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pH-insensitive fabrication of gold nanoparticles with high concentration by ultrasound-assisted electrochemical process via aid of chitosan

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ABSTRACT

In this work, we report a new pathway to prepare pure gold nanoparticles with high concentrations in acid solutions via the aid of chitosan without the addition of other stabilizers and reductants based on electrochemical methods. Interestingly, this fabrication of gold nanoparticles with high concentrations in solutions is pH-insensitive. The characteristics of prepared gold nanoparticles were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (HRXPS) measurements. Experimental results indicate the concentration and the particle size of Au nanoparticles prepared in 0.1N HCl are ca. 50 ppm and 12 nm in diameter, respectively. Similar experiment performed in 0.1N NaCl with the aid of chitosan shows that the corresponding concentration of prepared Au nanoparticles is ca. 100 ppm. Further similar experiments performed in 0.1N HCl and 0.1N NaCl without the aid of chitosan show that the corresponding concentrations of prepared Au nanoparticles are ca. 1 and 60 ppm, respectively.

1. Introduction

Noble metal nano-sized materials, such as gold and silver nanoparticles [1–3], have attracted much interest due to their unusual properties of optical [4], chemical [5], photoelectrochemical [6], and electronic [7] properties. The potential applications for nanoparticles, especially in the field of DNA detection [8,9] and catalysts modification [10,11], are rapidly growing because of their unique electronic structure and extremely large surface areas. As shown in the literature, the developed methods for noble metal nanoparticles fabrications include chemical reduction [12], sonochemical reduction [13], laser ablation [14], annealing from high-temperature solutions [15], metal evaporation [16], Ar^+ ion sputtering [17], ultrasound-assisted electrochemical reduction [18], and UV-, or, laser-, or microwave-assisted syntheses [19–21]. Meanwhile, some stabilizers, like sodium dodecyl sulfate [22], sugar ball [23] and poly(vinylpyrrolidone) [24] were used, and some stabilization technologies of thiol-ligand coatings [25] and polymer capping agents [26] were developed to prevent the prepared nanoparticles from aggregating. Huang et al. [27] reported a novel, simple, and convenient method for the preparation of water-soluble biofunctional Au nanodots for the detection of Concanavalin A and Escherichia coli. The Au nanodots were prepared through reduction of $HAuCl_4$ with tetrakis(hydroxymethyl)phosphonium chloride, which acts as both a reducing and capping agent. Lu et al. [28] reported a thiol-functionalized polyhedral oligomeric silsesquioxane (SH-POSS) as a protective group for the preparation of POSS-protected gold nanoparticles (POSS-Au NPs). The organic/inorganic hybrid SH-POSS NPs exhibited an interesting platelike morphology arising from steric hindrance between the isobutyl groups of SH-POSS. Bimetallic alloy nanoparticles consisting of two noble metals Pt–Ag supported on carbon with a variable dimension were successfully prepared by ethylene glycol (EG), as reported by Hwang et al. [29]. This work highlighted the viability of EG synthesis methodology yielding a range of particle size from 1.2 to 3.1 nm with 1:1 atomic composition but with different alloying extents by a simple control over the solution pH of the preparation medium. Brinas et al. [30] developed a method in preparing size-controllable Au nanoparticles capped with glutathione by varying the pH of the solution before reduction. This method is based on the formation of polymeric nanoparticle precursors, Au(I)-glutathione polymers, which change size and density depending on the pH. As reported by Guan et al. [31], the aggregation of histidine-functionalized Au nanoparticles induced by Fe^{3+} was identified to show pH-dependent character. At low pH value, the Fe^{3+} ion was effective to induce aggregation of the Au nanoparticles via its coordination with imidazole group of the histidine ligand. At pH value higher

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than 9, the histidine ligand provided an additional coordination site for the Fe^{3+} ion due to deprotonization of its α-NH_2 group.

Although the preparation of Au nanoparticles by a chemical reduction of commercial positively charged Au using suitable reductants was popularly used, the purity of prepared Au nanoparticles was an unavoidable issue. In this work, we report a new pathway based on electrochemical methods to prepare pure and Au nanoparticles with high concentrations in acid solutions from bulk Au substrates via the aid of natural chitosan. We aim to demonstrate that this fabrication of Au nanoparticles in solutions is pH-insensitive.

2. Experimental

2.1. Chemical reagents

The HCl electrolyte (p.a. grade) purchased from Acros Organics was used as received without further purification. Commercial chitosan powders (85% deacetylated) were purchased from First Chemical Works, Taiwan. All of the solutions were prepared using deionized 18.2 MΩ cm water provided from a MilliQ system.

2.2. 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 with bare surface area of 4 cm^2, a sheet of 2 cm × 4 cm stainless steel, and a KCl-saturated silver–silver chloride (Ag/AgCl) rod were employed as the working, counter, and reference electrodes, respectively. Before the oxidation–reduction cycles (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. Then the electrode was cycled in a deoxygenated aqueous solution of 40 mL containing 0.1N HCl and 1 g/L chitosan from −0.28 to +1.22 V vs. Ag/AgCl at 500 mV/s for 500 scans under slightly stirring. The durations at the cathodic and anodic vertexes are 5 and 5 s, respectively. After this roughening procedure, Au- and chitosan-containing complexes were left in this aqueous solution at pH 1.12. This strategy of electrochemically preparing $AuCl_4^-$ ions can ensure the purity of subsequently synthesized Au nanoparticles. Immediately, without changing the electrolyte, the gold working electrode was replaced by a platinum substrate with the same bare surface area of 4 cm^2. Then a constant cathodic overpotential of 0.6 V from the open circuit potential (OCP) of ca. 0.81 V vs. Ag/AgCl was applied under sonification and a slightly stirring to synthesize Au nanoparticles. The main purpose for using the ultrasonic generator is to avoid prepared Au nanoparticles depositing onto the electrode under ultrasound-assisted electrochemical reduction. The ultrasonic irradiation was performed by using an ultrasonic generator (model XL2000, Microson) and operated at 20 kHz with a barium titanate oscillator of 3.2 mm diameter to deliver a power of 100 W. Subsequently, the clear Au nanoparticles-containing solution was separated from chitosan by sonification and centrifugation. This Au-containing solution was placed in an ultrasonic bath (Branson 2510, 42 kHz) for 30 min and was further centrifugalized at 4000 rpm for 2 min to remove chitosan for preparing pure Au nanoparticles in an aqueous solution.

2.3. 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 be dried in a vacuum oven. Then the sample was examined by using a Philips Tecnai G2 F20 electron microscope with an acceleration voltage of 200 kV. Ultraviolet–visible absorption spectroscopic measurements were carried out on a PerkinElmer Lambda 35 spectrophotometer in 1 cm quartz cuvettes. For X-ray diffraction (XRD) measurements, instrument of ARL X'TRA Thermo with a supplemental capillary was used to examine the liquid sample. Before recording the high-resolution X-ray photoelectron spectroscopy (HRXPS), sample powders were obtained via centrifugation collections at 15,000 rpm for 3 min. In HRXPS measurements, a ULVAC PHI Quantera SXM spectrometer with monochromatized Al Kα 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.

3. Results and discussion

As shown in the literature, the chloride electrolyte used in the ORC treatment was generally selected since it can facilitate the metal dissolution–deposition process that is known to produce surface-enhanced Raman scattering (SERS)-active roughened surfaces [32]. Meanwhile, the Au-containing complexes were also left in the solution after roughening the Au substrate, as reported in our previous study [18]. On the other hand, chitosan is an ubiquitous biopolymer with a linear polysaccharide obtained by deacetylation of chitin [33,34]. By replacing the majority of aminoacetyl groups in chitin by the amine moieties chitosan molecules can be dissolved in acidic water. In such solution, chitosan is a positively charged polyelectrolyte due to the protonation of the amine groups. Chitosan has biological characteristics and physicochemical properties. This makes it attractive for many potential applications in food, pharmaceutical and cosmetic industries, and bioengineering [35]. In this work, chitosan was added in a 0.1N HCl solution to form static electricity attraction between positively charged chitosan and negatively charged $AuCl_4^-$ formed in the solution after the ORC treatment. This would be favorable for the subsequent reduction of capped $AuCl_4^-$ to form Au nanoparticles in the solution via ultrasound-assisted electrochemical reduction. Fig. 1 demonstrates the experimental processes for preparing gold nanoparticles by ultrasound-assisted

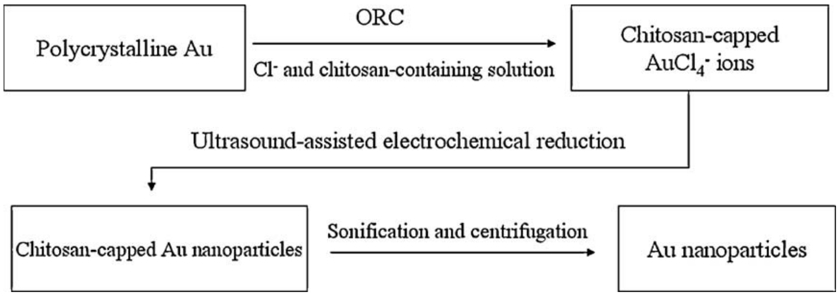

Fig. 1. Experimental processes for preparing gold nanoparticles.

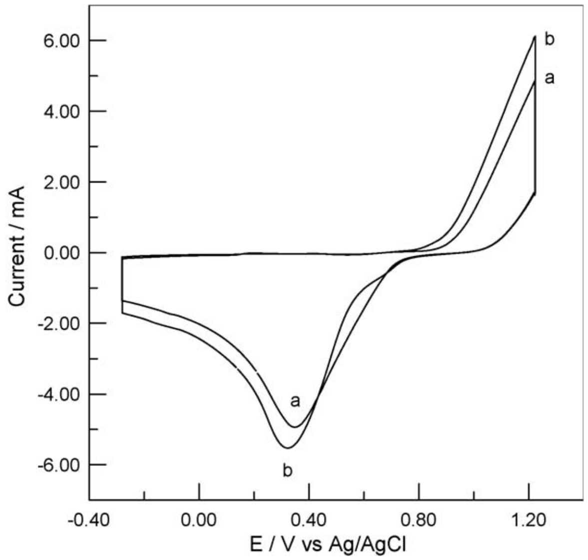

Fig. 2. Cyclic voltammogram at 500 mV/s of the 500th scan for electrochemically roughened gold substrates in different solutions: (a) 0.1N HCl; (b) 0.1N HCl containing 1 g/L chitosan.

electrochemical process via aid of chitosan. Fig. 2 shows the results of the 500th scan of cyclic voltammograms for the dissolution and redeposition of Au substrates in 0.1N HCl solutions with and without the addition of chitosan. Basically, these *I*–*E* curves are quite similar, but the area of the cathodic peak is increased due to the addition of chitosan, as demonstrated in curve b. This increase may also be ascribed to the remarkable increase of anodic dissolution of the Au substrate due to the presence of chitosan. As shown in our previous study [36], after the ORC procedure of roughening the Au substrate, yellow complexes of $AuCl_4^-$ would be produced in the solution after roughening the Au substrate. Then $AuCl_4^-$ can be adsorbed on the nitrogen of chitosan by following the mode of self-assembled monolayers (SAMs) [37,38]. Moreover, the $AuCl_4^-$ is readily adsorbed on the protonated chitosan via static electricity force. As expected, the transparent and colorless chitosan-containing solution was changed to yellow one after the ORC procedure in roughening the Au substrate. It reveals that $AuCl_4^-$ is readily adsorbed on chitosan as a precursor for the subsequent preparation of red Au nanoparticles in a solution.

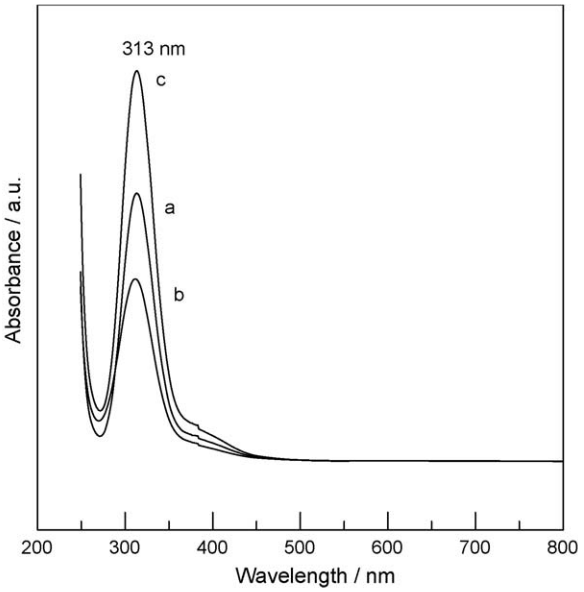

Fig. 3. UV–vis spectra of Au-containing complexes in solutions after roughing the Au substrates in different solutions: (a) 0.1N HCl; (b) 0.1N HCl and gradually dropping 1N NaOH into the solution to maintain the pH near 3; (c) 0.1N HCl containing 1 g/L chitosan.

As shown in Fig. 3, the absorbance maxima of $AuCl_4^-$ nanocomplexes all appear approximately at 313 nm [36] for prepared nanocomplexes in acidic solutions with and without chitosan, which are markedly different from those of zerovalent Au nanoparticles located at ca. 520 nm [39]. Spectrum b of Fig. 3 represents the pH-adjusted solution with pH 3, which was obtained via gradually dropping 1N NaOH into the solution after the ORC procedure for producing $AuCl_4^-$ nanocomplexes. This pH value is selected since it is corresponding to the considerable concentration of Au nanoparticles obtained in a solution after a subsequent reduction, as discussed later. Results from Fig. 3 indicate that chitosan is not a necessity for preparing $AuCl_4^-$ nanocomplexes in solutions via the ORC procedure. However, it plays an important role in the subsequent preparation of zerovalent Au nanoparticles in solutions. As shown in spectrum a of Fig. 4 (experiment performed in pH 1.12), after applying a cathodic overpotential of 0.6 V for obtaining zerovalent Au nanoparticles via ultrasound-assisted electrochemical reduction, the yellow $AuCl_4^-$ nanocomplexes-containing solution without the chitosan changes into transparent colorlessness. Moreover, the absorbance maximum of the solution originally located at 313 nm disappears. Instead, a new band of absorbance maximum appears at 531 nm, which represents a characteristic band of zerovalent Au nanoparticles [39]. These phenomena reveal that zerovalent Au nanoparticles with high concentrations are difficultly obtained in a more acidic solution without chitosan because most Au nanoparticles are easily redeposited on the working electrode. However, a considerable concentration of Au nanoparticles can be obtained in a solution of pH 3 without the aid of chitosan after ultrasound-assisted electrochemical reduction, as shown in spectrum b of Fig. 4. The absorbance maximum of the solution changes from at 313 to at 535 nm. More encouragingly, as shown in spectrum c of Fig. 4, the absorbance maximum of the solution changes from 313 to at 522 nm after heating the $AuCl_4^-$ nanocomplexes-containing solution in the presence of chitosan.

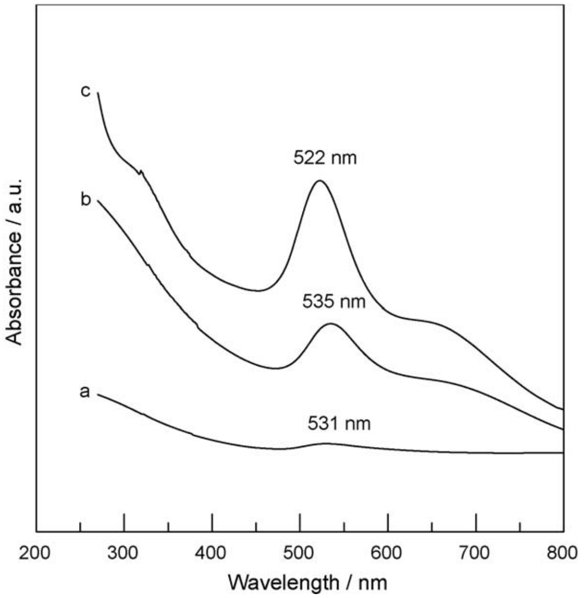

Fig. 4. UV–vis spectra of gold nanoparticles synthesized by ultrasound-assisted electrochemical reduction at constant cathodic overpotentials of 0.6 V from the OCP in the solutions after roughing the Au substrates in different solutions: (a) 0.1N HCl; (b) 0.1N HCl and gradually dropping 1N NaOH into the solution to maintain the pH near 3; (c) 0.1N HCl containing 1 g/L chitosan.

Also, the solution color changes from yellow to more deeply red after applying a cathodic overpotential of 0.6 V for obtaining zerovalent Au nanoparticles via ultrasound-assisted electrochemical reduction. These results indicate that zerovalent Au nanoparticles with high concentrations are successfully synthesized. Further inductively coupled plasma-mass spectrometer (ICP-MS) analyses indicate that the concentrations of the synthesized zerovalent Au nanoparticles in 0.1N HCl solutions with and without chitosan are ca. 50 and 1 ppm, respectively. Other metal elements, excluding Na, are not detected in the prepared Au nanoparticles-containing solution via the aid of chitosan. No aggregation of Au nanoparticles is observed in an ambient atmosphere for at least 3 months for the Au nanoparticles-enriching solution. The concentration of the synthesized zerovalent Au nanoparticles in solution with pH 3 without the aid of chitosan, which is corresponding to spectrum b of Fig. 4, is ca. 20 ppm. We also try to synthesize red zerovalent Au nanoparticles in 0.1N NaCl solutions (ca. pH 6.67) with and without the aid of additions of 1 g/L chitosan and follow the same electrochemical method discussed above. The experimental results indicate that the concentrations of the synthesized zerovalent Au nanoparticles in 0.1N NaCl solutions with and without chitosan are ca. 100 and 60 ppm, respectively. Examining the data revealed from the experiments performed in 0.1N NaCl and 0.1N HCl solutions with and without chitosan, it was found that the concentration of synthesized Au nanoparticles without the aid of chitosan is increased by 60-fold of magnitude via changing the electrolyte of HCl into NaCl. However, this change in electrolyte just can increase the concentration of Au nanoparticles by 2-fold of magnitude in the presence of chitosan. Therefore, we think the fabrication of Au nanoparticles in solutions is pH-insensitive due to the contribution of the capping effect of chitosan.

The dispersion and the particle size of prepared Au nanoparticles in 0.1N HCl solutions with the aid of chitosan are examined by using TEM images, as shown in Fig. 5. The nanoparticles with an average diameter of ca. 12 ± 6 nm demonstrate no aggregation and fairly even dispersion for preparing the Au nanoparticles with the aid of chitosan via the ultrasound-assisted electrochemical reduction. Fig. 6 shows the prepared Au size distributions corresponding to Fig. 5. The average diameter of prepared Au nanoparticles in solutions can be also determined from experiments of dynamic light scattering (model LB-550, HORIBA). The result indicates that the average diameter of prepared Au nanoparticles is ca. 11 ± 5 nm. Fig. 7 shows the corresponding moiré patterns of the Au nanoparticles demonstrated in Fig. 5. It exhibits a one-dimensional fringe lattice due to moiré interference, indicating that these nanoparticles are themselves crystalline [40]. Also, (1 1 1) lattice fringes with an interplanar spacing of 2.36 Å were also measured for almost all of the lattice planes. This is reasonable since the low index plane (1 1 1) has the lowest surface energy [41]. The crystalline orientations of prepared Au nanoparticles with the aid of chitosan were further analyzed by XRD. As shown in Fig. 8, the predominant peak of the prepared Au nanoparticles in an aqueous solution is located at 38.2°, which can be assigned to the (1 1 1) faces of Au. Other minor peaks located at 44.4°, 64.6° and 77.6° are assigned to the (2 0 0), (2 2 0), and (3 1 1) faces of Au, respectively, according to the XRD handbook. As reported in the literature regarding an in situ electrochemical scanning tunneling microscopy study of the structural changes of silver surfaces following an ORC treatment, the low index plane (1 1 1) has the

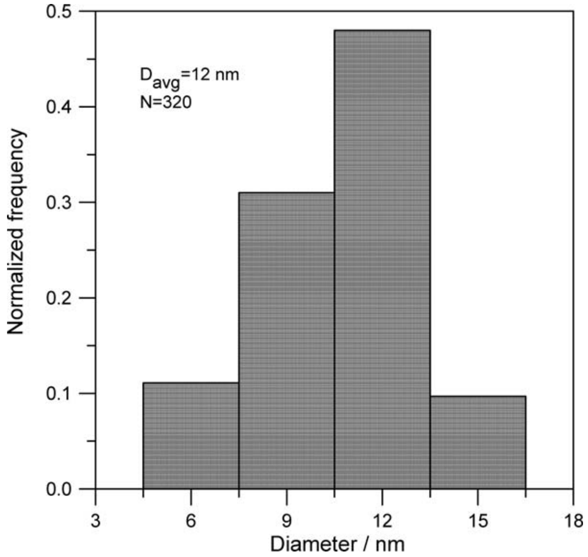

Fig. 6. Au size distributions corresponding to Fig. 5.

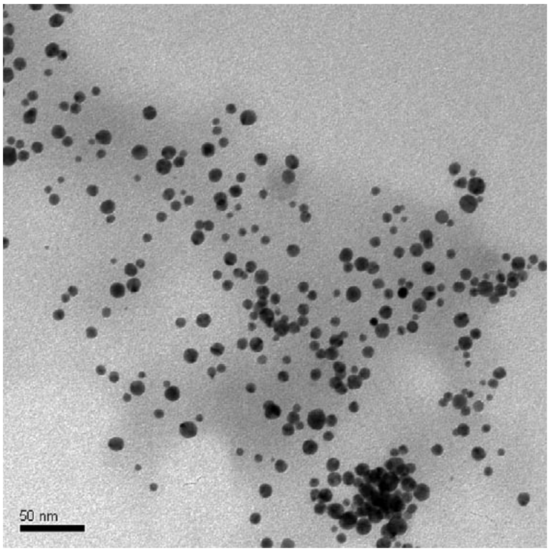

Fig. 5. TEM micrograph of prepared Au nanoparticles with the aid of chitosan, showing size and dispersion; scale of nano-bar being 50 nm.

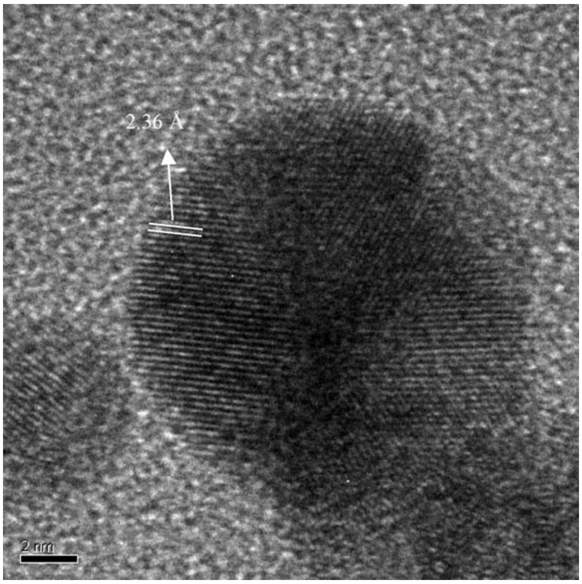

Fig. 7. High-resolution TEM micrograph of prepared Au nanoparticles with the aid of chitosan, showing the (1 1 1) lattice fringes with an interplanar spacing of 2.36 Å; scale of nano-bar being 2 nm.

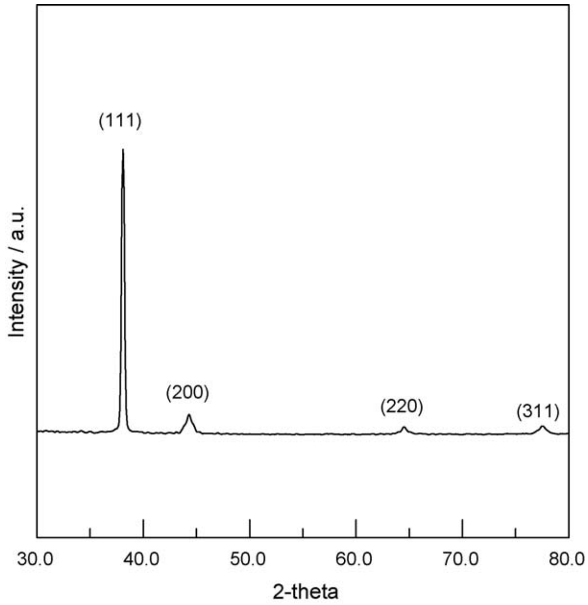

Fig. 8. XRD patterns of prepared Au nanoparticles with the aid of chitosan.

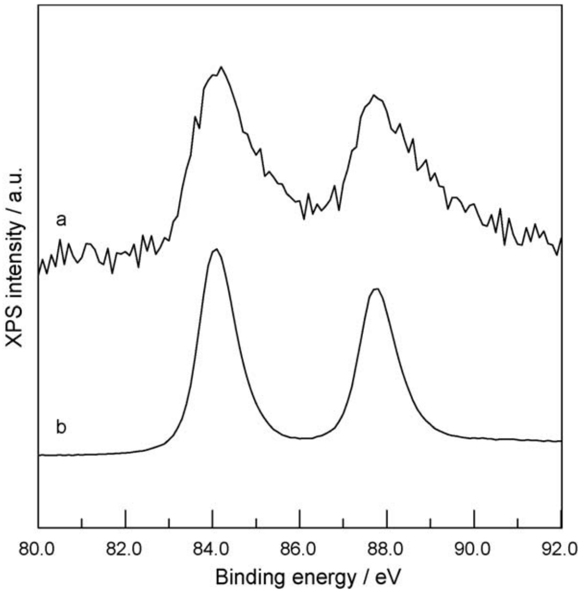

Fig. 10. HRXPS Au $4f_{7/2-5/2}$ core-level spectra of prepared Au nanoparticles with the aid of chitosan (curve a), and the Au substrate before the ORC treatment (curve b).

lowest surface energy [42]. The growth of this crystal plane becomes apparent after experiment. Since Au and Ag have the same forms of crystal lattices, the XRD peaks at (2 0 0), (2 2 0) and (3 1 1) have a very low intensity in comparison to the (1 1 1) peak is reasonable. Therefore, Au nanoparticles of predominant (1 1 1) face with high concentrations in solutions can be synthesized proposed in this work. Moreover, the prepared Au nanoparticles are stable in solutions for at least 3 months, but the solutions are free of other stabilizers. It reveals that chitosan can work as a stabilizer.

The main contribution of this work is to prepare pure Au nanoparticles. Thus the assistant of natural chitosan should be completely separated from the prepared Au nanoparticles, which was accomplished via sonification and centrifugation procedures mentioned in the experimental section. Here we use HRXPS to examine this issue. Fig. 9 shows the HRXPS survey spectrum of the prepared Au nanoparticles with the aid of chitosan. It is well known chitosan is composed of H, C, N and O elements. The absence of N signal confirms that the prepared Au nanoparticles are successfully separated from chitosan. The C and O signals shown in Fig. 9 are unavoidable from contaminant even though samples do not contain components of carbon and oxygen, which are always happened in HRXPS experiments. Fig. 10 displays the HRXPS Au $4f_{7/2-5/2}$ core-level spectra of the prepared Au nanoparticles via the aid of chitosan (spectrum a) and the Au substrate used for the ORC procedure (spectrum b). As shown in spectra a and b, the doublet peaks located at 84 and 87.7 eV can be assigned to Au(0) [43]. Basing on these two similar spectra, the Au nanoparticles prepared by ultrasound-assisted electrochemical methods via the aid of chitosan in this study can be confirmed to be in an elemental state.

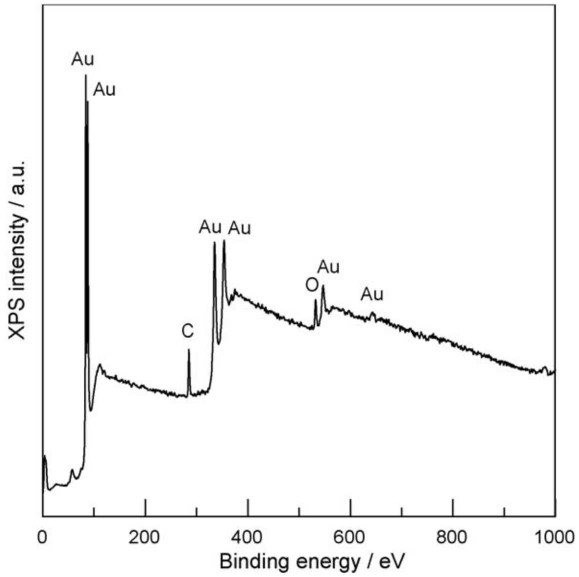

Fig. 9. HRXPS survey spectrum of prepared Au nanoparticles with the aid of chitosan.

4. Conclusions

In this work, pure and Au nanoparticles with high concentrations are successfully synthesized in 0.1N HCl solutions based on electrochemical methods via the aid of natural chitosan. Experimental results indicate the concentration and the particle size of prepared Au nanoparticles are ca. 50 ppm and 12 nm in diameter, respectively. Moreover, this fabrication of Au nanoparticles in solutions is pH-insensitive due to the contribution of the capping of chitosan. The prepared Au nanoparticles in solutions are stable in an ambient atmosphere for at least 3 months. This new approach provides a pathway to prepare pure and Au nanoparticles with high concentrations in acidic solutions, which can be applicable to biologically corresponding fields.

Acknowledgments

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