ELEC-L321101 Post-Graduate Studies in Micro- and Nanosciences (Fall 2021)

Manuscript Reviewing (CS)

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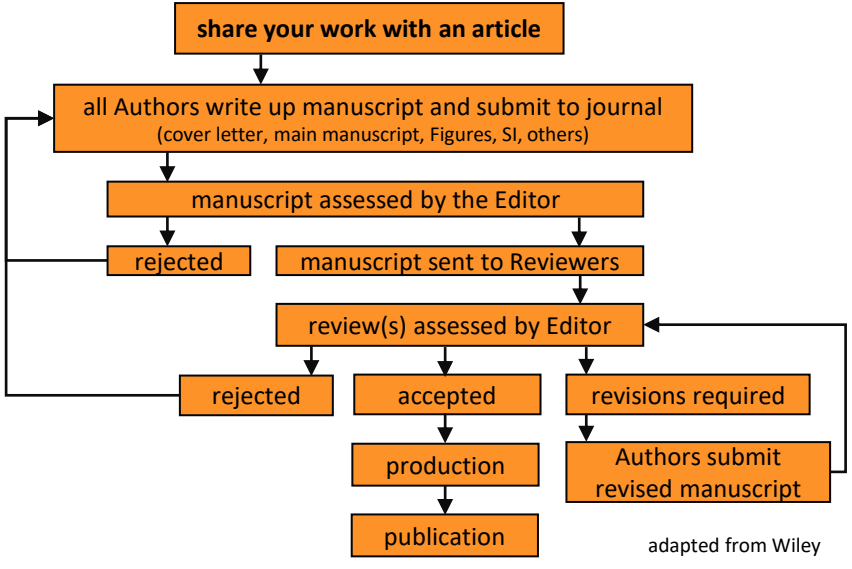
Manuscript Submission Process



My Approach in Reviewing Manuscripts

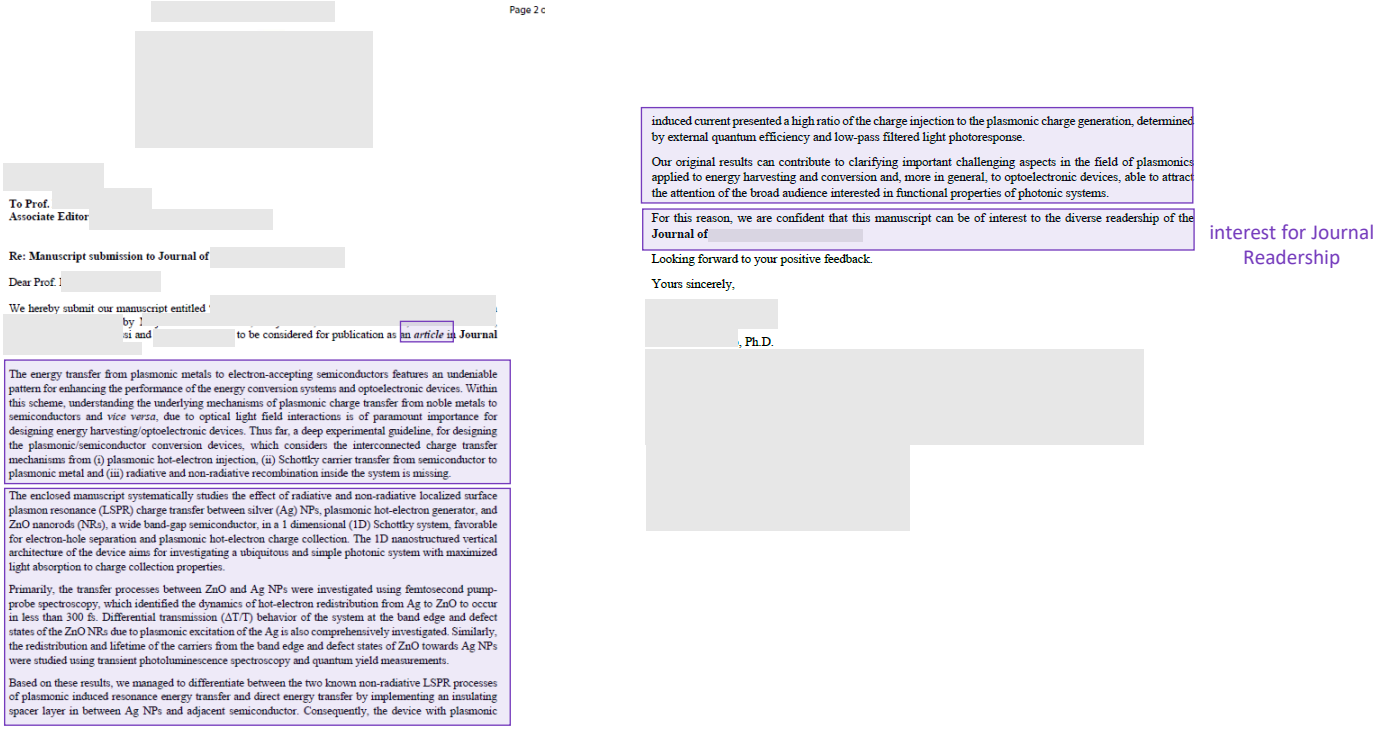
All papers, if scientifically sounding and scholarly presented, are worth being published

(…in the right journal)

match scope and quality expected for the Journal

improve quality of the paper (clarity, presentation, etc.)

The Editor Perspective: Cover Letter



Page 2 c

To Prof.
Associate Editor

Re: Manuscript submission to Journal of

Dear Prof.

We hereby submit our manuscript entitled
by
and to be considered for publication as an *article* in Journal

The energy transfer from plasmonic metals to electron-accepting semiconductors features an undeniable pattern for enhancing the performance of the energy conversion systems and optoelectronic devices. Within this scheme, understanding the underlying mechanisms of plasmonic charge transfer from noble metals to semiconductors and *vice versa*, due to optical light field interactions is of paramount importance for designing energy harvesting/optoelectronic devices. Thus far, a deep experimental guideline, for designing the plasmonic/semiconductor conversion devices, which considers the interconnected charge transfer mechanisms from (i) plasmonic hot-electron injection, (ii) Schottky carrier transfer from semiconductor to plasmonic metal and (iii) radiative and non-radiative recombination inside the system is missing.

The enclosed manuscript systematically studies the effect of radiative and non-radiative localized surface plasmon resonance (LSPR) charge transfer between silver (Ag) NPs, plasmonic hot-electron generator, and ZnO nanorods (NRs), a wide band-gap semiconductor, in a 1 dimensional (1D) Schottky system, favorable for electron-hole separation and plasmonic hot-electron charge collection. The 1D nanostructured vertical architecture of the device aims for investigating a ubiquitous and simple photonic system with maximized light absorption to charge collection properties.

Primarily, the transfer processes between ZnO and Ag NPs were investigated using femtosecond pump-probe spectroscopy, which identified the dynamics of hot-electron redistribution from Ag to ZnO to occur in less than 300 fs. Differential transmission ($\Delta T/T$) behavior of the system at the band edge and defect states of the ZnO NRs due to plasmonic excitation of the Ag is also comprehensively investigated. Similarly, the redistribution and lifetime of the carriers from the band edge and defect states of ZnO towards Ag NPs were studied using transient photoluminescence spectroscopy and quantum yield measurements.

Based on these results, we managed to differentiate between the two known non-radiative LSPR processes of plasmonic induced resonance energy transfer and direct energy transfer by implementing an insulating spacer layer in between Ag NPs and adjacent semiconductor. Consequently, the device with plasmonic induced current presented a high ratio of the charge injection to the plasmonic charge generation, determined by external quantum efficiency and low-pass filtered light photoresponse.

Our original results can contribute to clarifying important challenging aspects in the field of plasmonics applied to energy harvesting and conversion and, more in general, to optoelectronic devices, able to attract the attention of the broad audience interested in functional properties of photonic systems.

For this reason, we are confident that this manuscript can be of interest to the diverse readership of the **Journal of**

Looking forward to your positive feedback.

Yours sincerely,

, Ph.D.

manuscript details

main context for the submission

main results and why is the submission important for the field

interest for Journal Readership

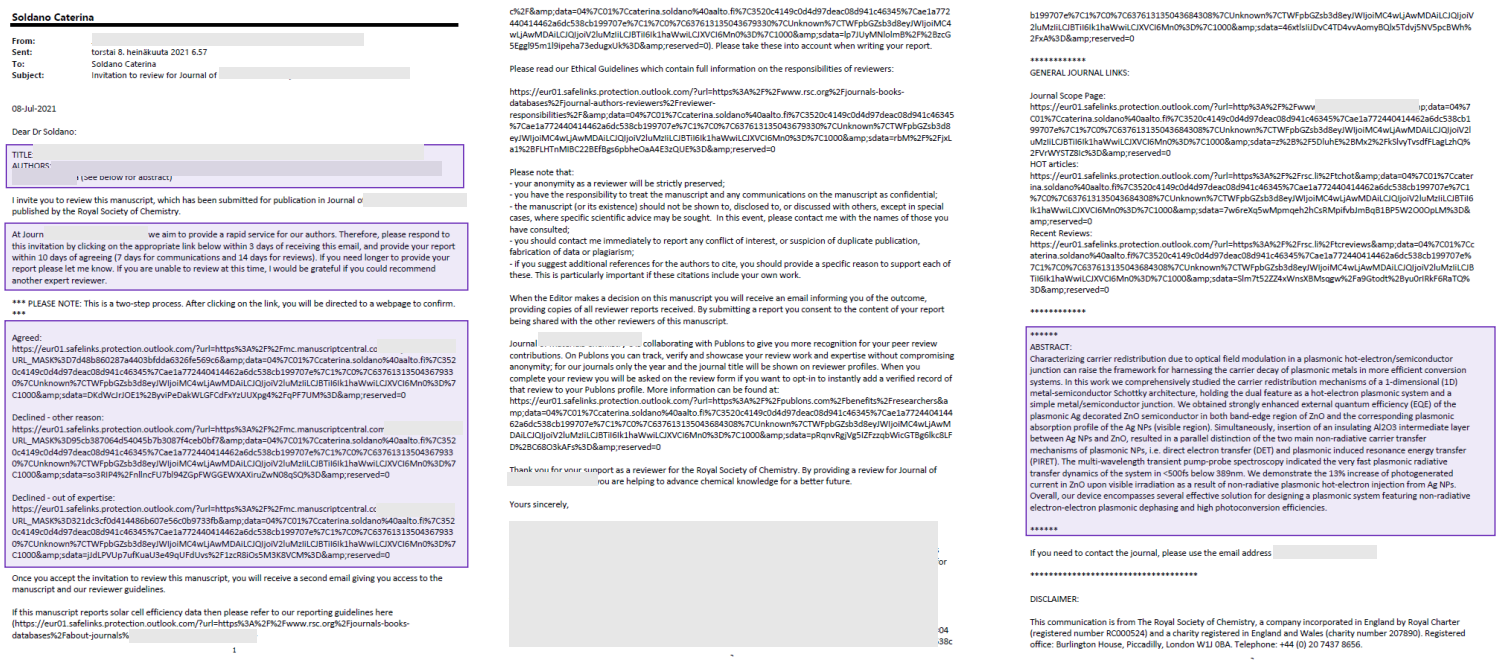
The Reviewer Perspective: Invitation to Review

conflict of interest

timeframe for review

accept or decline to review

is the manuscript in my field of expertise?



Soldano Caterina

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To: Soldano Caterina
Subject: Invitation to review for Journal of

08-Jul-2021

Dear Dr Soldano:

TITLE:
AUTHORS:

I invite you to review this manuscript, which has been submitted for publication in Journal o
published by the Royal Society of Chemistry.

At Journ we aim to provide a rapid service for our authors. Therefore, please respond to this invitation by clicking on the appropriate link below within 3 days of receiving this email, and provide your report within 10 days of agreeing (7 days for communications and 14 days for reviews). If you need longer to provide your report please let me know. If you are unable to review at this time, I would be grateful if you could recommend another expert reviewer.

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c%2F&data=04%7C01%7Ccaterina.soldano%40aalto.fi%7C3520c4149c0d4d97deac08d941c46345%7Cae1a772440414462a6dc538cb199707e%7C1%7C0%7C637613135043679330%7CUnknown%7CTWFpbGZsb3d8eyJWIjoiMC4wLjAwMDAiLCJQIjoiV2luMzIiLCJBTiI6Ik1haWwiLCJXVCI6Mn0%3D%7C1000&sdata=lp7JUyMNlolm8%2F%2BzcG5Egg95m1J9Ipeha73edugxUk%3D&reserved=0). Please take these into account when writing your report.

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Thank you for your support as a reviewer for the Royal Society of Chemistry. By providing a review for Journal of you are helping to advance chemical knowledge for a better future.

Yours sincerely,

or

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ABSTRACT:
Characterizing carrier redistribution due to optical field modulation in a plasmonic hot-electron/semiconductor junction can raise the framework for harnessing the carrier decay of plasmonic metals in more efficient conversion systems. In this work we comprehensively studied the carrier redistribution mechanisms of a 1-dimensional (1D) metal-semiconductor Schottky architecture, holding the dual feature as a hot-electron plasmonic system and a simple metal/semiconductor junction. We obtained strongly enhanced external quantum efficiency (EQE) of the plasmonic Ag decorated ZnO semiconductor in both band-edge region of ZnO and the corresponding plasmonic absorption profile of the Ag NPs (visible region). Simultaneously, insertion of an insulating Al2O3 intermediate layer between Ag NPs and ZnO, resulted in a parallel distinction of the two main non-radiative carrier transfer mechanisms of plasmonic NPs, i.e. direct electron transfer (DET) and plasmonic induced resonance energy transfer (PIRET). The multi-wavelength transient pump-probe spectroscopy indicated the very fast plasmonic radiative transfer dynamics of the system in <500fs below 389nm. We demonstrate the 13% increase of photogenerated current in ZnO upon visible irradiation as a result of non-radiative plasmonic hot-electron injection from Ag NPs. Overall, our device encompasses several effective solution for designing a plasmonic system featuring non-radiative electron-electron plasmonic dephasing and high photoconversion efficiencies.
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If you need to contact the journal, please use the email address

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- at least 2 Reviewers (depending on journal)
- Blind Review: Authors do not know Reviewer(s) identity (most common, recently option to disclose Reviewer(s) identity at the end of the review process)

  Double-Blind: both Authors and Rewiewer(s) do not know each other´s identity

The Reviewer Perspective: What is Expected?

good practice to become familiar what is expected from Reviewer

from MDPI (it might vary with publisher/journal)

	YES	can be improved	must be improved	not applicable
Does the introduction provide sufficient background and include all relevant references				
Is research design appropriate?				
Are the methods adequately described?				
Are the results clearly presented?				
Are the conclusion supported by the results?				
	high	average	low	no-answer
Originality & novelty				
Significance of content				
Quality of presentation				
Scientific soundness				
Interest to the Readers				
Overall merit				

Do you have any potential conflict of interest with regards to this paper? (Y/N)

Did you detect plagiarism? (Y/N)

Did you detect inappropriate self-citations by authors? (Y/N)

Do you have any other ethical concerns about this study? (Y/N)

English language & style

( ) extensive editing of English language and style are required
( ) moderate English changes are required
( ) English language and style are fine/minor spell check required.
( ) I don´t feel qualified to judge about English language and style

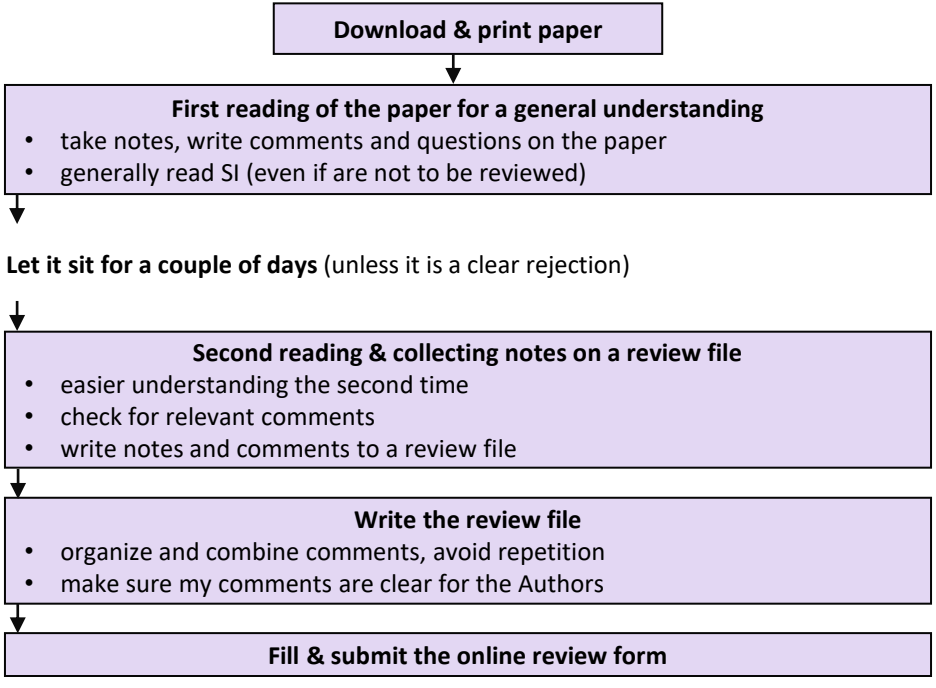
Overall Recommendation

( ) Accept in the present form
( ) Accept after minor revision (minor spell check/format style required)
( ) Reconsider after major revision
( ) Reject (article has serious flaws, more experiments needed, research not conducted correctly)

Reviewer Comments to Editor (private)

Reviewer Comments to Author(s) (write here Reviewer´s comments or upload a file)

My Reviewing Approach



(*My*) Reviewer Comments

manuscript info

_Reviewer comments

Title:

Authors:

Manuscript ID:

brief summary of the main findings

The Authors present a very detailed study of the photo-physics and optical properties in a very interesting hybrid system, Ag-decorated ZnO NRs and further investigate the effect of the insertion of a thin alumina coating on the same system. Different studies based on several characterization techniques support the Author´s claims.

my recommendation

The manuscript provides sufficient data to support the Author´s statement. I support publication but I will suggest the Authors to address comments below to improve the overall quality.

general comments on concepts, DOE, results, related to the all paper

General comments:

- I seem not to find explicit mentioning of the nanoparticle size (although this can be approximately estimated from high-magnification SEM images). This information and relative consideration in the context of the system here studied are extremely relevant since plasmonic effects are size-dependent.
- What is the nature of the NPs – NRs interaction? Are for example NPs physisorbed on the surface, chemically bonded? What does it change when the alumina coating is introduced (with Author finding a slightly higher degree of aggregation?).

  Is it possible to define a surface roughness for the ZnO NRs? This might provide some additional information on the decoration process with/without ALD coating.

  What the Author could expect if for example a continuous monolayer of Ag NPs would be deposited on ZnO NRs? Is there a "threshold" value of coverage for which plasmonic effect are present and/or quenched?
- How does alumina bandgap compared and locate compared to Ag and ZnO? Are alumina films 4nm thick "thin enough" to enable tunneling in the absence of an external applied field?
- How reasonable is to compare Ag-decorated NRs with properties of Ag NPs in solution?

detailed comments on paper

Some more detailed comments:

- Figure 2: EQE dependence on wavelength.

  It seems that part of the description might be in the text (page 7, below Figure 2) " range of 300-500nm, the ZnO ...."

  The text hereby mentioned several orders of magnitude difference compared to bare ZnO. However from the picture it is possible to roughly estimate maybejust one order of magnitude difference.

  Inset: what does it mean scaled up (simply multiplied? shifted vertically?). Panel (c) is a bit confusing since main panel and inset seems to mismatch and the relative description is not very clear.

- In page 6, Authors attribute the shift in LSPR to the change of Ag NPs dielectric constant environmental medium. In which way a change in dielectric constant of the NPs surrounding environment would impact theirs results? Adding an extra 4nm layer of alumina, which has a very similar dielectric permittivity to the one of ZnO should not affect very much the dielectric environment.
- Figure 3.b: Authors finds very little differences between investigated samples, which however do not affect the average PL-lifetime of the ZnO visible emission. What does this outcome suggest? I would also suggest a different choice of plot format, to highlight the different curves

Some minor comments:

- IPCE is mentioned in the experimental section, but there is no mention either in the manuscript description nor in the Supporting Information. Only EQE is reported and discussed in the manuscript.
- Minor format issue and spelling errors throughout the manuscript should be reviewed upon acceptance

minor comments (*i.e.* format, spelling, small mistakes, etc.)

Reviewer Online Submission (Details)

	YES	can be improved	must be improved	not applicable
Does the introduction provide sufficient background and include all relevant references	X			
Is research design appropriate?	X			
Are the methods adequately described?	X			
Are the results clearly presented?	X			
Are the conclusion supported by the results?	X			
	high	average	low	no-answer
Originality & novelty	X			
Significance of content	X			
Quality of presentation	X			
Scientific soundness	X			
Interest to the Readers	X			
Overall merit	X			

Do you have any potential conflict of interest with regards to this paper? (Y/N) N

Did you detect plagiarism? (Y/N) N

Did you detect inappropriate self-citations by authors? (Y/N) N

Do you have any other ethical concerns about this study? (Y/N) N

English language & style

( ) extensive editing of English language and style are required
( ) moderate English changes are required
(X) English language and style are fine/minor spell check required.
( ) I don´t feel qualified to judge about English language and style

Overall Recommendation

( ) Accept in the present form
(X) Accept after minor revision (minor spell check/format style required)
( ) Reconsider after major revision
( ) Reject (article has serious flaws, more experiments needed, research not conducted correctly)

Reviewer Comments to Editor (private)

Dear Editor,
I recommend the publication of the manuscript in its present form. Minor revisions (see list) can improve the overall quality.
BR,
~~Caterina Soldano~~

Reviewer Comments to Author(s) (write here Reviewer´s comments or upload a file)

See attached file (or you can copy and paste here your comments)

Authors Perspective: Response to Reviewer 1 & 3

Authors response: *point-by-point* answer to the Reviewer(s)

Reviewer general intro & recommendation

Reviewer comment

Authors response

Answers to reviewers' comments

(Our answers in plain text)

Reviewer 1:

The manuscript "[illegible] was a comprehensive study of carrier photogeneration and decay in 1-dimensional ZnO nanorods coupled to Ag plasmonic clusters in presence/absence of an Al_2O_3 spacing layer. In this work, the authors studied the carrier redistribution mechanisms of a 1-dimensional (1D) metal-semiconductor Schottky architecture, holding the dual feature as a hot-electron plasmonic system and a simple metal/semiconductor junction. The authors obtained strongly enhanced external quantum efficiency (EQE) of the plasmonic Ag decorated ZnO semiconductor in both band-edge regions of ZnO and the corresponding plasmonic absorption profile of the Ag NPs (visible region). Besides, the photogenerated current in ZnO can be enhanced by 18% upon visible irradiation as a result of non-radiative plasmonic hot-electron injection from Ag NPs. "This is an interesting and novel work that deserves publication in Journal of [illegible] few minor issues are to be noted and the paper can be published after minor revision."

1. The authors need to explain a bit in more details the relatively wide absorption profile of the Ag NPs from almost 390 nm to 455.

We thank the reviewer on this critical note. The wide range of the plasmonic dephasing in the absorption spectra of the implemented silver nanoparticles (Ag NPs) can be assigned to dipole plasmon resonance of nearly spherical metal NPs and it is in good agreement with the quasistatic and Mie theory predictions obtained through solving the Maxwell equation for spherical particles[0].

At the same time, we consider the possibilities in (i) variation of the size distribution of the Ag NPs synthesized using polyol method. The variation of the particle size, in fact, can modify the absorption/extinction spectra of the plasmonic NPs, altering the position and broadening the visible light absorption of the Ag NPs[2]. In addition, (ii) the possibility of synthesizing geometrically distorted NPs via the aforementioned synthesis method cannot be neglected, in a way that the particles do not comply to a perfect spherical shape and often present different geometries with sharp edges and distorted shapes. This often promotes formation of the distinct *hot-spots* in the plasmonic NPs resonance.

We acknowledge that the mentioned note by the reviewer is rather critical. We added the highlighted points on the wide absorption edge of the used Ag NPs in the revised manuscript.

2. How does such wide range affect the hot carrier harvesting of the system?

Thanks for the note. We emphasize that the role of the plasmonic NPs in our system is to perform hot-carrier injection to the semiconductor in the visible range, where relevant hot-carriers can be exploited by the semiconductor. Similar to our results, identical conclusions were obtained in different studies, where the plasmonic excitation's intensity and the controlled position of the excitation on the absorption profile of the plasmonic NPs, directly correspond to the rate of hot-carrier injection[0]. In a way that higher intensities of plasmonic excitations and/or direct excitation on the plasmonic profile of the NPs increase the steady-state concentration of the energetic charge carriers in the adjacent semiconductor.

In our system, we denoted similar behavior using our controlled illumination photoresponse analysis (figure 6), where exciting the sample on the plasmonic profile of the Ag NPs resulted in different ranges of current densities. We observed the highest obtained currents by shifting the absorption excitation of the Ag decorated samples at the center of the plasmonic profile, with the most intense plasmonic absorption (395 nm). Conversely, the excitation of the samples at the ultimate end of the plasmonic profile of the Ag NPs at 495 nm, where we observed the decay of the Ag NPs plasmonic excitation, resulted in rather insignificant current densities. We further attributed the observed trend to the carrier injection properties of the system.

3. The authors should explain the reason behind the slight red shift in the PL NB emission of the samples after Ag uptake. Does that correspond to Förster carrier transfer, density of defects, etc?

Thanks for the critical note. We observe no red-sift on the PL near-band emission of the ZnO after Ag uptake. On the other hand, we report a drastic quenching of the PL NB on the silver decorated sample. We attribute this behavior in the PL emission of the ZnO defect states to the non-radiative Förster energy transfer (FET), as emphasized by the reviewer. In FET mechanism, the hot-carriers non-radiatively transfer from band-edge states of the ZnO NRs PL (a blue-shifted emitter) to Ag NPs, a red-shifted absorber constituent, through simple dipole-dipole coupling as schematically presented in Figure 1[3]. This phenomenon is in agreement with the absorption profile of the bare Ag NPs and the defect emission of the ZnO NRs presented in Figure 2 and Figure 3 of the MS. Consequently, we observed a significant quenching of the band edge PL emission of the ZnO NRs.

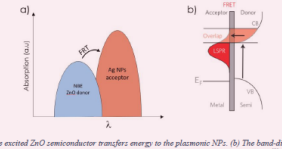


Figure 1: (a) FET, the excited ZnO semiconductor transfers energy to the plasmonic NPs. (b) The band-diagram corresponding to the förster energy transfer from semiconductor to the adjacent absorber metal[3].

We understand that our statements in the MS might not be sufficient for describing the mentioned phenomenon. We have further highlighted this section in the MS.

Reviewer 3:

The manuscript entitled "[illegible] describes the experimental study of energy/charge transfer from silver plasmonic particles to wide banagap ZnO semiconducting nanorods and vice-versa under UV and visible photoexcitation. This topic is highly important for the design of effective light harvesters in energy conversion devices under white light irradiation, due to the large extinction coefficient of plasmonic particles, which enable strong light absorption in very limited film thickness. It is also important in the broader field of optoelectronic devices, where monochromatic radiation can be applied. The authors give an in-depth characterization of hot-electron dynamics under UV and visible excitation. A comprehensive approach is applied, which involves static and transient photoluminescent, static optical absorption, ultra-fast absorption in pump-probe configuration and light-induced photocurrent measurements. The conclusions of the manuscript are based on a solid ground and correct interpretation of the experimental findings. The manuscript is very well-written and technically sound. Moreover [illegible] is urgent and timely, and can be of interest for the readership of the Journal

I support its publication after minor revisions, as detailed below.

1. In Figure S1, what induces aggregation of the Ag nanoparticles and does that impact the authors' findings?

We appreciated the critical point raised by the reviewer. Due to the nature of the deposition method for Ag NPs uptake on ZnO NRs surface (low voltage electrophoretic deposition), the Ag NPs are attached to the ZnO surface via only weak electrostatic bonding. We note that the reduced surface roughness of the Al_2O_3 coated NRs can be a motivation for slight aggregation of the Ag NPs. Yet determining the surface roughness of the samples due to the nature of their 1dimensional nanostructured geometry is rather unfeasible through atomic force microscopy or other techniques. However, as peer review suggested, we note that further discussions is required on the effect of Ag decoration in their plasmonic carrier harvesting. More subtexts were added to the *morphological discussions* of the MS.

*2. In Figure 1e, the authors indicate additional reflections in the XRD pattern by a *. Where do these reflections arise from and why?*

We appreciate the reviewer's critical note. The asterisks (*) corresponds to the reflection peaks arising from the fluorinated doped tin oxide (FTO) substrate. We have added a clear description on the captions of the Figure 1 in the MS.

3. The authors investigate the effect of Ag plasmonic particles on ZnO nanorods. Do they also expect similar results in the case of ZnO thin films? Is the interest in nanorods dictated by the possible application in devices, or the exposure of lateral faces of ZnO rods (which is of course different from thin films) may have a role in modulating charge dynamics?

Thanks for the comment. The main motivation of employing a 1D forest of ZnO nanorods (NRs) is to promote a higher light harvesting system that features sufficient downward band-bending characteristic and at the same time higher carrier transfer properties, a suitable platform for the acquisition of hot plasmonic carriers. The previous studies, show that the Wannier unoccupied states present in ZnO NRs are potentially of interest for considerable plasmonic hot-carrier collection properties[2].

Likewise, our device architecture is mainly intended to exploit the non-radiative hot-carrier injection from NPs with reduced radiative recombination and higher light harvesting properties. In agreement with the point raised by the reviewer, the carrier mobility and the light harvesting properties in the 1D ZnO NRs are relatively superior compared to the thin-film counter parts (even with the same crystalline structure).

We mainly consider this system as a platform for designing a hot-carrier conversion device. However, implication of such a system in a PV platform requires a practical design, in which efficient separation of the photoexcited plasmonic positive and negative ions are enabled.

4. The authors claim that they highlight very clearly the different effect of DET and PIRET processes, but this is not said in a very clear way, especially in the Conclusions section, where the authors should focus in summarizing what are the peculiar effects of DET and PIRET on the optoelectronic properties of the system. I would recommend additional elaboration.

We appreciate the reviewer's suggestion. The effect of the distinguished hot-carrier transfer phenomena, DET and PIRET, and the prospect of their applications is further discussed in the *conclusion* section of the MS.

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Authors Perspective: Response to Reviewer 2 (CS)

Reviewer 2:

The Authors present a very detailed study of the photo-physics and optical properties in a very interesting hybrid system, Ag-decorated ZnO NRs and further investigate the effect of the insertion of a thin alumina coating on the same system. Different studies based on several characterization techniques support the Author's claims. The manuscript provides sufficient data to support the Author's statement. I support publication but I will suggest the Authors to address comments below to improve the overall quality.

1. I seem not to find explicit mentioning of the nanoparticle size (although this can be approximately estimated from high-magnification SEM images). This information and relative consideration in the context of the system here studied are extremely relevant since plasmonic effects are size-dependent.

We appreciate the reviewer's suggestion. We have highlighted the effect of the Ag NPs size dependence and their size distributions in the plasmonic carrier-transfer of the system. Based on our morphological characterizations we have reported the NPs size distribution further in the text. Sub-sections were added to the text in the discussions corresponding to plasmonic absorption profile of the samples. We have determined the average size distribution of the Ag NPs employed in our work to be around 5-40 nm based on the statistical observation of the decorated samples and our previous TEM analysis. We have considered both SEM analysis and previous TEM investigations of the samples for the reported size distributions.

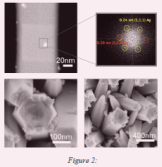


Figure 2:

2. What is the nature of the NPs – NRs interaction? Are for example NPs physisorbed on the surface, chemically bonded? What does it change when the alumina coating is introduced (with Author finding a slightly higher degree of aggregation?). Is it possible to define a surface roughness for the ZnO NRs? This might provide some additional information on the decoration process with/without ALD coating. What the Author could expect if for example a continuous monolayer of Ag NPs would be deposited on ZnO NRs?

Is there a "threshold" value of coverage for which plasmonic effect are present and/or quenched?

We thank the peer review for raising these points. The Ag NPs are attached to the ZnO surface via only weak electrostatic bonding. The NPs decorate the ZnO NRs via electrophoretic deposition method using only the synthesized Ag suspension as electrolyte. Special care was given during the deposition to prevent the oxidation of the Ag NPs and/or ionization of the ZnO NRs as mentioned in the experimental section of the MS. The electrophoretic deposition of the Ag NPs provided a quantitative method for the uptake of Ag NPs, in a way that the amount of the deposited Ag NPs could be manipulated by changing the duration of electrodepositions. We added a more clarifying subtext to the *experimental section* of the MS.

We also agree with the reviewer on the effect of reduced surface roughness of the Al_2O_3 coated NRs as a possible reason for slight aggregation of the Ag NPs. Yet determining the surface roughness of the samples due to the nature of their 1dimensional nanostructured geometry is rather unfeasible through atomic force microscopy or other surface techniques. However, as peer review suggested we note that further discussions is required on the effect of Ag decoration in their plasmonic carrier harvesting. More subtexts were added to the *morphological discussions* and the *experimental section* of the MS.

We have previously investigated the effect of the Ag concentration in the optical plasmonic coupling of the samples as shown in Figure 3 (a). Our result indicated that even after conformal coverage of the ZnO NRs with Ag NPs (Figure 3 (C)) the corresponding plasmonic optical coupling of the system in the visible range (~420 nm) is still observable. However, the obtained plasmonic absorption shoulder of the Ag NPs on the reflectance spectra of the ZnO NRs presents a broader profile in the samples with conformal coverage of Ag NPs. This behavior can be assigned to the possible distortion and aggregation of the deposited Ag NPs on the samples (Figure 3(c)). In addition, previous studies elucidated the effect of *hot-spot* formations through interactions of localized surface plasmons resonance (LSPR) of the plasmonic NPs in direct contact with each other[2]. In our work we decided to minimize the self-interactions of the Ag NPs and solely investigate the effect of their hot-carrier mechanisms towards semiconductor. We have further clarified our point in the *morphological discussion* of the MS.

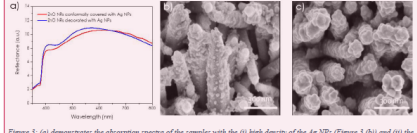


Figure 3: (a) demonstrates the absorption spectra of the samples with the (i) high density of the Ag NPs (Figure 3 (b)) and (ii) the samples conformally covered with the deposited Ag NPs on ZnO NRs (Figure 3 (c)) respectively.

3. How does alumina bandgap compared and locate compared to Ag and ZnO? Are alumina films 4nm thick "thin enough" to enable tunneling in the absence of an external applied field?

It is rather a critical point mentioned by the reviewer. We have systematically investigated the effect of the Al_2O_3 layer thickness on the photocurrent contribution of the Ag NPs plasmonic response, using external quantum efficiency (EQE) of the system as shown in Figure 4 (a)-(b). As expected thicker alumina 10 nm yield higher series resistance and marginal decrease in the EQE of the system, presenting no possible derived signal related to the samples. As the alumina thickness decreases, the contribution from the Ag plasmon resonance becomes more prominent and reaches its maximum. On the other hand, we have not selected the 1 nm thick alumina spacer layer as the nominal sample for the presented MS studies, since we required to assure the direct contact of the Ag NPs with the ZnO NRs is prevented for investigating the PIRET hot-carrier transfer of the system. In that sense, the 4 nm thick Al_2O_3 spacer layer is selected as the sample, for which we ensured the homogenous coverage of the ZnO NRs using Rutherford backscattering (RBS) as presented in supporting information Figure S2.

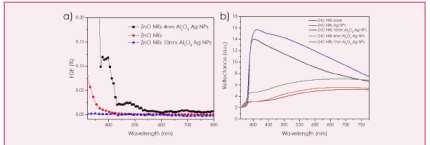


Figure 4: (a) external quantum efficiency of the Ag NPs decorated ZnO NRs with different thickness of alumina interlayer. (b) Diffused reflectance spectra of the ZnO/Ag NPs samples with different alumina interlayer thickness were compared to bare ZnO NRs.

4. How reasonable is to compare Ag-decorated NRs with properties of Ag NPs in solution? Some more detailed comments.

The highlighted point by the peer review is rather important. LSPR of the plasmonic NPs depends strongly on nanoparticles shape, size, composition, and on the refractive index of immediate environment and its dielectric function according to Mie theory. In our work we have employed the bare Ag NPs suspension in ethanol (in transient pump probe measurements Supplementary information Figure S5) solely to understand the possibility of the LSPR excitation of Ag NPs through interband excitations at 266 nm. In fact, our result indicated that the timeframes and the decay dynamics of the interband excitation of Ag NPs in ethanol are nearly identical to the composite samples. Further, subsections were added to the *discussions* in the text to clarify the highlighted points.

5. Figure 2: EQE dependence on wavelength. It seems that part of the description might be in the text (page 7, below Figure 2) "range of 300- 500nm, the ZnO …." The text hereby mentioned several orders of magnitude difference compared to bare ZnO. However from the picture it is possible to roughly estimate maybe just one order of magnitude difference. Inset: what does it mean scaled up (simply multiplied? shifted vertically?). Panel (c) is a bit confusing since main panel and inset seems to mismatch and the relative description is not very clear.

We thank the reviewer for this comment. In the MS we mentioned the increase of several orders of magnitude according to the analysis of the overall EQE values, considering the EQE curves not only in the range of Ag NPs absorption profile, but also that of the bare ZnO sample of which we consider the non-radiative carrier transfer from Ag NPs to the ZnO demonstrate a significant improvement in derived current of the samples. Similar experimental evidence were obtained in the photoresponses of the samples of which the uptake of Ag NPs increase the overall current and the spectral range of the bare ZnO NRs. We simply calculated the collected current per incident photon of the bare ZnO and ZnO/Ag NPs sample in the range 320 nm to 550 nm. Our consequent calculations determine nearly 2.5 folds increase in the EQE values of the sample decorated with Ag NPs compared with bare ZnO NRs we have further added this values to the EQE discussion of the text.

The purpose of the inset of the figure 2 (c) in the MS, is to simply highlight the plasmonic carrier injection of the sample with Al_2O_3 intermediate layer. In that sense, we simply reduced the spatial offset of the ZnO/Ag curve and that of the ZnO/Al_2O_3/Ag.

6. In page 6, Authors attribute the shift in LSPR to the change of Ag NPs dielectric constant environmental medium. In which way a change in dielectric constant of the NPs surrounding environment would impact theirs results? Adding an extra 4nm layer of alumina, which has a very similar dielectric permittivity to the one of ZnO should not affect very much the dielectric environment.

Thanks for the note. The frequency and width of the surface plasmon absorption depends on the size and shape of the metal nanoparticles as well as on the dielectric constant of the metal itself and the surrounding medium. The plasmon absorption has linear dependence on the aspect ratio of the plasmonic NPs and the dielectric constant of the medium according to the Mie relations[3,4]. We attributed the slight shift in the plasmonic absorption spectrum of the bare Ag NPs to the changes of the refractive index and environmental dielectric constant of the samples suspended in ethanol as opposed to the Ag decorated ZnO NR samples in solid -state. As mentioned by the peer review, similar changes are not expected for the sample with Al_2O_3 intermediate layer, since the refractive index of the thin Al_2O_3 layer does not present remarkable changes compared to bare ZnO NRs. We have investigated the optical changes of the samples before and after Al_2O_3 depositions in the Supplementary Information Figure S3. We added further discussions regarding the effect of dielectric constant of the environmental medium in the *pump-probe discussion* of the MS.

7. Figure 3.b: Authors finds very little differences between investigated samples, which however do not affect the average PL-lifetime of the ZnO visible emission. What does this outcome suggest? I would also suggest a different choice of plot format, to highlight the different curves some minor comments.

We appreciate the reviewer's comment. Our PL data suggested a slight increase of the average decay time-constant (τ_{RI}), from which we concluded that the transfer of the charges from ZnO to Ag NPs increases the possible dynamics of the electron recombination due to increase in the carrier population density in ZnO NRs electronic structure. In contrary, the sample with Al_2O_3 layer presented a negligible change of PL time constants indicating that 4 nm Al_2O_3 layer can significantly block the transfer of the charges from ZnO NRs to Ag NPs. We concluded that the overall fast PL decay of our samples even after integration of the Ag NPs is mainly related to the fact that the plasmonic carrier transfer of the Ag NPs towards ZnO NRs contributes to the non-radiative carrier transfer mechanisms. We further support our findings by simply introducing a two-step model taking in to account the quantum yield of the samples.

We fully appreciate the suggestion of the reviewer regarding the format change of the Figure 3(b) in the MS. We have modified the style of the Figure 3 (b) to a more concise plot format.

8. IPCE is mentioned in the experimental section, but there is no mention neither in the manuscript description nor in the Supporting Information. Only EQE is reported and discussed in the manuscript. Minor format issue and spelling errors throughout the manuscript should be reviewed upon acceptance.

Thanks for the note, we have corrected the mentioned errors.

Authors Perspective: Re- Submission

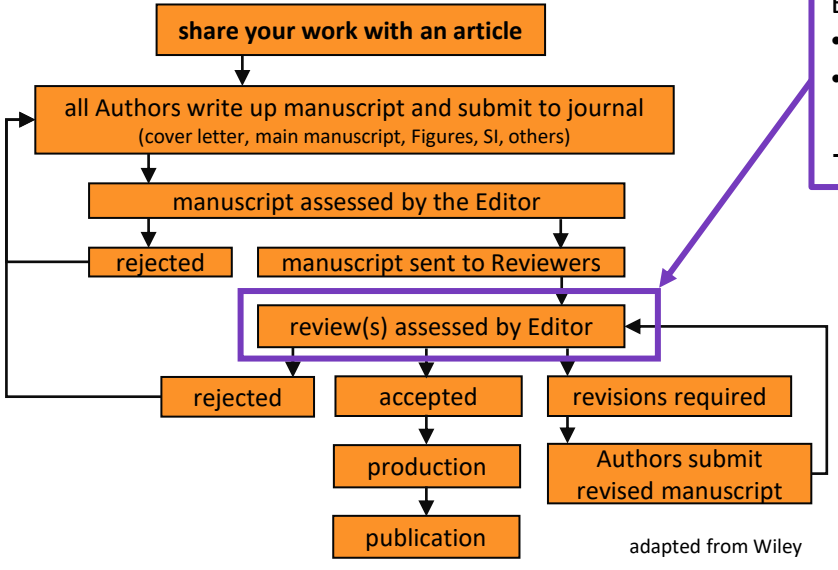
Authors then submit:

- revised manuscript (changes highlighted)
- *point-to-point* Response to Reviewer(s)
- (optional) updated cover letter (typically this is shorter than the first time)

Revised manuscript

- **not ALL comments raised by the Reviewer(s) have to be included in the revised version** (if relevant and appropriate)
- **OK not to agree with Reviewer(s)** comments, however you **HAVE to prove/support your statement**
- changes might include format, additional paragraphs, re-wording, new references, etc….

Editor Perspective: Reviewer Comments



adapted from Wiley

Editor will assess:
- Reviewer(s)´ recommendation
- Authors response to Reviewer(s)

→ **ACCEPT**, **REJECT** or **FURTHER REVISIONS**

<u>As Author:</u>

only once I went through two-rounds peer review (as corresponding author), typically one round

<u>As Reviewer:</u>

- typically see paper twice (original submission and revised manuscript)
- accepted with minor/no revision several papers
- rejected one paper based on plagiarism (with a very "strong" email to the Editor) - I was very surprised!
- rejected three papers based on English issues

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Slowed canonical progress in large fields of science

Johan S. G. Chu[a,1] and James A. Evans[b,c,d]

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Publish or perish: Where are we heading?

"Surely you were aware when you accepted the position, Professor, that it was publish or perish."

J Res Med Sci. **19** (2), 87 (2014)