Improved Rapid Preparation of Polyelectrolyte-protected Gold Nanoparticles through a Microwave-based Thermal Process

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This work demonstrates the improved, size-controlled preparation of polyelectrolyte-protected gold nanoparticles, carried out by microwave radiation of an aqueous solution containing chloroauric acid and amine-containing polyelectrolyte.

Nanosized particles of noble metals hold promise for use as advanced materials with novel electronic, optical, and thermal properties as well as catalytic properties because of their potential applications in the fields of physics, chemistry, biology, medicine, material science, and their different interdisciplinary fields.[1] Therefore the synthesis and characterization of metal nanoparticles have attracted considerable attention from a fundamental and practical point of view.[2] To date, a variety of methods have been developed to prepare metal particles and many reviews can now be available.[3] However, chemical reduction of gold slats is still a general route. Since nanoparticles tend to be fairly unstable in solution, special precautions have to be taken to avoid their aggregation or precipitation. The most common strategy is the use of protective agent, which not only prevents their aggregation, but also results in functionalized particles.[4]

Polyelectrolytes have been widely used as both building blocks for the creation of multilayer thin films[5] and excellent colloid protective agents to sterically and electrostatically stabilize colloids.[6] Polyelectrolyte-protected nanoparticles have been commonly prepared via a two-step method where gold salt was first mixed with polyelectrolyte, followed by the addition of a reducing agent under rapid stirring. More recently, Sun et al. have developed a simple heat-treatment-based method for preparing polyelectrolyte-protected gold nanoparticles in a single process, carried out by heating an aqueous solution containing chloroauric acid and amine-containing polyelectrolyte without the additional step of introducing other reducing agents and protective agents.[7] However, this conventional heating method suffers from both the larger ($\approx$25 nm in diameter) and uncontrollable particle size.

Microwave chemistry has experienced an exponential growth rate, in both industry and academia. Microwave irradiation as an efficient heating method has been widely used in chemistry since 1986.[8] The microwave-based fast, simple, energy-efficient synthetic route has also been developed for the preparation of metal nanoparticles.[9] I present herein a microwave-based improved preparation of polyelectrolyte-protected gold nanoparticles, carried out by microwave radiation of a solution containing chloroauric acid and the same amine-containing polyelectrolyte as that used by Sun et al. in their study.[7] It suggests that this microwave-based thermal process can produce smaller gold nanopatrticles ($\approx$4 nm in diameter) and provide better control over particle size by varying the molar ratio of polyelectrolyte to gold.

Chloroauric acid and linear polyethylenimine (LPEI, MW: 423) were purchased from Aldrich. All reagents were used without further purification. The water used was purified through a Millipore system. Three samples were prepared according to the following procedure: Firstly, 200 µL of 0.024 M chloroauric acid aqueous and x µL of 0.056 M LPEI aq solution was mixed together with molar ratio 5:1, 8:1, and 15:1 of LPEI (repeating unit) to gold, corresponding to samples 1, 2, and 3, respectively. Each solution was diluted to 20 mL with water, then subjected to heat-treatment in a domestic microwave oven operated at 100% power of 600 W for two minutes.

UV–vis spectra were collected on a CARY 500 Scan UV–vis–near infrared (UV–vis–NIR) spectrophotometer. Samples for TEM characterization were prepared by placing a drop of gold colloidal sample on carbon-coated copper grid and dried at room temperature. TEM measurements were made on a JEOL 2010 transmission electron microscopy operated at an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were collected on an ESCLAB MKII using Mg as the exciting source.

The formation of gold nanoparticles was confirmed by UV–vis spectra of three samples (Figure 1). The maxima of the plasmon resonance band were located at 530, 517, and 534 nm, for samples 1, 2, and 3, respectively, indicating the formation of gold nanoparticles.[10] It is worthwhile mentioning that all these colloidal samples were quite stable for several months without observable aggregation, indicating that LPEI serves as a very effective protective agent for the formation of gold nanoparticles.

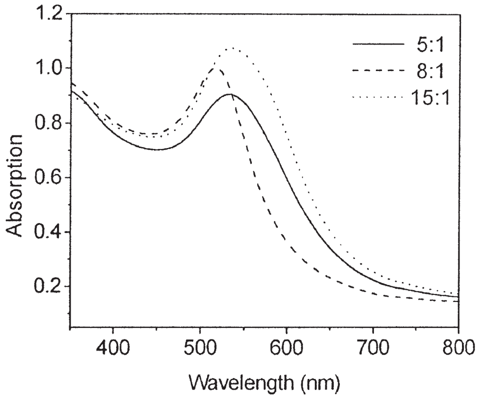

Figure 1. UV–vis spectra of three samples prepared with LPEI to gold ratio 5:1, 8:1, 15:1.

The TEM images also provide another piece of evidence for the formation of gold nanoparticles, as shown in Figure 2. Clearly, gold particles of samples 1 and 2 are both spherical in shape and the particles of sample 3 are irregular in shape. Although a fraction of particles of samples 1 and 3 seem to have sintered, however, a closer examination reveals that these particles are not in direct physical contact. Gold particle aggregates can result

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in the occurrence of longitudinal plasmon resonance.[11] No longitudinal plasmon resonance occurs in UV–vis spectra of three samples, indicating the absence of particle aggregates. Therefore, these differences observed in TEM images can be partly attributed to the different sizes, but not different aggregated forms of gold particles. Also mentioned here is that it is, however, impossible to obtain reliable overall information about the nanocomposites existing in solution by using TEM because of the fact that evaporation of solvent and high vacuum used for sample preparation and characterization in this technique may lead to secondary aggregations on the grid and to the expansion of the flattened nanoparticles. Evidently, the gold particle size can be controlled by the variation of molar ratio of LPEI (repeating unit). At the molar ratio 3:1, larger gold particles ($\approx$8 nm) are observed. As the molar ratio is increased to 8:1, smaller gold particles ($\approx$4 nm) are noticed, which can be attributed to that high molar ratio provides more LPEI molecules to interact with a gold particle produced and limits particle growth. However, as the molar ratio is higher (15:1), the mean particle size is increased unexpectedly to 7 nm and the formation reason of larger particles at this molar ratio is unclear at present. Also mentioned here is that reproducible results can be obtained in my present study.

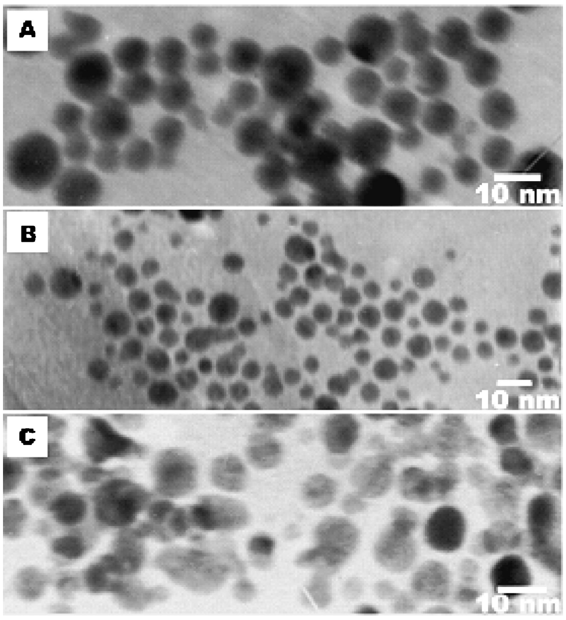

Figure 2. Typical TEM images of three samples prepared with LPEI to gold ratio (A) 5:1, (B) 8:1, and (C) 15:1.

Obviously, the size of as-prepared gold nanoparticles is smaller than that obtained by conventional heating method,[7] which can be attributed to that microwave irradiation can heat uniformly the reaction container, leading to a more homogeneous nucleation and shorter crystallization time compared with those for conventional heating.

To further confirm the formation of Au atoms from chloroauric acid, XPS was used to identify the change in oxidation states for Au after the microwave irradiation reaction had occurred. Figure 3 shows the XPS spectra of precipitate of sample 1. That the Au $4f_{7/2}$ peak appears at a binding energy of 83.5 eV and the Au $4f_{5/2}$ peak appears at a binding energy of 87.6 eV indicates the formation of metallic gold.[12]

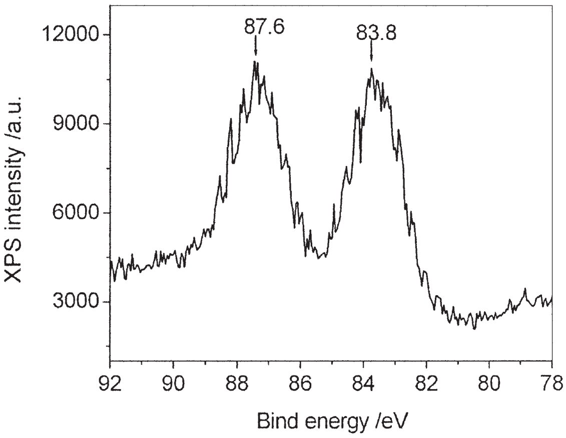

Figure 3. XPS spectra of precipitate obtained by centrifuging sample 1.

In conclusion, microwave irradiation was proven to be a more effective method than traditional heating method[7] for preparing polyelctrolyte-protected gold nanoparticles from a chloroauric acid/amine-containing polyelectrolyte aqueous solution in that it is fast and more importantly, can provide more control over the particle size.

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