nature portfolio

Peer Review File

Spatiotemporal photon distribution control on active sites enables bio-inspired methane-to-methanol conversion

Corresponding Author: Professor Ying Zhou

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The work by Y. Li et. al., focuses on the catalytic conversion of methane to methanol using impregnated nanoparticles of CdS with Pt. The Pt is proposed to exist in different oxidation states that favor conversion of methane to methanol through a temporary adsorption of methane to the surface. I was left with many questions regarding this manuscript that I would hope the reviewers could address.

1. I was confused by the connection to biomimetics in the abstract of this paper. There doesn't seem to be any connection to biology in this system (the authors argue that the coordination of dioxygen to a diiron center satisfies this connection), however there is little connection to diiron or any enzymatic science. The authors are not attempting to do careful synthetic work to create an artificial mimic of the active sites used in these systems. If anything, this could be motivated by a more controlled heterogeneous catalysis route similar to what is argued in their first paragraph. The ability to limit the overoxidation of the methane to carbon monoxide through light absorbing materials is as impactful as the biomimetic route and is likely more relevant to their overall paper. I would suggest the authors look at J.Am.Chem.Soc, 2024, 146, 25989-25999 and the references therein for inspiration.
2. I wouldn't agree with the author's statement of a "model" substrate. There are many peaks within the XRD and the SAED images that show polycrystalline nanomaterials are present in the sample. Although polycrystalline substrates are interesting on their own, these are far from "model" substrates. It would be useful for the authors to highlight what areas are Pt and what are CdS in their TEM images. A comment or two on the number and distribution of SAED spots would also be helpful. Another question is what is the distribution of particle sizes? Are they all a single distribution? Multi-distribution?
3. The arguments made regarding the oxidation state that the Pt is in are difficult to follow. The authors suggest it is some sort of oxidized Pt but say it is not Pt(IV). I do not agree with this assessment based on their available data. First, their Reference 25 clearly put the contribution at 72.1 eV as a Pt(II) species, while the contribution at 73.6 eV is most likely a Pt(IV) species (I'm leaving out the spin-orbit pair Pt 4f5/2 peak for simplicity). This isn't surprising given the chloroplatinic acid species heated in aqueous solution is most likely to form Pt (IV) species upon deposition. With the two different available oxidation states, regardless of what formal charge they have, why isn't there multiple contributions in the XAFS? I wouldn't expect the different oxidation states to have the same coordination numbers around them. Can the authors explain the lack of structure in their XAFS based on the presence of multiple species in the XPS? If the assumption is that all of the Pt is at the surface, then the XPS and XANES/XAFS should show similar results.
4. Did the authors observe any Cl in their XPS? It would be useful to increase the size of Supplementary Figure 6 and label all peaks in the survey spectra.
5. Did the authors take CO DRIFTS spectra without the Pt on their CdS particles? They explain what peaks are not there but it would be useful to explain the peaks that are there. In the 1% Pt/CdS sample, there is clearly a red shift in the desorption peaks that is not present in the 2% Pt/CdS sample. Can the authors suggest why and how this is? Why does the peak envelope at 2050 cm-1 change between the different samples? The peak at ~2200 cm-1 is not the same between the two samples, why is this?
6. The caption in Figure 2 made it difficult to understand which sub-figure was related to the different letterings.
7. Can the authors explain the shift in the UV-vis DRS spectra for the Pt1/CdS at 480 nm?
8. Would the authors expect multiple different relaxation pathways given the different oxidation states of Pt? Why are they only observing a single Pt pathway?
9. The shifts measured in Figure 4 are very small. They are also shifting with the same magnitude and direction which leads me to wonder if the authors are just measuring a charging effect on their samples. If the Pt is accepting an electron and the S

is sitting with a long-lived hole species, then I would expect to see a Pt shifted to lower binding energy with the S shifted to higher binding energy. How were the samples mounted in the XPS spectrometer? Was the spectrometer properly calibrated? There are very few details regarding the photoelectron spectroscopy. It would be good to include this in the main text given its significance.
10. At higher temperatures, I would have expected the rate of the reaction to increase and therefore more methanol to be observed. Can the authors provide more commentary on why they observe the opposite effect?
11. In Figure 5d, were all of the systems characterized in this study or are they putting this in comparison with other work that has been done in the literature? If the latter, they should reference where they got all of the data.
12. What is the relationship between relative humidity and the adsorption of water at the different sites on these systems?
13. The lack of recognition of multiple Pt oxidation states within the interpretation of the reaction mechanism makes this difficult to grasp what the true nature of the Pt in this scheme. Which of the Pt oxidation states are responsible for the oxygen reduction? Is the Pt being reduced during this process?
14. Can the authors comment more on their subtraction during the DRIFTS experiment and be more explicit in how to interpret the data? For example, my interpretation of the peaks is that they have desorbed all species from the heating and then began flowing gas into their chamber from 0 to 20 min. At the 20 min mark, they zero'ed out their spectra and then began illuminating their samples. So, the adsorption spectra should all be positive peaks showing increases in the adsorption of the molecules as a function of time. The illumination would be positive peaks for new species, negative peaks for loss of species, and zero that show no change. Is that correct? If so, why do they see a negative peak around the 1036 cm-1 for CdS for the adsorption time of CH2OH? This only seems to happen for CdS and not for any of the other samples.
15. Can the authors explain the changes in the peak envelopes just below 1000 cm-1? What about at 1250 cm-1?
16. In the ESR spectra for Pt1/CdS under H2O/O2/CH4, why is the highest peak at ~3400G show so little intensity?

Overall, the quality of the data appears to be quite high but many of their conclusions would have stronger support with further explanation based on the previous points. I'm not convinced that the impact of this paper is all that significant given that there are others who have shown similar results with related systems. It also impacted the perceived novelty of the work. The authors have done a quality job referencing their work and it was easy to access during review.

Reviewer #2

(Remarks to the Author)
In the manuscript, authors reported a combined experimental and theoretical work to study the effects of photogenerated charge carrier manipulation in methane-to-methanol conversion by constructing multifunctional active sites. Revealed by TA, in situ XPS, etc., electron and hole were trapped in similar timescale and then further localized on Pt and unsaturated sulfur sites for the spatiotemporal control, realizing the efficiency and highly selective methane conversion. Overall, the novelty of this work is prominent, and it matches with the requirement of Nature Communications. The results presented here provide substantial evidence supporting the proposed conclusions. It is believed that the findings in this work will be of the broad interests to readers in the field of energy materials. However, there are some issues that need to be identified and addressed in the present form.
Main concerns:
1.Supplementary Fig. 8 displays the ultra-violet and visible diffuse reflectance spectra of samples, and it is clear that there is additional tail absorption from 500 to 800 nm, which may be associated with Pt. However, in TAS (Fig. 3), authors claimed that the bleach signals in this region should only be ascribed to CdS without considering Pt species. Please explain this phenomenon and supply necessary proof in the manuscript.
2.As to photodynamics in Fig. 3 d-f, the conclusion "2 at 397.0 ps is only featured with GSB and tail bleach has been completely removed. It demonstrates the hole on interband state is further trapped and 2 should be ascribed to the intrinsic recombination of CdS" needs to be further identified. The recombination of excited electron with trapped hole can also promote the decline of tail bleach, so why 2 was ascribed to band edge recombination and secondary trapping?
3.In terms of time-resolved spectroscopies, authors claimed the influence of pump laser pulse fluency on photodynamics, which standardized the whole process; simultaneously, it was also noticed that the wavelength of pump laser was set to 400 nm. Why did authors choose this parameter and please explain it in the manuscript.

Other concerns:
1.Photodynamics revelations demonstrated the importance of active sites, but authors hardly mentioned the influence of Pt to band structure of photocatalysts. In this case, it is advised to depict the valence band and conduction band position of CdS, Pt1/CdS and Pt2/CdS, which is imperative to discuss carrier behavior from the perspective of thermodynamics.
2.Apart from the mentioned C1 products, were C2H6 or C2H4 also detected in current system?
3.HCHO was detected using colorimetric method, the fundamental mechanism of colorimetric method is suggested to be supplied in the manuscript.

Reviewer #3

(Remarks to the Author)
In this manuscript, the authors used CdS-supported Pt catalyst to realize the photocatalytic oxidation of methane to methanol, a significant topic. The CH3OH production rate over the optimal catalyst reaches 12.7 μmol-1·g-1·min-1 with a selectivity of 83.5%. My comments are given as follows:

1. What is the oxidant for methane oxidaiton? In the experimental section, the authors only introduced CH4 into the reactor without any oxidant. Did they used some solvent (e.g., H2O) or other sacrificial agent?

2. The authors used Pt to modify CdS with different contents. What are the structures of 1%Pt/CdS and 2%Pt/CdS? Only one sample was provided in EXAFS spectrum (Fig. 2c) and fitting (Supplementary Table 2). What is the local coordination structure of 2%Pt/CdS?

3. In Supplementary Table 2, Pt was mistakenly written as "Pd". Pt atoms are coordinated with both Cd and S atoms. However, the scheme of the sturcture given in Fig. 2g shows that Pt only coordinates with S atom. I am wondering that how the Pt atoms are anchored with CdS, will Pt atoms replace some Cd, or dop as interstitial atoms?

4. The catalytic peformance of 1%Pt/CdS and 2%Pt/CdS are strongly different. 2%Pt/CdS tends to catalyze methane to HCHO, CH3OH and CO2, while 1%Pt/CdS favors the selective formation of methanol. What is the reason?

5. What is the role of Pt for methane oxidation? It seems that the introduction of Pt suppresses the migration of photogenerated carriers (Supplementary Fig. 15). The photocurrent of CdS is much higher than that of 1%Pt/CdS and 2%Pt/CdS. It is contradictory to the most reported cases.

6. CdS tends to be oxidized under light irradition. The authors should give the data of the spent photocatalyst to verify its stability.

7. The authors are suggested to test the long-term durality test for 1%Pt/CdS.

8. In Fig. 6f, the author gave the detailed reaction pathways of 1%Pt/CdS and 2%Pt/CdS for methane converison. I think they should provide more evidences. For example, no signals of O2- radicals were observed in EPR, but which were invloved in the pathway. Same radicals were involved for methane oxidation over Why 1%Pt/CdS and 2%Pt/CdS (OH and O2-), why the reation pathways are greatly different?

Reviewer #4

(Remarks to the Author)
The critical mechanism of photocatalytic methane to methanol conversion using Pt-loaded CdS catalysts with special focus on the spatial and temporal distribution of photo-excited charge carriers was systematically investigated in this manuscript. And a clear picture on the correlation between catalyst structure and catalytic performance has been provided, which is important for the catalyst development in the field of green energy utilization. The paper is well written and has a concrete storyline but the following issues need to be stressed before it can be agreed for publication.
1. There were only two contrast groups in current work, named 1%Pt/CdS and 2%Pt/CdS. It is suggested for authors to make more samples for photocatalytic methane to methanol evaluation.
2. In the TA tests, why authors added BQ? The purpose needs to be clarified. Besides that, would the addition of such additives change the intrinsic structures of the catalysts? The factors and mechanism should be ruled out.
3. The time-resolved spectroscopic studies were conducted with the fs-laser pulse and it reflected photodynamics in ultrafast timescale. But authors reckon electron and hole can be further localized on Pt and unsaturated sulfur, of which the corresponding timescale is beyond the time-window of TAS. How did authors deduce this conclusion and the validity of the spectroscopic characterizations related to the catalytic mechanism in general need to be discussed.
4. As to electrochemical characterizations, was transient photocurrent response tested under open circuit potential? The applied potential should be illustrated in the manuscript.
5. Since the SVD analysis is still quite new compared with conventional single wavelength kinetic fitting for TA results (Angew. Chem. Int. Ed. 2024, 63, e202401255; Adv. Mater. 2024, 36, 2303287), I suggest the author provide detailed description on how the SVD fitting is implemented and the basic interpretation or theory about the fitting process to facilitate the non-expert readers. Moreover, some expressions need to be checked, e.g. 1Σ excitons in line 200 was also written as 1S excitons, etc. (Adv. Mater. 2014, 26, 2954-2961; Nano Energy 2016, 28, 319-329; ACS Catal. 2022, 12, 10115-10126).

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I want to applaud the authors on addressing the concerns outlined. Based on many of their responses I am more supportive of their conclusions but am still not convinced of the impact of their work. There are more concerns with their central conclusion that justifies the impact – that the Pt center is responsible for adsorption of oxygen, and free S groups are responsible for CH4 adsorption. If the authors could provide responses to the following, it may add clarity more clarity to their conclusions:
1. In the authors response to comment 1.3, they re-fit their XPS spectra and show their new fits in supplementary figure R3. If one looks closely at the Pt 4f spectra for each sample, they will see a change in slope around 74.5 eV and a second contribution to the Pt spectra. This is clearly a multivalent Pt species on the surface and exists for all samples with Pt. The contribution is much smaller, granted, in the 1% species but it there. My concern rests on the author's central point that the Pt species is acting as this sink of O2 for the mechanism. Which Pt species? Why do they just observe a single pathway in the

transient spectroscopy if there are multiple Pt species? Why do they only observe a single Pt species in the XAFS when there are clearly multiple valences in the XPS? In the authors supplementary figure R35, the Pt envelope clearly shows multivalence too. Why isn't there consistency between the different photoelectron spectra?
2. Further to the previous point, there is some indication that there could be Cl 2p in the 1% Pt. What were the parameters that the Cl 2p was taken? Did the authors use a larger pass energy to ensure that they could observe small amounts on the surface? The reason for my concern with this is that Cl is often a recombination center when adsorbed on the surface. If the samples are not perfectly clean of Cl, there could be changes to many of the different techniques used in the author's study – DRIFTS and TAS – to make their central argument.
3. I do not agree with the comment 1.8 the author's response. The oxidation and coordination environment are still not confirmed and this convolutes the conclusions from the ultrafast photodynamics experiment. I could accept that a generic Pt species is what creates this behavior but it still isn't clear to me what the role of the oxidation state is. Perhaps this is irrelevant? If so, will any electron trapping metal provide the same behavior? Do unsaturated S-sites normally adsorb CH_4?
4. What indications are there that there is an explicit Pt-S bond? Is this from the EXAFS?
5. From comment 1.9, the authors cite Nat. Commun. 2024, 15, 4807 (I tried to find the other references but they were difficult to find due to the authors formatting) as a reference for their small shifts. In that article, those authors do show the expected shifts for electron trapping and hole trapping that was referred to in the initial review. In this work, the authors do not show this phenomenon. Can the authors comment on how they are coming to their conclusion given that they are not observing similar effects from the literature in their photoelectron spectra?
6. In response to Reviewer 3, the authors claim that the Pt has replaced part of Cd to form the Pt-S configuration. Have the authors considered that the Pt will deposit on top of Cd and attenuate its signal, thus producing a lower Cd:S ratio? Did the authors use appropriate sensitivity values to get their ratios? Is any of the Pt oxidation states of similar size to Cd^{2+} to replace it in the crystal structure?
7. The lower photocurrent seems to scale with the amount of Pt. The Pt seems to be acting as a recombination center rather than a reaction site. Can the authors comment on this?

Reviewer #2

(Remarks to the Author)
I have carefully read the author's revisions. I think the manuscript is now in an acceptable state and can be published.

Reviewer #3

(Remarks to the Author)
All the comments have been addressed, and this manuscript can be accepted with the current version.

Reviewer #4

(Remarks to the Author)
The revised manuscipt has been improved and acceptance is suggested.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I want to thank the authors for their useful discussion on their paper. While I am still not convinced of their interpretation of the photoelectron spectra, I believe this merits publication and scrutiny by the wider community to further investigate their claims.

Reviewer #5

(Remarks to the Author)
Despite numerous efforts to support the authors' proposal for unique catalytic sites and charge dynamics, the claim of exclusively monovalent Pt^{2+} on the surface is not properly demonstrated. The XPS Pt 4f spectra clearly show a shoulder peak possibly for Pt^{4+}. The response to this concern is not convincing. Reviewer #1's concern about mixed valence is well-founded. In addition, given that H_2PtCl_6 (Pt^{4+}) is used as the precursor, no explicit reduction step is described and the chemical pathway from Pt^{4+} to Pt^{2+} remains unclear. It is also doubtful that Pt species are atomically dispersed in this study since the TEM image of separated Pt atoms are not provided. Therefore, further data analyses and computational simulations should be considered with more solid investigation and proper structural hypothesis.
1. HAADF-STEM should be carried out to confirm the separated Pt atoms on CdS surface.
2. The claim that Pt is coordinated with sulfur sites is not convincing. EPR spectra of CdS samples before and after Pt deposition should be provided.
3. The XPS discussion regarding Figure 4 is not convincing, as all elements appear shifted by the same value. This shift may result from the C 1s (284.8 eV) calibration, which is broad and prone to be shifted.
4. No standard sample containing Pt-S bond, or other Pt^{2+} states, is measured and compared in XAS. Analysis on the EXAFS and XANES lacks details, what is the Pt-S model and how does this model fit into the EXAFS spectra?

5. In Figure 5c, in addition to selectivity, it is essential to report the Faradaic efficiency to evaluate the actual process efficiency. Faradaic efficiency quantifies the percentage of charge carriers effectively used for methane-to-methanol conversion. Selectivity alone does not account for holes consumed in reactions.
6. To me the reply to reviewer #1's concerns about photocurrents is not really convincing.
7. Bandgap evaluation based on IPCE spectra should be carried out.
8. XRD for all samples after reaction need to be provided.
9. Literature citations need to be improved proficiently, and the foundation of the concept needs to be cited properly rather than just some recent related papers.

Reviewer #6

(Remarks to the Author)
I have carefully reviewed the entire manuscript as well as the exchange between Reviewer 1 and the authors. Overall, I find the conclusions and findings in the paper to be convincing and carefully presented.
With regard to the main point of debate—the oxidation state of the Pt species—I did notice a very slight shoulder on the high-binding-energy side of the main Pt^{2+} peak, around 73.6 eV. However, given the generally weak core-level signal of the sample, I would be very cautious about directly assigning this feature to a new Pt species. Several alternative explanations are possible, including surface charging, the presence of surface adsorbates during measurement, or baseline artifacts, as the authors have already pointed out. I therefore agree with the authors that the oxidation state of Pt should be established through complementary characterization methods. Indeed, both XAS and TA studies provide consistent evidence supporting the monovalent nature of the Pt species.
In addition, the authors confirmed that there is no residual chloroplatinic acid in the sample, which rules out the major possibility suggested by Reviewer 1.
In general, XPS is a highly surface-sensitive technique that can be subject to significant uncertainties, especially when the overall signal intensity is low. To rigorously validate the electronic structure of the target sample, complementary techniques are essential, rather than overinterpreting noisy XPS spectra through curve fitting alone. This is precisely the approach taken by the authors, and I find their response to Reviewer 1 to be convincing and well-reasoned.
Summary, this manuscript presents a novel innovative concept supported by extensive characterization data. however , before publication, several following issues still need to be addressed.
1. There appears to be an error in the unit labels within the Fig. 2b and 2c. The unit for vertical coordinate should be the angstrom, symbolized as 'Å', not the ampere, which is symbolized as 'A'. Additionally, adding a detailed legend description to the EXAFS fitting parameters table (Supplementary Table 2-3) is crucial for reflecting the rigor of the data. For example, J.Am.Chem.Soc, 145, 2698-2707.
2. In Fig. 6, it is recommended to clearly indicate the correspondence between the electron/hole enrichment sites and the reaction pathways, for example, holes are enriched at the S sites while electrons are enriched at the Pt sites.
3. It is recommended to supplement the test data for apparent quantum efficiency to allow for a more comprehensive evaluation of the photocatalytic efficiency.
4. It appears that the font or size of "μ" in Fig. 5 is inconsistent with others. It is recommended to optimize its font style and size to ensure visual uniformity.
5. The paper indicates that the introduction of Pt accelerates the charge carrier recombination rate, yet it enhances the catalytic performance. Does this imply that a longer charge carrier lifetime is not necessarily better?

Version 3:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I would like to thank the authors for their diligence and patience in this review. I do have a few other questions based on their discussions with my colleagues in their response:

• In the HAADF-STEM image, the authors point to several changes in contrast on the 1% Pt/CdS in a single area but it is not distributed across the particle. The same can be said for the 2% Pt/CdS image. Is this a proper representation of the photocatalyst surfaces in each case? I would expect for the 2% Pt/CdS to have double the amount of Pt on the surface, but this doesn't seem to be the case. Can the authors provide some explanation for this?
• In the EPR spectra, this change is very small and could be attributed to changes in the background. Did the authors also run the 2% Pt/CdS to observe a starker change in the EPR?
• Adsorbed CO2 isn't likely to shift the photoelectron spectra in the way the authors indicate. It is not clear whether the shifts mean anything other than some sort of charging effect. More information on how the samples for photoelectron characterization are mounted in the methods section would be appreciated.
• Can R14 be split into multiple panels and the data enlarged so that we can see more subtle changes in the XRD spectra? The current presentation is difficult to discern any changes other than major changes in the largest peaks.

Overall, I think the authors have done a lot of work to address our reviewer comments. The interpretation of the photoelectron spectra still concerns me. There seems to be enough supporting evidence of bulk techniques for the authors claims, but their core argument/interpretation does center on the interaction of Pt with the surface of the CdS particles, thus a surface

sensitive characterization technique should be the most supportive of their claims. I would continue with my last comment that it merits publication and that the authors and the field should take the opportunity to investigate this further.

Reviewer #6

(Remarks to the Author)
The authors have addressed fully my concerns. Now the manuscript can be accepted for publication in Nature Communications.

Version 4:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I have no further comments on this manuscript and would like to thank the authors for their discussions

Manuscript: NCOMMS-25-21495

Spatiotemporal control of photon distribution on active sites: Bridging bio-inspired methane-to-methanol conversion

Response to the Reviewers' Comments

Reviewer #1

The work by Y. Li et. al., focuses on the catalytic conversion of methane to methanol using impregnated nanoparticles of CdS with Pt. The Pt is proposed to exist in different oxidation states that favor conversion of methane to methanol through a temporary adsorption of methane to the surface. I was left with many questions regarding this manuscript that I would hope the reviewers could address.

Reply to reviewer: Thanks for reviewer's comments. In the revised manuscript, we have re-analyzed the electronic state and coordination environment of Pt species based on the combination of the data from XPS, XAFS, XRD, TEM, SAED and in situ DRIFTS CO adsorption probe tests. It is found that Pt species in 1%Pt/CdS and 2%Pt/CdS both stay in valence of +2 and are coordinated with S to form Pt-S configurations (*see Response 1.2, 1.3, 1.4 and 1.5*). The role of Pt in the carrier dynamics and reaction paths as well as its stability in photocatalysis have been discussed (*see Response 1.8, 1.9, 1.13, 1.14, 1.15 and 1.16*). Furthermore, experimental conditions of temperature and humidity have been investigated and discussed for their contributions to ultimate performance (*see Response 1.10 and Response 1.12*). The constructive comments and suggestions are addressed in detail as follow, and we hope that these alterations could meet your expectation.

Comment 1.1 I was confused by the connection to biomimetics in the abstract of this paper. There doesn't seem to be any connection to biology in this system (the authors argue that the coordination of dioxygen to a diiron center satisfies this connection), however there is little connection to diiron or any enzymatic science. The authors are not attempting to do careful synthetic work to create an artificial mimic of the active sites used in these systems. If anything, this could be motivated by a more controlled heterogeneous catalysis route similar with what is argued in their first paragraph. The ability to limit the overoxidation of the methane to carbon monoxide through light absorbing materials is as impactful as the biomimetic route and is likely more relevant to their overall paper. I would suggest the authors look at J. Am. Chem. Soc, 2024, 146, 25989-25999 and the references therein for inspiration.

Reply to reviewer: Thanks for reviewer's comment. We are sorry that our previous descriptions on photocatalyst design cannot well display our motivation and raise reviewer's confusion. To

present our ideas in a better approach, the inspire of this work is necessarily reclaimed. Methane monooxygenase (MMO) exhibits excellent performance in the bio-catalytic conversion of CH_4 to CH_3OH, and its catalytic process is worthy of learning and simulation. In our work, we were specifically inspired by the ordered sequence of this MMO catalytic process, rather than its Fe active site structure. This core concept of process-inspired design has been explicitly emphasized in the abstract and introduction of the revised manuscript, which is highlighted on Page 2-3.

Comment 1.2 I wouldn't agree with the author's statement of a "model" substrate. There are many peaks within the XRD and the SAED images that show polycrystalline nanomaterials are present in the sample. Although polycrystalline substrates are interesting on their own, these are far from "model" substrates. It would be useful for the authors to highlight what areas are Pt and what are CdS in their TEM images. A comment or two on the number and distribution of SAED spots would also be helpful. Another question is what is the distribution of particle sizes? Are they all a single distribution? Multi-distribution?

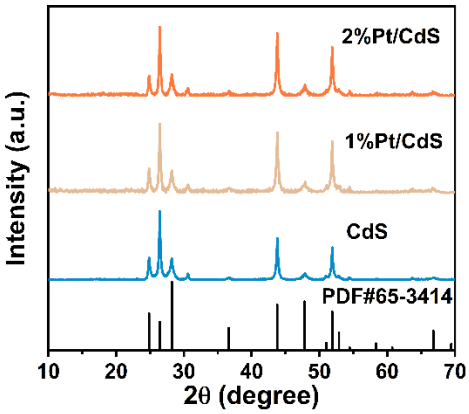
Reply to reviewer: Thanks for reviewer's comment. Our response to reviewer's comment are presented in detail as follow:

(1) Naming CdS as a model catalyst

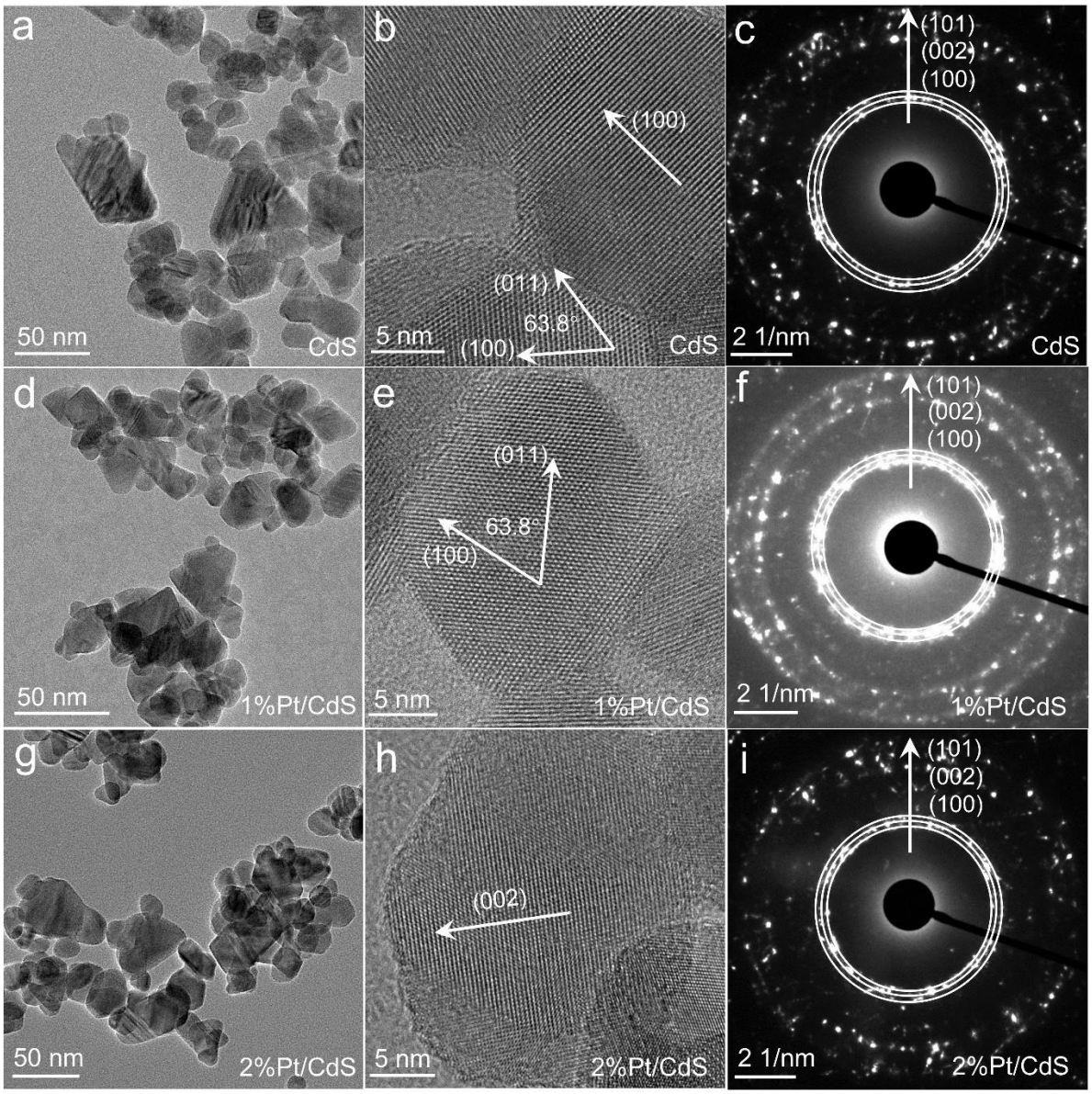
CdS has been extensively employed as a typical photocatalyst in prior studies owing to its superior light-harvesting properties and facile surface tunability. Consequently, in the previous version of our manuscript, CdS was named as a model catalyst. In accordance with the reviewer's suggestion, this terminology has been revised to 'typical photocatalyst' to more accurately reflect its role in demonstrating fundamental reaction principles.

(2) Size and distribution of Pt nanostructures:

As shown in Supplementary Fig. R1, the primary diffraction peaks at around 24.9°, 26.5° and 28.2° in XRD can be indexed to (100), (002) and (101) of hexagonal CdS (PDF#65-3414), which are relatively sharp and narrow. The measurable lattice fringes in HRTEM (Supplementary Fig. R2b) includes typical (100) and (011) of CdS. Selected area electron diffraction (SAED) images (Supplementary Fig. R2c) demonstrate the polycrystalline property of substrate materials, where the obvious diffraction rings all correspond to hexagonal CdS crystal. In contrast, no characteristic peaks corresponding to Pt metallic nanoparticles or Pt-related composites were detected in the XRD, TEM, and SAED patterns of 1%Pt/CdS and 2%Pt/CdS, confirming the high-dispersity of Pt on the surface of CdS. Combined analysis of XPS and XAFS data demonstrates that Pt exists in the +2 oxidation state and forms Pt-S bonds with CdS. (Detailed discussions on Pt valence and coordination are provided in *Response 1.3*) Corresponding revisions have been implemented on Page 5 line 112 of the revised manuscript with highlighted modifications.



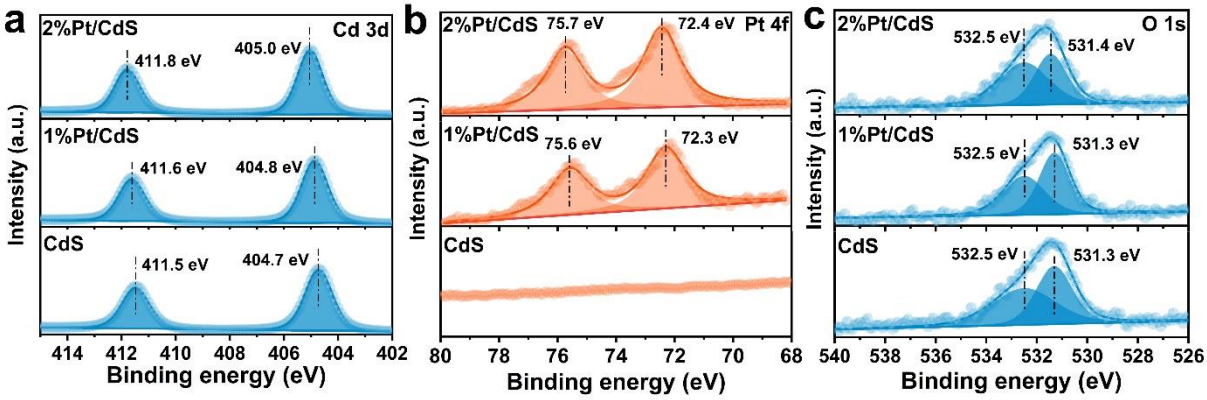
Supplementary Fig. R1 XRD of CdS, 1%Pt/CdS and 2%Pt/CdS.



Supplementary Fig. R2 TEM, high-resolution TEM and selected area electron diffraction (SAED) images of CdS **a-c**, 1%Pt/CdS **d-f** and 2%Pt/CdS **g-i**.

Comment 1.3 The arguments made regarding the oxidation state that the Pt is in are difficult to follow. The authors suggest it is some sort of oxidized Pt but say it is not Pt(IV). I do not agree with this assessment based on their available data. First, their Reference 25 clearly put the contribution at 72.1 eV as a Pt(II) species, while the contribution at 73.6 eV is most likely a Pt(IV) species (I'm leaving out the spin-orbit pair Pt $4f_{5/2}$ peak for simplicity). This isn't surprising given the chloroplatinic acid species heated in aqueous solution is most likely to form Pt (IV) species upon deposition. With the two different available oxidation states, regardless of what formal charge they have, why isn't there multiple contributions in the XAFS? I wouldn't expect the different oxidation states to have the same coordination numbers around them. Can the authors explain the lack of structure in their XAFS based on the presence of multiple species in the XPS? If the assumption is that all of the Pt is at the surface, then the XPS and XANES/XAFS should show similar results.

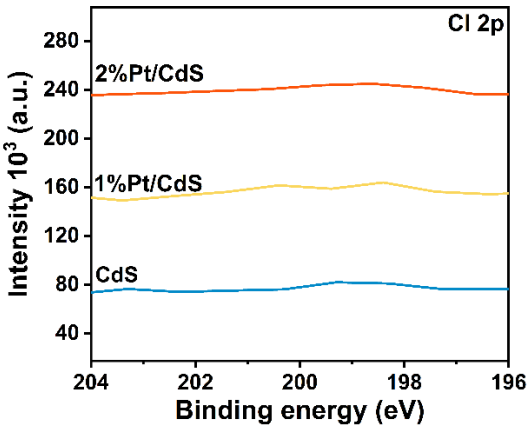
Reply to reviewer: Thanks for reviewer's comment and suggestions. In the XPS fitting of last version of manuscript, we referred to several works to identify the possible peaks. Among them, the doublets at 73.6 eV ($Pt_{7/2}$) mainly referred to the Pt loaded on the oxide surface (J. Am. Chem. Soc. 2024, 146, 16363-16368), and this peak might correspond to Pt^{4+}. Pt with +2 valence can be fitted at a binding energy of 72.1 eV ($Pt_{7/2}$). Due to this mixed valence state, in our last version, we mainly stated that Pt was in an oxidation state and did not specify its specific valence state. However, on the suggestion of the reviewers, we examined the fitting of XPS and ultimately determined that there is only Pt^{2+} in Pt_1/CdS and Pt_2/CdS based on the following considerations. Firstly, Cl 2p signal was not detected in XPS, indicating that there is no chloroplatinic acid residual over material surface (see details in *Responses 1.4*). Secondly, we analyzed the coordination of the material in combination with XAFS and found that the average environment of Pt in the material is unique and not the result of the superposition of multiple coordination structures. Finally, by referring to multiple literatures related to Pt/CdS (Angew. Chem. Int. Ed. 2023, 62, e202306452; Angew. Chem. Int. Ed. 2023, 62, e202301239), we found that it was not common to detected Pt^{4+} on the surface of CdS. Therefore, we refitted the Pt 4f signal of XPS and found that when there is only one couple of doublets, the signal can still be well fitted. The corresponding substance was Pt^{2+}(Supplementary Fig. R3b). Meanwhile, EXAFS fitting also proves that Pt grows on the surface of CdS through Pt-S bonds, and forms a Pt-S coordination structure. Here, we sincerely express our gratitude to the reviewers for constructive suggestions. Necessary revisions have been made in the corresponding parts of the article (in revised manuscript Page 6 line 132).



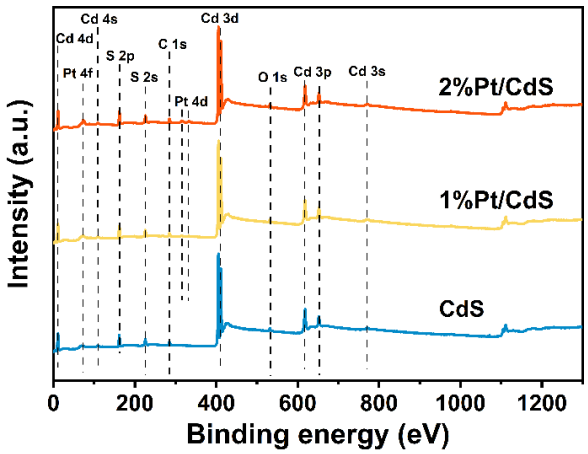
Supplementary Fig. R3 X-ray photoelectron Cd 3d **a**, Pt 4f **b**, O 1s **c** fine spectra of CdS, 1%Pt/CdS and 2%Pt/CdS.

Comment 1.4 Did the authors observe any Cl in their XPS? It would be useful to increase the size of Supplementary Figure 6 and label all peaks in the survey spectra.

Reply to reviewer: Thanks for this comment. To verify the potential presence of residual Cl on the surface of 1%Pt/CdS and 2%Pt/CdS, XPS high-resolution Cl 2p spectra were analyzed. As shown in Supplementary Fig. R4, no characteristic peaks assigned to Cl species were observed, confirming the effective elimination of chloroplatinic acid precursor which is the only source of Cl species. Moreover, to respond reviewer's comment, XPS full spectra have been enlarged while the detected signals are all labelled, including Cd 4d, Cd 4s, Pt 4f, S 2s and so on. Corresponding revisions have been implemented on Page 6 line 133 of the revised manuscript with highlighted modifications.



Supplementary Fig. R4 The Cl 2p spectra of CdS, 1%CdS and 2%CdS.



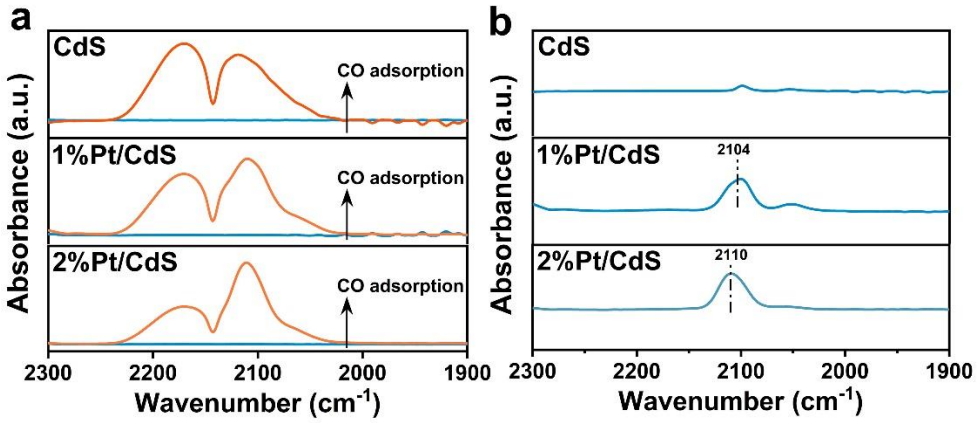
Supplementary Fig. R5 X-ray photoelectron full spectra of CdS, 1%CdS and 2%CdS.

Comment 1.5 Did the authors take CO DRIFTS spectra without the Pt on their CdS particles? They explain what peaks are not there but it would be useful to explain the peaks that are there. In the 1% Pt/CdS sample, there is clearly a red shift in the desorption peaks that is not present in the 2% Pt/CdS sample. Can the authors suggest why and how this is? Why does the peak envelope at 2050 cm^{-1} change between the different samples? The peak at ~2200 cm^{-1} is not the same between the two samples, why is this?

Reply to reviewer: Thanks for this comment. Before responding to reviewer's questions, we need to make more descriptions on CO adsorption/desorption experiment details. Before carrying out CO adsorption, inert gas (Ar) was firstly used to purge the impurities on the surface of photocatalyst. After the purging is completed, CO was introduced into the infrared reactor for adsorption until the adsorption saturation is reached. However, in CO adsorption process, the collected IR signal is rather complex and non-specific, because the vibration signal of the gaseous CO molecules will overlap with the signal of the adsorbed CO molecules. Therefore, it is necessary to further use inert gas to purge the material surface to remove the excess gaseous CO molecules and then observe the vibration of the adsorbed CO molecules. During the process of removing gaseous CO molecules, the originally overlapping infrared signals are separated and the deviation of the infrared signal peak can be observed. The phenomenon observed in experiments are illustrated as follow.

After adsorption saturation (Supplementary Fig. R6a), the adsorption signal of gaseous CO was mainly observed on the surface of CdS. In contrast, the infrared signals on the surfaces of 1%Pt/CdS and 2%Pt/CdS showed complex due to the superposition of multiple vibrations. After continuous purging with inert gas (Supplementary Fig. R6b), the vibration signals related to CO on the CdS surface disappeared rapidly, while on the surface of 1%Pt/CdS and 2%Pt/CdS, weak CO adsorption signals retained at 2110~2104 cm^{-1}, corresponding to the adsorbed CO on $Pt^{\delta+}$. However, due to the high dispersity of Pt, compared with typical signals (~2084 cm^{-1}), this vibration

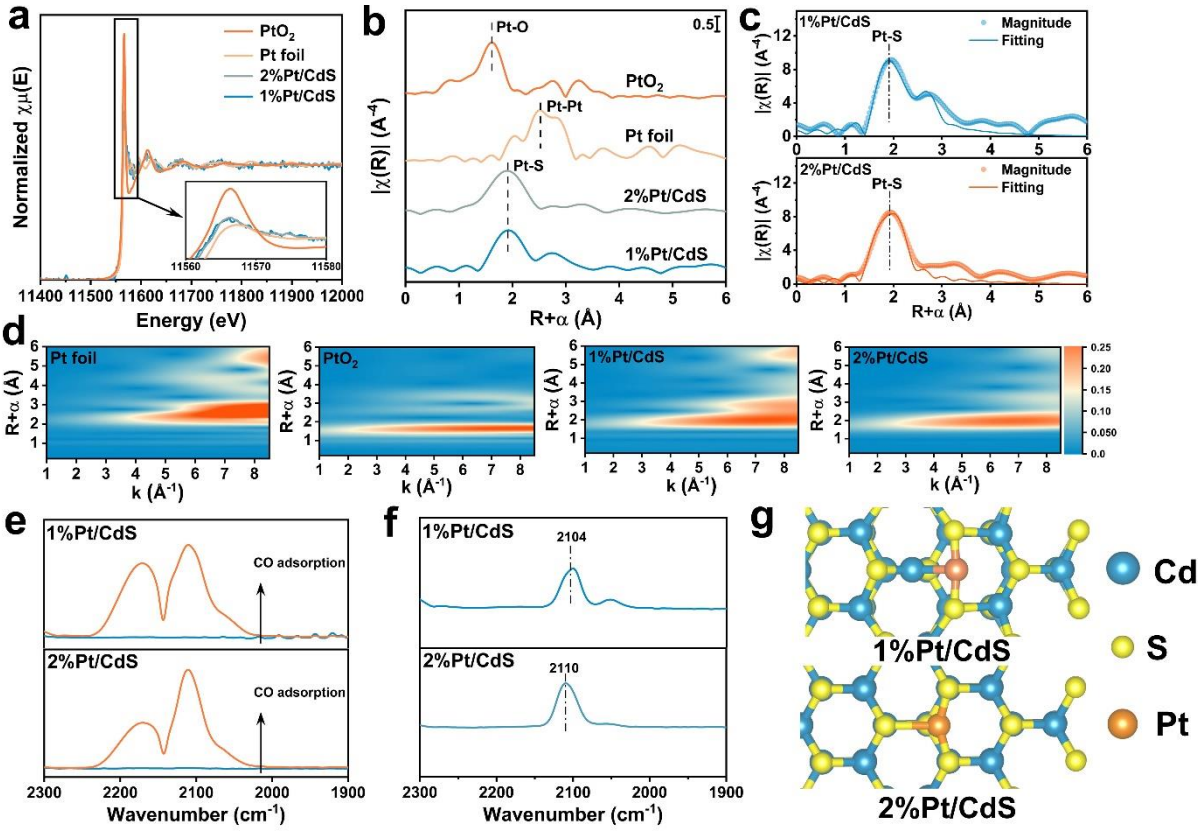
has changed (Nat. Commun. 2017, 8, 16100; ACS Catal. 2022, 12, 3634-3643). It is speculated that the anchored Pt over CdS could have strong affinity with CO. Ultimately, combining CO adsorption/desorption experiments with XPS and XAFS, it can be disclosed that Pt is in the form of Pt-S bonds with +2 valence. The revisions have been made in the corresponding parts of the article (in revised manuscript Page 7 line 164).



Supplementary Fig. R6 CO adsorption **a** and CO desorption **b** in-situ DRIFTS of CdS, Pt_1/CdS and Pt_2/CdS. (These data were smoothed during processing)

Comment 1.6 The caption in Figure 2 made it difficult to understand which sub-figure was related to the different letterings.

Reply to reviewer: Thanks for reviewer's suggestion. We have revised the caption to well deliver the information in the figure, which is shown in Supplementary Fig. R7. Corresponding revisions have been implemented on Page 8 line 181 of the revised manuscript with highlighted modifications.

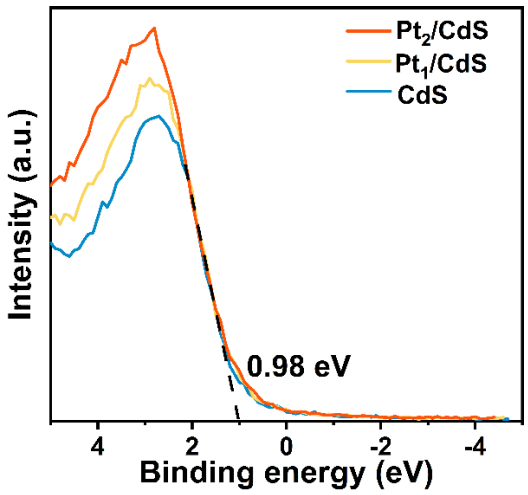


Supplementary Fig. R7 XANES spectra of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **a**; Fourier-transformed k^3-weighted EXAFS of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **b**; R-space fitting results for 1%Pt/CdS and 2%Pt/CdS (The R-space data are presented without phase correction) **c**; EXAFS wavelet transformation (WT) for Pt foil, PtO_2, 1%Pt/CdS and 2%Pt/CdS **d**; CO adsorption **e** and desorption **f** in-situ DRIFTS of 1%Pt/CdS and 2%Pt/CdS (Ar gas flow was used to remove extra gaseous CO and the desorption curve was collected after 20 min Ar flow); The proposed structure for Pt-S configuration for 1%Pt/CdS and 2%Pt/CdS **g**.

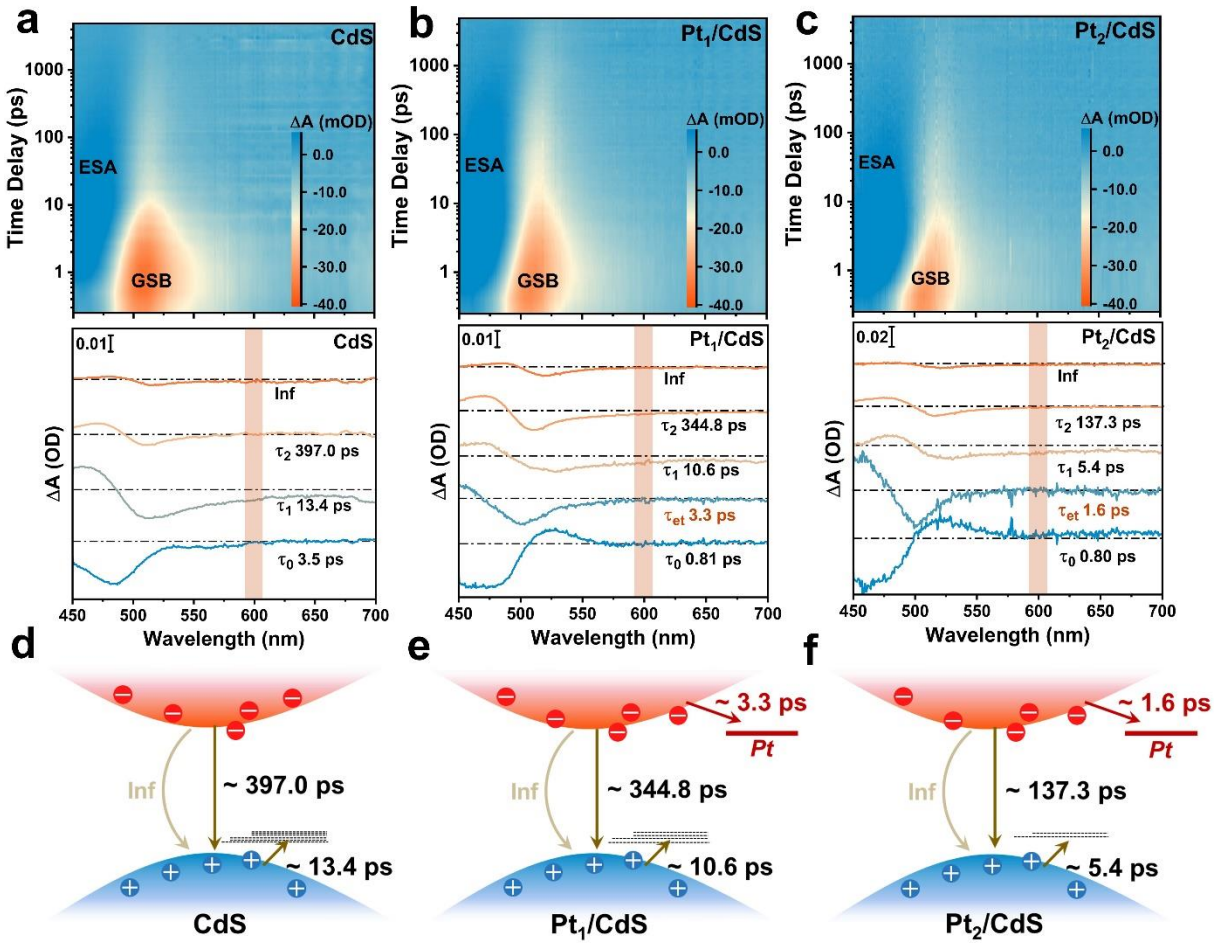
Comment 1.7 Can the authors explain the shift in the UV-vis DRS spectra for the Pt_1/CdS at 480 nm?

Reply to reviewer: Thanks for reviewer's comments. It is noted that the absorption peak near 480 nm was shifted to a certain extent in the UV-vis DRS spectra, but this shift is not related to the intrinsic absorption change of CdS due to the following analysis. Firstly, as shown in Supplementary Fig. R8, it can be found that the valence band positions of CdS, Pt_1/CdS and Pt_2/CdS are basically same. Meanwhile, in TAS, the wavelengths corresponding to the ground state bleaching signals of CdS, Pt_1/CdS and Pt_2/CdS are consistent (Supplementary Fig. R9), indicating that the absorption edge of CdS has not moved either. Above results prove that Pt has not changed the band structure and intrinsic absorption of CdS. As for the wavelength shift observed the UV-vis DRS spectra, we speculate that the Pt on the surface of Pt_1/CdS scatters a part of incident light during the diffuse

reflection process, thereby causing a weak wavelength shift in the absorption signal after normalization.



Supplementary Fig. R8 XPS valence band spectra of CdS, Pt_1/CdS and Pt_2/CdS.



Supplementary Fig. R9 Transient absorption spectroscopy (TAS) where 400 nm beam light was used as pump light and a continuous white light ranging from 450 to 700 nm was used as probe light: two-dimensional contour plots of TAS with the associated global fitting results of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c**. The diagram exhibiting the excited-state carrier relaxation of CdS **d**, Pt_1/CdS **e** and Pt_2/CdS **f**.

Comment 1.8 Would the authors expect multiple different relaxation pathways given the different oxidation states of Pt? Why are they only observing a single Pt pathway?

Reply to reviewer: Thanks to reviewer's comment. Due to the confirmation of the oxidation state and coordination environment of Pt, the role of Pt in relaxation paths was further revealed based on excited-state dynamics studying. From the perspective of ultrafast photodynamics, when Pt species was loaded on CdS, the TAS global fitting results showed that extra time-component (~ 3.3 ps) appeared in contrast to CdS, which is associated with electron trapping. Moreover, transient photocurrent response and in-situ XPS demonstrated that electron trapped by Pt are further localized on photocatalyst surface. For surface reaction, Pt can work as electron-rich center to preferably adsorb O_2 for ·OH formation ($O_2 + e^- \rightarrow \cdot O_2^-$, $\cdot O_2^- + H^+ \rightarrow \cdot OOH$, $\cdot OOH + H^+ + e^- \rightarrow \cdot OH$) while CH_4 is adsorbed on unsaturated sulfur sites (such as Pt_1/CdS). In this case, CH_3OH overoxidation was inhibited.

Comment 1.9 The shifts measured in Figure 4 are very small. They are also shifting with the same magnitude and direction which leads me to wonder if the authors are just measuring a charging effect on their samples. If the Pt is accepting an electron and the S is sitting with a long-lived hole species, then I would expect to see a Pt shifted to lower binding energy with the S shifted to higher binding energy. How were the samples mounted in the XPS spectrometer? Was the spectrometer properly calibrated? There are very few details regarding the photoelectron spectroscopy. It would be good to include this in the main text given its significance.

Reply to reviewer: Thanks for reviewer's comments and these comments are responded in detail as follows:

(1) The details on the sample preparation and energy calibration for in-situ XPS.

To prepare sample for in-situ XPS testing, an amount of photocatalyst was mixed with electroconductive resin to form homogeneous mixture. The mixture was processed by compression to prepare a film which was immediately placed on the specimen stage of in-situ XPS spectrometer. The chamber where the sample stage was located was evacuated and then XPS data collection was carried out. XPS in the light field was collected after 5 min monochromatic light irradiation. During the data collection period, monochromatic light will continue to be shone. Finally, the binding energy of in-situ was calibrated referenced on C 1s at 284.8 eV. The revisions have been made in Page 20 line 519 of revised manuscript.

(2) The overall energy shifts in in-situ XPS

We agree with author's view and it was ever expected to see that the binding energy of S 2p

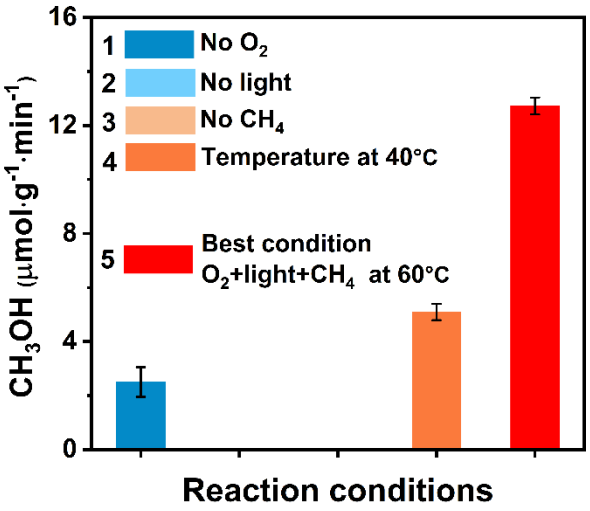
was positively shifted while Pt 4f was negatively shifted. As to current results that XPS spectra are overall shifted, we speculated that it is caused by carrier diffusion over photocatalyst surface. Based on the experimental procedures of in-situ XPS (in revised manuscript Page 20 line 519), XPS in the light field was collected after 5 min irradiation and in that case the dominated carriers could rapidly diffuse and influence the overall surface charge distributions. Moreover, Pt is bonded on CdS through Pt-S bond, and the carrier diffusions between them could be exaggerated, which promote the whole process.

(3) The minor energy shifts in in-situ XPS

The transfer and localization of carriers is a dynamic process that needs to compete with the recombination behavior of carriers. At the time scale that in-situ XPS can characterize, the excitation and recombination of carriers have reached a dynamic equilibrium, and thus the charge accumulation that can be observed on the material surface will not be obvious. The binding energy offset within the range of 0-0.2 eV is a relatively common value in in-situ XPS tests (Angew. Chem. Int. Ed. 2023, 62, E 2022, 18688; Nat. Commun. 2024, 15, 4807). Secondly, for the localization of surface electrons and holes, we also referred to other test results in our research. For example, in the photocurrent test, we found that the electron outflow from the surface of the Pt_1/CdS working electrode was significantly lower than that of CdS, indicating that the strong electron capture and localization effect of Pt inhibited the transfer of electrons to the external circuit. Taking the phenomenon mentioned above in considerations, we reckoned that the minor energy shift in in-situ XPS is acceptable and they can reflect the carrier distribution on photocatalyst surface.

Comment 1.10 At higher temperatures, I would have expected the rate of the reaction to increase and therefore more methanol to be observed. Can the authors provide more commentary on why they observe the opposite effect?

Reply to reviewer: Thanks for reviewer's comment. We are sorry to the unclear descriptions which have raised misunderstanding in last version of manuscript. The contrast experimental (Supplementary Fig. R10) were carried out to determine the contributions of experimental factors (including light, temperature, O_2, and CH_4) to ultimate performance (photocatalyst was Pt_1/CdS). Among them, group "current condition" referred to the best experimental conditions (CH_4+O_2+light at 60°C) which have been used to compare performance between CdS, Pt_1/CdS and Pt_2/CdS. Hence, consistent with the reviewer's comment, the activity increased when the temperature was raised from 40°C to 60°C under light irradiation. The "current condition" has been revised as "the best conditions (CH_4+O_2+light at 60°C)" in Page 20 line 519 of revised manuscript.



Supplementary Fig. R10 The contrast photocatalytic experiment to determine the optimized experimental conditions (photocatalyst was Pt_1/CdS). Error bars represent standard deviations obtained from at least two independent measurements

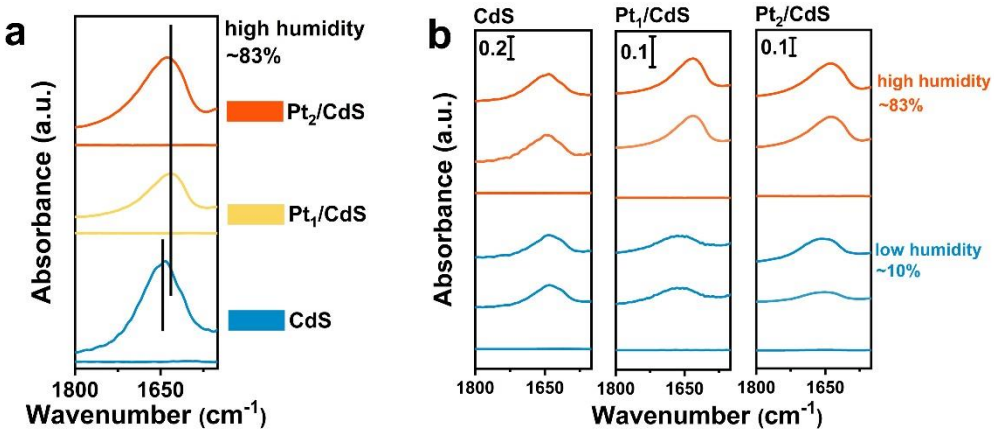
Comment 1.11 In Figure 5d, were all of the systems characterized in this study or are they putting this in comparison with other work that has been done in the literature? If the latter, they should reference where they got all of the data.

Reply to reviewer: Thanks for reviewer's comment. The contrast experiments (Supplementary Fig. R10, Figure 5d in manuscript) were all carried out in our photocatalytic system through selectively removing O_2, light or CH_4 as well as lowing temperature.

Comment 1.12 What is the relationship between relative humidity and the adsorption of water at the different sites on these systems?

Reply to reviewer: Thanks for reviewer's comments. In response to the reviewers' comments, we explored the influence of humidity on the adsorption sites of H_2O using in-situ DRIFTS. In our photocatalytic evaluation experiments, the photocatalyst was pre-dispersed in ultrapure water with a high environmental humidity. Therefore, we firstly characterized the adsorption of H_2O under high humidity conditions (~83%). As shown in the Supplementary Fig. R11, in contrast to CdS, the H_2O vibration signals over Pt_1/CdS and Pt_2/CdS have shifted under high humidity conditions, indicating that the adsorption sites of H_2O have changed. For CdS, it is speculated that since a large amount of unsaturated sulfur are enriched on its surface, H_2O could be adsorbed on the unsaturated sulfur sites. While for Pt_1/CdS and Pt_2/CdS, the changes in the adsorption sites should be caused by Pt, as H_2O has been adsorbed onto Pt sites. Furthermore, as humidity was decreased to a low level (~10%), the vibration signals over CdS, Pt_1/CdS and Pt_2/CdS are not altered but the signals

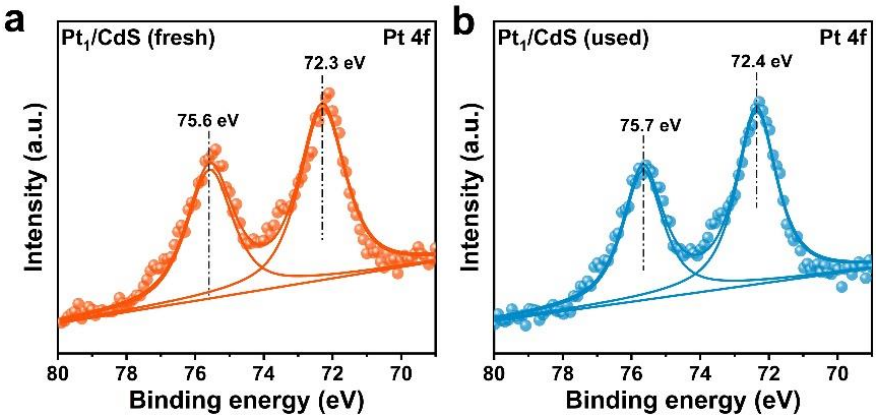
intensity drops. This phenomenon illustrates that in low humidity, H_2O adsorption sites over photocatalyst are still same with that in high humidity, while the amount of adsorbed H_2O could decrease.



Supplementary Fig. R11 The adsorption of H_2O on photocatalyst surface in high humidity **a**; the contribution of humidity to H_2O adsorption on photocatalyst surface **b**. (These data were smoothed during processing)

Comment 1.13 The lack of recognition of multiple Pt oxidation states within the interpretation of the reaction mechanism makes this difficult to grasp what the true nature of the Pt in this scheme. Which of the Pt oxidation states are responsible for the oxygen reduction? Is the Pt being reduced during this process?

Reply to reviewer: Thanks for reviewer's comment. Based on Response 1.13, we have determined that only Pt^{2+} (Pt $4f_{7/2}$ at ~72.3 eV) over Pt_1/CdS which is responsible for the oxygen reduction. Moreover, to demonstrate the stability of Pt-S configurations in photocatalysis, XPS of used Pt_1/CdS was tested. Displayed in Supplementary Fig. R12, XPS Pt 4f fine spectra were not negatively shifted while no Pt^0 species appeared after photocatalytic reaction, which indicated that Pt species were not further reduced. The involved contents have been supplemented in Page 13 line 322 of revised manuscript.



Supplementary Fig. R12 XPS Pt 4f fine spectra of fresh Pt_1/CdS **a** and used Pt_1/CdS **b**.

Comment 1.14 Can the authors comment more on their subtraction during the DRIFTS experiment and be more explicit in how to interpret the data? For example, my interpretation of the peaks is that they have desorbed all species from the heating and then began flowing gas into their chamber from 0 to 20 min. At the 20 min dark, they zeroed out their spectra and then began illuminating their samples. So, the adsorption spectra should all be positive peaks showing increases in the adsorption of the molecules as a function of time. The illumination would be positive peaks for new species, negative peaks for loss of species, and zero that show no change. Is that correct? If so, why do they see a negative peak around the 1036 cm^{-1} for CdS for the adsorption time of CH_2OH? This only seems to happen for CdS and not for any of the other samples.

Reply to reviewer: Thanks for reviewer's comments and these comments are responded in detail as follows:

(1) The specific experimental procedures of in-situ DRIFTS

In-situ DRIFTS experiments were carried out in a sealed reactor which can place sample and allow probe light to transmit. At first, background signals were collected as basic lines to zero out the spectra. Then, the reactant gas (H_2O+CH_4+ O_2) was introduced into the reactor for adsorption. During the adsorption process, DRIFTS spectra was constantly collected until the characteristic signals was not growing. Furthermore, the spectra were zeroed out for the second time and the simulated light was turned on. Then DRIFTS spectra were further recorded.

(2) The information of peaks at ~1036 cm^{-1}

We reckon that no signal appeared at around 1036 cm^{-1} over CdS during adsorption process. Spectra at 1036 cm^{-1} look negative because the signals around it are strongly positive, such as S-*CH_4 signal at around 1013 cm^{-1} and continuous bands from 1035 to 1200 cm^{-1}. The overlapping

of different signals made 1036 cm^{-1} seem negative, but it can hardly be regarded as a signal. As to why this phenomenon was only detected on CdS, we supposed it could be related with surface structure. The unsaturated sulfur over CdS might be beneficial to reactant adsorption so that the continuous band and S-*CH_4 are both stronger. But unsaturated sulfur sorely can hardly manipulate electron, so that CH_4 selective conversion under light irradiation was inhibited.

Comment 1.15 Can the authors explain the changes in the peak envelopes just below 1000 cm^{-1}? What about at 1250 cm^{-1}?

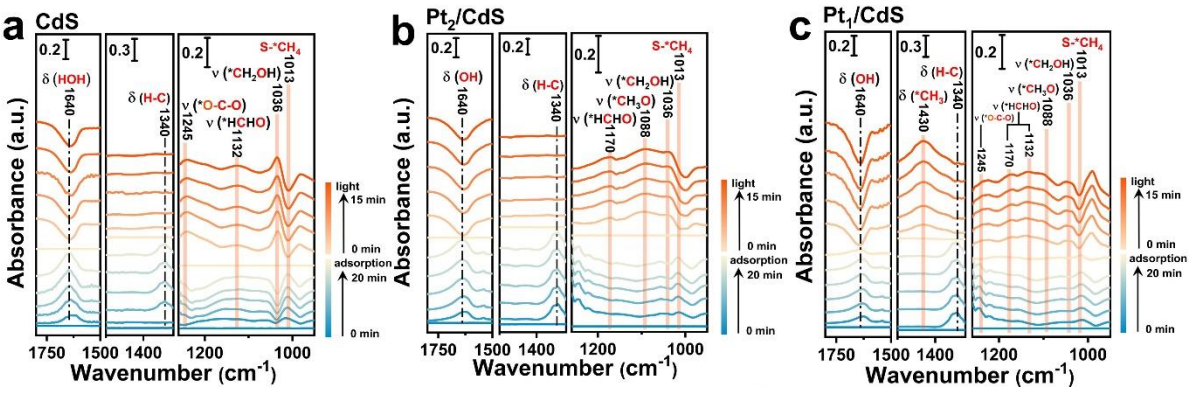
Reply to reviewer: Thanks for reviewer's comment. The responses are presented in detail as follow:

(1) The information of peaks at ~1245 cm^{-1}

The characteristic peaks at ~1245 cm^{-1} in DRIFTS are ascribed to ν(*O-C-O) (Nat. Communications, 2021, 12, 1675) which is associated with CO_2 adsorbed on photocatalysts surface. Additional descriptions on this phenomenon have been made on Page 15 line 355 of revised manuscript to respond reviewer's comment.

(2) In-situ DRIFTS below 1000 cm^{-1}

Restricted attention has been given to the signal below 1000 cm^{-1} in this work due to these two main concerns. Importantly, the signals in Infrared fingerprint area (below 1000 cm^{-1}) are generally complex and overlapping while exhibits poor characteristics. Extracting information in this region is not widely adopted (J. Am. Chem. Soc. 2025, 147, 9134-9146; Angew. Chem. Int. Ed. 2024, 63, e202408379; Nat. Commun. 2024, 15, 564). On the other hand, sufficient information about CH_4 conversion has been obtained in the region beyond 1000 cm^{-1}, so that a complete CH_4 oxidation path can be built (CH_4→CH_3OH→HCHO→CO_2) in this case. Accordingly, we presented the in-situ DRIFTS as Supplementary Fig. R13 show.

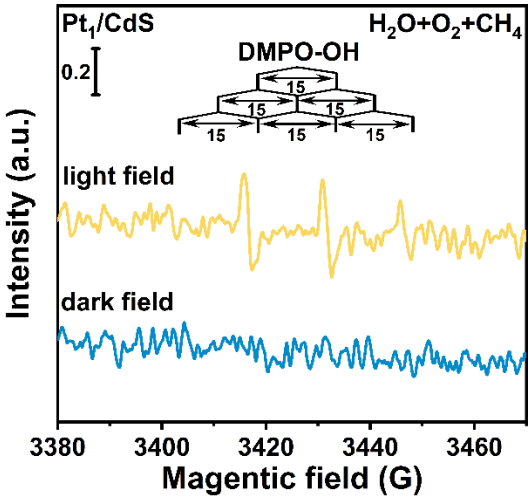


Supplementary Fig. R13 In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CdS **a**, Pt_2/CdS **b** and Pt_1/CdS **c** in the atmosphere of CH_4 + O_2 + H_2O mixture under

light irradiation: the sample surface has been fully absorbed with reactants before the light irradiation (These data were smoothed during processing).

Comment 1.16 In the ESR spectra for Pt_1/CdS under $H_2O/O_2/CH_4$, why is the highest peak at ~3400G show so little intensity?

Reply to reviewer: Thanks for reviewer's comment. Regarding this issue, we suppose it might be caused by the magnetic field or baseline fluctuations during the testing process (Supplementary Fig. R14). Although the signal is not obvious at ~3400 G, it can still be determined that ·OH has been generated. Firstly, the intensity ratio of four ·OH EPR signals is about 1:2:2:1, and highest peaks should be located at central area, corresponding to signals at around ~3415 G, and ~3430 G. Secondly, the typical EPR signal are symmetrically distributed in the spectra. As the signal at around ~3445 G is found, it can be speculated that another signal should appear at ~3400 G. Finally, the signal interval of ·OH should strictly follow that $A_N=A_H=$ 15 G, and the phenomena detected in our EPR results match with this rule. Based on these results, we determine the formation of ·OH in reaction system.



Supplementary Fig. R14 The EPR of Pt_1/CdS in the atmosphere of $H_2O+O_2+CH_4$. (These data were smoothed during processing)

Reviewer #2

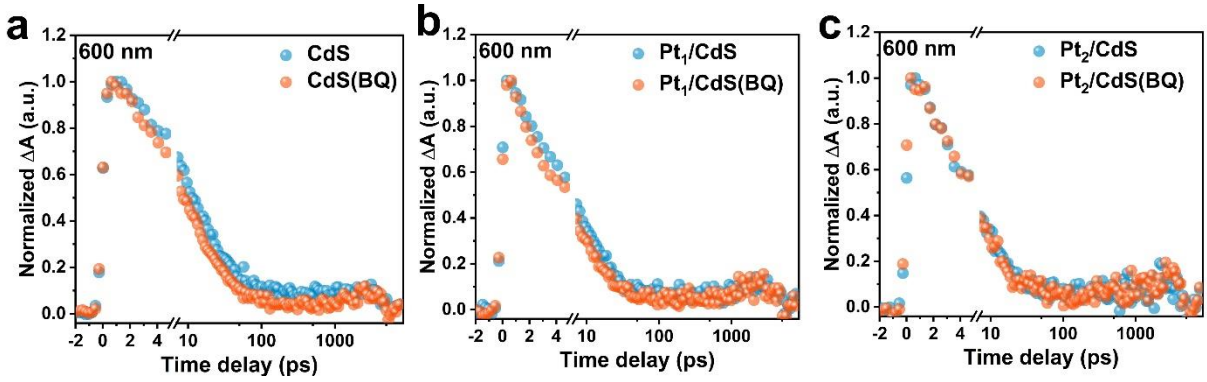
In the manuscript, authors reported a combined experimental and theoretical work to study the effects of photogenerated charge carrier manipulation in methane-to-methanol conversion by constructing multifunctional active sites. Revealed by TA, in situ XPS, etc., electron and hole were trapped in similar timescale and then further localized on Pt and unsaturated sulfur sites for the spatiotemporal control, realizing the efficiency and highly selective methane conversion. Overall, the novelty of this work is prominent, and it matches with the requirement of Nature Communications. The results presented here provide substantial evidence supporting the proposed conclusions. It is believed that the findings in this work will be of the broad interests to readers in the field of energy materials. However, there are some issues that need to be identified and addressed in the present form.

Reply to reviewer: We are grateful to reviewer for the positive and constructive suggestions. Due to space limitations in the previous version of our manuscript, we have not provided a detailed explanation of the testing objectives and procedures for the TA as well as the related analysis. In the revised manuscript, we have expanded this section (*see Response 2.1, 2.2 and 2.3*). Furthermore, band structure of samples is investigated through analyzing XPS valence band spectra, demonstrating the consistence of band edge position of CdS, Pt_1/CdS and Pt_2/CdS (*see Response 2.4*). Additional analysis of C_2 products is added in the revised manuscript (*see Response 2.5*). As to the detailed mechanism of colorimetric method (*see Response 2.6*), the necessary descriptions have been added in the manuscript. As follow, the point-to-point responses are presented in detail and we hope could meet reviewer's expectation.

Comment 2.1 Supplementary Fig. 8 displays the ultra-violet and visible diffuse reflectance spectra of samples, and it is clear that there is additional tail absorption from 500 to 800 nm, which may be associated with Pt. However, in TAS (Fig. 3), authors claimed that the bleach signals in this region should only be ascribed to CdS without considering Pt species. Please explain this phenomenon and supply necessary proof in the manuscript.

Reply to reviewer: Thanks for reviewer's comment. The TAS signals related to Pt were excluded due to the following reasons. Firstly, in our TAS tests, 400 nm pump light with pulse fluency of ~5 $\mu J \cdot pulse^{-1} \cdot cm^{-2}$ was adopted to excite samples and there was only single exciton dynamics. In this case, Pt of which the unoccupied states are far more than CdS can make scarce contributions to TAS. Besides, the BQ-trapping experiments provided additional supports to it (Supplementary Fig. R15). The bleach signals at 600 nm were not altered by BQ, and this phenomenon was same over CdS, Pt_1/CdS and Pt_2/CdS, illustrating this signal is still contributed by CdS rather than Pt. To

respond reviewer's comment, the descriptions on these phenomena have been supplemented in our revised manuscripts and Supplementary information so that it can enhance reader's comprehensions (In revised manuscript Page 9 line 215 and revised Supplementary Information Page 14 line 129).



Supplementary Fig. R15 The kinetic decay curves at 600 nm to determine the contribution of p-benzoquinone (BQ) to excited-state carrier relaxation: CdS **a**, Pt_1/CdS **b**, Pt_2/CdS **c**.

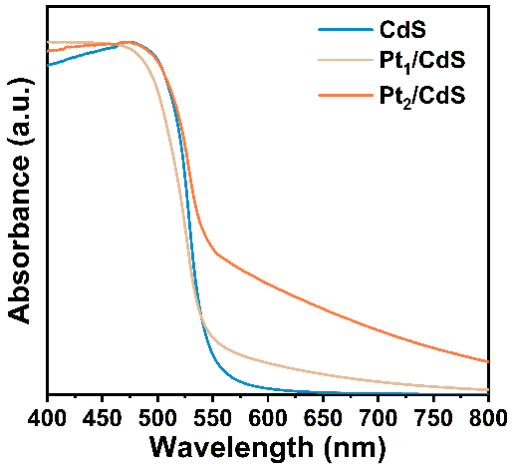
Comment 2.2 As to photodynamics in Fig. 3 d-f, the conclusion "τ_2 at 397.0 ps is only featured with GSB and tail bleach has been completely removed. It demonstrates the hole on interband state is further trapped and τ_2 should be ascribed to the intrinsic recombination of CdS" needs to be further identified. The recombination of excited electron with trapped hole can also promote the decline of tail bleach, so why τ_2 was ascribed to band edge recombination and secondary trapping?

Reply to reviewer: Thanks for reviewer's comment. Taking CdS as an example, it is noted that under light irradiation, in-situ XPS binding energy is positively shifted, indicating the hole localization on the surface. Thus, it is reasonable to speculate that the trapped hole are not recombined and they own prolonged lifetime so that can be further transferred and localized on unsaturated sulfur site. Moreover, the trapped carrier generally own longer lifetime (ACS Nano 2021, 15, 2, 2281-2291; Angew. Chem. Int. Ed. 2021, 60, 20811-20816), and the timescale for its recombination could be beyond the time-window of TAS. Taking these factors into consideration, we ascribe τ_2 to band-edge recombination process.

Comment 2.3 In terms of time-resolved spectroscopies, authors claimed the influence of pump laser pulse fluency on photodynamics, which standardized the whole process; simultaneously, it was also noticed that the wavelength of pump laser was set to 400 nm. Why did authors choose this parameter and please explain it in the manuscript.

Reply to reviewer: Thanks for reviewer's comment. According to the steady-state absorption of CdS, Pt_1/CdS and Pt_2/CdS, the intrinsic absorption for 400 nm proton were prominent over three

sample (Supplementary Fig. R16). Thus 400 nm pump light can well excite the sample to produce photogenerated carriers. Moreover, carriers excited by 400 nm pump light can cool down to band edge so that visible probe light can also detect them. Besides, from the perspective of instrument, 400 nm pump laser source is stable and sufficient over most of laser source, which is the preconditions for high-quality TAS signals. Referenced on the reported works, 400 nm pump light were commonly used for CdS-based materials TAS signal collection (J. Am. Chem. Soc. 2023, 145, 40, 21886–21896; Angew. Chem. Int. Ed. 2023, 62, e202218688; J. Am. Chem. Soc. 2015, 137, 10224-10230). To illustrate the necessity of 400 nm pump light, additional revisions have been supplemented in revised manuscript (in revised manuscript Page 19 line 485).

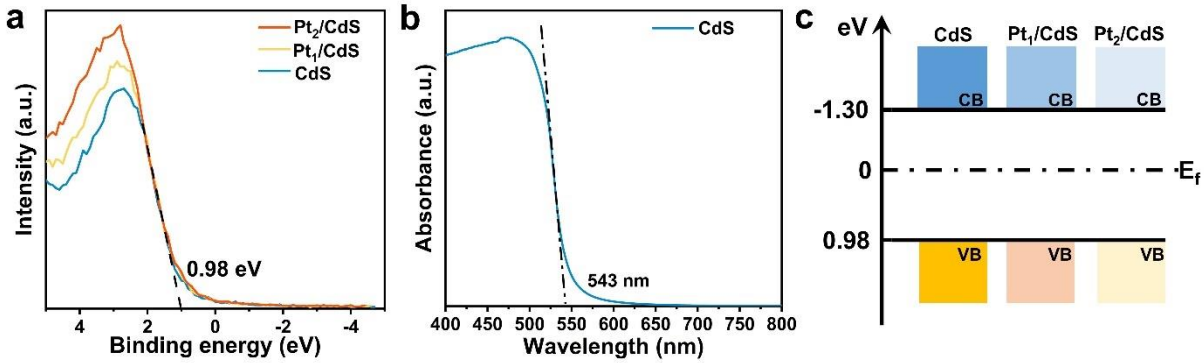


Supplementary Fig. R16 Ultraviolet-visible diffuse and reflectance (UV-vis DRS) spectra of CdS, Pt_1/CdS and Pt_2/CdS.

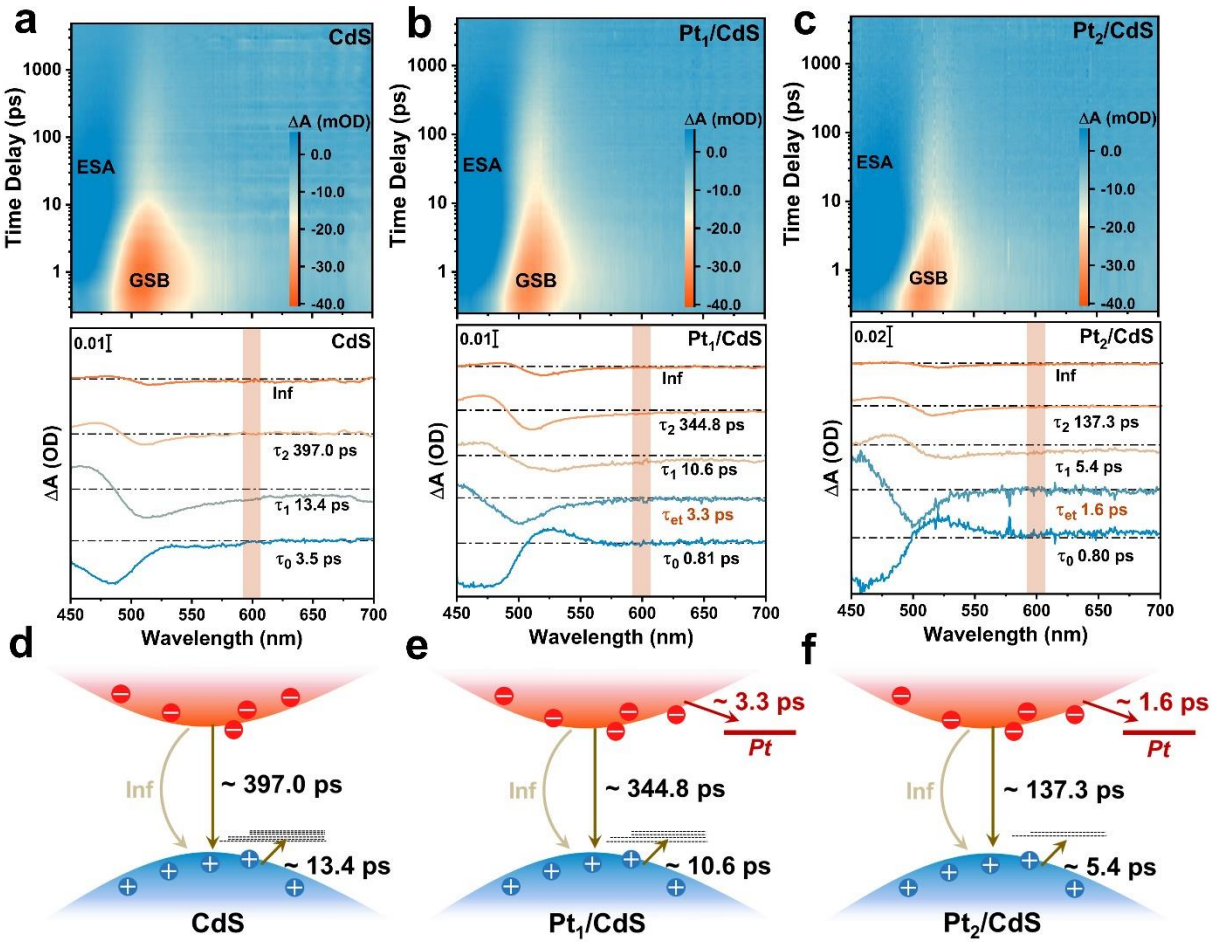
Comment 2.4 Photodynamics revelations demonstrated the importance of active sites, but authors hardly mentioned the influence of Pt to band structure of photocatalysts. In this case, it is advised to depict the valence band and conduction band position of CdS, Pt_1/CdS and Pt_2/CdS, which is imperative to discuss carrier behavior from the perspective of thermodynamics.

Reply to reviewer: Thanks for reviewer's comment. The band structure of CdS, 1%Pt/CdS and 2%Pt/CdS was necessarily investigated through determining the valance band position from XPS. As displayed in Supplementary Fig. R17, the intersection points of the tangent line with the coordinate axis are almost identical among CdS, 1%Pt/CdS and 2%Pt/CdS, illustrating that the valence band position of CdS were not altered with the introduction of Pt. Moreover, in TAS (Supplementary Fig. R18), the ground-state bleach signal of CdS, Pt_1/CdS and Pt_2/CdS were both probed by ~505 nm light, demonstrating their same band gap. Accordingly, we conclude that the band structure of substrate materials are not influenced by Pt which mainly plays a role in photogenerated carrier manipulation. To respond reviewer's suggestion, additional descriptions on

photocatalyst band structure have been supplemented in revised manuscript (in revised manuscript Page 8 line 195).



Supplementary Fig. R17 XPS valence band spectra of CdS, Pt_1/CdS and Pt_2/CdS **a**; the absorption edge of CdS **b**; the band structure of CdS, Pt_1/CdS and Pt_2/CdS **c**.



Supplementary Fig. R18 Transient absorption spectroscopy (TAS) where 400 nm beam light was used as pump light and a continuous white light ranging from 450 to 700 nm was used as probe light: two-dimensional contour plots of TAS with the associated global fitting results of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c**. The diagram exhibiting the excited-state carrier relaxation of CdS **d**, Pt_1/CdS **e** and Pt_2/CdS **f**.

Comment 2.5 Apart from the mentioned C_1 products, were C_2H_6 or C_2H_4 also detected in current system?

Reply to reviewer: Thanks for reviewer's comment. Supplementary Table R1 summarizes the photocatalytic CH_4 oxidation reactions over CdS and Pt_x/CdS (X=0.5~2.0) where Pt_1/CdS exhibited prominent performance in CH_3OH selective production. To respond reviewer's suggestions, we further scrutinized the C_2 products, including C_2H_6, C_2H_4 and CH_3OH in our system and Pt_1/CdS was used as photocatalyst. Based on the data recorded in gas chromatograph, no any C_2 products have been found. There results and related discussions have been added to the revised manuscript (On page 13 line 305 of revised manuscript).

Supplementary Table R1 CH_4 conversion rate and product generation rate.

Samples	CH_3OH production rate ($\mu mol \cdot g^{-1} \cdot min^{-1}$)	HCHO production rate ($\mu mol \cdot g^{-1} \cdot min^{-1}$)	CO_2 production rate ($\mu mol \cdot g^{-1} \cdot min^{-1}$)	The average selectivity of CH_3OH (%)
CdS	5.07	2.37	0.69	62.3
$Pt_{0.5}$/CdS	7.65	2.09	0.49	74.8
Pt_1/CdS	12.72	2.13	0.39	83.5
$Pt_{1.5}$/CdS	9.54	2.11	0.48	78.7
Pt_2/CdS	7.88	2.71	0.41	71.7

Comment 2.6 HCHO was detected using colorimetric method, the fundamental mechanism of colorimetric method is suggested to be supplied in the manuscript.

Reply to reviewer: Thanks for reviewer's comment. HCHO owns electrophilic properties and it can react with pentane-2,4-dione to form colored substances. In the presence of ammonium salts (such as ammonium acetate), HCHO undergoes a condensation reaction with pentane-2,4-dione to form yellow 3,5-diacetyl-1,4-dihydro-2,6-lutidine (DDL) which has a characteristic absorption peak at 412 nm (HCHO + pentane-2,4-dione + $NH_4^+ \rightarrow$ DDL + H_2O). By measuring DDL, HCOH amount can be determined. The specific experimental procedures of colorimetric method include: Firstly, colorimetric reagent solution was prepared through dissolving 15 g ammonium acetate, 0.3 mL of acetic acid and 0.2 mL pentane-2,4-dione in 95.5 mL deionized water. Secondly, 0.5 mL liquid in photocatalytic reactors and 0.5 mL of colorimetric reagent solution was dissolved in 2.0 mL deionized water, and then maintained at 80°C for 10 mins with water bath. Furthermore, the ultra-violet and visible absorption spectroscopy of the mixed liquid was measure. The absorbance at 412

nm is proportional to the concentration of HCHO in the liquid. Finally, to well exhibit the procedure and mechanism of colorimetric method, we supplemented the contents above in experimental sections (In revised manuscript Page 21 line 560).

Reviewer #3

In this manuscript, the authors used CdS-supported Pt catalyst to realize the photocatalytic oxidation of methane to methanol, a significant topic. The CH_3OH production rate over the optimal catalyst reaches 12.7 $\mu mol \cdot g^{-1} \cdot min^{-1}$ with a selectivity of 83.5%. My comments are given as follows:

Reply to reviewer: Thanks for pointing out the issues that need to be addressed in the manuscript. In response to reviewer's concerns with the photostability and the coordination environment of photocatalyst, additional tests have been carried out. In specific, the photocatalytic durability of our best sample was explored by conducting cycle experiments and analyzing the XPS of used sample (*see Response 3.6 and 3.7*). The stable CH_3OH production and selectivity can be observed in three rounds while no photocorrosion was found over used sample. Moreover, the local coordination of Pt in 2%Pt/CdS was disclosed by fitting data in R-space with a proposed configuration (*see Response 3.2 and 3.3*). Pt in 2%Pt/CdS is still coordinated with S atom, which is close to that of 1%Pt/CdS. In addition, the role of Pt in carrier dynamics modulation and reaction path determinations have been further illustrated (*see Response 3.4 and 3.5*). As follow, the point-to-point responses have been presented in detail.

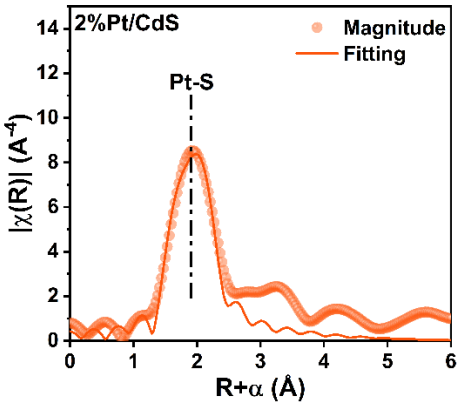
Comment 3.1 What is the oxidant for methane oxidation? In the experimental section, the authors only introduced CH_4 into the reactor without any oxidant. Did they used some solvent (e.g., H_2O) or other sacrificial agent?

Reply to reviewer: Thanks for reviewer's comments. For our photocatalytic evaluation experiments, the sealed glass photoreactor was poured photocatalyst-dispersed solution and then exhausted with diluted oxygen gas (10 vol% in N_2 gas) and 5 mL CH_4. The reactants for our experiments included O_2, H_2O and CH_4. Among them, O_2 worked as oxidant to promote CH_4 conversion to CH_3OH, while H_2O was used to disperse photocatalyst and provide protons for ·OH formation ($O_2 + e^- \rightarrow \cdot O_2^-$, $\cdot O_2^- + H^+ \rightarrow \cdot OOH$, $\cdot OOH + H^+ + e^- \rightarrow \cdot OH$).

Comment 3.2 The authors used Pt to modify CdS with different contents. What are the structures of 1%Pt/CdS and 2%Pt/CdS? Only one sample was provided in EXAFS spectrum (Fig. 2c) and fitting (Supplementary Table 2). What is the local coordination structure of 2%Pt/CdS?

Reply to reviewer: Reviewer's comments are really appreciated. In response to reviewer's suggestions, the coordination environment of 2%Pt/CdS was investigated through fitting the EXAFS in R space as displayed in Supplementary Fig. R19. Pt in 2%Pt/CdS was also coordinated with S (~2.3 Å) in the first shell while only Pt-S contribution could be observed in R space. It is speculated that with the increasing of Pt amount, the coordination environment becomes homogeneous and regular. Necessary revisions have been made on Page 8 line 180 of revised

manuscript and Page 37 of revised supplementary information.



Supplementary Fig. R19 R-space fitting results for 2%Pt/CdS (The R-space data are presented without phase correction)

Supplementary Table R2 Curve-fit parameters of Pt L_3-edge EXAFS of 2%Pt/CdS based on optimized crystal model.

	S_0^2	δ^2	E_0 (eV)	R (Å)	N	R-factor
Pt-S¹	0.98	▮	6.313	2.22	1.35	0.016
Pt-S²		▮		2.38	2.53	

Comment 3.3 In Supplementary Table 2, Pt was mistakenly written as "Pd". Pt atoms are coordinated with both Cd and S atoms. However, the scheme of the structure given in Fig. 2g shows that Pt only coordinates with S atom. I am wondering that how the Pt atoms are anchored with CdS, will Pt atoms replace some Cd, or dope as interstitial atoms?

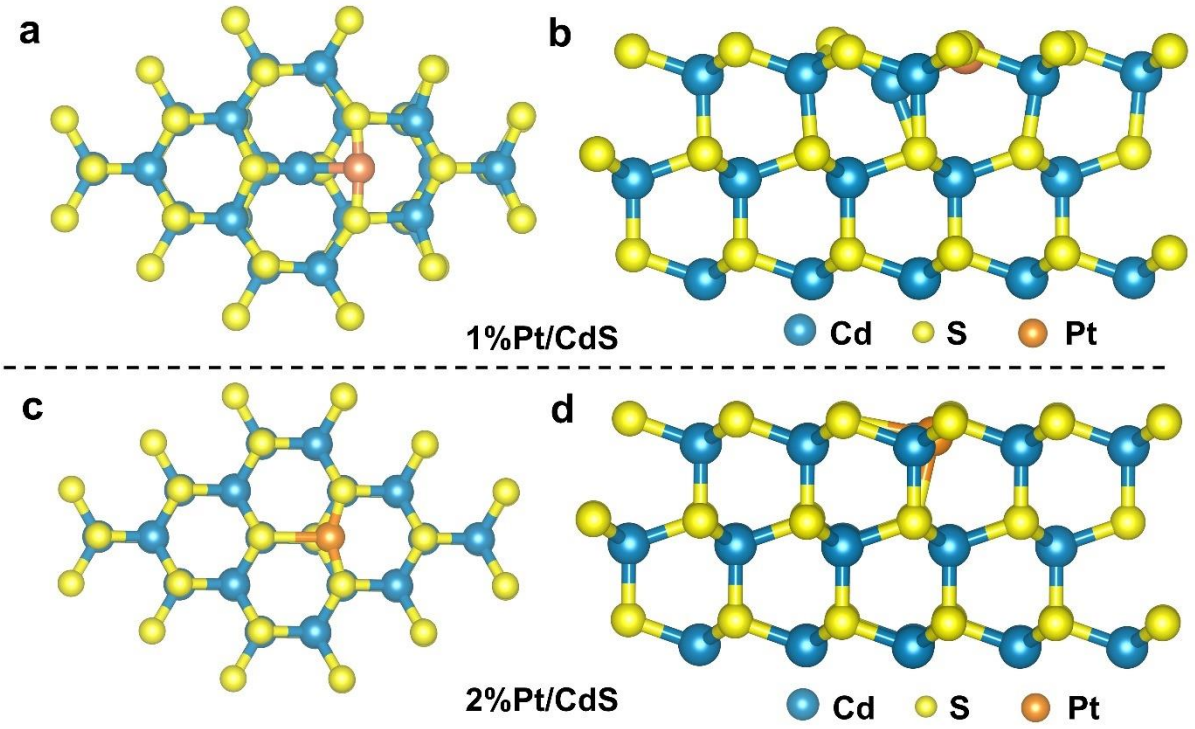
Reply to reviewer: Thanks for reviewer's comments and these comments are responded in detail as follows:

(1) Optimizing the expression for chemical element

We apologize for labelling element Pt as Pd in the last version of manuscript and it is sincerely appreciated for reviewer to point it out. In the revised manuscript and Supplementary Information, all the contents have been comprehensively checked so that the key points can be accurately delivered to readers.

(2) The coordination of Pt in 1%Pt/CdS in Fig. 2g

The contribution of Pt-Cd was observed in the second shell for 1%Pt/CdS while there is no any Pt-Pt of Pt-O contribution. Fig. 2g in the last version of manuscript displayed the coordination of Pt in Pt_1/CdS but the top view can hardly display all details. In this regard, the coordination of Pt was also shown from other views as Supplementary Fig. R20 show. Revisions have been made on



Supplementary Fig. R20 The top view and side view of proposed 1%Pt/CdS **a** and 2%Pt/CdS **b** configurations.

(3) The way that Pt atoms are anchored with CdS

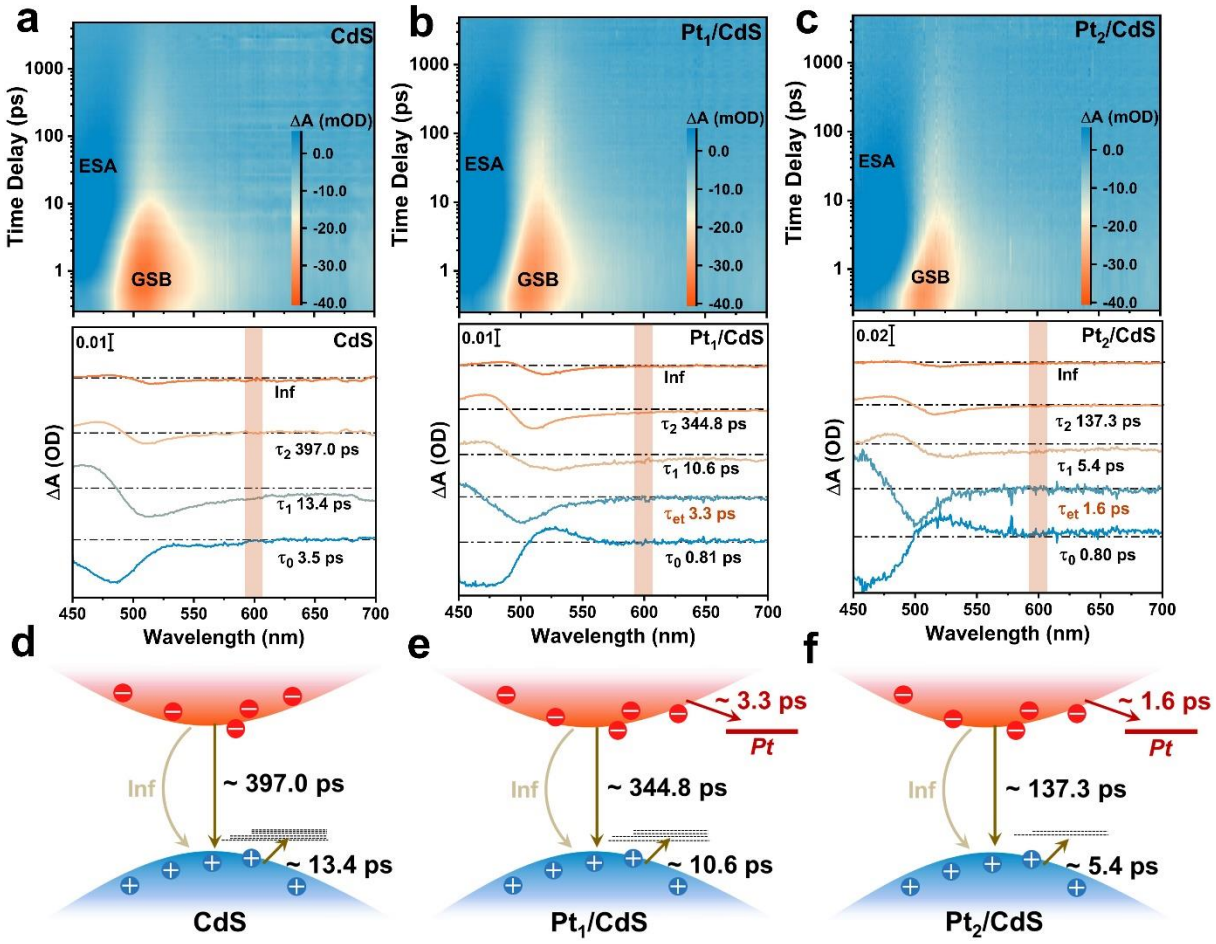
To investigate the way that Pt was anchored on CdS, the atomic ratio over CdS, Pt_1/CdS and Pt_2/CdS was scrutinized through XPS. As shown in Supplementary Table R3, Cd ratio was gradually decreased over Pt_1/CdS and Pt_2/CdS, while sulfur ratio was increased. Thus, it can be concluded that Pt has replaced a part of Cd to formed Pt-S configuration. The phenomenon also matches with the detected Pt-Cd coordination in the second shell, arising from crystal structure deformation.

Supplementary Table R3 The Cd, S and Pt atomic ratio on the surface of CdS, 1%Pt/CdS and 2%Pt/CdS.

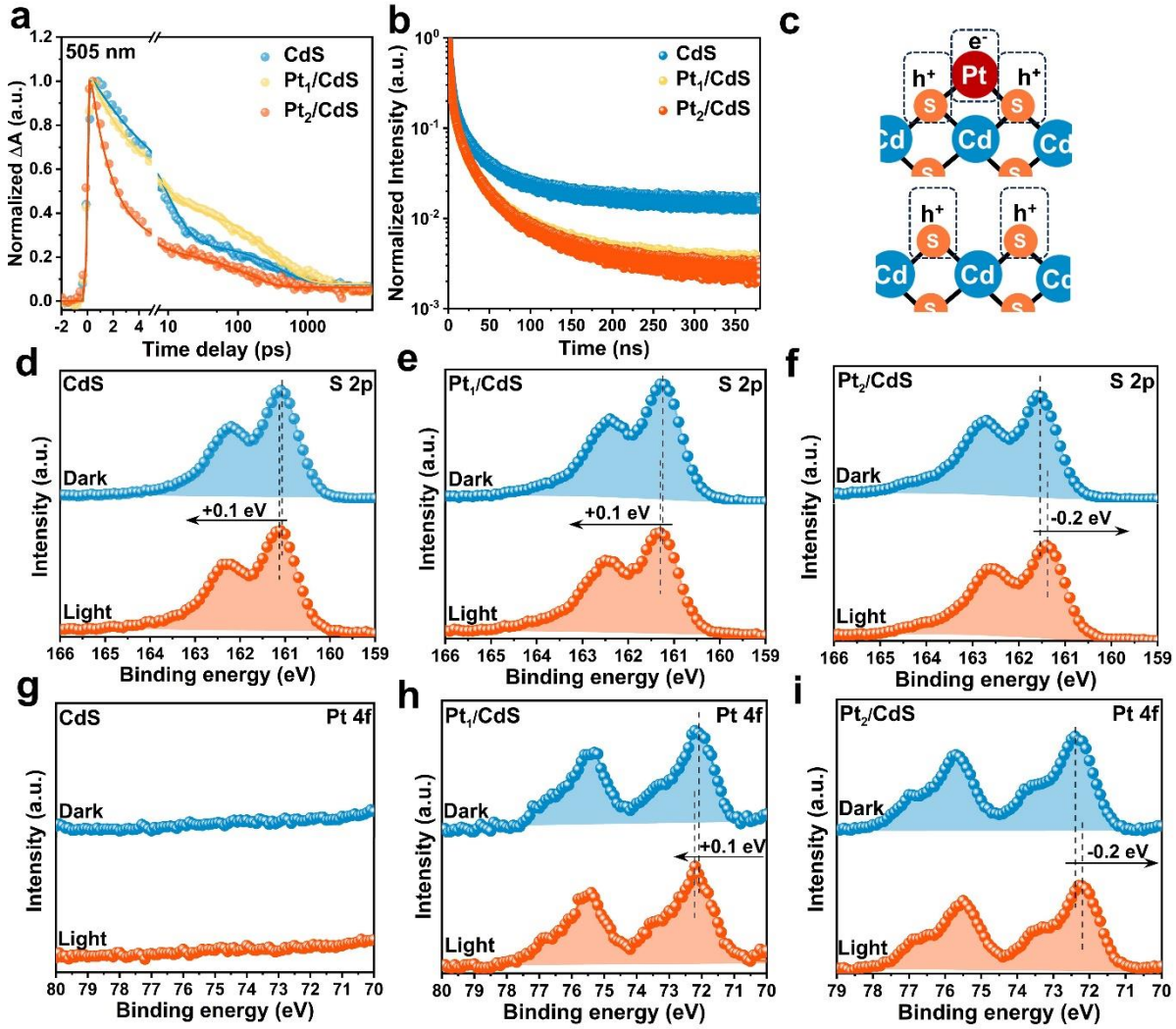
	Samples		
	CdS	1%Pt/CdS	2%Pt/CdS
Cd	48.1	45.6	43.0
S	51.9	53.1	54.3
Pt	0	1.3	2.7

Comment 3.4 The catalytic performance of 1%Pt/CdS and 2%Pt/CdS are strongly different. 2%Pt/CdS tends to catalyze methane to HCHO, CH_3OH and CO_2, while 1%Pt/CdS favors the selective formation of methanol. What is the reason?

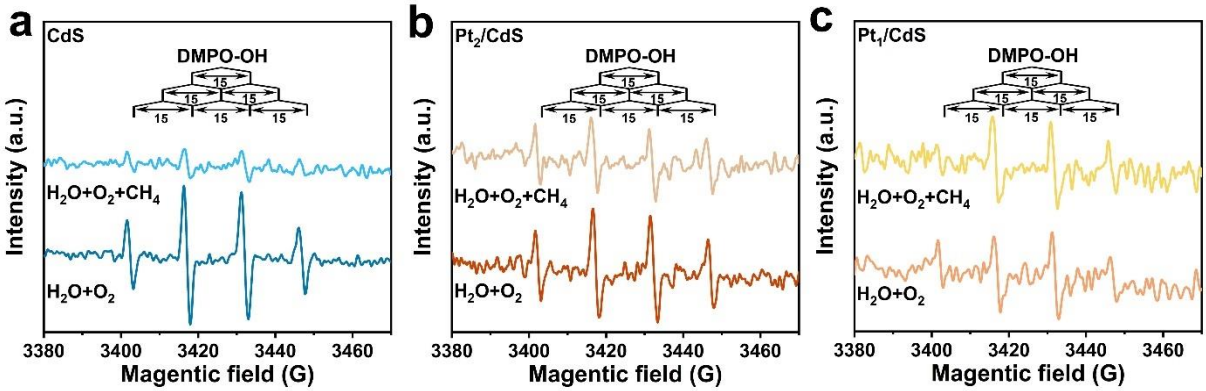
Reply to reviewer: Thanks for reviewer's comment. According to transient absorption spectroscopy (in Supplementary Fig. R21) and in-situ XPS (in Supplementary Fig. R22), unsaturated sulfur and Pt sites can separately trap hole and electron, then further localizing them on photocatalyst surface. For Pt_1/CdS, in-situ EPR indicated that ·OH formation sites and CH_4 activation site are separated, as when CH_4 was introduced into system, the detected ·OH amount were not decreased (in Supplementary Fig. R23). Then, based on DFT calculation (in Supplementary Fig. R24), it can be noted that CH_4 should be preferably anchored on unsaturated sulfur sites, which also indicated that O_2 should be reduced over Pt sites to form ·OH. Such as a reaction process is closely like bio-enzyme to catalyze CH_4 to CH_3OH, and it boosts overall efficiency. However, over Pt_2/CdS, the excessive Pt has changed the reaction path. In in-situ EPR, the introduction of CH_4 in system decreased the detected ·OH amount, illustrating the overlapping of CH_4 activation sites and ·OH formation sites. Considering that Pt has dominated Pt_2/CdS surface, CH_4 activation and ·OH formation could both be carried on Pt sites. Such a process promotes CH_3OH overoxidation to HCHO and CO_2.



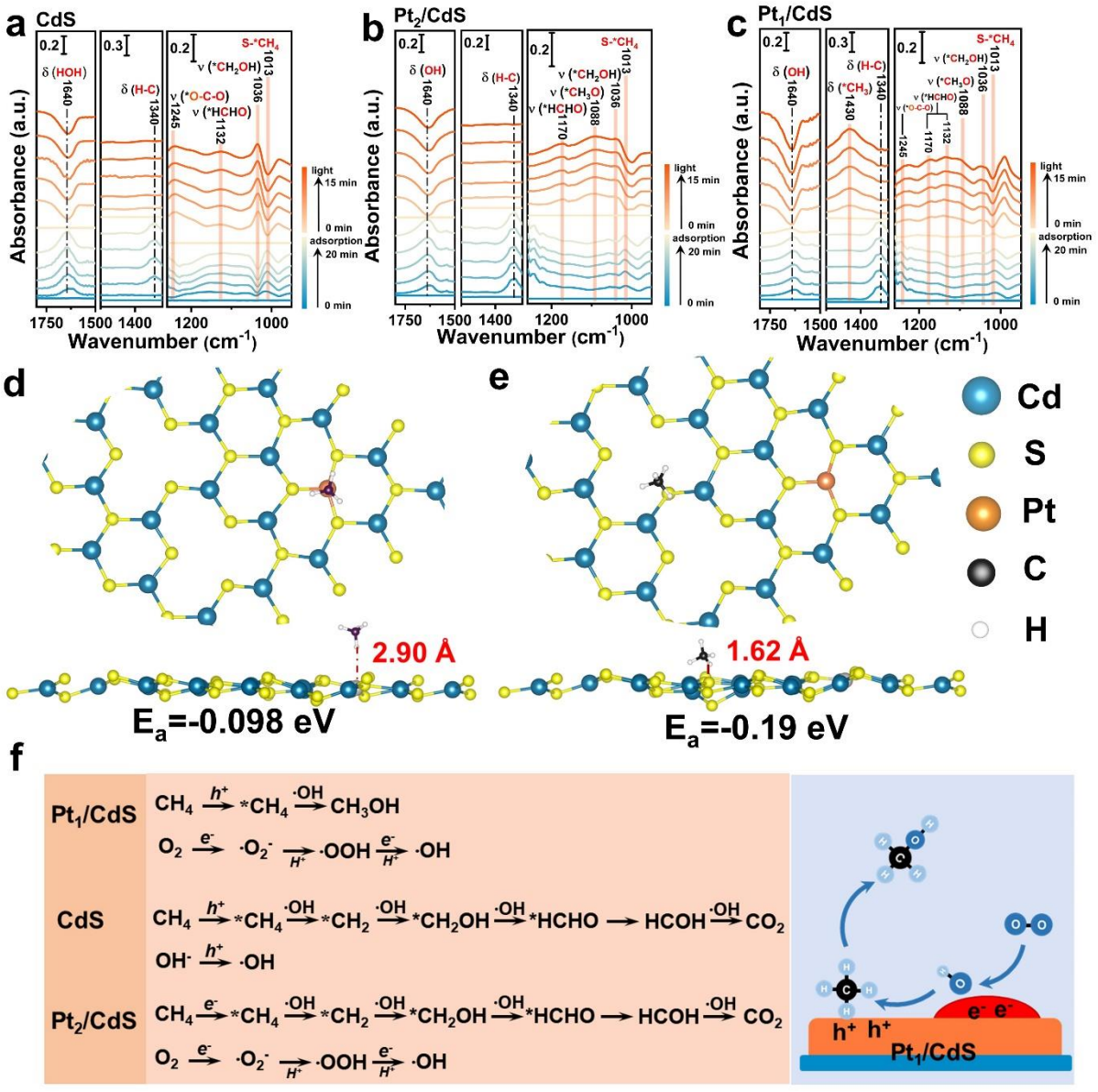
Supplementary Fig. R21 Transient absorption spectroscopy (TAS) where 400 nm beam light was used as pump light and a continuous white light ranging from 450 to 700 nm was used as probe light: two-dimensional contour plots of TAS with the associated global fitting results of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c**. The diagram exhibiting the excited-state carrier relaxation of CdS **d**, Pt_1/CdS **e** and Pt_2/CdS **f**.



Supplementary Fig. R22 TAS kinetic decay curves at 505 nm of CdS, Pt_1/CdS and Pt_2/CdS: the scatter plots are experimental data and linear plots are the corresponding fitting curves **a**. Time-resolved photoluminescence (TRPL) spectra of CdS, Pt_1/CdS and Pt_2/CdS **b**. A diagram showing the carrier distribution on photocatalyst surface **c**. High-resolution X-ray photoelectron Pt 4f and S 2p fine spectra in dark and light field: CdS **d&g**, Pt_1/CdS **e&h** and Pt_2/CdS **f&i**.



Supplementary Fig. 23 In-situ electron paramagnetic resonance (EPR) spectroscopy of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c** under different testing conditions (These data were smoothed during processing).



Supplementary Fig. 24 In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CdS **a**, Pt_2/CdS **b** and Pt_1/CdS **c** in the atmosphere of CH_4 + O_2 + H_2O mixture: the sample surface has been fully adsorbed with reactants before the light irradiation (These data were smoothed during processing). Geometry optimized configuration of CH_4 adsorbed on Pt sites **d** and unsaturated sulfur sites **e.** Schematic diagram illustrating the CH_3OH production through stepwise reaction path **f**.

Comment 3.5 What is the role of Pt for methane oxidation? It seems that the introduction of Pt suppresses the migration of photogenerated carriers (Supplementary Fig. 15). The photocurrent of CdS is much higher than that of Pt_1/CdS and Pt_2/CdS. It is contradictory to the most reported cases.

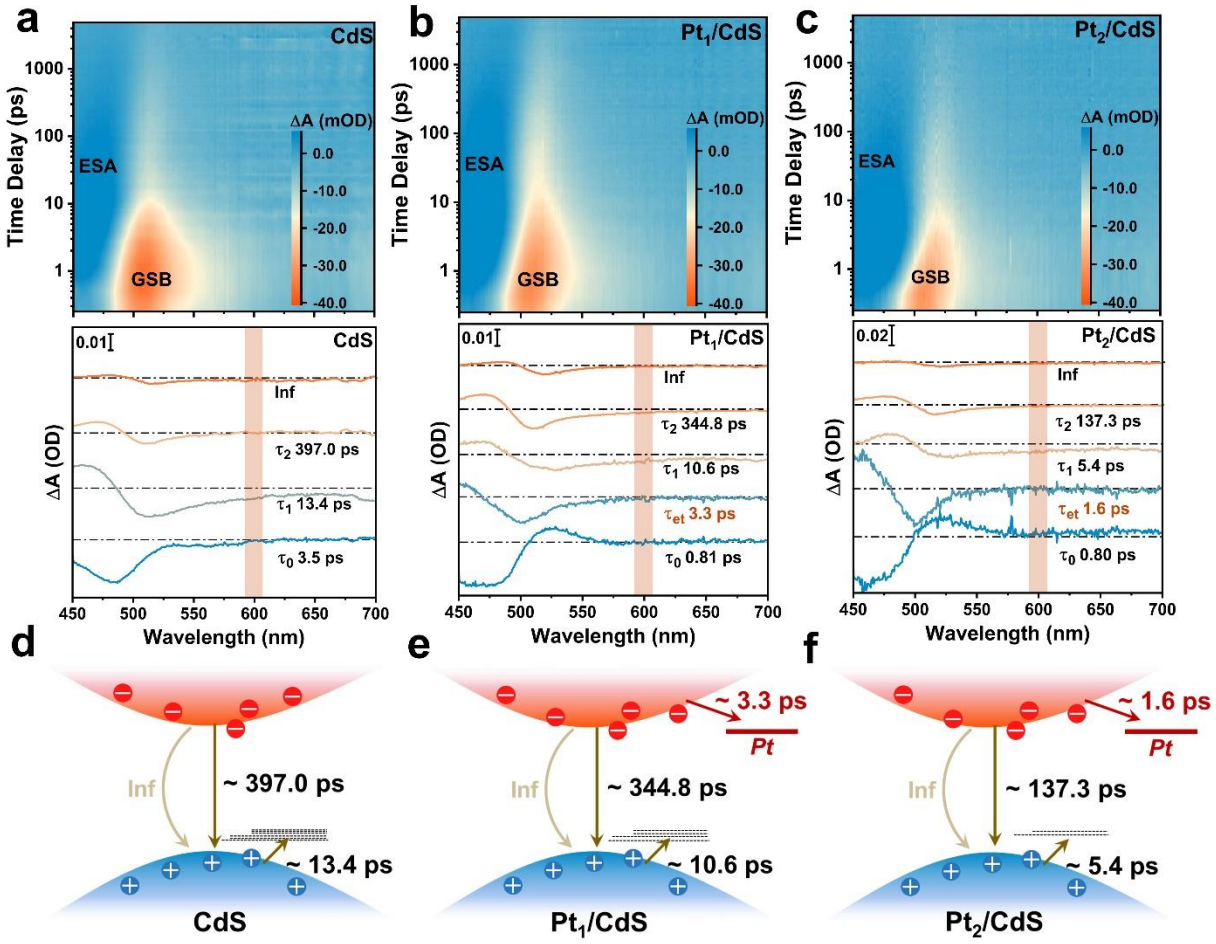
Reply to reviewer: Thanks for reviewer's comment. Our responses are presented in detail as follows:

(1) The role of Pt in methane oxidation

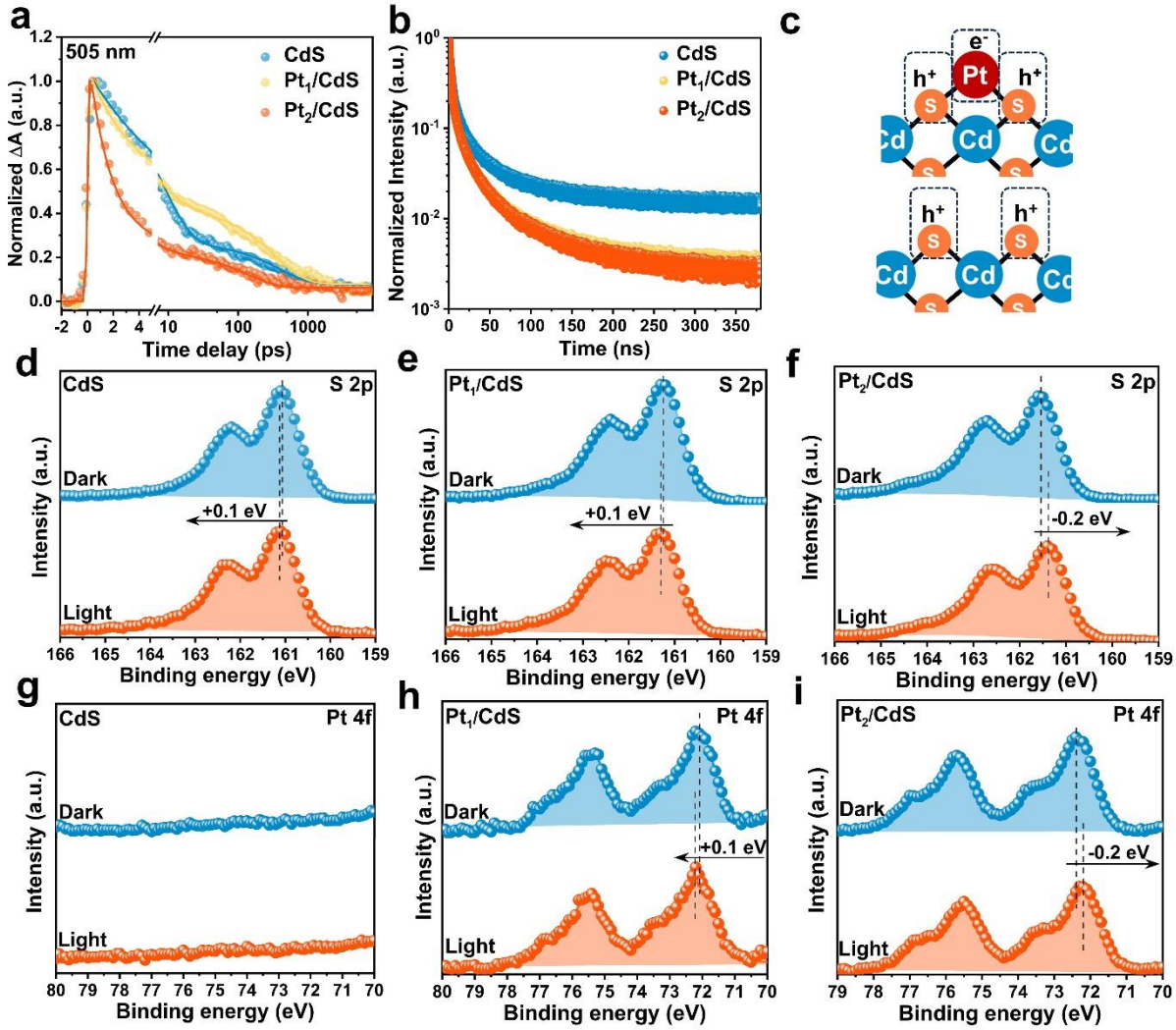
Pt mainly works as active site to modulate electron behavior while preferably adsorb O_2 to prevent the overlapping of ·OH formation sites and CH_4 activation sites so that overoxidation can be inhibited. In specific, based on excited-state dynamics studying (Supplementary Fig. R25-R27), it is demonstrated that Pt can trap electron in picosecond timescale (~3.3 ps) and further localize electron in the timescale equal to surface reactions. During the surface reaction, O_2 is preferably adsorbed on Pt and conversed to ·OH through electron-injection (see more details in Response 3.4) while CH_4 is adsorbed and activated on unsaturated sulfur sites. Finally, ·OH combine with activated CH_4 to form CH_3OH.

(2) The lower photocurrent intensity over 1%Pt/CdS and 2%Pt/CdS

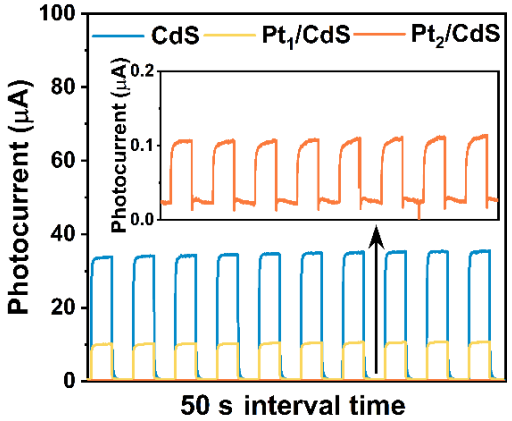
This phenomenon might be induced by strong electron trapping of Pt. In transient photocurrent response (Supplementary Fig. R27), the positive photocurrent observed over CdS, Pt_1/CdS and Pt_2/CdS indicated the electron transfer from working electrode to counter electrode under artificial light irradiation. Due to the strong electron trapping of Pt, rapid electron transfer into external circuit over Pt_1/CdS and Pt_2/CdS was obviously inhibited. Same phenomena were also reported and discussed in recent work (Nat. Sustain. 2024, 7, 1171-1181) which also considered the electron trapping to decreased photocurrent.



Supplementary Fig. R25 Transient absorption spectroscopy (TAS) where 400 nm beam light was used as pump light and a continuous white light ranging from 450 to 700 nm was used as probe light: two-dimensional contour plots of TAS with the associated global fitting results of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c**. The diagram exhibiting the excited-state carrier relaxation of CdS **d**, Pt_1/CdS **e** and Pt_2/CdS **f**.



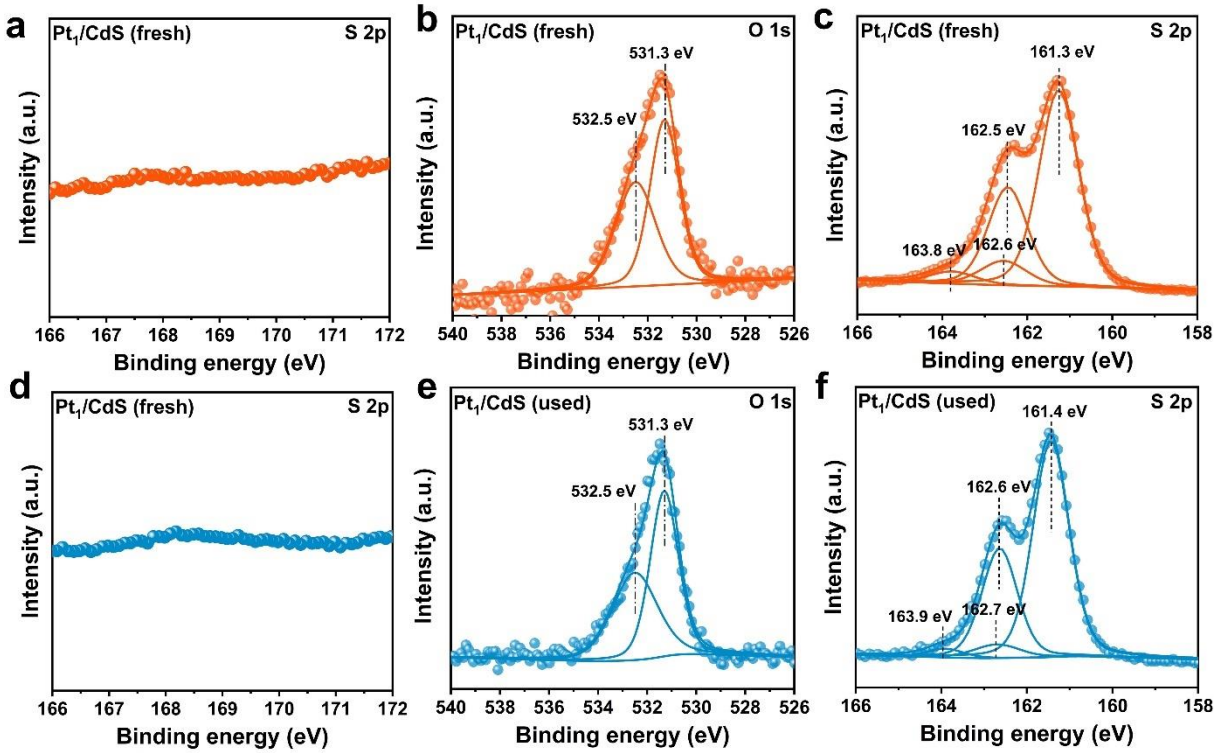
Supplementary Fig. R26 TAS kinetic decay curves at 505 nm of CdS, Pt_1/CdS and Pt_2/CdS: the scatter plots are experimental data and linear plots are the corresponding fitting curves **a**. Time-resolved photoluminescence (TRPL) spectra of CdS, Pt_1/CdS and Pt_2/CdS **b**. A diagram showing the carrier distribution on photocatalyst surface **c**. High-resolution X-ray photoelectron Pt 4f and S 2p fine spectra in dark and light field: CdS **d&g**, Pt_1/CdS **e&h** and Pt_2/CdS **f&i**.



Supplementary Fig. R27 Transient photocurrent response of CdS, Pt_1/CdS and Pt_2/CdS (embedding picture shows the enlarged Pt_2/CdS photocurrent image).

Comment 3.6 CdS tends to be oxidized under light irradiation. The authors should give the data of the spent photocatalyst to verify its stability.

Reply to reviewer: Thanks for reviewer's comments. In response to reviewer's suggestions, XPS of used Pt_1/CdS was recorded to verify the structural stability of photocatalyst. Typically, the oxidized CdS should be feathered with the appearance of SO_4^{2-} and lattice oxygen signals in XPS. In Supplementary Fig. R28, SO_4^{2-} signals at ~168.0 eV (J. Am. Chem. Soc. 2021, 143, 6533−6541) and lattice oxygen (ACS Catal. 2024, 14, 10, 7788-7794) at ~ 530.0 eV were both absent over used Pt_1/CdS. The prominent signals in S 2p are still indexed to S^{2-} in crystal ($2p_{3/2}$ at ~161.3 eV, $2p_{1/2}$ at ~162.5 eV) and unsaturated sulfur ($2p_{3/2}$ at ~162.4, $2p_{1/2}$ at ~163.6 eV). Above results exclude the photocorrosion and sample's stability is verified. In revised manuscript, additional descriptions on XPS of used photocatalyst have been supplemented (in Page 13 line 318 of revised manuscript).

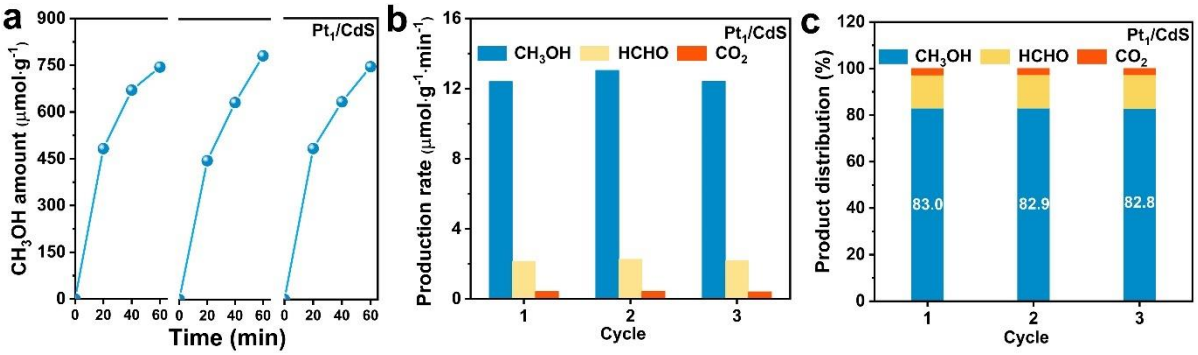


Supplementary Fig. R28 XPS S 2p for SO_4^{2-} **a,** O 1s **b** and XPS S 2p for S^{2-} **c** of fresh Pt_1/CdS; XPS S 2p for SO_4^{2-} **d,** O 1s **e** and XPS S 2p for S^{2-} **f** of used Pt_1/CdS.

Comment 3.7 The authors are suggested to test the long-term durability test for 1%Pt/CdS.

Reply to reviewer: Thanks for reviewer's comments. The cycle experiments have been carried out in this work to characterize the long-term stability of Pt_1/CdS. Displayed in Supplementary Fig. S29, similar CH_3OH production rate was observed in the first three rounds and the corresponding

product selectivity are also close, indicating its photocatalytic stability in 360 min. In revised manuscript, additional descriptions on cycle experiments have been supplemented (on Page 13 line 316 of revised manuscript).



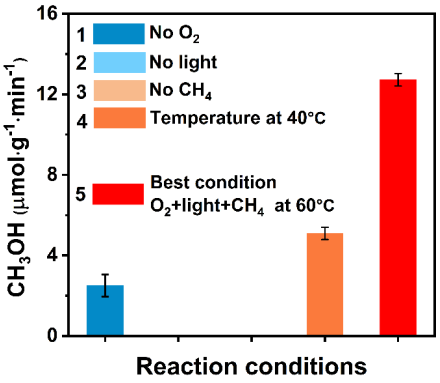
Supplementary Fig. R29 Photocatalytic CH_4 to CH_3OH cycle experiments over Pt_1/CdS: the influence of cycle number to CH_3OH production rate **a**; the statistic average production rate of different products **b** and photocatalytic products distributions **c**.

Comment 3.8 In Fig. 6f, the author gave the detailed reaction pathways of 1%Pt/CdS and 2%Pt/CdS for methane conversion. I think they should provide more evidences. For example, no signals of O_2^- radicals were observed in EPR, but which were involved in the pathway. Same radicals were involved for methane oxidation over Pt_1/CdS and Pt_2/CdS ($\cdot OH$ and $\cdot O_2^-$), why the reaction pathways are greatly different?

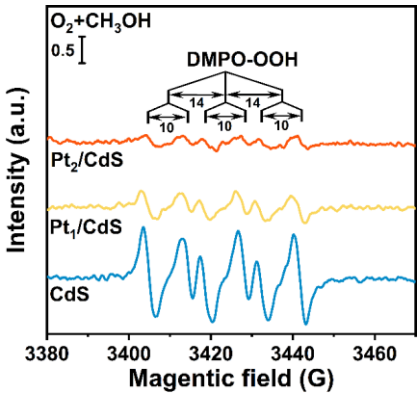
Reply to reviewer: Thanks for reviewer's comment. Our responses to reviewer's comment are presented in detail as follows:

(1) The demonstrations on $\cdot O_2^-$ radicals in reaction path.

Based on photocatalytic contrast experiments showed in Supplementary Fig. R29, O_2 was crucial to efficient CH_3OH formation. As oxidant, O_2 was firstly reduced to $\bullet O_2^-$ radicals and then to $\cdot OOH$ and $\cdot OH$ ($O_2 + e^- \rightarrow \cdot O_2^-$, $\cdot O_2^- + H^+ \rightarrow \cdot OOH$, $\cdot OOH + H^+ + e^- \rightarrow \cdot OH$) which is the active oxygen species in CH_4 conversion. The above reaction paths were widely considered in previous works (ACS Catal. 2024, 14, 955-964; Angew. Chem. Int. Ed. 2024, 63, e202408379; Nat. Commun. 2023, 14, 2690). Importantly, although no signal of $\cdot O_2^-$ and $\cdot OOH$ radicals were observed in EPR, we reckoned it results from the rapid radical hydrogenation and relatively excessive $\cdot OH$ signals, which weakened the signals of $\cdot O_2^-$ and $\cdot OOH$. To demonstrate the existence of $\cdot O_2^-$ and $\cdot OOH$ in our system, we dispersed samples in aerobic methanol ($CH_3OH + O_2$) where CH_3OH can remove $\cdot OH$ and exaggerate $\cdot OOH$ signal. In Supplementary Fig. R30, $\cdot OOH$ are all detected over CdS, Pt_1/CdS and Pt_2/CdS. In this case, $\cdot OOH$ was only produced through O_2 reduction where $\cdot O_2^-$ is the involved intermediate ($O_2 + e^- \rightarrow \cdot O_2^-$, $\cdot O_2^- + H^+ \rightarrow \cdot OOH$). This result demonstrates the participation of $\cdot O_2^-$ in photocatalytic CH_4 conversion.



Supplementary Fig. R30 The contrast photocatalytic experiment to determine the optimized experimental conditions (photocatalyst was Pt_1/CdS). Error bars represent standard deviations obtained from at least two independent measurements.



Supplementary Fig. R31 In-situ electron paramagnetic resonance (EPR) spectroscopy of CdS, Pt_1/CdS and Pt_2/CdS in the conditions of O_2 + CH_3OH (These data were smoothed during processing).

(2) The reaction path discrepancy of Pt_1/CdS and Pt_2/CdS

The discrepancy of reaction paths over Pt_1/CdS and Pt_2/CdS might be caused by the distribution of unsaturated sulfur and Pt on the surface. Over Pt_1/CdS, Pt and unsaturated sulfur work in synergy that electron-rich Pt preferably adsorb O_2 to produce ·OH ($O_2 + e^- \rightarrow \cdot O_2^-$, $\cdot O_2^- + H^+ \rightarrow$ ·OOH, ·OOH + $H^+ + e^- \rightarrow$ ·OH) while hole-rich unsaturated sulfur sites adsorb CH_4 for activation. However, the excessive Pt sites over Pt_2/CdS have dominated photocatalyst surface so that ·OH formation and CH_4 activation could both be carried out on electron-rich Pt sites (*see more details in Response 3.4*). In that case, ·OH is still produced through O_2 reduction and the its conversion process is identical with Pt_1/CdS. But ·OH could further attack CH_4, leading to the undesired overoxidation.

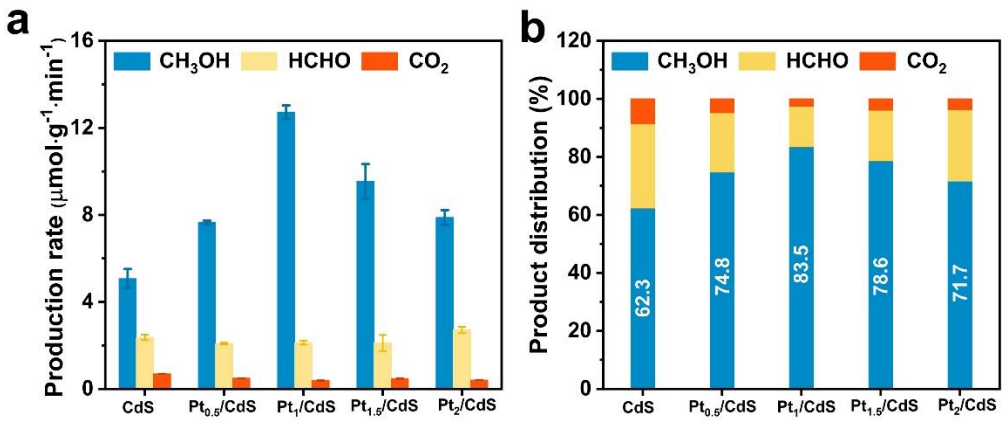
Reviewer #4

The critical mechanism of photocatalytic methane to methanol conversion using Pt-loaded CdS catalysts with special focus on the spatial and temporal distribution of photo-excited charge carriers was systematically investigated in this manuscript. And a clear picture on the correlation between catalyst structure and catalytic performance has been provided, which is important for the catalyst development in the field of green energy utilization. The paper is well written and has a concrete storyline but the following issues need to be stressed before it can be agreed for publication.

Reply to reviewer: We thank reviewer for the constructive suggestions. In our revised manuscript, additional contrast experiments have been conducted to demonstrate the priority of Pt_1/CdS in photocatalytic CH_4 to CH_3OH, and the principle of trapping agents in TAS as well as the mechanism of kinetic global fitting are also supplemented. In specific, samples of $Pt_{0.5}$/CdS and $Pt_{1.5}$/CdS have been prepared as contrast groups and their photocatalytic CH_4 to CH_3OH performance are evaluated (*see Response 4.1*). According to the photocatalytic performance evaluation, $Pt_{0.5}$/CdS and $Pt_{1.5}$/CdS are both inferior to Pt_1/CdS, demonstrating the best performance of Pt_1/CdS in current system. Moreover, the mechanism that BQ works as TAS trapping agent and how Pt and unsaturated sulfur contribute to photodynamics have been illustrated in detail (*see Response 4.2 and 4.3*). Finally, the advantages of SVD global fitting in excited-state dynamics studying are further presented so that it can well inspire non-expert readers (*see Response 4.5*). As follow, the point-to-point response are presented in detail.

Comment 4.1 There were only two contrast groups in current work, named 1%Pt/CdS and 2%Pt/CdS. It is suggested for authors to make more samples for photocatalytic methane to methanol evaluation.

Reply to reviewer: Thanks for reviewer's comments. Samples of $Pt_{0.5}$/CdS and $Pt_{1.5}$/CdS have been prepared as contrast group and their corresponding photocatalytic CH_4 to CH_3OH performance have been evaluated. As displayed in Supplementary Fig. R32, the overall performance $Pt_{0.5}$/CdS and $Pt_{1.5}$/CdS, including CH_3OH production rate and CH_3OH selectivity, is still inferior to marked Pt_1/CdS, indicating the scare or excessive Pt sites can hardly maximize the synergy of Pt and unsaturated sulfur in photocatalysis. To respond reviewer's comment, the supplementary experimental results have been added in our revised manuscript (In revised manuscript Page 13 line 309).



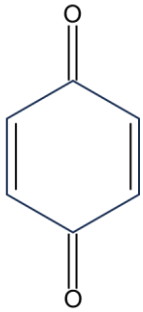
Supplementary Fig. R32 Photocatalytic CH_4 oxidation performance evaluation: the contribution of Pt amount to the statistic average products production rate **a** and products distributions **b**. Error bars represent standard deviations obtained from at least two independent measurements.

Comment 4.2 In the TA tests, why authors added BQ? The purpose needs to be clarified. Besides that, would the addition of such additives change the intrinsic structures of the catalysts? The factors and mechanism should be ruled out.

Reply to reviewer: Thanks for reviewer's comment. These comments are responded in detail as follows:

(1) The role of BQ in photodynamics investigation

BQ is a type of organic molecule where there are two symmetrical ketone functional groups in their structure (Supplementary Fig. R33), so that BQ exhibit oxidizing properties and it can actively attract photogenerated electron, simultaneously facilitating excited carrier relaxation in TAS. Reflected in TAS results, kinetic decay of electron signals could be accelerated in the circumstance that BQ is adsorbed on photocatalyst. Thus, BQ trapping experiments are widely conducted to identify the contributions of electron to time-resolved spectroscopy and investigate photodynamics (J. Phys. Chem. Lett. 2019, 10, 566−573; J. Am. Chem. Soc. 2012, 134, 10337−10340; J. Am. Chem. Soc. 2018, 140, 7791−7794). In our work, due to the limited influence of BQ on 600 nm TAS signal, we ascribed the tail bleach in TAS to hole-related trapping process, which is importance in our photodynamics revelation.



p-benzoquinone (BQ)

Supplementary Fig. R34 The structural formula of p-benzoquinone (BQ)

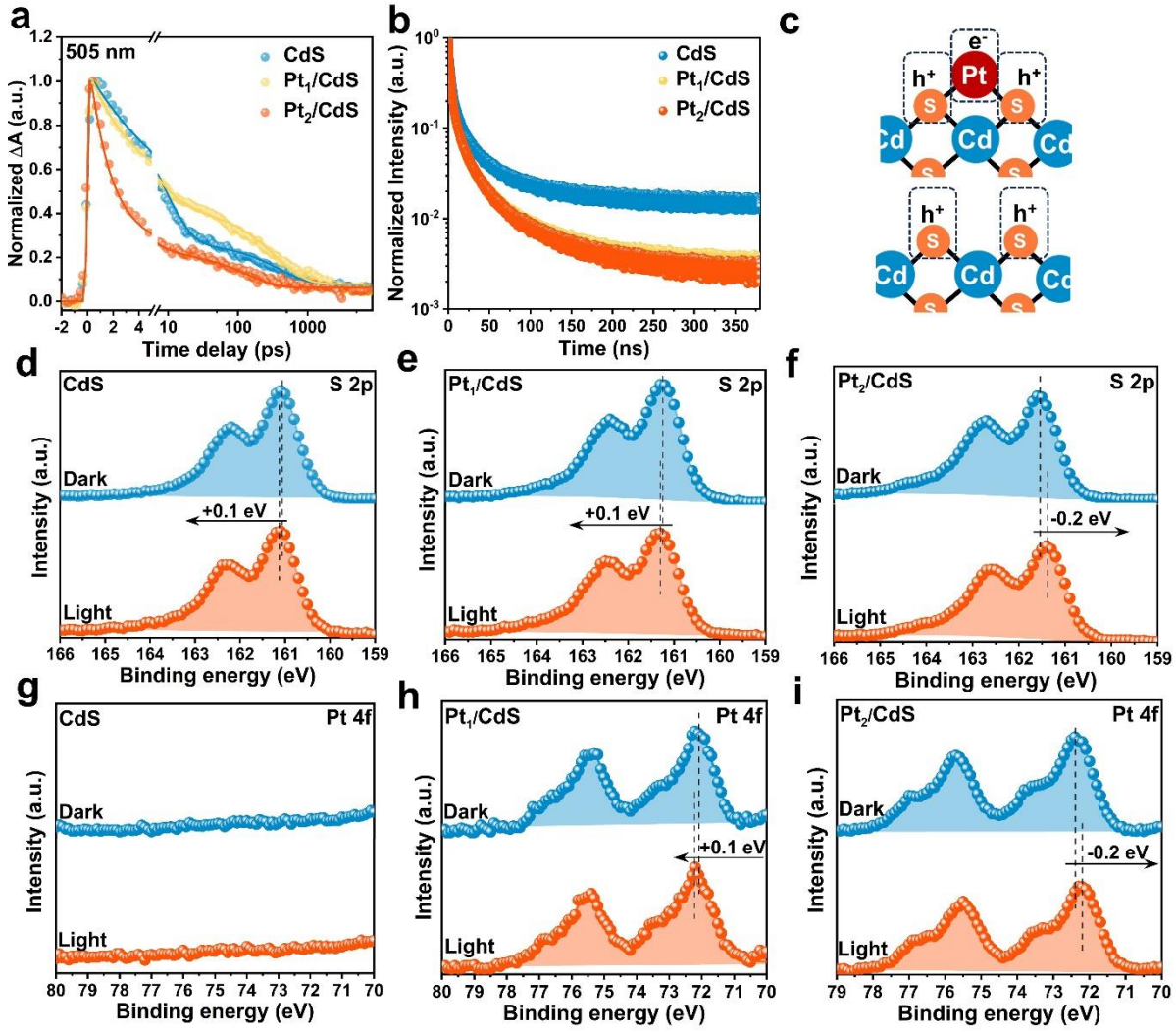
(2) The influence of BQ on intrinsic structures of the catalysts

As to this point, we believed there was restricted influence of BQ on photocatalysts. To commence with, in TAS testing, photocatalysts samples were immersed in BQ solution for trapping agent adsorption, and BQ amount is strictly controlled in a low level. Importantly, BQ has been used to research CdS-based materials photodynamics and no work found its contributions to catalyst intrinsic structure (J. Am. Chem. Soc. 2012, 134, 10337−10340; J. Am. Chem. Soc. 2018, 140, 7791−7794), which lay a foundation for our experiments. To respond reviewer's comment, the mechanism of BQ trapping have been supplemented in our revised manuscript to enrich the contents (In revised manuscript on Page 19 line 493).

Comment 4.3 The time-resolved spectroscopic studies were conducted with the fs-laser pulse and it reflected photodynamics in ultrafast timescale. But authors reckon electron and hole can be further localized on Pt and unsaturated sulfur, of which the corresponding timescale is beyond the time-window of TAS. How did authors deduce this conclusion and the validity of the spectroscopic characterizations related to the catalytic mechanism in general need to be discussed.

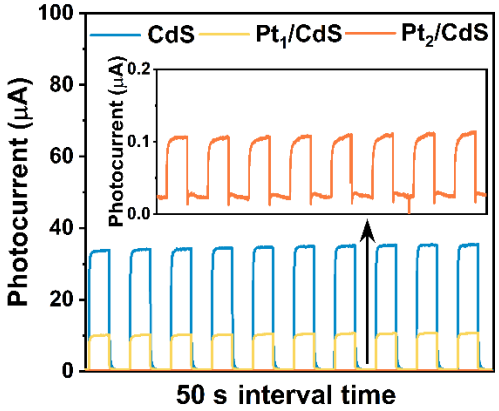
Reply to reviewer: Thanks for reviewer's comments. Kinetic decay fitting disclosed that Pt site and unsaturated sulfur can separately trap electron (~3.3 ps) and hole (~10.6 ps) in picosecond timescale. However, photocatalytic reduction and oxidation reaction were generally carried out in more than millisecond timescale, and it is difficult to demonstrate that the trapped carrier can have such a long lifetime and participate in photocatalysis. To fill the blank in this process, a series of characterizations which are able to unveils the photodynamics in slow timescale have been additionally adopted. For example, TRPL and steady state PL were firstly combined together (Supplementary Fig. R35). It was found that TRPL average photoluminescence lifetime of CdS was reduced to 49.1 ns with Pt sites formation, while simultaneously steady-state PL intensity drops. Thus, we concluded that the electron trapped by Pt sites own long lifetime and it returns to ground-

state through a non-radiative channel. Furthermore, additional characterizations including in-situ XPS and transient photocurrent response (Supplementary Fig. R36) were also carried out. As to in-situ XPS, the element binding energy shifts under light irradiation was slightly positive over CdS, demonstrating the hole localization is favorable in this case. While for Pt_1/CdS and Pt_2/CdS, the binding energy shift gradually became negative with the increasing of Pt amount, which illustrates the strong correlation between Pt and surface electron localization. Transient photocurrent response provided more evidences. The positive photocurrent was detected over CdS, and it indicated the electron transfer from working electrode to counter electrode. Noting that due to the strong trapping of Pt, the photocurrent intensity over Pt_1/CdS and Pt_2/CdS were remarkably lower than CdS, further disclosing the long-lifetime localization of carrier on Pt active sites. Accordingly, we assumed that Pt sites and unsaturated sulfur can separately trap electron and hole in picosecond timescale, and further localize carriers on photocatalyst surface so that they could participate in reactions.



Supplementary Fig. R35 TAS kinetic decay curves at 505 nm of CdS, Pt_1/CdS and Pt_2/CdS: the

scatter plots are experimental data and linear plots are the corresponding fitting curves **a**. Time-resolved photoluminescence (TRPL) spectra of CdS, Pt_1/CdS and Pt_2/CdS **b**. A diagram showing the carrier distribution on photocatalyst surface **c**. High-resolution X-ray photoelectron Pt 4f and S 2p fine spectra in dark and light field: CdS **d&g**, Pt_1/CdS **e&h** and Pt_2/CdS **f&i**.



Supplementary Fig. R36 Transient photocurrent response of CdS, Pt_1/CdS and Pt_2/CdS (embedding picture shows the enlarged Pt_2/CdS photocurrent image).

Comment 4.4 As to electrochemical characterizations, was transient photocurrent response tested under open circuit potential? The applied potential should be illustrated in the manuscript.

Reply to reviewer: Thanks for reviewer's comments. The transient photocurrent response in this work was tested under open circuit potential (OCP). The open circuit potential (OCP) of working electrode would be observed until the value get relatively stable (the sensitivity was set to 10^{-4} V). Corresponding OCP over CdS, Pt_1/CdS and Pt_2/CdS are -0.4103 V, -0.1301 Vand -0.1105 V, respectively. The revisions made in experimental sections have been supplemented on Page 20 line 545 of revised manuscript.

Comment 4.5 Since the SVD analysis is still quite new compared with conventional single wavelength kinetic fitting for TA results (Angew. Chem. Int. Ed. 2024, 63, e202401255; Adv. Mater. 2024, 36, 2303287), I suggest the author provide detailed description on how the SVD fitting is implemented and the basic interpretation or theory about the fitting process to facilitate the non-expert readers. Moreover, some expressions need to be checked, e.g. 1Σ excitons in line 200 was also written as 1S excitons, etc. (Adv. Mater. 2014, 26, 2954-2961; Nano Energy 2016, 28, 319-329; ACS Catal. 2022, 12, 10115-10126).

Reply to reviewer: Thanks for reviewer's comment. Single wavelength kinetic fitting is a common and widely adopted method to analyze kinetic decay, of which the mechanism is relatively simple. However, for complex system dynamics, single wavelength kinetic fitting is not that efficient compared with SVD global fitting. SVD global analysis is a unified separable nonlinear model which

can describe all measurements collected over multiple independent variables. SVD involves eliminating the less important parts in dataset and producing an accurate approximation data, for which sufficient exponential decays and their amplitudes will be adopted to fit. Then the feature and timescale of specific dynamic processes can be assigned. In this regard, the photodynamics can be visualized in a more intuitive way. In our revised manuscript, additional description for SVD global fitting has been supplemented so that it can be well presented to non-expert readers (in revised manuscript Page 9 line 210 and Page 19 line 500). Finally, the expressions that reviewers mentioned have been checked and we revise “1Σ excitons” with “1S excitons” (in revised manuscript Page 9 line 206).

Manuscript: NCOMMS-25-21495A

Spatiotemporal control of photon distribution on active sites: Bridging bio-inspired methane-to-methanol conversion

Response to the Reviewers' Comments

Reviewer #1

I want to applaud the authors on addressing the concerns outlined. Based on many of their responses I am more supportive of their conclusions but am still not convinced of the impact of their work. There are more concerns with their central conclusion that justifies the impact – that the Pt center is responsible for adsorption of oxygen, and free S groups are responsible for CH_4 adsorption. If the authors could provide responses to the following, it may add clarity more clarity to their conclusions:

Reply to reviewer: We are grateful to the reviewer for the positive and appreciative of our work and pointing out the issues that need to be solved in the manuscript. In the revised manuscript, we comprehensively analyzed all relevant data to further confirm the electronic state and coordination of Pt, conclusively establishing that Pt in both 1%Pt/CdS and 2%Pt/CdS is anchored via Pt-S bonds in the valence state of +2 (*see Response 1.1, 1.4, and 1.6*). Furthermore, we have definitively demonstrated that all Pt-S configurations significantly enhance electron trapping during photodynamics (see *Response 1.3*). Critically, these findings align with our previous conclusions. Importantly, we re-emphasize and provide clear evidence that residual Cl has been completely removed, confirming the thorough elimination of precursors (see *Response 1.2*). To address the reviewer's specific concerns, we have provided detailed supplementary explanations for the phenomena observed in in-situ XPS and photocurrent responses (see *Response 1.5 and 1.7*). The constructive comments and suggestions are addressed in detail as follow, and we hope that these alterations could meet your expectation.

Comment 1.1 In the author's response to comment 1.3, they re-fit their XPS spectra and show their new fits in supplementary figure R3. If one looks closely at the Pt 4f spectra for each sample, they will see a change in slope around 74.5 eV and a second contribution to the Pt spectra. This is clearly a multivalent Pt species on the surface and exists for all samples with Pt. The contribution is much smaller, granted, in the 1% species but it there. My concern rests on the author's central point that the Pt species is acting as this sink of O_2 for the mechanism. Which Pt species? Why do they just observe a single pathway in the transient spectroscopy if there are multiple Pt species? Why do they only observe a single Pt species in the XAFS when there are clearly multiple valences in the XPS? In the author's supplementary figure R35, the Pt envelope clearly shows multivalence

too. Why isn't there consistency between the different photoelectron spectra?

Reply to reviewer: Thanks for this comment, and these comments are responded in detail as follows:

(1) The doublet peak fitting in XPS

Addressing the reviewer's observation regarding the slope change near 74.5 eV and potential secondary contribution in Pt XPS spectra, we attribute these features primarily to overlap of Pt 4f spin-orbit split signals (3.3 eV splitting) rather than higher-valence Pt species, particularly given the significant spectral overlap within 74.0-75.0 eV. Simultaneously, Pt is still the minor component (< 5%) compared with Cd and S. While Pt 4f fine spectra was extended acquisition cycles, the possible interference from background contributions can hardly be ignored, further promoting the possible fluctuations of fine spectra at ~74.5 eV. On this basis, we also considered the phenomenon detected in other characterizations. Based on XAFS structural evidence (Supplementary Fig. R1), R-space fitting reveals an exclusive Pt-S coordination environment without detectable Pt-O or Pt-Cl bonds, precluding the existence of Pt^{4+} species (e. PtO_2 and H_2PtCl_6). Moreover, XPS elemental quantification confirms effective removal of Cl impurities (see more details in *Response 1.2*), further substantiating complete elimination of platinum precursors (Supplementary Fig. R2). To avoid data overinterpretation, we deliberately constrained the fitting complexity and maintain a couple of doublets. In addition, the complementary analysis of XAFS and XPS data addressing this matter is detailed in *Response 1.4*.

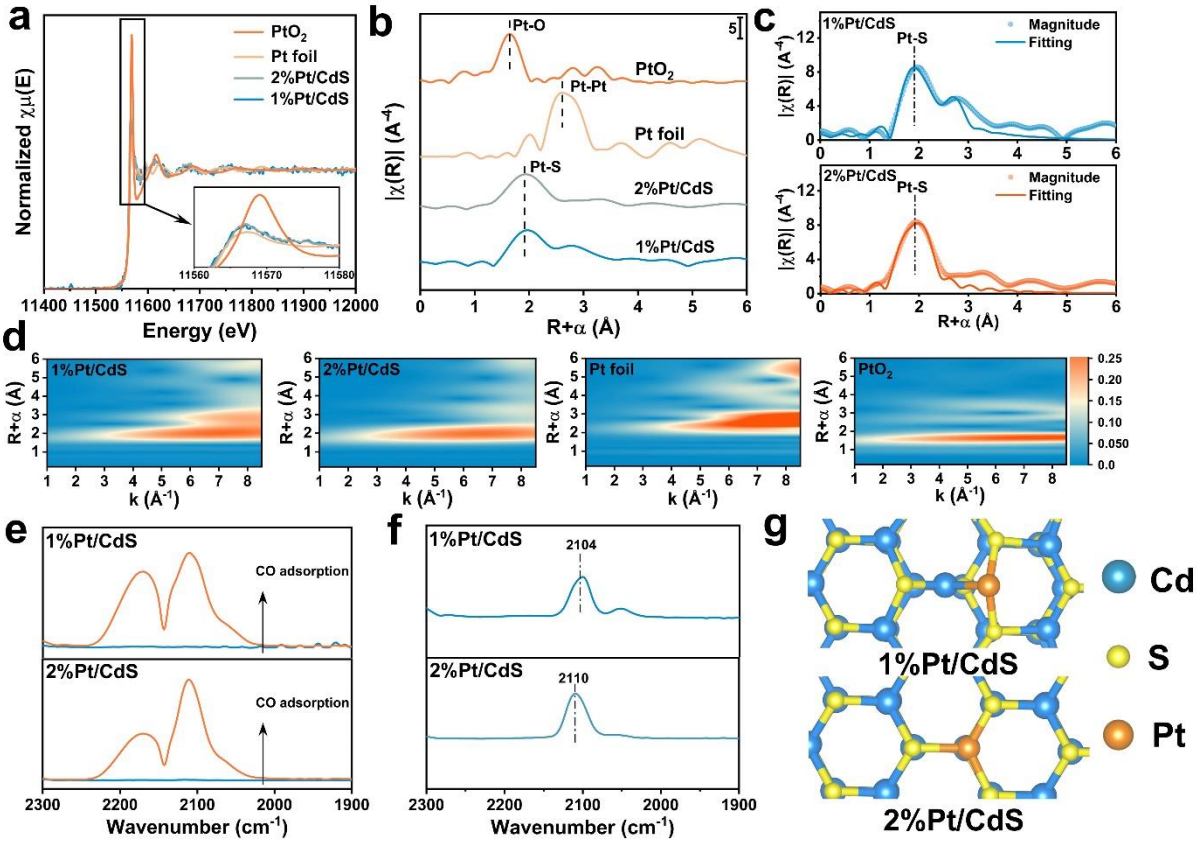
(2) The phenomenon observed in transient photodynamics

Regarding ultrafast dynamics analysis, global fitting of carrier kinetics reveals that both Pt_1/CdS and Pt_2/CdS exhibit exclusively one additional time component (strongly correlated with electron trapping as there is no any bleach at 600 nm) compared to pristine CdS (Supplementary Fig. R3b and Fig. R3c). This confirms Pt-induced rapid electron trapping. Given that the ubiquitous Pt-S coordination over Pt_1/CdS and Pt_2/CdS, we deduce consistent carrier transfer pathways across highly dispersed Pt atoms. Therefore, our theoretical calculations and surface reaction pathway analyses are based on the Pt-S single atom coordination model, wherein Pt localizes electrons to adsorb O_2 (forming ·OH) while unsaturated sulfur sites localize holes for CH_4 adsorption.

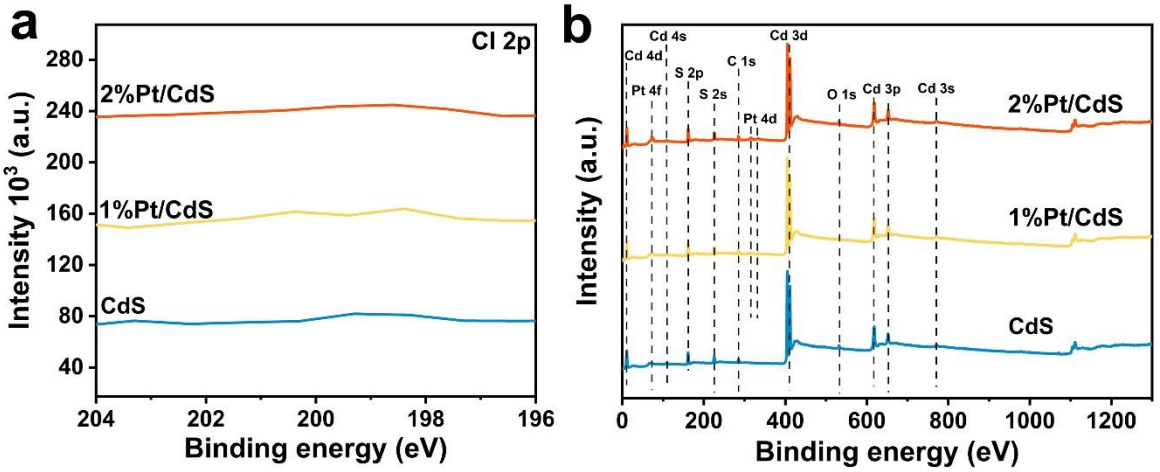
(3) The spectra discrepancy between XPS and in-situ XPS

Owing to the specialized optical configuration required for in-situ XPS measurements, our conventional XPS (Supplementary Fig. R4) and in-situ XPS (Supplementary Fig. R5) analyses were conducted on distinct spectrometers (Specific descriptions were provided on page 20 of

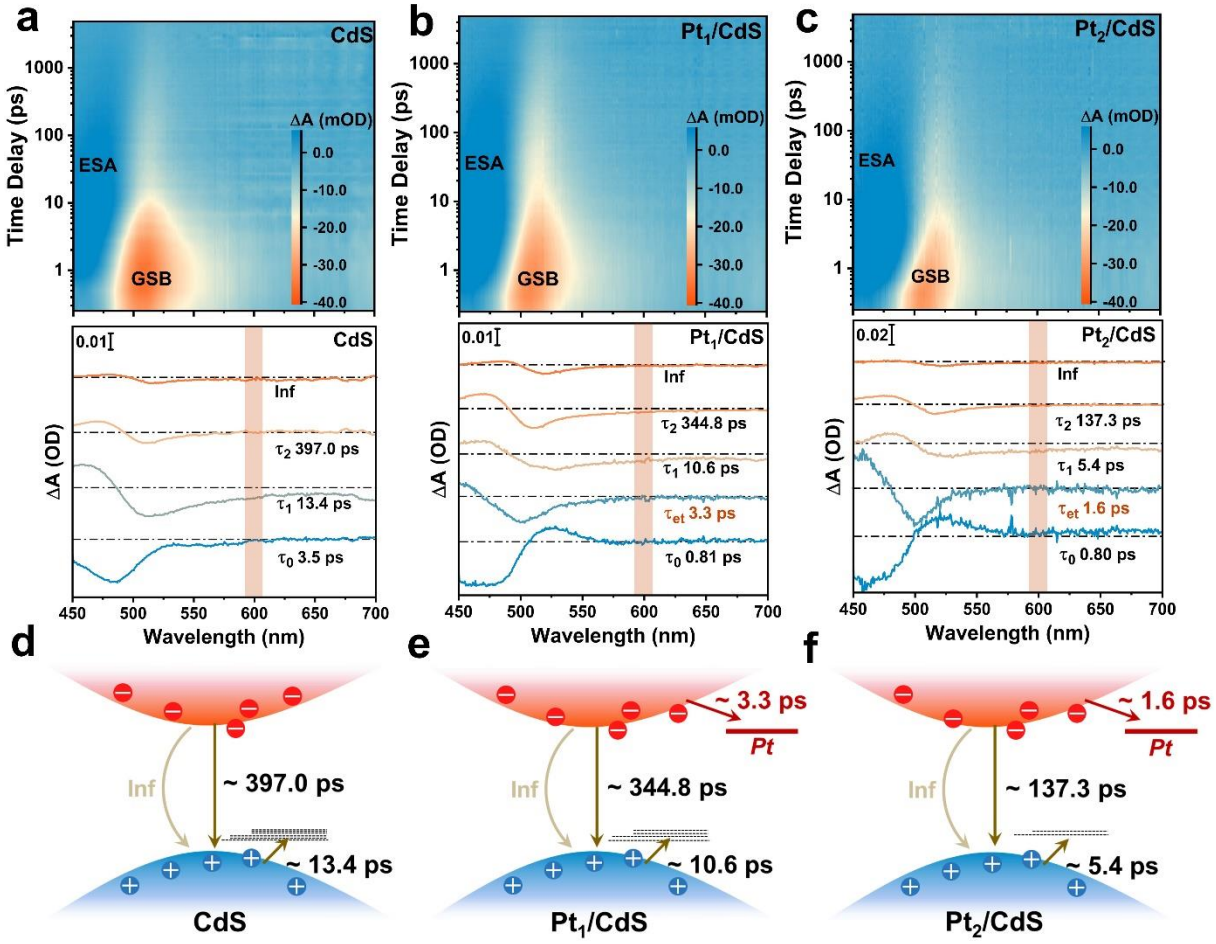
revised manuscript and page 4 of revised Supplementary Information). To ensure maximal data fidelity, conventional XPS spectra underwent deliberately optimized acquisition parameters with extended dwell times. Conversely, in-situ XPS focused exclusively on tracking light-induced binding energy shifts, hence employing shorter acquisition cycles that inherently yield noisier spectral profiles.



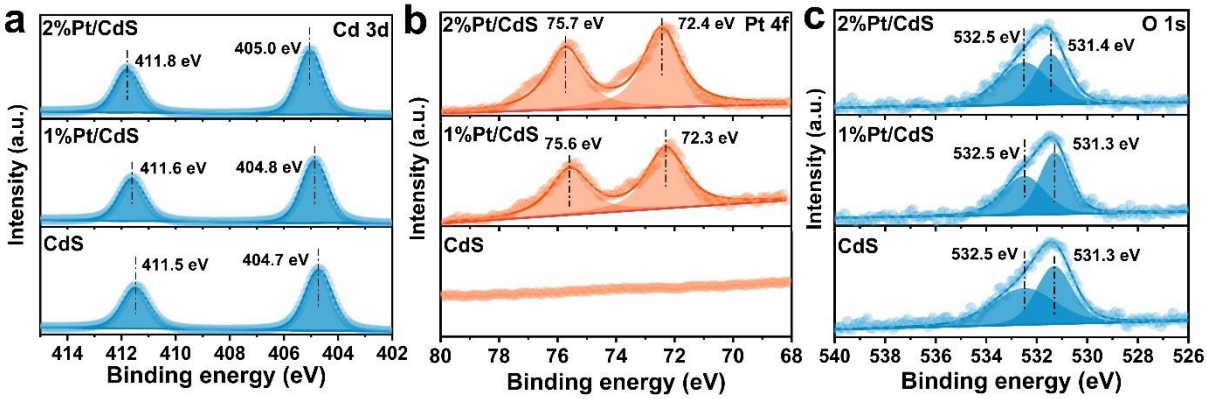
Supplementary Fig. R1 XANES spectra of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **a**; Fourier-transformed k^3-weighted EXAFS of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **b**; R-space fitting results for 1%Pt/CdS and 2%Pt/CdS (The R-space data are presented without phase correction) **c**; EXAFS wavelet transformation (WT) for Pt foil, PtO_2, 1%Pt/CdS and 2%Pt/CdS **d**; CO adsorption **e** and desorption **f** in-situ DRIFTS of 1%Pt/CdS and 2%Pt/CdS (Ar gas flow was used to remove extra gaseous CO and the desorption curve was collected after 20 min Ar flow); The proposed structure for Pt-S configuration over 1%Pt/CdS and 2%Pt/CdS **g**.



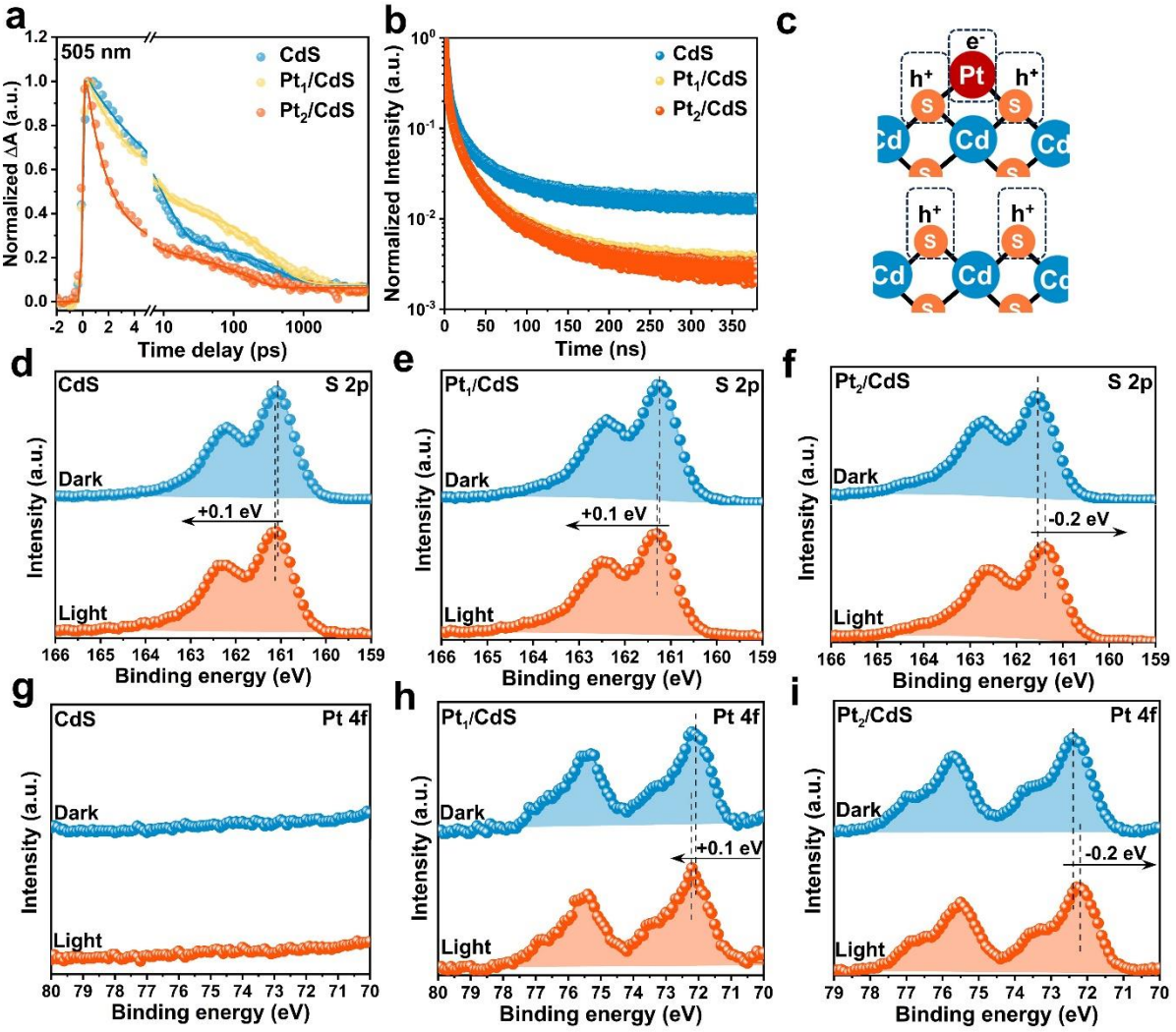
Supplementary Fig. R2 X-ray photoelectron Cl 2p spectra **a** and full spectra **b** of CdS, 1%Pt/CdS and 2%Pt/CdS.



Supplementary Fig. R3 Transient absorption spectroscopy (TAS) where 400 nm beam light was used as pump light and a continuous white light ranging from 450 to 700 nm was used as probe light: two-dimensional contour plots of TAS with the associated global fitting results of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c**. The diagram exhibiting the excited-state carrier relaxation of CdS **d**, Pt_1/CdS **e** and Pt_2/CdS **f**.



Supplementary Fig. R4 X-ray photoelectron Cd 3d **a**, Pt 4f **b**, O 1s **c** fine spectra of CdS, 1%Pt/CdS and 2%Pt/CdS.



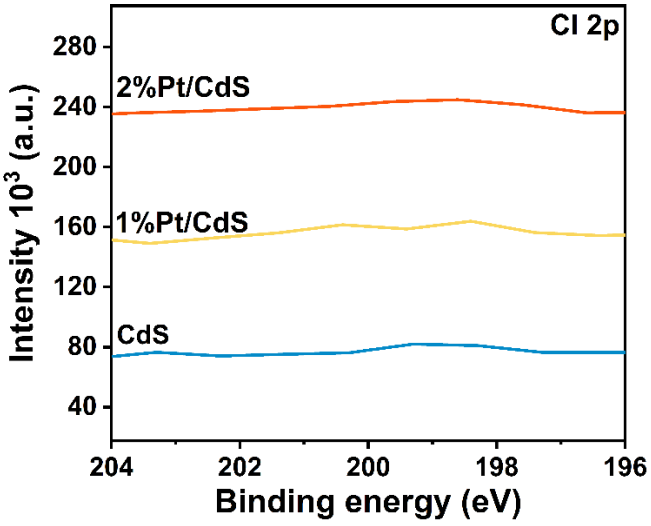
Supplementary Fig. R5 TAS kinetic decay curves at 505 nm of CdS, Pt_1/CdS and Pt_2/CdS: the scatter plots are experimental data and linear plots are the corresponding fitting curves **a**. Time-resolved photoluminescence (TRPL) spectra of CdS, Pt_1/CdS and Pt_2/CdS **b**. A diagram showing

the carrier distribution on photocatalyst surface **c**. X-ray photoelectron S 2p and Pt 4f fine spectra in dark and light field: CdS **d&g**, Pt_1/CdS **e&h** and Pt_2/CdS **f&i**.

Comment 1.2 Further to the previous point, there is some indication that there could be Cl 2p in the 1% Pt. What were the parameters that the Cl 2p was taken? Did the authors use a larger pass energy to ensure that they could observe small amounts on the surface? The reason for my concern with this is that Cl is often a recombination center when adsorbed on the surface. If the samples are not perfectly clean of Cl, there could be changes to many of the different techniques used in the author's study – DRIFTS and TAS – to make their central argument.

Reply to reviewer: Thanks for reviewer's comments and these comments are responded in detail as follows:

To definitively confirm the absence of Cl residues and attribute apparent spectral features to baseline artifacts, we provide Cl 2p spectra of pure CdS as a reference alongside Pt/CdS samples (Supplementary Fig. R6). Crucially, both Pt_1/CdS and Pt_2/CdS exhibit near-identical spectral profiles to the Cl-free CdS control, with all observed variations attributable solely to baseline fluctuations. This experimental evidence conclusively establishes no detectable Cl residues exist on Pt/CdS surfaces. For absolute scientific rigor, we explicitly emphasize that any potential residual Cl falls below the detection threshold of XPS, as verified by direct comparison of unsmoothed spectral data.



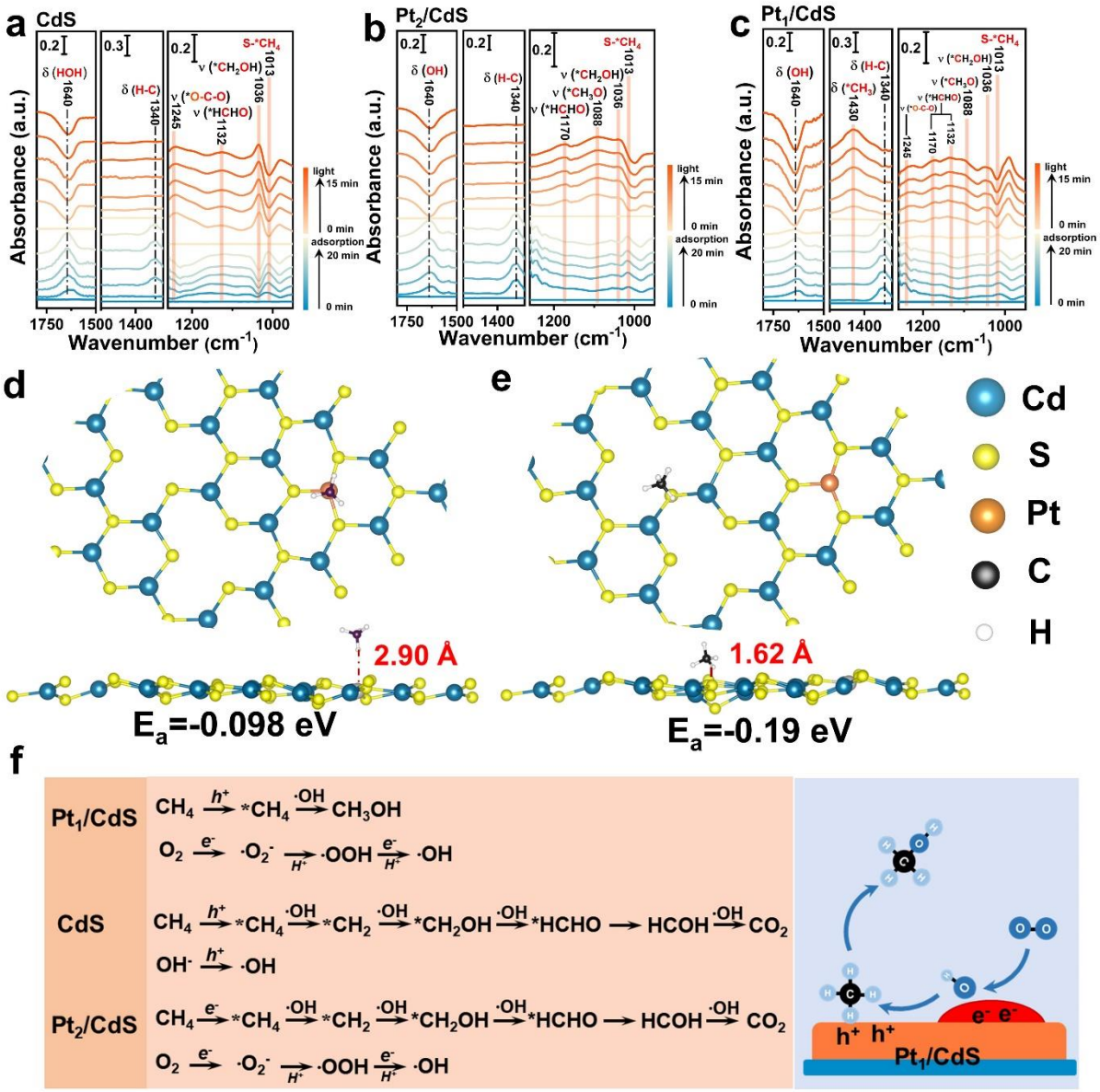
Supplementary Fig. R6 Cl 2p spectra extracted from XPS full spectra.

Comment 1.3 I do not agree with the comment 1.8 the author's response. The oxidation and coordination environment are still not confirmed and this convolutes the conclusions from the ultrafast photodynamics experiment. I could accept that a generic Pt species is what creates this behavior but it still isn't clear to me what the role of the oxidation state is. Perhaps this is irrelevant? If so, will any electron trapping metal provide the same behavior? Do unsaturated S-sites normally

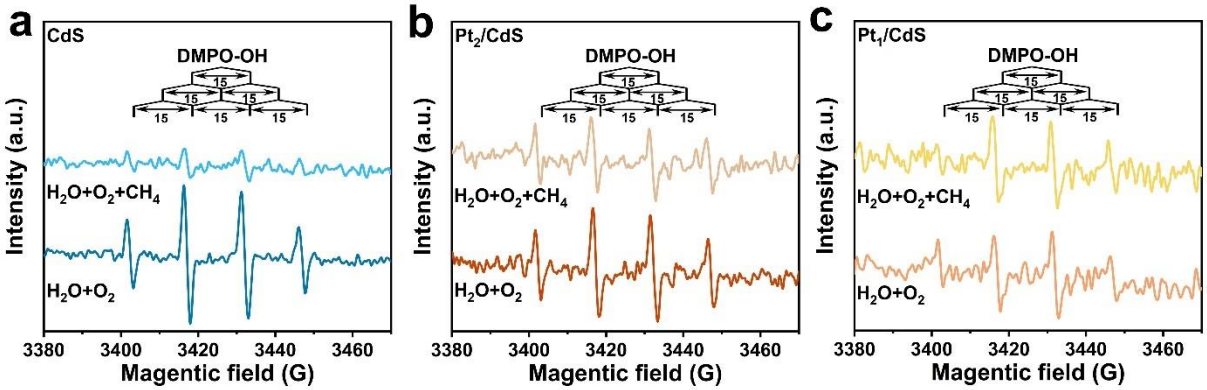
adsorb CH_4?

Reply to reviewer: Thanks for reviewer's comment. As we have claimed in *Response 1.1*, exclusively monovalent Pt^{2+} species in Pt-S configurations are uniformly present on both Pt_1/CdS and Pt_2/CdS. Our ultrafast kinetic analysis reveals that the modified carrier dynamics in CdS originate from a singular electron transfer process – specifically, electron trapping at these Pt^{2+} sites. Regarding the reviewer's query on oxidation state effects, the absence of mixed-valence Pt in our system directly underpins the observed unified electron transfer pathway.

Regarding selective CH_4 adsorption at unsaturated sulfur sites, while unsaturated sulfur atoms serve as potential active sites, their CH_4 adsorption/desorption behaviors were jointly determined by DRIFTS and theoretical calculations (Supplementary Figure R7). In in-situ DRIFTS, during reactant adsorption, characteristic vibrational peaks at ~1013 cm^{-1} emerged uniformly across CdS, Pt_1/CdS and Pt_2/CdS, corresponding to the S-*CH_4 configuration, confirming CH_4 adsorption at unsaturated sulfur sites. Moreover, DFT calculations revealed stronger absolute adsorption energies for CH_4 at unsaturated sulfur sites when co-existing with monodisperse Pt atoms, indicating thermodynamically favored adsorption. In-situ EPR (Supplementary Figure R8) demonstrated non-overlapping adsorption sites for O_2 and CH_4 on Pt_1/CdS, that CH_4 adsorbs preferentially at sulfur sites, while O_2 migrates to adjacent Pt sites. This spatial separation underpins the proposed dual-active-site mechanism.



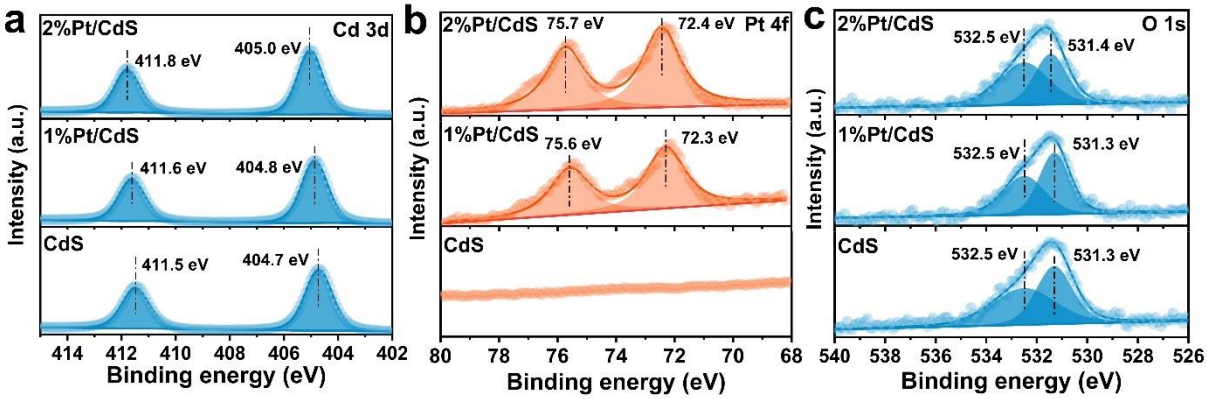
Supplementary Fig. R7 In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CdS **a**, Pt_2/CdS **b** and Pt_1/CdS **c** in the atmosphere of CH_4 + O_2 + H_2O mixture: the sample surface has been fully adsorbed with reactants before the light irradiation (These data were smoothed during processing). Geometry optimized configuration of CH_4 adsorbed on Pt sites **d** and unsaturated sulfur sites **e.** Schematic diagram illustrating the CH_3OH production through stepwise reaction path **f**.



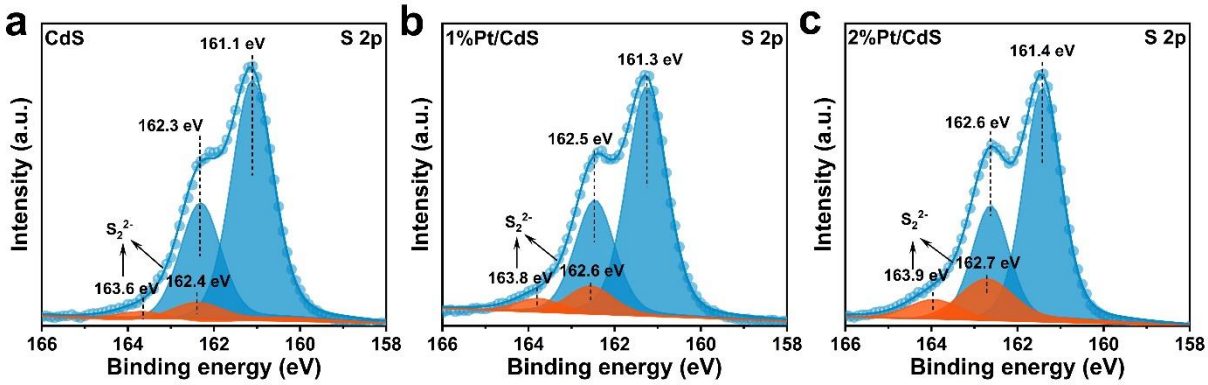
Supplementary Fig. R8 In-situ electron paramagnetic resonance (EPR) spectroscopy of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c** under different testing conditions. (These data were smoothed during processing)

Comment 1.4 What indications are there that there is an explicit Pt-S bond? Is this from the EXAFS?

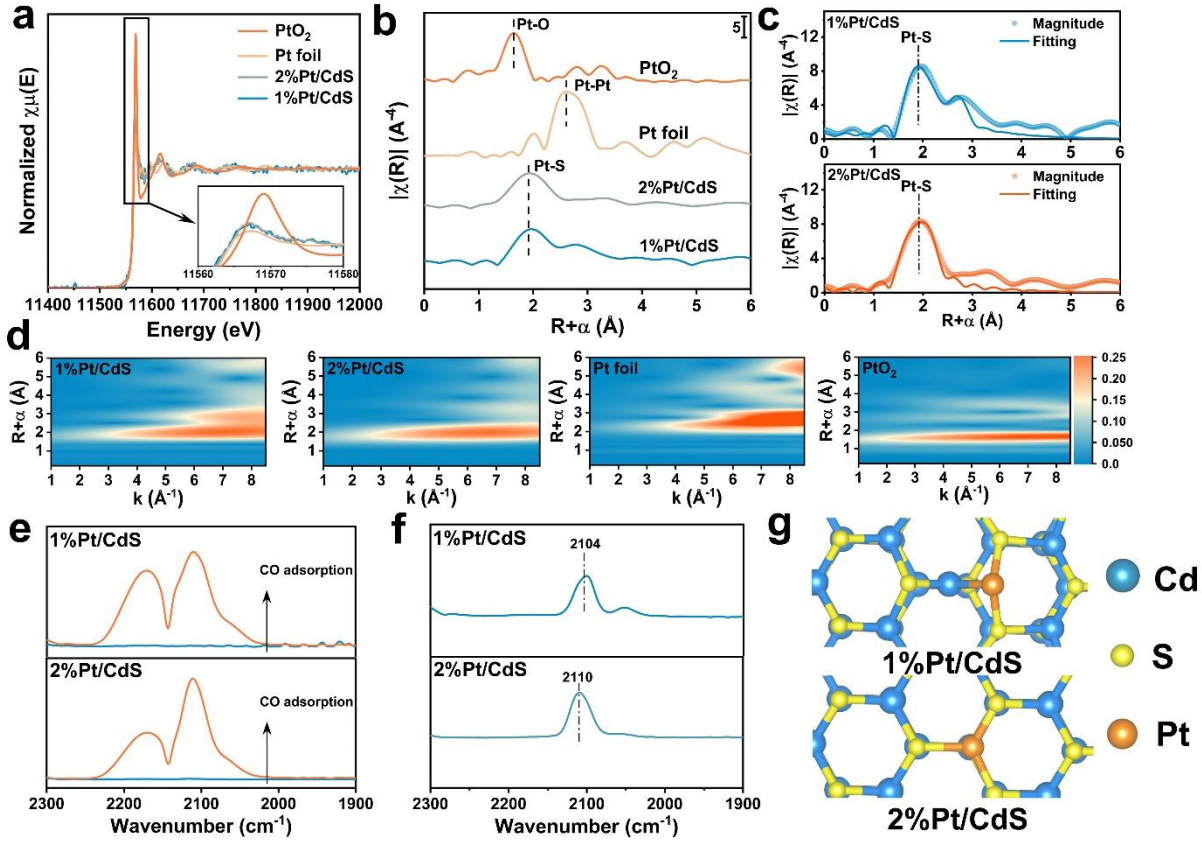
Reply to reviewer: Thanks for reviewer's comment. We concluded Pt-S configurations over Pt_1/CdS and Pt_2/CdS referenced on XPS and EXAFS fitting results. Reflected in XPS O 1s, S 2p and Pt 4f, there is no any lattice oxygen (~530.1 eV) and metallic Pt (~70.6 eV) while only sulfide can be detected, excluding the possible Pt-O and Pt-Pt bonds. Simultaneously, in FT-k^3 EXAFS, the dominating peaks over Pt_1/CdS and Pt_2/CdS can hardly match well standard Pt foil and PtO_2, but can be well fitted by our proposed configurations where Pt was anchored on CdS through Pt-S bond. Taking all these results into consideration, we determined the existence of Pt-S bonds.



Supplementary Fig. R9 X-ray photoelectron Cd 3d **a**, Pt 4f **b**, O 1s **c** fine spectra of CdS, 1%Pt/CdS and 2%Pt/CdS.



Supplementary Fig. R10 X-ray photoelectron S 2p fine spectra of CdS **a**, 1%Pt/CdS **b** and 2%Pt/CdS **c**.



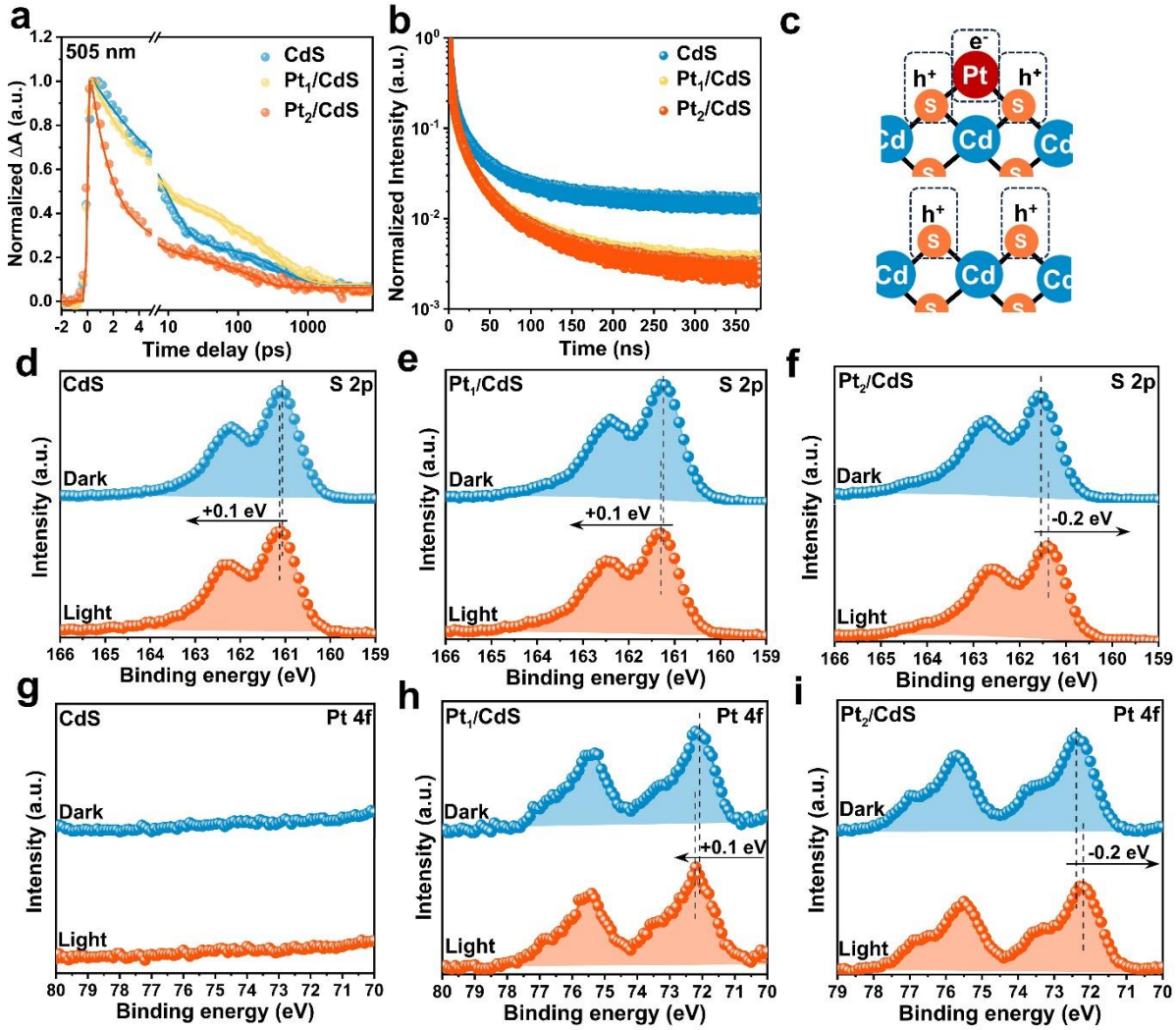
Supplementary Fig. R11 XANES spectra of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **a**; Fourier-transformed k^3-weighted EXAFS of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **b**; R-space fitting results for 1%Pt/CdS and 2%Pt/CdS (The R-space data are presented without phase correction) **c**; EXAFS wavelet transformation (WT) for Pt foil, PtO_2, 1%Pt/CdS and 2%Pt/CdS **d**; CO adsorption **e** and desorption **f** in-situ DRIFTS of 1%Pt/CdS and 2%Pt/CdS (Ar gas flow was used to remove extra gaseous CO and the desorption curve was collected after 20 min Ar flow); The proposed structure for Pt-S configuration over 1%Pt/CdS and 2%Pt/CdS **g**.

Comment 1.5 From comment 1.9, the authors cite Nat. Commun. 2024, 15, 4807 (I tried to find

the other references but they were difficult to find due to the authors formatting) as a reference for their small shifts. In that article, those authors do show the expected shifts for electron trapping and hole trapping that was referred to in the initial review. In this work, the authors do not show this phenomenon. Can the authors comment on how they are coming to their conclusion given that they are not observing similar effects from the literature in their photoelectron spectra?

Reply to reviewer: Thanks for reviewer's comment. We are sorry that the inappropriate format of cited references, which lead to the difficult searching. Currently, the complete reference information and DOI number have been supplied so that they can be correctly found (Angew. Chem. Int. Ed. 2023, 62, e202218688. 10.1002/anie.202218688; Nat. Commun. 2024, 15, 4807. 10.1038/s41467-024-49004-7).

In our prior response, the cited references primarily serve to demonstrate that binding energy shifts of 0.0 to 0.2 eV are commonly observed during in-situ XPS characterization. However, the referenced systems are all heterojunction materials with well-defined dual phases. In such configurations, charge carriers tend to accumulate and delocalize preferentially within one phase after crossing the heterojunction interface, resulting in a binding energy increase in one phase and decrease in the other – consistent with the authors' expectations. Conversely, our material does not constitute a conventional heterojunction system, lacking distinct phase separation. The covalent Pt-S bonding facilitates efficient carrier diffusion between Pt and S atoms. Consequently, the observed binding energy shifts are governed by the primary carrier localization sites. For CdS and Pt_1/CdS, unsaturated sulfur sites dominate hole localization, manifesting as positive binding energy shifts under photoexcitation. While for Pt_2/CdS, excessive Pt sites become the predominant localization centers, leading to negative binding energy shifts under identical conditions.



Supplementary Fig. R12 TAS kinetic decay curves at 505 nm of CdS, Pt_1/CdS and Pt_2/CdS: the scatter plots are experimental data and linear plots are the corresponding fitting curves **a**. Time-resolved photoluminescence (TRPL) spectra of CdS, Pt_1/CdS and Pt_2/CdS **b**. A diagram showing the carrier distribution on photocatalyst surface **c**. X-ray photoelectron S 2p and Pt 4f fine spectra in dark and light field: CdS **d&g**, Pt_1/CdS **e&h** and Pt_2/CdS **f&i**.

Comment 1.6 In response to Reviewer 3, the authors claim that the Pt has replaced part of Cd to form the Pt-S configuration. Have the authors considered that the Pt will deposit on top of Cd and attenuate its signal, thus producing a lower Cd:S ratio? Did the authors use appropriate sensitivity values to get their ratios? Is any of the Pt oxidation states of similar size to Cd^{2+} to replace it in the crystal structure?

Reply to reviewer: Thanks for reviewer's comments and these comments are responded in detail as follows:

(1) Whether Pt deposit on the top of Cd and cause a lower Cd:S ratio

We assume that Pt could replace a part of Cd to form Pt-S configuration rather than simply

deposition, because it is notice that as Pt amount was increased, Cd amount was decreased while S amount was also increased (Supplementary Table R1). This phenomenon indicated that overall metal-to-sulfur radio was changed and original Cd have been extracted. More importantly, if Pt were deposited on CdS surface, it should be expected to see that both S and Cd amount both declined with Pt amount growing, but this trend was not detected.

(2) The size of Pt and Cd atom

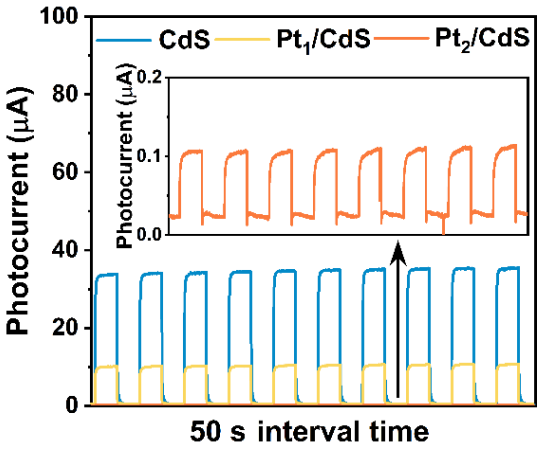
Referenced on standard database, the radius of Pt^{2+} and Pt^{4+} are ~0.85 Å and ~0.70 Å, respectively, while that of Cd^{2+} is ~0.92 Å. This phenomenon indicated Pt^{2+} is more prone to take the place of Cd^{2+} of CdS to form Pt-S configuration.

Supplementary Table R1 The Cd, S and Pt atomic ratio on the surface of CdS, 1%Pt/CdS and 2%Pt/CdS.

	Samples		
	CdS	1%Pt/CdS	2%Pt/CdS
Cd	48.1	45.6	43.0
S	51.9	53.1	54.3
Pt	0	1.3	2.7

Comment 1.7 The lower photocurrent seems to scale with the amount of Pt. The Pt seems to be acting as a recombination center rather than a reaction site. Can the authors comment on this?

Reply to reviewer: Thanks for reviewer's comment. The positive photocurrent indicates the electron transferring from working electrode (made of photocatalyst) to counter electrode (Pt foil) under applied voltage, and it was revealed that the photocurrent intensity of CdS decreased with the growing of Pt amount (Supplementary Fig. R13). Here, we understand the reviewer's concerns with this phenomenon, that Pt could become the recombination center over photocatalysts. But in our work, Pt sites over Pt_1/CdS and Pt_2/CdS have been demonstrated the strong trapping for photogenerated electron in ultrafast timescale, which is faster than photocurrent formation. In this regard, less photogenerated electron could enter the circuit and the observed photocurrent intensity was decreased. Same phenomenon was also reported by Tang et al. (Nat. Sustain. 2024, 7, 1171-1181. 10.1038/s41893-024-01401-y) who explored the contributions of metal sites to photocurrent intensity.



Supplementary Fig. R13 Transient photocurrent response of CdS, Pt_1/CdS and Pt_2/CdS (embedding picture shows the enlarged Pt_2/CdS photocurrent image).

Reviewer #2

I have carefully read the author's revisions. I think the manuscript is now in an acceptable state and can be published.

Reply to reviewer: We thank for the Reviewer for the appreciative evaluation of our work.

Reviewer #3

All the comments have been addressed, and this manuscript can be accepted with the current version.

Reply to reviewer: We deeply thank the reviewer for this comment.

Reviewer #4

The revised manuscript has been improved and acceptance is suggested.

Reply to reviewer: We sincerely appreciate the reviewer's evaluations and recommended acceptance of our work.

Manuscript: NCOMMS-25-21495

Spatiotemporal control of photon distribution on active sites: Bridging bio-inspired methane-to-methanol conversion

Response to the Reviewers' Comments

Reviewer #1

I want to thank the authors for their useful discussion on their paper. While I am still not convinced of their interpretation of the photoelectron spectra, I believe this merits publication and scrutiny by the wider community to further investigate their claims.

Reply to reviewer:

We would like to express our sincere gratitude to the reviewer for the thorough examination of our work. While our previous responses may not have fully addressed all the concerns, we are committed to actively collaborating with Reviewer #5 and Reviewer #6 to further improve the discussion regarding atomic-level coordination, structural fundamentals, and stability-related issues.

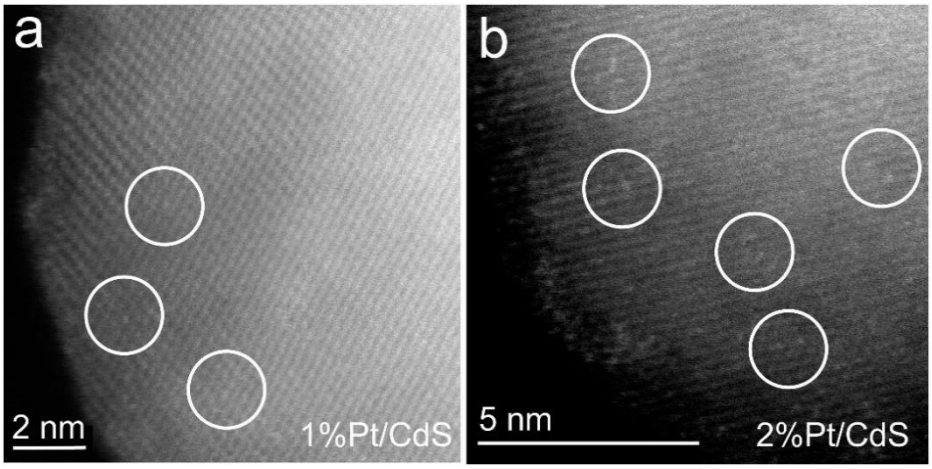
Reviewer #5

Despite numerous efforts to support the authors' proposal for unique catalytic sites and charge dynamics, the claim of exclusively monovalent Pt^{2+} on the surface is not properly demonstrated. The XPS Pt 4f spectra clearly show a shoulder peak possibly for Pt^{4+}. The response to this concern is not convincing. Reviewer #1's concern about mixed valence is well-founded. In addition, given that H_2PtCl_6 (Pt^{4+}) is used as the precursor, no explicit reduction step is described and the chemical pathway from Pt^{4+} to Pt^{2+} remains unclear. It is also doubtful that Pt species are atomically dispersed in this study since the TEM image of separated Pt atoms are not provided. Therefore, further data analyses and computational simulations should be considered with more solid investigation and proper structural hypothesis.

Reply to reviewer: We sincerely thank the reviewer for the comprehensive review and constructive suggestions on our work. In response to these comments, we have conducted additional characterizations including HAADF-STEM, EPR, XRD, AQE, and IPCE to address concerns on Pt dispersion, defects, stability, efficiency, and band structure (*see Responses 5.1, 5.2, 5.5, 5.7, and 5.8*). We have also supplemented descriptions and analyses for in-situ XPS and XAFS to clarify doubts (*see Responses 5.3, 5.4, and 5.6*). Finally, literature citations have been revised for stronger foundational support (*see Response 5.9*). Point-by-point responses are detailed below.

Comment 5.1 HAADF-STEM should be carried out to confirm the separated Pt atoms on CdS surface.

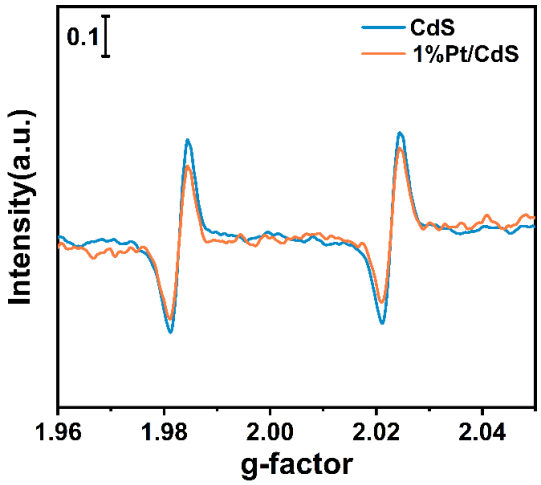
Reply to reviewer: Thanks for reviewer's comments. In response of reviewer's suggestions, HAADF-STEM have been carried to investigate the dispersity of Pt over CdS. As shown in Supplementary Fig. R1a, sporadic Pt atoms can be observed in the lattice of 1%Pt/CdS due to the contrast difference, although the overall density remains low. In the case of 2%Pt/CdS, the density of Pt atoms increases significantly with the higher Pt loading. These findings collectively indicate the high dispersity of Pt. The related descriptions for HAADF-STEM have been added in revised manuscript (line 173, page 7) and revised supplementary information (page 13).



Supplementary Fig. R1 HAADF-STEM of 1%Pt/CdS **a)** and 2%Pt/CdS **b)**.

Comment 5.2 The claim that Pt is coordinated with sulfur sites is not convincing. EPR spectra of CdS samples before and after Pt deposition should be provided.

Reply to reviewer: Thanks for reviewer's comments. Electron paramagnetic resonance (EPR) measurements of CdS and 1%Pt/CdS have been conducted to characterize the effect of Pt loading on the surface defects of CdS, specifically the unsaturated sulfur sites. As illustrated in Supplementary Fig. R2, the signals in EPR are ascribed to unpaired electrons induced by unsaturated sulfur. It is noteworthy that the decline of EPR signal intensity was observed after the deposition of Pt, indicating a decrease in the concentration of unsaturated sulfur. Further analysis, combined with XPS and XAFS results (see more details in response 5.4), suggests that Pt likely interacts with unsaturated sulfur to form Pt-S bonds, leading to the nucleation of Pt on the CdS surface as our previous conclusions indicates. EPR of CdS and 1%Pt/CdS have been supplemented in revised manuscript (line 140, page 6) and revised supplementary information (page 11).



Supplementary Fig. R2 EPR of CdS and 1%Pt/CdS.

Comment 5.3 The XPS discussion regarding Figure 4 is not convincing, as all elements appear shifted by the same value. This shift may result from the C 1s (284.8 eV) calibration, which is broad and prone to be shifted.

Reply to reviewer: Thanks for reviewer's comments and we would be delightful to discuss this issue further with the reviewer. Regarding the overall shift in the XPS spectra, we had also considered during our analysis that it might be due to a shift in the C 1s peak (from adsorbed CO_2) during the calibration process. However, we also noticed that the extent of the shift is not consistent across the three samples (CdS, Pt_1/CdS and Pt_2/CdS). Specifically, the overall shift changes from slightly positive to noticeably negative as the Pt content increases. This suggests that the shift cannot be attributed solely to the C 1s calibration (otherwise, the shift should be consistent across all three samples). Taking into account the previously obtained carrier dynamics analysis, we believe that the increasing Pt content alters the localization of electrons and holes on the surface of photocatalyst, thereby causing the shift in the XPS spectra.

Comment 5.4 No standard sample containing Pt-S bond, or other Pt^{2+} states, is measured and compared in XAS. Analysis on the EXAFS and XANES lacks details, what is the Pt-S model and how does this model fit into the EXAFS spectra?

Reply to reviewer: Thanks for reviewer's valuable comments. These comments are responded in detail as follows:

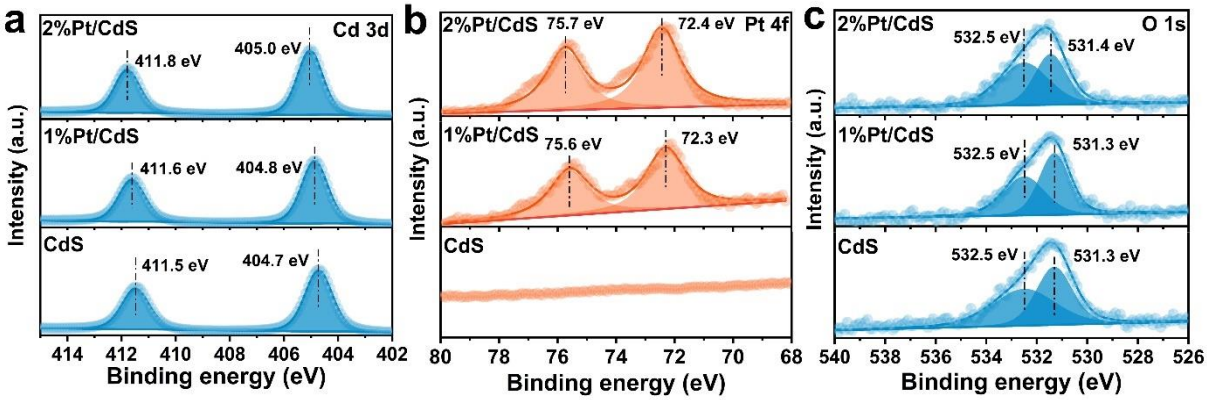
(1) No standard sample containing Pt-S

To directly prove the presence of Pt-S bonds in Pt_1/CdS and Pt_2/CdS, the most straightforward approach is to compare with standard samples containing Pt-S. However, at the XAFS test stations, standard reference materials like PtS and PtS_2 are not common, and the standard database also lacks corresponding data. Therefore, when conducting XANES comparisons, we can only compare the absorption signals of the samples with those of Pt foil and PtO_2 to rule out the existence of elemental Pt and Pt oxides (Pt-O bonds) in the material.

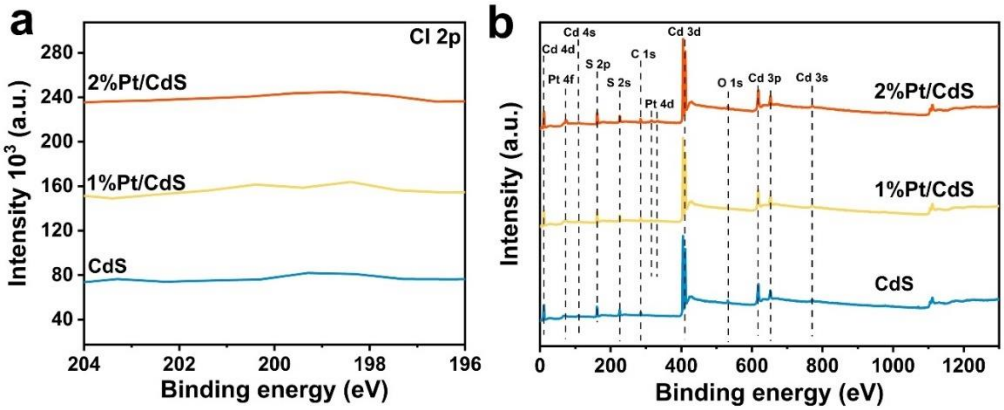
（2）How Pt-S models fit EXAFS

EXAFS fitting is a typical 'black box' process, which involves establishing a possible crystal model and then fitting it with the test data. The correctness of the model is judged by observing the rationality of the fitting parameters. In XPS testing, we found that the valence state of Pt is +2 and there is no lattice oxygen (Supplementary Fig. R3) or Cl (Supplementary Fig. R4) on the material surface. Therefore, we speculated that Pt is most likely to coordinate with S to form a Pt-S configuration. Thus, we established two crystal models and adjusted the distribution of Pt-S

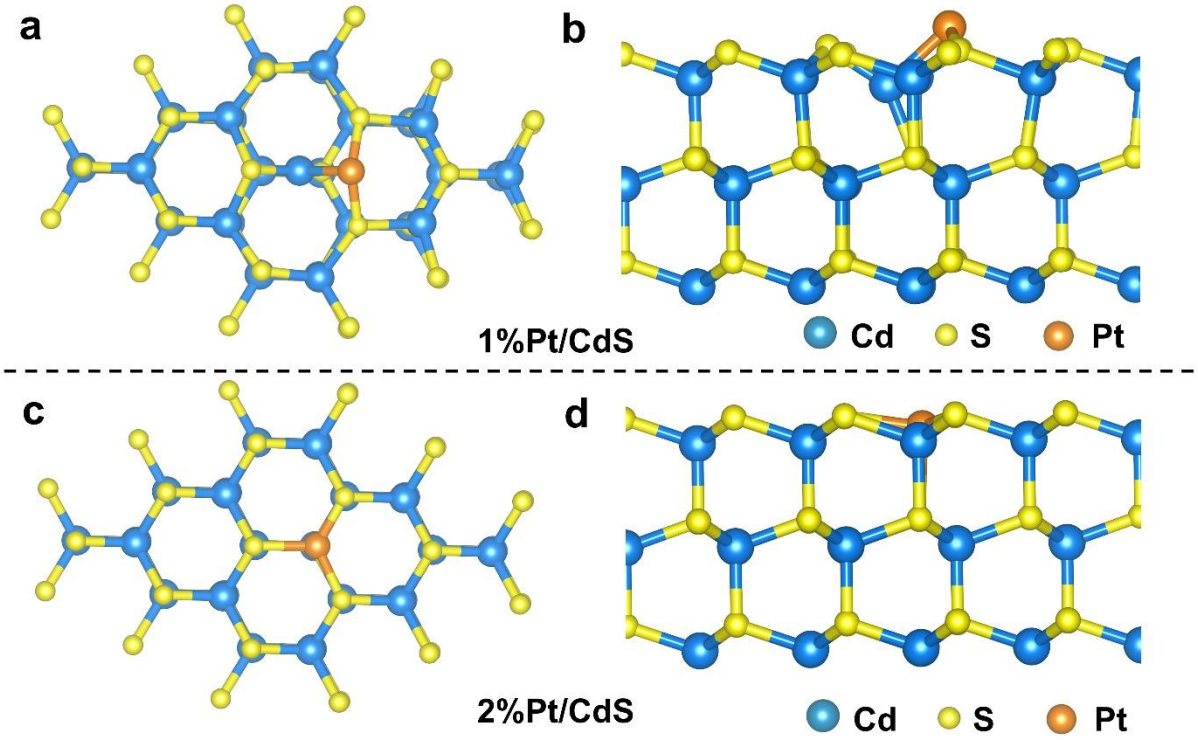
configuration on the CdS surface to match the Fourier transform signal of EXAFS (Supplementary Fig. R5 and Supplementary Fig. R6c). Since the first coordination of Pt atoms in our self-built model is the Pt-S bond, we believe that the first shell of Pt_1/CdS and Pt_2/CdS should also be the Pt-S bond. By comparing with previous works (Angew. Chem. Int. Ed. 2023, 62, e202306452; Adv. Mater. 2024, 21, 2411339), it can also be found that the radiation distance corresponding to the Pt-S bond is indeed in this range (~2.3 Å). Therefore, we believe that there is a Pt-S bond in the material.



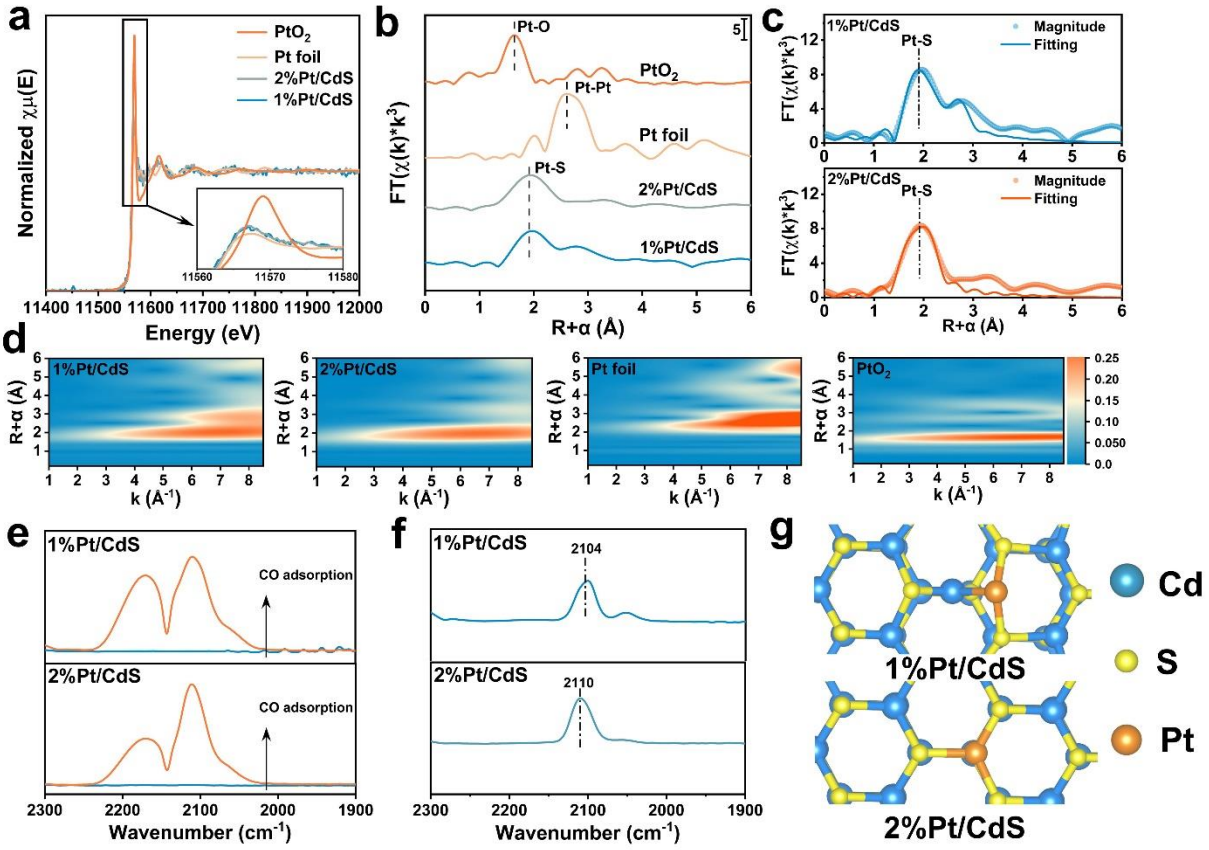
Supplementary Fig. R3 X-ray photoelectron Cd 3d **a**, Pt 4f **b**, O 1s **c** fine spectra of CdS, 1%Pt/CdS and 2%Pt/CdS.



Supplementary Fig. R4 X-ray photoelectron Cl 2p spectra **a** and full spectra **b** of CdS, 1%Pt/CdS and 2%Pt/CdS.



Supplementary Fig. R5 The top view and side view of proposed 1%Pt/CdS **a** and 2%Pt/CdS **b** configurations.

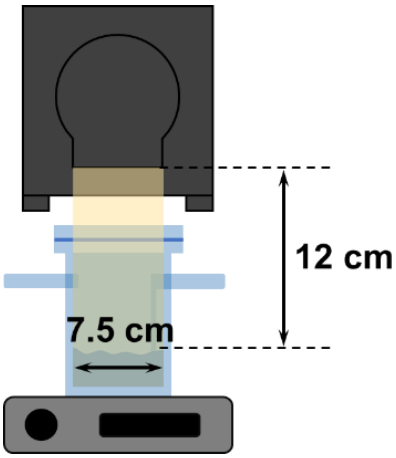


Supplementary Fig. R6 XANES spectra of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and

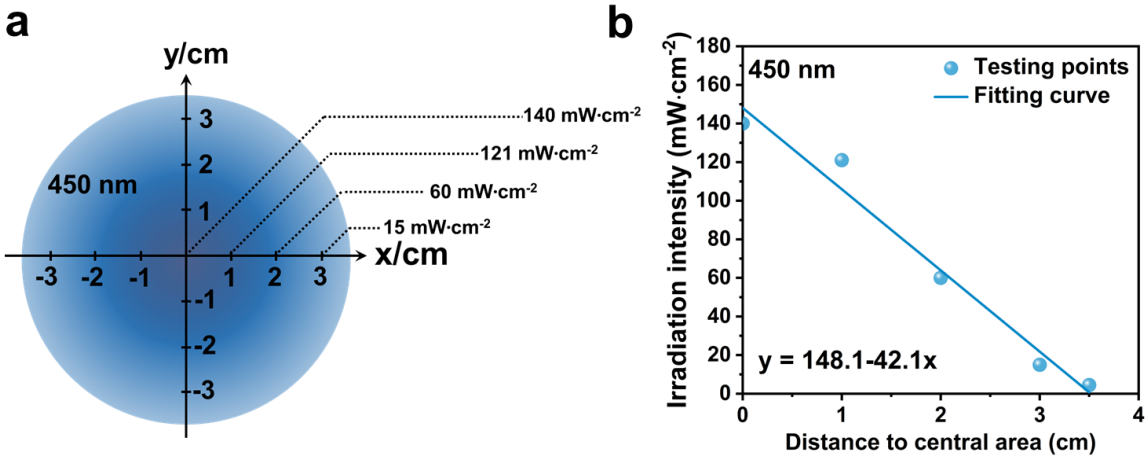
PtO_2 **a**; Fourier-transformed k^3-weighted EXAFS of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **b**; R-space fitting results for 1%Pt/CdS and 2%Pt/CdS (The R-space data are presented without phase correction) **c**; EXAFS wavelet transformation (WT) for Pt foil, PtO_2, 1%Pt/CdS and 2%Pt/CdS **d**; CO adsorption **e** and desorption **f** in-situ DRIFTS of 1%Pt/CdS and 2%Pt/CdS (Ar gas flow was used to remove extra gaseous CO and the desorption curve was collected after 20 min Ar flow); The proposed structure for Pt-S configuration over 1%Pt/CdS and 2%Pt/CdS **g**.

Comment 5.5 In Figure 5c, in addition to selectivity, it is essential to report the Faradaic efficiency to evaluate the actual process efficiency. Faradaic efficiency quantifies the percentage of charge carriers effectively used for methane-to-methanol conversion. Selectivity alone does not account for holes consumed in reactions.

Reply to reviewer: Thank you for the reviewer's comment. Faradaic efficiency requires current density measurement (Equation R1), which is challenging in our heterogeneous photocatalytic dispersion system. Instead, we measured apparent quantum efficiency (AQE) per literature methods (J. Am. Chem. Soc. 2025, 147, 38, 34959-34971; Nat. Commun. 2025, 16, 7612; Adv. Funct. Mater. 2025, 35, 2422726) using Equations R2-R4 to quantify photon utilization. It is found that AQE at 450 nm is 0.06% for Pt_1/CdS (Supplementary Fig. R7, Fig. R8 and Table R1). Detailed AQE methods have been added to the revised manuscript (line 341, page 13; line 606, page 22) and supplementary information (page 33).



Supplementary Fig. R7 The schematic illustrations on photocatalytic set-up and the parameters.



Supplementary Fig. R8 The diagram illustrating the irradiation intensity fluctuation of 450 nm monochromatic light in irradiation area **a)**; The fitting curve of irradiation attenuation in irradiation area **b)**.

$$\eta_F = \frac{N_F}{N_T} = \frac{m \times n \times F}{I \times t} \times 100\% \qquad \text{Equation R1}$$

$$Number\ of\ incident\ photon = \frac{P \times t \times \lambda}{h \times c} \qquad \text{Equation R2}$$

$$AQE = \frac{Number\ of\ electron}{Number\ of\ incident\ photon} \qquad \text{Equation R3}$$

$$P_{450\,nm} = \int_{-3.75}^{3.75} dy \int_{-3.75}^{3.75} 148.1 - 42.1\sqrt{x^2 + y^2}\, dx \qquad \text{Equation R4}$$

Supplementary Table R1 The parameters for CH_3OH production AQE determination.

Wavelength (λ, nm)	Power of light (P, mW)	Number of incident photon	Amount of CH_3OH in 1 h (μmol)	Number of electron	AQE (%)
450	1535.30	1.25×10^{22}	4.08	7.37×10^{18}	0.06

Comment 5.6 To me the reply to reviewer #1's concerns about photocurrents is not really convincing.

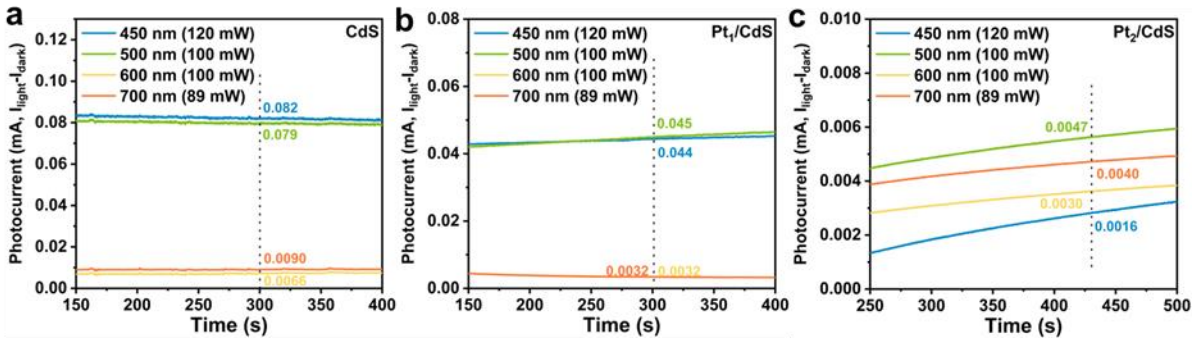
Reply to reviewer: Thank you for the reviewer's comments. While higher activity might suggest higher photocurrent, factors like carrier lifetime, light absorption, and applied fields influence results. TAS shows prolonged carrier lifetime (quantified from Fig. R14), indicating Pt traps electrons ultrafast, suppressing recombination and extending lifetimes. Reduced photocurrent likely stems from this trapping, limiting electron entry into external circuits, as supported by recent work (Nat.

Sustain. 2024, 7, 1171-1181).

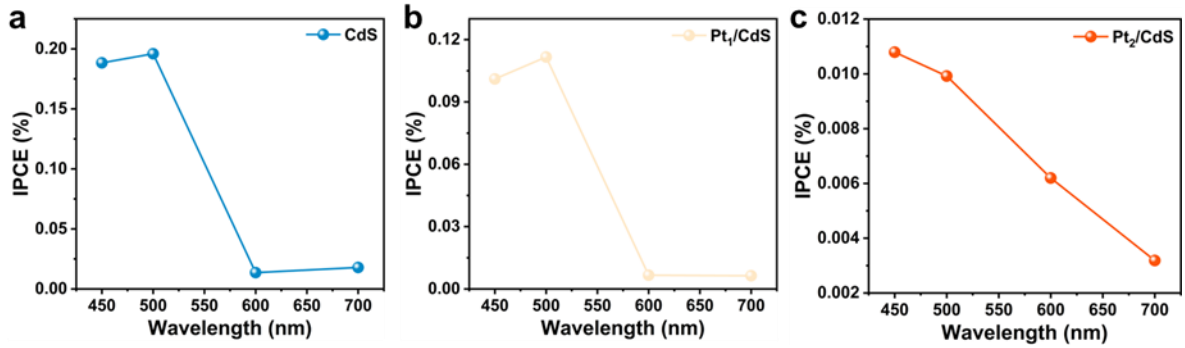
Comment 5.7 Bandgap evaluation based on IPCE spectra should be carried out.

Reply to reviewer: Thank you for the reviewer's comments. IPCE measurements were performed per literature (Adv. Energy Mater. 2021, 11, 2003233; Equation R5, Supplementary Fig. R9-R10, Table R2). IPCE is highest at 400-500 nm, negligible >600 nm. IPCE onset at ~540 nm corresponds to a bandgap of ~2.30 eV, matching continuous absorption spectra (Supplementary Fig. R13c, bandgap ~2.28 eV). XPS valence band spectra (Supplementary Fig. R11a) and TAS (Supplementary Fig. R12) confirm unchanged valence band and bandgap across samples, with Pt primarily modulating carriers (Supplementary Fig. R12 and R13). Descriptions have been added to the revised manuscript (line 203, page 8).

$$IPCE = \frac{1240(V \times nm) \times |I_{ph}(mA)|}{P_{mono}(mW) \times \lambda(nm)} \qquad \text{Equation R5}$$



Supplementary Fig. R9 The photon-induced current in the circuit where the working electrode made of CdS film **a),** Pt_1/CdS film **b)** and Pt_2/CdS film **c)**.

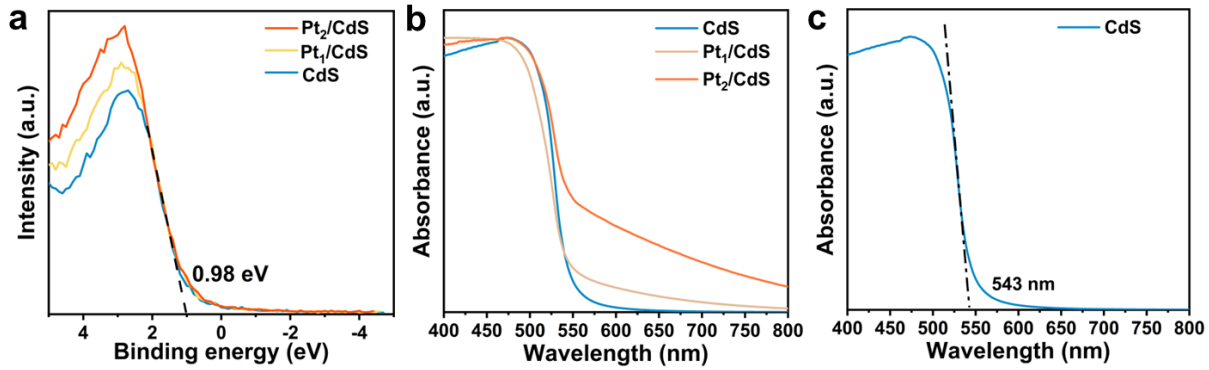


Supplementary Fig. R10 IPCE of CdS, Pt_1/CdS and Pt_2/CdS.

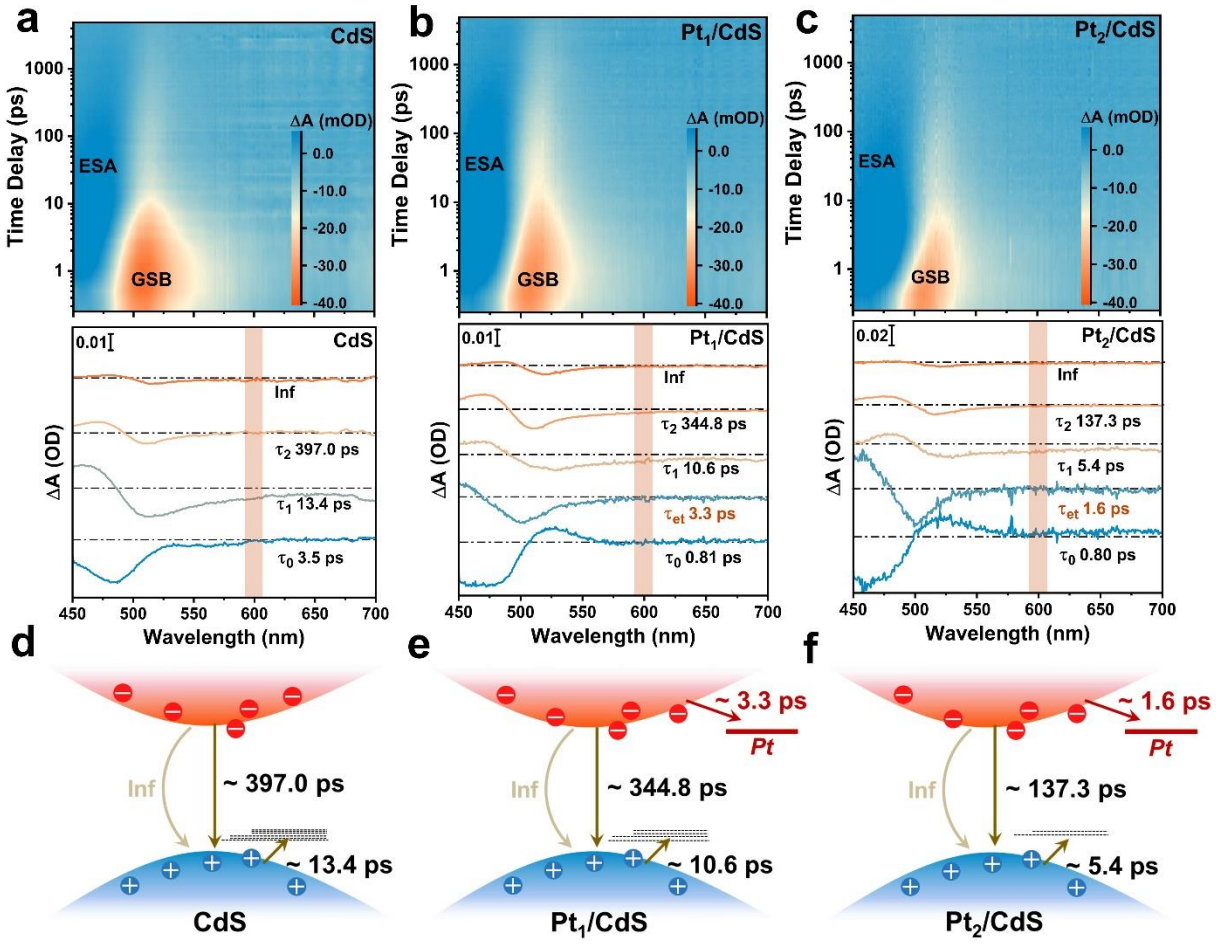
Supplementary Table R2 The parameters for IPCE determination.

Samples	Wavelength (nm)	Photocurrent intensity (mA)	Power of light (mW)	IPCE (%)

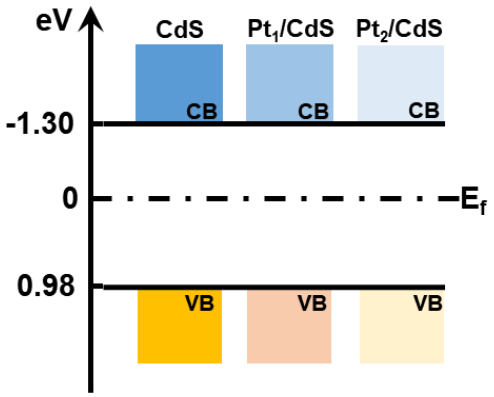
CdS	450	0.082	120	0.19
	500	0.079	100	0.20
	600	0.0066	100	0.014
	700	0.009	89	0.018
Pt_1/CdS	450	0.044	120	0.10
	500	0.045	100	0.11
	600	0.0032	100	0.0066
	700	0.0032	89	0.0064
Pt_2/CdS	450	0.0047	120	0.011
	500	0.004	100	0.0099
	600	0.003	100	0.0062
	700	0.0016	89	0.0032



Supplementary Fig. R11 XPS valence band spectra of CdS, Pt_1/CdS and Pt_2/CdS **a**; the steady-state absorption edge of CdS **b**; the band structure of CdS, Pt_1/CdS and Pt_2/CdS **c**.



Supplementary Fig. R12 Transient absorption spectroscopy (TAS) where 400 nm beam light was used as pump light and a continuous white light ranging from 450 to 700 nm was used as probe light: two-dimensional contour plots of TAS with the associated global fitting results of CdS **a**, Pt_1/CdS **b** and Pt_2/CdS **c**. The diagram exhibiting the excited-state carrier relaxation of CdS **d**, Pt_1/CdS **e** and Pt_2/CdS **f**.

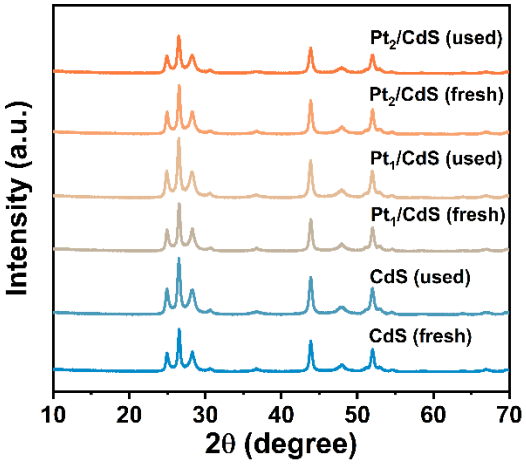


Supplementary Fig. R13 The band structure of CdS, Pt_1/CdS and Pt_2/CdS

Comment 5.8 XRD for all samples after reaction need to be provided.

Reply to reviewer: Thanks for reviewer's comments. XRD of all samples after photocatalytic

reactions have been recorded and they are used to compare with fresh samples. As displayed in Supplementary Fig. R14, the typical diffraction peaks of used samples can well match with fresh ones while no additional peaks appeared, illustrating the crystal stability of CdS, Pt_1/CdS and Pt_2/CdS. In the revised manuscript (line 332, page 13) and revised supplementary information (Page 29), we have supplemented additional descriptions on the contents above.



Supplementary Fig. R14 XRD of fresh and used photocatalysts.

Comment 5.9 Literature citations need to be improved proficiently, and the foundation of the concept needs to be cited properly rather than just some recent related papers.

Reply to reviewer: Thanks for reviewer's comments. We have revised the article in response to the issues related to references, which specifically include: (revised manuscript line 58, page 3) In recent works, simulating the active center of methane monooxygenase (MMO) for catalysts designs have made progress in modulating CH_4 to CH_3OH[9-15]. Not just the precisely constructing biomimetic active sites over photocatalysts, we are also inspired with the sequence of crucial steps, which requires the additional focus on temporal modulations; (revised manuscript line 73, page 3) Conversely, it is common that engineered photocatalysts employ photoinduced-electron-enriched active centers to facilitate efficient O_2-to-ROS conversion ($O_2 + e^- \rightarrow \cdot O_2^-$, $\cdot O_2^- + H^+ \rightarrow \cdot OOH$, $\cdot OOH + H^+ + e^- \rightarrow \cdot OH$)[16-18]. (revised manuscript line 164, page 7) Compared with typical signals (~2084 cm^{-1}), the wavenumber was increased[30-32]. It is speculated that the anchored Pt over CdS could have strong affinity with CO. (revised manuscript line 215, page 9) To determine the contribution of excited electron and hole to the tail bleach, electron trapping agent p-benzoquinone (BQ)[36,37] was used to quench the signal.

Reviewer #6

I have carefully reviewed the entire manuscript as well as the exchange between Reviewer 1 and the authors. Overall, I find the conclusions and findings in the paper to be convincing and carefully presented.

With regard to the main point of debate—the oxidation state of the Pt species—I did notice a very slight shoulder on the high-binding-energy side of the main Pt^{2+} peak, around 73.6 eV. However, given the generally weak core-level signal of the sample, I would be very cautious about directly assigning this feature to a new Pt species. Several alternative explanations are possible, including surface charging, the presence of surface adsorbates during measurement, or baseline artifacts, as the authors have already pointed out. I therefore agree with the authors that the oxidation state of Pt should be established through complementary characterization methods. Indeed, both XAS and TA studies provide consistent evidence supporting the monovalent nature of the Pt species.

In addition, the authors confirmed that there is no residual chloroplatinic acid in the sample, which rules out the major possibility suggested by Reviewer 1.

In general, XPS is a highly surface-sensitive technique that can be subject to significant uncertainties, especially when the overall signal intensity is low. To rigorously validate the electronic structure of the target sample, complementary techniques are essential, rather than overinterpreting noisy XPS spectra through curve fitting alone. This is precisely the approach taken by the authors, and I find their response to Reviewer 1 to be convincing and well-reasoned.

Summary, this manuscript presents a novel innovative concept supported by extensive characterization data. however， before publication, several following issues still need to be addressed.

Reply to reviewer: We sincerely appreciate the reviewer's positive assessment and valuable suggestions, which affirm the manuscript's conclusions while highlighting areas for improvement. In response to these, we have recorded apparent quantum efficiency (AQE) to evaluate light utilization in methane-to-methanol reactions (*see Response 6.3*). We have also revised figure labels, chemical symbols, and units for clarity (*see Responses 6.1, 6.2, and 6.4*). Finally, additional explanations on carrier lifetime and catalytic performance have been provided (*see Response 6.5*). These revisions strengthen the manuscript's rigor and clarity, aligning with the reviewer's positive assessment. Point-by-point responses are detailed below.

Comment 6.1 There appears to be an error in the unit labels within the Fig. 2b and 2c. The unit for vertical coordinate should be the angstrom, symbolized as ‘Å’, not the ampere, which is symbolized as ‘A’. Additionally, adding a detailed legend description to the EXAFS fitting parameters table (Supplementary Table 2-3) is crucial for reflecting the rigor of the data. For example, J.Am.Chem.Soc, 145, 2698-2707.

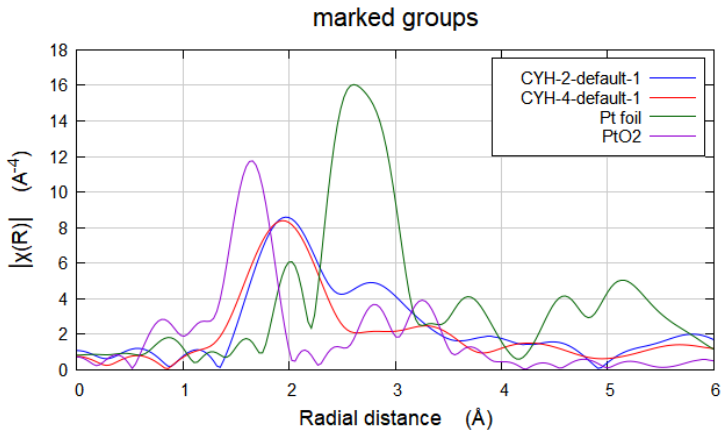
Reply to reviewer: We are very grateful for these conductive comments. These comments are responded in detail as follows:

(1) The unit for vertical coordinate

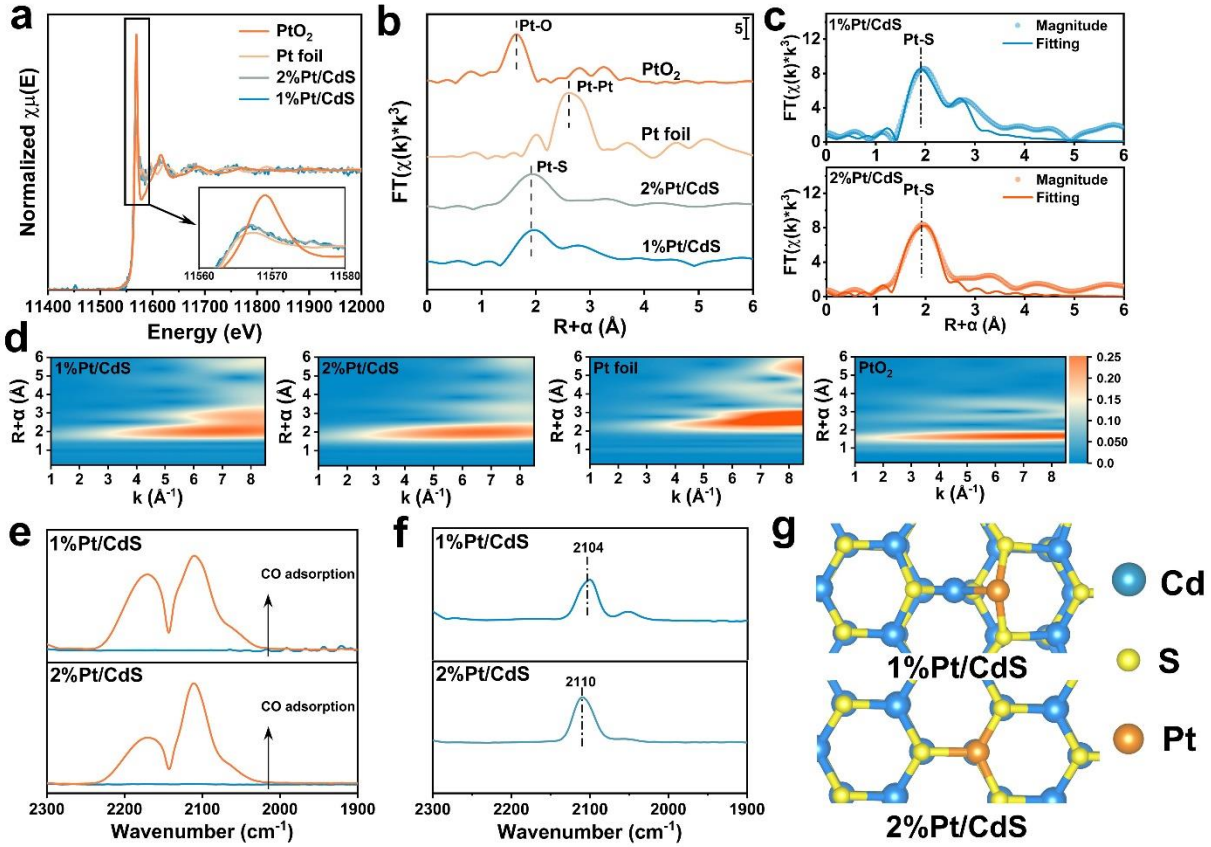
The unit of the vertical coordinate in Fig. 2b and 2c was referred to the analysis software of XAFS (Athena, Artemis). Here, the symbol “A” represents the intensity of the Fourier-transformed signals, not ampere nor the length unit angstrom (Supplementary Fig. R15). However, considering that this representation might cause ambiguity, we modified the vertical coordinate of the picture according to the reference recommended by the reviewer (Supplementary Fig. R16).

（2）The legend descriptions on EXAFS fitting parameters table

Thanks for the reviewers' suggestions. We have revised the descriptions of the XAFS fitting data table in accordance with the recommended literature, adding the necessary data fluctuation range, which can better present the fitting results (Supplementary Table 3 and Supplementary Table 4).



Supplementary Fig. R15 Fourier-transformed k^3-weighted EXAFS of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 (This figure was exported by Athena software)



Supplementary Fig. R16 XANES spectra of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **a**; Fourier-transformed k^3-weighted EXAFS of 1%Pt/CdS and 2%Pt/CdS versus that of Pt foil and PtO_2 **b**; R-space fitting results for 1%Pt/CdS and 2%Pt/CdS (The R-space data are presented without phase correction) **c**; EXAFS wavelet transformation (WT) for Pt foil, PtO_2, 1%Pt/CdS and 2%Pt/CdS **d**; CO adsorption **e** and desorption **f** in-situ DRIFTS of 1%Pt/CdS and 2%Pt/CdS (Ar gas flow was used to remove extra gaseous CO and the desorption curve was collected after 20 min Ar flow); The proposed structure for Pt-S configuration over 1%Pt/CdS and 2%Pt/CdS **g**.

Supplementary Table R3 Curve-fit parameters of Pt L_3-edge EXAFS of 1%Pt/CdS based on optimized crystal model.

	S_0^2	δ^2	ΔE_0 (eV)	R (Å)	N	R-factor
Pt-S[1]	0.98	0.0012 ± 0.0032	7.17 ± 2.87	2.33	2.58 ± 0.82	0.017
Pt-Cd[2]		-0.0018 ± 0.0097		2.79	1.00 ± 1.71	

S_0^2 was set as 0.98; σ^2: Debye-Waller factors; ΔE^0: the inner potential correction; R: bond distance; N: coordination numbers; R factor: goodness of fit.

Supplementary Table R4 Curve-fit parameters of Pt L_3-edge EXAFS of 2%Pt/CdS based on optimized crystal model.

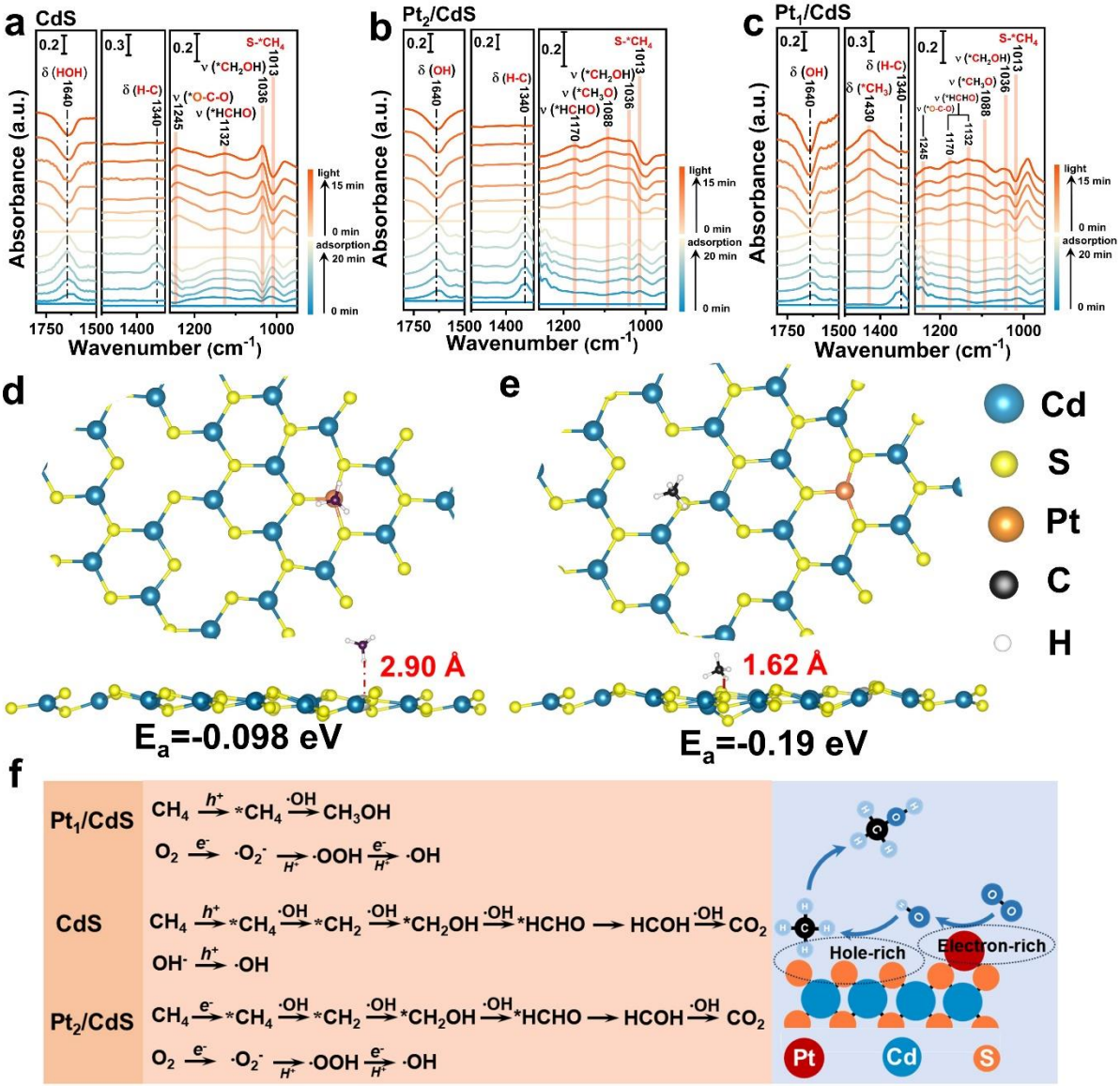
	S_0^2	δ^2	E_0 (eV)	R (Å)	N	R-factor

Pt-S^1	0.98	-0.00013 ± 0.0086	5.98 ± 5.0028	2.28	2.75 ± 1.87	0.019
Pt-S^2		-0.0060 ± 0.0055		2.42	1.10 ± 0.00	

S_0^2 was set as 0.98; σ^2: Debye-Waller factors; ΔE^0: the inner potential correction; R: bond distance; N: coordination numbers; R factor: goodness of fit.

Comment 6.2 In Fig. 6, it is recommended to clearly indicate the correspondence between the electron/hole enrichment sites and the reaction pathways, for example, holes are enriched at the S sites while electrons are enriched at the Pt sites.

Reply to reviewer: Thanks for reviewer's suggestions. To clarify the collaboration between S sites and Pt sits in charge carrier dynamics modulation, Fig. 6f have been carefully revised so that it can emphasize the preferable localization of S and Pt for hole and electron (Supplementary Fig. R17).

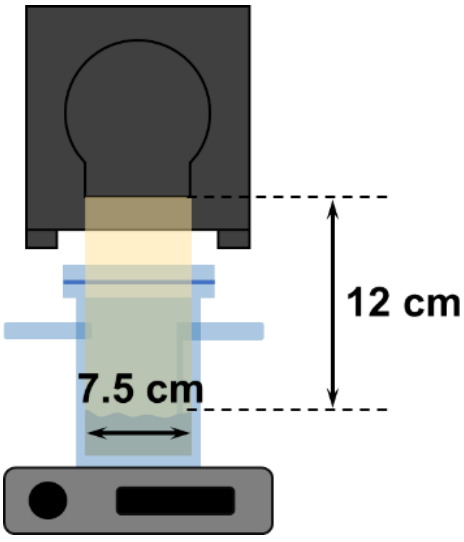


Supplementary Fig. R17 In-situ diffuse reflectance infrared Fourier transform spectroscopy

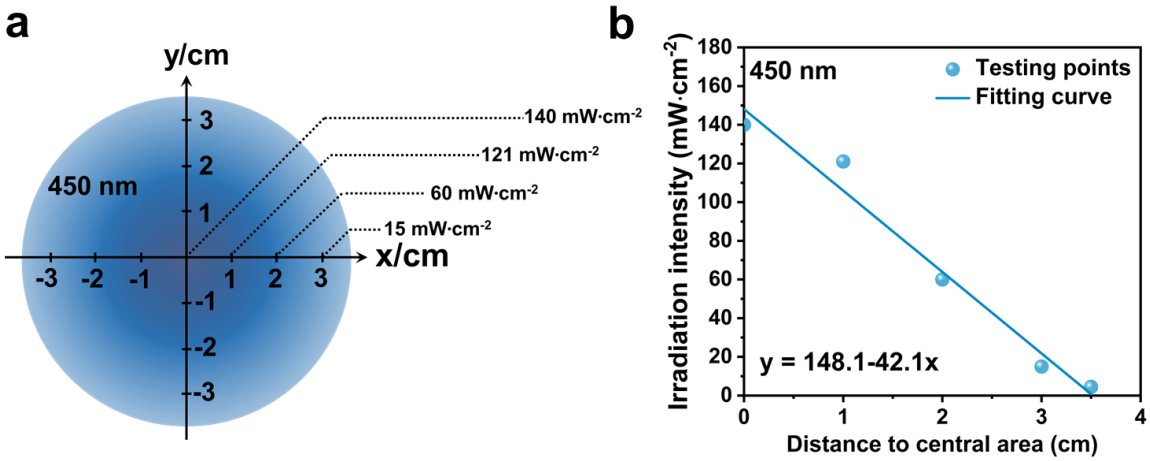
(DRIFTS) of CdS **a**, Pt_2/CdS **b** and Pt_1/CdS **c** in the atmosphere of CH_4 + O_2 + H_2O mixture: the sample surface has been fully adsorbed with reactants before the light irradiation (These data were smoothed during processing). Geometry optimized configuration of CH_4 adsorbed on Pt sites **d** and unsaturated sulfur sites **e.** Schematic diagram illustrating the CH_3OH production through stepwise reaction path **f**.

Comment 6.3 It is recommended to supplement the test data for apparent quantum efficiency to allow for a more comprehensive evaluation of the photocatalytic efficiency.

Reply to reviewer: Thank you for the reviewer's comment. We have performed AQE measurements per recent works (J. Am. Chem. Soc. 2025, 147, 38, 34959-34971; Nat. Commun. 2025, 16, 7612; Adv. Funct. Mater. 2025, 35, 2422726) using Equations R6-R8 to quantify photon utilization. Monochromatic light (450 nm) was obtained via filters on a Xe lamp (Supplementary Fig. R18). Incident photon numbers were calculated via double integration of irradiation intensity (Supplementary Fig. R21). It is found that AQE at 450 nm is 0.06% for Pt_1/CdS. These data enhance the evaluation of photocatalytic efficiency and have been added to the revised manuscript (pages 13 and 22) and supplementary information (page 34).



Supplementary Fig. R18 The schematic illustrations on photocatalytic set-up and the parameters.



Supplementary Fig. R19 The diagram illustrating the irradiation intensity fluctuation of 450 nm monochromatic light in irradiation area **a)**; The fitting curve of irradiation attenuation in irradiation area **b)**.

$$Number\ of\ incident\ photon = \frac{P \times t \times \lambda}{h \times c} \qquad \text{Equation R6}$$

$$AQE = \frac{Number\ of\ electron}{Number\ of\ incident\ photon} \qquad \text{Equation R7}$$

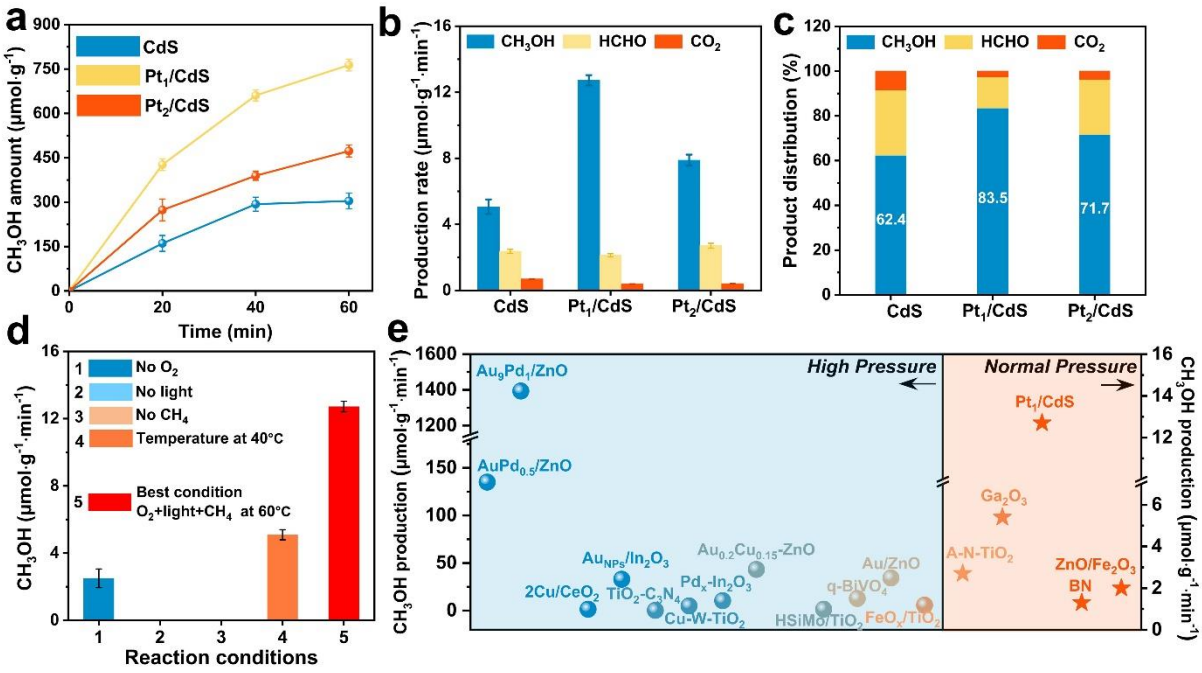
$$P_{450\,nm} = \int_{-3.75}^{3.75} dy \int_{-3.75}^{3.75} 148.1 - 42.1\sqrt{x^2 + y^2}\,dx \qquad \text{Equation R8}$$

Supplementary Table R6 The parameters for CH_3OH production AQE determination.

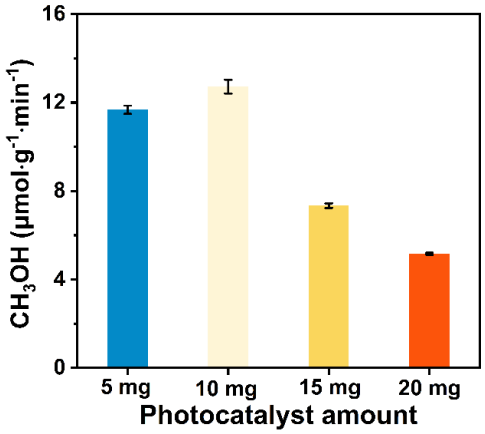
Wavelength (λ, nm)	Power of light (P, mW)	Number of incident photon	Amount of CH_3OH in 1 h (μmol)	Number of electron	AQE (%)
450	1535.30	1.25×10^{22}	4.08	7.37×10^{18}	0.06

Comment 6.4 It appears that the font or size of "μ" in Fig. 5 is inconsistent with others. It is recommended to optimize its font style and size to ensure visual uniformity.

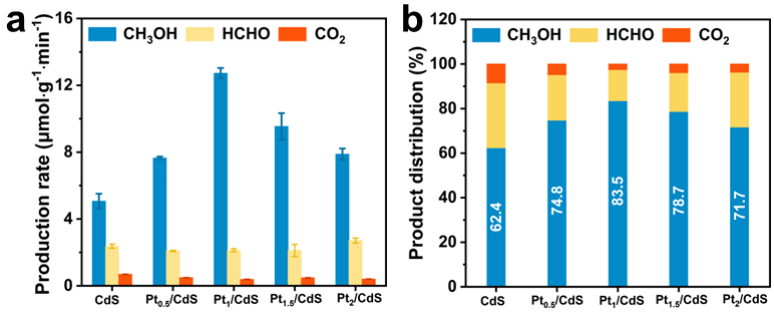
Reply to reviewer: Thanks for reviewer's comments and comprehensive scrutinization on our figures. In the revised manuscript, the Roman numerals and chemical symbols in the figures (especially Supplementary Fig. R20) and context have been carefully revised. It is expected that the current version can explicitly deliver the crucial information to readers.



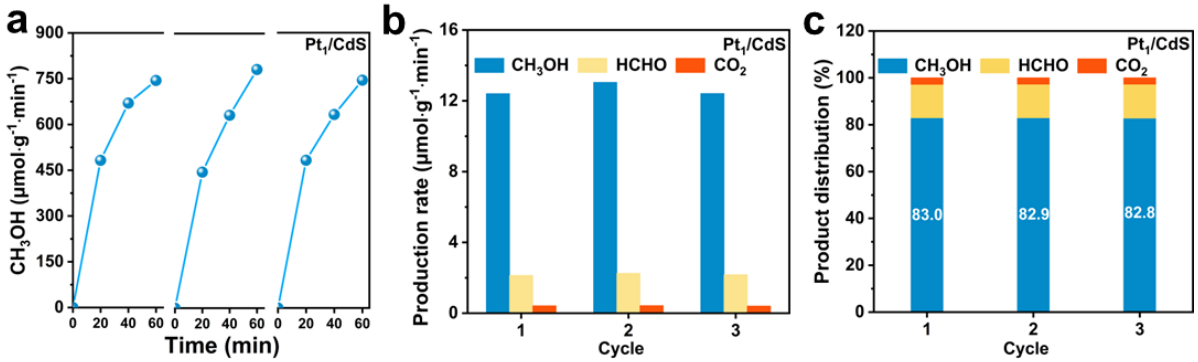
Supplementary Fig. R20 Photocatalytic CH_4 oxidation performance evaluation: the contribution of Pt amount to CH_3OH production rate **a**; the statistic average production rate of different products **b** and photocatalytic products distributions **c**; The contrast photocatalytic experiment to determine the optimized experimental conditions (photocatalyst was Pt_1/CdS) **d**. The representative works on CH_4 photooxidation to CH_3OH (The data are collected and calculated based on the information provided in the experimental sections) **e**. Error bars represent standard deviations obtained from at least two independent measurements.



Supplementary Fig. R21 Photocatalytic CH_4 oxidation performance evaluation: contrast experiments to determine the optimized photocatalyst amount. CH_3OH production rate equals to CH_3OH amount in 1 h divided by irradiation time. Error bars represent standard deviations obtained from at least two independent measurements



Supplementary Fig. R22 Photocatalytic CH_4 oxidation performance evaluation: the contribution of Pt amount to the statistic average products production rate **a** and products distributions **b**. Error bars represent standard deviations obtained from at least two independent measurements



Supplementary Fig. R23 Photocatalytic CH_4 to CH_3OH cycle experiments over Pt_1/CdS: the linear graph showing the CH_3OH amount in the system **a**; the average CH_3OH, HCHO and CO_2 production rate in every cycle **b**; the average product distribution in every cycle **c**. Error bars represent standard deviations obtained from at least two independent measurements

Comment 6.5 The paper indicates that the introduction of Pt accelerates the charge carrier recombination rate, yet it enhances the catalytic performance. Does this imply that a longer charge carrier lifetime is not necessarily better?

Reply to reviewer: Thanks for reviewer's comments. As to this issue, we need to give more descriptions on the role of Pt in photocatalysis. Although some material characterization do not directly indicate the increase of carrier lifetime, such as TRPL, from an overall perspective, we still believe that the loading of Pt promotes carrier separation, which is beneficial to the enhancement of photocatalytic activity. Firstly, on the ultrafast timescale (picosecond timescale), TAS analysis proves that Pt rapidly captures the photogenerated electrons of CdS, forming an electron localization state. This capture process limits the intrinsic band edge recombination of CdS. Further, on the nanosecond timescale, although TRPL indicates that the fluorescence lifetime of Pt_1/CdS and Pt_2/CdS is shorter, TRPL mainly responds to the radiative recombination process, that is, the intrinsic recombination of CdS. However, electrons captured by the trapped state (Pt) generally return to the ground state through a non-radiative process and have a longer lifetime. This inference

can be drawn from the steady-state fluorescence test results. The steady-state fluorescence intensity of Pt_1/CdS and Pt_2/CdS is significantly lower than that of CdS, indicating that Pt inhibits the rapid radiative recombination of CdS and allows the captured electrons to return to the ground state through a non-radiative process with a longer lifetime.

Manuscript: NCOMMS-25-21495

Spatiotemporal control of photon distribution on active sites: Bridging bio-inspired methane-to-methanol conversion

Response to the Reviewers' Comments

Reviewer #1

I would like to thank the authors for their diligence and patience in this review. I do have a few other questions based on their discussions with my colleagues in their response. Overall, I think the authors have done a lot of work to address our reviewer comments. The interpretation of the photoelectron spectra still concerns me. There seems to be enough supporting evidence of bulk techniques for the authors claims, but their core argument/interpretation does center on the interaction of Pt with the surface of the CdS particles, thus a surface sensitive characterization technique should be the most supportive of their claims. I would continue with my last comment that it merits publication and that the authors and the field should take the opportunity to investigate this further.

Reply to reviewer: We would like to express our sincere gratitude to the reviewer for the comprehensive evaluation, which has significantly improved the quality of our manuscript. Regarding the interpretation of Pt valence states, we fully appreciate the reviewer's thoughtful concerns and the opportunity to refine our analysis for greater rigor. Accordingly, we have revised the descriptions of Pt valence states in the latest version to make them more measured and nuanced (***see more details in the revised manuscript***). We believe this wording strengthens our core arguments while leaving sufficient space for future researchers to further explore the valence states and functions of Pt based on our work.

Moreover, point-to-point responses have been made to positively respond the reviewer's comments. Firstly, we have enriched our descriptions on in-situ XPS and presented more details of experiments and analysis (***see response 1.3***). Recommended EPR spectra for CdS, 1%Pt/CdS and 2%Pt/CdS have been supplemented (***see response 1.2***) and XRD of fresh and used samples have been partially enlarged to display the crucial information in a better way (***see response 1.4***). Moreover, we also give more explanations to HAADF-STEM analysis, which is expected to solve the confusion of reviewer (***see response 1.1***). Our responses are presented in detail as follow:

Comment 1.1 In the HAADF-STEM image, the authors point to several changes in contrast on the 1% Pt/CdS in a single area but it is not distributed across the particle. The same can be said for the 2% Pt/CdS image. Is this a proper representation of the photocatalyst surfaces in each case? I would expect for the 2% Pt/CdS to have double the amount of Pt on the surface, but this doesn't seem to be the case. Can the authors provide some explanation for this?

Reply to reviewer: Thanks for reviewer's comments. This comment will be responded in details

as follow:

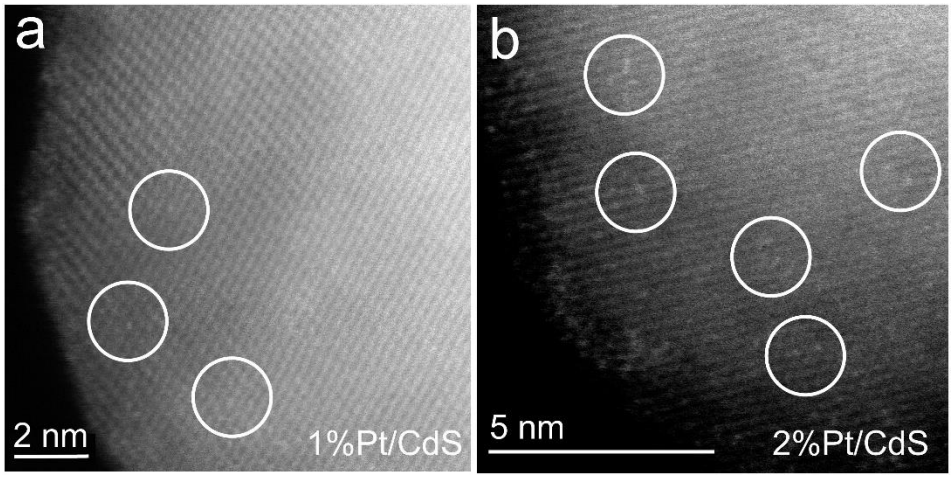
(1) Explanation for the non-uniform distribution of Pt across the particles.

In HAADF-STEM image, the identification of uniformly dispersed Pt atoms primarily relies on the contrast difference. Due to the higher relative atomic mass of Pt compared to Cd and S, Pt atoms appear brighter in the images. Regarding the reviewer's question concerning the dispersion of Pt, we attribute the absence of observed uniform distribution across the entire particle to two main reasons. Firstly, the highly dispersed Pt atoms exist predominantly as single atoms with minimal mutual interference, resulting in a random distribution. This phenomenon is also reported in other studies (J. Am. Chem. Soc.145, 13169-13180 (2023)). Secondly, we speculate that this is related to the thickness of the CdS particles. In the central region of the particles, the increased crystal thickness, combined with the fact that the contrast difference between Pt and Cd is not 'absolutely large', may have prevented HAADF from effectively capturing the relevant signals.

(2) The explanation on the signals intensity over 2%Pt/CdS.

We share the reviewer's expectation that the 2%Pt/CdS sample should exhibit approximately twice the signal intensity of 1%Pt/CdS sample in the images. However, as the loading amount increases, we cannot assume that interatomic interference grows in a strictly linear manner. Although XAFS fitting results indicate that Pt in 2%Pt/CdS still exhibits a Pt-S coordination, its overall configuration is not identical to that of the 1% Pt sample. This suggests the presence of interactions among Pt atoms, leading to the clustering of some Pt single atoms within certain regions in HAADF images. Therefore, the overall dispersion does not directly correlate with the nominal loading amount.

In summary, HAADF-STEM reveals the high dispersity of Pt over 1%Pt/CdS and 2%Pt/CdS, and this result can support the results of XAFS, TEM and etc.

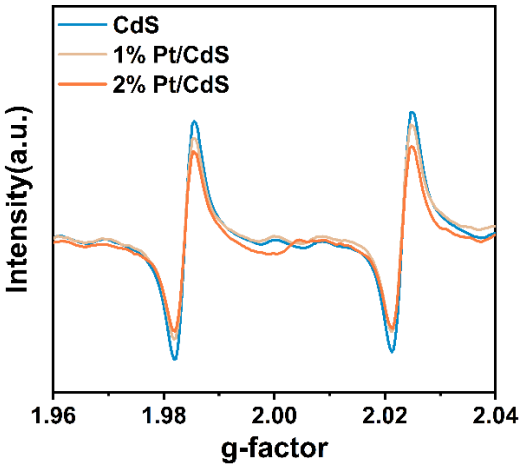


Supplementary Fig. R1 HAADF-STEM of 1%Pt/CdS **a** and 2%Pt/CdS **b**.

Comment 1.2 In the EPR spectra, this change is very small and could be attributed to changes in

the background. Did the authors also run the 2% Pt/CdS to observe a starker change in the EPR?

Reply to reviewer: We thank reviewer for this comment. To display the change in EPR, CdS 1%Pt/CdS and 2%Pt/CdS have been all supplemented in revised Supplementary Information (Page 11). As Supplementary Fig. R2 displays, the EPR signals of CdS decline as the loading amount of Pt is increasing, illustrating that Pt are bonded with unsaturated sulfur which induce crystal defects. The related descriptions for EPR are also supplemented on Page 6 of revised manuscripts.



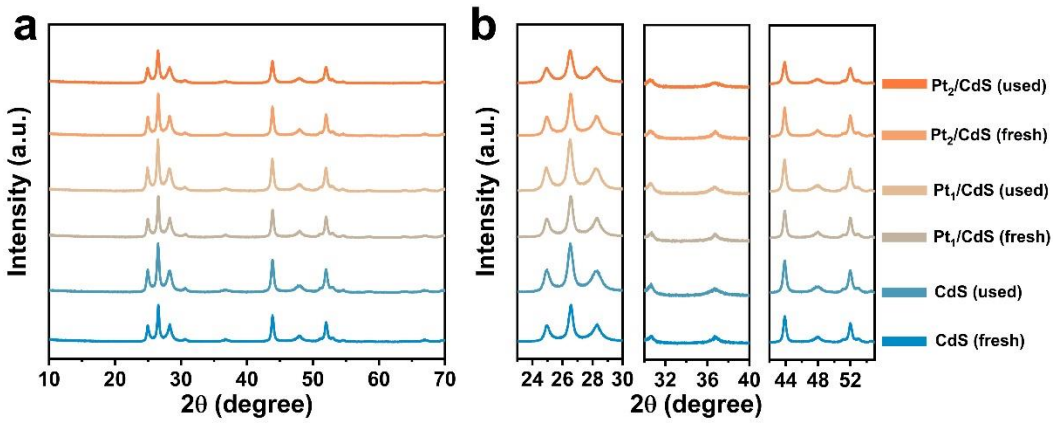
Supplementary Fig. R2 EPR of CdS, 1%Pt/CdS and 2%Pt/CdS.

Comment 1.3 Adsorbed CO_2 isn't likely to shift the photoelectron spectra in the way the authors indicate. It is not clear whether the shifts mean anything other than some sort of charging effect. More information on how the samples for photoelectron characterization are mounted in the methods section would be appreciated.

Reply to reviewer: Thanks for reviewer's comment. We are sorry our previous descriptions on XPS calibrations are not clearly presented. It should be emphasized that our in-situ XPS measurements were conducted under vacuum conditions; therefore, the charge accumulation observed on the material surface should originate from the material itself rather than from other external processes. Furthermore, during the energy calibration of XPS, we consider that adsorbed carbon species (C 1s 284.8 eV) does not substantially affect the binding energy shift. Accordingly, all spectra were calibrated based on this premise, which allowed us to identify the systematic deviation in binding energy. Specifically, as the Pt loading increases, the degree of electron localization at the material surface is enhanced, leading to an overall negative shift in binding energy across the surface. To better clarify our testing and interpretation procedures, we have supplemented the experimental details related to the in-situ XPS characterization in the revised supplementary information (Page 4), aiming to present the relevant information more comprehensively to readers.

Comment 1.4 Can R14 be split into multiple panels and the data enlarged so that we can see more subtle changes in the XRD spectra? The current presentation is difficult to discern any changes other than major changes in the largest peaks.

Reply to reviewer: Thanks for reviewer's comment and suggestions. To well present the details of XRD, the continuous spectra (from 10 to 70°) have been divided into three panels (23 to 30°, 30 to 40°, 42 to 55°) where the typical diffraction peaks of as-prepared samples are enlarged. As Supplementary Figure R3 displays, the detected diffraction peaks of CdS, Pt_1/CdS and Pt_2/CdS can be all indexed to hexagonal CdS, while they are stable and not altered after photocatalysis, illustrating the crystal stability of photocatalysts. The related descriptions for XRD are also supplemented on Page 13 of revised manuscripts.



Supplementary Fig. R3 XRD of fresh and used photocatalysts: full spectra **a)** and partially enlarged spectra **b)**.

Reviewer #6

The authors have addressed fully my concerns. Now the manuscript can be accepted for publication in Nature Communications.

Reply to reviewer: We extend our sincere gratitude to the reviewer for the thorough scrutiny and acceptance of our work.