

SYNTHESIS OF GOLD NANORODS WITH DIFFERENT ASPECT RATIO FOR ORGANIC PHOTOVOLTAICS

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1. Introduction

Organic photovoltaic cells (OPV) are attracting much attentions due to low-cost raw materials, high-throughput processing, low weight and mechanical flexibility [1-3]. Incorporation of noble metals, mainly gold nanoparticles, is promising for OPV applications. Gold nanorods are able to confine resonant photons and to induce coherent surface plasmon oscillation of their conduction band electrons. At the resonant frequency, called the local surface plasmon resonance-LSPR, a large enhancement of the particle light absorption and scattering occur [4]. The photocurrent LSPR enhancement from spherical Au nanoparticles is limited to a region around 530 nm [5] but rod-like Au nanostructures are attractive because their longitudinal plasmon absorption can be tuned from visible, over NIR up to the infrared region by simply manipulating the aspect ratio. This provides unique opportunity for utilizing the low energy part of the solar spectrum [1]. The plasmon band of Au nanorods is split in two: the longitudinal plasmon band, corresponding to light absorption and scattering along the long axis of the particle, and the transverse plasmon band, corresponding to light absorption and scattering along the short axis of the particle [6,7]. Gold nanorods can be prepared by wet chemical synthesis in aqueous solutions with good dispersion, their size, shape, density being easily controlled by reaction conditions. This approach is less expensive comparing with other methods, e.g. laser ablation, electron beam lithography, etc [1].

In this article, we describe the modified seed-mediated growth synthesis of Au nanorods in aqueous medium according to C. Murphy [6] designed for applications in photovoltaic devices with different aspect ratio (redshift of longitudinal LSPR). It is a method which is divided into two different steps. The first one is preparation of spherical gold particles by metal salts reduction in water which serve as a seeds to the formation of nanorods. In the second step, the rods grow from these seeds applying a structure-directing agent, namely cetyltrimethylammonium bromide (CTAB).

The absorption spectra showing different plasmon resonance wavelengths for nanorods with various aspect ratios were detected by the UV/VIS/NIR spectrophotometry (SolidSpec 3700, Shimadzu). Stability of nanorod solutions was examined by the zeta potential measurement on Zetasizer Nano ZS 90 (Malvern Instrument).

2. Experimental procedures

2.1. Chemicals

Gold(III) chloride hydrate (52%) Au basis, hexadecyltrimethylammonium bromide (CTAB, 98%), sodium borohydride (98%) were obtained from Sigma-Aldrich (Slovakia); sodium citrate (99%), L-ascorbic acid (99%) were obtained from mikrochem (Slovakia).

2.2. Preparation of gold nanorods

Preparation is divided into two parts- synthesis of *seed solution* and *growth solution*.

Preparation of the seed solution:

- 1) chloroauric acid (2 mM) in water was reduced by ascorbic acid (0.11 M) at room temperature and added to the sodium hydroxide solution (0.1 M)
- 2) chloroauric acid (0.02 M) was reduced in water environment under ambient atmosphere at room temperature with a sodium borohydride (0.1M) and electrostatically stabilized by sodium citrate (0.01 M)
- 3) 1 ml solution (step 2) was added to the mixture (step 1) under stirring to achieve 5 nm seed particles

Growth of seeds:

growth solution: HAuCl₄ (0.24 mM) and CTAB were mixed at room temperature with an ascorbic acid to reduce the gold ions.

- 1) the seed solution (1 ml) was added to the growth solution (9 ml) which contained a weak reducing agent, namely ascorbic acid, which is an ideal secondary reducing agent; it reduces the gold precursor Au³⁺ to Au¹⁺ in the growth step and CTAB which supports the controlled growth of the final nanorod shape
- 2) the solution from step 1 (1 ml) was added to the growth solution (9 ml)
- 3) the solution from step 2 (10 ml) is added to the growth solution (90 ml)

In the next step, the Au nanorods were centrifuged to decrease of size distribution, to remove abundant CTAB surfactant and redispersed in water.

3. Synthesis and diagnostics of nanorods

To obtain various nanorod aspect ratios, a modified seed-mediated growth synthesis was used. This method involves surfactant-directed growth of nanorods from spherical seeds which were prepared by reduction of a metal salt (chloroauric acid) with a mild reducing agent (ascorbic acid) in the water environment, in air, at room temperature. Subsequently the sodium hydroxide was added. Adding a proper amount of sodium hydroxide produces concentrated uniform spherical gold nanoparticles with low size distribution but with poor stability. To obtain a stable nanoparticle solution, a second colloidal solution was prepared composed of chloroauric acid which has been reduced with strong reducing agent (sodium borohydride) and capped with a citrate group (sodium citrate). Afterwards the first and second solutions were mixed to yield 5 nm spherical seed particles which are stable for several months.

The application of the "structure-directing" agent- CTAB is crucial for obtaining nanorods. It has been demonstrated that the presence of bromide ions is crucial to making gold nanorods [6]. The affinity of bromide for gold is slight, hence high concentrations of bromide would be required to drive the ion onto gold surface. Therefore, lowering the amount of CTAB in solution, which would lower the Br⁻ concentration, would favour spherical particles. This is

indeed the case, since very high concentrations of CTAB are required to synthesize nanorods using seed-mediated growth method. The concentration of CTAB in reaction mixture is a critical parameter for nanorod growth. In our case, three different concentrations of CTAB (0.015 M; 0,025 M; 0.045 M) were used. Gradual addition of growth solution during the reaction produced a colour change from the light pink to intense violet, suggesting the presence of ligand-substituted anions such as $[\text{AuCl}_3\text{Br}]^-$, or CTAB-Au(III) complexes, or both. Addition of the ascorbic acid into the reaction mixture leads to a colour change from intensive violet to colourless suggesting that the Au (III) complexes were initially reduced to aqueous Au (I) anions, such as $[\text{AuCl}_2]^-$, rather than Au (0). Ascorbic acid is not capable of fully reducing the metal salt all the way to the elemental metal; but upon addition of the seeds, the reaction is thought to take place on the seed surface and be autocatalytic, to produce larger nanoparticles.

The presence of gold nanorods with various aspect ratios in colloidal solution has been monitored by UV/VIS spectrophotometer and scanning electron microscopy. The absorption spectra (Figs. 1-3). exhibit two plasmonic peaks whose position and shape depend on two factors: size dispersion and aspect ratio of particles. The absorption maximum from transverse plasmon band depends on diameter of the seed particles and was recorded approximately at 530 nm. The position of the longitudinal plasmon band redshift depends on the aspect ratio of nanorods and was recorded at 670 nm for 0.015 M concentration of CTAB (Fig. 1), at 700 nm for 0.025 M concentration of CTAB (Fig. 2), and 725 nm for 0.045 M CTAB (Fig. 3). The samples for scanning electron microscopy SEM (JEOL 7500F) studies were prepared by casting a drop (100 μl) of the nanoparticle solution onto a silicon substrate and air-drying. Comparison of SEM images and UV/VIS spectra shows that the aspect ratio leads to the redshift of the longitudinal plasmon band $\text{LSPR}_{\text{long}}$, providing thus possibility of tuning the absorption spectrum.

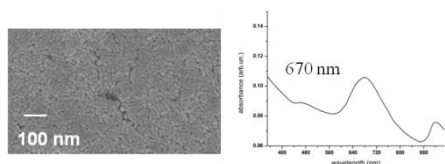


Fig.1. SEM image and UV/VIS spectrum of Au nanorods with aspect ratio ~ 20 and 0.015 M CTAB concentration deposited on silicon substrate.

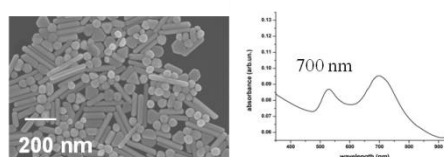


Fig.2. SEM image and UV/VIS spectrum of Au nanorods with aspect ratio ~ 40 and 0.025 M CTAB concentration deposited on silicon substrate.

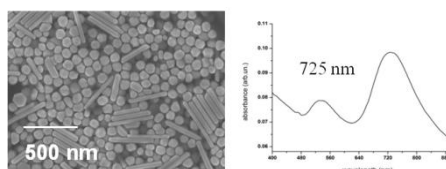


Fig.3. SEM image and UV/VIS spectrum of Au nanorods with aspect ratio ~ 60 and 0.045 M CTAB concentration deposited on silicon substrate.

4. Conclusion

In summary, we investigated shape manipulation of gold nanorods by different concentrations of the "structure directing" CTAB surfactant accompanied by a redshift in the $\text{LSPR}_{\text{long}}$ band of the absorption spectrum for application in the organic photovoltaic cells.

Our results demonstrate that the aspect ratio of Au nanorods can easily be changed by changing the concentration of CTAB. Enhanced concentration of CTAB surfactant redshifts $LSRP_{long}$ while opposite takes place at reduced CTAB concentration. However, the concentration of CTAB in the reaction mixture can be reduced only to a certain limit in order to maintain the stability of the gold nanoparticles in solution. The zeta potential measurements of nanoparticles in a colloidal solution (46.9 mV at 0.015 M CTAB; 37.6 mV at 0.025 M CTAB; 35.9 at 0.045 M CTAB) monitoring the thickness of the electrical double layer around the nanoparticles show sufficient stability of Au nanorods for all CTAB concentrations. The presented method of Au nanorod synthesis with various aspect ratios and adjustable plasmon bands has direct implications for preparation of tailored plasmonic nanostructures for organic photovoltaic cells.

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