STRATEGIES TO ENHANCE THE PHOTOSTABILITY OF PLASMONIC PARTICLES

Fulvio Ratto[1,], Lucia Cavigli[1], Sonia Centi[1], Boris Khlebtsov[2], Alessio Milanesi[1,3], Claudia Borri[1], Patrizia Bogani[4], Nikolai Khlebtsov[2,5], Roberto Pini[1]*

1 Istituto di Fisica Applicata 'Nello Carrara', CNR, Via Madonna del Piano, 10, 50019 Sesto Fiorentino (FI), Italy
2 Institute of Biochemistry and Physiology of Plants and Microorganisms, RAS, 13 Prospekt Entuziastov, Saratov 410049, Russia
3 Dipartimento di Chimica 'Ugo Schiff', Università di Firenze, Via della Lastruccia, 3-13, 50019 Sesto Fiorentino (FI), Italy
4 Dipartimento di Biologia, Università di Firenze, Via Madonna del Piano, 6, 50019 Sesto Fiorentino (FI), Italy
5 Saratov State University, 83 Ulitsa Astrakhanskaya, Saratov 410026, Russia
**f.ratto@ifac.cnr.it*

We discuss strategies to improve the stability of photoacoustic conversion from gold nanorods by protecting their shape against overheating by the use of various containment shells, or the implementation of concepts for faster heat dissipation.
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1. Abstract

Plasmonic particles are emerging as a versatile solution for a broad variety of unmet needs at the crossroads of biomedical optics, sensing and imaging, owing to their unique efficiency to enhance, absorb and scatter light. In particular, gold nanorods stand out as a hopeful material combining favourable photophisical and biochemical features for critical applications as the photoacoustic imaging and photothermal ablation of cancer, or, for instance, for photothermal cycling for gene amplification.
However, in some cases, the great efficiency of photothermal conversion of gold nanorods may turn into an issue and a practical limitation, as the input energy may trigger their overheating, reshaping and bleaching, by the effect of premelting, before the pathways of thermal relaxation to the environment may patch over the problem. In particular, in a regime of optical pulses of interest in photoacoustic imaging, typical damage thresholds of gold nanorods fall around few mJ/cm^2 [1,2,3,4], which is below relevant maximum permissible exposure limits, and so amount to a real bottleneck. Here, we discuss different approaches to enhance the photostability of gold nanorods.
The most obvious strategy is to improve their thermal stability, by constraining their shape through the addition of rigid or soft shells. Rigid shells, such as mesoporous organosilica [3] (see Figure 1a), represent an effective tool that may also enable more perspectives for controlled drug release. However, we show that soft shells such as self-assembled monolayers of aromatic thiols are a lightweight alternative that ensures surprising efficiency.
Another possibility is to speed up the thermal coupling to the environment by lowering the thermal resistance at the gold/water interface, for instance, through a rational design of the surface-to-volume ratio of the particles. Examples of this kind are the use of smaller particulates [1], or the addition of rough overlayers obtained by the deposition and galvanic replacement of silver shells (see Figure 1b). We note that this strategy is rather counterintuitive, because a larger surface-to-volume ratio means a lower thermal stability. But this effect is often more than counterbalanced by that of heat dissipation.
Another option that places less emphasis on the side of materials engineering is to redistribute the input energy among more particles through customization of the optical source. In this context, the introduction of unpolarised light, LED lamps or supercontinuum lasers may all represent possible roadmaps to involve larger fractions of gold nanorods in their heterogeneous mixtures.

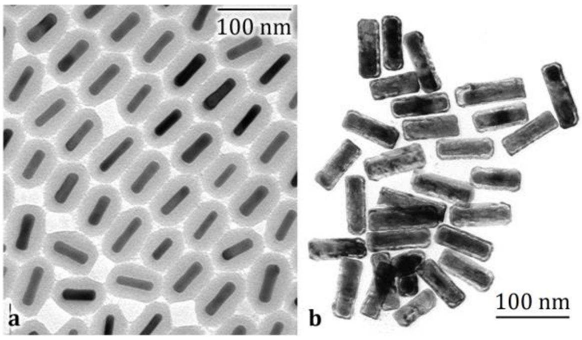

Figure 1: Transmission electron micrographs of gold nanorods coated with mesoporous organosilica (a) or a rough Ag/Au overlayer (b)

We discuss cases where one solution may be more pertinent than the other, as well as synergistic combinations that collectively target a readier penetration of plasmonic particles into the biomedical practice.
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