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Synthesis and tuning of gold nanorods with surface plasmon resonance

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ABSTRACT

Gold nanostructures in general and gold nanorods in particular due to their plasmon resonance has been employed for many applications, such as biosensors. For the biosensors uses, gold nanorods remain popular and reproducibility of them is the most important and critical. In the present work we used six different CTAB (Hexadecyltrimethylammonium bromide) products and one BDAC (Benzyldimethylhexadecylammonium chloride) with varying silver nitrate concentration in the seed-mediated growth of gold nanostructures. We synthesized gold nanorods with varying aspect ratio up to 5.5 with a longitudinal surface plasmon resonance peak from 670 to 950 nm. We obtained excellent rod-shape gold nanostructures witch were reliable and reproducible with our method based on common seed-mediated growth. The synthesized nanostructures were characterized by UV–visible spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction (XRD). Here, we report our method in more detail as a user-friendly guide for the production of gold nanorods and tuning of their aspect ratios.

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1. Introduction

People have studied the gold nanorods due to their ability in inducing the localized surface plasmon oscillations of the conduction band electrons and confining resonant photons in an small cell [see Ref. [1] and details therein]. This strong plasmonic light scattering and light absorption allows for the sensing applications [2]. The surface plasmon resonance (SPR) can thus been produced with interaction between gold nanoparticles and incident light, which cause the electrons undergo a collective coherent oscillation in resonance with the frequency of light and a charge separation between the free electrons and the ionic metal core. The key issue is that the SPR condition is strongly dependent on the particle size, shape and structure of sample. Although many researchers have worked and studied the spherical gold nanoparticles as good candidate in medical applications, some recent studies and our present study demonstrated that gold nanorods due to their strong SPR bands in the visible, IR region and electron oscillations in one of two directions (It depends on the polarization of the incident light: the short and long axes) can be so desirable issue (see next sections). Thus LSPRs band is split into two bands due to the cylindrical symmetry and excitation of collective oscillations of conduction electrons of nanorods and two peaks seen in the UV–vis spectrum [3].

Gold nanorods is popular for plasmonic applications. Because of the unique properties, the ability to synthesis in high quality using seeded crystallization form solution, the adjustability of plasmon resonance by varying the aspect ratio (AR, ratio of the length to the width of gold nanorod), excellent tunability and biocompatibility, they are attractive candidates for biological, biomedical and biosensing applications [1,2]. Some of these applications depend on anisotropic optical and electronic properties such as LSPR, which can be tuned and controlled by the aspect ratio (AR, ratio of the length to the width of gold nanorod) [2,4].

Gold nanorods exhibit a weak transverse surface plasmon resonance that fixed at around 520 nm (±10 nm) and intense longitudinal surface plasmon resonance, whose wavelength can adjust

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Table 1
Stock solutions with their concentrations.

Material (product code)	Concentration (M)	Volume (mL)	Weight (g)
CTAB (52370)	0.1	100	3.7964
CTAB (H5882)	0.1	100	3.7189
CTAB (H9151)	0.1	100	3.6813
CTAB (227165000)	0.1	100	3.6813
CTAB (A15235)	0.1	100	3.7189
CTAB (219374)	0.1	100	3.7189
BDAC (B4136)	0.1	50	1.9805
$HAuCl_4$ (520918)	0.01	50	0.1971
HCl (1003171000)	1	50	[a]

[a] For make 50 mL solution of HCl 1 M, we slowly added 4.106 mL of stock solution (HCl 37%, 12.18 M) to 12.5 mL DIW. Adjusted the final volume of solution to 50 mL with DIW.

Table 2
Fresh solutions with their concentrations that used in our experiments.

Material (Product Code)	Concentration (M)	Volume (mL)	Weight (g)
Vitamin C (A0278)	0.1	1	0.0176
$AgNO_3$ (209139)	0.006	1	0.0010
$NaBH_4$ (198072)	0.01	10	0.0039

to 650–1300 nm [1,5–7]. Therefore, fast, easy, efficient and reliable methods for synthesis of gold nanorods with a broad range of LSPR is necessary and highly desirable [6,8].

The most popular method to produce gold nanorods is seed-mediated growth, which was pioneered by Murphy et al. [9] and was developed by El-Sayed et al. [10]. There are several modified methods based on the original techniques [11–20]. Although the synthetic methods are clear and simple, the possibility of reproducing them is low, because there are many tips and tricks for achieving sufficient reproducibility [6] also synthesis of gold nanorods depend on many parameter that must be met, including quality of water, chemical suppliers [6], ambient temperature of synthesis and etc.

Smith and Korgel used CTAB products from different suppliers and reported "good" CTABs to gold nanorods formation [17,18]. We used two of the same CTABs (one "good" CTAB and one "suspect" CTAB) and four new CTAB products for comparison and report the result with full details of gold nanorods synthesis method.

2. Experimental

2.1. Materials and suppliers

Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥99.9% trace metals basis, ALDRICH), Silver nitrate ($AgNO_3$, ≥99.0%, ACS reagent, SIGMA-ALDRICH), Sodium borohydride ($NaBH_4$, 98%, ALDRICH), L-Ascorbic acid (Vitamin C, reagent grade, SIGMA), Benzyldimethylhexadecylammonium chloride (BDAC, SIGMA), Hexadecyltrimethylammonium bromide (CTAB) obtained from 5 suppliers (52370, ≥96.0%, SIGMA-ALDRICH), (H5882, ≥98%, SIGMA), (H9151, ≥99% BioXtra, SIGMA), (227165000, 99+%, ACROS), (A15235, 98%, Alfa Aesar), (219374, ≥98% by TLC, Merck), Hydrochloric acid (HCl, 37%, Merck). HPLC-grade water (deionized water, DIW) was used in all of the experiments. Prior to use, all glassware was washed with soap and water, soaked in aqua regia (15 min) (volume ratio $HCl/HNO_3 = 3/1$), rinsed extensively with DIW and dried.

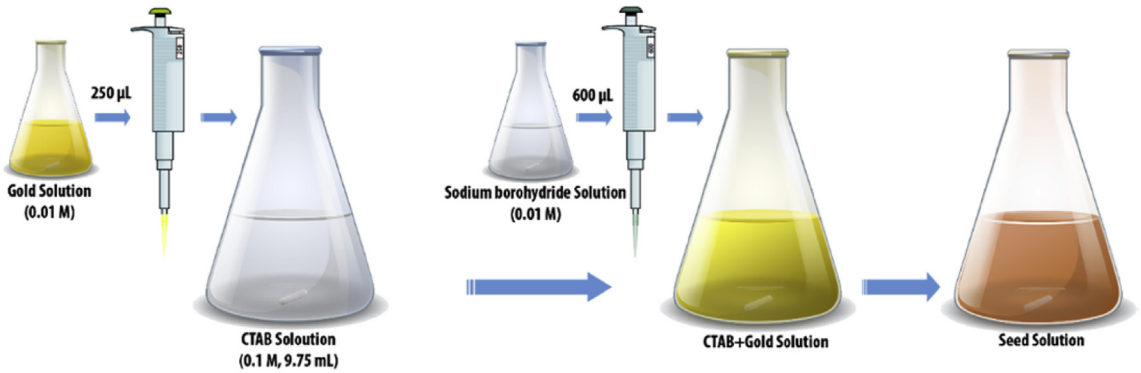

Fig. 1. Scheme of preparing the seed solution.

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