

Optical properties of Au/Ag nanorods as imaging labels for biological applications

Boris N. Khlebtsov^{a,b}, Vladimir Bogatyrev^b, Vitaliy Khanadeev^b and Nikolai G. Khlebtsov^{a,b}

^aInstitute of Biochemistry and Physiology of Plants and Microorganisms,
Russian Academy of Sciences, 13 Pr. Entuziastov, Saratov 410049, Russia

^bSaratov State University, 155 Moskovskaya St., Saratov 410026, Russia

ABSTRACT

We describe experimental results on synthesis and optical properties of gold nanorods with silver coating. The formation of silver nanoshell were controlled by the shift of plasmon resonances (PR) of extinction and light scattering, by appearance of characteristic Ag peaks in the EDX spectra of samples, by TEM data, and by visual inspection of changes in colloid colors. The basic advantage of the described protocol is the fine controlled tuning of the extinction and light scattering PRs of two-layered nanorods from NIR to 550 nm with an accuracy of about of 10 nm. Such particles may find promising applications in biophotonics, bioimaging of cellular structures, contrasting of OCT tissue images, and other fields.

INTRODUCTION

For optical imagings at the cell and tissue levels, the most popular labels are quantum dots (QD), fluorescence labels rather than noble metal nanoparticles. The fluorescent labels (as well as QDs) have several disadvantages at the biology imaging field such as: the quenching of fluorescence and the biological toxicity of most QDs. Furthermore, there are difficulties in the functionalization of QDs while transferring the particles from primary the organic synthesis phase to a water-saline environment, which needs to be done with all biospecific molecular probes. Most of these difficulties may be overcome by using PR particles, but the optical properties of these particles should be tuned in a proper manner to ensure the desired resonance quality and position. In particular, the solid gold and silver spheres are poor candidates for multicolor labeling, as their size-dependent spectral tuning covers rather narrow spectral intervals.

Among the numerous particle structures made available through the existing synthetic technologies [1] the gold nanorods are of significant interest for applications to optical imaging [2], because its scattering spectra can easily be tuned to a wide spectral band [3]. However, the maximum of scattering spectra of such particles belongs only in NIR range. The change of nanorods the material from gold into silver can solve this problem and allow making labels in whole visible and NIR range. Unfortunately, despite of gold, there are no any reproducible protocols for silver nanorods synthesis. These two points give us idea to make a novel type of nanoparticles – Au/Ag nanorods

with good and reproducible protocol of synthesis (like from gold nanorods) and with narrow and tunable in whole visible-NIR range scattering peak (like from silver nanorods).

RESULTS AND DISCUSSION

Ag/Au nanorods were prepared using two-stage protocol (see Fig. 1). At the first stage the gold nanoparticles we use here as template were produced by the seeded-growth technique of Nikoobath et al. [4] in a highly concentrated aqueous surfactant solution. The average thickness of the particles was 11 ± 0.8 nm and length 40 ± 3 nm which correspond the plasmon resonant peak at 810 nm.

For silver coating we first remove excessive growth solution from the gold rods, which contains additional silver and gold ions, by centrifuging once and re-dispersing in 0.1 M CTAB. 0.8 ml of the gold rods solution is diluted in 4 ml of 1 wt % aqueous polyvinyl pyrrolidone (PVP, Aldrich). To the mixture of PVP, CTAB and gold nanoparticles, different amounts of 1 mM AgNO_3 (Sigma-Aldrich, typically $180\mu\text{L}$) and typically $100\mu\text{L}$ 0.1 M ascorbic acid (Sigma) were added. Raising the pH by adding $200\mu\text{L}$ of 0.1 M NaOH (Merck) initiates the coating reaction and leads to a color change within a few minutes. We keep the molar ratio between AgNO_3 , ascorbic acid and NaOH constant (0.6:25:50) when the concentration of silver nitrate is changed.

The freshly prepared silver-coated gold nanorods solutions show strong colors, varying from red, blue, bluish green, to purplish red, with an increasing thickness of silver coating. Also we saw great changes in extinction and scattering spectra of suspensions (see Fig. 1). For this kind of gold nanorods template we observed the spectral tuning in range from 810 nm to 590 nm depends on

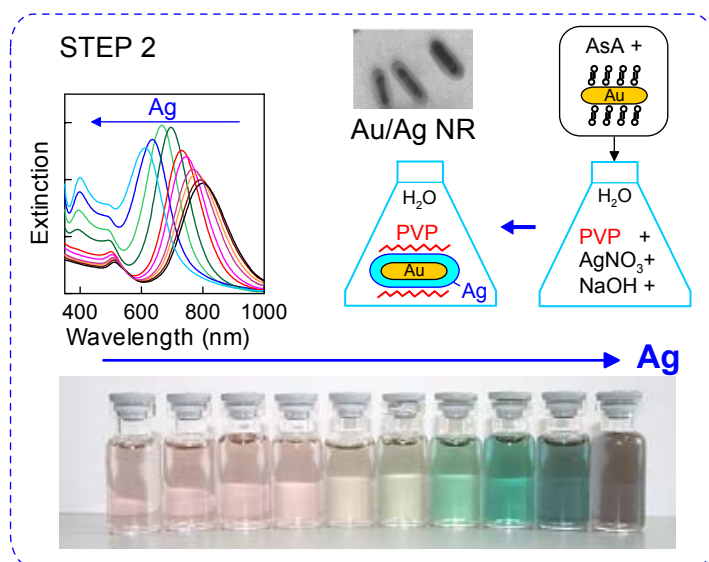


Fig. 1 Scheme of Au/Ag nanorods synthesis together with extinction spectra and image of obtained suspensions

silver concentration and the silver shell thickness. Our TEM measurement shows a different thickness of homogeneous silver layer coated on the surface of gold nanorods for different amounts of silver added (the thickness of silver layer varying from 1 to 4 nm). The same results we also obtained by using another gold nanorods (plasmon resonance 700 nm) sample as template for silver

coating. But in this case our spectral tuning was in range from 700 to 500 nm (data not shown). Long-term storage at room temperature causes the coated nanorods to decompose and the solution takes on a yellowish color, characteristic of silver nanoparticles. We have found that the optical properties of gold/silver nanorods can be stabilized by addition of polyacrylic acid. Also this approach has been described before for gold nanorods biofunctionalization [5].

To summarize, the basic advantage of the described protocol is the fine controlled tuning of the

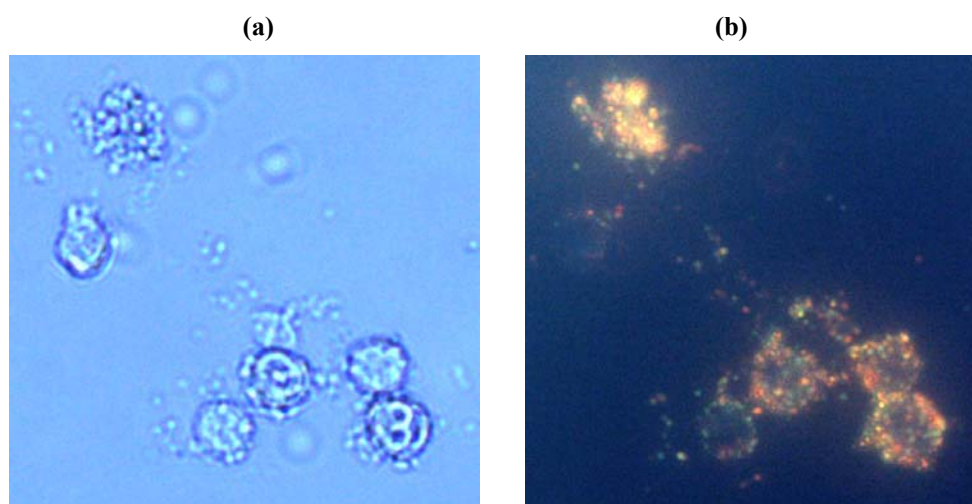


Fig. 2 Regular (a) and dark-field (b) microscopy images of rat macrophages cells labeled with Au/Ag rod.

extinction and light scattering resonance of two-layered Au/Ag nanorods from NIR to 550 nm with an accuracy of about of 10 nm. Such particles may find promising applications in biophotonics, bioimaging of cellular structures, contrasting of OCT tissue images, and other fields. As an example Fig. 2 shows regular and dark-field microscopy images of rat macrophages cells labeled with Au/Ag rod. Colored spots correspond single nanoparticles (deposited on the cell surface) scattering.

REFERENCES

-
1. Y. Xia, N. J. Halas, *MRS Bulletin* **30** (2005) 338.
 2. I. H. El-Sayed, X. Huang, M. A. El-Sayed, *Nano Lett.* **5** (2005) 829.
 3. K.-S. Lee, M. A. El-Sayed, *J. Phys. Chem. B.* **109** (2005) 20331.
 4. B. Nikoobakht, M.A. El-Sayed, *Chem. Mater.* **15** (2003) 1957.
 5. C. Murphy, *Chem. Comm.* (2008) 544