



Improved galvanic replacement growth of Ag microstructures on Cu micro-grid for enhanced SERS detection of organic molecules



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ABSTRACT

Galvanic growth of Ag nano/micro-structures on Cu micro-grid was systematically studied for surface-enhanced Raman scattering (SERS) applications. Detailed characterizations via FE-SEM and HR-TEM showed that processing parameters, (reaction time, Ag⁺ concentration, and PVP addition) all substantially affect thermodynamics/kinetics of the replacement reaction to yield substrates of significantly different microstructures/homogeneities and thus varied SERS performances (sensitivity, enhancement factor, and reproducibility) of the Ag substrates in the detection of R6G analyte. PVP as an additive was shown to notably alter nucleation/growth behaviors of the Ag crystals and promote the deposition of dense and uniform Ag films of nearly monodisperse polyhedrons/nanoplates through suppressing dendrites crystallization. Under optimized synthesis (50 mM of Ag⁺, 30 s of reaction, and 700 wt.% of PVP), Ag substrates exhibiting a high Raman signal enhancement factor of $\sim 1.1 \times 10^5$ and a low relative standard deviation of ~ 0.13 in the repeated detection of 10 μM R6G were obtained. The facile deposition and excellent performance reported in this work may allow the Ag microstructures to find wider SERS applications. Moreover, growth mechanisms of the different Ag nano/micro-structures were discussed based on extensive FE-SEM and HR-TEM analysis.

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1. Introduction

Since Fleischmann et al. first discovered the surface-enhanced Raman scattering (SERS) phenomenon in 1974 [1], mechanistic and synthetic studies have been widely pursued for decades [2–6]. Due to its high sensitivity, SERS is nowadays being extensively explored for applications in the areas of chemical, biochemical, and environmental monitoring [7–9]. It is commonly accepted that the SERS effect mainly comes from localized surface plasmon resonance (LSPR) generated by the electromagnetic interaction of nanometer-sized metallic structures (hot spots) [10, 11]. Cu, Au and Ag are generally advantageous for SERS [12–15], among which Ag has received wider investigations and various kinds of Ag substrates have been successively developed, such as aggregated colloids [16, 17], carbon nanotube/Ag composite [18], semiconductor/Ag composite [19,20], and Ag nanosheet-coated inverse opal film [21].

Photochemical reaction [22,23], templating [24], ultrasonication assisted templating [25], and surfactant assisted reduction/stabilization [26] are commonly used strategies in the practical synthesis of SERS substrates. Though having their own respective advantages, they are either complicated or high time/money cost and some are not capable of producing SERS substrate in large area. As a facilely accessible, low cost,

and time efficient technique, galvanic replacement deposition (such as the Ag⁺/Cu system in this work) has thus been widely investigated [27–29]. Due to the high reactivity of the Ag⁺/Cu pair (standard electrode potential: Ag⁺/Ag = 0.80 V; Cu²⁺/Cu = 0.34 V), however, replacement generally proceeds in an extremely fast and uncontrollable manner, and as a consequence irregular Ag dendritic structures are frequently resulted, which may in turn lead to irreproducible SERS signals in practical application. It can be said that galvanic synthesis of large area and homogenous SERS substrates still remains a great challenge, and relentless efforts are being devoted to better controlling the uniformity and microstructure of the galvanic Ag crystals. Gao et al., for example, successfully assembled a film of cross-linked/parallel-linked Ag nanosheets with extremely high packing density on a Cu/Cu₂O plate via dipping it into a trisodium citrate solution before adding AgNO₃ and HNO₃ solution. The citrate ions and Cu₂O layer were both used to weaken the reaction process while trisodium citrate solution was specifically responsible for the growth of Ag nanosheet. However, this technique seems inefficient and complex [30]. Ke et al., on the other hand, deposited homogeneously distributed Ag nanoparticles on a well confined Cu micro-square patterned plate by galvanic reaction for SERS arrays. The pattern was achieved via microcontact printing of HDT monolayers on a gold substrate followed by electrochemical deposition of Cu [31]. Albeit excellent SERS performance was demonstrated therein, the advantages of this technique were offset by the complicated synthetic procedure and expensive equipment/chemicals.

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We recently reported controllable deposition of Ag NCs on brookite/rutile for SERS via photocatalytic reduction [32], where poly(vinylpyrrolidone) (PVP) as an additive exhibited tremendous ability in morphology engineering of the resultant Ag NCs. Inspired by this, PVP was introduced in this work into the fast galvanic replacement reaction system of Ag^+/Cu to produce homogeneous Ag substrates for efficient and reproducible SERS applications. Cu micro-grid for TEM analysis was employed as a sacrificial substrate for Ag deposition since it is commercially readily available, facilely transferable, and has well defined micropatterns. Systematic studies on the effects of reaction time, AgNO_3 concentration, and PVP content on the growth mechanism and morphology evolution of Ag have led to Ag substrates of well controlled microstructures and excellent SERS performances. The facile synthetic technique developed herein may allow Ag microstructures to find better and wider applications in highly sensitive, efficient, and reliable analyte determination via SERS.

2. Experimental methods

2.1. Chemicals and materials

Hydrochloric acid (HCl, 36%), silver nitrate (AgNO_3 , 99.9%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%), acetone (CH_3COCH_3 , 99.5%), and Rhodamine 6G (R6G, $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, practical grade) were all purchased from Wako Pure Chemical Industries (Osaka, Japan). Poly(vinylpyrrolidone) (PVP, $(\text{C}_6\text{H}_9\text{NO})_x$, $M_w = 10,000 \text{ g mol}^{-1}$) was purchased from Sigma-Aldrich Inc. (MO, USA). Copper micro-grid (200 meshes) was purchased from Nisshin EM Co. Ltd. (Tokyo, Japan). The water used throughout the experiment was taken from a Milli-Q purification system (MA, USA).

2.2. Galvanic deposition of Ag

2.2.1. Pretreatment of Cu micro-grid

To clean off possible surface contaminants, Cu grid was first immersed in a 3.6% hydrochloric acid solution for 3 min, followed by sequential washing with ethanol, water, and acetone before drying with N_2 flow.

2.2.2. Ag deposition on Cu micro-grid

The as-treated Cu micro-grid was immersed in 3 mL of a base solution (1, 2, 4, 6, 10, 20, and 50 mM of AgNO_3 , respectively) for certain time (from 10 to 120 s). When PVP was used, its content was varied from 3 to 700 wt.% (mass ratio against AgNO_3). The substrate after reaction was sequentially soaked in ethanol, water, and acetone, and finally dried by N_2 gas flow. All the above operations were performed under ambient conditions.

2.3. Characterization and SERS measurements

Morphologies of the Ag crystals were observed by field-emission scanning electron microscopy (FE-SEM, model S-5000, Hitachi Co. Ltd., Tokyo) operated at 10 kV and transmission electron microscopy (TEM, Model FEM-3000F, JEOL Ltd., Tokyo) under an acceleration voltage of 300 kV.

Rhodamine 6G (R6G) was dissolved in ethanol to make an analyte solution (10 μM for enhancement factor determination, 0.1 M for bare Cu micro-grid, and 0.1 μM for sensitivity analysis). The sample for SERS test was immersed in the analyte solution for 30 min and then dried in the air. Raman spectra were taken under ambient conditions on a micro-Raman spectrophotometer (Model Jobin Yvon T64000, Horiba Co. Ltd., Tokyo) with a 170 μW Ar^+ laser (514 nm) as the excitation source. The acquisition time was 20 s, the signal was acquired under two accumulations, and the laser spot was $\sim 1 \mu\text{m}^2$ under a $90\times$ air objective lens.

The enhancement factor (EF) of as-made Ag substrate can be assayed using the equation

$$EF = (I_{\text{Ag}}/I_{\text{Cu}})(N_{\text{Cu}}/N_{\text{Ag}}) \quad (1)$$

where I_{Ag} and I_{Cu} represent intensities of the selected Raman peak of the R6G molecules adsorbed on Ag substrate and bare Cu micro-grid (Fig. S4), respectively, and N_{Cu} and N_{Ag} are the number of surface adsorbed R6G molecules. The I value was defined in this work as the difference between the intensity of the selected Raman peak and the average intensity of the left- and right-hand tails of the spectrum baseline. In addition, the average of five measurements, taken from randomly selected spots, was used to denote the I value (see Fig. S6 for example). The N value, on the other hand, is represented by the concentration of R6G in each case.

Raman signal reproducibility of the Ag decorated surface was evaluated with relative standard deviation (RSD) calculated using the equation

$$RSD = \sqrt{\frac{\sum_{i=1}^n (EF_i - \overline{EF})^2}{n-1}} / \overline{EF} \quad (2)$$

where \overline{EF} is the average enhancement factor and n is 5 in this work.

3. Results and discussion

3.1. Growth process

Surface of the Cu micro-grid turned rougher by HCl treatment, as compared in Fig. S1, and may thus provide more active sites for Ag deposition. It can also be said from the SEM images that surface contaminants have been effectively removed. It is well known that, without the participation of any surfactant, the growth of Ag NCs may be dominated by either thermodynamics or kinetics. Under thermodynamic control, the crystal tends to assume a shape that has a minimal total interfacial free energy during nucleation/growth, that is, the crystal will express a maximal coverage of low energy facets and/or a minimal surface area for a certain volume. Crystal morphology may deviate from that favored by thermodynamics under kinetic control, and thus Ag NCs with artificially designed shapes can be obtained by precisely manipulating synthesis parameters. Since the Ag^+/Ag pair has a larger standard electrode potential (+0.799 V) than Cu^{2+}/Cu (+0.337 V), galvanic replacement would readily take place when the Cu micro-grid is immersed into AgNO_3 solution. To better follow morphology evolution of the deposited Ag particles, experiments were performed under the low Ag^+ concentration of 1 mM and the results are shown in Fig. 1. It can be seen that Ag nanoparticles (up to $\sim 25 \text{ nm}$), aggregated into uniform and roughly spherical shaped clusters of $\sim 60 \text{ nm}$, have been formed after only 10 s of reaction (Fig. 1a and inset), indicating a quite high reaction rate. The 30 s product tends to be platelets of $\sim 100 \text{ nm}$ in lateral size, though the polyhedral aggregates found in Fig. 1a are still observable. Closer observation (the inset) reveals that each nanoplate consists of numerous smaller crystallites (subunits). In view that single crystalline Ag platelets are usually evolved from seeds having stacking faults [33,34], the above results may suggest that Ag nuclei having stacking faults, favored by the high reaction kinetics, have been formed at the initial stage of the replacement reaction, and the nanoplates shown in Fig. 1b are then formed via growth of the defected nuclei and possibly also via "oriented attachment" of subunits [35,36]. Aside from size growth, the nanoplates in the 60 s product have denser and smoother surfaces, indicating merging of the subunits via coarsening to eliminate interfaces and to form single crystallites. Prolonging the reaction to 120 s does not change the overall morphology of the product but produced significantly bigger Ag nanoplates of $\sim 200 \text{ nm}$ in lateral size.

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