Response Letter

Dear Editors,

I am writing to respond to the reviewers' critical comments on our manuscript entitled, "Superabsorption of light by nanoparticles" NR-COM-08-2015-005468, which we aim for publication in Nanoscale.

As a group of authors interested in high quality input we know that unbiased and professional review is an important part of a publication process. This way we would like to stress you attantion to the second comment of the first reviewer. He had listed a number of publications, however, it is hard to belive that this list is unbiased after looking to the authors names; several authors from Jiangxi Normal University are listed in all of this publications (it looks like some names have two spelling options with and without the dash). We provide our findings here:

1. ACS Applied Materials Interfaces, 7, 4962-4968 (2015)
   Zhengqi Liu, Xiaoshan Liu, Shan Huang, Pingping Pan, Jing Chen, Guiqiang Liu, and Gang Gu
   DOI: 10.1021/acsami.5b00056

2. Materials Letters 158, 262-265 (2015)
   Zhengqi Liu , Guiqiang Liu, Xiaoshan Liu, Shan Huang, Yan Wang, Pingping Pan, Mulin Liu
   http://dx.doi.org/10.1016/j.matlet.2015.06.029

3. Applied Physics Letters, 104, 081116 (2014)
   Zheng-qi Liu, Hui-bai Shao, Gui-qiang Liu, Xiao-shan Liu, Hai-qing Zhou, Ying Hu, Xiang-nan Zhang, Zheng-jie Cai, and Gang Gu
   http://dx.doi.org/10.1063/1.4867028

4. Nanotechnology, 24, 155203 (2013)
   Zheng-qi Liu, Gui-qiang Liu, Hai-qing Zhou, Xiao-shan Liu, Kuan Huang, Yuan-hao Chen, and Guo-lan Fu
   doi:10.1088/0957-4484/24/15/155203

We would like to thank the editor and two anonymous reviewers for their constructive comments, which helped us to improve the manuscript. Below, we address all comments point-by-point, discussing the subsequent modifications.

Reviewer #1 comments

> 1. The authors claimed Combined effect of these resonances is presented to produce the flat and relative broadband electric resonance response. Nevertheless, the broadened absorption band is not very broad. Is there any further way to predict a broadband light absorption. For instance, a broadband absorption in the whole visible spectral range. Maybe, a possible way of using the dispersed size scale nanoparticles should be added for improving the study.

This comment touches two aspects of broadband performance, namely, properties of a stanalone particle and in interaction with other particles. The first case, as it was correctly mentioned with the reviewer, has some limiations. We can design a band, which will be broader of a typical band for a given multipole, however, width is not extremly large. To illustrate this we have run an optimization with a goal to provide a prediefined separation between multipole resonanses (Fig. 1). Our observation is the following: while the separation is small enough compared to a multiple resonance width the optimizer was successful to find desings with electric and magnetic dipole. If the separation is large the absorption band splits into two. For large separation is is also possible to obtain two resonanses of the electric dipole response, located at predefined position (Fig. 1(e,f)). Still there are not so many possibilities here to design a good broadband. To control the bandwidth at a given spectral position we need to involeve relatively large particles. This leads to appereance of resonances (and absorbtion) out of the designed band which are hard to control or suppress in disscussed triple-layer structure.

To answer the second part of the comment, related to possiblity of usage of the pariticle array with dispered sizes, we designed two particles with best absorption effeciency at 475 nm and 525 nm (outer radius 34 and 38 nm) and simulatied them both with FDTD method using Lumerical FDTD Solutions. Sketch of the simulated system and final results are in Fig. 2. To verify our FDTD we fist simulated absorption of standalone spheres, the obtained postions and amplitudes of resonances to corresponde well with Mie caclulations. Next step was to find out the possible interactions between two spheres, so we run a simulation in dimer configuration with zero separation between spheres and with 10 and 30 nm separation. The resulting spectra has a strong contribution from standalone resonances, while coupling effects seems to be minor. This can be easily explained from field distribution in Fig. 4(c) of the manuscript. Positioning spheres in H-k plane we are exploting the feature of field being highly localized inside the the sphere. For sure arranging spheres in other plane, increasing the number of spheres can change the amount of coupling between the spheres. As an example we tested arragement of sphers in E-k plane Fig. 2(c); for zero separation the intraction between spheres is strong, however, due to near-field nature of this coupling it rapidly decays with the separation width Fig. 2(d), for separation of 30 nm responses of individual particles dominate in overall spectra for both planes of polarization. This way we show that in principle it is possible to construct an absoption band of an array of dispersed particles simply optimizing the properties of every single sphere carefully tuning the distance between particles (which still is much smaller than the wavelength).

We changed the manuscript from "As a result, one can design spectrally-selective absorbers or broadband absorbers with almost arbitrary prescribed properties." to "As a result, one can design absorbers with broadened spectra or spectrally-selective absorbers with almost arbitrary prescribed properties. Due to strong localization of electric dipole field (espatially in H-k plane) it is also possible to desing dispersed size arrays particles by defining their individual properties for composite absorption spectra; we obtained rather small coupling between particles during additional simulation using FDTD method."

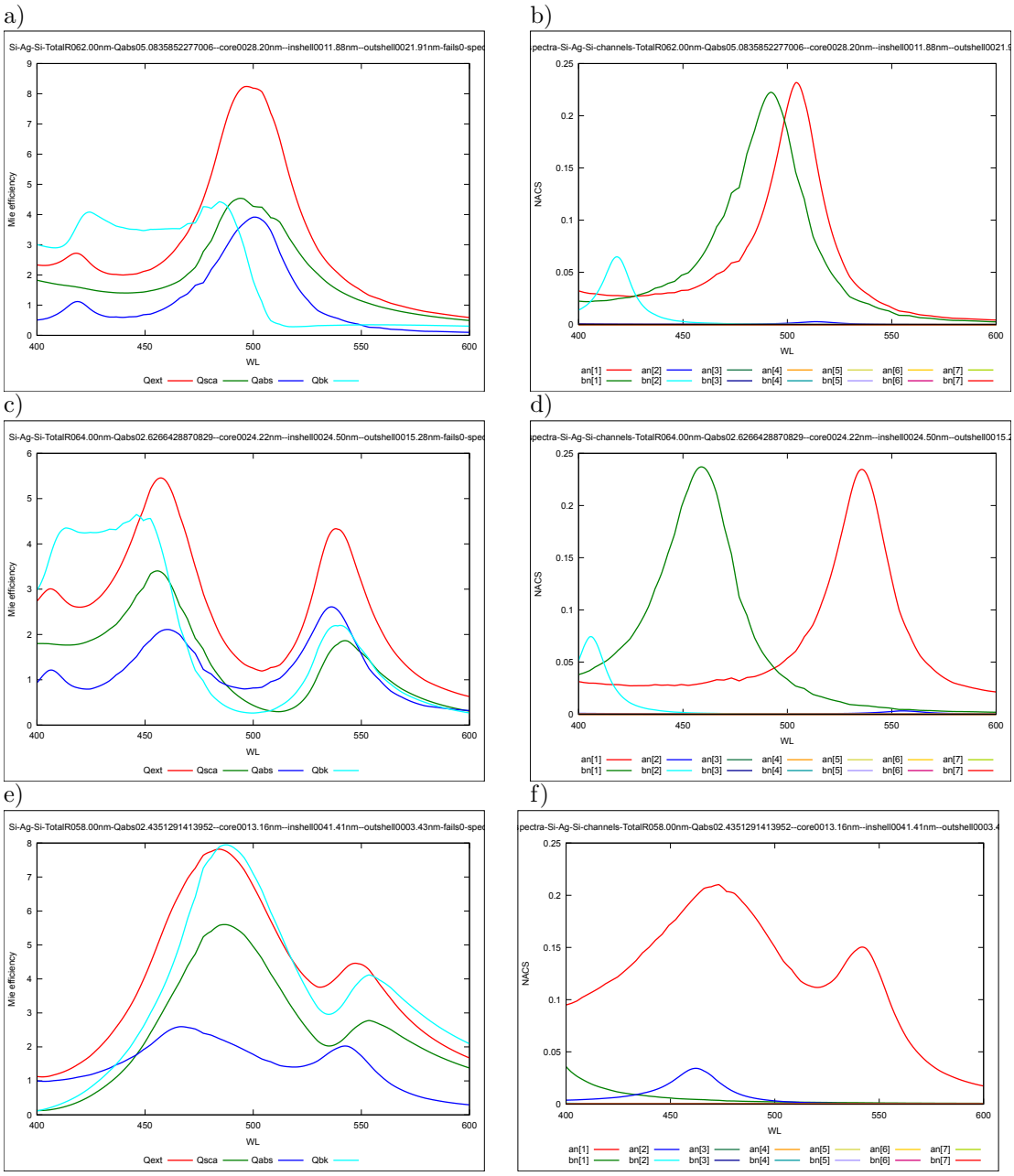


Figure 1: Single particle desings for separation between dipole resonances of 20 nm (a-b) and 80 nm (c-f). Left column with figures (a,c,e) contains spectra of Mie efficiency for extinction (Qext), scattering (Qsca), absorption (Qabs, blue curve) and backscattering (Qbk). Right column (b,d,f) presents contibution of multipoles to the spectra (red and green stands for electric and magnetic dipoles, blue and cyan corresponds to quadrupole electric and magnetic modes, respectively). It is interesting to note that for 80 nm separation optimizer was able to find a desing with two resonances of a dipole mode (f). We suppose that the latter most likely has the same nature as the response presented in Fig. 3(c,d) of the manuscript: there are several resonances of an electric dipole response binded to different layers of the particle.

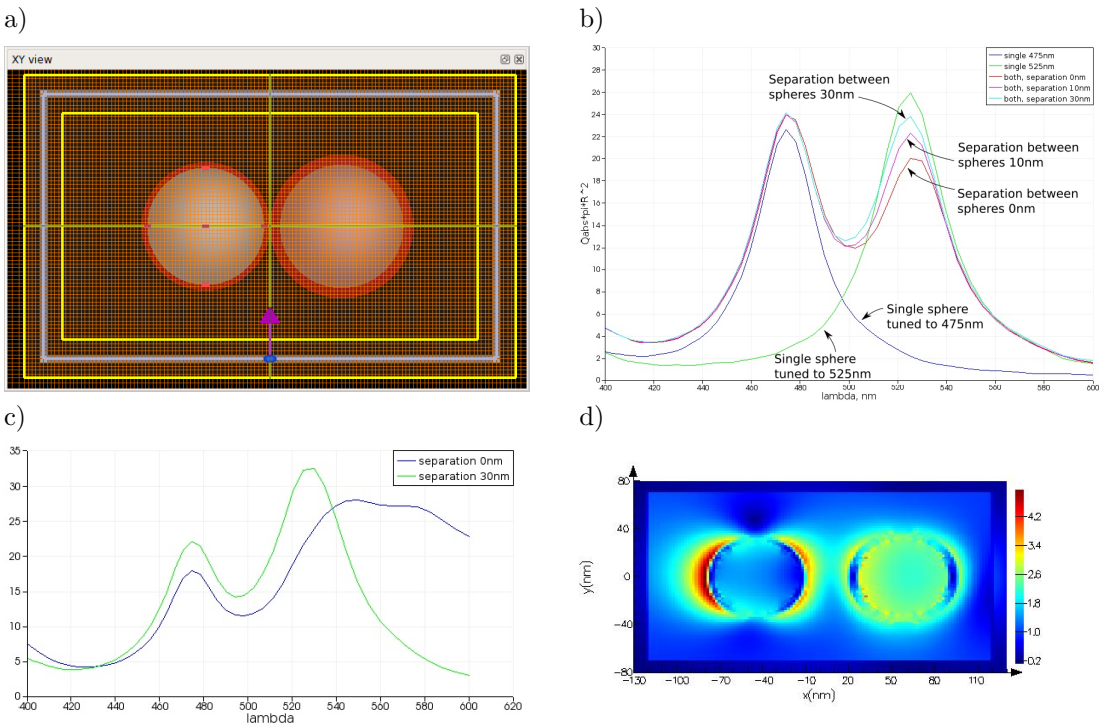


Figure 2: (a) Fullwave simulation prepared in Lumerical FDTD. (b) Absorption spectra of standalone spheres and in dimer configuration with separation between spheres of 0, 10, and 30 nm, particles are in H-k plane (c) Separation 0 and 30 nm for particles in E-k plane (d) Field distribution at 500nm of incedent wavelength for particles in E-k plane with separation of 30 nm.

> 2. To achieve super-absorption behavior, it is interesting to know what will happen when the multilayered nanoparticles are closely packed as the plasmonic crystal. As reported in the previous papers [ACS Applied Materials & Interfaces, 7, 49624968 (2015); Materials Letters 158, 262265 (2015); Applied Physics Letters, 104, 081116 (2014); Nanotechnology, 24, 155203 (2013)], the packed plasmonic crystals have been demonstrated to show broadband light coupling and confinement. Thereby, it would be interesting to show improved broadband light absorption based on the plasmonic crystal of this proposed multilayered nanoparticles.

We would like to thank the reviewer for provided citations, some of them turned to be really interesting. In order to reply this comment first of all we checked all the citations provided.

ACS Applied Materials & Interfaces, 7, 4962-4968 (2015) titled "Automatically Acquired Broadband Plasmonic-Metamaterial Black Absorber during the Metallic Film-Formation" uses metal film formation process to achive very wideband performance. However, the absorption in this case is highly dependable on the thickness of the underlaying silica layer. This way we can argue against the conlusion of the paper "These results also confirm that an ultrathin meta-surface layer (less than 10 nm) structure can produce nearly ideal broadband light absorption" - to achieve experimentally observed performance the whole system (including silica layer and gold under-layer) is needed. A more detailed simulation can give some answers, however, we expect that most of the absorbtion happends in the gold under-layer, while the metasurface and silica layer serves to be kind of an impedance matcher. This proposal is confirmed with the experemental results in Fig. 5 of the paper, for 100 nm silica layer the absorption is low. At the same time the wideband performance can be related to the fractal-type surface, as it is shown in Fig. 2(f) Moreover, it should be relativly easy to estimate the thermal behaviour of such a metasurface, as soon as isolated particles on the top of the silica have no heat transfer with electrons to the substrate. If we suppose that most of the light is absorbed in top layer this should lead to overheating of the metasurface due to extreamly low geometrical volume. For this case in steady state we should expect a large temperature gradient as soon as gold thermal condutivity 310 $W/(m \cdot K)$ is about 200 fold larger than silica $1.4W/(m \cdot K)$. Measuring temperature via infrared radiation from both sides of the sample can provide hints to distinguish the absortption origin.

Anyway, albiet of the exciting experimental results obtained in the paper they exploit phsycal effect that differs a lot from the one proposed in our manuscript; our particles were desinged to absorb the incident power by themselfs, and they work perfectly in a stand-alone mode. This can be extremly conviniet, for example, for nanophotonics application, when the available volume to place an absorber can be very limited. Same overheating question can also appear here, limiting the operational power range.

Applied Physics Letters, 104, 081116 (2014) titled "$\lambda^3/20000$ plasmonic nanocavities with multispectral ultra-narrowband absorption for high-quality sensing" is cleary not related to "broadband light coupling and confinement" and was probably listed by an accident.

Nanotechnology, 24, 155203 (2013) titled "Near-unity transparency of a continuous metal film via cooperative effects of double plasmonic arrays" describes light interaction with a gold film, which has an array of gold spheres positioned on top, bottom, or both sides of the film. Provided simulations show a strong field enhancement between the spheres. Absorption related part of the paper references [18-21], where [20] is Le F, Brandl D W, Urzhumov Y A, Wang H, Kundu J, Halas N J, Aizpurua J and Nordlander P 2008 ACS Nano 2 707 titled "Metallic Nanoparticle Arrays: A Common Substrate for Both Surface-Enhanced Raman Scattering and Surface-Enhanced Infrared Absorption". In this paper absorption spectra in Fig. 5(b) calculated with electrostatic plasmon hybridization method showes, as it was stated with a reviewer, a significat increase of the band when packing particles to an array. This broadering originates from the appearance of collective mode (or, in other words, the hybridization of plasmon responce of several particles) with additional impact from retardation effects. It can be of great intereset (including applied examples) to apply the same approch from our manuscript to this system. It should be possible to optimize simultniously geometry of individual particles and their positioning in array to degenerate several absorption resonances of such collective modes in order to achieve superabsorption. However, we do not have any working code for plasmon hybridization method to check it with our optimizer.

Using brute force approach with FDTD simulation looks to be rather computationaly expensive without any prior analytical estimations.

However, as a proof of concept, we simulated with FDTD method the 3x3 rectangular array of spheres (to provide a good coupling both in E and H direcitons) with the separation of 4 nm (so it is only 2 mesh cells to resolve the separation in the used coarse grid, selected to get a resonable timing of a 3D full-wave simulation) Fig 3(a). Several collective modes can be recognized from field distribution while changing the incident wavelength Fig 3(c-e) (it can be interesting to compare this results with Fig 4 of Le et al. paper) . However, for used materials, nanoparicle and array designs, spectral range, and plane of polarization we observed a blue shift of absoption responce (it looks to be dominated with silver plasmon resonance) Fig 3(b), which is opposite to results of Le et al. in Fig. 5(b) of their paper.

Materials Letters 158, 262265 (2015) titled "Dielectric shell modulated plasmonic crystal for novel light absorption meta-surface" provide another type of plasmonic coupling. In contrast to most other works with hot spots located between the particles it this paper field distributions presented in Fig 2 (b-d) is mostly localized inside the particles and in Fig 2 (e) it is about the same order inside and between the particles. It looks to be quite reasonable as far as relatively small metallic core (d=25 nm) is covered with thick dielectric shell (d=65 nm). This way due to relatively small coupling between the particles we should expect to find this resonances in a stand-alone particle, which was easy to reproduce. The result of Mie calcultion for gold sphere (material data is from P. B. Johnson and R. W. Christy. Optical Constants of the Noble Metals, Phys. Rev. B 6, 4370-4379 (1972)) of diameter d=25 nm covered with lossless and dispersionless dielectric with refractive indes n=2.5 and d=65 nm in Fig. 5. However, there was the only one electric dipole resonance at 637 nm, futhermore, 3D FDTD simulation of such a particle with a gold substrate (as is was used in the paper) and periodic boundary condition for a HCP array lead to appearance of a peak at 666 nm (for polarization oriented to far neighbor) in Fig 5(c) in contrast with the simulation presented in Fig. 1(b) of the paper with several resonances in range 700-1100 nm. We do not have a good explanation for such a disagreement.

This way it looks that using particle array adds a whole banch of new physical features which deserve a separate investigation. No changes to the manuscript were done.

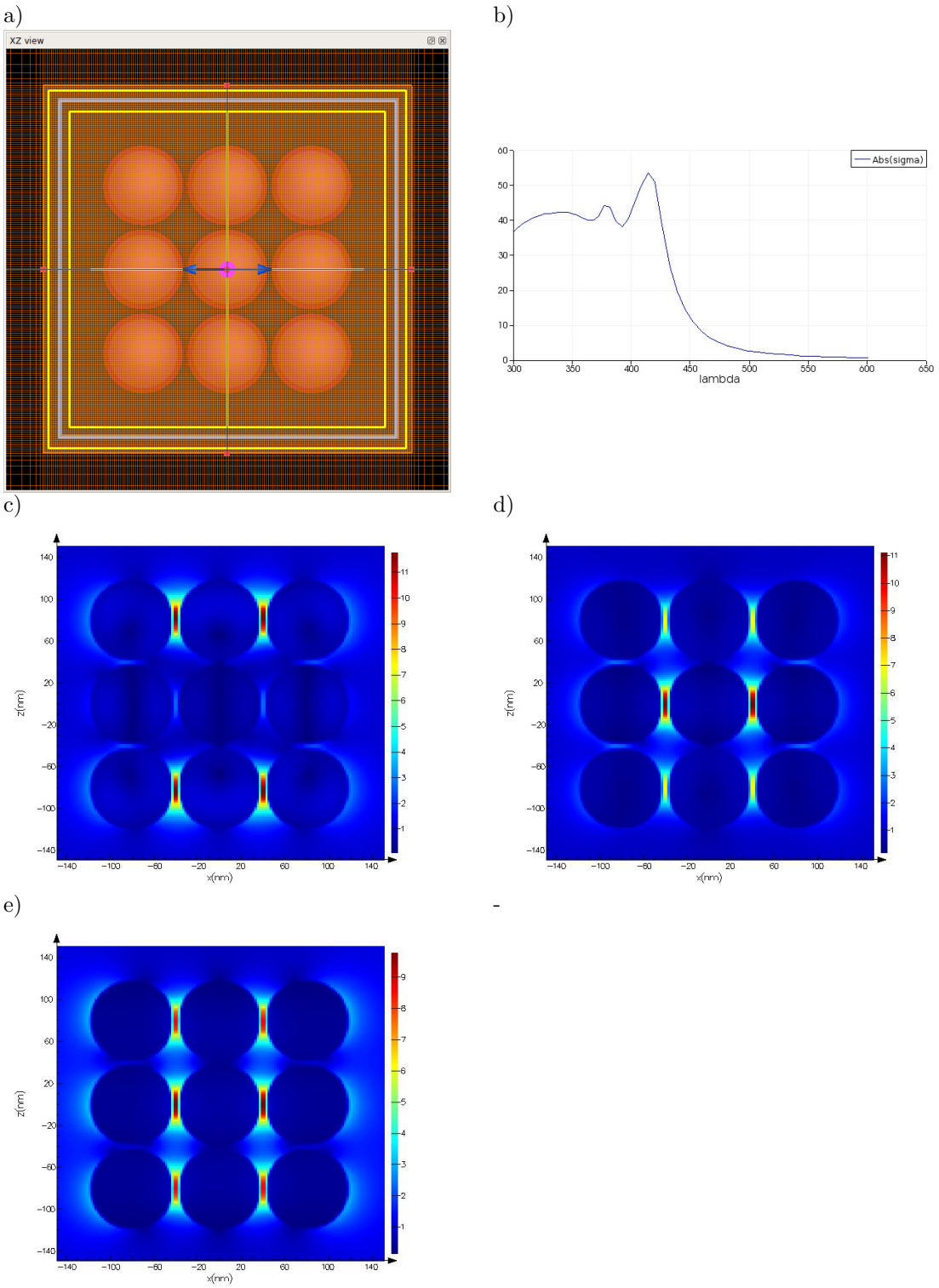
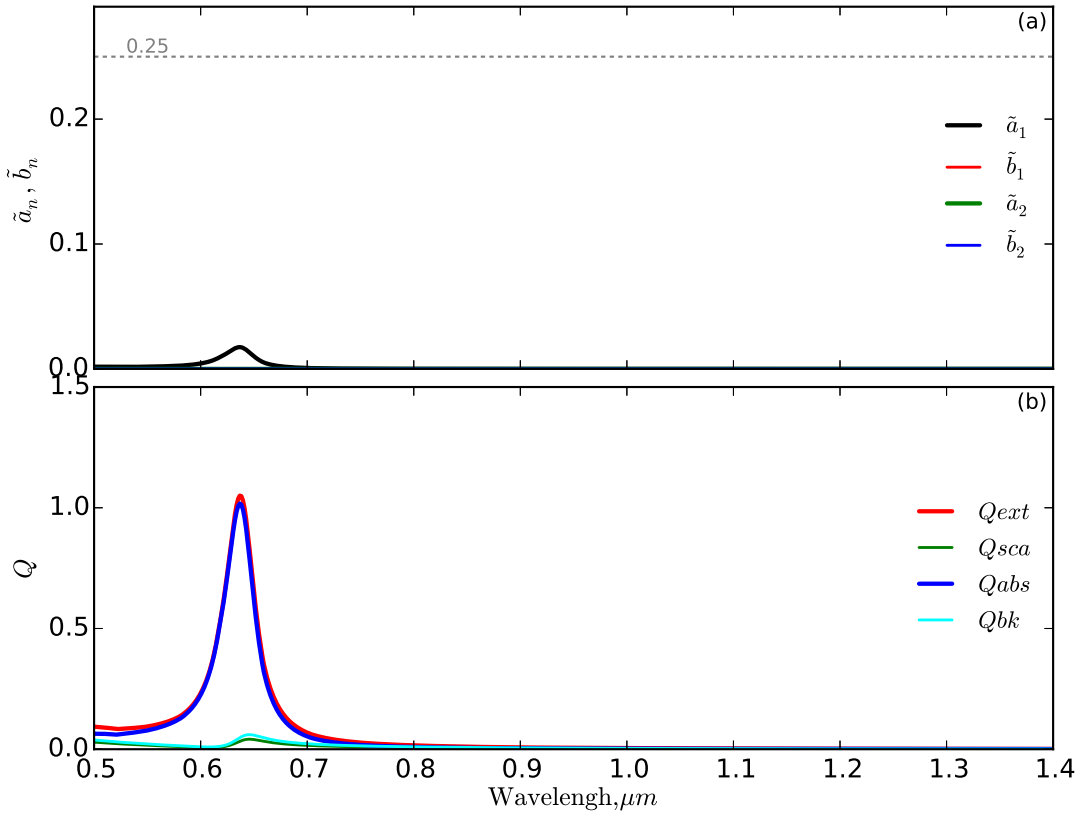


Figure 3: FDTD simulation of 3x3 grid of spheres optimized for absorption at 525 nm(a) Full-wave simulation prepared in Lumerical FDTD. (b) Cross-section absorption spectra (c,d,e) Field distribution at 408, 452, and 600nm of incident light.



c)

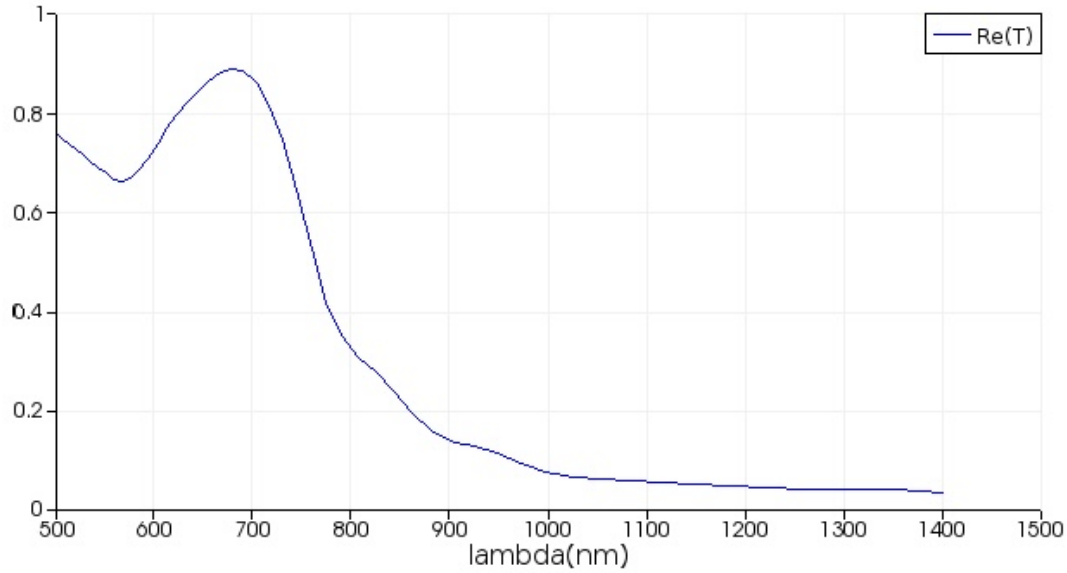


Figure 4: Mie simulation for core-shell particle with gold core (a) Mie absorption coefficients (b) Mie efficency for scattering, absorbtion, extinction and backscattering.(c)

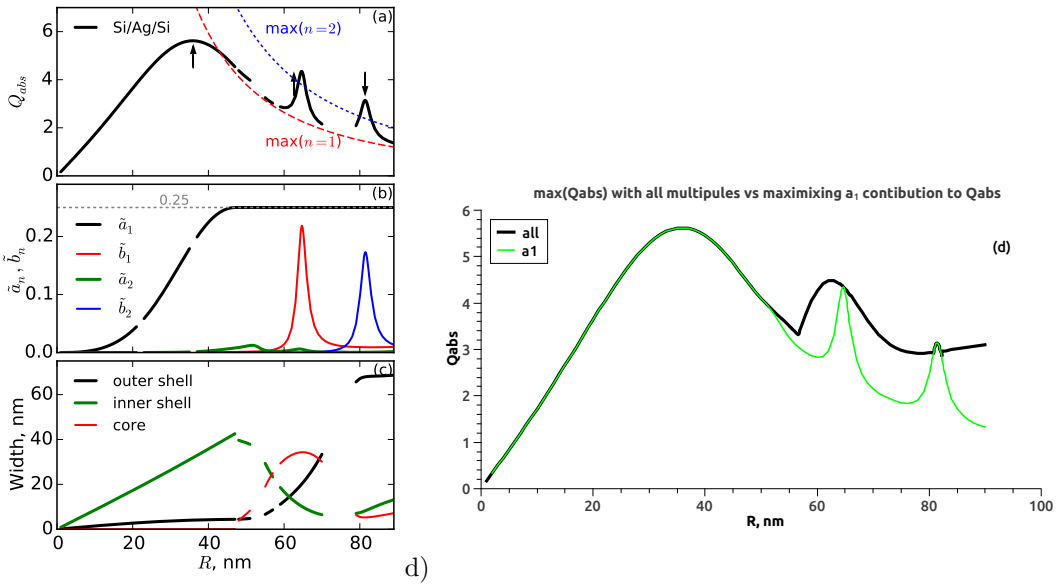


Figure 5: Mie simulation for core-shell particle with gold core (a) Mie absorption coefficients (b) Mie efficency for scattering, absorbtion, extinction and backscattering.(c)

Reviewer #2 comments

> 1. As we can find from the manuscript, the highest absorption efficiency is achieved for a Si/Ag core-shell structure, which is not located in the super absorbing regime. Moreover, the authors also claimed that from practical aspect, the core-shell structure (not in the super absorbing regime) could be easier and cheaper to fabricate than three layered structure (in the super absorbing regime). Therefore, the authors should clearly clarify what are the advantages or significances of the super absorption nanoparticles?

We added a sentence to the end of first paragraph of page 3 right column after "From a practical point of view, it is quite important that the maximum can be reached in a bi-layer structure, instead of a triple-layer, since it should be easier and cheaper to fabricate."

New sentencs: "At the same time the best absorption efficency for large particles (with $R >$ 60 nm for provided materials and layers order) was achieved with superabsorption designs, which can be relevant for the case of layer thickness fine control is not available."

> 2. In Fig. 2, we noticed a discontinuity at 80 nm. The authors explain it as the design supporting electric dipole and magnetic quadrupole has larger ACS. However, this explanation is not clearly to me since it is lacking physics behind this phenomenon. The authors should clarify why the magnetic quadrupole only plays a significant role in this small wavelength range.

The sort answer it that it was not possible to fit magnetic quadroupole to the particle of smaller size, however, it is hard to keep it been efficient for larger sizes. However, the contribution of the electric diple is also very important.

To present this idea in more details we run an optimization with changed fitness function - we requested to maximize the impact of electric dipole to the absorption efficiency.

> 3. In Fig. 3 (c), the authors observed a flat top of electric dipole resonance. They attributed this flat resonance to the excited several electric dipole resonances with close resonance frequencies. Nevertheless, as we can see in Fig. 3 (d), even without considering the resonances located in outer and inner shell, the resonance inside the core is much broader than the other two cases. The authors should explain this broadened resonance clearly.

> 4. Some sentences are not clear to me. For instance, there is a strong conterplay between the increased absorption for larger particles vs size for smaller particles. In summary, I do not think the manuscript is acceptable at its current stage.

Sincerely Yours,
On behalf of the authors,
Konstantin Ladutenko