



SYNTHESIS OF SILVER NANOCUBES AND APPLICATION IN SERS

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ABSTRACT

This work describes a rapid route to prepare monodispersed silver nanocubes. By adding a trace amount of sodium tetrahydridoborate and hydrochloric acid to the conventional polyon synthesis, the reaction time was significantly shortened from 16-26 h to 4-5 h, increasing both the rate of production and uniformly the shape of monodispersed nanocubes of 40; 60 and 70 nm in size. The synthesized Ag nanocubes have been characterized by UV-vis, TEM, and XRD. Our results show that the SERS technique is able to detect Rd3B within wide concentration range, i.e. $10^{-14} - 10^{-8}$ M, with lower limit of detection (LOD) being 10^{-14} M. It demonstrates that the Ag nanocubes have potential applications in SERS for the detection of biomolecules and biomarkers (or dye molecules) to early detection and diagnosis of cancers or serious diseases.

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1 INTRODUCTION

In many last decades, metal nanostructures have been extensively studied because of their potential applications in catalysis, photography, optics, electronics, optoelectronics, information storage, biological and chemical sensing, and surface-enhanced Raman scattering (SERS) (Halperin, 1986; Lewis, 1993; Nie and Emory, 1997; Novak *et al.*, 2000; Taton *et al.*, 2000; Templeton *et al.*, 2000; El-Sayed *et al.*, 2001; Kim *et al.*, 2001; Maier *et al.*, 2001; Nicewarner-Peña *et al.*, 2001; Chen and Yang, 2002; Dick *et al.*, 2002; Kamat, 2002; Kim *et al.*, 2002; Murphy and Jana, 2002; Nath and Chilkoti, 2002; Thanh and Rosenzweig, 2002; Roll *et al.*, 2003; Teng *et al.*, 2003; Tkachenko *et al.*, 2003).

Noble metals such as Ag, and Au exhibit surface plasmon excitation by incident light. Chemical enhancement arises through electronic resonance and charge transfer between a molecule and a metal surface; this results in an increase in the polarizability of the molecules. Anisotropic nanomateri-

als (e.g. nanocubes) have enhanced plasmon modes due to transverse and longitudinal polarizations caused by topological differences (Wang *et al.*, 2000; Chan *et al.*, 2003; Wang *et al.*, 2005; Durr *et al.*, 2007). The SERS signal intensity can be affected by electromagnetic enhancement and chemical enhancement, the former being much stronger. Electromagnetic enhancement takes place under conditions of surface plasmon excitation. The electromagnetic field of light on the nanoparticle surface is greatly enhanced by amplification of both the incident laser field and the scattered Raman field through their interaction with the surface.

In general, the impact of metal nanostructures is continually increasing as our group become more capable of producing them with well-controlled sizes and shapes for fine-tuning their properties and further development of emerging applications. It has been demonstrated that the optical and magnetic properties of a metal nanostructure are highly dependent not only on the size of the structure (hollow vs solid) (Kottmann *et al.*, 2001; Sershen *et al.*, 2002; Jackson *et al.*, 2003), but also on the

shape (with various Dimensions of 0D, 1D, 2D, 3D, etc...) (Dick *et al.*, 2002; Kamat, 2002; Kelly *et al.*, 2003; Chen *et al.*, 2006). For example, the surface plasmon resonance (SPR) peak of gold or silver nanorods can shift from the visible to near-infrared (near-IR) region by increasing their aspect ratios (Kim *et al.*, 2002; Murphy and Jana, 2002). Silver nanostructures have been synthesized with a range of different shapes, including spheres, discs, rods, wires, stars, prisms, right bipyramids, and cubes (Jana *et al.*, 2001; Jin *et al.*, 2001; Sun and Xia, 2002; Lin *et al.*, 2003; Wiley *et al.*, 2006).

In this work, we have modified a rapid method called polyol synthesis with using a trace amount of sodium tetrahydridoborate (NaBH_4) as a reductant agent, increasing reaction rate. In addition, our recent success in synthesizing silver nanostructures with well-defined shapes and surfaces (e.g. nanocubes bounded by $\{100\}$ crystallographic planes) also provides a number of model systems to systematically investigate the template-engaged replacement reaction on the nanometer scale (Yu *et al.*, 1997; Jin *et al.*, 2001; Sun and Xia, 2002; Jin *et al.*, 2003; Sun *et al.*, 2003). Herein, we have used Ag nanomaterials with structure 3D (3 Dimension) of nanocube particle to further studies on the SERS mechanism and applications are of great interest, showing that the Ag nanocubes exhibit a good SERS for the detection of Rd3B molecules due to the generation of many "hot spots" by electrostatic force (attract force) between Rd3B molecules and Ag nanocubes' surfaces.

2 MATERIALS AND METHODS

2.1 Materials

Ethylene glycol (EG), silver nitrate (AgNO_3), poly(*N*-vinylpyrrolidone) (PVP; $M_w \approx 55,000$), Rhodamine 3B (Rd3B; $\geq 99\%$), hydrochloric acid (HCl; 36-37%), sodium tetrahydridoborate (NaBH_4), ethanol ($\text{C}_2\text{H}_5\text{OH}$; $\geq 99.5\%$) and acetone (CH_3COCH_3 ; $\geq 99.5\%$) were purchased from Acros and Sigma-Aldrich. All solutions were prepared using deionized water from a MilliQ system.

2.2 Preparation of silver nanocubes

Silver nanocubes (Ag NCBs) were synthesized according to a modification of a previously reported method (Karthikeyan and Loganathan, 2012). Typically, in a 100 mL round-bottomed flask, EG (5 mL) was heated at 140°C in an oil bath with magnetic stirring for 40 min. Next, solutions of the following reagents were added by a micropipette in succession: 1) NaBH_4 (10 mM in EG; 20 μL); 2) after 2 min, quickly, HCl (3 mM in EG; 1 mL); 3) after another 10 min, at a rate of 45 mL/h, AgNO_3 (94 mM in EG; 3 mL) and PVP (147 mM (based

on the repeating unit) in EG; 3 mL). Upon injection of the solution of AgNO_3 , the reaction mixture changed color from milky white, through transparent light yellow and red to ochre while being heated at 140°C . Respectively, after 240; 260 and 300 min, the solution was centrifuged (10000 rpm; 15 min), the precipitated Ag NCBs were washed with acetone, ethanol and then H_2O to remove excess EG and PVP and re-dispersed in deionized water. The average edge length of the Ag NCBs as prepared were ~ 40 ; ~ 60 and 70 nm.

2.3 Characterization

The UV-Vis (absorbance) spectra of particle solutions were measured on a Shimadzu UV-675 spectrophotometer. Transmission electron microscopy (TEM) was recorded on a Philips Tecnai F20 G2 FEI-TEM microscope (accelerating voltage 200 kV). Specimens were prepared by dropping on a copper grid and drying at 60°C in an oven. The powder X-ray diffraction (XRD) pattern of the Ag NCB sample was investigated on a Rigaku Dmax-B diffractometer with a $\text{Cu K}\alpha$ source operated at 40 kV and 100 mA. A scan rate of 0.05 deg^{-1} was used for 2θ between 30° and 90° . Raman measurements were performed on a Renishaw 2000 confocal Raman microscope system. A He-Ne laser operating at $\lambda = 532 \text{ nm}$ was used as the excitation source with a laser power of 20 mW. All Raman spectra were obtained at 10 s exposure time. The laser line was focused onto the sample in backscattering geometry using a 10x objective providing scattering area of $\sim 0.25 \text{ mm}^2$.

2.4 Preparation of SERS substrates

Droplets (50 μL of a 1.18×10^{10} particle mL^{-1} solution) of Ag NCB (with various dimensions of 40 and 70 nm) were spread on silicon wafers ($\sim 1 \text{ cm}^2$), respectively. Aqueous Rd3B solution (10^{-8} M ; 5 μL droplets) was spread on the Ag NCBs' surfaces and kept in the dark for 1 h at room temperature prior to testing. For Rd3B quantification, samples with concentration of 10^{-8} , 10^{-10} , 10^{-12} , 10^{-14} , 10^{-15} , and 10^{-16} M were used. SERS spectra for all samples were measured in triplicate within 10 min over 3 different areas on the sample focus for 10 s (at 25°C). These measurements are reproducible with comparable measurement errors.

3 RESULTS AND DISCUSSION

3.1 Characterization and properties of the silver nanocubes

The UV-Vis spectra of Ag NCBs (40; 60 and 70 nm in edge length) exhibited a main, respective broad band with maximum peaks at 434; 450 and 479 nm and shoulders at 351; 347 and 346 nm.

Figure 1 shows absorption spectra that were obtained with various dimensions of Ag nanocubes at different reaction times of (a) 240 min; (b) 260 and (c) 300 min, respectively.

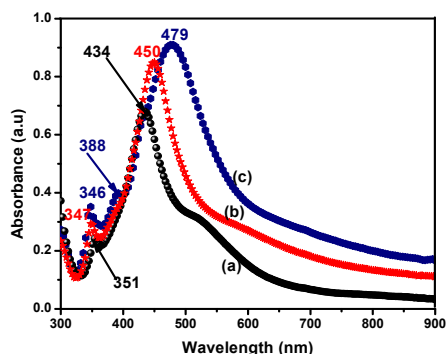


Fig. 1: UV-vis spectra of silver nanocubes dispersed in aqueous solution AgNCBs (a) ~40 nm, (b) ~60 nm, and (c) ~70 nm, respectively

The presence of BH_4^- and Cl^- anions greatly accelerated the polyol synthesis of silver nanocubes due

to a dramatic increase in the reduction rate of silver ions (Ag^+). During the synthesis, we could easily monitor the progress of the nanoparticle production through its color changes and then characterize the evolution of shape using transmission electron microscope (TEM). Figure 2 shows representative TEM images of Ag NCB samples with various particle sizes of 40; 60 and 70 nm and with different reaction times of 240; 260 and 300 min, respectively.

The X-ray diffraction (XRD) pattern of Ag NCBs is also shown in Figure 3. The diffraction peaks located at 38.1° , 44.3° , 64.7° , 77.56° and 81.88° can be indexed to the (111), (200), (220), (311), and (222) planes respectively, of the face-centered cubic (fcc) structure of Ag (JCPDS No. 87-0720). The (200) peak of Ag NCB sample is more intense than the (111) peak that dominates the JCPDS pattern mainly because the cubes are joined at the $\{100\}$ facets and the powder standard is overwhelmed by the lower energy $\{111\}$ facets.

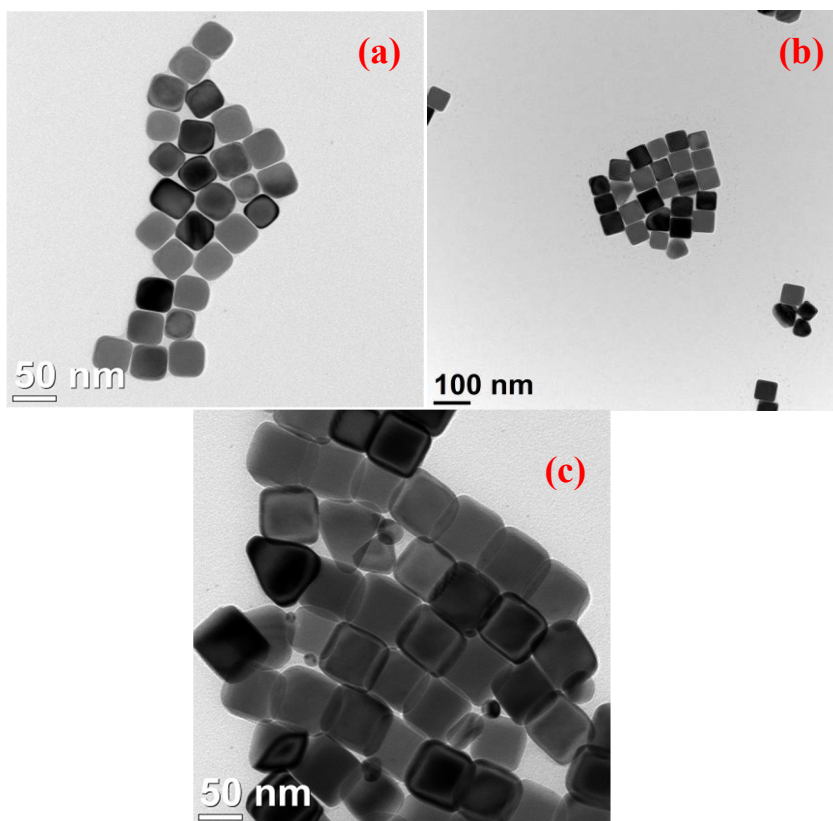


Fig. 2: TEM images of Ag NCBs with different reaction times and dimensions of (a) (240 min; 40 nm); (b) (260 min; 60 nm); and (c) (300 min; 70 nm), respectively

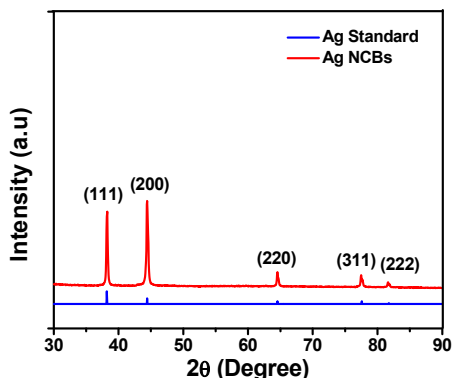
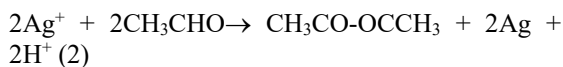


Fig. 3: XRD pattern of Ag NCBs with particle size of 70 nm

3.2 The formation mechanism of the silver nanocubes

In a typical polyol synthesis, silver atoms are formed by reducing AgNO_3 precursor with ethylene glycol through the following mechanism (Blin *et al.*, 1989; Wiley *et al.*, 2005):



Accordingly, we propose the mechanism depicted in equation (1)-(2) for the growth of Ag nanocubes. When the AgNO_3 solution is injected into the EG-HCl/ NaBH_4 solution at 140°C , Ag ions will quickly be reduced by EG (through reactions of (1) and (2)) and NaBH_4 to $\text{Ag}^{(0)}$. Herein, NaBH_4 also plays an important role because they can increase reaction rate of Ag ions to generate a lot of Ag nuclei and then form $\text{Ag}^{(0)}$ atoms to obtain Ag nanocubes (Ag NCBs) structure. Besides, polyvinylpyrrolidone (PVP) is used as one of the most common shape-directing agents in forming of Ag NCBs. These PVP molecules bind strongly to silver surfaces through the quaternary ($-\text{NH}$) and ($-\text{C}=\text{O}$) group and forms a bilayer structure around the particles, thus hindering the retention of most analytes.

3.3 SERS measurement of the silver nanocubes

The SERS intensity of Rd3B on the silicon substrate shown no signal, and the highest signal was found on Ag NCBs with particle size ~ 70 nm (Figure 4 a, c). As shown in Figure 4(c), the peak at ca. 773 cm^{-1} is assigned to the C–H out-of-plane bending mode. The peak at ca. 1148 cm^{-1} is assigned to

the C–H in-plane bending mode. The peaks at ca. 1379 , 1528 , 1585 and 1667 cm^{-1} are assigned to typical aromatic ring vibrations of Rd3B. The enhancement factor of Ag NCBs (~ 70 nm) was about 12 fold-magnitude and 9 times stronger than that of Rd3B on the silicon substrate and on the Ag NCBs (~ 40 nm)– see Figure 4(c, a, b), respectively. This interesting result may be due to the interaction between Ag NCBs in the presence of Rd3B molecules via electrostatic force on their surfaces. The electrostatic force on Ag NCBs' surfaces has been created favorable conditions for the generation of many “hot-spots” at the junction between two nanocubes, increasing the electromagnetic field enhancement.

Since Rd3B was used as a probe molecule in SERS studies it should be very stable and without adsorption in near-infrared region. The Ag NCBs (~ 70 nm) has been shown to be non-destructive, flexible and used to enhance SERS intensity of Rd3B molecules with limit of detection (LOD) at the lowest concentration of Rd3B on the Raman signal (Figure 5). Besides, the SERS spectra is dependent on Rd3B molecules' concentration with typical aromatic ring vibrations of Rd3B (e.g., 1148 , 1216 , 1379 , 1528 and 1667 cm^{-1}). Lowest concentration (10^{-14} M) of Rd3B in solution can still be detected. Accordingly, the present method may also be used in the relatively quantitative detection of biomolecules in organisms with the advantages of simplicity and sensitivity.

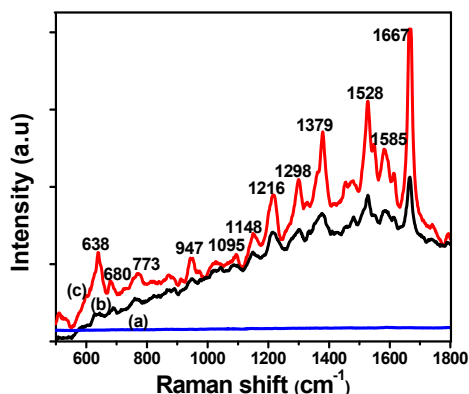


Fig. 4: Raman spectra of Raman spectra of (a) 10^{-8} M rhodamine 3B (Rd3B) on the silicon wafer and 10^{-8} M Rd3B on the silver nanocubes (Ag NCBs) with various dimensions of (b) ~ 40 nm and (c) ~ 70 nm, respectively

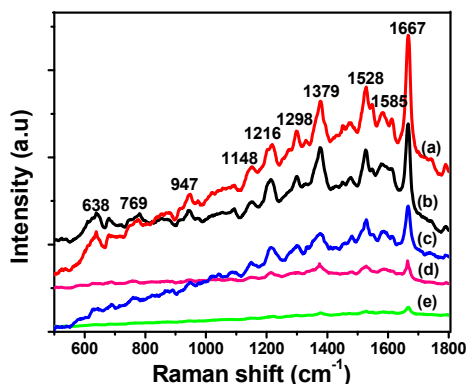


Fig. 5: Representative SERS spectra of rhodamine 3B (Rd3B) on silver nanocubes (Ag NCBs) at concentrations of: (a) 10^{-8} M; (b) 10^{-10} M; (c) 10^{-12} M; (d) 10^{-13} M and (e) 10^{-14} M, respectively

4 CONCLUSIONS

In this work, we have successfully modified a method that utilizes low concentrations of BH_4^- and Cl^- anions to manipulate the polyol process and thus increase both the rate of production with short reaction time (~ 3 -5 h) and uniformly the shape of monodispersed nanocubes of 40; 60 and 70 nm in size. Moreover, these silver nanocubes (Ag NCBs) have been also used to detect and determine quantity of Rd3B dye molecules. Herein, Rd3B molecules can be detected at very low concentration with lower limit of detection (LOD) being 10^{-14} M. It demonstrates that the Ag nanocubes have potential applications in SERS for the detection of biomolecules or dye molecules.

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