Size-Controlled Synthesis of Gold Nanoparticles from Bulk Gold Substrates by Sonoelectrochemical Methods

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Size-controlled gold nanoparticles, ranging from 2 to 15 nm in diameter, were first prepared from gold substrates in 0.1 N HCl aqueous solutions without the addition of any stabilizers by sonoelectrochemical methods. First, an Au substrate was cycled in a deoxygenated aqueous solution containing 0.1 N HCl from −0.28 to +1.22 V vs Ag/AgCl at 500 mV/s with 100 scans. The durations at the cathodic and anodic vertexes are 10 and 5 s, respectively. After this process, Au- and Cl-containing complexes were left in the solution. The Au working electrode was then immediately replaced by a Pt electrode, and cathodic overpotentials of 0.2, 0.4, and 0.6 V from the open circuit potential (OCP) of ca. 0.82 V vs Ag/AgCl were applied under sonification to synthesize Au nanoparticles. The prepared nanoparticles increase in size from 2 to 15 nm with the increase of the cathodic overpotential applied from 0.2 to 0.6 V. Furthermore, the ratio of Au nanoparticles to Au-containing nanocomplexes in solutions can be controlled by adjusting the sonoelectrochemical reduction time.

Introduction

In the past decade, nanostructured materials have been the focus of scientific research[1,2] due to their unusual optical,[3] chemical,[4] photoelectrochemical,[5] and electronic[6] properties. The number of potential applications for nanoparticles, especially in the field of proteins detection[7] and catalysts modification,[8] are rapidly growing because of their unique electronic structure and extremely large surface areas. The developed methods for nanoparticles fabrication include chemical reduction,[9] sonochemical reduction,[10] laser ablation,[11] annealing from high-temperature solutions,[12] metal evaporation,[13] Ar$^+$ ion sputtering,[6] etc. Meanwhile, some stabilizers, like sodium dodecyl sulfate[10] and sugar ball,[14] were used, and some stabilization technologies of thiol-ligand coatings[15,16] and polymer capping agents[17,18] were developed to prevent the prepared nanoparticles from aggregating.

It is useful to develop effective methods for the size- and shape-controlled synthesis of metal nanoparticles; these properties can significantly affect their corresponding characterization.[17,19] Henglein and Meisel[20] reported a radiolytic control on the size of colloidal gold nanoparticles in solutions. Kobayashi et al.[21] reported a sol−gel processing of silica-coated gold nanoparticles for the preparation of gels with different particle sizes and shapes. Wang et al.[22] reported polyelectrolyte multilayers for preparing silver nanoparticles composites with controlled metal concentrations and particle sizes by adjusting the pH value of solutions. Generally, the advantages of electrochemical methods over the chemical ones are the high purity of the particles and the control of particle size by adjusting applied potentials or current densities.[17,23]

In the studies of surface-enhanced Raman scattering (SERS), the electrochemical oxidation−reduction cycles (ORC) procedure[24,25] is a better way to produce SERS-active metal substrate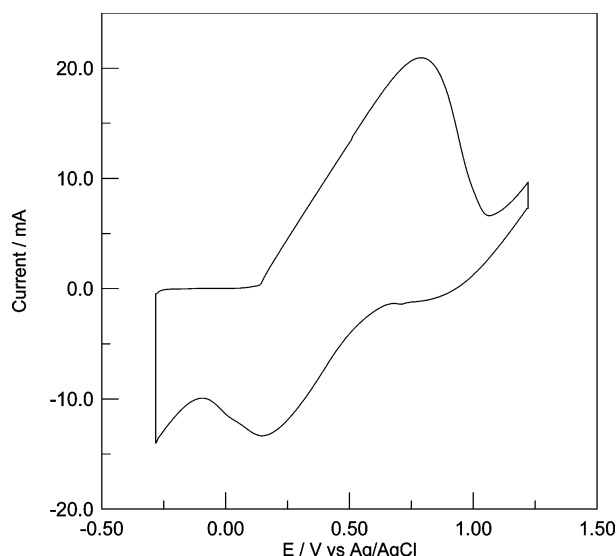s because a controllable and reproduced surface roughness can be easily generated.[26,27] In the previous studies of SERS spectroscopy of polypyrrole (PPy),[24,28] we reported the evidence of a chemical effect on SERS of PPy electrodeposited on gold roughened by electrochemical oxidation−reduction cycles (ORC) and the relationship between crystalline orientations of gold and SERS with PPy deposited on it. Most of the research on SERS is generally focused on the surface of roughened substrates.[29,30] In this work, we first use an electrochemical ORC roughening procedure to obtain gold-containing complexes in a 0.1 N HCl aqueous solution from a gold substrate. Size-controlled gold nanoparticles are then immediately synthesized in the same solution without addition of any stabilizer by a sonoelectrochemical reduction method with different overpotentials.

Experimental Section

Chemical Reagents. The HCl reagent (p.a. grade) purchased from Acros Organics was used as received without further purification. All of the solutions were prepared using deionized 18 MΩ cm water provided from a MilliQ system.

Preparation of Gold Nanoparticles. All of the electrochemical experiments were performed in a three-compartment cell at room temperature, 22 °C, and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). First, a sheet of gold foil with bare surface area of 4 cm^2, a sheet of 2 × 4 cm^2 platinum, and a KCl-saturated silver−silver chloride (Ag/AgCl) rod 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 slurries to a mirror finish. The electrode was then cycled in a deoxygenated aqueous solution of 100 mL containing 0.1 N HCl from −0.28 to +1.22 V vs Ag/AgCl at 500 mV/s with 100 scans. The durations at the cathodic and anodic vertexes were 10 and 5 s, respectively. This ORC procedure corresponded to the maximum SERS spectroscopy of PPy deposited on the roughened Au substrate.[31] After this roughening procedure, Au- and Cl-containing complexes were left in this aqueous solution at pH 6.7. Immediately,

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Figure 1. Cyclic voltammogram at 500 mV/s of the 100th scan for gold electrode in 0.1 N HCl.
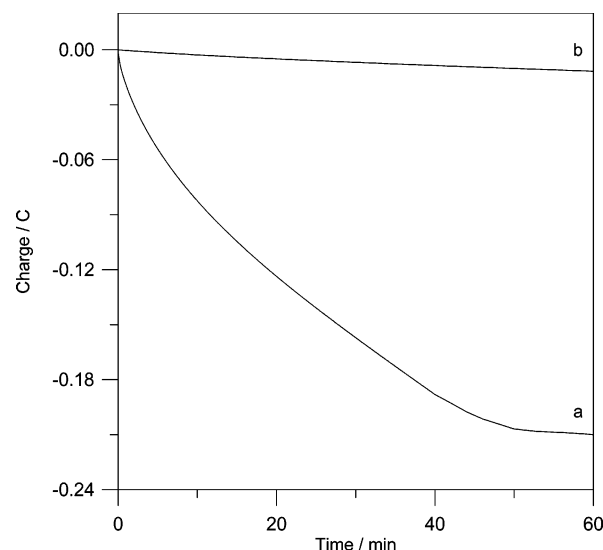

Figure 2. Coulometric curves of Au nanoparticles prepared in Au complexes-containing solutions at a cathodic overpotential of 0.2 V from the OCP of 0.82 V vs Ag/AgCl with sonification (a), and a reference experiment with the same preparation conditions in 0.1 N HCl but no Au complexes in the solution (b).

without changing the electrolyte, the gold working electrode was replaced by a platinum substrate with the same bare surface area of 4 cm^2, and different cathodic overpotentials of 0.2, 0.4, and 0.6 V from the open circuit potential (OCP) of ca. 0.82 V vs Ag/AgCl were applied under sonification and a slight stirring for 60, 20, and 7 min, respectively, to synthesize Au nanoparticles. The ultrasonic irradiation was performed by using an ultrasonic generator (model XL2000, Microson) and was operated at 20 kHz with a barium titanate oscillator of 3.2 mm diameter to deliver a power of 100 W.

Characteristics of Gold Nanoparticles. A single drop of the sample-containing solution was placed on a 300 mesh Cu/carbon film transmission electron microscopy (TEM) sample grid and was allowed to dry in a vacuum oven. The sample was then examined via a JEOL JEM-4000 EX electron microscope with an acceleration voltage of 400 kV. Before the XPS spectra were recorded, a few drops of the samples were evaporated on an amorphized graphite substrate. A Physical Electronics PHI 1600 spectrometer with monochromatized Mg Kα radiation at 15 kV 250 W and an energy resolution of 0.1−0.8% $\Delta E/E$ was used. To compensate for surface charging effects, all XPS spectra were referred to the C 1s neutral carbon peak at 284.6 eV. Ultraviolet−visible absorption spectroscopic measurements were carried out on a Perkin-Elmer Lambda 25 spectrophotometer in 1 cm quartz cuvettes.

Results and Discussion

In the ORC treatment, the chloride electrolyte was selected because this facilitates the metal dissolution−deposition process that is known to produce SERS-active roughened surfaces.[32] Figure 1 shows the typical triangular voltammetry curve obtained at 500 mV/s on gold in 0.1 N HCl. As shown in previous studies,[24,28] after the ORC procedure of roughening the Au substrate, it would leave some unreduced species, possibly positively charged Au clusters, on the Au surface. Meanwhile, the Au-containing complexes might be present in the solution after roughening the Au substrate for 100 scans in this study. XPS analyses show that positively charged Au- and negatively charged Cl-containing complexes indeed exist in this solution.

Figure 2a illustrates the sonoelectrochemically cathodic reduction process at an overpotential of 0.2 V from positively
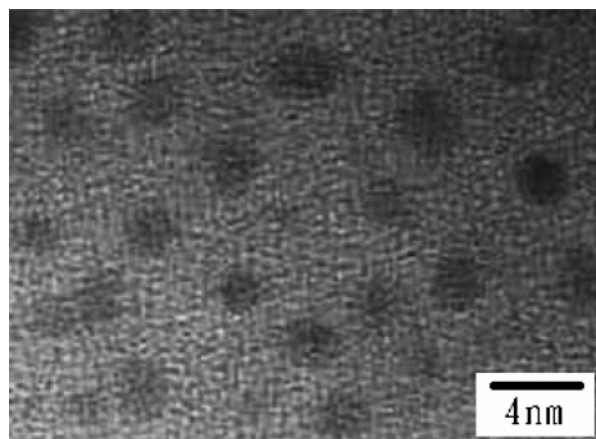
Figure 3. TEM micrograph of Au nanoparticles, prepared at a cathodic overpotential of 0.2 V from the OCP of 0.82 V vs Ag/AgCl with sonification, showing size and dispersion.

charged Au-containing complexes to elemental Au nanoparticles. Clearly, after 50 min, the gold reduction is significantly slowed; instead, the evolution of hydrogen from water becomes the domain reaction in this step. To realize the degree of the competitive reaction of hydrogen evolution, a blank experiment without the positively charged Au-containing complexes in solution was performed, as shown in Figure 2b. Comparing this plot with Figure 2a, it is found that the hydrogen evolution is insignificant at the cathodic potential used in this study, and it would not interfere with the synthesis of gold nanoparticles. During the sonoelectrochemical reduction for 60 min, the solution was continuously stirred. Therefore, the depressed reaction over 50 min may mean that the synthesis of gold nanoparticles is wholly completed. This can be confirmed from the later discussions in XPS and UV−vis spectra.

The dispersion and the particle size of the gold nanoparticles prepared at a cathodic overpotential of 0.2 V with sonification in an aqueous solution are examined via the TEM micrograph, as shown in Figure 3. The nanoparticles with a diameter of ca. 2 nm demonstrate no aggregation and fairly even dispersion. In preparing well-dispersed metal nanoparticles in aqueous solutions by electrochemical reduction methods, one necessary
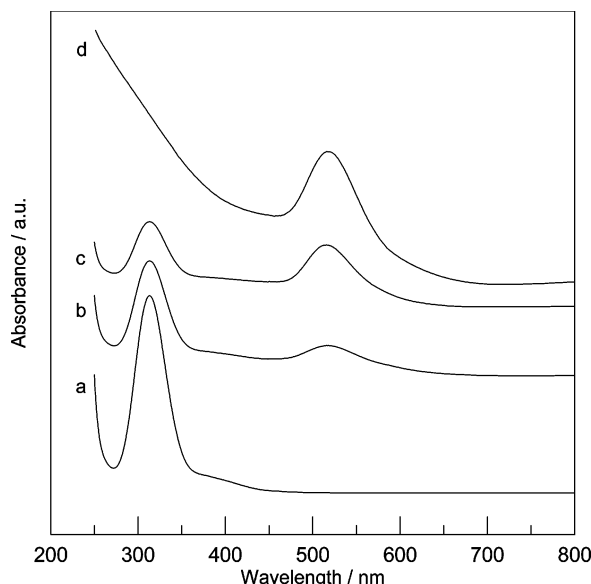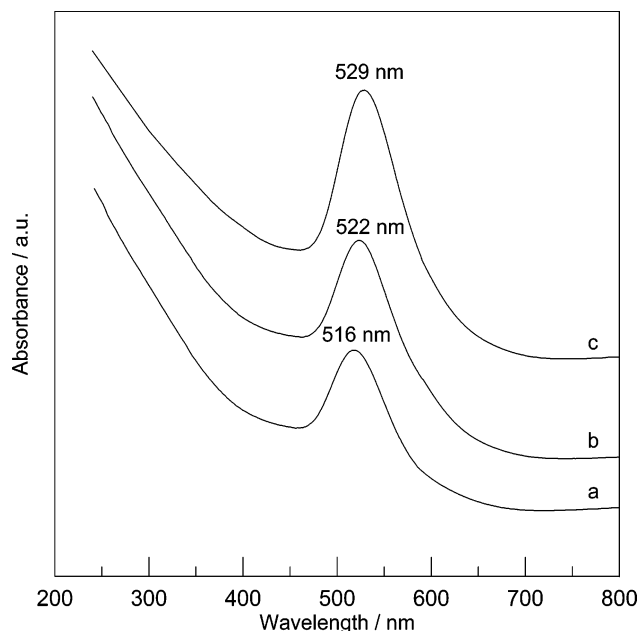
Figure 4. UV−vis spectra of Au-containing colloidal solutions: (a) Au-containing complexes after roughing the Au substrate; gold nanoparticles synthesized by sonoelectrochemical reduction at a cathodic overpotential of 0.2 V from the OCP of 0.82 V vs Ag/AgCl for (b) 4 min, (c) 20 min, and (d) 60 min, respectively, in the solution containing Au complexes prepared in this work.

Figure 5. UV−vis spectra of gold nanoparticles synthesized by sonoelectrochemical reduction at different cathodic overpotentials from the OCP of 0.82 V vs Ag/AgCl in the solution containing Au complexes: (a) 0.2 V; (b) 0.4 V; (c) 0.6 V.

Figure 6. XPS Au $4f_{7/2-5/2}$ core-level spectra of Au-containing complexes in solutions after roughing the Au substrate (curve a), gold nanoparticles synthesized by sonoelectrochemical reduction at an overpotential of 0.2 V in the solution containing Au complexes (curve b), and the gold substrate before the roughening procedure (curve c).

requirement is to accelerate the transfer of gold clusters formed from the cathodic vicinity to the bulk solution. The sonification and the mechanical stirring used in this study can satisfy this requirement. Further experiments indicate that only the mechanical stirring would result in serious deposition of Au nanoparticles on the substrate. Similarly, only sonification would cause the diffusion issue for the reactant of Au-containing complexes. Meanwhile, the prepared Au nanoparticles demonstrate a predominate (111) orientation, as confirmed by XRD analyses.

As shown in spectrum a of Figure 4, the absorbance maximum of Au-containing complexes before the sonoelectrochemical reduction appears approximately at 309 nm, which is markedly different from that of zerovalent Au located at ca. 520 nm[33,34] and can be confirmed from the XPS analysis. Correspondingly, the appearance of the characteristic absorbance maximum at ca. 516 nm, as shown in spectrum b of Figure 4, after the sonoelectrochemical reduction at an overpotential of 0.2 V for 4 min reveals that the elemental Au(0) nanoparticles can be readily synthesized by the electrochemical reduction at room temperature under ultrasonication in the solution containing Au complexes, which was prepared in this study. By increasing the reduction time to 20 min, the characteristic absorption maximum bands of the Au-containing complexes and the elemental Au nanoparticles decrease and correspondingly increase, respectively, as illustrated in spectrum c of Figure 4. By integrating their individual area of absorption bands, it shows that the contents of the elemental Au nanoparticles in the whole Au particles are ca. 20% and 60% for the reduction times of 4 and 20 min, respectively. This quantitative result is consistent with that evaluated from the coulometric plot, as shown in Figure 2. No characteristic absorption band of positive charged Au at 309 nm appearing in Figure 4d indicates that the reduction reaction is almost complete at 60 min.

Figure 5 demonstrates the absorption maximum bands of gold nanoparticles synthesized by sonoelectrochemical reduction at different cathodic overpotentials. The absorption maximum band at 516 nm with a cathodic overpotential of 0.2 V performs red
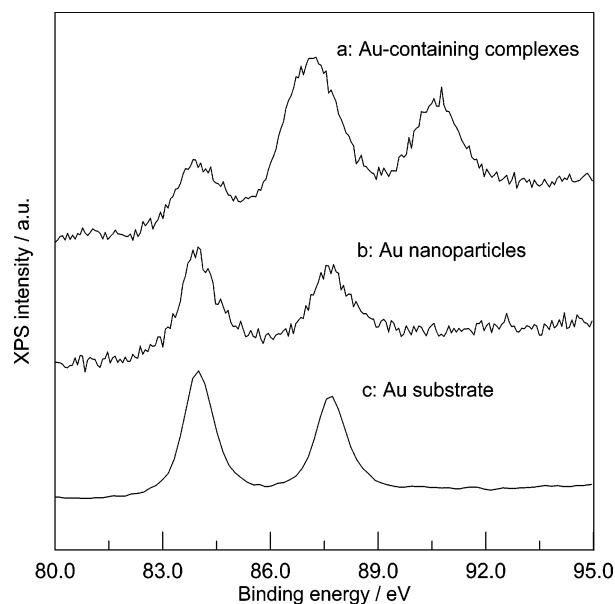
shifts to 522 and 529 nm when more cathodic overpotentials of 0.4 and 0.6 V, respectively, were used. The corresponding complete reduction times were 7, 20, and 60 min for the applied cathodic overpotentials of 0.6, 0.4, and 0.2 V, respectively. Clearly, the advantage of employing more cathodic overpotential is shortening of the reaction time; however, the obtainable particle sizes become larger. TEM analyses show that the particles sizes are ca. 2, 5, and 15 nm for applying cathodic overpotentials of 0.2, 0.4, and 0.6 V, respectively.

Figure 6 displays the XPS Au $4f_{7/2-5/2}$ core-level spectra of the positively charged Au-containing complexes (spectrum a) and the elemental Au nanoparticles (spectrum b) before and after the sonoelectrochemical reduction at an overpotential of

0.2 V, respectively, and the Au substrate used for the ORC procedure (spectrum c). As shown in spectra b and c, the doublet peaks located at 84 and 87.7 eV can be assigned to Au(0).[35] Based on these two similar spectra, the Au nanoparticles prepared by sonoelectrochemical methods in this study can be confirmed to be in an elemental state. Comparing spectrum a, representing the positively charged Au-containing complexes, with spectrum b or c, representing the elemental nanoparticles Au(0), it is found that there are extra oxidized components of Au shown in the higher binding energy side. The oxidized Au shown in spectrum a can be assigned to monovalent Au(I) and trivalent Au(III) at 85.2 and 86.7 eV, respectively.[36] No further deconvolution was made, and the term of positively charged Au was adopted in this study.

Conclusions

We have developed a sonoelectrochemical pathway to synthesize size-controlled gold nanoparticles ranging from 2 to 15 nm in diameter in aqueous solutions from gold substrates without the addition of any stabilizers. The prepared nanoparticles size increases with the increase of the cathodic overpotential applied. Furthermore, the ratio of Au nanoparticles to Au-containing nanocomplexes in solutions can be easily controlled by adjusting the sonoelectrochemical reduction time. The study of the potential application of this methodology to other noble metals or bimetals is currently underway.

References and Notes

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