

Reviewer: 1

Recommendation: Reconsider after major revisions noted.

Comments:

The authors tackle an important existing issue pertinent to plasmon-driven photochemistry, namely the ability to distinguish confidently between the role of hot charge carriers (electron and holes) from that of the local heating following plasmon excitation and decay. They do this by following the kinetics of the silver shell growth over gold nanoparticles purportedly due to the reduction of silver ions in solution both in the dark, at various ambient temperatures, and under illumination. Of course the nub of the issue here, as in previous studies is to estimate confidently the local temperatures that accompanies illumination so as to reliably ascribe the observed rate of silver reduction to one versus the other mechanism. The authors do this by carrying out a calculation of the local temperature increase under illumination using traditional heat absorption and conduction equations. The issue here, as with other such studies is that the thermal calculations as described by the authors calculate steady state temperatures. Such calculations normally cannot account for sometimes rather high temperatures that arise locally. Such high local temperatures arise from the fact that heat dissipation in the immediate neighborhood of illuminated nanoparticles are not efficient and can often lead to higher temperatures (as reported in some early enhanced photochemistry studies) than what is true for the average temperatures on larger length scales, as computed using heat conduction experiments derived for macroscopic heat condition processes. Nevertheless, I believe what the authors have achieved is a step forward and with the appropriate caveats (as well as some editing for language and spelling- British spelling seems to be used) it should be published.

We would like to briefly address the comment of reviewer 1, who writes:

"The issue here, as with other such studies is that the thermal calculations as described by the authors calculate steady state temperatures. Such calculations normally cannot account for sometimes rather high temperatures that arise locally. Such high local temperatures arise from the fact that heat dissipation in the immediate neighborhood of illuminated nanoparticles are not efficient and can often lead to higher temperatures (as reported in some early enhanced photochemistry studies) than what is true for the average temperatures on larger length scales, as computed using heat conduction experiments derived for macroscopic heat condition processes."

We think the reviewer may be referring to the effect due to the presence of a finite heat conductance at the surface of a metallic nanoparticle, sometimes referred to as the Kapitza resistance. Such resistance can lead to inefficient heat dissipation and higher steady-state temperatures than the ones calculated with our equation (1).

However, it has been shown that for gold nanoparticles stabilized by cetyltrimethylammonium-based surfactants, the Kapitza resistance is essentially negligible (see reference 41 in our manuscript: G. Baffou and R. Quidant, Thermo-plasmonics: using metallic nanostructures as nano-sources of heat, *Laser and Photonics Reviews* 7, 171–187 (2013)). Furthermore, even a large deviation from the calculated steady-state **local temperatures** would have a negligible effect on the activation mechanism of our reaction, as

the estimated local temperature increase is of the order of milliKelvins. What is important in our reactions is instead the **local heat generation**, which follows directly from an energy conservation law: all the optical power that is absorbed by the nanoparticles is converted into heat. It is such calculated heat generation that we use as input for our COMSOL modeling and that leads to quantitative agreement between the predicted and measured temperatures.

In order to better explain this point and answer the reviewer's concern we added the following sentence (in bold) in the section entitled "Light propagation and heat transfer":

"From the absorbed power and the nanoparticle density, we can then calculate the local increase in the surface temperature of the Au nanoparticles, δT , using eq (1). **The use of eq (1) is justified, as it has been shown that temperature deviations due to a finite interface conductivity are negligible for Au nanoparticles capped with cetyltrimethylammonium salts.**⁴¹"

Reviewer 1 also suggests to edit the manuscript "*for language and spelling- British spelling seems to be used*", but we could not find any occurrence of British spelling or any typos in the text.

Reviewer: 2

Recommendation: Publish as is in ACS Nano; no revisions needed.

Comments:

Kamarudheen et al. present a combined experimental and numerical study of photo-induced growth of silver in a solution of gold nanoparticles, and separate the effect of plasmon-induced heating from hot-carrier effects. Mechanisms for this interesting growth phenomenon have been hotly debated for many years, and the detailed simulations combining photon scattering and fluid dynamics presented here convincingly show the substantial effect of collective heating at high densities of plasmonic nanoparticles. In addition the paper is written clearly, organized well and is suitable for publication in ACS Nano in its present form.