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Tuning the plasmon resonances of gold nanoparticles by controlling their size and shape

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The optical properties of noble metal nanoparticles are tunable throughout the visible and near-infrared region of the spectrum as a function of their size, shape, aggregation state, and local environment. In this work, we report the synthesis of gold nanoparticles of different size (from 18 to around 100 nm) and shape (spheres, rods, stars) and demonstrate the tunability of their surface plasmon resonances. Transmission electron microscopy and UV-VIS absorption spectroscopy were employed for characterization.

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1. Introduction

When the size of a material is reduced to the nanometer length scale (which is the length scale of the electronic motion), its electronic and thus optical and chemical properties change tremendously. In semiconductor nanoparticles, the property change results from quantum confinement of the electronic motion [1]. In metals, the properties of the surface become dominant and give nanoparticles new properties [2]. As for example, when noble metals interact with visible light, the coherent collective oscillation of free electrons - which is called surface plasmon resonance (SPR) - induces large surface electric fields which greatly enhance the radiative properties of gold and silver nanoparticles [3]. This makes the absorption cross-section of these nanoparticles orders of magnitude stronger than the strongest absorbing molecules and the scattered light becomes orders of magnitude more intense than the fluorescence of organic dyes.

Spherical gold nanoparticles show a single, strong SPR absorption band in the visible region around 520 nm. The absorption results from the dipole oscillations of the free electrons with respect to the ionic core of nanoparticles. On the contrary, for particles of anisotropic shapes, several plasmon resonance modes could appear from visible to near infrared (NIR) associated with the various orientations of the particle axes relative to the electric field of light [4]. The SPR resonances which appear in NIR region of spectrum are of significant biological importance, as NIR domain represents the only spectral window for both therapeutic and imaging applications in tissue because the tissue do not have significant absorption in this range of wavelengths. Therefore, the synthesis of gold nanoparticles which exhibit strong NIR absorption is essential for applications in biochemical sensors [5], biological imaging and medial therapeutics [6] as well as substrates for surface-enhanced vibrational spectroscopy [7]. However, the synthesis of noble-metal nanoparticles of anisotropic shape (nanorods, prisms, cubes, star shape, core-shells) in high yield remains a challenge for laboratories, requiring complex and time-consuming steps such as morphology transformation or seeded growth process.

In previous papers we have proposed a we-chemistry strategy for fabrication of multilayers of gold nanoparticles [8] and studied organic molecules deposited on gold nanoparticles [9].

This work is aimed at tuning the SPR of gold nanoparticles from visible to NIR spectral region by controlling their size and shape via chemical synthesis routes.

2. Experimental

In our experimental protocol, the following reagents were used: tetrachloroauric acid ($HAuCl_4$), trisodium citrate, cetyltrimethyl ammonium bromide (CTAB), sodium borohydride, silver nitrate and ascorbic acid from Merck, Germany.

For the synthesis of spherical gold nanoparticles, the citrate reduction method has been employed as described in literature [10].

For the synthesis of nanorods and star-shape particles, a seed-mediated growth method at room temperature in two steps has been employed [9, 10]. In the first step a seed spheres solution of 3-5 nm gold nanocrytals was prepared. In the second step, the growth of gold nanorods from as prepared seed nanoparticles in presence of CTAB, sodium borohydride, $AgNO_3$ and ascorbic acid was used. The nanorods were concentrated and separated from solution by centrifugation. The supernatant, containing mostly CTAB molecules and gold ions, was removed and the solid part containing rods was redispersed in ultrapure water. The as synthesized nanorods in water are coated with a bilayer of CTAB molecule being stable at room temperature for many months. For the synthesis of star shapes of gold, in the first step the seed particles were prepared in absence of surfactant. The protocol for synthesis of star shape is similar with that of gold nanorods.

A JEOL JEM 1010 transmission electron microscope was used to picture the gold nanoparticle's size and shape. The UV–vis absorption spectra of colloidal solution were recorded with a Jasco V-530 UV–vis spectrophotometer using unpolarized light.

3. Results and discussion

The absorption spectrum of gold nanospheres in water is shown in figure 1. The SPR absorption occurs at 520 nm, as predicted by the following Mie formulae for isolated, round shape particles:

$$\sigma_{\text{ext}}(\omega) = 9\,\frac{\omega}{\text{c}}\,\varepsilon_{\text{m}}^{3/2}\,\text{V}\,\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_{\text{m}}]^2+\varepsilon_2(\omega)^2} \qquad (1)$$

where V is the particle volume, ω is the angular frequency of the exciting light, c is the speed of light, and a_{m} and $\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega)$ are the dielectric functions of water and the gold, respectively. From the above equation, it can be seen that the peak position of the surface plasmon absorption band is dependent on the size of the metal nanoparticles as well as the dielectric constant of the metals as well as the medium surrounding the particles. Indeed, following the same experimental procedure and modifying the ration between reagents, we synthesized nanospheres with size ranging from 20 nm to ~100 nm. The measured SPR bamds are slightly red shifted from the spectrum shown in Fig. 1 (see the doted vertical line in figure 1). With increasing the nanosphere diameter from 20 to 100 nm, the redshift was from 520 to 560 nm and the bandwidth increases a little bit as the particle diameter increases [13]. Previosly, we demonstrated that self-assemblies of such gold nanoparticles on solid substrate can serve as very useful Surface Enhanced Raman Scattering (SERS) substrate to detect molecules adsorbed on gold by using different laser lines [14,15]. However, the SPR tunability of such spherical particles with their size remains limited to be useful for most biomedical applications in the NIR window. For current in vivo imaging and therapeutic applications, the optical resonance of the nanoparticles is strongly desired to be shifted from visible to the near-infrared (NIR) region, where the tissue transmissivity is the highest [13].

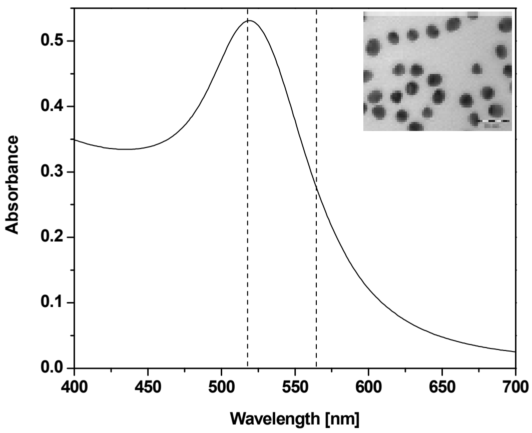

Fig. 1. UV-VIS absorption spectrum of 18 nm gold nanospheres. The inset shows the TEM image of gold nanospheres

We noticed that by modifying the diameter of nanospheres there is not enough shift for the SPR band. Therefore, we adopt a different solution and make changes in the shape of nanoparticles by introducing morphological transformation from spheres to nanorods or another complex shape like star-shape. Thus, by changing the shape of gold nanoparticles we were able to tune the SPR band much more exetensivly. Indeed, as prepared nanorods exhibit a new plasmon band located at higher wavelengths, in addition to the plasmon band around 520 nm (see Fig. 2). Gold nanorods have two plasmon absorption peaks, the shorter wavelength band is attributed to the transverse surface plasmon resonance while the band which appears at longer wavelength corresponds to the longitudinal surface plasmon resonance [10]. For the spectrum in Fig. 1 the corresponding dimensions of synthesized gold nanorods as resulted from TEM picture are 90 ± 10 nm in length and 10 ± 1 nm in diameter (see inset in figure 2). We mention that the nanorods are characterized by their aspect ratio which is the ratio of the nanorod's long axis to the short one. The absorption of the gold nanorod is very sensitive to the aspect ratio of rods [11], the longitudinal plasmon absorption bands being tunable by chemical synthesis from the visible to the near-IR. In our work the longitudinal plasmon band has been shifted from 670 to 1017 nm as function of the particle aspect ratio.Simulation methods have also demonstrated a linear dependence of the longitudinal mode maximum with the aspect ratio of nanorods while transverse and multipolar modes remain unchanged [13].

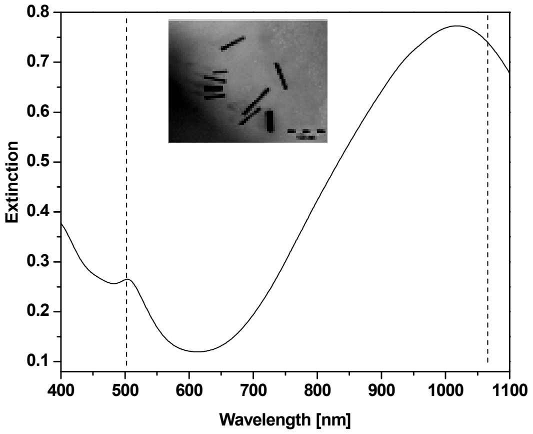

Fig. 2.UV-VIS extinction spectrum of nanorods. The inset shows the TEM image of gold nanorods

The third synthesized nanoparticles were of star like shape. It can be seen form Fig. 3 that such nanostructures exhibit two close peaks situated in the visible and NIR region of the spectrum. A transmission electron microscopy image of synthesized nanostar is presented in inset to figure 3.In the case of gold stars the peak centered at 724 nm is assigned to be similar to the longitudinal plasmon resonance due to the elongated structure of nanostars. The 637 nm peak could represent the transverse plasmon resonance of the tips, which is also seen for gold nanorods, or partially to the presence of slightly asymmetric spherical colloids in the solution [11,12]. The origins of plasmon resonances in such particles is difficult to identify and could be assigned to the hybridization between plasmons associated with the core of particle and the individual tips of the particle. It is plausible that the low-energy bonding nanostar plasmons are primarily composed of tip located plasmons but with a contribution from the core plasmons [16]. The size of nanostar of ~100 nm was determined from TEM image.

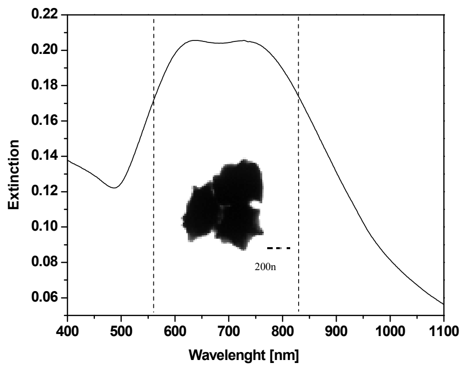

Fig. 3. UV-VIS extinction spectrum of star shaped gold nanoparticles. The inset represent the TEM image of star shaped gold particles.

4. Conclusions

In this work we have demonstrated the tunability of plasmon resonances of gold nanoparticles by changing their size and shape. Thus, the positions of surface plasmon resonance peaks could be continuously shifted from the visible, i.e from 520 nm for gold nanospheres to the near infrared region, i.e. 1100 nm for long gold nanorods. Moreover, the SPR tunability by controlling the aspect ratio (in the case of nanorods) or by inducing complex morphological transformation (in the case of nanostars), makes such nanostructures the ideal candidates for contrast agents in biomedical imaging or SERS application in near-infrared region. Our future work proceeds toward bio-functionalizing of the surface of as synthesized nanoparticles in order to render them biocompatible with intracellular components.

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