



Highly effective surface-enhanced Raman scattering-active gold substrates prepared by using electrochemical methods in the presence of hexadecyltrimethylammonium bromide



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ABSTRACT

As shown in the literature, Au nanoparticles (NPs) were popularly used in the fields of catalyst and surface-enhanced Raman scattering (SERS). Meanwhile, cationic surfactants of hexadecyltrimethylammonium bromide (CTAB) were generally employed in syntheses of Au nanorods (NRs). In this work, CTAB is used to prepare highly effectively SERS-active Au substrates via electrochemical oxidation-reduction cycles (ORCs) for the first time. Based on the effectively SERS-active Au substrate prepared under assistance of CTAB, the SERS of Rhodamine 6G (R6G) exhibits a higher intensity by more than one order of magnitude, as compared with that of R6G adsorbed on a SERS-active Au substrate without the assistance of CTAB in preparation. Experimental results indicate that the quantities of adsorption sites for the developed SERS-active Au substrates are large enough to accommodate considerable ranges of analyte concentrations. The aging of SERS enhancement capability can be markedly depressed on this substrate. Moreover, its potential application in the trace detection of monosodium urate (MSU)-containing solution in gouty arthritis can be promised using this SERS-active Au substrate with CTAB.

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1. Introduction

With the development of nano-sized materials, Raman spectroscopies have been widely employed to investigate the nano-structures of titania [1,2], heterogeneous individual and single- and double-wall carbon nanotubes [3,4], and grapheme [5,6]. However, only poor information can be provided due to weak signal or interference from noise in Raman spectroscopy [7,8]. This issue was successfully resolved by using surface-enhanced Raman scattering (SERS), of which nearly 10^6 -fold enhancement of Raman spectra of surface species provides a dramatic example for the modification of the optical properties of molecules near solid-state surfaces in view of its unique sensitivity and excellent frequency

resolution [9,10]. In SERS studies based on Au and Ag nanoparticles (NPs), metal NPs colloids in solutions [11,12] and metal NPs deposited on substrates [13,14] were two generally employed systems. Among other techniques used to obtain rough metal substrates with SERS-activities [15,16], a controllable and reproducible surface roughness can be generated through the electrochemical oxidation-reduction cycles (ORCs) [17,18].

It is very useful for developing effectively size- and shape-controllable syntheses of metal NPs due to these characteristics can significantly affect their correspondingly optical and electronic properties [19,20]. Size and shape of NPs are often kinetically decided via a balance of the rates of nucleation to facet-specific growth or aggregative coarsening processes [21]. Therefore, molecules of hexadecyltrimethylammonium bromide (CTAB) were popularly employed for the syntheses of various shapes of Au and Ag NPs [22,23]. It is thought that CTAB binds preferentially to certain crystal faces of the growing metal seeds, which leads to anisotropic 1D growth for a small number of NPs (4–15%) [24,25]. As reported by Bullen et al. [21], the chemical kinetics of the silver-mediated growth of Au nanorods prepared by the reduction of Au precursor in aqueous CTAB solution has been

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systematically studied using spectroscopic monitoring and electron microscopy. The rate of monomer depletion $-d[\text{Au}^{III}]/dt$ has a linear dependence on both $[\text{Au}^{III}]$ and seed nuclei concentration at 30 °C. Particle growth is significantly retarded by CTAB and KBr, with the order ca. -1 for $[\text{Br}^-]$. As reported by Song et al. [26], plasmon-resonant Au nanostars (NSTs) with magnetic cores were synthesized by a multistep sequence from superparamagnetic Fe_3O_4 NPs and evaluated as optical contrast agents under magnetomotive (MM) imaging conditions. Core-shell $\text{Fe}_3\text{O}_4/\text{Au}$ NPs were prepared in nonpolar organic solvents with nanometer control over shell thickness and with good epitaxy to the Fe_3O_4 surface. Anisotropic growth was performed in micellar solutions of CTAB under mildly reducing conditions, resulting in NSTs with physical features similar to those produced from colloidal Au seeds. As reported by Sun et al. [27], aggregation of citrate-reduced Ag NPs induced by CTAB was studied. These nanoparticle aggregates can be “tuned” to yield maximum SERS enhancement as different concentrations of CTAB were added. It was found that the maximum enhancement was achieved when 0.05 mM CTAB was added. A facile and reversible method for assembling and disassembling Au nanorods using a common chelating agent, ethylenediaminetetraacetic acid (EDTA), was reported by Sreeprasad and Pradeep [28]. Assembly was induced by the electrostatic interaction between the CTAB bilayer present on Au nanorods and EDTA. It was found that SERS activity of the system could be tuned by controlling the concentration of EDTA and the metal ion of Pb(II). As shown in the literature, CTAB was mainly used to control the particle sizes and shapes of metal NPs colloids in solutions. The corresponding SERS effects based on CTAB-assisted preparations of metal colloids are unstable, therefore, the prepared metal colloids are necessarily aggregated on substrates for reliable SERS measurements. However, the sizes and shapes of metal colloids from CTAB-assisted preparations are difficultly maintained during particle aggregations. To our knowledge, the effects of the addition of CTAB in preparing roughened metal substrates on the corresponding SERS effects were less discussed in the literature. In this work, Au substrates are roughened by electrochemical ORC procedure in 0.1 M HCl aqueous solution containing different concentrations of CTAB. The improved SERS performances are investigated in details.

2. Experimental section

2.1. Chemical reagents

Electrolytes of HCl, surfactants of CTAB, and probe molecules of Rhodamine 6G (R6G) reagents (p.a. grade) purchased from Acros Organics were used as received without further purification. All of the solutions were prepared using deionized 18.2 M Ω cm water provided from a MilliQ system.

2.2. Preparation of SERS-active Au substrates

All electrochemical experiments were performed in a three-compartment cell at room temperature, 24 °C, and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). A sheet of gold foil with a bare surface area of 0.238 cm², a 2 × 2 cm² platinum sheet, and a silver–silver chloride (Ag/AgCl) electrode were employed as the working, counter and reference electrodes, respectively. Before the ORC treatment, the gold electrode was mechanically polished (model Minimet 1000, Buehler) successively with 1 and 0.05 μm of alumina slurry to a mirror finish. Then the electrode was cycled in a deoxygenated 0.1 M HCl aqueous solution containing 0.01 (or 0.001) g/L CTAB from -0.28 to $+1.22$ V vs Ag/AgCl at 500 mV/s for 25 scans under slight stirring. The durations at the cathodic and anodic vertices are 10 and 5 s,

respectively. This ORC treatment is responsible for the strongest SERS effect observed on the roughened Au electrode, as shown in our previous report [29]. Finally, the potential was hold at the cathodic vertex before the roughened Au electrode was taken from the solution and rinsed thoroughly with deionized water to remove surfactants of CTAB. For comparison, roughened Au substrates without the additive of CTAB were also prepared by using the same roughening procedure. For SERS measurements, the roughened Au substrates were incubated in 2×10^{-5} M R6G aqueous solutions for 30 min. Then the substrates were rinsed thoroughly with deionized water, and finally dried in a dark vacuum-dryer for 1 h at room temperature for subsequent test.

2.3. Characterization of SERS-active Au substrates

The surface morphologies of Au substrates were examined by using scanning electron microscopy (SEM, model S-4700, Hitachi, Japan). For high resolution X-ray photoelectron spectroscopy (HRXPS) measurements, a ULVAC PHI Quantera SXM spectrometer with monochromatized Al K α radiation, 15 kV and 25 W, and an energy resolution of 0.1 eV was used. To compensate for surface charging effects, all HRXPS spectra are referred to the C 1s neutral carbon peak at 284.8 eV. Raman spectra were obtained (Renishaw InVia Raman spectrometer) by using a confocal microscope employing a diode laser operating at 785 nm with an output power of 1 mW on the sample. A 50 \times , 0.75 NA Leica objective was used to focus the laser light on the samples. The laser spot size is ca. 1–2 μm . A thermoelectrically cooled charge-coupled device (CCD) 1024 × 256 pixels operating at -60 °C was used as the detector with 1 cm⁻¹ resolution. All spectra were calibrated with respect to silicon wafer at 520 cm⁻¹. In measurements, a 90° geometry was used to collect the scattered radiation. A holographic notch filter was used to filter the excitation line from the collected light. The acquisition time for each measurement was 10 s. Replicate measurements of five times on different areas were made to verify the recorded spectrum was a true representation of each sample. The relative standard deviation is within 5% based on the strongest band intensity of R6G on the Raman spectrum. Also, different batches of the as synthesized substrates were measured by using the same conditions for three times. The relative deviation from the average value is less than 5% for an individual sample based on the strongest band intensity of R6G on the Raman spectrum. The aging test was performed via placing the samples in an atmosphere of 50% relative humidity (RH) and 20% volume concentration (v/v) of O₂ in the mixture of O₂ and N₂ at 30 °C for 60 days.

3. Results and discussion

3.1. Characterization of SERS-active Au substrates

In the ORC treatment, the chloride electrolyte was selected since this facilitates the metal dissolution–deposition process that is known to produce SERS-active roughened surfaces [30]. Meanwhile, the AuCl_4^- complexes were produced in the solution during the anodic scan in the ORC treatment for roughening the Au substrate, as reported in our previous study [31]. These negatively charged AuCl_4^- complexes are easily combined with the cationic surfactants of CTAB due to electrostatic attraction. On the other hand, it is generally accepted that CTAB adsorbs onto Au NRs in a bi-layer fashion, with the trimethylammonium headgroup of the first monolayer facing the Au surface in the CTAB-assisted synthesis of rod-shaped NPs in aqueous surfactant media [32]. However, the exact mechanism of formation of CTAB-capped Au NRs remains unclear [33]. In this work, CTAB was added in a chloride-containing solution to cap complexes of

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