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SUPPLEMENTARY INFORMATION

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Stoichiometric methane conversion to ethane using photochemical looping at ambient temperature

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Supplementary Information for

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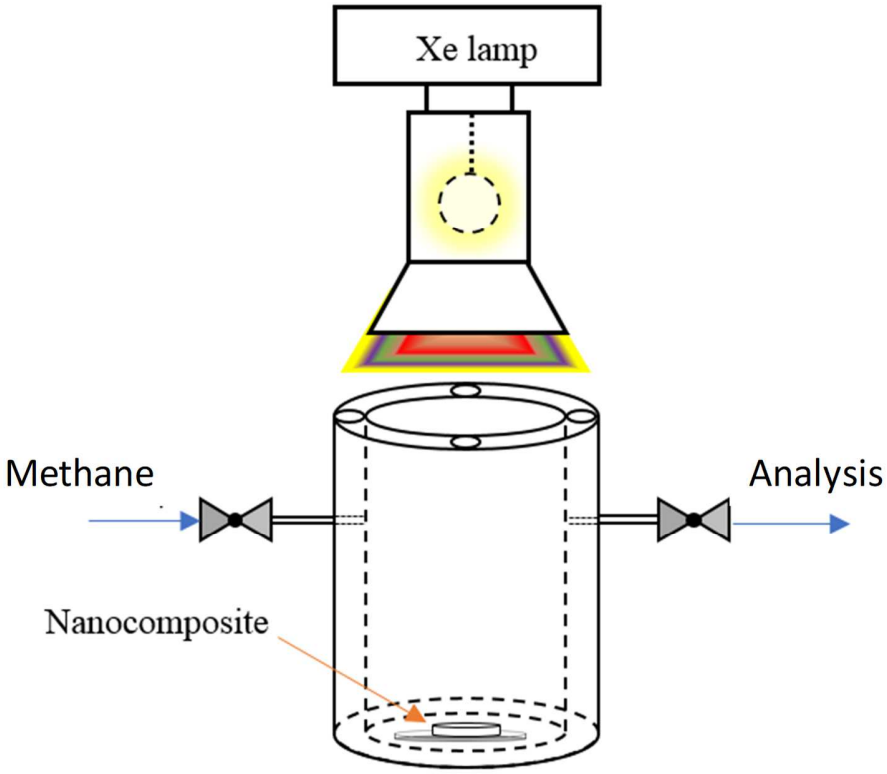
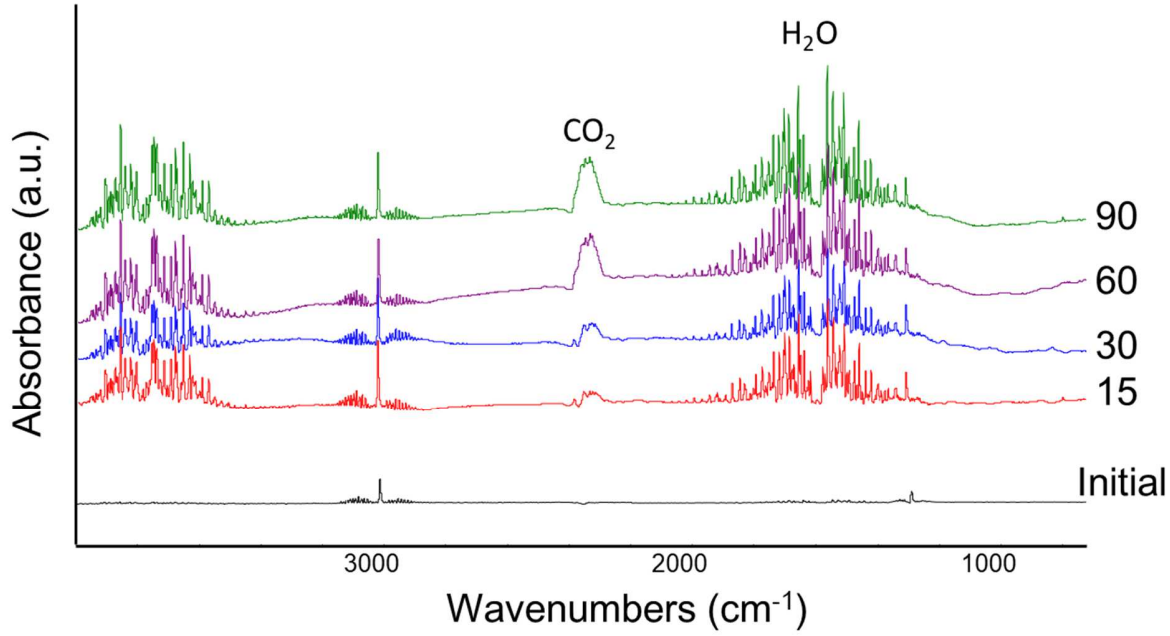
by Xiang Yu, Vladimir L. Zholobenko, Simona Moldovan, Di Hu, Dan Wu, Vitaly V. Ordomsky and Andrei Y. Khodakov**

Supplementary Table 1. BET specific surface area measured for the Ag-HPW/TiO_2 nanocomposites with different ratio of HPW/TiO_2.

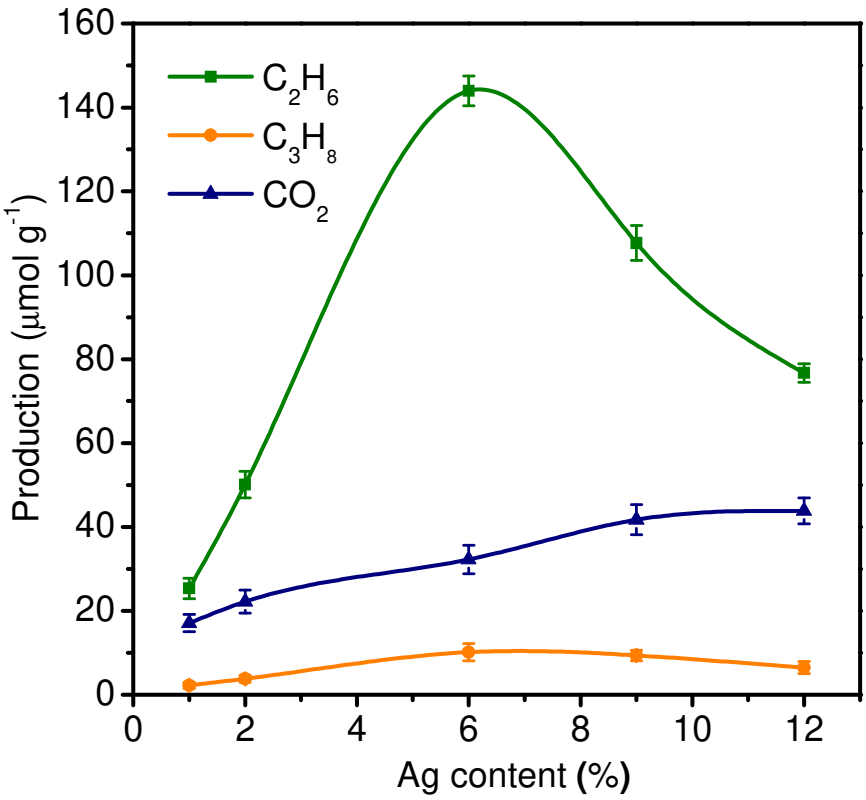
Ag-HPW/TiO_2 (the ratio of HPW/TiO_2)	BET (m^2/g)
0.15	40
0.30	36
0.60	31
0.90	25
1.2	18



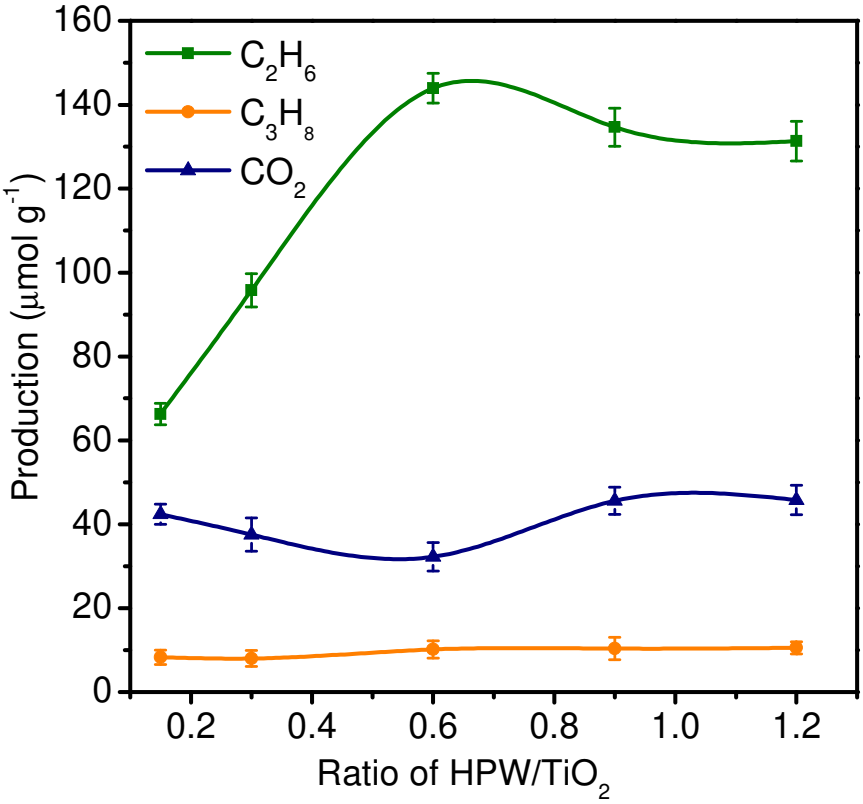
Supplementary Fig. 1. Schema of photochemical reactor



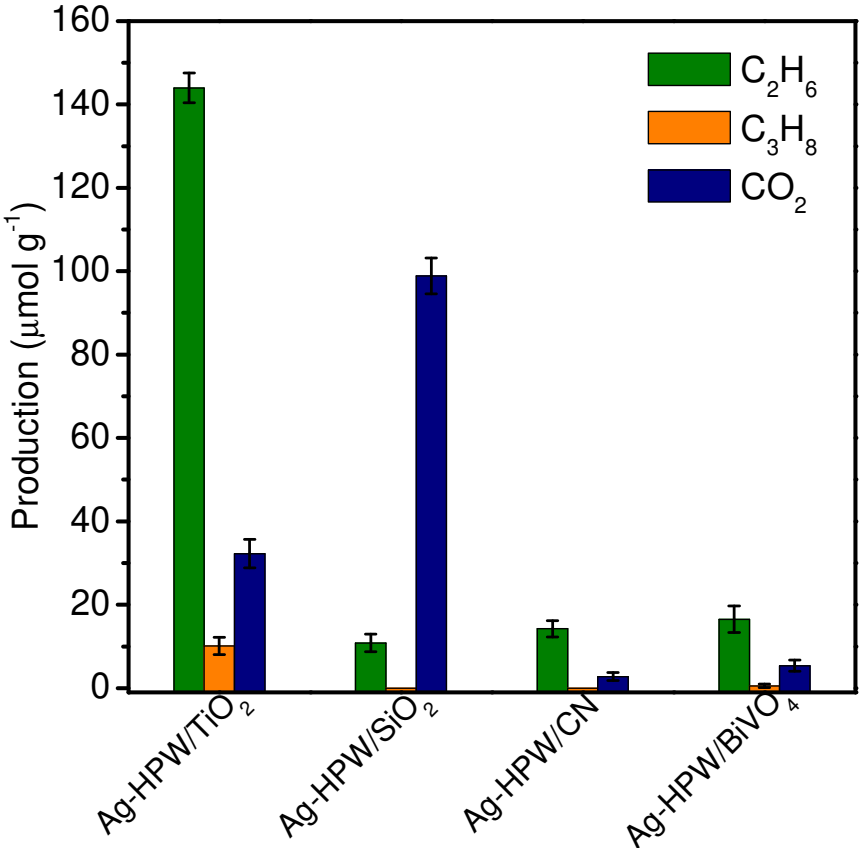
Supplementary Fig. 2. FTIR spectra of gaseous phase during photochemical coupling of methane over Ag-HPW/TiO2 as a function of reaction time. The reaction has been performed in FTIR cell by light treatment of the pellet Ag-HPW/TiO_2 at 1 bar of methane.



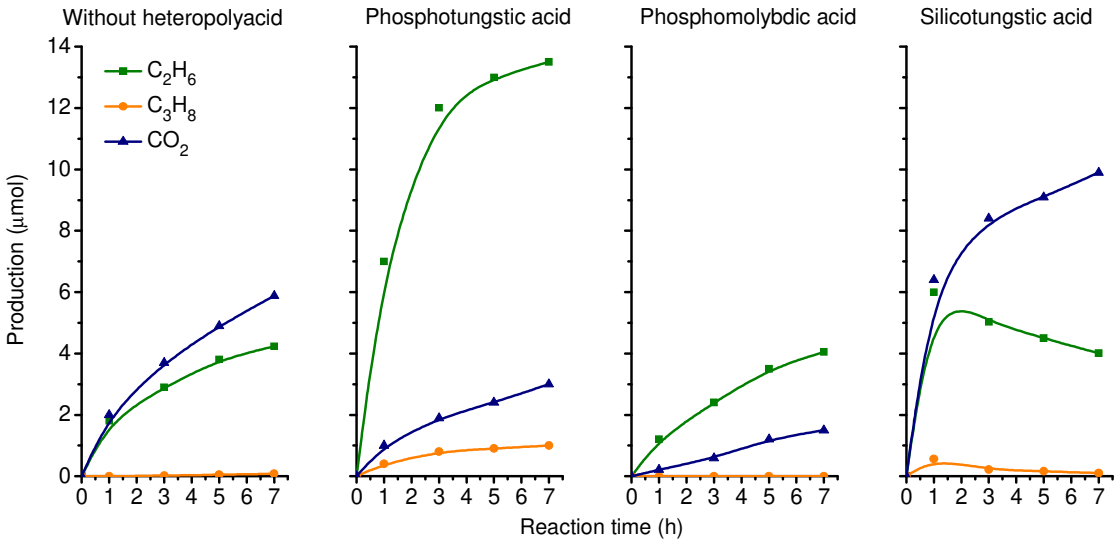
Supplementary Fig. 3. Production of ethane, propane and carbon dioxide over Ag-HPW/TiO_2 with different Ag loadings. The lines are guides to the eye. Reaction conditions: nanocomposite, 0.1 g; gas phase pressure, CH_4 0.3 MPa; irradiation time, 7 h. The experiments in each case were performed for three times. The error bar represents the relative deviation, which is within 5%.



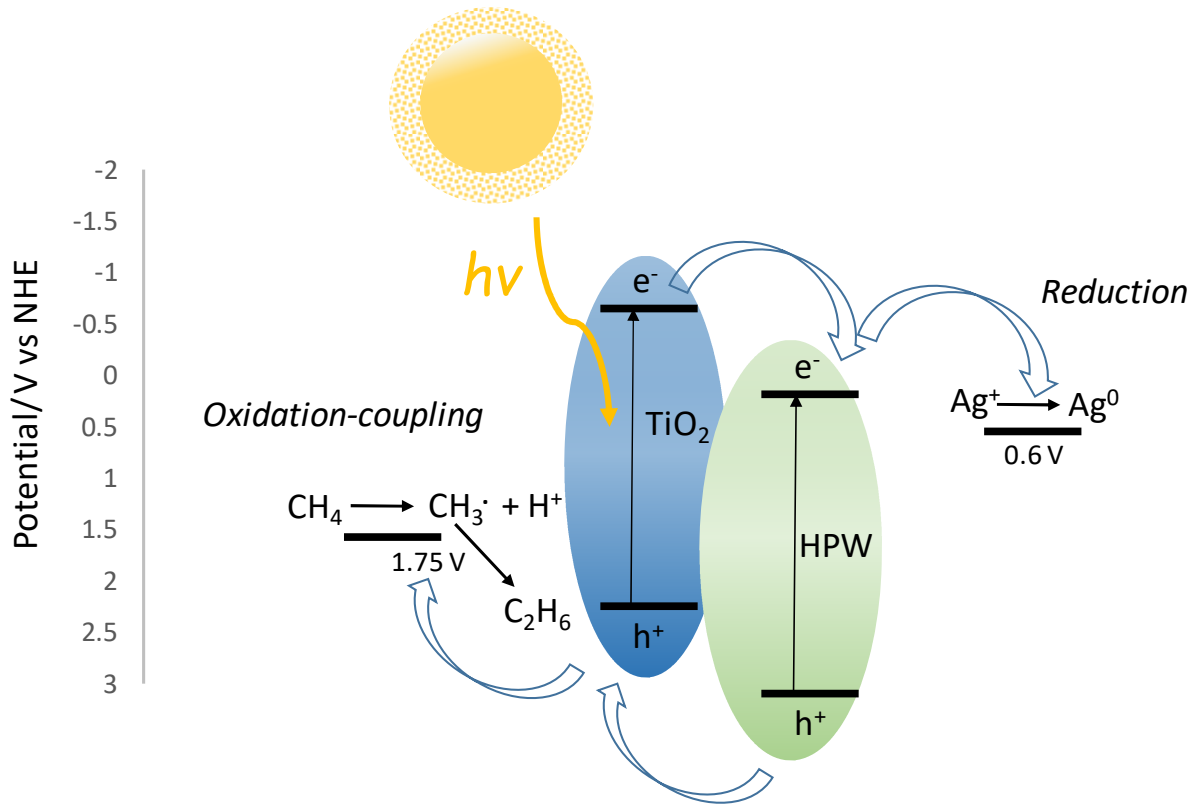
Supplementary Fig. 4. Production of ethane, propane and carbon dioxide over Ag-HPW/TiO_2 with different ratio of HPW/TiO_2. The lines are guides to the eye. Reaction conditions: nanocomposite, 0.1 g; gas phase pressure, CH_4 0.3 MPa; irradiation time, 7 h. The experiments in each case were performed for three times. The error bar represents the relative deviation, which is within 5%.



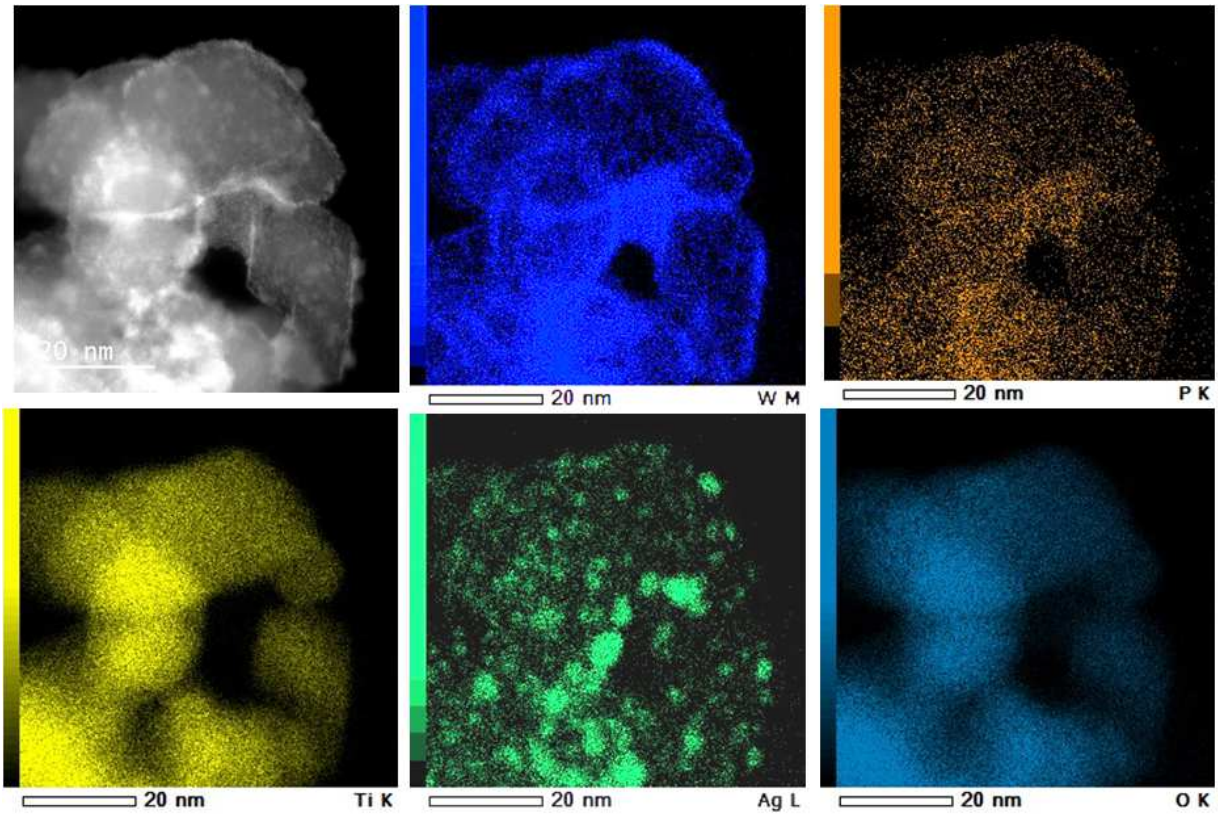
Supplementary Fig. 5. Production of ethane, propane and carbon dioxide on silver-heteropolyacid on different semiconducting supports. Reaction conditions: nanocomposite, 0.1 g; gas phase pressure, CH_4 0.3 MPa; irradiation time, 7 h. The experiments in each case were performed for three times. The error bar represents the relative deviation, which is within 5%.



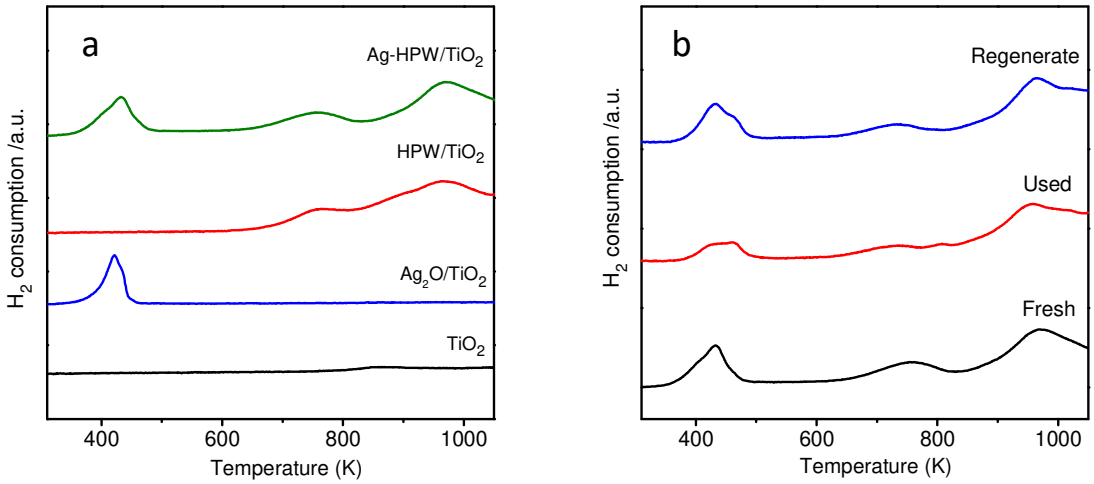
Supplementary Fig. 6. Production of ethane, propane and carbon dioxide during photochemical conversion of methane on the Ag-HPW/TiO_2 nanocomposites prepared using different heteropoly acids. The lines are guides to the eye. Reaction conditions: nanocomposite, 0.1 g; gas phase pressure, CH_4 0.3 MPa.



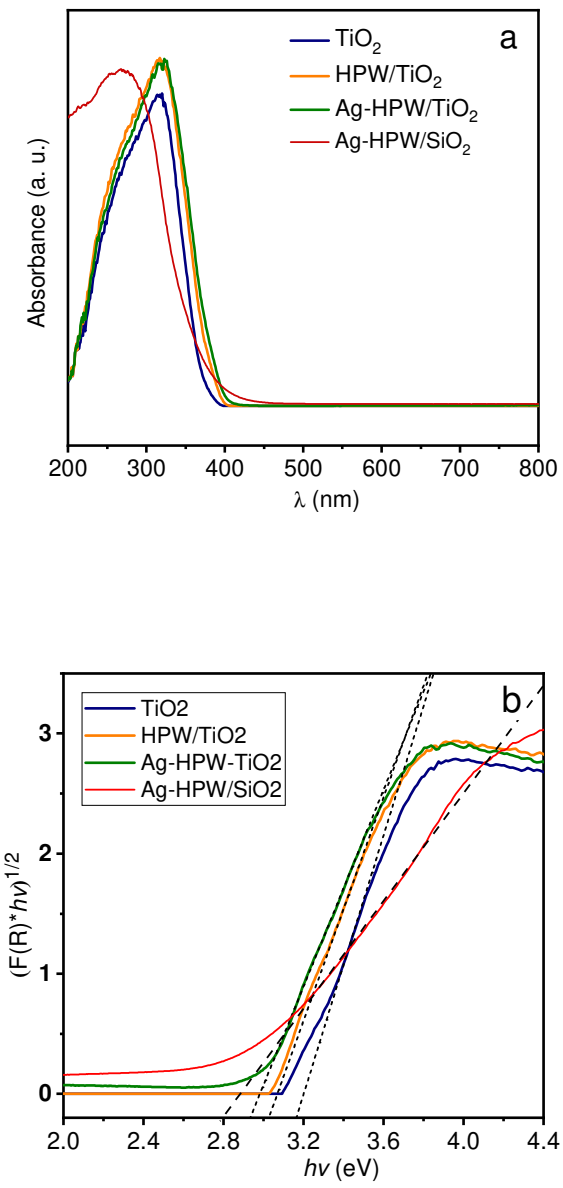
Supplementary Fig. 7. Band levels and elementary steps in methane coupling. Band levels are given versus NHE.



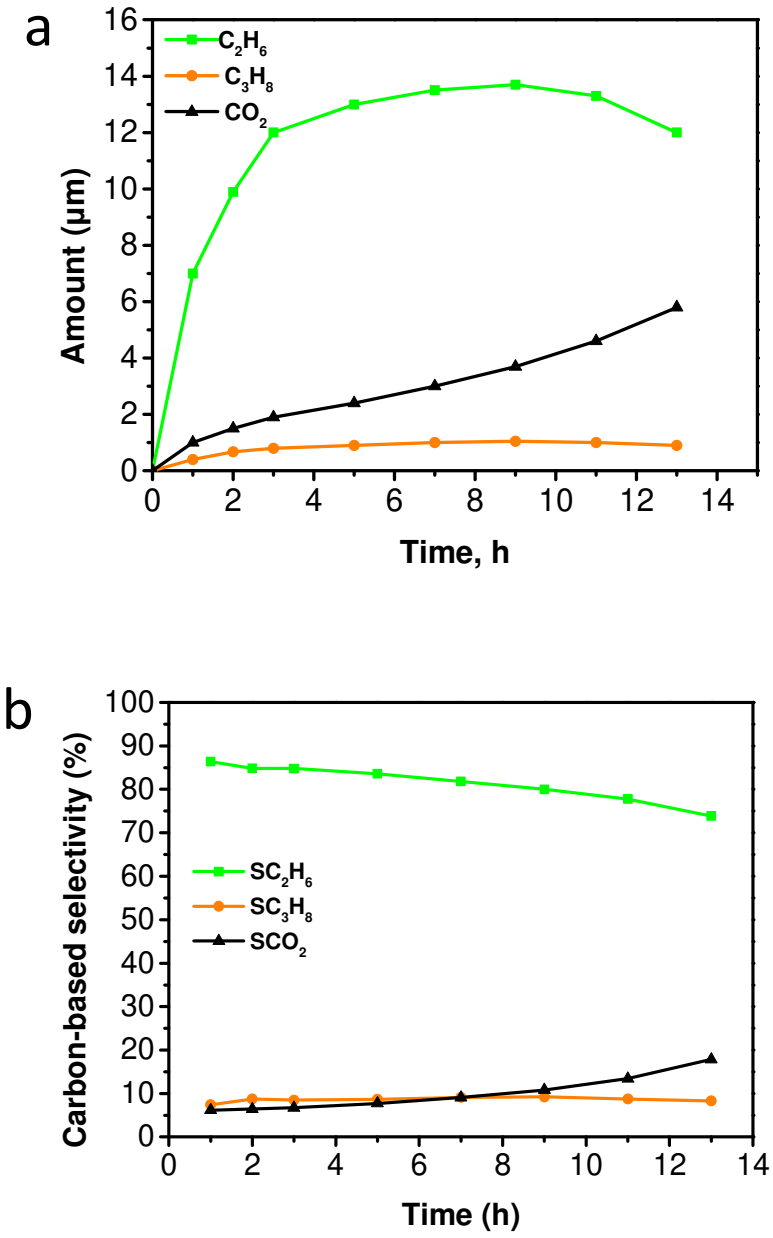
Supplementary Fig. 8. STEM-EDX elemental maps of the fresh sample showing the location of the Ag nanoparticles on the surface of the HPW embedding the TiO_2 crystals.



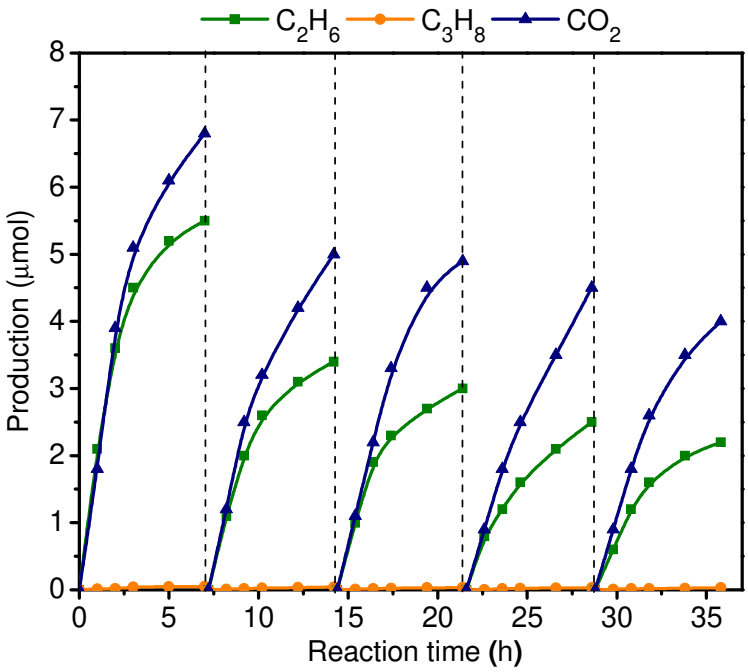
Supplementary Fig. 9. H_2-TPR profiles (a) of TiO_2 based composites and (b) fresh, used and regenerated Ag-HPW/TiO_2. Conditions: 5%H_2 in Ar, ramping rate 10°C/min.



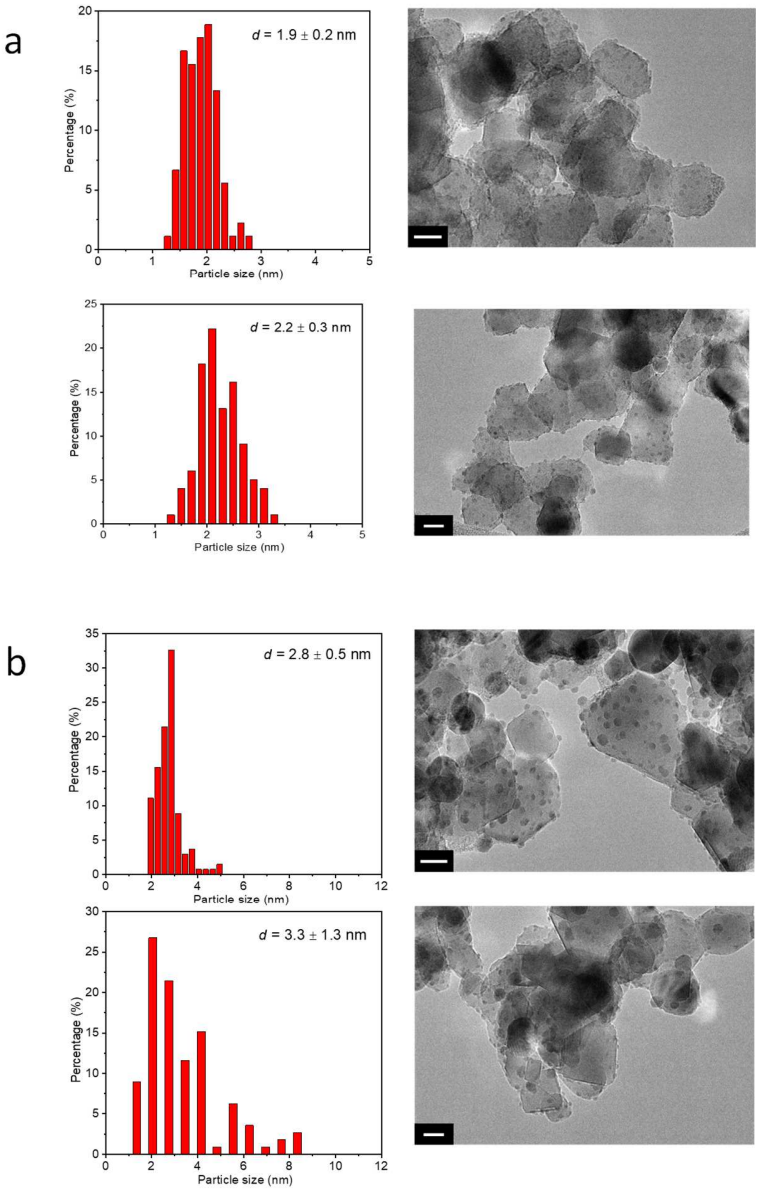
Supplementary Fig. 10. (a) UV-Vis spectra of HPW/TiO_2, TiO_2, Ag-HPW/TiO_2 and samples; (b) $[F(R\infty)h\nu]^{1/2}$ versus *hν* for HPW/TiO_2, TiO_2 and Ag-HPW/TiO_2 samples



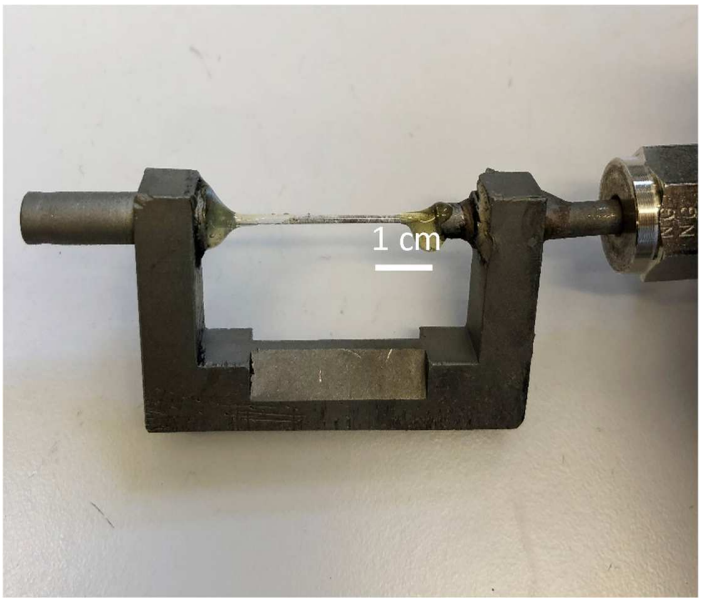
Supplementary Fig. 11. (a) Productions of ethane, propane and carbon dioxide, and (b) selectivity on carbon basis as functions of the reaction time over Ag-HPW/TiO_2 nanocomposite. The lines are guides to the eye.



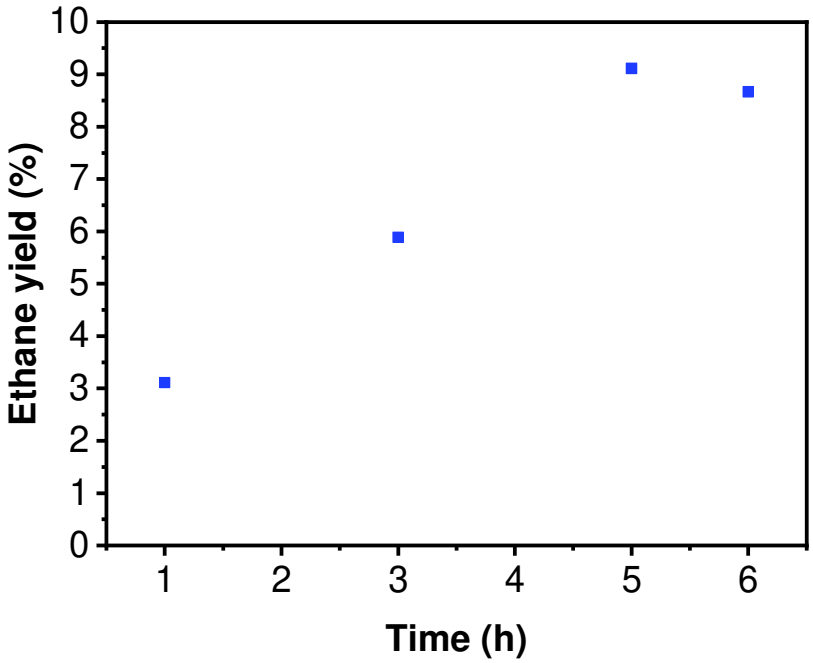
Supplementary Fig. 12. Production of ethane, propane and carbon dioxide during the reaction-regeneration cycles in the course of photochemical coupling of methane on Ag/TiO_2 . The lines are guides to the eye. Reaction conditions: nanocomposite, 0.1 g; gas phase pressure, CH_4 0.3 MPa.



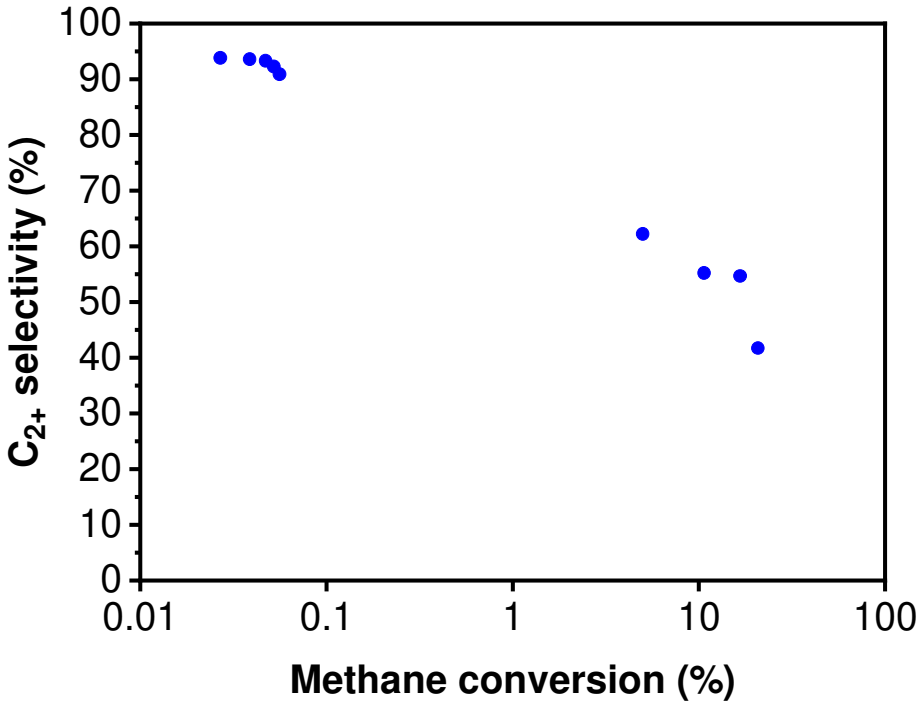
Supplementary Fig. 13. TEM images of fresh and used sample after photochemical coupling of methane: (a) Ag-HPW/TiO_2, (b) Ag/TiO_2 . Scale bar: 10 nm(c) (d) Size statistics of Ag particles of fresh and used nanocomposites. The mean size of nanoparticles was estimated by counting ~200 particles.



Supplementary Fig. 14. Capillary photoreactor with reduced gas volume used for high conversion methane coupling experiments. Scale bar: 1 cm



Supplementary Fig. 15. Ethane yield as a function of reaction time in the capillary reactor.



Supplementary Fig. 16. Selectivity to higher hydrocarbons as a function of methane conversion.