

jz-2024-029984.R1

Name: Peer Review Information for "A Contactless Method for Measuring the Redox Potentials of Metal Nanoparticles"

First/Second/Third Round of Reviewer Comments

Reviewer: 1

Comments to the Author

A Contactless Method for Measuring the Redox Potentials of Metal Nanoparticles

In this article, the authors investigate/describes a novel contactless approach to measure the redox potential of gold nanoparticles, aimed at avoiding traditional electrode-based measurements that may alter the nanoparticles' intrinsic electrochemical properties.

I consider the paper very well-presented and the work well accomplished with some specific test on this system under study such SPR and related electrochemical testing. Also, the issue under study in the paper match well with the journal scope.

Here are some critical points regarding its strengths and areas for improvement:

1. Please state on text what does the arrow in figure 1d mean.
2. The study focuses solely on gold nanoparticles (the title stated metallic , what means limited scope hindering the applicability to other nanoparticles otherwise. The later have no even stated , inferred or included in a little outlook section. Including other metals like silver or platinum would demonstrate the broader applicability of this method.
3. I think the outlook section aimed to unveil further works is important in this study as this work apparently suppose a breakthrough to measure redox potential for nanoparticles. In this case you will have to include the suitability use of the method for nonmetallic NP such ZnO.

4. Since zeta potential influences both colloidal stability and the electronic structure at the particle surface, zeta potential values across different nanoparticle samples would introduce variability in redox potential measurements, complicating the assessment of size-dependent trends. Zeta potential maybe also related somehow to Ostwald ripening as mentioned by authors. Just include any remark that zeta potential could affect results. Also, in the same line, authors do take into account ligand interaction with the NP which do really affects E° .

Reviewer: 2

Comments to the Author

This manuscript describes a method to measure the redox properties of Au nanoparticles (NPs) of different size by combining the NPs with Fe^{3+} and CTAB and allowing the oxidation/reduction reaction (reduction of Fe^{3+} to Fe^{2+} and oxidation of Au NPs) to reach equilibrium. The spectroscopic measurement of Fe^{2+} and the known standard potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ allows them to measure the size-dependent standard potential of Au NPs. This is a very creative way to measure this interesting property in a "contactless" way, avoiding the effect of the electrode in determining these values, which is how it was done previously. The use of CTAB to ensure that Au oxidizes to $\text{Au}(\text{I})\text{Br}_2\text{:CTA}^+$ micelle complex and knowledge of the $K(\text{AuBr}_2^-)$ and $K(\text{AuBr}_2\text{:CTA}^+)$ allows the measurement of the Au/Au^+ standard reduction potential as a function of Au NP size. The calculated values are compared to Plieith theory and related to other experimental and theoretical considerations appropriately. This work provides a creative measurement approach and new physical insights about the size-dependent properties of metal NPs in solution that are important to the field and potential applications of NPs. I only found some minor considerations that the authors need to address prior to publication as described below:.

- 1). The following sentence is confusing: "If more or fewer particles are used at the beginning of the reaction, the equilibrium, equation (4) above, will shift to a new point, and $E^\circ(\text{Au}^+/\text{AuNP})$ will depend on the particle size at this new equilibrium."
- 2) The authors should explain the chemical assay in the main text better. The general method of analysis should be briefly mentioned instead of putting it fully in SI.
- 3) Did the authors measure the Fe^{2+} formed in a solution of Fe^{3+} , CTAC and CTAB to see how much forms due to other potential reducing agents in solution? This is important to show.
- 4) The B value and K_m only have 1 significant figure but the measured potentials have 3 significant figures, even though they depend on B and K_m . I think they report too many sig figs for standard potential and the error is greater than listed.
- 5) SI page 1: Should be " AuCl_4^- " instead of " AuCl_4 ".

6) SI: The synthesis should not just refer to another paper. Give at least a general description, such as stabilizer, reducing agent, and method of controlling size (seeded growth or stabilizer:AuCl₄-amount, for example).

7) Authors need to be clear in the main text that the concentrations were determined by the Fe phenanthroline detection method and all other concentrations were calculated assuming AuBr₂- as the 100% product. Any other assumptions should be noted and it should be made clear that UV-vis of the Au NPs was not used for analysis but only to determine when the reaction reached equilibrium.

8) A list of assumptions are needed and a table is needed to give all the solution conditions and final concentrations to make it clearer. When CTAC or other changes are made, then that should be listed in the table. This could be put in SI.

9) Do CTA+/Electrode interactions that are not present in solution affect the measurement on electrodes in a different way than what happens in solution? Is there a strong effect on the kinetics of the reaction with varying CTA+ concentration?

10) I don't believe that HRTEM has the resolution to distinguish 0.283 nm distance from 0.288 nm distance? What is the uncertainty in the 0.283 nm value? Also, normally when lattice contraction occurs, it occurs more significantly at the surface atoms as compared to the interior layers, so it may not be uniform throughout the entire NPs.

Author's Response to Peer Review Comments:

We would like to thank all reviewers for their fruitful comments which helped to improve our manuscript greatly. In the attached document below, all reviewers' comments are copied below without any omission, and our point-by-point responses are colored in blue. Accordingly, we have attached the clean version of the revised manuscript and the annotated version with track change.

We would like to thank all reviewers for their fruitful comments which helped to improve our manuscript greatly. In this document, all reviewers' comments are copied below without any omission, and our point-by-point responses are colored in blue. Accordingly, we have attached the clean version of the revised manuscript and the annotated version with track change.

Reviewer 1

In this article, the authors investigate/describes a novel contactless approach to measure the redox potential of gold nanoparticles, aimed at avoiding traditional electrode-based measurements that may alter the nanoparticles' intrinsic electrochemical properties.

I consider the paper very well-presented and the work well accomplished with some specific test on this system under study such SPR and related electrochemical testing. Also, the issue under study in the paper match well with the journal scope.

Here are some critical points regarding its strengths and areas for improvement:

1. Please state on text what does the arrow in figure 1d mean.

Authors' response: The caption in Figure 1d was modified as follows:

“(d) and (e) Time-lapsed UV-Vis spectra (arrow indicates the reaction progress) and kinetic trace at plasmon resonance of a typical reaction between 10.9 nm nanoparticles and Fe^{3+} .”

2. The study focuses solely on gold nanoparticles (the title stated metallic, what means limited scope hindering the applicability to other nanoparticles otherwise. The later have no even stated, inferred or included in a little outlook section. Including other metals like silver or platinum would demonstrate the broader applicability of this method.

Authors' response: The below sentences were added in the conclusion (page 4) to highlight that our method should not be limited to only gold nanoparticles.

“Furthermore, this method can be adapted to other nanoparticles as long as a redox reaction between the particles and a redox couple in solution is established, and the Nernst equation can be applied at reaction equilibrium to determine the standard reduction potentials of the nanoparticles”.

3. I think the outlook section aimed to unveil further works is important in this study as this work apparently suppose a breakthrough to measure redox potential for nanoparticles. In this case you will have to include the suitability use of the method for nonmetallic NP such ZnO.

Authors' response: As addressed in comment #2, the current method is applicable to other nanoparticles, including metal oxide nanoparticles, as long as a redox reaction between the nanoparticles and a probed redox couple reaches equilibrium.

4. Since zeta potential influences both colloidal stability and the electronic structure at the particle surface, zeta potential values across different nanoparticle samples would introduce variability in redox potential measurements, complicating the assessment of size-dependent trends. Zeta potential maybe also related somehow to Ostwald ripening as mentioned by authors. Just include any remark that zeta potential could affect results. Also, in the same line, authors do take into account ligand interaction with the NP which do really affects E°

Author's response: This is an interesting point to raise. It is reasonable to suspect that zeta potential might influence the chemistry at the nanoparticles' surface, potentially affecting our measured E° . However, we do not believe that zeta potential is directly related to E° . First, there is no strong evidence in literature suggesting that zeta potential depends on particle size, whereas E° does depend on size. Second, zeta potential is defined as the electrical potential at the slipping plane, which is relatively far from the active surface of the nanoparticles where the redox reaction occurs.

Reviewer: 2

Recommendation: This paper is publishable subject to minor revisions noted. Further review is not needed.

Comments:

This manuscript describes a method to measure the redox properties of Au nanoparticles (NPs) of different size by combining the NPs with Fe^{3+} and CTAB and allowing the oxidation/reduction reaction (reduction of Fe^{3+} to Fe^{2+} and oxidation of Au NPs) to reach equilibrium. The spectroscopic measurement of Fe^{2+} and the known standard potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ allows them to measure the size-dependent standard potential of Au NPs. This is a very creative way to measure this interesting property in a "contactless" way, avoiding the effect of the electrode in determining these values, which is how it

was done previously. The use of CTAB to ensure that Au oxidizes to Au(I)Br₂⁻:CTA⁺ micelle complex and knowledge of the K(AuBr₂⁻) and K(AuBr₂⁻:CTA⁺) allows the measurement of the Au/Au⁺ standard reduction potential as a function of Au NP size. The calculated values are compared to Pliech theory and related to other experimental and theoretical considerations appropriately. This work provides a creative measurement approach and new physical insights about the size-dependent properties of metal NPs in solution that are important to the field and potential applications of NPs. I only found some minor considerations that the authors need to address prior to publication as described below:

1. The following sentence is confusing: "If more or fewer particles are used at the beginning of the reaction, the equilibrium, equation (4) above, will shift to a new point, and E°(Au⁺/AuNP) will depend on the particle size at this new equilibrium."

Author's response: We improve such sentence in the manuscript as follows:

"In other words, changing the number of particles only influences the number of gold atoms oxidized per particle, resulting in a different particle size at the reaction equilibrium. Therefore, if the number of gold nanoparticles used at the beginning of the reaction is different, the equilibrium (as described by equation (4) above) will shift to a new point to reflect the new equilibrium size. Thus, E°_{Au⁺/AuNP} will also reflect the particle size at this new equilibrium, but not the number of particles."

2. The authors should explain the chemical assay in the main text better. The general method of analysis should be briefly mentioned instead of putting it fully in SI.

Author's response: The chemical assay was briefly introduced by adding the following sentences on page 3 of the main text.

"Briefly, the Fe²⁺ concentration can be quantified by chemical assay using the absorbance of the Fe(II)phenanthroline complex and a standard curve. The Fe²⁺ concentration was then used to determine the concentrations of Fe³⁺, CTA_{mic}AuBr₂, and Br⁻ at equilibrium. Furthermore, the extinction at the localized surface plasmon resonance of the gold nanoparticles was monitored to observe the reaction equilibrium but not necessarily to quantify the amount of elemental Au etched (see SI)."

3. Did the authors measure the Fe²⁺ formed in a solution of Fe³⁺, CTAC and CTAB to see how much forms due to other potential reducing agents in solution? This is important to show.

Author's response: This is a great comment. We performed this control and did not observe Fe²⁺ formed in the absence of gold nanoparticles. A section in the SI was added and the sentence "A control reaction in the absence of gold nanoparticles showed that no Fe²⁺ product formed" was added in the main text.

4. The B value and Km only have 1 significant figure but the measured potentials have 3 significant figures, even though they depend on β and Km. I think they report too many sig figs for standard potential and the error is greater than listed.

Author's response: As shown in Figure 2b, when we change Km from 5x10⁵ to 13x10⁵, E⁰ only changes from 1.82V to 1.84V. This indicates that the propagation of error in Km does not amplify the error in E⁰, due to the mathematical form of the Nernst equation. Moreover, the errors of E⁰ from multiple experimental runs are also quite small as compared to E⁰ itself.

5. SI page 1: Should be "AuCl₄⁻" instead of "AuCl₄".

Author's response: This error was corrected.

6. SI: The synthesis should not just refer to another paper. Give at least a general description, such as stabilizer, reducing agent, and method of controlling size (seeded growth or stabilizer:AuCl₄⁻ amount, for example).

Author's response: A few paragraphs were added in the SI describing the gold nanoparticle synthesis.

7. Authors need to be clear in the main text that the concentrations were determined by the Fe phenanthroline detection method and all other concentrations were calculated assuming AuBr₂⁻ as the 100% product. Any other assumptions should be noted and it should be made clear that UVvis of the Au NPs was not used for analysis but only to determine when the reaction reached equilibrium.

Author's response: This issue was clarified in the main text with the following sentences:

On page 2: "Note that UV-Vis spectroscopy was used to observe the reactions as they progressed to their equilibrium points (Figure 1 d&e, and Figure S2)."

On page 3: "Furthermore, the extinction at the localized surface plasmon resonance of the gold nanoparticles was monitored to observe the reaction equilibrium but not necessarily to quantify the amount of elemental Au etched (see SI)."

8. A list of assumptions are needed and a table is needed to give all the solution conditions and final concentrations to make it clearer. When CTAC or other changes are made, then that should be listed in the table. This could be put in SI.

Author's response: A table was constructed on page 5 of the SI with the volumes of the typical reaction conditions.

9. Do CTA⁺/Electrode interactions that are not present in solution affect the measurement on electrodes in a different way than what happens in solution? Is there a strong effect on the kinetics of the reaction with varying CTA⁺ concentration?

Author's response: We might expect CTA⁺/electrode interactions to influence the voltammetry measurements due to electrostatic effects. As previously reported by Zamborini and coworkers (*Langmuir* **2014**, *30*, 13075-13084), the electrostatic charge from the molecular linkers (i.e. ligands) used to support the metallic nanoparticles induced a variation in the interfacial potential distribution across the electrodes and nanoparticles interface. As a result, this change caused an observed shift in the oxidation peaks of the electrostatically deposited metallic nanoparticles. Considering CTAC and CTAB are surfactant and would behave similarly to linkers on an electrode surface, we may expect to see a shift in the oxidation potential in the CTA⁺-stabilized gold nanoparticles.

Regarding the second question, Figure 1f shows a sharp kinetic effect that is observed at the cmc of CTA⁺. This kinetic effect is solely caused by the formation of the micelles, which function to "solubilize" the Au complexes into solution.

10. I don't believe that HRTEM has the resolution to distinguish 0.283 nm distance from 0.288 nm distance? What is the uncertainty in the 0.283 nm value? Also, normally when lattice contraction occurs, it occurs more significantly at the surface atoms as compared to the interior layers, so it may not be uniform throughout the entire NPs.

Author's response: We added more details for our HRTEM measurement in the SI, and the reported value of 0.283 nm has the uncertainty of 0.005 nm (see the update in the SI), which is just enough to compare to the 0.288 nm value from the bulk gold.

We appreciate the comment on the possibility of non-uniformed lattice contraction. We now added this phase in the SI to address this comment: "Assuming the lattice contraction is uniform throughout the entire nanoparticle, the interatomic distance was then used to calculate the effective atomic volume...."

Additional Questions: Urgency:
High

Significance: High

Novelty: High

Scholarly Presentation: High

Is the paper likely to interest a substantial number of physical chemists, not just specialists working in the authors' area of research?: Yes