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Peer Review File

Observation of Nanoparticle Coalescence during Core-Shell Metallic Nanowire Growth in Colloids via Nanoscale Imaging

Corresponding Author: Professor Xiaohui Song

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)
This manuscript presents an interesting study on the deposition mechanism of noble metals onto AuAg nanowires (NWs), employing a combination of cutting-edge techniques, including in-situ low-pressure transmission electron microscopy (LPTEM), cryo-TEM, deep learning, and atomic-scale 3D electron tomography. The authors provide valuable insights into the fundamental mechanisms driving the growth of core-shell nanowires and the various phenomena that influence their structure, such as nucleation, nanoparticle attachment, and Ostwald ripening. The findings offer substantial contributions to the design and application of noble metal nanocrystals which is benefiting to chemistry and materials science, and the use of advanced electron microscopy methods is a significant strength of this work which could be applied broadly. I suggest the manuscript can be accepted in Nature Communication after minor revision. Below are the comments for the author's improvement:

Q1: Beam Effect: While the author has conducted both in-situ and ex-situ experiments to investigate the formation mechanism of core-shell nanowires, this is not sufficient. The effect of beam dose needs to be addressed. For example, how does the strength of the beam dose affect the experimental results? This aspect should be discussed further.

Q2: Electron Tomography: The author uses nanoscale and atomic-scale 3D TEM reconstructions to demonstrate how different metal deposits lead to varying final morphologies of the core-shell nanowires. How is the accuracy of these 3D reconstructions assessed? A discussion on the reliability of these results is necessary to strengthen the conclusions.

Q3: Use of Ligands: Were ligands used during the synthesis of the nanowires? This needs to be clearly stated, as the packing of ligands can influence the deposition of precious metals on the surface of the nanowires.

Q4: Different Types of AuAg Seed Nanowires: To demonstrate that the morphology of the core nanowire does not affect the deposition of precious metals, the author synthesized two different AuAg alloy nanowires. What are the differences between the two? Why can AuAg alloys grow into both chiral and non-chiral nanowires? A more detailed explanation of this point would be useful.

Q5: The deposition experiments with Au, Pd, and Pt confirm that the growth of core-shell nanowires is a complex process, exhibiting both similarities and differences. Has the author considered testing the deposition of other metals? Exploring additional metal deposition experiments would help extend the conclusions and enhance the generalizability of the findings.

Q6: Effect of Colloidal and Liquid-phase Environment: Has the author considered the influence of the liquid-phase environment on the deposition of precious metals in colloidal systems? For instance, factors like pH and precursor types can affect the deposition process. Discussing these aspects would improve the reliability of the conclusions.
Q7: Does the strain shown in Fig.5 is the driving force for double helix nanowire formation?

Suggestions:
1 The introduction should more clearly outline previous studies on nanowire growth mechanisms and their conclusions. This would help readers better understand the significance of the current work.

2 It would be beneficial to include a table summarizing the various TEM experimental conditions, along with comparisons to

related literature. This would aid in the reproducibility of the experiments.

3 The analysis of nanowire strain in Figure 5, particularly in relation to the growth mechanism, is not sufficiently clear. A more in-depth discussion of this connection is needed to clarify the results.

Reviewer #2

(Remarks to the Author)
This manuscript investigates the mechanism of Pd/Au/Pt nanoparticle deposition on AuAg nanowires (NWs) through advanced techniques such as Cryo-TEM and 3D electron tomography. A combination of used analysis methods are intriguing and the question that authors would like to answer is important; however, the major drawback in this work is that the proposed mechanism based on the observations, as dictated in the title, is far from what people would accept as a general core/shell nanowire growth mechanism. Thus, with this current data, I worry that the mechanism drawn from the in situ observation is limited only for a very specialized case of the nanowire growth that authors studied in this work. Without being convinced with the importance of the observation presented in the work, it is not recommended to publish this work in Nature Communications. In addition, there are several technical points that require revisions.
Questions:
1. Figure 1C vs. Figure 2: In the data shown in Figure 1C, the deposition mechanism is completed within 30 seconds, while in Figure 2, some nanoparticles remain even after 5 minutes. Could you explain the difference between these two observations?
2. Nanoparticle Coalescence Section: In the "Nanoparticle Coalescence Revealed by Electron Tomography" section, could you clarify the exact duration for the completion of the reaction?
3. Chiral vs. Achiral Nanowires: The analysis in the manuscript distinguishes between chiral and achiral nanowires in the front and back sides, respectively. Could you provide more detailed information regarding the differences between these two types of nanowires?
4. Incomplete Data Involvement: The study includes Au/Pd/Pt nanoparticles, but some datasets, such as the Pt deposition on achiral AuAg nanowires and several 3D tomography results, are not fully incorporated. More detailed analysis and clearer inclusion of all relevant data are necessary to strengthen the findings.
5. Ostwald Ripening (Figure 4e): Ostwald ripening is mentioned in Figure 4e, but more detailed explanation is required to help the reader better understand the data and its significance in the context of the study.
6. Local Strain Analysis of Au@AuAg Core-Shell Nanowires Section:
o Are the nanowires in this section chiral or achiral? Please clarify.
o Is Figure 5F identical to other figures in Figure 5? If they are the same, this should be clearly indicated in the figure legend.

Additional Suggestions:
• Title Suggestion: The current title does not fully reflect the specific focus of the manuscript. It is too broad and does not emphasize the core topic clearly. A more specific title related to the Pd/Au/Pt nanoparticle deposition mechanism on AuAg nanowires would be more appropriate.
• Consistency of Terminology: Throughout the manuscript, the terms "chiral" and "achiral" are used to describe AuAg nanowires. However, in the supporting material, the terms "BCB nanowire" and "straight nanowire" (or "core-shell nanowire") are used interchangeably. It would be helpful to maintain consistent terminology throughout the manuscript to ensure clarity for the reader.
• In Situ Images (Figure 1b and Supporting Figure S3): The in situ images in Figure 1b are the same as those in Supporting Figure S3, but Figure 1b is described in terms of time, while Figure S3 is described in terms of frames. Please clarify and ensure consistent terminology when describing these images.
• Discussion of AuAg NWs Diameters: The manuscript discusses several diameters of AuAg nanowires in the supporting information, but this is not mentioned in the main text. It would be helpful to include a more detailed description of the findings related to the various diameters of the nanowires in the manuscript.

Image and Data Verification:
1. TEM Image Scale Bars: In Figure 2, the images are marked with the same scale bar (A-C, E-G), but the diameters appear to differ significantly. Additionally, similar discrepancies are observed in the supporting figures, such as Figure S12. Could you please confirm that these images were taken at the same magnification? It is crucial to ensure that the correct magnification is applied and clearly marked in the figure legends.
2. Red Arrows, Circles, and Boxes in Figure 2: Figure 2 contains red arrows, red circles, and a box, but these features are not explained in the manuscript. Please provide further details in the text to clarify their significance.
3. Figure S12 Title Discrepancy: In Figure S12, the title refers to "Pd deposition," but the manuscript mentions "Au deposition." Please correct this inconsistency in both the figure legend and the text.
4. Supporting Figures S19 & S20 vs. S21 & S22: Supporting Figures S19 & S20 are identical to Figures S21 & S22. Please ensure that the correct data is presented in the manuscript and make the necessary corrections.
5. Figure 3 and Data Numbering: In Figure 3, panel 3g presents Au data, but the manuscript refers to the data as if it were from a different figure. Please revise the text to ensure that the correct data number is cited.
6. Figure S24e Omission: There is no mention of Figure S24e in the manuscript. Please address this oversight.

Reviewer #3

(Remarks to the Author)

The paper by Yang et al. presents a multi-modal imaging workflow, integrating LPTEM, cryo-EM, and electron tomography to investigate the growth mechanism of nanocrystals. Three steps are proposed for the seed-mediated growth of noble metals on 1D nanowires: initial heterogeneous nucleation, particle attachment, and coalescence. The consistency between LPTEM and cryo-EM results highlights a generalized growth mechanism applicable to both in situ and ex situ (bulk solution synthesis) experiments, showcasing the strength of the proposed approach. However, I have several questions for the authors regarding specific observations and explanations:

1. In addition to growth mechanism, which can vary with different synthetic methods, I think the authors want to highlight their workflow combining LPTEM with cryo-EM, as well as electron tomography, to give a comprehensive overview of the growth process. However, the necessity of cryo-EM is not well explained. For example, people can also quench the reaction and take conventional TEM imaging, which may be more suitable for reactions involving high temperatures. Can authors explain more on why cryo-EM is necessary?
2. In Figure 1: (1) how stable is the nanowire over a longer time period, such as the 30 seconds used in Figure 1c? (2) Dose rate should be added to either the main text or figure caption; (3) How is the diameter calculated? It seems the nanowires are tracked by “atoms” or segments instead of contours.
3. In Movie S2, there appears to be motion or drift of the nanowire. Given the small viewing area and the possibility of the nanowire being obscured/blocked by the viewing window, could the authors comment on the accuracy of the tracked area?
4. Can authors clarify the composition of the “mixed solution” used for LPTEM? It is important to mention what is the reducing agent used in the LPTEM experiment.
5. In Movie S3, there is no obvious evidence of particle attachment. Besides, there is no obvious increase in the diameter of the nanowires while the nanoparticles in the background (Pd nanoparticles?) all gradually disappeared. Instead of coalescence, is it possible that the Pd, like those highlighted in red, is actually etched?
Besides, it is interesting that in Movie S4, the beam induced self-nucleation of Pd, while etching of particles seems to exist in Movie S3. Can authors comment on these contradicting phenomena?
6. For Figure 3, the authors claimed that it “clearly reveals the presence of nanoparticles adhering to the nanowire surfaces”. However, from Figure 1, it seems that not all “atoms” are tracked in nanowires. Besides, the edge of the reconstructed nanowire in Figure 3 is also very blurring. Could the authors provide further clarification on the reliability of the evidence supporting particle attachment? For example, maybe adding EDX of similar areas to show the “attached particle” is really made of Pd.
7. The authors mentioned that “interfacial fusion between the nanoparticles and nanowires was observed along the Pd (111) direction”. How the (111) direction (should be ⟨111⟩ direction?) is derived? From lattice spacing?
8. In Figure 4c, it seems there is galvanic replacement between Pt and AuAg alloy nanowire?
9. The authors attribute the surface roughness of Pd and Pt-coated nanowires to “differences in lattice matching between the various metal crystals”. In addition to the lattice mismatch between Au and Pd (5.3%) or Pt (3.9%), the authors can also check the atom diffusivity and bond energy. It is possible that Pd and Pt tend to self-nucleate and slow to diffuse, while Au is the opposite.
10. In Figure 5, what is the scale for stress distribution? Also, is it stress or strain? What do vertical and horizontal directions mean?
11. Can authors provide more explanation on how strain is calculated? What are the unstrained diffraction vectors mentioned in the supporting information? It is suggested to add one more figure to Supporting Information to show the strain analysis process.
12. The authors mentioned that “higher stress in the central region is likely induced by the deposition of external Au atoms, while higher stress at the boundary may result from structural features at the boundary”. How does the strain look like in pristine AuAg nanowires? Besides, what is the motivation for strain analysis? It should be clarified at the beginning of this section.

Reviewer #4

(Remarks to the Author)
In their Manuscript “Understanding Core-Shell Nanowires Development in Colloidal Synthesis through Nanoscale Imaging” the authors study metal deposition on AuAg seed nanowires using liquid phase and cryo transmission electron microscopy. The results are evaluated extensively using advanced computational methods. While the study is done well from an experimental and data analysis point of view, the scientific analysis and structure of the main manuscript is quite lacking. First of all, it is not really clear what the main outcome of this study was. To see heterogeneous nucleation on a seed crystal with concurrent homogeneous nucleation of particles that can attach to the seed crystal is hardly surprising. Other results such as the proposed Ostwald ripening are poorly supported by the data. Furthermore, a lot of the extensive microscopy and analysis work is not really brought into context and explained at all. This is somewhat exemplified by the ratio of content in the main manuscript compared to the content in the supplementary. While I believe that an extensive supplementary is generally a good thing, having 41 supplementary figures (in addition to other items) for such a short article (~2500 words, 5 figures) begs the question whether the authors chose the right publication format. Maybe a longer format article with more display items would be more suitable. Furthermore, there does not seem to be a good reason for the application of some of the techniques in the first place. For instance, using deep learning to measure the nanowire area in the first part of the manuscript seems highly questionable. Neither are the results convincing nor is there a reason to do that kind of analysis at all (especially without a critical appraisal of the validity of the results). Other analysis techniques fall in a similar category like the morphology analysis (S34 c&d, no explanation given on how it was performed), or the curvature analysis (S24) which leaves open a lot of questions. It seems to me that the authors just tried everything they could think of (liquid and cryo TEM, Atomic resolution tomography, deep learning analysis, GPA and custom strain measurement…) to see what sticks instead of carefully planning and conducting dedicated experiments and analyses.
On a further note, I don’t want to criticize style in general, however words/phrases such as ‘impressively’, ‘for the first time’

should not be used describe one's own research (e.g. 'Impressively, in Figure 3d, e, we unexpectedly observed in[…]').

I suggest the authors think about how to restructure their manuscript for clarity and accuracy. They should write a concise and convincing story that is well supported by their findings without unnecessarily analyses. Frankly, a few proper EDX measurements would make the whole story way more comprehensible as a lot of what the authors report hinges on the spatial distribution of elements.

Therefore, without major changes I cannot recommend the manuscript for publication at this point.

A (non-exhaustive) list of further points follows below:
1. In the initial LPTEM part the authors describe their wires as chiral, however the images showing the proposed BCB structure are not really convincing (Figure S1). The wires simply appear as polycrystalline, not like a regular arrangement of tetrahedra. Maybe the authors can make this clearer.
2. Figure 1 a: Why do the authors color the whole nanowire in green? If it is 'remarkably stable' as they claim there is no need for obfuscation by coloring. Let the reader see what is really there. I guess the original images are shown in S2, which begs the question why they are shown twice. What does the green color mean? This is not referenced in the caption.
3. Figure 1b: Again: Why color the wire? I can see the lattice planes much better without the color. Also, the color is neither explained in the figure caption nor in the main text. In supplementary figure 3 almost the same images are shown again and finally the origin of the color is mentioned, but without further detail let alone a reason why a deep learning analysis was performed. In the main text the deep learning is only briefly mentioned in the context of S4.
4. Further on Figure 1b: The authors claim that the increase in the wire thickness is due to Pd deposition. It would be nice to have some sort of confirmation that it is actually Pd (e.g. post mortem EDX) and not just redistribution of AuAg. The authors do show an EDX in figure S8 but apart from issues with the EDX mentioned later on, it is not clear whether that is comparable to the wires shown in fig 1 b.
5. Fig. 1c: Rather than deposition this seems to be more like dissolution due to the electron beam. In the very first frame there is a number of particles visible that gradually disappear over time. At the same time the wires appear to get slightly thinner. How can this be described as deposition? There is clearly less material (in a solid state) there than before. Also, the red circles obfuscate the images (in the video it is much clearer). The corresponding Figure S6 shows a few more frames from the same experiment, however the caption must be wrong as it talks about lattice 'stripes' and coloring which are clearly not visible in this magnification.
6. Regarding the EDX map in supplementary figure S8. First of all, the authors did not state whether they show raw counts or quantified the results. Secondly, the authors need to show a raw spectrum to confirm that the Pd peak is actually there. Otherwise this could just be noise.
7. Fig. 1d: Nice schematic. Unfortunately, it is not supported at all by the findings presented so far. Neither are there helical wires (which I believe is not the same as a chiral wire) nor is there any evidence for the presented growth mechanism. So far, the authors have simply presented one instance in which wires get slightly thicker and one in which wires get slightly thinner. Later on, the authors present more convincing results and in the supplementary there are plenty of examples of helixal wires, but at this point I just have to wonder why Figure 1 was put together this way.
8. Figures S11 and S18: To show the elemental distribution 'within' a core shell structure you would need to construct a linescan perpendicular to the wire. Currently these figures serve no purpose.
9. Figure 2 D&H. Measuring the lattice spacing in high resolution is an extremely unreliable way of distinguishing between metals that are so similar in structure (as noted by the authors the 111 plane distance is 0.22, 0.23 and 0.24 nm for Pd,Pt and Au). EDX would offer a clear and straightforward proof.
10. How can the authors claim to see Ostwald ripening? All they show is that one particle in a particle agglomerate shrinks which is hardly surprising to see in a liquid cell TEM.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The author addressed all my comments, I would recommend its publish. Thanks.

Reviewer #2

(Remarks to the Author)
All concerns are well addressed. I support a publication of this mansucript.

Reviewer #3

(Remarks to the Author)
The authors have prepared extensive discussion and additional data, which address some of the comments I had raised regarding the manuscript. However, there are still some remaining and new questions emerging:

1. The authors claim that Fe, Ni, Cu, and Ru can be deposited onto AuAg nanowires using ascorbic acid at room temperature. However, all these metals are hard to be reduced, and their typical synthetic methods usually require high

temperatures. Can authors double-check the valence of these metals in the shell, e.g., using XPS? I suspect the shell might not be metallic Fe, Ni, Cu, or Ru.
2. For the formation of double-helical morphology, the author mentioned that “this phenomenon is attributed to the strong internal strain within the chiral seed nanowires, which originates from the intrinsic chirality of the as-synthesized AuAg alloy nanowires”.
(1) The phenomenon is induced by chirality of AuAg nanowires, which originates from their internal strain? I assume the authors want to explain coating of shell increases the internal strain of the nanowire, leading to larger extent of chirality and thus higher possibility of forming double-helical structures?
(2) In Figure 5, please provide strain range (in %) and label/explain x and y direction in the image/caption.
(3) In Figure 5, if the authors want to claim the additional strain from Au deposition induces double-helical structure, they need to compare the strain in Au-coated and pristine AuAg nanowires.
3. For the accuracy of reconstruction, the authors provided R-factor and claimed the consistency between experimental projection images and the corresponding projections of the reconstructed 3D model. There are two questions here:
(1) The R-factor is calculated based on the nanowire shown in Figure S39, where the reconstruction seems not to be at atomic resolution. How about those shown in Figure 3, which are claimed to be atomic resolution?
(2) The tilting angle for reconstructions in Figure 3 should be provided.
(3) For reconstruction, missing wedge effect actually contributes a lot to the error, which cannot be reflected by consistency in projection images. I would suggest authors find another way to verify their accuracy, such as creating a model with a similar wire-like shape and comparing the model with its reconstruction from the same tilting angles.
4. The authors mentioned that “we utilize low-dose LPTEM imaging to investigate the shaping process of core-shell nanowire crystals during seed-induced growth without the presence of any organic ligands”. However, based on experimental section, both PVP and DMF were used during synthesis (also confirmed by XPS), which can serve as capping agents blocking certain facets of Ag, Au, or even AuAg nanowires. This could affect the deposition of atoms and the final shape of the nanocrystals. I would suggest either removing this claim or explain whether PVP and DMF will induce surface capping or not.
5. In line 280-282, the authors claim “the ⟨111⟩ surface of noble metals has the lowest surface energy, prompting nanoparticles and nanowires to come into contact and fuse along this plane to minimize the overall free energy of the system”.
(1) <111> usually refers to direction instead of surface.
(2) If {111} gives the lowest surface energy, then this surface should be more exposed instead of being covered/fused?
(3) Will potential PVP and DMF binding to nanowire surface affect the direction of fusion?
6. The authors propose a three-step deposition process – heterogeneous nucleation, nanoparticle attachment, and coalescence – as a generalized mechanism for metal deposition on nanowires. Though authors explored different metals and varying amounts of reducing agents, (1) imaging evidence is only provided for Pd and Au deposition; (2) there are a lot more parameters that can be tuned, like even higher temperatures and milder reducing agents, which may lead to missing/reversing order of certain steps. I suggest the authors describe their findings as a potential deposition mechanism, rather than a generalized mechanism.

There are also some minor questions:
7. In line 225, the author mentioned that “the number of attached Au nanoparticles is significantly smaller”, but it is hard to get this conclusion from Figure 2. Also, in Figure 2, it is better to label the images of AuAg@Pd and AuAg@Au, making the figure clearer to audience.
8. In lines 338-339, how is the conclusion “while the pH value of the solution is not so crucial” obtained?
9. In line 257, “Figure 3D and 3F” should be “3C and 3E”? The authors should double-check all the figure numbers in the manuscript.
10. For the diameters provided in the manuscript, standard errors should be provided to further verify the diameter increase and reliability of the conclusion.
11. The abbreviation “NW” is not defined in the manuscript, and “NW” and “nanowires” are used randomly. Similar for “double-helix” and “double-helical” nanowire. Please double check the abbreviations and words and make sure they are consistent throughout the paper.

Reviewer #4

(Remarks to the Author)
The authors have carefully revised their manuscript and answered the questions in detail.The additional provided results and discussion improve the manuscript and demonstrate the intensive work that went into the study.

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)
I still recommend that the authors double-check the strain range in Figure 5, as ±45% or ±30% strain in nanocrystals is highly uncommon. Other than that, the authors have addressed all my comments. Thanks!

Following are detailed responses to the reviewers' comments:

It is noticed that changes to the manuscript and supplementary information are highlighted in yellow.

To Reviewer #1:

This manuscript presents an interesting study on the deposition mechanism of noble metals onto AuAg nanowires (NWs), employing a combination of cutting-edge techniques, including in-situ low-pressure transmission electron microscopy (LPTEM), cryo-TEM, deep learning, and atomic-scale 3D electron tomography. The authors provide valuable insights into the fundamental mechanisms driving the growth of core-shell nanowires and the various phenomena that influence their structure, such as nucleation, nanoparticle attachment, and Ostwald ripening. The findings offer substantial contributions to the design and application of noble metal nanocrystals which is benefiting to chemistry and materials science, and the use of advanced electron microscopy methods is a significant strength of this work which could be applied broadly. I suggest the manuscript can be accepted in Nature Communication after minor revision. Below are the comments for the author's improvement:

Comment 1: Beam Effect: While the author has conducted both in-situ and ex-situ experiments to investigate the formation mechanism of core-shell nanowires, this is not sufficient. The effect of beam dose needs to be addressed. For example, how does the strength of the beam dose affect the experimental results? This aspect should be discussed further.

Response 1: We appreciate the reviewer's insightful comment regarding the potential effect of the electron beam dose on our experimental results. The beam effect is indeed a critical factor in in-situ nanoscale imaging experiments, and we have taken steps to carefully evaluate and mitigate its influence during our study. Below, we provide a detailed discussion on this matter as below:

1) During our in-situ experiments, we systematically controlled the electron beam dose to minimize any potential artifacts caused by beam-induced effects. Specifically, we maintained a low beam dose rate (the beam dose rate in our experiments is 7.0-8.5 $e \cdot Å^{-2} \cdot s^{-1}$) during imaging to reduce the likelihood of

beam-induced heating, sample charging, or structural modifications. Additionally, we ensured that the total beam exposure time (total time t< 5 min) was minimized by limiting the duration of high-resolution imaging to only the critical moments required to capture the dynamic formation processes of the core-shell nanowires (Supplementary note 1).

2) In addition, we have also taken the effect of electron beam irradiation into consideration. Therefore, we investigated the growth mechanism through ex-situ experiments and utilized cryo-TEM techniques to minimize the impact of the electron beam to the greatest extent possible. It is inserted in the revised manuscript as "To address the first question raised above regarding the influence of experimental conditions, such as the electron beam and solution volume, cryo-electron microscopy (cryo-EM) was employed to capture intermediates during nanowire growth directly from the original solution. This approach eliminates the potential artifacts caused by electron beam irradiation, small solution volumes, or material decomposition, allowing for the most accurate preservation and visualization of the native morphological features of the intermediate products"

3) We acknowledge that beam effects are an inherent limitation of in-situ electron microscopy studies, and we highlight this as an important consideration for future investigations. Advanced techniques, such as dose fractionation or the use of complementary non-invasive methods (e.g., X-ray or optical imaging), could further validate the findings and provide additional insights into the formation mechanism of core-shell nanowires (Supplementary note 1).

Comment 2: Electron Tomography: The author uses nanoscale and atomic-scale 3D TEM reconstructions to demonstrate how different metal deposits lead to varying final morphologies of the core-shell nanowires. How is the accuracy of these 3D reconstructions assessed? A discussion on the reliability of these results is necessary to strengthen the conclusions.

Response 2: We appreciate the reviewer's valuable suggestion, which has helped to enhance the quality of our manuscript. A discussion on the accuracy of the 3D tomography has been inserted in the revised supplementary (Supplementary note 2, Figure S), which is copied as the follow:

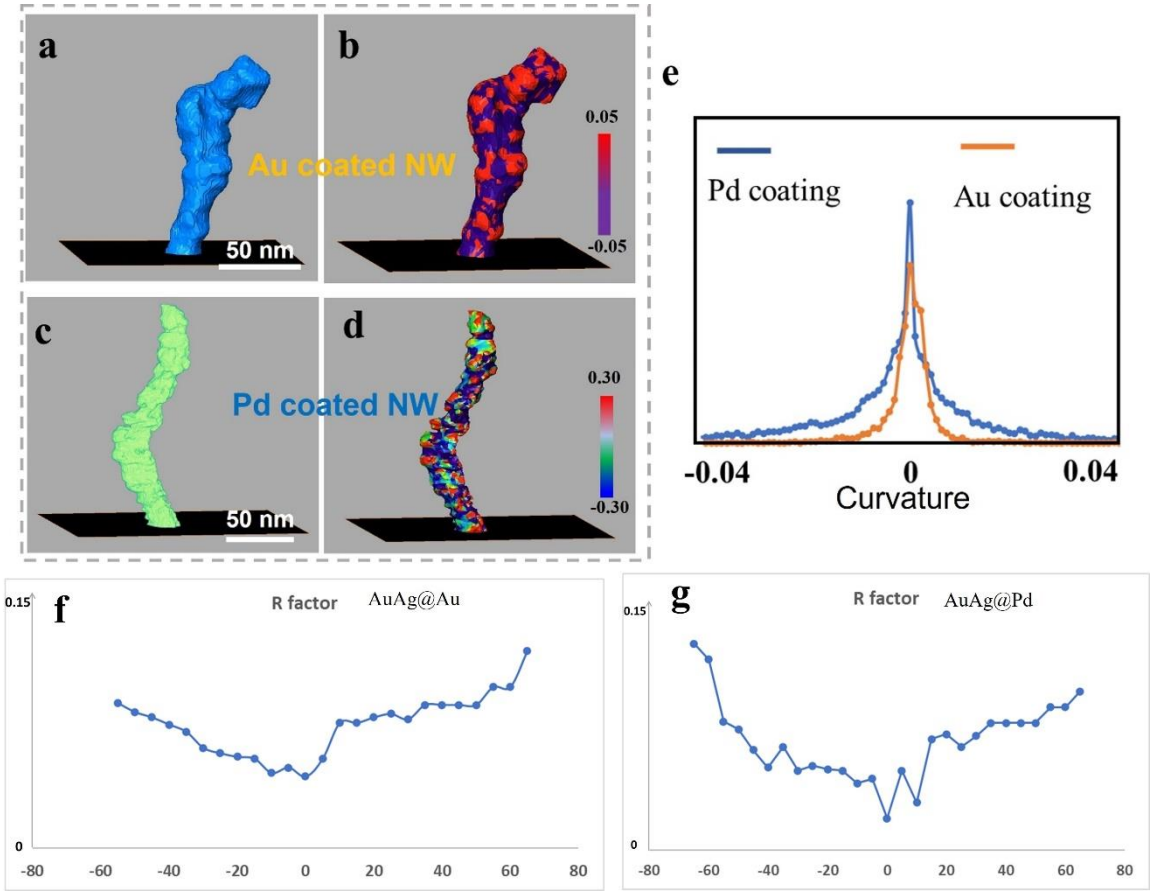

Figure S39: Characterization of core-shell nanowire surface curvature (metal deposition on non-chiral seed nanowire). (a) 3D reconstruction of AuAg@Au nanowire (Au coated on seed nanowire). (b) surface curvature color map showing the local curvature is small (<0.05). (c) 3D reconstruction of AuAg@Pd

nanowire (Pd coated on seed nanowire). (d) surface curvature color map showing the local curvature is large after Pd deposition. (f) the R-factor value (or residual factor) of 3D tomography for AuAg@Au sample as shown in a and b. (g) the R-factor value (or residual factor) of 3D tomography for AuAg@Pd sample as shown in c and d.

The accuracy of electron tomography: The R-factor value (or residual factor) is a quantitative metric used to evaluate the accuracy and reliability of 3D reconstructions, including those obtained through electron tomography. It provides a measure of how well the reconstructed 3D model matches the experimental data, such as the experimental projection images used in the reconstruction process.

The R-factor is typically expressed as a normalized difference between the experimental projection images and the corresponding projections of the reconstructed 3D model. Mathematically, it can be written as:

$R = (\sum | I_{exp} - I_{recon} |)/(\sum | I_{exp} |)$

I_{exp}: Intensities of the experimental projection images

I_{recon}: Intensities of the projections generated from the reconstructed 3D model.

The summation is taken over all pixels and all projection angles.

Comment 3: Use of Ligands: Were ligands used during the synthesis of the nanowires? This needs to be clearly stated, as the packing of ligands can influence the deposition of precious metals on the surface of the nanowires.

Response 3: We appreciate the reviewer's valuable suggestion, which has helped to enhance the quality of our manuscript. Thank you for your comment. We confirm that no ligands were used during the synthesis of the nanowires. This was further verified through XPS characterization (Figure S2), which showed no evidence of ligand-related peaks in the spectra. The absence of ligands ensures that their packing does not influence the deposition of precious metals on the surface of the nanowires, allowing us to study the deposition process without interference from surface-bound organic molecules. The relative discussion has been inserted in the revised manuscript copied as the follow:

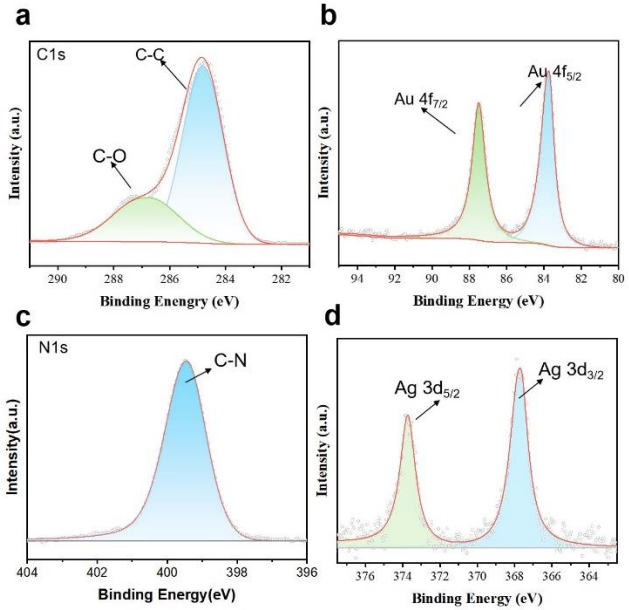

Figure S2. XPS spectra of the chiral AuAg seed nanowire. (a) C, (b) Au, (c) N, and (d) Ag XPS spectrum showing that there is no organic ligand on the seed nanowire surface since we did not apply any organic molecule as ligand or surfactant.

“Some recent work focus on the design and synthesis of nanowires with the control of organic ligands which is a kind of template or surfactant to induce the metal deposition”. “In this study, we utilize low-dose LPTEM imaging to investigate the shaping process of core-shell nanowire crystals during seed-induced growth without the presence of any organic ligands (Figure S2)”.

Comment 4: Different Types of AuAg Seed Nanowires: To demonstrate that the morphology of the core nanowire does not affect the deposition of precious metals, the author synthesized two different AuAg alloy nanowires. What are the differences between the two? Why can AuAg alloys grow into both chiral and non-chiral nanowires? A more detailed explanation of this point would be useful.

Response 4: We appreciate the reviewer's valuable suggestion, which has helped to enhance the quality of our manuscript. First, from a synthesis perspective, the AuAg chiral seed nanowires were synthesized at room temperature, while the AuAg non-chiral seed nanowires were synthesized at 40°C. Second, there are significant differences in their crystal structures: the AuAg chiral seed nanowires exhibit the characteristic "Boerdijk-Coxeter-Bernal" crystal structure (Figure 1A, and Figure S1), whereas the AuAg non-chiral seed nanowires are typical nanowires that grow along the <111> direction (Figure S29).

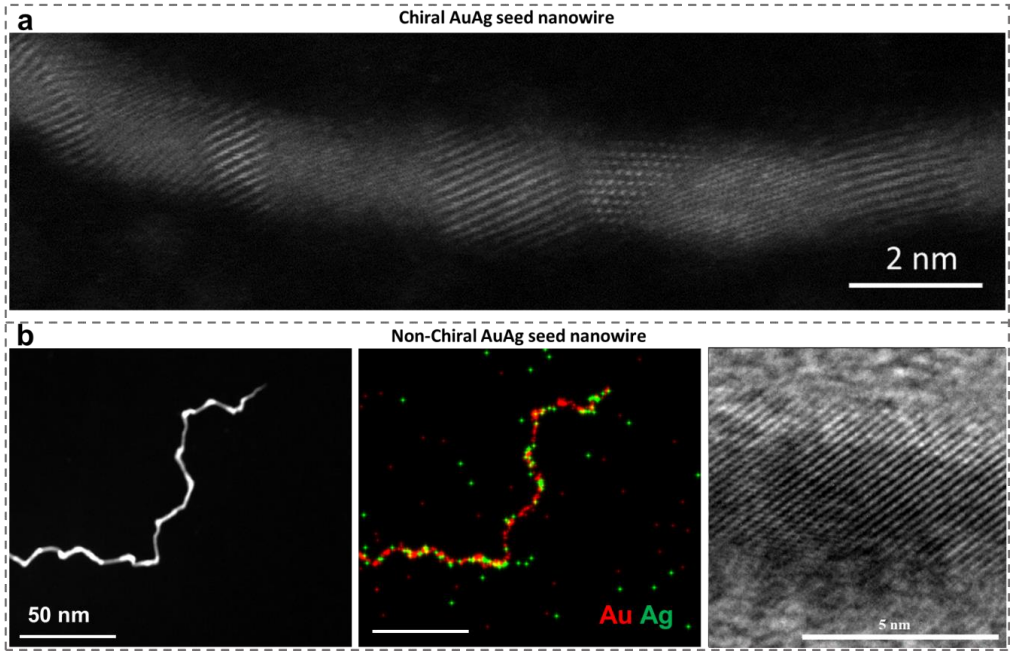

Figure 1 (for review only). Two different types of AuAg seed NWs. (a) HRSTEM image of chiral AuAg seed nanowire, and (b) the EDX color map showing the alloy nanowire composition, and the HRTEM image of the AuAg alloy non-chiral seed nanowire growth from <111> direction, which showing different lattice with chiral seed nanowire.

These experimental details and structural differences have been clearly stated in the revised version of the manuscript. The relative discussion in the revised manuscript is copied as the follow: "First, we monitored the coating process of Pd on chiral AuAg NWs (see Figure S1 for initial morphology) using LPTEM (see Methods for operation details). It is noted that this chiral nanowire is also named 'Boerdijk-Coxeter-Bernal' Nanowire based on previous reports39, 40, 41as shown in Figure 1A, which is identified by both HRSTEM image and the corresponding FFT image. There is no organic ligand presence as shown in XPS spectra (Figure S2) in the solution since we try to study the metal deposition on clean nanowire surface", and "The fourth question regarding the proposed

hypothesis pertains to whether the crystal structure of the seed nanowires influences nanoparticle attachment during outer-layer metal deposition and whether Ostwald ripening occurs. To address this issue, non-chiral seed nanowires (Figure S29) were applied to conduct similar metal deposition experiments. The chiral AuAg seed nanowires were synthesized at room temperature, while the non-chiral AuAg seed nanowires were synthesized at 40°C, with all other experimental conditions kept identical. After synthesis, the nanowires underwent four rounds of washing. XPS analysis confirmed the absence of any organic ligands on the surface of all seed nanowires (Figure S2)".

Comment 5: The deposition experiments with Au, Pd, and Pt confirm that the growth of core-shell nanowires is a complex process, exhibiting both similarities and differences. Has the author considered testing the deposition of other metals? Exploring additional metal deposition experiments would help extend the conclusions and enhance the generalizability of the findings.

Response 5: Thank you for your insightful comment. We appreciate your suggestion to explore the deposition of additional metals to further generalize our findings. In the revision, we have conducted additional experiments with other metals, including Ag, Fe, Cu, and Ru, to test the versatility of the deposition process on both chiral (Figure 3F-I) and non-chiral seed nanowire (Figure 4D). The results from these experiments are consistent with our conclusions, demonstrating that the metal coalescence with nanowire during the growth of core-shell nanowires is indeed a universal phenomenon, although the specific deposition behavior can vary slightly depending on the type of applied metal. The relative discussion in the revised manuscript is copied as the follow:

"The third question regarding the proposed hypothesis concerns the generality of the mechanism. To address this, experiments were designed to deposit different metals onto chiral seed nanowires. As shown in Figures 3F-I, metals including Fe, Ni, Cu, and Ag were investigated (Figure S27 and Figure S28). Experimental observations revealed that the deposition of all these metals resulted in the formation of double-helical structures, along with evidence of nanoparticle coalescence. However, the yield of double-helical nanowires varied depending on the specific metal used, decreasing in the order of Cu > Ag > Fe > Ni. Furthermore, EDX mapping confirmed the successful deposition of the outer-layer metals. Furthermore, as shown in Figure 3F, the fusion of Fe nanoparticles with nanowires primarily occurs along the (110) direction, whereas Ag nanoparticles exhibit fusion along the <111> direction shown in Figure 3I. Combining these observations with previous results for Pd, Au, and Ag deposition, a general trend of phase emerges: noble metal nanoparticles tend to fuse along the <111>

direction, while this is not the case for transition metals. This phenomenon may be attributed to the following reasons: First, the <111> surface of noble metals has the lowest surface energy, prompting nanoparticles and nanowires to come into contact and fuse along this plane to minimize the overall free energy of the system[52]. This energy-driven process makes the <111> direction the preferred orientation for fusion. Second, differences in surface energy among metals influence their fusion tendencies, with metals exhibiting lower surface energy (e.g., Cu and Ag) more readily diffusing across surfaces and fusing with other metals[53]. All the above phenomena deviate from traditional studies on nanowire growth mechanisms[54, 55, 56, 57, 58, 59]. However, the deposition behavior of Ni cannot be fully explained by these mechanisms", and "The universality is not limited by the crystalline structure of the seed nanowires or the type of deposited metal. As shown in Figure 4D, deposition experiments involving Pd, Au, Ni, Cu, and Ru (Figure S32-35) further confirm this mechanism. In the absence of any organic ligands, metal deposition on AuAg seed nanowires consistently exhibits both NP attachment following self-nucleation and atomic layer deposition driven by heterogeneous nucleation. These conclusions are supported by the observed increase in the diameter of the resulting core-shell nanowires and the formation of surface knot-like structures. Importantly, these phenomena closely resemble the deposition behavior observed on chiral nanowires, further supporting the proposed mechanism".

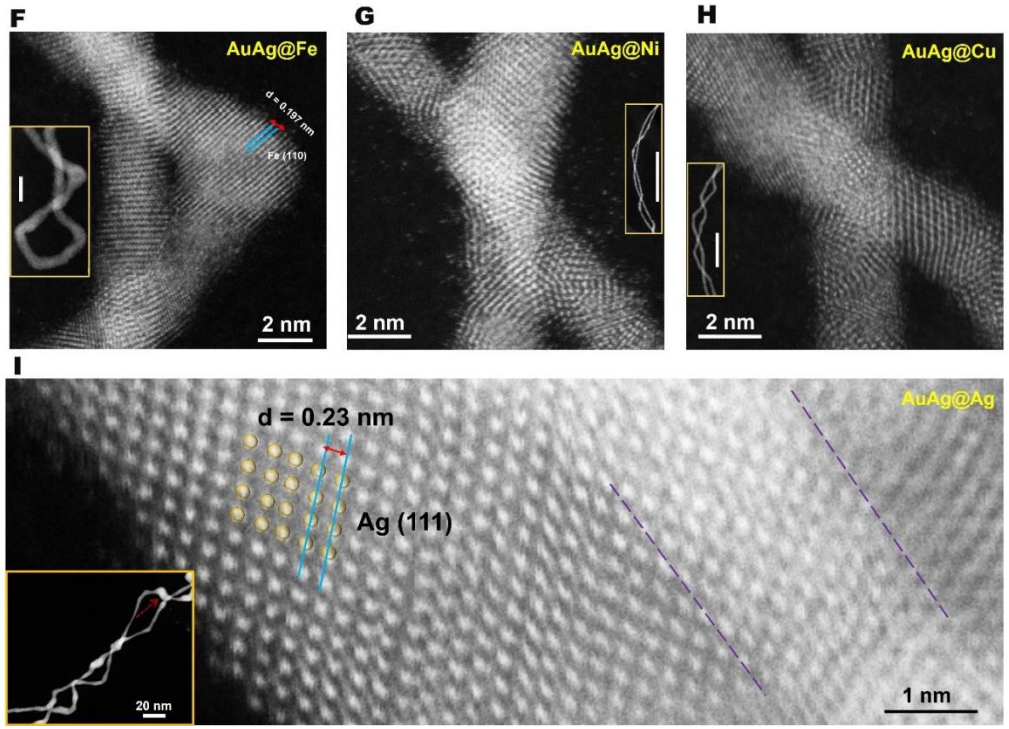

Figure 3: (F) HRSTEM image of Fe coated chiral AuAg NWs, showing the core-shell morphology as well as the attached nanoparticle coalescence in Fe(110) direction. The inserted image is the whole double helix nanowire with scale bar: 5 nm. **(G)** HRSTEM image of Ni coated chiral AuAg NWs, showing the core-shell morphology in atomic resolution. The inserted image is the whole double helix nanowire with scale bar: 50 nm. **(H)** HRSTEM image of Cu coated chiral AuAg NWs, showing the core-shell morphology in atomic resolution. The inserted image is the whole double helix nanowire with scale bar: 20 nm. **(I)** HRSTEM image of Ag coated chiral AuAg NWs, showing the core-shell morphology as well as the attached nanoparticle coalescence in Ag<111> direction.

Comment 6: Effect of Colloidal and Liquid-phase Environment: Has the author considered the influence of the liquid-phase environment on the deposition of precious metals in colloidal systems? For instance, factors like pH and precursor types can affect the deposition process. Discussing these aspects would improve the reliability of the conclusions.

Response 6: Thank you for your thoughtful comment and for highlighting the importance of the liquid-phase environment in the deposition process. In response to your suggestion, we have conducted additional experiments to investigate the effects of pH and precursor types on the deposition of precious metals in colloidal systems. Our results indicate that while a pH value is around 4-7 is generally suitable for the deposition process, the reducing agent's strength and ability play a more critical role in determining the efficiency and dynamic of metal deposition (Figure S40). These findings suggest that the reducing agent's properties outweigh pH variations in influencing the overall process. The relative discussions in the revised manuscript and revised supplementary materials are copied as follow:

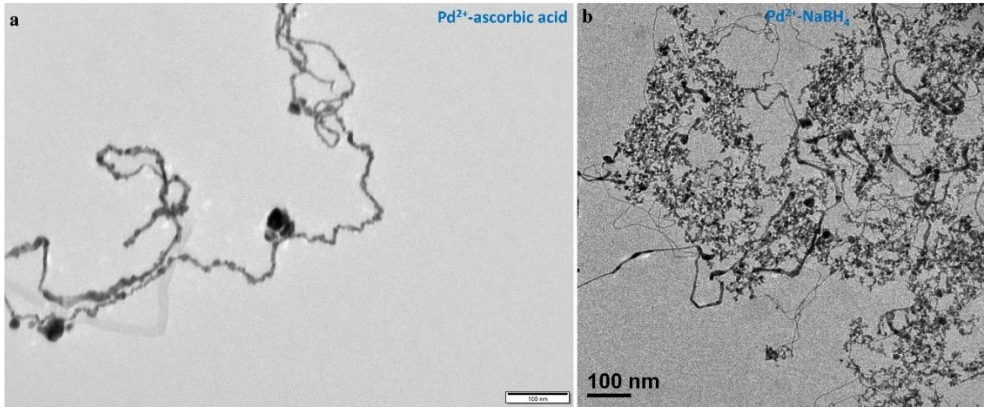

Figure S40. Reducing agent effect on the Pd deposition dynamics on non-chiral nanowire. (a) TEM image of core-shell nanowire while ascorbic acid being applied as reducing agent. (b) TEM image of core-shell nanowire while sodium borohydride being applied as reducing agent. It is clear to see that faster

reduction reaction speed leading to heavy homogeneous nucleation, which is not good for the nanoparticle-attachment growth mode as proposed. Note: it is the experiment of metal deposition on non-chiral AuAg seed nanowire. The pH value of the solution is not as crucial as the other factors based on our experiments.

"Another issue needed to consider it that whether the M^{+x} to M reduction reaction affect its deposition dynamics on AuAg seed nanowire without the present of organic ligands. Control experimental results indicate that when a strong reducing agent, such as sodium borohydride (Figure S40b), is used, Pd homogeneous nucleation dominates. This leads to the formation of a large number of Pd nanoparticles in the solution, with relatively few nanoparticles attaching to the nanowire surface. In contrast, when a weaker reducing agent, such as ascorbic acid (Figure S40a), is used, heterogeneous nucleation becomes dominant, resulting in noticeable nanoparticle coalescence on the nanowire surface. These findings suggest that the redox reaction rate in the solution plays a significant role in determining the mechanism of Pd deposition while pH value is not so crucial"

Comment 7: Does the strain shown in Fig.5 is the driving force for double helix nanowire formation?

Response 7: Thank you for your insightful comment. We have realized that we did not make a clear discussion in the original manuscript. Here, we believe that the strain within the nanowire domain play an important role in the double helix formation based on the literature as well as our understanding. Hence, we inserted the relative discussions in the revised manuscript, which is copied as the follow: Although ultrathin metallic double-helix nanowires were synthesized long agoe, there has been no effective method to investigate the influence of internal stress on their structure. In this study, we employed coding technique to analyze the internal stress within ultrathin double-helix nanowires. This stress arises from the packing of interpenetrated icosahedral or decahedral units in the BCB seed nanowires (Figure S42). Understanding this stress contributes to a deeper comprehension of their helical formation mechanism and provides insights for controlling the chirality and yield of double-helix nanowires.

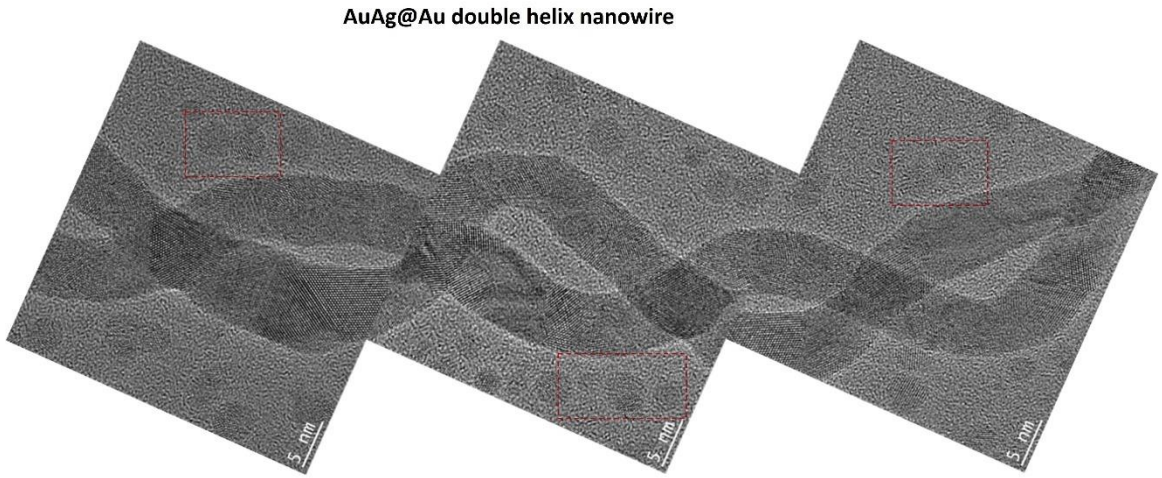

Figure S42. HRSTEM image of AuAg BCB@Au double helical nanowire. The same sample as shown in Figure 5C-G in the main text. The red box highlights Au nanoparticles due to homogeneous nucleation. Note: it is the product of Au deposition on chiral AuAg seed nanowire.

Suggestions:

1 The introduction should more clearly outline previous studies on nanowire growth mechanisms and their conclusions. This would help readers better understand the significance of the current work.

Reply: We thank the reviewer for the good suggestion to improve the quality of our manuscript. We inserted the relative discussion in the revised manuscript which is copied as the follow:

Previous research has revealed that the morphology, composition, and diameter of gold nanowires can be controlled by varying the concentration of growth solutions and reaction conditions[15, 16]. Some recent work focus on the design and synthesis of nanowires with the control of organic ligands which is a kind of

template or surfactant to induce the metal deposition[17, 18, 19]. Precise control over synthetic parameters is necessary to achieve metal nanowires with specific diameters for applications in electronics and sensing[20, 21].

However, more details about the growth process of crystals and the underlying mechanisms (especially in the case of metal core-shell nanowire synthesis) still need to be discovered in order to better control the crystal composition, size, shape, facet, phase, and surface properties as well as explain some interesting phenomena during the growth process. While the growth mechanisms of nanoparticles are generally better understood due to their simpler structure[22, 23, 24, 25], established methodologies, and extensive research, the complexities inherent in core-shell nanowire growth-such as their 1D nature and dependency on surface interactions, as well as surface ligands-present challenges that continue to require detailed investigation[25, 26], even though some of the recent reports revealed the helical nanowire morphology depending on chiral organic ligands[27, 28].

2 It would be beneficial to include a table summarizing the various TEM experimental conditions, along with comparisons to related literature. This would aid in the reproducibility of the experiments.

Replye We thank the reviewer for the good suggestion to improve the quality of our manuscript. We inserted the relative table in the revised supplementary (Table S4).

3 The analysis of nanowire strain in Figure 5, particularly in relation to the growth mechanism, is not sufficiently clear. A more in-depth discussion of this connection is needed to clarify the results.

Reply: Thank you for your insightful comment. We have realized that we did not make a clear discussion in the original manuscript. Here, we believe that the strain within the nanowire domain play an important role in the double helix formation based on the literature as well as our understanding. Hence, we inserted the relative discussions in the revised manuscript, which is copied as the follow: Although ultrathin metallic double-helix nanowires were synthesized long ago[51], there has been no effective method to investigate the influence of internal stress on their structure. In this study, we employed coding technique to analyze

the internal stress within ultrathin double-helix nanowires. This stress arises from the packing of interpenetrated icosahedral or decahedral units in the BCB seed nanowires (Figure S42). Understanding this stress contributes to a deeper comprehension of their helical formation mechanism and provides insights for controlling the chirality and yield of double-helix nanowires.

To Reviewer #2:

It is noticed that Changes to the manuscript and supplementary information are highlighted in yellow.

Main comment: This manuscript investigates the mechanism of Pd/Au/Pt nanoparticle deposition on AuAg nanowires (NWs) through advanced techniques such as Cryo-TEM and 3D electron tomography. A combination of used analysis methods are intriguing and the question that authors would like to answer is important; however, the major drawback in this work is that the proposed mechanism based on the observations, as dictated in the title, is far from what people would accept as a general core/shell nanowire growth mechanism. Thus, with this current data, I worry that the mechanism drawn from the in situ observation is limited only for a very specialized case of the nanowire growth that authors studied in this work. Without being convinced with the importance of the observation presented in the work, it is not recommended to publish this work in Nature Communications. In addition, there are several technical points that require revisions.

Response to the main comment: Thank you for your detailed feedback and for recognizing the importance of our research question and the advanced techniques we employed. We appreciate your concerns regarding the generality of the proposed mechanism and have taken significant steps during the revision process to address these points through additional experiments and refined analysis.

1. To test the generality of the deposition mechanism, we have extended our study to include the deposition of other types of metals, such as Ag, Pt, Fe, Ni, and Cu, in addition to noble metals, on both chiral (Figure 2F-H and Figure 3F-I) and non-chiral nanowires (Figure 4C-D). These experiments allowed us to observe differences and similarities in the deposition processes, providing a broader perspective on the mechanism.

2. Our results show that for noble metals (Pd, Au, Pt), the deposition mechanism involves a competitive interplay between homogeneous nucleation and heterogeneous nucleation, which is consistent across different nanowire systems (Figure 2). However, for non-noble metals such as Fe, Ni, and Cu, we observed distinct behaviors, suggesting that the deposition mechanism is influenced by the specific chemical properties of the metal precursors and the seed nanowire (Figure 4).

3. One key finding across all systems is that nanoparticle coalescence during metal deposition on seed nanowires is a common phenomenon. This observation enriches the classical nanocrystal growth theory by highlighting the role of coalescence in the formation of core-shell structures, which we believe is a universal feature of the deposition process. The title has been updated to "Observation of Nanoparticle Coalescence during Core-Shell Metallic Nanowire Growth in Colloids via Nanoscale Imaging"

4. Based on these additional experiments and findings, we have revised the manuscript to better highlight our hypothesis and the innovative aspects of our work. While we acknowledge that the mechanism, we propose may not yet represent a fully generalized theory for all core-shell nanowire growth, we believe our findings provide significant insights into the fundamental processes involved and offer a framework for future studies.

5. Apologies for the lack of clarity in the writing logic of the previous draft. In the revised version, we have carefully re-evaluated the writing structure and adopted a problem-driven approach to gradually unveil the proposed mechanism which is highlighted in yellow color in the revised manuscript. This improvement is largely thanks to the valuable questions raised by the reviewers, which have helped us gain a deeper understanding of the key innovations of our work and the importance of effectively conveying them.

We hope these additional experiments and the refined presentation of our work address your concerns and demonstrate the broader relevance and importance of our findings. Thank you again for your constructive feedback, which has been invaluable in strengthening our study.

Comment 1: 1. Figure 1C vs. Figure 2: In the data shown in Figure 1C, the deposition mechanism is completed within 30 seconds, while in Figure 2, some nanoparticles remain even after 5 minutes. Could you explain the difference between these two observations?

Response 1: We sincerely appreciate the reviewer for pointing out the seemingly contradictory aspects in the original draft. First, we apologize for the misunderstanding related to the data in Figure 1C of the original manuscript. This phenomenon may have been caused by electron beam-induced etching. To address this, we conducted new in situ liquid-phase TEM experiments and successfully captured the attachment of Pd nanoparticles (Figure 1C), which still occurs within tens of seconds. However, this differs significantly from the 5-minute timescale shown in Figure 2. The reasons are as follows which is copied from the revised manuscript:

The experiment in Figure 1 was conducted using in situ liquid-phase TEM, which allows for direct observation of nanoparticle attachment. However, it is challenging to fully account for the effects of the electron beam in this setup.

To minimize the influence of the electron beam, we performed ex situ experiments by freezing samples at different time points to capture the intermediate structures. This method enables us to more accurately determine the structural evolution of intermediates without interference from the electron beam. As a result, the experimental conditions and reaction environments for the two figures are fundamentally different. In the revised manuscript, we have provided a detailed explanation of this discrepancy and supplemented our findings with quantitative analysis of the nanowire structure using TEM 3D reconstruction techniques. Relevant discussions can be found in the revised manuscript, which is copied as the follow:

Comment 2: Nanoparticle Coalescence Section: In the "Nanoparticle Coalescence Revealed by Electron Tomography" section, could you clarify the exact duration for the completion of the reaction?

Response 2:

We sincerely appreciate the reviewer for raising this critical question. Through repeated experiments, combining both in situ and ex situ methods, we have observed the following: 1) The speed of nanoparticle (NP) coalescence is influenced by the type of metal in the deposited layer. For metals such as Pd, Au, and Pt, the coalescence occurs more rapidly because these metals have interfacial energies similar to that of the AuAg alloy seed nanowires. In situ TEM experiments show that the coalescence process can be completed within tens of seconds. 2) In contrast, for metals like Ru and Fe, the deposition and coalescence processes are slower. These findings highlight the role of interfacial energy in determining the coalescence dynamics. (Line 341-357 in the revised manuscript)

Comment 3: Chiral vs. Achiral Nanowires: The analysis in the manuscript distinguishes between chiral and achiral nanowires in the front and back sides, respectively. Could you provide more detailed information regarding the differences between these two types of nanowires?

Response 3: We appreciate the reviewer's valuable suggestion, which has helped to enhance the quality of our manuscript. First, from a synthesis perspective, the AuAg chiral seed nanowires were synthesized at room temperature, while the AuAg non-chiral seed nanowires were synthesized at 40°C. Second, there are significant differences in their crystal structures: the AuAg chiral seed nanowires exhibit the characteristic "Boerdijk-Coxeter-Bernal" crystal structure (Figure 1A, and Figure S1), whereas the AuAg non-chiral seed nanowires are typical nanowires that grow along the <111> direction (Figure S29).

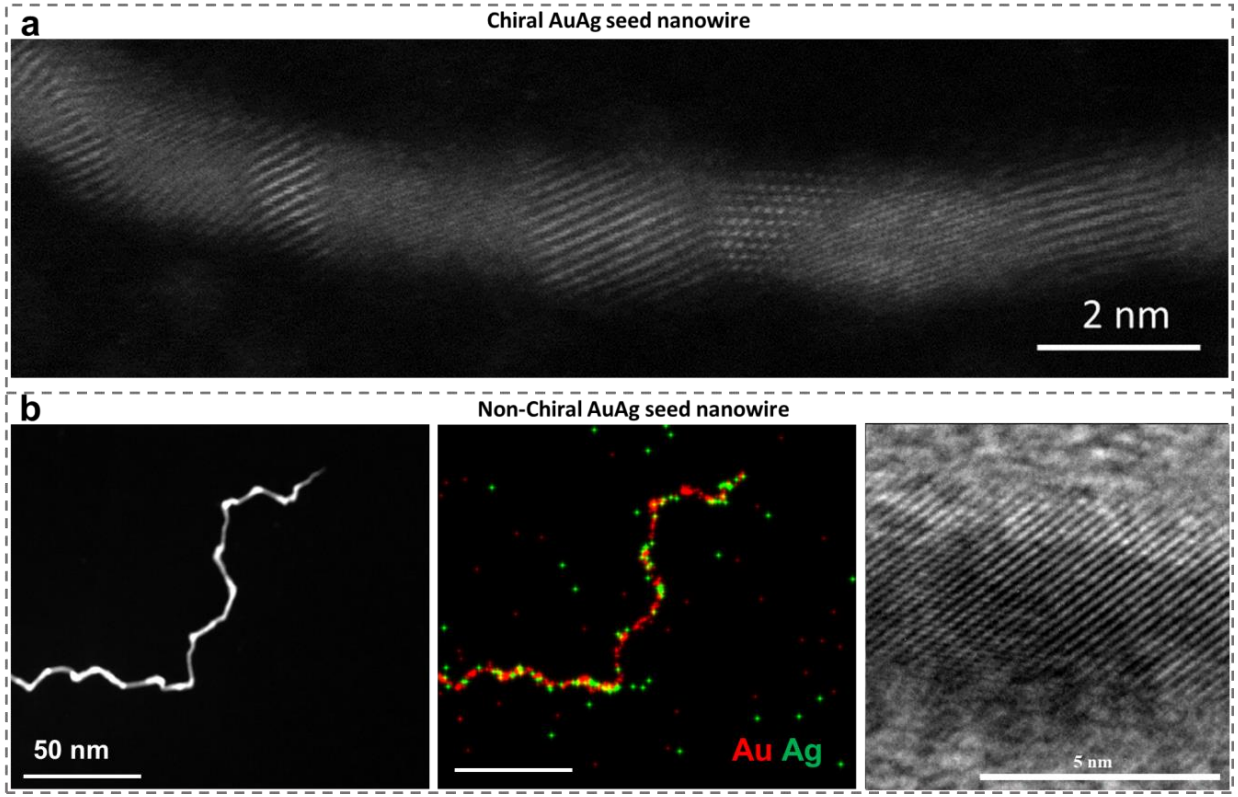

Figure 1 (for review only). Two different types of AuAg seed NWs. (a) HRSTEM image of chiral AuAg seed nanowire, and (b) the EDX color map showing the alloy nanowire composition, and the HRTEM image of the AuAg alloy non-chiral seed nanowire growth from <111> direction, which showing different lattice with chiral seed nanowire. The images have been inserted in the revised manuscript and revised supplementary information.

These experimental details and structural differences have been clearly stated in the revised version of the manuscript. The relative discussion in the revised manuscript is copied as the follow: "First, we monitored the coating process of Pd on chiral AuAg NWs (see Figure S1 for initial morphology) using LPTEM (see Methods for operation details). It is noted that this chiral nanowire is also named 'Boerdijk-Coxeter-Bernal' Nanowire based on previous reports[39, 40, 41] as shown in Figure 1A, which is identified by both HRSTEM image and the corresponding FFT image. There is no organic ligand presence as shown in XPS spectra (Figure S2) in the solution since we try to study the metal deposition on clean nanowire surface", and "The fourth question regarding the proposed hypothesis pertains to whether the crystal structure of the seed nanowires influences nanoparticle attachment during outer-layer metal deposition and whether Ostwald ripening occurs. To address this issue, non-chiral seed nanowires (Figure S29) were applied to conduct similar metal deposition experiments. The chiral AuAg seed nanowires were synthesized at room temperature, while the non-chiral AuAg seed nanowires were synthesized at 40°C, with all other experimental conditions kept identical. After synthesis, the nanowires underwent four rounds of washing. XPS analysis confirmed the absence of any organic ligands on the surface of all seed nanowires (Figure S2)".

Comment 4: Incomplete Data Involvement: The study includes Au/Pd/Pt nanoparticles, but some datasets, such as the Pt deposition on achiral AuAg nanowires and several 3D tomography results, are not fully incorporated. More detailed analysis and clearer inclusion of all relevant data are necessary to strengthen the findings.

Response4: We sincerely thank the reviewer for their valuable feedback. We apologize for the lack of clarity and logical presentation in the initial draft, which failed to fully convey the significance of the experimental data. In response to the reviewer's comments, we have conducted a thorough reanalysis and rewriting of all relevant content, incorporating additional experimental data obtained during the revision process. The revised manuscript has been updated as follows:

1). Through structural analysis of the double-helix nanowires after the deposition of Pd, Pt, Au, and Ag, we found that the coalescence of these noble metal nanoparticles predominantly occurs along the <111> direction. (Line 304-312 in the revised manuscript)

2). In contrast, structural analysis of nanowires following the deposition of Fe, Cu, and Ni revealed that these metals do not deposit along the <111> direction.

3). Regarding the deposition kinetics, we observed that noble metals deposit on AuAg seed nanowires at a faster rate compared to other metals. This is likely due to their closer surface energy compatibility with the AuAg alloy. (Line 277-288 in the revised manuscript)

4). The accuracy of electron tomography: The R-factor value (or residual factor) is a quantitative metric used to evaluate the accuracy and reliability of 3D reconstructions, including those obtained through electron tomography. It provides a measure of how well the reconstructed 3D model matches the experimental data, such as the experimental projection images used in the reconstruction process. (Line 259-270 in the Supporting information)

5). Additionally, we have revised the manuscript's structure and writing style to adopt a problem-driven approach. This better highlight the relationship between experimental design, data analysis, and observed phenomena. Clear evidence has also been provided to support the proposed mechanisms. (Line 172-180 in the revised manuscript)

We hope these revisions address the reviewer's concerns and significantly strengthen the clarity and impact of the manuscript. Thank you again for your constructive suggestions.

Comment 5: Ostwald Ripening (Figure 4e): Ostwald ripening is mentioned in Figure 4e, but more detailed explanation is required to help the reader better understand the data and its significance in the context of the study.

Response 5: We appreciate the reviewer's insightful comment regarding the need for a more detailed explanation of Ostwald ripening in Figure 4e (Figure 5A in the revised manuscript). To address this:

1). To ensure the reproducibility of our experiments, we conducted additional experiments under identical conditions. These new experiments provided more pronounced evidence of the Ostwald ripening phenomenon, further validating its occurrence and significance.

2). Ostwald ripening is observed as smaller Pd nanoparticles (NPs) dissolve and redeposit onto larger ones, driven by surface energy minimization. This process results in the formation of surface "knots," which reflect localized growth and restructuring on the nanowire surface, as shown in Figure 5A and Figure S41.

3) Additionally, we note that the metal type plays a critical role in Ostwald ripening due to differences in surface energy and atomic mobility. For Pd on the AuAg nanowire surface, the high atomic diffusivity and surface energy compatibility facilitate the observed ripening and restructuring behavior.

The relative discussion could be found in the revised manuscript, which is copied as the follow:

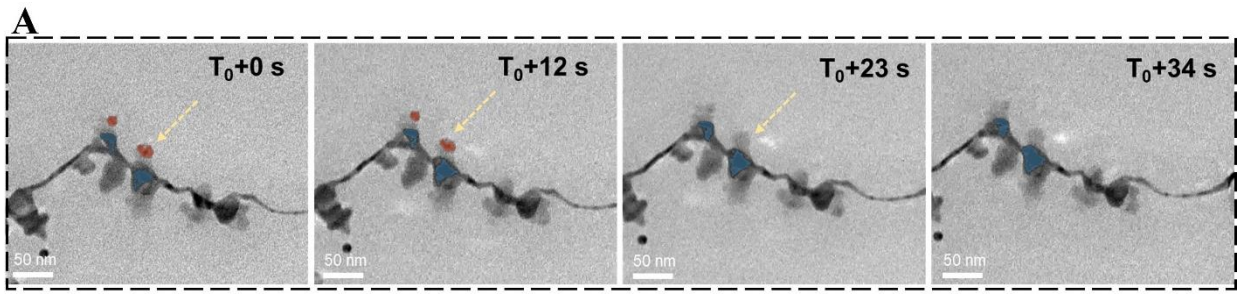

Figure 5. (A) The snapshot image illustrates the LPTEM observation of Ostwald ripening among attached Pd nanoparticles highlighted in red and blue color. The yellow arrow shows the position of the Ostwald ripening which gives a surface with lots of knots as an evidence of nanoparticle attachment.

These findings indicate that the growth mechanism of metal core-shell nanowires during colloidal synthesis is a complex competitive process involving three key steps: heterogeneous nucleation, homogeneous nucleation, and nanoparticle attachment & coalescence. Additionally, this process encompasses phase coalescence and Ostwald ripening. Figure 5A illustrates the Ostwald ripening observed via LPTEM, which contributes significantly to variations in the nanowire morphology highlighted in red and blue color, surface characteristics, and size highlighted by yellow arrow due to the dissolve and redeposition (Figure S41, Movie S8). This ripening process leads to the formation of surface "knots," representing localized growth and restructuring on the nanowire. However, Oswald ripening was not observed in transition metals deposition experiments even we tried lots of times. It seems that the metal type significantly influences Ostwald ripening due to differences in surface energy and atomic mobility. Noble metals like Au, Ag, and Pd exhibit pronounced ripening due to higher atomic diffusivity and surface energy compatibility. In contrast, transition metals like Fe, Ni, Cu, and Ru show limited ripening due to lower diffusivity and surface energy mismatch.

Comment 6: Local Strain Analysis of Au@AuAg Core-Shell Nanowires Section:1. Are the nanowires in this section chiral or achiral? Please clarify.2.Is Figure 5F identical to other figures in Figure 5? If they are the same, this should be clearly indicated in the figure legend.

Response 6: We sincerely apologize for not clearly addressing these points in the initial draft. In the revised manuscript, we have made the following modifications to clarify the concerns raised:

1). We have explicitly stated that the nanowires discussed in this section are derived from chiral seed nanowires, resulting in the formation of double-helical (chiral) Au@AuAg core-shell nanowires. This clarification has been added to the text (Line 360-379 in the revised manuscript).

2). We have provided an explanation for the formation of the double-helical structure, emphasizing the role of chiral seed nanowires and the growth dynamics that lead to this unique morphology (Line 360-379 in the revised manuscript).

3). We have clearly indicated in the figure legend that Figure 5F and other figures (e.g., Figure 5C and 5G) are derived from the same double-helical nanowire (Line 756-760 in the revised manuscript). This ensures that the connection between the different characterizations is explicitly stated.

4). We have expanded the discussion on the local strain analysis at the nanoscale, highlighting its critical role in understanding the formation mechanism of the double-helical structure (Line 366-379 in the revised manuscript). This analysis provides insights into how strain distribution influences the structural evolution of the nanowires.

These revisions have been incorporated to improve clarity and address the reviewer's concerns. We thank the reviewer for their valuable suggestions, which have helped enhance the quality of our manuscript.

Additional Suggestions from the reviewer:

• Title Suggestion: The current title does not fully reflect the specific focus of the manuscript. It is too broad and does not emphasize the core topic clearly. A more specific title related to the Pd/Au/Pt nanoparticle deposition mechanism on AuAg nanowires would be more appropriate.

Reply: We agree with the reviewer's comments and the title has been updated to "Observation of Nanoparticle Coalescence during Core-Shell Metallic Nanowire Growth in Colloids via Nanoscale Imaging"

• Consistency of Terminology: Throughout the manuscript, the terms "chiral" and "achiral" are used to describe AuAg nanowires. However, in the supporting material, the terms "BCB nanowire" and "straight nanowire" (or "coreshell nanowire") are used interchangeably. It would be helpful to maintain consistent terminology throughout the manuscript to ensure clarity for the reader.

Reply: We sincerely apologize for the confusion caused by inconsistent naming of the nanowires in the initial draft. To address this issue, we have made the following changes in the revised manuscript: i) Throughout both the main text and the Supporting Information (SI), we have standardized the terminology by consistently using "chiral" and "non-chiral" to distinguish between the seed nanowires; ii) We have explicitly clarified that all the resulting double-helix nanowires are formed due to the use of chiral seed nanowires. This has been clearly indicated at every relevant point in the revised manuscript; iii) Similarly, we have explicitly clarified that all the resulting straight nanowires are formed due to the use of non-chiral seed nanowires. This has also been clearly indicated at every relevant point in the manuscript and revised supplementary information.

• In Situ Images (Figure 1b and Supporting Figure S3): The in situ images in Figure 1b are the same as those in Supporting Figure S3, but Figure 1b is described in terms of time, while Figure S3 is described in terms of frames. Please clarify and ensure consistent terminology when describing these images.

Reply: We sincerely apologize for the inconsistency in how the in-situ liquid-phase TEM experimental data was described in the initial manuscript. In the revised manuscript, we have standardized the description of time across both the main text and the Supporting Information (SI) by uniformly using seconds as the unit.

- Discussion of AuAg NWs Diameters: The manuscript discusses several diameters of AuAg nanowires in the supporting information, but this is not mentioned in the main text. It would be helpful to include a more detailed description of the findings related to the various diameters of the nanowires in the manuscript.

Reply: We appreciate the reviewer's insightful comment regarding the diameter analysis. Under identical conditions (same precursor concentration, 30-minute growth), AuAg@Au nanowires have a smaller average diameter (5.3 nm) than AuAg@Pd and AuAg@Pt nanowires (6.3–6.4 nm). This suggests Au nanoparticle coalescence is more uniform, likely due to Au's interfacial energy being closer to that of the AuAg seed nanowire compared to Pd and Pt. The relative discussion has been copied here "By the diameter survey of AuAg@Au, AuAg@Pd, and AuAg@Pt nanowires (Table S1-3), we observed that under identical experimental conditions-namely, the same precursor concentration and a growth time of 30 minutes-the average diameter of AuAg@Au nanowires is 5.3 nm, which is smaller than the average diameters of AuAg@Pd and AuAg@Pt nanowires, which range from 6.3 to 6.4 nm. This result suggests that the coalescence of Au nanoparticles is more uniform, leading to smaller particle sizes compared to the coalescence of Pd and Pt. This difference may be attributed to the fact that Au has a more similar interfacial energy with the AuAg seed nanowire compared to Pd and Pt"

Image and Data Verification:

1. TEM Image Scale Bars: In Figure 2, the images are marked with the same scale bar (A-C, E-G), but the diameters appear to differ significantly. Additionally, similar discrepancies are observed in the supporting figures, such as Figure S12. Could you please confirm that these images were taken at the same magnification? It is crucial to ensure that the correct magnification is applied and clearly marked in the figure legends.

2. Red Arrows, Circles, and Boxes in Figure 2: Figure 2 contains red arrows, red circles, and a box, but these features are not explained in the manuscript. Please provide further details in the text to clarify their significance.

3. Figure S12 Title Discrepancy: In Figure S12, the title refers to "Pd deposition," but the manuscript mentions "Au deposition." Please correct this inconsistency in both the figure legend and the text.

4. Supporting Figures S19 & S20 vs. S21 & S22: Supporting Figures S19 & S20 are identical to Figures S21 & S22.Please ensure that the correct data is presented in the manuscript and make the necessary corrections.

5. Figure 3 and Data Numbering: In Figure 3, panel 3g presents Au data, but the manuscript refers to the data as if it were from a different figure. Please revise the text to ensure that the correct data number is cited.

6. Figure S24e Omission: There is no mention of Figure S24e in the manuscript. Please address this oversight.

Reply: We sincerely thank the reviewer for pointing out errors in the original manuscript, and we apologize for these oversights. In the revised manuscript, we have made the following corrections: 1) adjusted the scale bars in the TEM and STEM images, 2) added explanations for relevant labels in the figure captions and main text, 3) removed duplicate images in the supplementary information, 4) corrected figure citation errors, and 5) clearly referenced figures and tables from the SI in the main text while removing irrelevant data.

To Reviewer #3:

It is noticed that Changes to the manuscript and supplementary information are highlighted in yellow.

The paper by Yang et al. presents a multi-modal imaging workflow, integrating LPTEM, cryo-EM, and electron tomography to investigate the growth mechanism of nanocrystals. Three steps are proposed for the seed-mediated growth of noble metals on 1D nanowires: initial heterogeneous nucleation, particle attachment, and coalescence. The consistency between LPTEM and cryo-EM results highlights a generalized growth mechanism applicable to both in-situ and ex-situ (bulk solution synthesis) experiments, showcasing the strength of the proposed approach. However, I have several questions for the authors regarding specific observations and explanations:

Comment 1: In addition to growth mechanism, which can vary with different synthetic methods, I think the authors want to highlight their workflow combining LPTEM with cryo-EM, as well as electron tomography, to give a comprehensive overview of the growth process. However, the necessity of cryo-EM is not well explained. For example, people can also quench the reaction and take conventional TEM imaging, which may be more suitable for reactions involving high temperatures. Can authors explain more on why cryo-EM is necessary?

Response 1: We sincerely thank the reviewer for raising this critical and insightful question, which helps us refine the innovative aspects of our study. The necessity of using cryo-EM and electron tomography in this work is explained as follows:

1). Cryo-EM: While in situ liquid-phase TEM (LPTEM) allows us to observe nanoparticle (NP) coalescence, the influence of the electron beam on the reaction cannot be fully quantified. Although quenching the reaction and using conventional TEM imaging can capture intermediate products, this approach has limitations: (i) during the drying process, NPs may overlap with the nanowires, complicating structural analysis, and (ii) the quenching process itself may alter the metal deposition kinetics, introducing potential artifacts. Additionally, prior studies have shown that the ultrathin nature of the seed nanowires (diameter <2 nm) and the resulting BCB-structured nanowires (diameter <8 nm) makes them highly susceptible to structural damage under electron beam exposure during conventional TEM or STEM imaging. Cryo-EM helps preserve the native state of these delicate structures and minimizes such artifacts. (Line 192-199 in the revised manuscript)

2). Electron Tomography: Traditional 2D HRSTEM imaging cannot effectively distinguish between NP coalescence and the overlapping of NPs due to their physical positions. Electron tomography, on the other hand, provides a 3D reconstruction, enabling us to quantify the surface roughness of nanowires. This is crucial for understanding how different metal depositions influence NP coalescence mechanisms. (Line 244-255 in the revised manuscript)

We hope this explanation clarifies why cryo-EM and electron tomography are essential to our workflow, complementing LPTEM to provide a comprehensive and artifact-minimized understanding of the growth process. Thank you again for your valuable feedback.

Comment 2: In Figure 1: (1) how stable is the nanowire over a longer time period, such as the 30 seconds used in Figure 1c? (2) Dose rate should be added to either the main text or figure caption; (3) How is the diameter calculated? It seems the nanowires are tracked by "atoms" or segments instead of contours.

Response 2: We thank the reviewer for raising this important question. We have addressed the concerns as follows: i) The AuAg chiral seed nanowires demonstrated excellent stability during the in-situ liquid-phase TEM experiments, remaining intact even after 5 minutes of continuous beam irradiation (Figure S1); ii) The beam dose rate has now been explicitly added to the figure captions for clarity; iii) In this analysis, we not only tracked the changes in the area but also calculated the average diameter of the entire nanowire for a more comprehensive evaluation. The above revisions have been inserted into the revised manuscript (Line 688-697 in the revised manuscript).

Comment 3: In Movie S2, there appears to be motion or drift of the nanowire. Given the small viewing area and the possibility of the nanowire being obscured/blocked by the viewing window, could the authors comment on the accuracy of the tracked area?

Response 3: We sincerely thank the reviewer for raising this critical scientific question, which has prompted us to carefully evaluate the reliability of our data. We address the concern as follows: i) To further support the accuracy of our analysis, we have included additional supporting data in the Supplementary Information (SI), which demonstrates significant changes in the overall area of the nanowire region as a result of Pd deposition (Figure S4). This provides strong evidence for the observed phenomenon; ii) The accuracy of the tracked area is based on a deep learning approach, and we have made every effort to rigorously evaluate its reliability. The regression function curve (Figure S5 and S6), included in the SI, provides a quantitative assessment of the method's performance; iii) We acknowledge that sample drifting occurred during the experiment, which is indeed a limitation of the current setup. This challenge motivated us to adopt

complementary techniques, such as cryo-electron microscopy and 3D electron tomography, to further validate the findings and improve the robustness of our analysis. The corresponding discussion has been inserted into the revised manuscript (Line 332-347 in the supporting information).

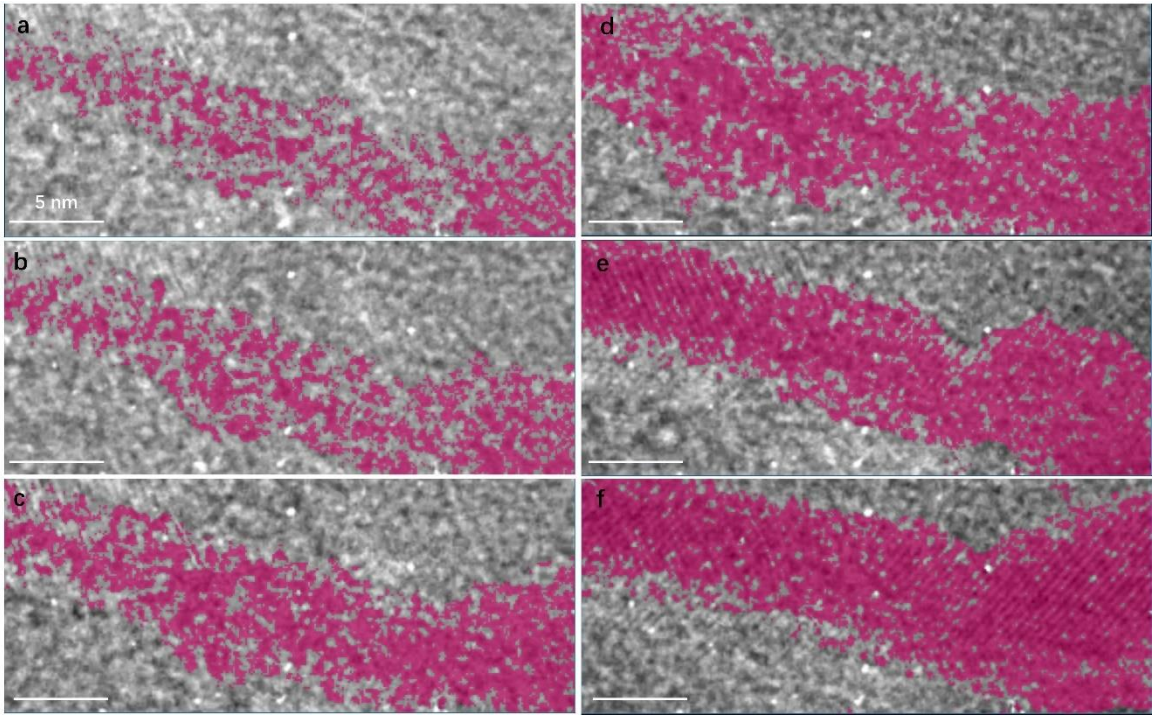

Figure S4. These screenshots depict the kinetic process of Pd depositing on the surface of AuAg BCB NW observed under in-situ TEM in liquid phase as shown in Figure 1B in the main text (from **a** to **f**, *t* = 0 s, 0.5 s, 2.5 s, 4 s, 5.8 s, and 6.5 s). The red color shows coding process to quantify the area change of the nanowire during Pd deposition. It is evident from the images that there is noticeable growth of lattice stripes. The AuAg BCB@Pd nanowire was marked during deep learning analysis.

Comment 4: Can authors clarify the composition of the "mixed solution" used for LPTEM? It is important to mention what is the reducing agent used in the LPTEM experiment.

Response 4: We sincerely thank the reviewer for raising this critical question. In a commonly performed Pd coating experiment, 50 μL of the as-purified AuAg NWs aqueous solution was introduced into 200 μL of aqueous L-ascorbic acid solution (concentration: 0.2 M) under vortex. Subsequently, 60 μL of H_2PdCl_4 solution (volume ratio: H_2O/DMF = 1:1) was added. The final mixture was allowed to sit undisturbed at room temperature for 30 min to complete the Pd deposition. For LPTEM experiment, 0.3μLof the above solution will be dropped on the graphene film. Hence, the reducing agent is L-ascorbic acid, and the mixed solution is the growth solution of the nanowire. (Line 412-423 in the revised manuscript)

Although we observed nanoparticle (NP) coalescence under these experimental conditions, there are clear challenges, such as the impact of the electron beam and the difficulty in controlling the initial stages of the reaction. Therefore, cryo-electron microscopy (cryo-EM) is considered a more reliable method for studying intermediates in ex situ experiments. By comparison, we believe that the influence of the electron beam accelerates metal deposition in in situ experiments (occurring within tens of seconds), whereas in ex situ experiments, the process typically takes several minutes. (Line 383-389 in the revised manuscript)

Comment 5: In Movie S3, there is no obvious evidence of particle attachment. Besides, there is no obvious increase in the diameter of the nanowires while the nanoparticles in the background (Pd nanoparticles?) all gradually disappeared. Instead of coalescence, is it possible that the Pd, like those highlighted in red, is actually etched? Besides, it is interesting that in Movie S4, the beam induced self-nucleation of Pd, while etching of particles seems to exist in Movie S3. Can authors comment on these contradicting phenomena?

Response 5: We sincerely thank the reviewer for raising this critical question. In response, we conducted additional experiments and obtained new data to support our conclusion: during the Pd deposition process, both heterogeneous nucleation leading to atomic layer deposition and self-nucleation followed by nanoparticle attachment were observed (Figure 1C, and Figure S7, Movie S3). Furthermore, subsequent atomic-scale SREM image analysis revealed that this deposition behavior also occurs during Pt deposition (Figure S18). The corresponding discussion has been incorporated into the revised manuscript (Line 143-154, 231-235 in the revised manuscript).

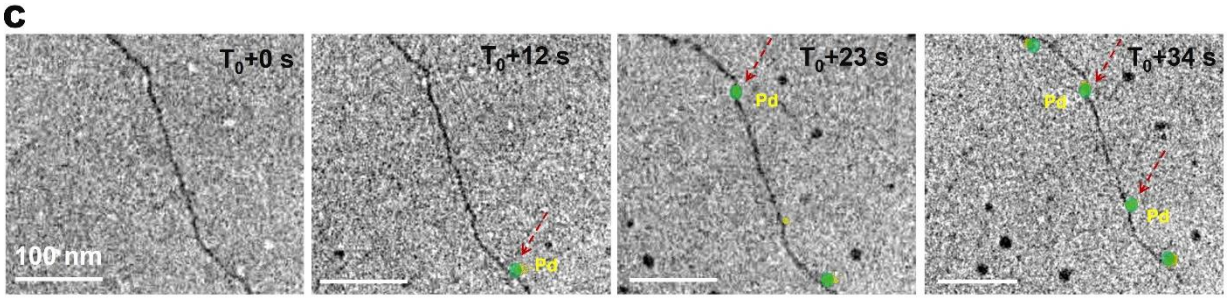

Figure 1. (C) Snapshot image depicts the dynamic process of Pd nanoparticle deposition directly on a AuAg NW in colloids: the greenred circle highlights some attached Pd nanoparticles on AuAg seed nanowire followed by covalence whose positions are labelled by red arrows.

Comment 6: For Figure 3, the authors claimed that it "clearly reveals the presence of nanoparticles adhering to the nanowire surfaces". However, from Figure 1, it seems that not all "atoms" are tracked in nanowires. Besides, the edge of the reconstructed nanowire in Figure 3 is also very blurring. Could the authors provide further clarification on the reliability of the evidence supporting particle attachment? For example, maybe adding EDX of similar areas to show the "attached particle" is really made of Pd.

Response 6: We sincerely thank the reviewer for raising this critical scientific question, which has significantly deepened our understanding of this work. To address the issue, we conducted repeated atomic-scale STEM imaging analyses of the samples and confirmed the coalescence of Pd nanoparticles (NPs) along the <111> direction (Figure 2F-G). Additionally, we observed atomic layer deposition of Pd atoms, a discovery made possible by the application of cryo-electron microscopy. These results indicate that during the Pd deposition process, both heterogeneous nucleation leading to atomic layer deposition and self-nucleation followed by nanoparticle attachment occur, representing two competing mechanisms. Furthermore, EDX mapping confirmed the Pd deposition behavior (Figure 2H). These experimental findings not only compensate for the limitations of electron tomography but also provide us with new insights. The corresponding discussion has been incorporated into the revised manuscript (Line 212-220 in the revised manuscript).

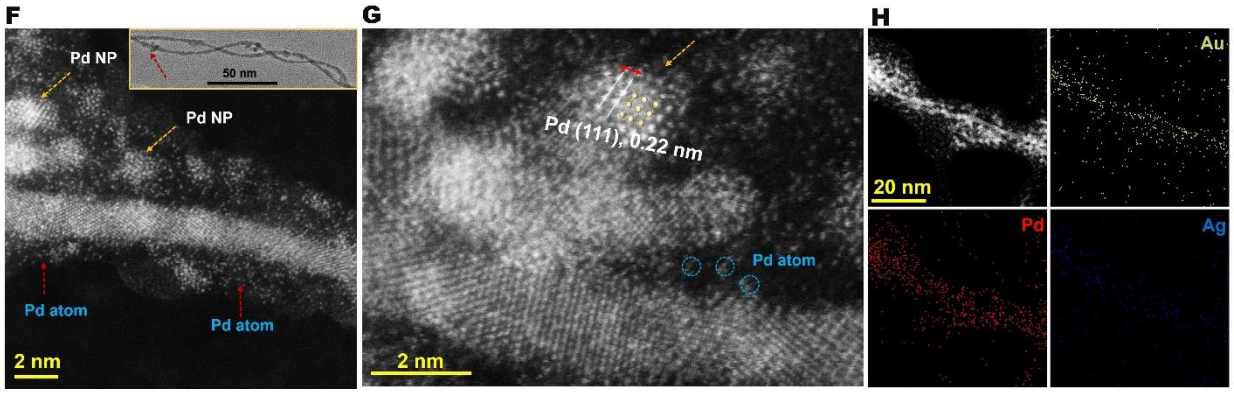

Figure 2. (F and G) STEM image of the Pd coated chiral AuAg NWs in atomic resolution showing both Pd atom deposition (red arrow) and Pd nanoparticle coalescence (yellow arrow) in Pd<111> direction on AuAg seed nanowire captured by cryogenic STEM after 1 min growth in colloid. (H) EDX maps confirm the Pd element deposition on the seed nanowire correspondingly as in figure F.

Comment 7: The authors mentioned that "interfacial fusion between the nanoparticles and nanowires was observed along the Pd (111) direction". How the (111) direction (should be ⟨ 111⟩ direction?) is derived? From lattice spacing?

Response 7: We sincerely thank the reviewer for raising this important question. We address the concern as follows: i) The observation of the interfacial fusion between the nanoparticles and nanowires along the Pd ⟨111⟩ direction is indeed based on the measurement of lattice spacing. Using high-resolution TEM (HRTEM) images, we measured the lattice spacing at the interface and identified it as corresponding to the Pd ⟨111⟩ planes. This identification is supported by the agreement between the measured lattice spacing and the known value for Pd ⟨111⟩; ii) The lattice spacing measurement is a reliable method for determining the crystallographic orientation in our case. The high-quality HRTEM images allowed us to clearly resolve the lattice fringes, ensuring the accuracy of the measurement. Additionally, the ⟨111⟩ direction is consistent with the expected growth and fusion behavior of Pd under the experimental conditions, further corroborating our observation. The corresponding discussion has been incorporated into the revised manuscript (Line 244-255 in the revised manuscript).

Comment 8: In Figure 4c, it seems there is galvanic replacement between Pt and AuAg alloy nanowire?

Response 8: We thank the reviewer's comments. The following discussion has been updated in the revised manuscript: The phenomenon of Pt deposition observed in Figure 4C could potentially be attributed to galvanic replacement between Pt and the AuAg alloy nanowire. However, similar nanoparticle formation was also observed in our experiments involving Ni deposition, which supports our hypothesis. It is possible that the galvanic replacement between Pt and the AuAg alloy nanowire may explain why the nanoparticles appear larger in the Pt deposition experiment.

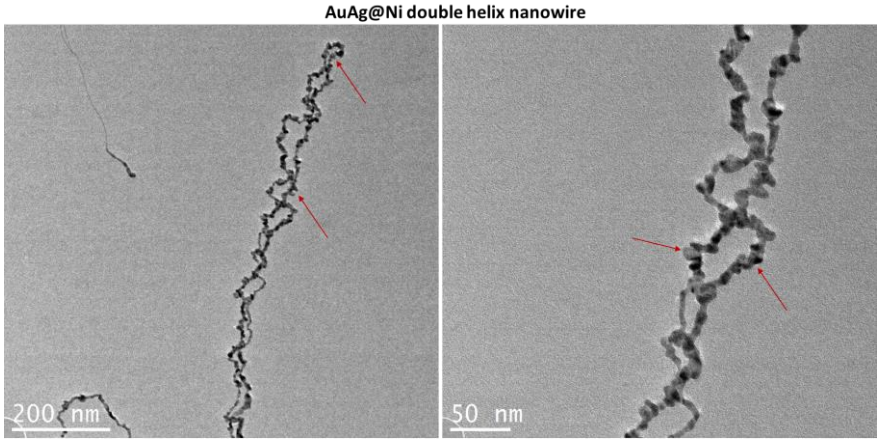

Figure 2 (for review only). Ni deposition on chiral AuAg seed NWs. Since both gold and silver have higher (more positive) reduction potentials than nickel, they are more noble and less likely to be replaced by nickel under normal conditions. This makes galvanic replacement less favorable.

Comment 9: The authors attribute the surface roughness of Pd and Pt-coated nanowires to “differences in lattice matching between the various metal crystals”. In addition to the lattice mismatch between Au and Pd (5.3%) or Pt (3.9%), the authors can also check the atom diffusivity and bond energy. It is possible that Pd and Pt tend to self-nucleate and slow to diffuse, while Au is the opposite.

Response 9: We sincerely thank the reviewer for their valuable suggestions, which have greatly enhanced our understanding of this study. We have addressed this question from the following perspectives: i) A review of the literature indicates that the atomic diffusivity of different metals is indeed a key factor influencing the variations in coalescence behavior (Ref.54, Ref.55); ii) We conducted additional experiments with the deposition of other metals, such as Ag. Due to its relatively high atomic diffusivity, the resulting nanowire surfaces were smoother (Figure 3I). In contrast, metals like Fe and Ru exhibited more limited nanoparticle coalescence (Figure 4D). The corresponding discussion has been inserted into the revised manuscript (Line 271-277,313-320 in the revised manuscript).

Figure 3I

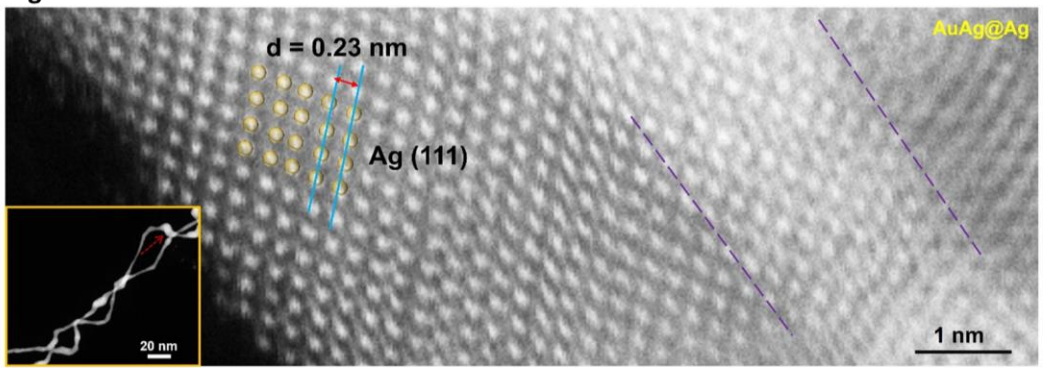

Figure 4D

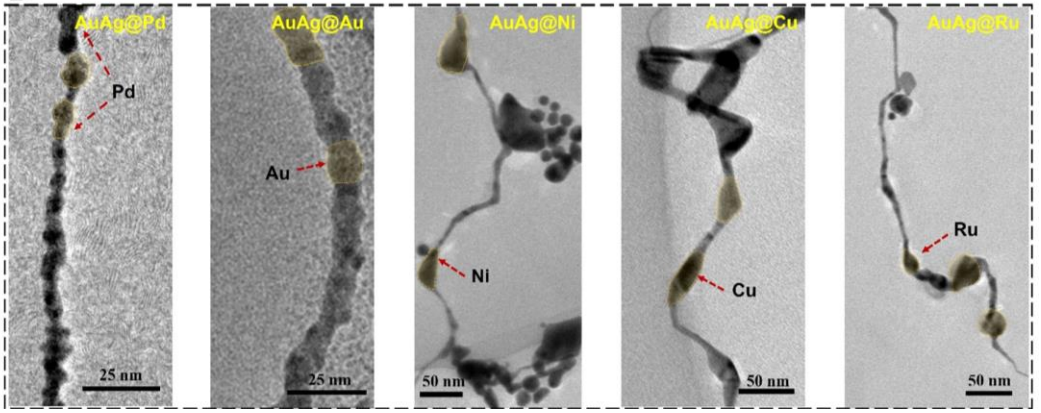

Figure 3I: HRSTEM image of Ag coated chiral AuAg NWs, showing the core-shell morphology as well as the attached nanoparticle coalescence in Ag<111> direction. Figure 4D: TEM images showing different types of metal deposition on non-chiral AuAg seed non-chiral nanowire giving a core-shell nanowire with nanoparticles attachment which includes Pd, Au, Ni, Cu, and Ru. The red arrows show the position of the nanoparticle coalescence which region is highlighted in red color on nanowire

Comment 10: In Figure 5, what is the scale for stress distribution? Also, is it stress or strain? What do vertical and horizontal directions mean?

Response 10: Thanks for the good question, and we are sorry for the confusion. We made the following corrections and explanation: 1) It should be strain not stress which was measured in our study; 2) The scale unit for the strain color map is dimensionless, as strain itself is defined as the change in length divided by the original length (e.g., $\varepsilon=\Delta L/L_0$); 3) vertical and horizontal directions represent ε_{xx} and ε_{yy}. The strain components, such as ε_{xx} and ε_{yy}, refer to the normal strain in the x and y directions, respectively. The corresponding discussion has been incorporated into the revised manuscript (Line 364-371 in the revised manuscript).

Comment 11: Can authors provide more explanation on how strain is calculated? What are the unstrained diffraction vectors mentioned in the supporting information? It is suggested to add one more figure to Supporting Information to show the strain analysis process.

Response 11: We sincerely thank the reviewer for raising this important question. We address the concern as follows:

1). Strain Calculation Method:

- In our study, we utilized a coding method that employs digital image correlation (DIC) to analyze the HRTEM images. This method allows for a more precise quantification of local displacements within the nanowire compared to traditional Geometrical Phase Analysis (GPA).
- The strain is calculated using the displacement field obtained from the coding method. Specifically, the strain components (e.g., ε_{xx}, ε_{yy}, and ε_{xy}) are derived from the spatial derivatives of the displacement field. For example: $\varepsilon_{xx}= \partial u/\partial x$, $\varepsilon_{yy}= \partial v/\partial y$ $\varepsilon_{xy}=(\partial u/\partial x +\partial v/\partial y)/2$.

2). Unstrained Diffraction Vectors:

- The unstrained diffraction vectors mentioned in the Supporting Information refer to the reciprocal lattice vectors that correspond to the ideal, unstrained crystal structure of the gold nanowire. These vectors are used as a reference to compare against the strained conditions observed in the HRTEM images.

- The unstrained diffraction vectors mentioned in the Supporting Information refer to the reciprocal lattice vectors that correspond to the ideal, unstrained crystal structure of the gold nanowire. These vectors are used as a reference to compare against the strained conditions observed in the HRTEM images.
- The relationship between the unstrained and strained diffraction vectors can be expressed as: $G_{strained} = (1+\varepsilon)\cdot G_{unstrained}$

where ε represents the strain tensor

The corresponding discussion has been incorporated into the revised supplementary information (Line 200-225 in the supporting information).

Comment 12: The authors mentioned that "higher stress in the central region is likely induced by the deposition of external Au atoms, while higher stress at the boundary may result from structural features at the boundary". How does the strain look like in pristine AuAg nanowires? Besides, what is the motivation for strain analysis? It should be clarified at the beginning of this section.

Response12: Thank you for your insightful comment. We have realized that we did not make a clear discussion in the original manuscript. Here, we believe that the strain within the nanowire domain play an important role in the double helix formation based on the literature as well as our understanding. Hence, we inserted the relative discussions in the revised manuscript, which is copied as the follow: Although ultrathin metallic double-helix nanowires were synthesized long ago[51], there has been no effective method to investigate the influence of internal stress on their structure. In this study, we employed coding technique to analyze the internal stress within ultrathin double-helix nanowires. This stress arises from the packing of interpenetrated icosahedral or decahedral units in the BCB seed nanowires (Figure S42). Understanding this stress contributes to a deeper comprehension of their helical formation mechanism and provides insights for controlling the chirality and yield of double-helix nanowires.

To Reviewer #4:

It is noticed that Changes to the manuscript and supplementary information are highlighted in yellow.

Main comment: In their Manuscript "Understanding Core-Shell Nanowires Development in Colloidal Synthesis through Nanoscale Imaging" the authors study metal deposition on AuAg seed nanowires using liquid phase and cryo transmission electron microscopy. The results are evaluated extensively using advanced computational methods. While the study is done well from an experimental and data analysis point of view, the scientific analysis and structure of the main manuscript is quite lacking. First of all, it is not really clear what the main outcome of this study was. To see heterogeneous nucleation on a seed crystal with concurrent homogeneous nucleation of particles that can attach to the seed crystal is hardly surprising. Other results such as the proposed Ostwald ripening are poorly supported by the data. Furthermore, a lot of the extensive microscopy and analysis work is not really brought into context and explained at all. This is somewhat exemplified by the ratio of content in the main manuscript compared to the content in the supplementary. While I believe that an extensive supplementary is generally a good thing, having 41 supplementary figures (in addition to other items) for such a short article (~2500 words, 5 figures) begs the question whether the authors chose the right publication format. Maybe a longer format article with more display items would be more suitable. Furthermore, there does not seem to be a good reason for the application of some of the techniques in the first place. For instance, using deep learning to measure the nanowire area in the first part of the manuscript seems highly questionable. Neither are the results convincing nor is there a reason to do that kind of analysis at all (especially without a critical appraisal of the validity of the results). Other analysis techniques fall in a similar category like the morphology analysis (S34 c&d, no explanation given on how it was performed), or the curvature analysis (S24) which leaves open a lot of questions. It seems to me that the authors just tried everything they could think of (liquid and cryo TEM, Atomic resolution tomography, deep learning analysis, GPA and custom strain measurement…) to see what sticks instead of carefully planning and conducting dedicated experiments and analyses.On a further note, I don't want to criticize style in general, however words/phrases such as 'impressively', 'for the first time' should not be used describe one's own research (e.g. 'Impressively, in Figure 3d, e, we unexpectedly observed in[…]').

I suggest the authors think about how to restructure their manuscript for clarity and accuracy. They should write a concise and convincing story that is well supported by their findings without unnecessarily analyses. Frankly, a few proper EDX measurements would make the whole story way more comprehensible as a lot of what the authors report hinges on the spatial distribution of elements.

Therefore, without major changes I cannot recommend the manuscript for publication at this point.

Response to the main comment: We sincerely thank the reviewer for the detailed and constructive feedback. We deeply regret that the initial submission fell short in terms of clarity, structure, and scientific analysis, and we apologize for the inconvenience caused. We fully agree with the reviewer's comments and have taken the following steps to address the identified issues:

1). Clarification of the main outcome of the study: We have refined the manuscript to clearly articulate the main outcome of this work. Specifically, we demonstrate that metal deposition on nanowires involves two distinct phenomena: (i) heterogeneous atomic-layer nucleation on the seed nanowire and (ii) homogeneous nucleation of nanoparticles (NPs) that subsequently attach to the nanowire. This dual process is identified as a universal phenomenon in liquid-phase nanomaterial synthesis, particularly in systems without organic ligands. This insight provides a more comprehensive understanding of metal deposition mechanisms.

2). NP coalescence and its kinetics as a key finding: We emphasize that the analysis of NP coalescence and its influencing kinetic factors is a central outcome of this study. This finding enriches the traditional understanding of nanocrystal growth theories, particularly in the context of ionic nanocrystal systems. The revised manuscript now provides a clearer explanation of how our results contribute to the broader field of nanomaterial synthesis.

3). Verification of results and reproducibility: To strengthen the reliability of our conclusions, we conducted additional experiments to validate the results, including studies on other types of metal deposition, further data analyses, and tests of experimental reproducibility. These additional experiments and their outcomes are now included in the revised manuscript.

4). Improved manuscript structure and writing style: To enhance clarity and logical flow, we adopted a question-driven writing approach. The manuscript now begins by presenting the key scientific questions and subsequently addresses them step by step. This structure ensures that each section is purpose-driven and logically connected to the overall narrative. Additionally, we have removed subjective and non-academic phrases (e.g., "impressively," "for the first time") and corrected formatting and stylistic issues throughout the manuscript.

5). Supplementary information and analysis methods: We have streamlined and reorganized the supplementary materials to ensure they complement the main manuscript without overwhelming the reader. Each analysis method, including deep learning-based nanowire area measurement, morphology analysis, and curvature analysis, is now properly justified and critically appraised. For example, we have clarified why deep learning was employed in the first part of the manuscript and provided a critical evaluation of its validity. Detailed explanations of the methods and their relevance to the study are now included in both the main text and supplementary information.

We believe these revisions significantly improve the clarity, structure, and scientific rigor of the manuscript. We thank the reviewer again for your valuable feedback, which has helped us substantially enhance the quality of our work.

A (non-exhaustive) list of further points follows below:

Comment 1: In the initial LPTEM part the authors describe their wires as chiral, however the images showing the proposed BCB structure are not really convincing (Figure S1). The wires simply appear as polycrystalline, not like a regular arrangement of tetrahedra. Maybe the authors can make this clearer.

Response 1: We appreciate the reviewer's valuable question and suggestion, which has helped to enhance the quality of our manuscript. First, from a synthesis perspective, the AuAg chiral seed nanowires were synthesized at room temperature, while the AuAg non-chiral seed nanowires were synthesized at 40°C. Second, there are significant differences in their crystal structures: the AuAg chiral seed nanowires exhibit the characteristic "Boerdijk-Coxeter-Bernal" crystal structure (Figure 1A, and Figure S1), whereas the AuAg non-chiral seed nanowires are typical nanowires that grow along the <111> direction (Figure S29). Also, the FFT image in Figure 1A confirms the BCB structure based on literature report (Ref.41, and Ref. 51).

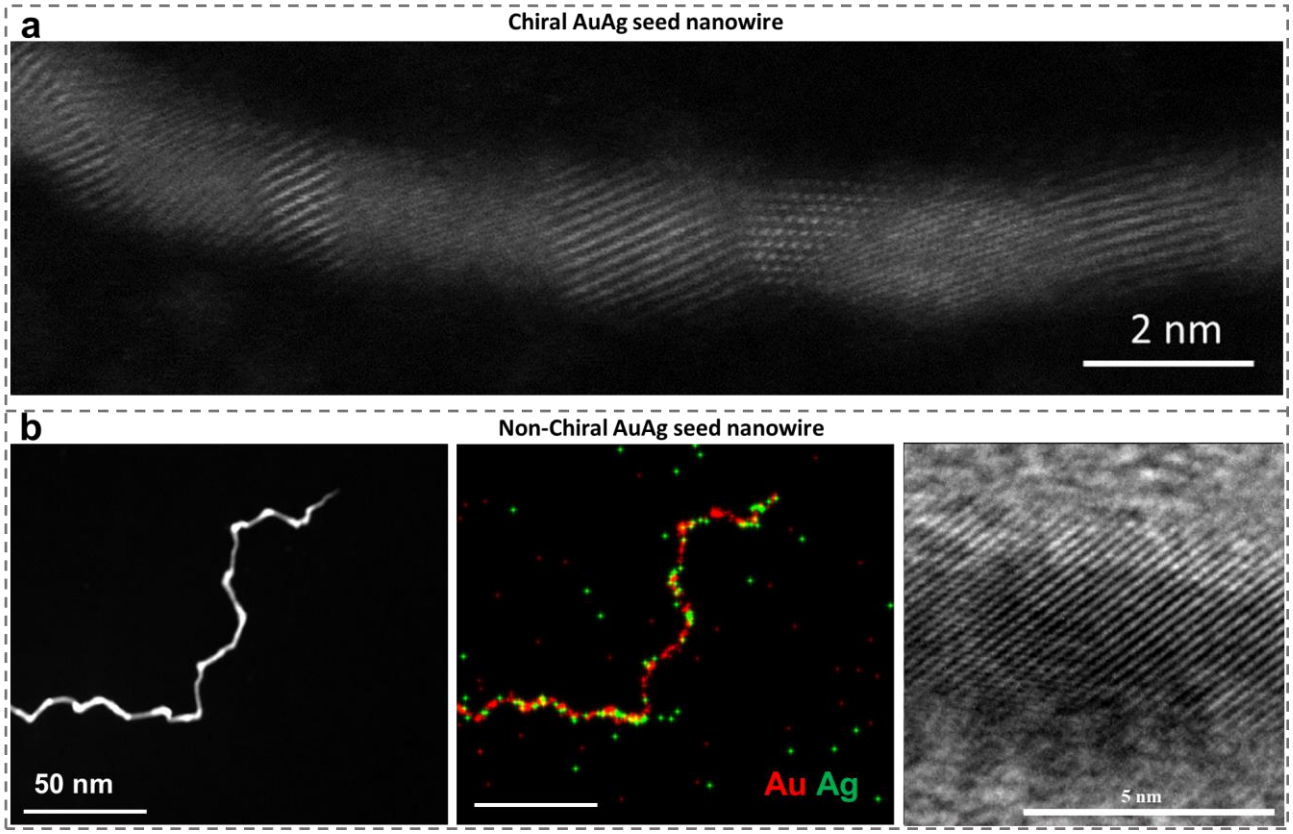

Figure 1 (for review only). Two different types of AuAg seed NWs. (a) HRSTEM image of chiral AuAg seed nanowire, and (b) the EDX color map showing the alloy nanowire composition, and the HRTEM image of the AuAg alloy non-chiral seed nanowire growth from <111> direction, which showing different lattice with chiral seed nanowire. The images have been inserted in the revised manuscript and revised supplementary information.

These experimental details and structural differences have been clearly stated in the revised version of the manuscript. The relative discussion in the revised manuscript is copied as the follow: "First, we monitored the coating process of Pd on chiral AuAg NWs (see Figure S1 for initial morphology) using LPTEM (see Methods for operation details). It is noted that this chiral nanowire is also named 'Boerdijk-Coxeter-Bernal' Nanowire based on previous reports[39, 40, 41] as shown in Figure 1A, which is identified by both HRSTEM image and the corresponding FFT image. There is no organic ligand presence as shown in XPS spectra (Figure S2) in the solution since we try to study the metal deposition on clean nanowire surface", and "The fourth question regarding the proposed hypothesis pertains to whether the crystal structure of the seed nanowires influences nanoparticle attachment during outer-layer metal deposition and whether Ostwald ripening occurs. To address this issue, non-chiral seed nanowires (Figure S29) were applied to conduct similar metal deposition experiments. The chiral AuAg seed nanowires were synthesized at room temperature, while the non-chiral AuAg seed nanowires were synthesized at 40°C, with all other experimental conditions kept identical. After synthesis, the nanowires underwent four rounds of washing. XPS analysis confirmed the absence of any organic ligands on the surface of all seed nanowires (Figure S2)".

Comment 2: Figure 1 a: Why do the authors color the whole nanowire in green? If it is 'remarkably stable' as they claim there is no need for obfuscation by coloring. Let the reader see what is really there. I guess the original images are shown in S2, which begs the question why they are shown twice. What does the green color mean? This is not referenced in the caption.

Response 2: We sincerely thank the reviewer for pointing out the issues regarding the presentation of Figure 1a and the associated explanation in the initial submission. We acknowledge that the original presentation was unclear and may have caused confusion. We have made the following modifications to address these concerns: i) n the revised manuscript, we have replaced the original Figure 1a with a detailed characterization of the crystal structure of the chiral seed nanowires. This change reflects the importance of confirming the chiral structure as a foundational aspect of this study. The high-resolution structural characterization is now presented in a clear and direct manner without unnecessary obfuscation; ii) The stability testing of the chiral seed nanowires in solution, including their behavior under electron beam irradiation, has been moved entirely to the SI. This ensures that the main manuscript remains focused on the most critical aspects of the study. In the SI, we have provided a clear explanation of the green coloring used in the images, which was intended to highlight the nanowire morphology during stability testing. We explicitly state that the green color does not alter or obscure the underlying data but was used for visual

clarity in those specific experiments. To avoid repetition, we have removed duplicate images from the main manuscript and SI. Each figure now serves a distinct purpose, and the revised captions provide clear and concise explanations of the data presented.

Comment 3: Figure 1b: Again: Why color the wire? I can see the lattice planes much better without the color. Also, the color is neither explained in the figure caption nor in the main text. In supplementary figure 3 almost the same images are shown again and finally the origin of the color is mentioned, but without further detail let alone a reason why a deep learning analysis was performed. In the main text the deep learning is only briefly mentioned in the context of S4.

Response 3: We thank the reviewer for highlighting the issues with Figure 1b and the associated explanation. We acknowledge that the use of color in the image and the lack of clarity regarding the deep learning analysis were problematic. To address these concerns, we have made the following revisions: i) In the revised manuscript, we have replaced the colored version of the nanowire with the original, unaltered TEM image (Figure 2B). This ensures that the lattice planes are clearly visible without any obfuscation. We believe this change improves the clarity and allows readers to directly observe the raw data. ii) We have eliminated the repetition of similar images between Figure 1b in the main manuscript and Supplementary Figure 3. Each image now serves a distinct purpose, and the redundancy has been resolved. iii) In the revised manuscript, we provide a clear explanation of why deep learning analysis was employed. Specifically, we used deep learning to analyze changes in the nanowire area and diameter during Pd deposition (Figure S4). This approach enables us to confirm atomic deposition while minimizing the effects of image drift and noise during TEM imaging. The rationale for using deep learning and its relevance to the study are now explicitly stated in the main text (Line 140-158 in the supporting information).

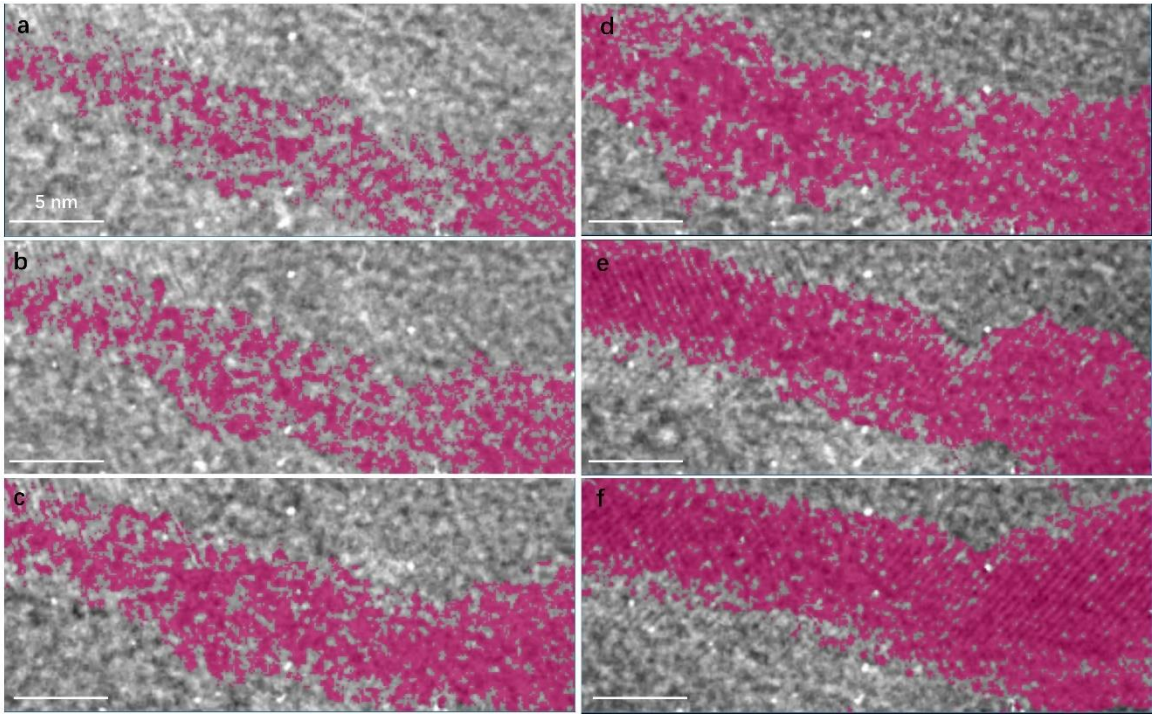

Figure S4. These screenshots depict the kinetic process of Pd depositing on the surface of AuAg BCB NW observed under in-situ TEM in liquid phase as shown in Figure 1B in the main text (from **a** to **f**, t = 0 s, 0.5 s, 2.5 s, 4 s, 5.8 s, and 6.5 s). The red color shows coding process to quantify the area change of the nanowire during Pd deposition. It is evident from the images that there is noticeable growth of lattice stripes. The AuAg BCB@Pd nanowire was marked during deep learning analysis.

Comment 4: Further on Figure 1b: The authors claim that the increase in the wire thickness is due to Pd deposition. It would be nice to have some sort of confirmation that it is actually Pd (e.g. post mortem EDX) and not just redistribution of AuAg. The authors do show an EDX in figure S8 but apart from issues with the EDX mentioned later on, it is not clear whether that is comparable to the wires shown in fig 1 b.

Response 4: We sincerely thank the reviewer for raising this critical scientific question, which has significantly deepened our understanding of this work. To address the issue that Pd do deposited on the seed nanowire as both single atom and Pd nanoparticle, we conducted repeated atomic-scale STEM imaging analyses of the samples and confirmed the coalescence of Pd nanoparticles (NPs) along the <111> direction (Figure 2F-G). Additionally, we observed atomic layer deposition of Pd atoms, a discovery made possible by the application of cryo-electron microscopy. These results indicate that during the Pd deposition process, both heterogeneous nucleation leading to atomic layer deposition and self-nucleation followed by nanoparticle attachment occur, representing two competing mechanisms. Furthermore, EDX mapping confirmed the Pd deposition behavior (Figure 2H). These experimental findings not only compensate for the limitations of electron tomography but also provide us with new insights. The corresponding discussion has been incorporated into the revised manuscript (Line 212-220 in the revised manuscript).

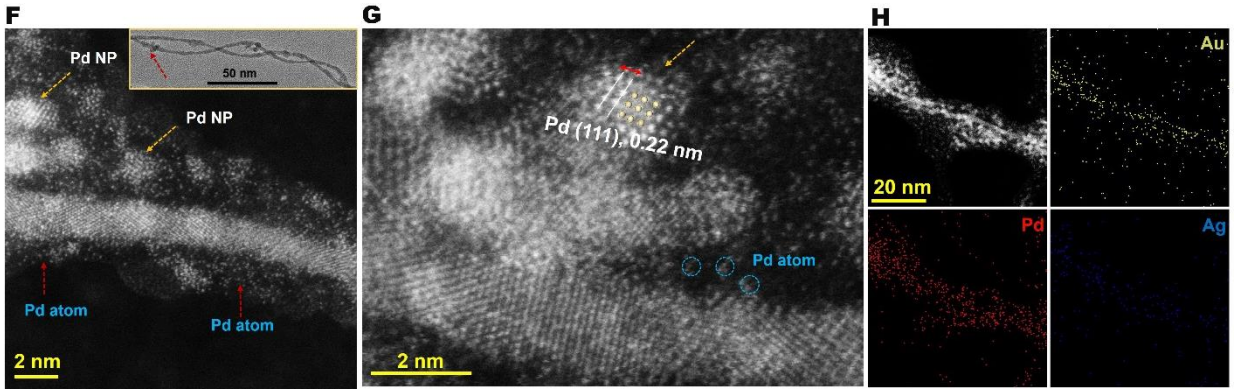

Figure 2. (F and G) STEM image of the Pd coated chiral AuAg NWs in atomic resolution showing both Pd atom deposition (red arrow) and Pd nanoparticle coalescence (yellow arrow) in Pd<111> direction on AuAg seed nanowire captured by cryogenic STEM after 1 min growth in colloid. (H) EDX maps confirm the Pd element deposition on the seed nanowire correspondingly as in figure F.

It is note that: to Figure 1B, it is challenge to get in-situ EDX maps due to Beam-Sample Interaction in Liquid Environment, Limited Signal from Thin Samples. Given these challenges, it is technically impractical to obtain fully consistent EDX mappings of the same sample during in situ liquid-phase HRTEM experiments. As an alternative, we used cryo-EM to freeze intermediate samples and perform EDX measurements under more stable and controlled conditions, providing reliable elemental analysis to address the reviewer's concerns.

Comment 5: Fig. 1c: Rather than deposition this seems to be more like dissolution due to the electron beam. In the very first frame there is a number of particles visible that gradually disappear over time. At the same time the wires appear to get slightly thinner. How can this be described as deposition? There is clearly less material (in a solid state) there than before. Also, the red circles obfuscate the images (in the video it is much clearer). The corresponding Figure S6 shows a few more frames from the same experiment, however the caption must be wrong as it talks about lattice ‘stripes’ and coloring which are clearly not visible in this magnification.

Response 5: We sincerely thank the reviewer for raising this critical question. In response, we conducted additional experiments and obtained new data to support our conclusion: during the Pd deposition process, both heterogeneous nucleation leading to atomic layer deposition and self-nucleation followed by nanoparticle attachment were observed (Figure 1C, and Figure S7, Movie S3). Furthermore, subsequent atomic-scale SREM image analysis revealed that this deposition behavior also occurs during Pt deposition (Figure S18). The corresponding discussion has been incorporated into the revised manuscript (Line 147-154 in the revised manuscript).

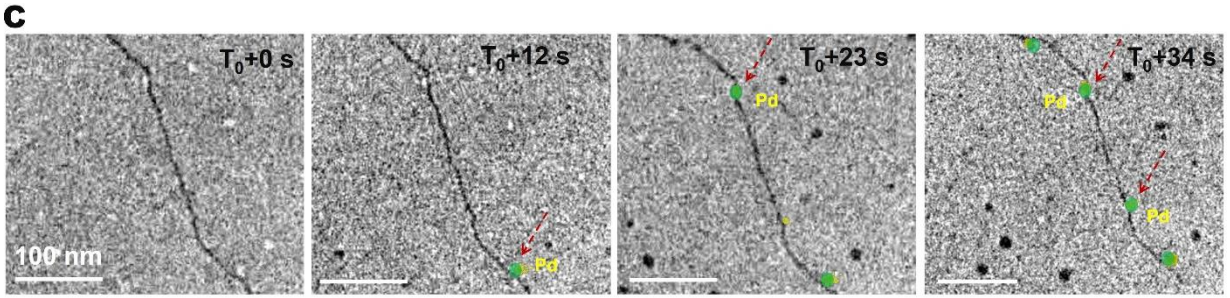

Figure 1. (C) Snapshot image depicts the dynamic process of Pd nanoparticle deposition directly on a AuAg NW in colloids: the greenred circle highlights some attached Pd nanoparticles on AuAg seed nanowire followed by covalence whose positions are labelled by red arrows.

Comment 6: Regarding the EDX map in supplementary figure S8. First of all, the authors did not state whether they show raw counts or quantified the results. Secondly, the authors need to show a raw spectrum to confirm that the Pd peak is actually there. Otherwise this could just be noise.

Response 6: We appreciate the reviewer's feedback regarding the EDX map in Supplementary Figure S8. To address the concerns: i) We have provided the corresponding EDX spectrum in the revised supplementary material to confirm the presence of the Pd peak, ensuring that it is not noise but a true signal from the sample (Figure S8-9). ii) We confirm that the EDX color maps shown in Supplementary Figure S8 represent raw data without further processing or quantification. This has now been explicitly stated in the revised figure caption for clarity. iii) To further strengthen our findings, we have performed similar characterizations for other metal elements in related deposition experiments. For these cases, we also provide corresponding EDX spectra to validate the presence of the elements (Figure S16-17, S27-28), demonstrating the reliability of our approach. The corresponding discussion has been incorporated into the revised manuscript (Line 355-367 in supporting information).

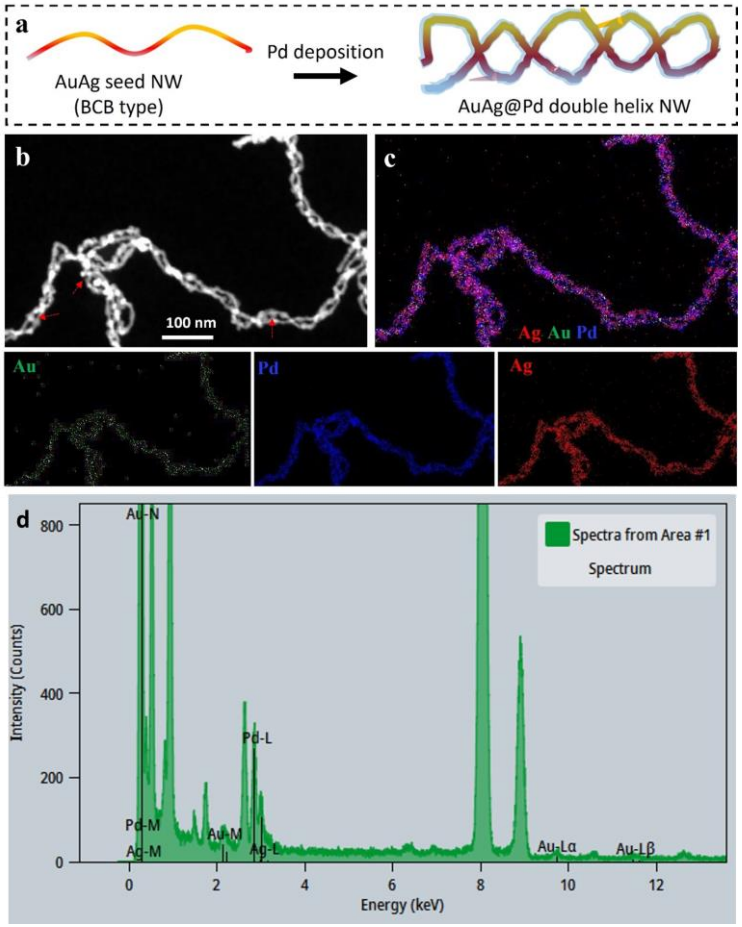
a
AuAg seed NW
(BCB type)
Pd deposition
AuAg@Pd double helix NW
b
100 nm
c
Ag Au Pd
Au
Pd
Ag
d
Au-N
Pd-L
Pd-M
Au-M
Ag-M
Ag-L
Au-Lα
Au-Lβ
Spectra from Area #1
Spectrum
Intensity (Counts)
Energy (keV)
0
200
400
600
800
0
2
4
6
8
10
12

Figure S8-9. Characterization of AuAg BCB@Pd double helical nanowire. (a) Schematics showing the experiment of Pd deposition on AuAg BCB seed nanowire giving a double helical nanowire. (b) STEM image (red arrow: Pd nanoparticle attachment on nanowire) and (c) raw EDX color maps showing the elemental presence within the nanowire domain. (e) the corresponding EDX spectrum of sample in a. This sample is similar as shown in Figure 1D.

Comment 7: Fig. 1d: Nice schematic. Unfortunately, it is not supported at all by the findings presented so far. Neither are there helical wires (which I believe is not the same as a chiral wire) nor is there any evidence for the presented growth mechanism. So far, the authors have simply presented one instance in which wires get slightly thicker and one in which wires get slightly thinner. Later on, the authors present more convincing results and in the supplementary there are plenty of examples of helixal wires, but at this point I just have to wonder why Figure 1 was put together this way.

Response 7: We thank the reviewer for their constructive feedback regarding Figure 1d and the associated interpretation. We have carefully considered the concerns and made the following revisions and adjustments in the revised manuscript:

1). We have redesigned the Figure 1 and adjusted the corresponding text to better align with the experimental findings presented in the manuscript. The revised Figure 1 now reflects the key observations more accurately and avoids overgeneralizations at this stage of the discussion. (Line 683-700 in the revised manuscript)

2). In the revised manuscript, we explicitly highlight that Pd deposition on the chiral seed nanowires occurs through multiple mechanisms, including (i) direct deposition at the atomic scale, originating from heterogeneous nucleation; and (ii) nanoparticle (NP)-level attachment, originating from self-nucleation. This distinction is now clearly stated and supported by experimental evidence presented later in the manuscript. (Line 159-171 in the revised manuscript)

3). We have acknowledged the limitations and open questions in the proposed hypothesis, such as the potential influence of the electron beam, whether the observed phenomena are isolated cases, and the role of deposition kinetics. These issues are now explicitly discussed in the revised text to provide a balanced and critical perspective. (Line172-180 in the revised manuscript)

4). To address the concern about whether NP coalescence is an isolated phenomenon, we have designed and performed additional experiments. These experiments demonstrate that NP coalescence is not a rare occurrence but is influenced by several factors, such as the type of metal, the strength of the reducing

agent, and other experimental conditions. These findings are now included in the revised manuscript and supplementary materials to provide a more comprehensive understanding of the process. (Line number 298-312 manuscript)

Comment 8: Figures S11 and S18: To show the elemental distribution 'within' a core shell structure you would need to construct a linescan perpendicular to the wire. Currently these figures serve no purpose.

Response 8: We thanks for the reviewer's good suggestion. A line scan for AuAg@Ag has been conducted to confirm the coating process forming core-shell nanowire (Figure S28). The corresponding discussion has been incorporated into the revised manuscript (Line 520-524 in supporting information).

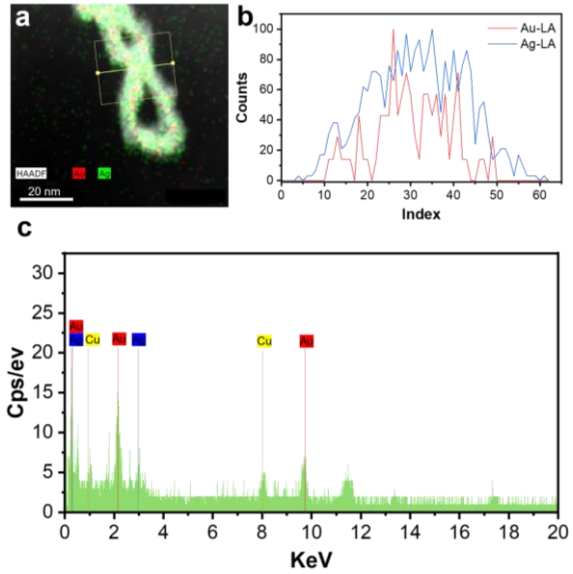

Figure S28. (a) EDX color map, and (b) EDX line scan of AuAg@Ag double helix nanowire. (c) EDX spectrum of AuAg@Fe double helix nanowire as shown in Figure 3I, which confirms the presence of Au, Ag elements. Note: product of Ag deposition on chiral AuAg seed nanowire.

Comment 9: Figure 2 D&H. Measuring the lattice spacing in high resolution is an extremely unreliable way of distinguishing between metals that are so similar in structure (as noted by the authors the 111 plane distance is 0.22, 0.23 and 0.24 nm for Pd,Pt and Au). EDX would offer a clear and straightforward proof.

Response 9: We thanks for the reviewer's good suggestion. EDX maps and spectra of different samples including AuAg@Pd (Figure 2F-H), AuAg@Pt (Figure S16-17), AuAg@Cu (Figure S33-34), AuAg@Ni, and AuAg@Ag, help us to confirm the metal attachment and coalescence. The corresponding discussion has been incorporated into the revised manuscript (Line 313-320 in the revised manuscript).

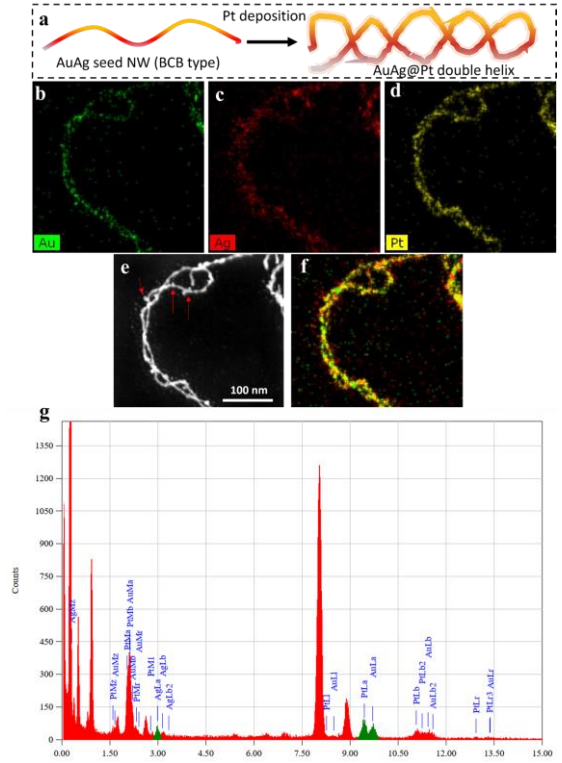

Figure S16. Characterization of AuAg BCB@Pt double helical nanowire. (a) Schematics showing the experiment of Pt deposition on AuAg BCB seed nanowire giving a double helical nanowire. (b-f) EDX color maps showing the elemental presence within the nanowire domain to confirm the double helical formation (red arrow: Pt nanoparticle attachment on the nanowire). (g) EDX spectra of the sample shown in a-f. Note: the STEM image in e showing the nanoparticles attached on the nanowire surface which is highlighted in red arrow.

Comment 10: How can the authors claim to see Ostwald ripening? All they show is that one particle in a particle agglomerate shrinks which is hardly surprising to see in a liquid cell TEM.

Response 10: We appreciate the reviewer's insightful comment regarding the need for a more detailed explanation of Ostwald ripening in Figure 4e (Figure 5A in the revised manuscript). To address this:

1). To ensure the reproducibility of our experiments, we conducted additional experiments under identical conditions. These new experiments provided more pronounced evidence of the Ostwald ripening phenomenon, further validating its occurrence and significance.

2). Ostwald ripening is observed as smaller Pd nanoparticles (NPs) dissolve and redeposit onto larger ones, driven by surface energy minimization. This process results in the formation of surface "knots," which reflect localized growth and restructuring on the nanowire surface, as shown in Figure 5A and Figure S41.

3) Additionally, we note that the metal type plays a critical role in Ostwald ripening due to differences in surface energy and atomic mobility. For Pd on the AuAg nanowire surface, the high atomic diffusivity and surface energy compatibility facilitate the observed ripening and restructuring behavior.

The relative discussion could be found in the revised manuscript, which is copied as the follow:

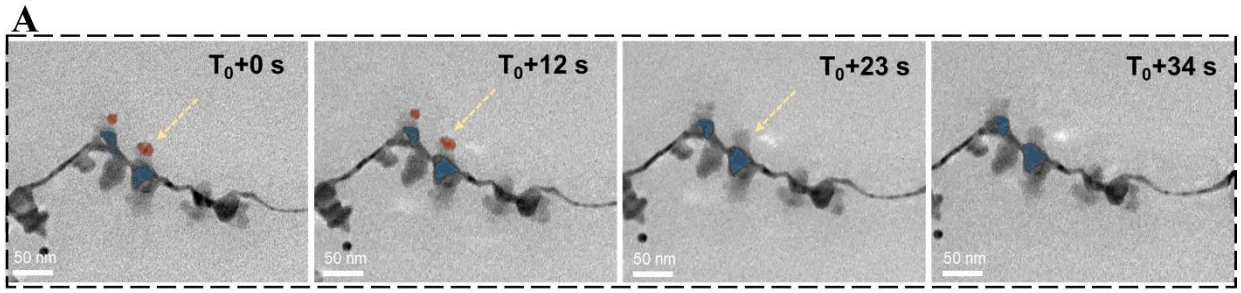

Figure 5. (A) The snapshot image illustrates the LPTEM observation of Ostwald ripening among attached Pd nanoparticles highlighted in red and blue color. The yellow arrow shows the position of the Ostwald ripening which gives a surface with lots of knots as an evidence of nanoparticle attachment.

These findings indicate that the growth mechanism of metal core-shell nanowires during colloidal synthesis is a complex competitive process involving three key steps: heterogeneous nucleation, homogeneous nucleation, and nanoparticle attachment & coalescence. Additionally, this process encompasses phase coalescence and Ostwald ripening. Figure 5A illustrates the Ostwald ripening observed via LPTEM, which contributes significantly to variations in the nanowire morphology highlighted in red and blue color, surface characteristics, and size highlighted by yellow arrow due to the dissolve and redeposition (Figure S41, Movie S8). This ripening process leads to the formation of surface "knots," representing localized growth and restructuring on the nanowire. However, Oswald ripening was not observed in transition metals deposition experiments even we tried lots of times. It seems that the metal type significantly influences Ostwald ripening due to differences in surface energy and atomic mobility. Noble metals like Au, Ag, and Pd exhibit pronounced ripening due to higher atomic diffusivity and surface energy compatibility. In contrast, transition metals like Fe, Ni, Cu, and Ru show limited ripening due to lower diffusivity and surface energy mismatch.

Following are detailed responses to the reviewers' comments:

It is noticed that changes to the manuscript and supplementary information are highlighted in yellow.

To Reviewer #3:

The authors have prepared extensive discussion and additional data, which address some of the comments I had raised regarding the manuscript. However, there are still some remaining and new questions emerging:

Comment 1: The authors claim that Fe, Ni, Cu, and Ru can be deposited onto AuAg nanowires using ascorbic acid at room temperature. However, all these metals are hard to be reduced, and their typical synthetic methods usually require high temperatures. Can authors double-check the valence of these metals in the shell, e.g., using XPS? I suspect the shell might not be metallic Fe, Ni, Cu, or Ru.

Response 1: We appreciate the reviewer's insightful comment regarding the valence states of these metals. To address this concern, we designed the following experiments:

i) Reduction feasibility studies:

Different types of reducing agents were applied in the core-shell nanowire synthesis at room temperature as well as 55˚C. For example, both FeSO4, and CuSO4 could be reduced by different types of reducing agents (L-ascorbic acid, $NaBH_4$) to giving double helical core-shell nanowires as shown in figure 1 (for review only). Also, we did the literature & text book survey to study the possibility of this redox reaction. It could be explained as the followings: 1) Ascorbic acid ($C_6H_8O_6$) can lose electrons and become oxidized to dehydroascorbic acid ($C_6H_6O_6$). This oxidation process is coupled with the reduction of metal ions.2) the standard reduction potential for the half-reaction involving Cu^{2+} is +0.34 V, while for Fe^{2+} it is -0.44 V. 3) The ability of ascorbic acid to reduce Fe^{2+} and Cu^{2+} ions is rooted in its capacity to donate electrons (reduce) while undergoing oxidation itself. The favorable thermodynamics of the reactions, as indicated by the standard reduction potentials, provide a driving force for these transformations (*Green Chem.*,

2011,13, 900; *Chem. Eng. J*., 2020,388, 124321). Ascorbic acid can also participate in redox reactions with nickel(II) nitrate and ruthenium(III) nitrate, but the specifics of the reactions depend on the oxidation states and the standard reduction potentials of the metal ions involved. We also did the control experiments to test different types of reducing agent and different temperatures (Fig. S45, Table S5), and the results are similar as using noble metals.

FIG 1 REDACTED

Figure 1 for review only: AuAg@Fe and AuAg@Cu double helix nanowire collected by using different types of reducing agents to reduce sulfate.

ii) XPS Characterization:

We did XPS characterization for three samples (AuAg@Cu, AuAg@Fe, AuAg@Ni) as suggested by the reviewer. As shown in figure 2 (for review only), The XPS spectrum shows that Cu, Fe, and Ni on the surface of the nanowires may exist as oxides. This could be due to two reasons: first, they may not have been fully reduced to their elemental forms; second, the sample may have been oxidized on its surface while exposed to air. The XPS spectra of these samples have been inserted in the revised supplementary materials (Fig.S39)

FIG 2 REDACTED

Figure 2 for review only: The XPS spectra data for Fe, Cu, and Ni were collected from the AuAg@Fe, AuAg@Cu, and AuAg@Ni double helix nanowires, respectively.

The relative clarification has been made in the revised manuscript, which is copied here (Line 349-353 in main text): These findings suggest that the redox reaction rate in the solution plays a significant role in determining the mechanism of Pd deposition. Taking into account parameters such as the yield of nanowires and the valence state of reduced metal products, environmental factors in the reaction solution, including pH (Table S4), reactant concentration, reducing agent concentration, and temperature (Table S5), may all influence the yield of core-shell nanowires.

Comment 2: For the formation of double-helical morphology, the author mentioned that "this phenomenon is attributed to the strong internal strain within the chiral seed nanowires, which originates from the intrinsic chirality of the as-synthesized AuAg alloy nanowires". (1) The phenomenon is induced by chirality of AuAg nanowires, which originates from their internal strain? I assume the authors want to explain coating of shell increases the internal strain of the nanowire, leading to larger extent of chirality and thus higher possibility of forming double-helical structures? (2) In Figure 5, please provide strain range (in %) and label/explain x and y direction in the image/caption. (3) In Figure 5, if the authors want to claim the additional strain from Au deposition induces double-helical structure, they need to compare the strain in Au-coated and pristine AuAg nanowires.

Response 2: We thank the reviewer for their constructive feedback, which significantly improved our mechanistic explanation. The explanation is listed as the followings: 1) Yes, we are sorry for the confusion of the previous description. The deposition of the second layer on the seed nanowire leads to the increase of the internal strain of the nanowire, which is also concluded from relative literature (*J. Am. Chem. Soc.*, 2011, 133(50), 20060-20063). We have made the corrections in the revised manuscript. 2) We have made the clarification in the revised manuscript as well as the image/caption. 3) We appreciate the reviewer's suggestion and have analyzed the stress evolution within pristine BCC AuAg seed nanowires and after the deposition of a single layer of gold atoms through

MD simulation (Fig. 5H-I and Fig. S50). The results reveal that the number of high-stress atoms significantly increases when the nanowire incorporates different metal layers. However, our simulation focuses on the cases after a monolayer of Au atoms is deposited, as the stress evolution between the initial deposition of atomic layers and the final complete deformation into a double-helix structure becomes far more complex. Additionally, due to the unique three-dimensional configuration of the double-helix structure, it is challenging to quantitatively analyze the stress evolution throughout the entire process using characterization techniques. To ensure our description is more objective, the revised manuscript is as follows (Line401-407): This strain arises from the packing of interpenetrated icosahedral or decahedral units in the BCB seed nanowires (Figure S47). The molecular dynamic simulation results (Figure 5H-I, Table S6-7) show that the stress within the nanowire increases as gold atoms are deposited on the outer layer. Specifically, depositing one layer of gold atoms causes the number of high-strain region atoms within the nanowire to increase by approximately 30% (Figure S50). This observation aligns with the experimental findings of stress within the nanowire and is consistent with previous literature[61].

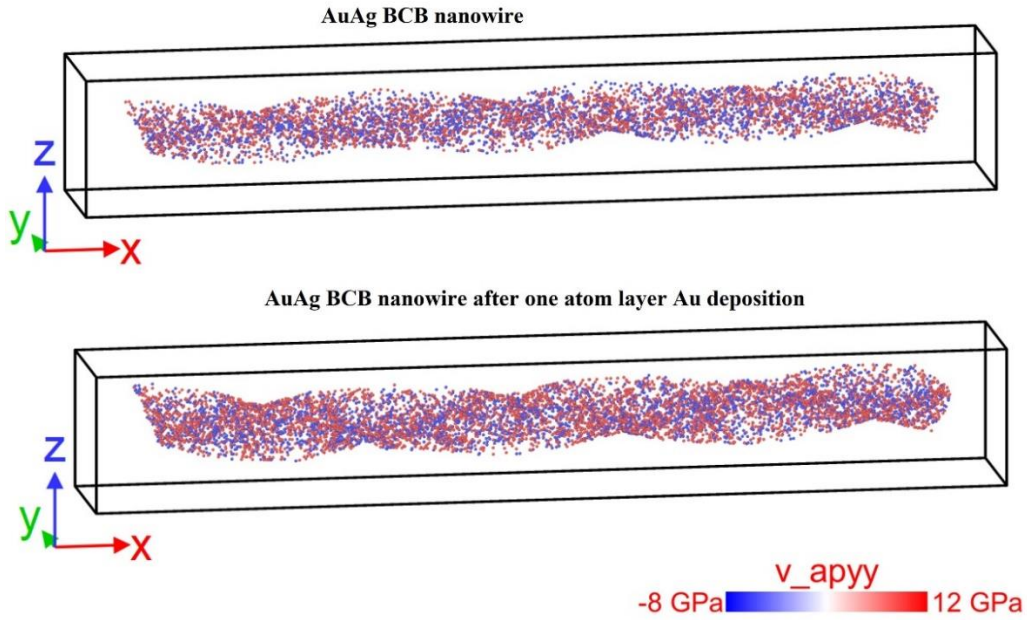

Figure S50. The color map represents a strain distribution in ε_{yy} direction map obtained from MD simulation of the pristine AuAg BCB nanowire and the one after one atom layer Au deposition, which showing higher strain within the nanowire due to Au atom deposition.

Comment 3: For the accuracy of reconstruction, the authors provided R-factor and claimed the consistency between experimental projection images and the corresponding projections of the reconstructed 3D model. There are two questions here: (1) The R-factor is calculated based on the nanowire shown in Figure S39, where the reconstruction seems not to be at atomic resolution. How about those shown in Figure 3, which are claimed to be atomic resolution? (2) The

tilting angle for reconstructions in Figure 3 should be provided. (3) For reconstruction, missing wedge effect actually contributes a lot to the error, which cannot be reflected by consistency in projection images. I would suggest authors find another way to verify their accuracy, such as creating a model with a similar wire-like shape and comparing the model with its reconstruction from the same tilting angles

Response 3: We appreciate the reviewer's rigorous scrutiny of our reconstruction methodology. In the revision, we have made clarifications for the atomic resolution electron tomography: 1) We have calculated the R-factor for atomic-scale 3D reconstructions and found that their overall accuracy is significantly lower compared to nanoscale reconstructions (Fig. S27). Furthermore, the precision of AuAg@Pd reconstructions is notably lower than that of AuAg@Au. This discrepancy may arise from the higher surface roughness reflected in atomic-scale 3D reconstructions compared to nanoscale ones, which also indicates that the surface roughness decreases upon Au coating compared to Pd coating. 2) We have included the tilting angles in the figure captions of the revised manuscript, despite their presence in the original supplementary information. 3) We agree with your observation that the R-factor does not fully capture the reconstruction quality, particularly concerning the missing wedge effect. Regrettably, we currently lack the capability for modeling atomic-scale structures, and therefore, we did not pursue this avenue. To ensure a more objective discussion, we have made the following revisions: first, we addressed the limitations of the R-factor in reflecting reconstruction precision, and second, we acknowledged the potential influence of the missing wedge effect in our atomic-scale 3D reconstructions. Additionally, we referenced relevant literature (Ref.51 in main text) to illustrate that such effects can be modeled and validated.

The relative discussion in the revised manuscript is copied as the follow (Line 258-261): It is notably that the missing wadge effect could lead to some errors in the 3D reconstruction which could be corrected via some published method even though the r-factor (Figure S27) showing the accuracy of the 3D tmography[51].

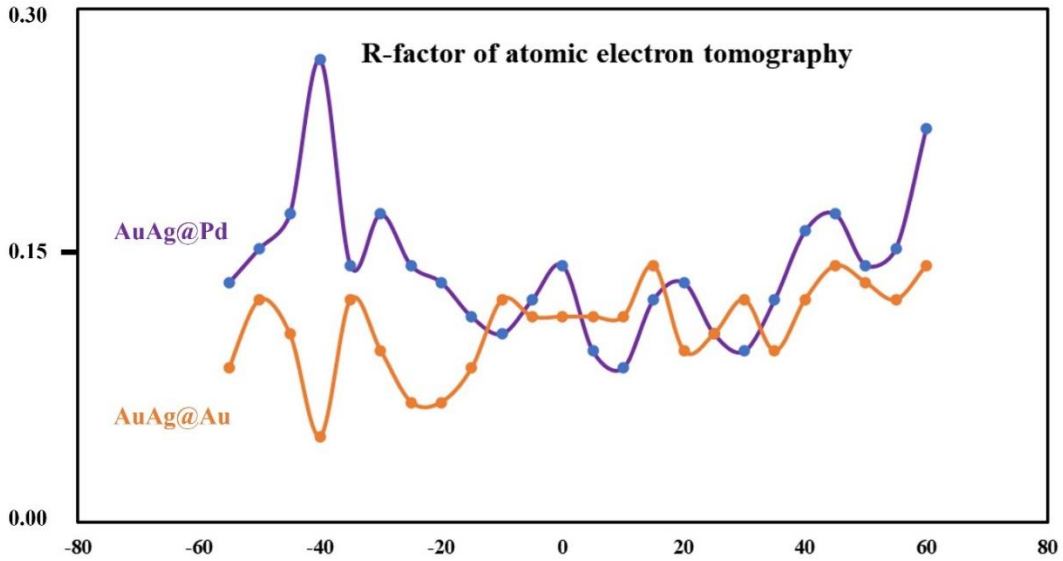

Figure S27 R-factor of the atomic resolution electron tomography of double helical nanowires as shown in Fig. 3C and Fig. 3F

Comment 4: The authors mentioned that "we utilize low-dose LPTEM imaging to investigate the shaping process of core-shell nanowire crystals during seed-induced growth without the presence of any organic ligands". However, based on experimental section, both PVP and DMF were used during synthesis (also confirmed by XPS), which can serve as capping agents blocking certain facets of Ag, Au, or even AuAg nanowires. This could affect the deposition of atoms and the final shape of the nanocrystals. I would suggest either removing this claim or explain whether PVP and DMF will induce surface capping or not.

Response 4: We thank the reviewer for highlighting the importance of the ligand effects. To clarify, we have conducted centrifugation treatments, leaving minimal ligands in the solution. For noble metals, ligand influence on deposition is possible, but PVP and DMF as ligands are unlikely to affect other transition metals or their influence differs. Nevertheless, our experimental results show no significant difference in the morphology of the products. Of course, we cannot rule out the assumptions suggested by the reviewers. Therefore, we have revised our manuscript (Line 92-96): In this study, we employ low-dose LPTEM imaging to investigate the shaping process of core-shell nanowire crystals during seed-induced growth, without the addition of any organic ligands in solution. Notably, the seed nanowires undergo multiple centrifugation and washing steps, which likely reduce the number of ligands on their surfaces. Additionally, no extra ligands or organic solvents are introduced during the reaction process.

Comment 5: In line 280-282, the authors claim "the ⟨ 111⟩ surface of noble metals has the lowest surface energy, prompting nanoparticles and nanowires to come into contact and fuse along this plane to minimize the overall free energy of the system". (1) <111> usually refers to direction instead of surface. (2) If {111} gives the lowest surface energy, then this surface should be more exposed instead of being covered/fused? (3) Will potential PVP and DMF binding to nanowire surface affect the direction of fusion?

Response 5: We appreciate the reviewer's precision in crystal notation and mechanistic reasoning. In response to the reviewer's comments, we have made several key modifications and discussions to enhance the clarity and robustness of our study:1) We have corrected the crystal face notation in our manuscript to ensure precision and avoid confusion. This adjustment is crucial for maintaining clarity in scientific communication. 2) . 3) Our experiments (Au, Pd, Cu, Fe, Ni deposition) currently do not clearly demonstrate the effects of ligands, as the ligand content in solution is relatively low. We acknowledge this limitation and suggest that future experiments with different ligands could provide clearer insights into their influence on the deposition process. The relative discussion has been inserted in the revised manuscript (Line 92-96 and Line 294-296): Finally, perhaps an interesting future research direction could involve studying how different types of organic ligands influence the deposition of an outer metal layer on nanowires and the direction of grain boundary fusion.

Comment 6: The authors propose a three-step deposition process – heterogeneous nucleation, nanoparticle attachment, and coalescence – as a generalized mechanism for metal deposition on nanowires. Though authors explored different metals and varying amounts of reducing agents, (1) imaging evidence is only provided for Pd and Au deposition; (2) there are a lot more parameters that can be tuned, like even higher temperatures and milder reducing agents, which may lead to missing/reversing order of certain steps. I suggest the authors describe their findings as a potential deposition mechanism, rather than a generalized mechanism.

Response 6: We thank the reviewer for emphasizing the need for cautious terminology. In response to the reviewer's suggestion, we have supplemented experiments on transition metals, such as Ni, revealing similar phenomena (Fig. S45 and Fig. 3 for review only). Additionally, experiments under different temperature and reducing agents have been conducted (Table S5). Our results suggest that the conclusions hold certain generality, but as a precaution, we have adopted your suggestion to revise "generality" to "hypothesis" and "potential mechanism" for a more cautious description.

FIG 3 REDACTED

Figure 3 for review only: the snapshot image illustrates the LPTEM observation of Ni nanoparticle coalescence with nanowire locally when $Ni(NO_3)_2$ was reduced by $NaBH_4$.

Comment 7: In line 225, the author mentioned that "the number of attached Au nanoparticles is significantly smaller", but it is hard to get this conclusion from Figure 2. Also, in Figure 2, it is better to label the images of AuAg@Pd and AuAg@Au, making the figure clearer to audience.

Response 7: We thank the reviewer for the good suggestion to improve the quality of our manuscript and we are sorry for the confusion in precious manuscript. We inserted the labels in the figure2. Also, the sentence has been modified from "the number of attached Au nanoparticles is significantly smaller" to "the number of attached Au nanoparticles is significantly decreased compared Pd deposition case".

Comment 8: In lines 338-339, how is the conclusion "while the pH value of the solution is not so crucial" obtained?

Response 8: We agree with the reviewer's concern that pH plays a significant role, hence we measured pH in reactions using various reducing agents, observing a broad range from 2.61 to 10.81 as shown below (Table S4), yet consistently obtained core-shell nanowires with similar morphologies. Despite this, we have refined our description, acknowledging that XPS results indicate different reducing agents and pH levels lead to varied reduction states and metallic valences, suggesting differing redox mechanisms. However, we did not account for yield variations in our analysis. Consequently, the relative discussion has been inserted in the revised manuscript (Line 348-352): These findings suggest that the redox reaction rate in the solution plays a significant role in determining the mechanism of Pd deposition. Taking into account parameters such as the yield of nanowires and the valence state of reduced metal products, environmental factors in the reaction solution, including pH (Table S4), reactant concentration, reducing agent concentration, and temperature (Table S5), may all influence the yield of core-shell nanowires.

Table S4. Measured pH values for reactions of $HAuCl_4$ and AuAg nanowires with different reducing agents: AA, $NaBH_4$, $N_2H_4 \cdot H_2O$.

Reducer	Test No. 1	Test No. 2	Test No. 3	Mean
AA (pH)	2.61	2.63	2.60	2.61
$NaBH_4$ (pH)	8.73	8.62	8.61	8.65
$N_2H_4 \cdot H_2O$ (pH)	10.22	10.14	10.18	10.18

Comment 9: In line 257, “Figure 3D and 3F” should be “3C and 3E”? The authors should double-check all the figure numbers in the manuscript.

Response 9: Figure 3C and Figure 3D are the same sample (AuAg@Pd) while Figure 3E represents sample AuAg@Au. We also double-checked all the figure numbers in the manuscript to make it accurate.

Comment 10: For the diameters provided in the manuscript, standard errors should be provided to further verify the diameter increase and reliability of the conclusion.

Response 10: The standard errors have been calculated and inserted in the revised supplementary information table and being clarified.

Comment 11: The abbreviation “NW” is not defined in the manuscript, and “NW” and “nanowires” are used randomly. Similar for “double-helix” and “double-helical” nanowire. Please double check the abbreviations and words and make sure they are consistent throughout the paper.

Response 11: We have modified the manuscript to make the names and abbreviations consistent in the revised manuscript, which is highlighted in yellow color by using “nanowires” and “double-helical” in the whole revised manuscript.

合肥工業大學
HEFEI UNIVERSITY OF TECHNOLOGY

Following are detailed responses to the reviewers' comments:

It is noticed that changes to the manuscript and supplementary information are highlighted in yellow.

To Reviewer #3:

Comment 1: I still recommend that the authors double-check the strain range in Figure 5, as ±45% or ±30% strain in nanocrystals is highly uncommon. Other than that, the authors have addressed all my comments.

Response 1: We appreciate the reviewer's insightful comment regarding the strain analysis, which is important for us to be accurate on data analysis. To address this concern, we double checked the analysis with our collaborator, prof. Colin Ophus from Stanford University. The corrections have been made in the revised manuscript as shown in Figure 5D and E, showing the color bar with (±2.0%). The analysis code has been uploaded too.