

First round of review

Reviewer: 1

Recommendation: *This paper is probably publishable, but should be reviewed again in revised form before it is accepted.*

Comments:

This manuscript presented the study of optical properties during UV irradiation and charge equilibration in dark via two core@shell nanoparticles. The mechanism of UV-induced changes in their plasmon resonance has been systematically investigated. I suggest its minor revision to publish in The Journal of Physical Chemistry:

Specific suggestions:

1. *The authors claimed the as-prepared core@shell nanoparticles were nearly monodisperse. However, one can see the standard deviation is up to 20%. On the other hand, after the coating of the TiO₂ shell, there were lots of free TiO₂ NPs in Figure 1b. Will the free TiO₂ NPs affect the following measurements? Can they be removed? Will the ligand hydroxypropyl cellulose detach from the surface during the UV irradiation?*

Author reply: We find that, compared to previous studies of charge equilibration in core@shell nanoparticles (see for example reference 21 in our manuscript), the core size distribution is nearly monodisperse and certainly sufficiently monodisperse to derive quantitative conclusions over the mechanism underlying the observed plasmon resonance shifts. If the reviewer disagrees, we are willing to edit the text according to his/her suggestion.

The TiO₂ nanoparticles can be partially removed by centrifugation. We refer to this in the main text where we write, *“The Ag@TiO₂ and Au@TiO₂ nanoparticles are finally centrifuged and redispersed in an ethanolic HPC solution to minimize water content and remove excess TiO₂ nanoparticles, which are a by-product of the sol-gel synthesis”*. Details of the centrifugation process are given in the Experimental section. To make it clear that the STEM images in Figure 1b correspond to the particles centrifuged and redispersed in an HPC aqueous solution we have edited the caption of Figure 1 and the sentence:

“(b) STEM images of (left) Ag@TiO₂ and (right) Au@TiO₂ nanoparticles [...].”

is now

“(b) STEM images of HPC-stabilized (left) Ag@TiO₂ and (right) Au@TiO₂ nanoparticles [...].”

The presence of remaining TiO₂ nanoparticles, however, does not significantly affect the following measurements, as LSPRs are exclusively sensitive to the immediate surrounding of the nanoparticles and therefore insensitive to the presence of other TiO₂ nanoparticles suspended in solution (see also our reply to the first comment of reviewer #2). This can be easily seen by comparing the UV-Vis spectra of Ag@TiO₂ nanoparticle suspensions before and after the centrifugation step (see figure below). The removal of a large fraction of TiO₂ nanoparticles strongly reduces the extinction in the spectral region of the TiO₂ bandgap (<300 nm), but it has no effect on the plasmon resonance of the core@shell nanoparticles.

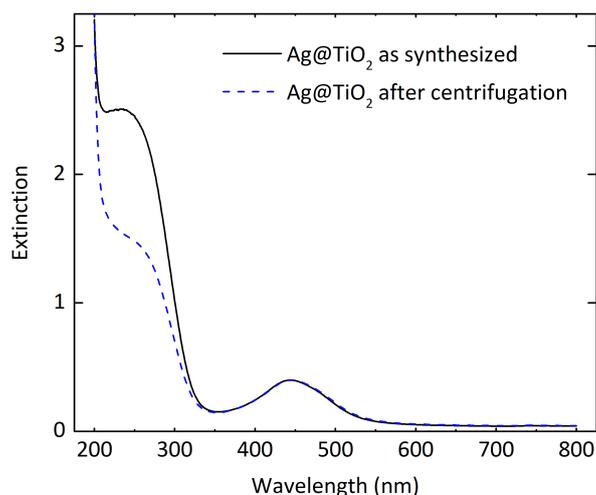


Figure 1. Extinction spectra of Ag@TiO₂ nanoparticle suspensions (*black solid line*) before and (*blue dashed line*) after centrifugation and redispersion in ethanol.

Finally, it is known that cellulose substrates are subject to polymerization in the presence of radicals, such as the ones produced by UV irradiation of oxygen (see for example [D. Roy et al., Cellulose modification by polymer grafting: a review, Chemical Society Reviews 38\(7\), 2046 \(2009\)](#)). In our study, however, we minimize the presence of oxygen and we observe reversible LSPR shifts over multiple cycles of UV irradiation and equilibration in the dark, indicating that the colloidal suspensions remain stable for the duration of the experiments. Interestingly (not shown in the manuscript), when irradiating with UV light at high HPC concentrations and in the presence of oxygen, we observed an irreversible red-shift of the LSPR and we speculated that this could have been due to aggregation of the core@shell nanoparticles as a consequence of oxygen radical-induced polymerization of HPC.

2. As the UV measurements were performed under the nitrogen purging, will the bubbling affect the accuracy of the result?

Author reply: It will not. The solution is initially purged for 20 minutes with the needle fully inserted into the solution, but during the UV irradiation experiments the needle is lifted above the liquid level to prevent the formation of bubbles.

3. How can air reduce Ag₂O as mentioned on Page 3 line 43 left column?

Author reply: This is a simple misunderstanding due to our unclear wording of the sentence on page 3, line 43. We of course do not claim that air reduces Ag₂O and we have modified the sentence from

“Another experimental evidence for the reduction of Ag₂O is the recovery of the initial LSPR peak position upon exposure to air at the end of the experiment (see Figure S3).”

to

“Another experimental evidence supporting the claim that the irreversible LSPR shift is due to the reduction of an interface Ag₂O layer, is the fact that the initial LSPR peak position can be recovered at the end of the experiment upon exposure of the solution to air (see Figure S3)”.

4. Other strategies to prepare well-defined nanomaterials via polymer as templates (Proc. Natl. Acad. Sci. U. S. A. 2018, 115, E1391; J. Am. Chem. Soc. 2017, 139, 12956; Small 2016, 12, 6714; Polym. Chem. 2015, 6, 5190; Energy Environ. Sci., 2017, 10, 402; Angew. Chem. Int. Ed. 2018, 57, 2046; J. Phys. Chem. B, 2016, 120, 4715) are suggested to be mentioned.

Author reply: Our manuscript focuses on the physical mechanism of charge equilibration in core@shell nanoparticles. We did not find any of the suggested synthetic papers necessary for our story and we therefore did not include the proposed citations.

Reviewer: 2

Recommendation: *This paper is probably publishable, but should be reviewed again in revised form before it is accepted.*

Comments:

This report provides insight into the nature of photocarrier generation in metal-TiO₂ core-shell heterostructure nanoparticles, based on spectroscopic analysis of the LSPR shift during UV photoexcitation. A primary conclusion is that all excited electrons reside in the oxide (or metal-oxide interface), with no injection into the metal core. The experimental method is thorough and the results are very well presented, so that I believe any researcher could reproduce the experiments. However, I think it would be inappropriate to publish the report at this time, based on some significant limitations in the data analysis and conclusions that are made. Moreover, the authors seem to have neglected the role of electrostatic interactions for influencing how electrons may be distributed non-uniformly in the nanoparticles when they are charged. In combination with ad hoc additions to the microscopic model used to interpret the results, such as swelling of the oxide layer in combination with interface chemical state filling, it seems that the presented model, while consistent with the observed data and plausible, still requires a few more checks before the conclusions of this study would be sufficiently convincing. Specific comments follow.

1) Figure 1B – *Based on the STEM images it seems that most of the colloidal particles contain no metal core. Is this an artifact of the imaging technique? Could all or most of the spectral changes observed during UV irradiation of the core-shell particles be explained as an increase of a large background (i.e. the photo-induced change of the pure TiO₂ colloid in Fig. 4a), if the authors assume an admixture of core-shell and pure TiO₂ particles at the same approximate ratio indicated in Fig 1b.*

Author reply: We would like to thank the reviewer for this very interesting point that deserves further discussion. So much so, that we have added a section in the Supporting Information to explain our reasoning (see the new section “Figure S10. Spectral effect of the presence of TiO₂ nanoparticles as by-products”). We also refer to this new SI section in the main text, where we included the following underlined sentence:

“As we have shown in Figures 3b and 3c, the UV-induced blueshift of the LSPR is always accompanied by an increase of the extinction maximum and a decrease of the FWHM. These effects cannot be due to the presence of pure TiO₂ nanoparticles as by-products in our core@shell nanoparticle suspensions (see Figure S10) and clearly indicate a reduced damping of the plasmon resonance as electrons are accumulated in the TiO₂ shell.”

To answer the first question of the reviewer, the presence of TiO₂ nanoparticles in the STEM images of Figure 1b is not an artifact, as in all our syntheses of core@shell nanoparticles the formation of pure TiO₂ nanoparticles of ~64 nm in diameter is a constant by-product (see also our reply to the first comment of reviewer #1).

It is interesting to calculate how much titanium dioxide is formed as pure TiO₂ nanoparticles and how much instead is condensed as a shell on our plasmonic cores. From the total amount of titanium precursor used, the Ag and Au nanoparticle concentrations and the average shell volume as measured by electron microscopy, we calculate that only 0.7% of the total amount of TiO₂ that is condensed in our sol-gel reactions is wrapped around our plasmonic cores. After the centrifugation and redispersion step, this percentage increases slightly to ~1.2% due to the partial removal of pure TiO₂ nanoparticles (see Figure 1 in the

reply to reviewer #1). We can therefore conclude that, even after purification of our core@shell nanoparticle suspensions, ~99% of the titanium dioxide present in solution is contained in pure TiO₂ nanoparticles and only ~1% in the shells of Ag@TiO₂ and Au@TiO₂ nanoparticles. It is therefore important to assess the influence of these TiO₂ nanoparticles on our extinction spectra. In order to do so, we focus on the changes of the extinction spectra of our suspensions before and after UV irradiation at 800 nm. At this wavelength, in fact, most of the extinction signal will be due to the scattering of light by the TiO₂ nanoparticles rather than to the LSPRs of Ag@TiO₂ ($\lambda \approx 446$ nm) and Au@TiO₂ ($\lambda \approx 550$ nm) or the interband transitions in Ag ($\lambda < 350$ nm) or Au ($\lambda < 730$ nm). To be more quantitative, we can calculate the theoretical extinction cross-sections of Ag@TiO₂, Au@TiO₂, and TiO₂ nanoparticles in ethanol at 800 nm, using Mie theory:

- Ag(35 nm diameter)@TiO₂(8 nm thickness): $\sigma_{\text{ext}} = 16.2 \text{ nm}^2$
- Au(35 nm diameter)@TiO₂(12 nm thickness): $\sigma_{\text{ext}} = 51.4 \text{ nm}^2$
- TiO₂(64 nm diameter): $\sigma_{\text{ext}} = 3.9 \text{ nm}^2$

Even though Ag@TiO₂ and Au@TiO₂ nanoparticles have extinction cross sections at 800 nm ~1 order of magnitude larger than TiO₂, the latter are ~2 orders of magnitude more abundant and will therefore dominate the extinction spectra at this wavelength.

In the figure below we compare the observed changes in the extinction spectra of Ag@TiO₂, Au@TiO₂, and TiO₂ ethanolic nanoparticle suspensions, upon UV irradiation for 10 minutes under N₂ purging (corresponding to Figure 2 and Figure 4a in the main text).

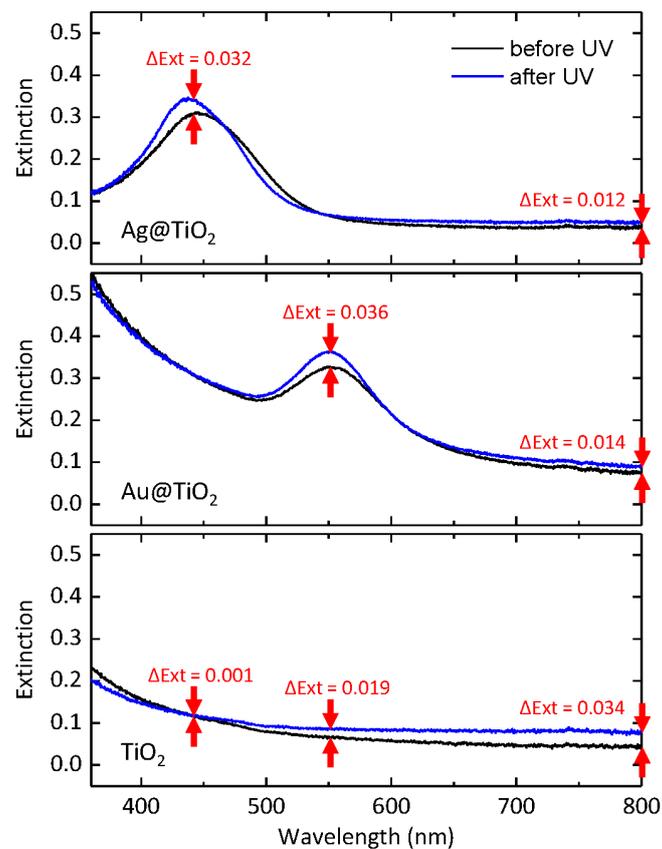


Figure 2. Extinction spectra of (top) Ag@TiO₂, (middle) Au@TiO₂, and (bottom) TiO₂ ethanolic nanoparticle suspensions (black lines) before and (blue lines) after 10 minutes of UV irradiation under N₂ purging.

The absolute changes in extinction at 800 nm for Ag@TiO₂, Au@TiO₂, and TiO₂ suspensions are 0.012, 0.014, and 0.034, respectively. We can therefore deduce that the Ag@TiO₂ and Au@TiO₂ suspensions have concentrations of TiO₂ nanoparticles corresponding to ~35% (0.012/0.034=0.35) and ~41% (0.014/0.034=0.41) of the concentration of TiO₂ nanoparticles in the pure TiO₂ suspension, respectively. These percentages allow us to estimate the relative contribution of the TiO₂ nanoparticles to the increase in extinction observed at the LSPRs of Ag@TiO₂ and Au@TiO₂:

1) The average LSPR wavelength of Ag@TiO₂ nanoparticles before and after UV irradiation is $\lambda_{\text{LSPR}}(\text{Ag@TiO}_2) = 442$ nm. At this wavelength, the absolute extinction increase for the Ag@TiO₂ suspension is 0.032 and for the TiO₂ suspension it is 0.001. Since we expect that the Ag@TiO₂ suspension contains ~35% of the TiO₂ nanoparticle concentration in the pure TiO₂ suspension, the contribution to the total increase in extinction by these pure TiO₂ particles will be 35% of 0.001, or 0.00035. This is about **1%** of the observed increase in extinction of the AgTiO₂ suspension at 442 nm and therefore negligible.

2) The average LSPR wavelength of Au@TiO₂ nanoparticles before and after UV irradiation is $\lambda_{\text{LSPR}}(\text{Au@TiO}_2) = 551$ nm. At this wavelength, the absolute extinction increase for the Au@TiO₂ suspension is 0.036 and for the TiO₂ suspension it is 0.019. Since we expect that the Au@TiO₂ suspension contains ~41% of the TiO₂ nanoparticle concentration in the pure TiO₂ suspension, the contribution to the total increase in extinction by these pure TiO₂ particles will be 41% of 0.019, or 0.0078. This is about **20%** of the observed increase in extinction of the AuTiO₂ suspension at 551 nm and therefore (almost) negligible.

To summarize our reasoning, the increase in extinction observed at the plasmon resonance wavelengths of our core@shell nanoparticles can almost entirely be attributed to a plasmonic effect rather than to a background contribution due to the presence of pure TiO₂ nanoparticles in solution.

2) Figure 2, 3 - Relatedly, for the analysis of the FWHM, were the baselines of the peaks corrected for somehow? It seems that the FWHM for the Au@TiO₂ particles (fig 1c, right) would contain the entire blue side of the spectrum without some correction, or assumption about the position of the baseline. Given the importance placed on interpreting changes to the FWHM for the proposed mechanism, details of the procedure for determining FWHM should be explained. This would also help clarify for the reader if the FWHM is actually changing during experiments, which is not possible to deduce by eye in Figure 2, especially if there are changes of the baseline consistent with Fig 4a.

Author reply: This is again a good point and we realized we did not provide details of how the full widths at half maximum of the LSPRs were calculated. This also led us to reconsider our fitting procedure, which now takes into account the presence of a background due to contributions from the bandgap of TiO₂ and from interband transitions in the metals. The FWHMs in the new version of the manuscript, which are now given in eV to be more easily compared with the change in damping due to chemical interface effects, confirm our previous interpretation, as can be seen in the updated version of Figure 3c.

All details of the fitting procedure are now included in the SI (see the new Figure S6) and mentioned in the main text, where we have replaced the sentence

“This is opposite to what we observe experimentally. Upon UV irradiation of both Ag@TiO₂ and Au@TiO₂ nanoparticles, in fact, we observe a narrowing of the FWHM and an increase in the extinction cross-section at the LSPR peak (Figures 3b and 3c).”

with

“This is opposite to what we observe experimentally, as shown in Figures 3b and 3c. Upon UV irradiation of both Ag@TiO₂ and Au@TiO₂ nanoparticles, in fact, we observe a narrowing of the FWHM (see also details in Figure S6) and an increase in the extinction cross-section at the LSPR peak.”

Given that the new fitted values of the FWHM are already given in electronvolts, we have also updated the main text (and the corresponding Figure S11 section) by replacing the paragraph

“To quantify the quenching of CID, we model the extinction spectra of Ag@TiO₂ nanoparticles with Mie theory, using a modified Drude approximation for the silver core in which the damping parameter, γ_{Ag} , is expressed as a sum of bulk and chemical interface damping:

$$\gamma_{Ag} = \gamma_{bulk} + \gamma_{CID} \quad (3)$$

We find that a decrease in γ_{CID} of ~ 0.01 eV can reproduce the experimentally measured increase in extinction cross-section and decrease in FWHM shown in figures 3b and 3c (see SI 11). Interestingly, a CID damping parameter of the order of tens of meV has also been recently reported for Au nanorods coated with thiol ligands²⁷. Furthermore, it has been suggested that a change in chemical interface damping could also affect the spectral position of the plasmon resonance, due to the dependence of the LSPR frequency on the damping parameter γ ²⁷. Such dependence could in principle qualitatively explain the observed LSPR shifts (Figure 3a), without invoking any swelling of the TiO₂ shells. However, for silver and gold, characterized in the Drude approximation by plasma frequencies of the order of ~ 10 eV, the measured variation in the damping parameter of ~ 0.01 eV has a negligible effect on the spectral position of the LSPR (see SI 11).”

with

“In Figure 3c we show that, upon UV irradiation, the linewidth of the plasmon resonances of Ag@TiO₂ and Au@TiO₂ decrease by a few tens of meV. Interestingly, a CID damping parameter of the order of tens of meV has also been recently reported for Au nanorods coated with thiol ligands²⁷. Furthermore, it has been suggested that a change in chemical interface damping could also affect the spectral position of the plasmon resonance, due to the dependence of the LSPR frequency on the damping parameter γ ²⁷. Such dependence could in principle qualitatively explain the observed LSPR shifts (Figure 3a), without invoking any swelling of the TiO₂ shells. However, for silver and gold, characterized in the Drude approximation by plasma frequencies of the order of ~ 10 eV, a variation in the damping parameter of the order of tens of meV has a negligible effect on the spectral position of the LSPR (see Figure S11).”

3) Starting on the last paragraph of page 3, the authors begin a discussion to justify the claim that electrons are not injected into the metal core. I find this argument very problematic because it assumes the excesses charges would be uniformly distributed within the metal core region. My intuition is that only the surface of the metal would exhibit appreciable changes in carrier density, within some screening length of the surface, but that the majority of the interior of the metal core would remain neutral.

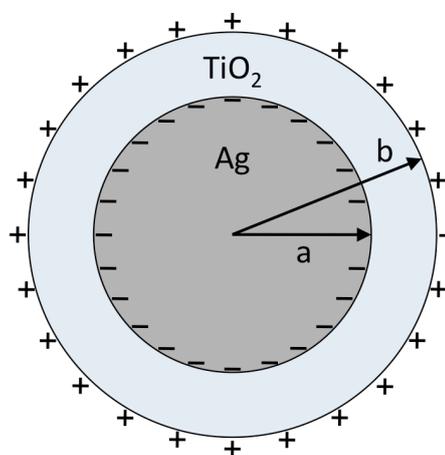
Author reply: Here we must disagree with the reviewer: it is not true that our argument assumes the excess charges to be *uniformly distributed within the metal*. Our argument is based on equation (1) in the main text, which expresses the increase in the Fermi energy of a coated metallic nanoparticle in solution. This equation, which we took from reference 38 (Scanlon et al., [Charging and Discharging at the Nanoscale: Fermi Level Equilibration of Metallic Nanoparticles, Chem. Sci. 6, 2705–2720 \(2015\)](#)), is nothing else but the equation for the electrostatic potential of a spherical conductor (see for example <http://hyperphysics.phy-astr.gsu.edu/hbase/electric/potsph.html#c1>), modified by the presence of a surfactant shell around the particle.

As it is true for any non-neutral conductor, the excess charges will certainly reside at the surface of the metallic nanoparticles to minimize electrostatic repulsion, but the spatial distribution of these charges has no influence on the calculated electrostatic potential, which is constant inside the metallic particle and decays as $1/r$ outside of it. As long as the nanoparticles remain metallic (and there is no reason to think otherwise), the calculated increase in the Fermi energy is therefore applicable to the entire particle.

When the authors go on to discredit the interpretation that the oxide layer may act as the dielectric layer of a capacitor defined by the metal core and the bulk solution (pg4 , line 20), they still assume an amount of charge accumulation that would be the amount required to uniformly modulate the carrier density of the metal core to give the observed shift of the LSPR peak. These separate discussions are physically nonsensical and incompatible, because again, the charges would be entirely localized to some surface layer on each side of the oxide.

Author reply: Again, we do not make any assumptions on the spatial distribution of the (supposedly) accumulated electrons in the metal nanoparticles and we agree with the reviewer that any excess charge will reside at the metal surface, due to electrostatic repulsion.

Using equation (1), we have shown that the accepted interpretation, which would assume that 34000 electrons are accumulated in the metallic cores while the holes are scavenged away by the solvent, would lead to an unphysical increase of the Fermi energy.



Here we are simply conceding a “best case scenario” in which the 34000 electrons which are needed to justify the observed plasmon resonance shift are indeed accumulated in the cores, while the holes are not diffusing away into the solvent, but instead are somehow localized at the TiO_2 /ethanol interface, to minimize the voltage increase in the metal (see sketch). In the text on page 4 we write “Using the electrostatic equation for a spherical capacitor and the relative static permittivity of TiO_2 leads to a predicted electric field across the shell of $\sim 4 \text{ V/nm}$, which is one to two orders of magnitude higher than the reported breakdown voltage of TiO_2 .^{40,43}”.

Such electric field is calculated using the standard electrostatic equation for a spherical capacitor (see <http://hyperphysics.phy-astr.gsu.edu/hbase/electric/capsph.html>):

$$\Delta V = \frac{Q}{4\pi\epsilon_0\epsilon_{TiO_2}} \left(\frac{1}{a} - \frac{1}{b} \right) = 33.7 \text{ V}$$

where

Q = total excess charge in the core needed to justify the blue shift in the LSPR

$$= 34000 \text{ electrons} \times 1.6 \times 10^{-19} \text{ C/electron}$$

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$$

$\epsilon_{TiO_2} = 26$ (see references 39 and 40 in the main text)

$$a = 17.5 \times 10^{-9} \text{ m}$$

$$b = 25.5 \times 10^{-9} \text{ m}$$

A voltage drop of 33.7 V across an 8 nm TiO_2 thickness corresponds to an average electric field of 4.2 V/nm that, as we argue in the manuscript, is much higher than the breakdown voltage of TiO_2 and therefore unphysical.

In summary, even conceding a best case scenario in which the electric field is minimized by the charge distribution in our core@shell nanoparticles, trying to explain the observed LSPR shifts with an electron accumulation in the metallic cores leads to unphysical results.

It is unclear what is the required number of electrons spatially limited to a surface layer (of a thickness that is not readily obvious but probably related to an electrostatic screening length), in order to reproduce spectral changes like those observed experimentally. This number of electrons may be much more physically reasonable, because the LSPR primarily interacts with those regions of electron density nearest the surface.

Author reply: We would like to reiterate that our calculations do not take into account any spatial distribution of the excess electrons and that we expect them to be at the metal surface, due to electrostatic repulsion. Interestingly, an answer to the reviewer's question comes from the work of Atwater's group at Caltech (see [A. M. Brown, M. T. Sheldon, and H. A. Atwater, Electrochemical Tuning of the Dielectric Function of Au Nanoparticles, ACS Photonics 2, 459-464 \(2015\)](#)).

In their paper the authors measure a plasmon resonance shift of ~2 nm upon applying a voltage of ~2 V to Au nanoparticles with a diameter of 60 nm. They treat the optical properties of their Au nanoparticles by correctly assuming that the excess electrons are accumulated to a surface region of the particle. In their conclusions they write: "the most non-neutral charge state of the shell, a decrease of electron density by 2% compared to bulk, occurred at +2.25 V applied bias and corresponds to roughly 12000 holes in the particle shell (calculated assuming a 2% change of charge density in a 3 nm thick shell of a 30 nm radius Au nanosphere)". In summary, in order to justify a small plasmon resonance shift (~2 nm), it is necessary to postulate the accumulation of (tens of) thousands of charge carriers, even assuming that all of them reside in a thin shell.

A fundamental difference between Atwater's results and ours, however, is that their experiments are conducted in the presence of the ionic liquid electrolyte diethylmethyl(2-

methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide (DEME) and in the absence of a TiO₂ shell around the nanoparticles. The capacitance of the electrical double layer (EDL) of DEME is extremely high (~0.12 F/m², see [Lu et al., Structure and Capacitance of Electrical Double Layers at the Graphene-Ionic Liquid Interface, Appl. Sci. 7, 939 \(2017\)](#)). The accumulation of 12000 holes in a Au nanoparticle of 30 nm in radius (surface area = 1.13e-14 m²) in the presence of such an electrolyte leads to a reasonable voltage drop at the metal/electrolyte interface:

$$V = \frac{Q}{C} = \frac{12000 \text{ holes} \times 1.6 \cdot 10^{-19} \text{ C/hole}}{0.12 \text{ F/m}^2 \times 1.13 \cdot 10^{-14} \text{ m}^2} = 1.4 \text{ V}$$

Note that a similar reasoning was offered by the group of prof. Mulvaney, when evaluating the plasmon resonance shifts occurring upon biasing Au nanorods in the presence of an electrolyte ([Novo et al, Electrochemical Charging of Single Gold Nanorods, JACS 131, 14664-14666 \(2009\)](#)). In their paper they write: *“The advantage of doing the experiments in fluids is that the double-layer capacitance of the particle is almost two orders of magnitude higher than that in air, due to the higher dielectric constant of water and the double layer screening by counterions (see Supporting Information Figure S3).”*

In our original version of the manuscript we had not properly underlined this difference. In the present version we have therefore changed the sentence

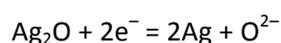
“First, the observed resonance shifts often lead to the prediction of large increases in the charge density of the metal nanoparticle (of the order of several percentages)^{15,21,23,24}, which would result in extremely high electric fields.”

with

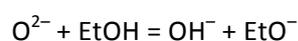
“First, the observed resonance shifts often lead to the prediction of large increases in the charge density of the metal nanoparticle (of the order of several percentages)^{21,23,24} which, in the absence of any electrical double layer screening from counterions in solution^{15,25}, would result in extremely high electric fields.”

Further, the reduction of the surface oxide of the metal core (or the proposed filling of chemical interface states) would be compatible with excess charges in the metal being localized to some surface layer. A more detailed analysis of this possibility seems very important.

Author reply: The reduction of the surface oxide does not necessarily lead to localized charges. The reduction reaction can be written as:



The oxygen anion O²⁻ can then be easily protonated by the solvent present in the pores of the TiO₂ shell:



Given the large porosity of the TiO₂ shells (~50%, see Figure S4), it is unlikely that these negatively charged species remain trapped at the Ag/TiO₂ interface and one could expect that they would diffuse into the bulk of the solution.

In the case of electrons trapped at the Ag/TiO₂ interface and leading to a quenching of the CID, these are indeed trapped electrons and could contribute to the development of an electrostatic potential. In the absence of a complete theory for the mechanism of chemical interface damping, however, it is at present impossible to correlate the measured shift in FWHM (few tens of meV) to a number of trapped electrons. A fundamental understanding of the physical mechanism of CID has recently emerged as one of the key open questions in the field at the 2018 Gordon Research Conference on Plasmonics and Nanophotonics, for example in the contributions of Stephan Link (Rice University) and Phillip Christopher (UCSB). What we feel confident in saying is that, if the observed damping effect needs to postulate the accumulation of tens of thousands of electrons, then we would have to abandon the CID hypothesis on the basis of our electrostatic considerations.

4.) Even if the claim is true that no electrons are injected into the metal, I would still expect the electrons to be non-uniformly distributed in the oxide shell, again due to electrostatic arguments. Can a gradient in the electron density in the oxide also provide spectral features like those that are observed, without invoking the other ad hoc aspects of the proposed model?

Author reply: This is an interesting point as indeed the electrons in the TiO₂ shells and in pure TiO₂ nanoparticles are likely to accumulate at the TiO₂/EtOH interface, because of electrostatic repulsion. As can be seen in Figure 4a and as we write in the manuscript “*The accumulation of electrons in TiO₂ is typically accompanied by an increase in its optical absorption in the visible^{21,44–46}, due to electrons trapped at Ti⁴⁺ sites²¹*”. These optical effects, which are most prominent in the red part of the spectrum, are however negligible at wavelengths close to the LSPR of the Ag@TiO₂ nanoparticles (Figure 4a in the manuscript) and it is therefore not possible to attribute the measured LSPR shifts to spectral features due to the accumulation of electrons in TiO₂.

Relatedly, during charging the particles will be surrounded by an electrochemical double layer from ions in solution. Could this local change of the components of the solution modify the refractive index surrounding the particles, also contributing to observed spectral shifts?

Author reply: In our experiments this cannot be the case. The formation of an electrical double layer (EDL) to justify the variation in the optical spectra of nanoparticles has been indeed already reported. In the already cited work by Atwater’s group at Caltech ([A. M. Brown, M. T. Sheldon, and H. A. Atwater, Electrochemical Tuning of the Dielectric Function of Au Nanoparticles, ACS Photonics 2, 459-464 \(2015\)](#)), references are provided to justify the formation of an EDL around the nanoparticles. In Reference 24 ([Jing et al, New Insights into Electrocatalysis Based on Plasmon Resonance for the Real-Time Monitoring of Catalytic Events on Single Gold Nanorods, Anal. Chem. 86, 5513 \(2014\)](#)) and Reference 26 ([Byers et al, Single-Particle Spectroscopy Reveals Heterogeneity in Electrochemical Tuning of the Localized Surface Plasmon, J. Phys. Chem. B 118, 14047 \(2014\)](#)) the nanoparticles are deposited on an ITO substrate and measurements are performed in presence of strong electrolytes like KNO₃, KCl, and NaCl in concentrations up to 0.1M. In Reference 30 ([Templeton et al, Solvent Refractive Index and Core Charge Influences on the Surface Plasmon Absorbance of Alkanethiolate Monolayer-Protected Gold Clusters, J. Phys. Chem. B](#)

[104, 564 \(2000\)](#)) the optical measurements are performed in presence of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄-NPF₆), a quaternary ammonium salt which is a strong electrolyte used in nonaqueous electrochemistry. In all of the reported references, the formation of an EDL around the nanoparticles is therefore justified. In our system, however, we do not have any strong electrolyte that can justify the formation of an EDL around our nanoparticles. The only chemical species that could act as a weak electrolyte could be the surfactant hydroxypropyl cellulose (HPC). However, the concentration of HPC in our system is 0.17 μM, almost 3 orders of magnitude lower than the concentration of the electrolytes reported in the above-cited papers. Moreover, the pH of our solutions is always close to neutral. We therefore think that the formation of an EDL around our nanoparticles due to the effect of UV light is highly unlikely to give any optical effect.

Another argument against the interpretation of our observed shifts as due to the formation of an EDL comes from the analysis of the timescales in which the LSPR partially recovers (Ag@TiO₂) or fully recovers (Au@TiO₂) its initial position. As can be seen from Figure 3a in the manuscript, these redshifts of the plasmon resonance are of the orders of (tens of) minutes. Even assuming that HPC could act as an EDL, upon switching off the UV light its optical effects should however disappear in less than a second as HPC's diffusion coefficient in ethanol is $\sim 4.4 \times 10^{-8}$ cm²/s (see [N. Yanagida and M. Matsuo, Morphology and mechanical properties of hydroxypropyl cellulose cast films crosslinked in solution, Polymer 33, 996 \(1992\)](#)).

Second round of review

Reviewer: 1

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

Comments:

It is good to know the authors have answered some of my questions. However, some revisions are still required to make the manuscript clear to readers.

1. Even though the core@shell nanoparticles with high standard deviation (20 %) can be used for the current study, the nanoparticles themselves are not qualified to be called nearly monodisperse. The authors are suggested to modify the related statement.

AUTHOR REPLY

In the abstract we have changed the sentence “*Here, we develop a nearly monodisperse synthesis*” into “*Here, we develop a two-step synthesis*”. We have removed the wording “*nearly monodisperse*” in the introduction, experimental section, results and discussion, and conclusion sections. Finally, in the conclusions, the sentence “*The use of nearly-monodisperse plasmonic nanoparticles [...]*” is now “*The use of plasmonic nanoparticles with controlled dimensions [...]*”.

2. In terms of N₂ purging during the experiment, it is better to add the detailed condition “The solution is initially purged for 20 minutes with the needle fully inserted into the solution, but during the UV irradiation experiments the needle is lifted above the liquid level to prevent the formation of bubbles.” to the manuscript. Otherwise, the reader will may still be confused of bubble generation.

AUTHOR REPLY

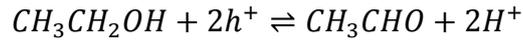
We have added the suggested sentence in the results and discussion section. The sentence “[...] *the ethanolic solution is purged for 20 minutes with N₂ gas before UV exposure, and the solution is kept under continuous nitrogen purging during the entire measurement*” has been replaced by “[...] *the ethanolic solution is purged for 20 minutes with N₂ gas before UV exposure, with a needle fully inserted into the solution. During the UV irradiation experiments, the N₂ purging is kept with the needle above the solution level to prevent the formation of bubbles that could influence the extinction measurements*”.

3. What is the mechanism of the reduction of the interface Ag₂O layer? A detailed discussion is needed.

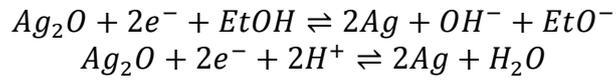
AUTHOR REPLY

We have added a detailed discussion of the reduction mechanism in section 2 of the supporting information, including the information we had already given in our reply to reviewer 2 in the first round of revision. The text we added in the SI is reproduced below:

“Upon shining UV light on Ag@TiO₂ core@shell nanoparticles, electron-hole pairs are generated inside the semiconductor. The holes are transferred to the TiO₂ surface, where they can oxidize ethanol to a variety of products, such as acetaldehyde, acetate, formaldehyde, and formate^{1,2}. These oxidation reactions are accompanied by the release of protons in solution. For example for the formation of acetaldehyde we can write the following reaction:



The photo-generated electrons can reduce the Ag₂O layer at the Ag/TiO₂ interface. The reduction can be assisted by the presence of ethanol or protons in the pores of the TiO₂ shell, according to the following reactions:



The presence of an ultrathin Ag₂O shell at the surface of Ag nanoparticles can significantly red-shift their localized surface plasmon resonances, as can be seen in the figure below.”

Reviewer: 2

Recommendation: This paper represents a significant new contribution and should be published as is.

Comments:

The authors of have done an excellent job of thoroughly addressing the referee comments, and I believe the manuscript is greatly improved. The manuscript is ready for publication.