Continuous Synthesis of Colloidal Metal Nanoclusters by Microwave Irradiation

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Received October 12, 1999

Polymer-stabilized metal colloids with small particle sizes and narrow size distributions were prepared by a continuous microwave synthesis. This synthesis method has good reproducibility for synthesizing uniform metal colloids in bulky amount.

Introduction

Nanoscopic materials have been attracting increasing interest for their unique chemical and physical properties and potential technological applications.[1] For decades, efforts have been made to prepare nanoscale metal colloids and clusters with narrow size distribution, which is important to the application in catalysis,[2−7] magnetism,[8] and electronics.[9] By means of chemical reduction,[10] UV photolysis,[11] thermal decomposition,[12] metal vapor deposition,[13] electrochemical synthesis,[14] and so on, stable nanoscale metal colloids could be synthesized. Very recently, some new approaches to the generation of metal nanoclusters have appeared in the literature. Synthesis of stable metal iron colloids by sonochemical decomposition[15] of iron-containing complexes such as $Fe(CO)_5$ was reported. Sun et al.[16] described a technique for the preparation of stable nanoparticles based on the rapid expansion of supercritical fluid solutions (RESS) coupled with chemical reduction. By microwave dielectric heating of poly(*N*-vinyl-2-pyrrolidone)/H_2PtCl_6 /NaOH/H_2O/ethylene glycol, nanoscale platinum colloids with a nearly uniform spherical shape were prepared.[17]

Quantity synthesis is a prerequisite for industrial application of metal clusters, as stated by Matijevic.[18] However, most of the reported methods could only be suitable for laboratory use and not for the large-scale generation of metal nanoclusters. For example, the alcoholic reduction method[3,5] will be unsuccessful when the volume of solution exceeds about 2 L. A method utilizing a combination of matrix effect and freeze-drying[19] was developed to achieve large-quantity production of metal nanoclusters; however, it suffered from batch manipulation. For industrialization, continuous flowing manipulation is an ideal means of obtaining products in bulk amounts. To the best of the authors' knowledge, no report focusing on continuous synthesis of nanoscopic metal clusters or colloids has appeared. In this article, we describe the continuous synthesis of large quantities of polymer-stabilized metal nanoclusters by microwave irradiation.

Experimental Section

Material and Instruments. Poly(*N*-vinyl-2-pyrrolidone) (PVP, MW = 40 000) was supplied by Fluka. Analytical grade reagents were purchased from Beijing Chemical Corporation.

Ultraviolet absorption spectrum measurements were carried out with an Unicam SP1750 ultraviolet spectrophotometer. Transmission electron microscopy (TEM) was performed with

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10.1021/cm990637l CCC: $19.00
Published on Web 01/04/2000

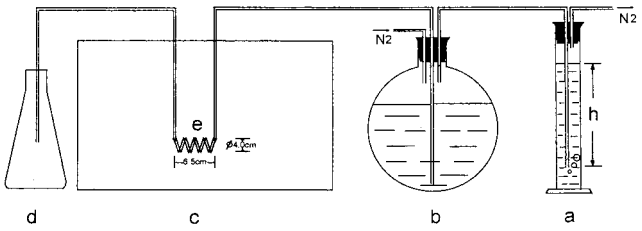

Figure 1. Reaction equipment system: (a) liquid column as a pressure regulator, (b) metal salt solution container, (c) microwave oven cavity, (d) metal cluster dispersion receiver, and (e) spiral tube reactor.

a Hitachi-9000 NAR apparatus. For TEM examination, ethylene glycol in a metal colloidal dispersion was removed by using acetone as a precipitate agent, and the solid residue (containing the metal clusters) was then redispersed in methanol. Specimens were prepared by placing a drop of the cluster dispersion upon a copper grid covered with a perforated carbon film and then evaporating the solvent. The particle diameters were measured from the enlarged photographs. The particle size distribution histograms were obtained on the basis of the measurement of about 300 particles.

Preparation of Polymer-Stabilized Metal Colloidal Cluster. The reaction system is schematically shown in Figure 1. The reactor comprised a 2.8 mm i.d. glass tubing coil (e) located inside the cavity of a domestic microwave oven (Galanz 2450 MHz, WP750). In a 3.0 L round-bottomed flask (b), 1.036 g of $H_2PtCl_6 \cdot 6H_2O$ (2.0 mmol) and 11.14 g of PVP (MW = 40 000, 0.10 mol in monomeric unit) were dissolved in 2.25 L of ethylene glycol, and a 250 mL ethylene glycol solution of NaOH (0.64 g, 16 mmol) was added dropwise with vigorous stirring to give a homogeneous yellow solution. The flask was then connected to the microwave heating system as shown in Figure 1. Nitrogen was conducted to the metal precursor container (b); thereby, adequate pressure was exerted in the round-bottomed flask, and as a result, reaction solution would flow steadily through the spiral tube (e). The flowing rate of the solution, and thus the irradiation time of the solution in the microwave oven cavity, could be regulated by changing the height of liquid column *h* (a). After microwave irradiation, the formed colloidal solution flowing out of the coil was gathered in the receiver (d).

Results and Discussion

UV−vis spectrophotometry was reported as an effective method to monitor the evolution of metal species in the synthesis of colloidal metal clusters,[20,21] because it could quantitatively measure the concentration of species in the solution based on their corresponding absorption spectrum. Under microwave irradiation (with the reaction system shown in Figure 1) at the maximum power output of 750 W, the flowing rate of the solution was adjusted so that the irradiation time of the solution kept in microwave oven cavity was 5, 10, 15, 20, 25, and 30 s, respectively. After irradiation for different time, the reaction solutions were sampled, respectively, for UV−vis spectroscopic measurement. Figure 2 shows the evolution of UV−vis spectra during the formation of platinum colloid. Under microwave irradiation, the temperature of the solvent, ethylene glycol, rose promptly, which may cause the rapid reduction of $PtCl_6^{2-}$ to Pt^0.[17,20] From Figure 2, we can see that the absorption peak of $PtCl_6^{2-}$ at 260 nm changes slightly

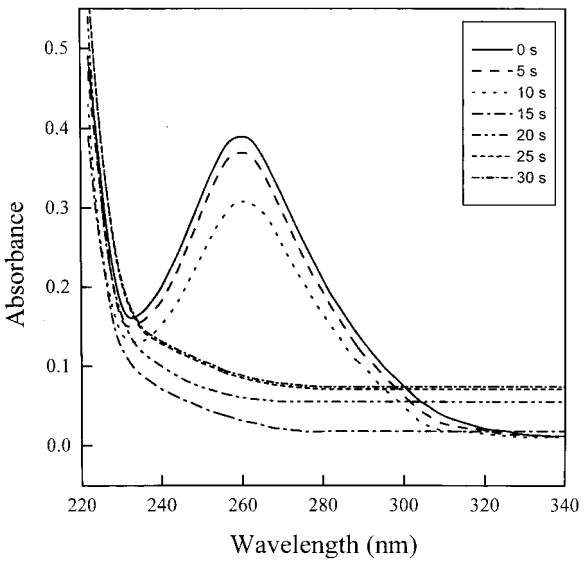

Figure 2. UV−vis spectra during the formation of platinum colloid in ethylene glycol system with continuous microwave irradiation.

at 5 s irradiation of the solution, and then it decreases rapidly with more irradiation and disappears completely at 15 s, which reveals that $PtCl_6^{2-}$ is entirely reduced to Pt^0. Then, Pt^0 atoms accumulate to form platinum clusters with lengthening irradiation, which is indicated by increasing absorbance of UV−vis spectra.[20,21] The formation of platinum clusters was also demonstrated by the observations from transmission electron microscopy (TEM).

A transmission electron microscopy photograph and the size distribution histogram of PVP-stabilized platinum colloid prepared with the continuous microwave method are shown in Figure 3a. It is indicated that the as-synthesized platinum colloid has small particle size (d_{av} = 1.46 nm) and narrow size distribution with a standard deviation σ = 0.25 nm. With irradiation time greater than 25 s, the solution in microwave cavity will boil; however, the platinum colloids so-synthesized have nearly the same particle size and the same size distribution, as verified by TEM. Thus, we set 25 s as the standard irradiation time for the preparation of platinum nanoclusters.

To examine the fluctuation of the results for the microwave continuous-synthesis process, two sets of experiments were carried out. One was that synthesis of 2.5 L of platinum colloidal dispersion (containing ∼0.5 g of metallic platinum) was accomplished for ∼3 h by the continuous manipulation. Multifold sampling of platinum colloidal dispersion was made at different periods, and the platinum colloids obtained were examined by TEM. The TEM results are given in Figure 4. From Figure 4, we can see that platinum colloids have nearly constant average particle diameter and standard deviation during the run, which reveals that there is no obvious fluctuation for the as-synthesized platinum colloidal dispersions. The other set of experiments was that more than 10 runs of continuous synthesis of platinum colloids (each containing 0.5 L of colloidal dispersion, i.e. ∼0.1 g of metallic platinum) were manipulated with the same equipment system, respectively. For each run, stable and transparent dark-brown

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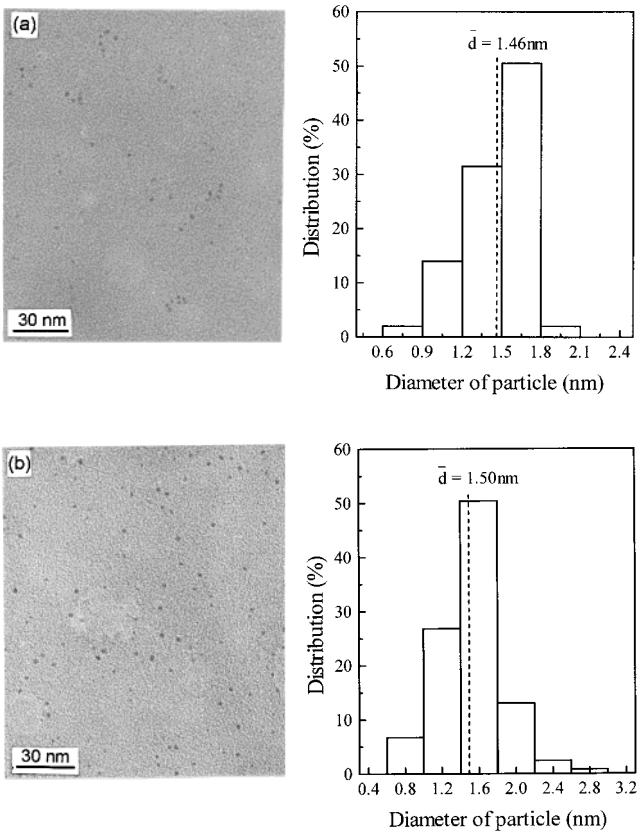

Figure 3. TEM photographs (left) and the corresponding particle size histograms (right) of platinum (a) and palladium (b) colloidal clusters.

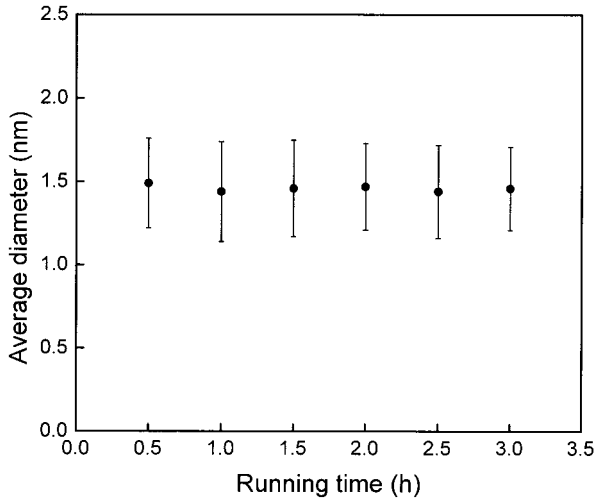

Figure 4. Average diameter with standard deviation of platinum colloids sampled at different running time of the continuous microwave synthesis.

platinum colloid was obtained. All as-synthesized platinum colloids were mixed together, and then, a sample was taken for TEM examination. TEM observation results showed that the average diameter of platinum colloidal particles was 1.52 nm and the standard deviation was 0.26 nm. Thus, it can be concluded that this continuous microwave method has good reproducibility. Palladium colloids (each containing ~0.2 g of metallic palladium) were synthesized with different molar ratio of NaOH:Pd from 0 to 8 in a similar fashion (Table 1). The average diameter and the size distribution of the palladium clusters decreased with the increase in molar ratio of NaOH:Pd. The TEM photograph with the size distribution of Pd5 is shown in Figure 3b.

Table 1. Preparation of PVP-Stabilized Palladium Colloids by Continuous Microwave Irradiation[a]

no.	NaOH:Pd (molar ratio)	av diam. (nm)	stand. dev. (nm)
Pd1	0	1.68	0.38
Pd2	2	1.59	0.37
Pd3	4	1.57	0.37
Pd4	6	1.52	0.34
Pd5	8	1.50	0.32

[a] PVP: Pd = 50:1 in molar ratio.

It should be mentioned that the continuous microwave synthesis offered platinum colloid with a smaller average diameter (d_{av} = 1.46 nm with σ = 0.25 nm) in comparison with the steady microwave synthesis (d_{av} = 2.0 nm with σ = 0.32 nm; see Yu et al.,[17] Table 1, no. 8). It is reasonable for continuous synthesis that the solution is in a flowing state, and because a flowing solution usually provides more crystal nuclei in it, the continuous synthesis causes the formation of smaller clusters, as verified by the stirring experiment.[17,22]

Microwaves are electromagnetic waves. The energy of the quantum of microwave is too small to break down chemical bonds or to influence the chemical equilibrium; so, we propose that the formation of nanometallic clusters is mainly attributed to a heating effect. Polar molecules can be heated quickly; however, nonpolar molecules cannot couple with microwaves. So, microwaves can heat the polar reaction solution to high temperature instantaneously and uniformly without heating the glass container. This is beneficial to avoiding the formation of colloidal particles on the wall of glass container. Therefore, with continuous microwave heating, there is little possibility of crystal nuclei forming on the wall of the glass coil and staining it, even if continuous preparation lasts for a long time. On the contrary, with conventional heating, we suspect that the wall temperature of the container is higher than that of the bulk solution because heat energy is conducted from outside. Therefore, a high-valence metal precursor near the wall has a tendency to be the first to be reduced to zerovalent metal particles, which is unfavorable to the formation of uniform colloidal particles, to say nothing of large-volume reaction containers.

A household microwave oven was the microwave source in our experiments. The microwave density is not homogeneous within the oven cavity.[23] The solution flowing through microwave oven will not absorb a completely uniform irradiation, which will hinder the formation of monodispersed colloidal metal particles. So, more uniform metal nanoclusters are expected with a more homogeneous microwave field, which can be accomplished with a special design. In addition, in our experiments, the maximum power output of the microwave oven was 750 W and the formation of platinum colloid required 25 s of microwave irradiation. According to this point, we designed the fine spiral tube to keep the solution in the microwave cavity for an adequate time. If we had a microwave oven with a much stronger

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power output, we could accomplish the scale-up synthesis of colloidal metal nanoclusters in a shorter time by expanding the volume of the reactor.

Microwave heating has many advantages compared with conventional heating, such as short heating time, easy heat control, low cost, and so on. One recent report[24] has described the microwave sintering of powdered metals into small solid rings, tubes, and gears. The sample inside a 2.45 GHz microwave oven can reach 1300 °C as it is heated from 5 min to 1 h. Thus, fine microstructure with better properties at lower cost can be offered by such microwave heating than by conventional heating. Therefore, many researchers may find the advantages of energy-saving, low-cost microwave heating valuable and attractive. In this paper, continuous microwave synthesis also provides a low-cost and easy-to-control method for producing uniform metal nanoparticles in bulk quantities with good reproducibility. It may be the fundamental to the industrialized manufacture of nanoscale metal colloids.

Acknowledgment. This work was supported by the National Nature Science Foundation of China (Contracts No. 29774037 and 29873058) and the Fund of the Chinese Academy of Sciences (Contract No. KJ 952-J1-508).

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