Synthesis and characterization of dendritic and porous Ag–Pd alloy nanostructures

Limiao Chen*, Younian Liu

College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China

ARTICLE INFO

Article history:
Received 3 June 2011
Accepted 6 August 2011
Available online 16 August 2011

Keywords:
Alloy
Synthesis
Morphology
Surface enhanced Raman scattering

ABSTRACT

Dendritic and porous Ag–Pd alloy nanostructures were successfully fabricated on the surface of silicon substrate using the co-reduction method and galvanic replacement reaction, respectively. The molar compositions of Ag and Pd in the alloy could be modulated by controlling the molar ratios of metal precursors and reaction time. The Ag–Pd alloy nanostructures were characterized by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray (EDX), and X-ray diffraction (XRD). The morphology and phase of Au–Pd alloy nanostructures were discussed as a function of molar ratios of metal precursors and reaction time. In addition, the morphology and composition-dependent surface-enhanced Raman scattering (SERS) of the as-synthesized Ag–Pd alloy nanostructures were investigated. The SERS enhancement factor was estimated and SERS mapping was performed to prove the homogeneity of these substrates. The results indicate that as-synthesized dendritic and porous Ag–Pd alloy nanostructures are good candidates for SERS spectroscopy.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

Bimetallic nanoparticles with core–shell or alloy nanostructure are of great significance because of the modification of properties observed, compared with monometals, not only due to size effects, but also as a result of the combination of different metals [1–3]. Catalytic, electronic, magnetic and optical properties of the bimetallic nanoparticles have been tailored compared with monometals [4–6]. Among the various bimetallic nanoparticles, Ag–Pd alloy nanoparticles have been widely explored as catalytic materials for a variety of reactions [7,8]. Recently much work has been devoted to fabricate Ag–Pd nanostructures with well-defined morphology because the grain size and morphology have a great impact on the chemical and/or physical properties of metal nanomaterials. For example, Ag–Pd nanorings, hollow triangular nanoplates and dendrites were successfully prepared by a simple galvanic replacement reaction using Ag nanoparticle, triangular nanoplates and wires as template, respectively [9–11]. Ag–Pd hollow nanoparticles were synthesized in ethylene glycol solution by the solvothermal method [12]. Ag–Pd clusters were prepared with a radiolysis method [13]. Ag–Pd alloy nanowires were deposited on pyrolytic graphite by electrochemical deposition at room temperature [14]. Despite all these efforts, it remains a challenge to synthesize Ag–Pd nanostructures with novel shapes and controllable molar composition by a simple and inexpensive method.

SERS is a powerful tool for the investigation of “in situ” catalytic reactions allowing the detection of both surface-adsorbed reagents and products [15–17]. In fact, for coinage metal substrates, constituted by colloidal nanoparticles or by nanostructured surfaces, huge enhancements of the Raman signal of the adsorbed molecules can be observed. Therefore SERS spectroscopy represents a very sensitive technique in the study of surface adsorption phenomena, because it is suitable for the detection of sub-monolayers and even single molecules. However, most catalysts are formed with SERS-inactive materials. To solve this problem, bimetallic nanoparticles composed by SERS-active metals (such as Ag and Au) and catalytically efficient metals (such as Pd, Ni and Pt) were recently prepared [11,17–22]. For example, Muniz-Miranda et al. [17] synthesized bimetallic Ag–Pd nanoparticles, which can reduce selectively nitrogroups to azogroups and provide satisfactory SERS enhancement to detect both reactants and reaction products. Han and co-workers [18] prepared flower-shaped porous Au–Pd alloy nanoparticles and found that high-quality SERS spectra can be obtained from these alloy nanoparticles although the SERS intensities are relatively weak compared with that obtained from Au nanoparticles. Recently, it has been shown that the Ag–Pd alloy nanostructure arrays give high SERS activity [11]. Although Ag–Pd bimetallic nanostructures have been synthesized and used as SERS substrates, there is still a need to improve the sensitivity and reproducibility.

In this work, dendritic and porous Ag–Pd alloy nanostructures were successfully deposited on the surface of silicon substrate using the co-reduction method and galvanic replacement reaction, respectively. The morphology and composition-dependent SERS activity of as-synthesized Ag–Pd alloy nanostructures were
investigated. It was found that the dendritic Ag–Pd nanostructures exhibit higher SERS activity than the porous Ag–Pd nanostructures, while the porous Ag–Pd nanostructures exhibit better reproducibility than the dendritic Ag–Pd nanostructures. For the Ag–Pd alloy nanoparticles with similar morphology, the SERS signal intensity decreases with increasing the Pd content.

2. Experimental

2.1. Synthesis of Ag–Pd dendrites

The typical preparation of Ag–Pd nanostructures by co-reduction was carried out as follows. AgNO₃ and Pd(NO₃)₂ were dissolved in aqueous HF solution (4.8 M) at room temperature to form a homogeneous solution. The molar ratios of AgNO₃/Pd(NO₃)₂ in the solutions were 3:1, 1:1 and 1:3. The commercial silicon wafer (1 × 1 cm²) was washed with water and acetone and then was etched with 5% HF aqueous solution for 3 min under room temperature to obtain fresh Si surface. The Si wafer was immediately placed into above solution (10 mL), which was kept still for 1–20 min under atmosphere ambient. After reaction, the sample together with the Si wafer were taken out from the reaction solution, rinsed with de-ionized water 3–5 times to remove contamination from the sample surface, and then dried under ambient conditions. The samples with different compositions of Ag and Pd will be referred as AgₓPdₙ, x and y are the molar composition in the bimetallic nanoparticles. For comparison, monometallic nanoparticles of Ag and Pd were also fabricated according the same procedures as described above.

2.2. Synthesis of Ag–Pd porous nanoparticles

Bimetallic Ag–Pd nanoparticles with porous structures were synthesized using Ag particles as template, which was synthesized by above co-reduction method. The synthesis of bimetallic Ag–Pd nanostructures was achieved simply by immersing the Ag nanoparticles together with the silicon substrate into the aqueous solution containing HF (0.005 M) and Pd(NO₃)₂ (0.01 M), which was kept still for 1–30 min under atmosphere ambient. After reaction, the sample together with the Si wafer were taken out from the reaction solution, rinsed with de-ionized water 3–5 times to remove contamination from the sample surface, and then dried under ambient conditions. The samples obtained by reaction for different time will be referred as AgₓPdₙ, x and y are the real molar composition in the bimetallic nanoparticles.

2.3. Characterization

 Morphologies and structures of the samples were characterized with scanning electron microscopy (SEM, Philips XL 30 FEG), transmission electron microscopy (TEM, Philips CM20, operated at 200 kV), and X-ray diffraction (XRD, Philips X’Pert MRD with Cu KR radiation). Ultraviolet–visible (UV–vis) spectra were recorded on a UV-2501 PC Spectrometer (Shimadzu). Raman measurements were conducted with a Renishaw 2000 laser Raman microscope equipped with a 633 nm laser of 2 μm spot size in diameter for excitation. All the spectra were acquired for 10 s with the laser power measured at the sample being 2.5 mW.

3. Results and discussion

Electroless deposition process is a simple and inexpensive method that has been often used for depositing a uniform dense metal membrane on any arbitrary geometry substrate [23]. Metal deposition on silicon substrate from aqueous HF solution is initiated by electrochemical reduction of metal ions, a process which is driven by the difference between the electron quasi Fermi energy in the silicon and the redox energy level of the metallic ions in solution. The detailed information about the mechanism of the electroless metal deposition on silicon substrate has been reported in other reports [24,25]. For Pd and Ag, the standard reduction potentials of the Pd⁰/Pd and Ag⁰/Ag pairs (0.83 and 0.80 V versus the standard hydrogen electrode (SHE), respectively) are higher than that of Si⁴+/Si (−1.2 V versus SHE), so the reaction occurred as follows:

\[2\text{Pd}^{1+}(aq) + \text{Si}^{6-}(aq) + 6\text{F}^-(aq) \rightarrow 2\text{Pd}(s) + \text{SiF}_6^{2-}(aq)\]  \hspace{1cm} (1)

\[4\text{Ag}^{2+}(aq) + \text{Si}^{6-}(aq) + 6\text{F}^-(aq) \rightarrow 4\text{Pd}(s) + \text{SiF}_6^{2-}(aq)\]  \hspace{1cm} (2)

The morphology and nanostructure of the Ag–Pd nanoparticles were studied using SEM, TEM and selected area electron diffraction (SAED). Typical low and high-magnification SEM images of the sample prepared from the aqueous solution of AgNO₃/Pd(NO₃)₂ mixtures in molar ratio of 3:1 are shown in Fig. 1a and b, which shows that as-synthesized particles are dendritic structures. The aggregation of the dendrites is flower-like, implying that these dendrites might grow radially from the same particle. The individual dendrite length is about 1–4 μm and composed of numerous side branches. Fig. 1c shows a typical TEM image of a dendritic nanostructure. It is clear that the nanodendrite is nearly symmetric, and the angles between the stem and the branches are in the range of 50–60°. It is also noted that the side branches growing on the stem can also act as a secondary stem to grow secondary side branches. As can be seen from the inset of Fig. 1c, the SAED pattern displays the clear spots indicating that the whole dendrite is a single crystal and can be indexed to (1 1 1) and (2 0 0) reflections from face-centered cubic (fcc) Ag–Pd, and the zone axis projection is along (0 1 1). The chemical compositions of the obtained Ag–Pd nanoparticles were determined by EDX analysis of the samples deposited on the TEM grids. The EDX spectrum testified the existing of the Ag and Pd elements, in which the peaks of the corresponding Ag and Pd elements were distinct (other peaks originated from the copper and carbon from the TEM grid). The molar composition of Ag and Pd in the alloy is about 79% and 21%, respectively. This shows that the compositions of nanoparticles were not consistent with those of feeding solutions. The elemental mapping images (Fig. 2) from electron energy loss spectroscopy (EELS) clearly show that Ag and Pd elements are uniformly distributed over the entire structure. Moreover, the elemental mapping of Ag is higher than that of Pd, which confirms the formation of homogeneous alloy with a higher Ag content. As-synthesized products are denoted as AgₓPdₙ.

Fig. 3 shows a high-magnification TEM image of the end of AgₓPdₙ dendrites and the corresponding HRTEM images at locations marked “I”, “II” and “III”. The HRTEM image (Fig. 3b) taken at the tip of the dendrite (location “I”) reveals clear lattice fringes with a measured d spacing of about 0.232 and 0.195 nm, which match well with the interplanar spacings of (1 1 1) and (2 0 0), respectively. The HRTEM image in Fig. 3c shows a connection region between a stem and the branches. It can be seen that continuous fringes run through both stem and branch. This suggests that the small branch is not a physical contact with the stem but an epitaxial growth. In other words, the small branch and the stem belong to the same crystal orientation. Fig. 3d shows the HRTEM image taken at location “III”. It can be seen that the two branches have different growth direction, growing along (1 1 1) and (2 0 0), respectively.

The effect of molar ratio of metal precursors in the solution on the morphology, size and phase of the final products was also investigated. Fig. 4a and b shows typical SEM images of the sample prepared from the aqueous solution of AgNO₃/Pd(NO₃)₂ mixtures.
in molar ratios of 1:1 and 1:3. As can be clearly seen, the products mainly consist of irregularly shaped dendrites. Moreover, the length of individual dendrite is shorter than that of dendrite in the Ag79Pd21 sample. The molar compositions of Ag in these samples are 54 and 24%, respectively. As-synthesized products are denoted as Ag54Pd46 and Ag24Pd76. Fig. 4c is the SEM image of the samples prepared from pure Pd(NO3)2 aqueous solution. It shows that the samples (Pd nanoparticles) still take on dendritic morphology, while the size of the particle becomes smaller compared with that of Ag–Pd nanoparticles. Fig. 4d is the SEM image of the samples prepared from the AgNO3 aqueous solution. It was found that most of the products (Ag nanoparticles) are sphere-like nanoparticles and only few dendrites were formed at the edge of the silicon substrate. These results indicate that the Pd content in the Ag–Pd nanostructures have influence in the morphology and size of the final product. The phase and purity of the as-prepared nanoparticles were further determined from the XRD pattern (Fig. 5). Each pattern exhibits two diffraction peaks in the range of $30^\circ < 2\theta < 60^\circ$, which can be indexed to diffraction from the (1 1 1) and (2 0 0) of the fcc structure of metallic Ag and/or Pd. In addition, the diffraction peaks of the bimetallic particles exhibit a shift from pure Ag to pure Pd as the Pd content increases. This also suggests that as-prepared nanoparticles were Ag–Pd alloys.

Dendritic growth of Pd and Pt nanostructures has been generally studied and a mechanism consisting of nanoparticle seeding followed by fast autocatalytic surface growth has been proposed [26]. In this proposed process, metal ions were slowly reduced and form metal nanoclusters. Once the nanoclusters reached the certain size (about 500 atoms), the reduction of metal ions was accelerated through an autocatalytic reduction process, which would be facilitated to a highly anisotropic mode to form dendritic nanostructures. This mode of formation might explain the growth mechanism of Ag–Pd and Pd nanoparticles with dendritic morphology.

Bimetallic Ag–Pd nanoparticles were also prepared via a galvanic displacement reaction using Ag nanoparticles (as shown in Fig. 4d) as template, which was synthesized by co-reduction method. Because the standard reduction potentials of the Pd2+/Pd pairs (0.83 V versus SHE) is higher than that of Ag+/Ag (0.80 V versus SHE), so the reaction occurred as follows:

$$2\text{Ag}(s) + \text{Pd}^{2+}(aq) \rightarrow \text{Pd}(s) + 2\text{Ag}^+(aq) \quad (3)$$

The reaction was confined to the vicinity of the particle surface, and Ag atoms migrate outward from the core during the reaction. The resultant nanoparticles are expected to be bimetallic and with hollow interiors, as shown by the following experiments.
The phase and purity of the products synthesized by immersing the Ag nanoparticles into the aqueous HF solution of Pd(NO₃)₂ for different times were further determined from the XRD pattern (Fig. 6). For the sample synthesized by reaction for 5 min, the spectrum is dominated by the peaks centered at 38.5° and 44.7°. The peak position is close to that of Ag, indicating a high Ag content.
in the alloy. Careful observation reveals that there is a small peak centered at 39.1°, indicating the presence of a small content of another Ag–Pd alloy phase in the sample. Upon increasing the reaction to 10 min, the intensity of the peak centered at 39.1° increased, while the peak centered at 38.5° disappeared, which support the formation of a homogeneous Ag–Pd alloy. As the reaction proceeded to 15 min, a new peak indexed as Pd was observed, while the intensity of the peak centered at 39.1° decreased greatly. Further increasing the reaction time (30 min) resulted in the pure Pd phase. These results indicated that optimized reaction time for formation Ag–Pd alloy with pure phase is 10 min. The morphology and microstructure of as-synthesized Ag–Pd nanoparticles were also studied using SEM, TEM, SAED and EELS. As shown in Fig. 7a, after the reaction conducted for 5 min sphere-like nanoparticles with rough surface was observed. The inset in Fig. 7a is the typical TEM image of as-synthesized nanoparticles. It was found that many small nanoparticles (about 10 nm in diameter) were adsorbed on the big particles. Corresponding EDX spectrum (Fig. 7b) and EELS mappings (Fig. 7d and e) of the nanoparticle show that the molar composition of Ag and Pd in the alloy is about 83% and 17%, respectively, and the Ag and Pd elements are uniformly distributed over the whole particles. The SAED pattern (Fig. 7c) displays that they are polycrystalline. Fig. 7f shows the SEM image of the product formed after a reaction time of 10 min. Each individual particle was composed of several small nanoparticles, which seem to interconnect to form porous nanostructure. Moreover, there are black spots on the particles’ surfaces (as indicated by arrows in Fig. 7f), which are assumed to be the pinholes formed by the dissolution of the silver template. The pinholes also can be clearly observed from the TEM image (the inset in Fig. 7f). The molar composition of Ag in the alloy is decreased to 65% with increasing the reaction time. As the reaction proceeded to 15 min, the nanoparticles with pinholes disappeared and pinecone-like nanoparticles were generated, accompanied by the appearance of few dendritic nanoparticles. The TEM observations showed that the pinecone-like nanostructures consist of many small nanoparticles (the inset in Fig. 7g). The molar composition of Ag in the alloy is decreased to 11% with increasing the reaction time. As-synthesized samples were denoted as Ag83Pd17, Ag54Pd46 and Ag11Pd89, respectively. It should be emphasized that the galvanic displacement reaction in this study can be easily used to fabricate other bimetallic nanostructures such as Au–Pd, Ag–Au, Ag–Pt and Au–Pt with various morphologies.

Bimetallic Ag–Pd nanostructures have potential applications in the investigation of “in situ” Pd catalytic reactions and detecting both surface-adsorbed reagents and products. Here, the SERS on Ag–Pd alloy nanostructures was investigated by using R6G as probe molecule. Loading of analyte onto the Ag–Pd nanostructures was accomplished by immersing the nanoparticles together with the silicon substrate (about 3 mm × 3 mm) into 100 μL aqueous R6G solution (10 nM) for 1 h. Fig. 8A shows typical SERS spectra of R6G adsorbed on Ag, Pd and Ag–Pd nanoparticles with different molar composition and morphologies. High-quality SERS spectra can be obtained from Pd and Ag–Pd alloy nanoparticles although the relative SERS intensities at the band of 1510 cm\(^{-1}\) are different. The strong and medium-strong Raman bands at 1648, 1575, 1510, 1361, 1310, and 1187 cm\(^{-1}\) are assigned to the xanthene ring stretch, ethylamine group wag and carbon–oxygen stretch of R6G [27]. Fig. 8B shows the average peak height of the 1510 cm\(^{-1}\) line for 40 SERS spectra of R6G obtained from Pd and Ag–Pd alloy nanoparticles, in which the background of the signal has been removed in drawing the graph. As can be seen, for the Ag–Pd alloy nanoparticles with similar morphology, the SERS signal intensity decreases with increasing the Pd content in the Ag–Pd alloy. The dendritic Ag79Pd21 nanoparticles exhibit the highest SERS intensity. The decrease in SERS intensity may be attributed to variation of the content of Ag in the alloy and morphology of Ag–Pd nanoparticles. On one hand, the SERS activity of Pd is much lower than that of Ag. The increase in Pd content may result in the decreased SERS enhancement ability directly. On other hand, when the Pd content increased from 21% to 100%, the morphology changed from dendrite to long stems and numerous side branches to irregularly shaped dendrites with few branches. According to theoretical and experimental studies, the largest SERS enhancement occurs at the gap between two metal nanoparticles [28,29]. As the morphology changes from dendrite to irregularly shaped dendrite, the number of the side branch decreases, therefore the number of gap between the branches or between the shafts and branches decreases and provide a more weak SERS enhancement. From Fig. 8 we also can find that the porous Ag65Pd35 exhibits higher SERS intensity than those of pinecone-like Ag54Pd46 nanoparticles. This may be due to the fact that the porous structure can supply more hot spots when used as SERS substrates.

The SERS enhancement factors (EF) for R6G adsorbed on Ag–Pd alloy and Pd nanoparticles were calculated according to the equation [30] \( EF = \left( I_{\text{SERS}}/I_{\text{bulk}} \right) \left( N_{\text{bulk}}/N_{\text{surface}} \right) \), where \( I_{\text{SERS}} \) and \( I_{\text{bulk}} \) denote the integrated intensities for the 1510 cm\(^{-1}\) band of the 10 nM R6G adsorbed on the surface of Ag–Pd alloy nanoparticles and 1.0 mM R6G on glass, respectively, whereas \( N_{\text{SERS}} \) and \( N_{\text{bulk}} \) represent the
corresponding number of R6G molecules excited by the laser beam. Loading of analyte onto the Ag–Pd and Pd nanostructures was accomplished by dropping 20 \( \mu \)L aqueous R6G solution onto the SERS substrates (about 3 mm \( \times \) 3 mm). The EFs of Ag–Pd alloy and Pd nanoparticles are evaluated to be \((1.1–6.8) \times 10^6\) and \(2.2 \times 10^5\), respectively.

The homogeneity of the SERS substrates (dendritic Ag\(_{79}\)Pd\(_{21}\) and porous Ag\(_{65}\)Pd\(_{35}\)) was detected by a 2D point by point SERS.
mapping of R6G molecules as shown in Fig. 9. For mapping measurement, the substrates were dipped into 100 µL aqueous R6G solution (10 nM) for 1 h and then dried naturally in air. The mapping areas were 30.0 × 33.0 µm² and 27.0 × 27.0 µm², respectively, and the scan step was 3 µm. A baseline-corrected peak intensity of a peak at 1510 cm⁻¹ is chosen for the acquisition of the SERS mapping. Red areas represent higher intensity of the SERS signal. Fig. 9a shows the mapping of R6G adsorbed on porous Ag₆₅Pd₃₅ nanoparticles. The relative SERS peak intensity of the collection spots all centered at a narrow range. These results indicate that the homogeneity of such substrates is pretty good. Fig. 9b shows the mapping of R6G adsorbed on dendritic Ag₇₉Pd₂₁ nanoparticles. It is clear that most SERS peak intensity is in a relative broad intensity window as shown by the contrast in color codes. These results indicate that the porous Ag₆₅Pd₃₅ nanoparticles exhibit better reproducibility than the dendritic Ag₇₉Pd₂₁ nanoparticles due to their uniform dispersion on the silicon substrate.

4. Conclusion

In summary, Ag–Pd alloy nanostructures have been synthesized by two different methods. In the first case, Ag–Pd alloy dendrites were deposited on the silicon substrate through the co-reduction of AgNO₃ and Pd(NO₃)₂ in aqueous HF solutions using silicon as a reducing agent. In the second case, porous Au–Pd alloy nanoparticles were synthesized by galvanic replacement reaction using Ag particles as template. Relative molar compositions between Ag and Pd in the dendritic and porous Ag–Pd alloy could be modulated by controlling the molar ratios between the metal precursors and reaction time, respectively. Raman analyses showed that the dendritic and porous Ag–Pd nanostructures are good SERS-active substrates. The enhancement factor was estimated to be on the order of 10⁸ using R6G as test probe molecules. For the Ag–Pd alloy nanoparticles with similar morphology, the SERS signal intensity decreases with increasing the Pd content in the Ag–Pd alloy. SERS mappings show that the porous Ag₆₅Pd₃₅ substrate exhibits better reproducibility and lower sensitivity compared with the dendritic Ag₇₉Pd₂₁ substrate.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 21101172).

References