JOURNAL OF Materials CHEMISTRY

Rapid synthesis of nanoscale colloidal metal clusters by microwave irradiation

Weixia Tu and Hanfan Liu*

PCLCC (Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation), Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China. E-mail: hfliu@infoc3.icas.ac.cn

Received 20th March 2000, Accepted 29th June 2000
Published on the Web 4th August 2000

Uniform and stable polymer-stabilized colloidal clusters of Pt, Ir, Rh, Pd, Au and Ru were synthesized by microwave irradiation with a modified domestic microwave oven. The as-synthesized colloidal clusters have small average diameters and narrow size distributions. The microwave method is characterized by rapid and homogeneous heating compared with conventional heating methods, although its thermal effects are similar to those of other heating methods.

Introduction

The intense interest in nanoscale metal clusters or colloids is a result of their theoretical importance and potential applications.[1] Their chemical and physical properties differ from those of bulk metals because of surface or quantum size effects.[2] Hence, the preparation of nanoscale metal clusters or colloids with desirable properties represents a significant challenge. Diverse approaches to the preparation of metal nanoparticles have been reported, such as chemical reduction,[3] UV photolysis,[4] thermal decomposition,[5] metal vapor deposition,[6] electrochemical synthesis[7] and sonochemical decomposition,[8] but, amongst them, chemical reduction has been most extensively studied. Turkevich *et al.*[3a] used citrate salts as reductants, while alcohol reduction and the polyol process were studied by Hirai and co-workers,[3c,9] Toshima and co-workers,[10] Figlarz and co-workers[11] and others.[12] Organohydroborides were also proposed by Bönnemann *et al.* as reductants for preparing metal colloids or nanoparticles.[13]

In recent years, microwave chemistry has made great progress in organic reactions,[14–16] molecular sieve preparation,[17,18] synthesis of inorganic complexes[19–21] and radiopharmaceuticals,[22,23] while applications of microwaves in plasma chemistry,[24] analytical chemistry[25] and catalysis[26] have also been reported.

It is generally accepted that there are a number of characteristics specific to microwaves as agents for promoting chemical reactions: (i) the quantum energy of microwaves (10^{-5} eV) is much lower than that of chemical bonds so that microwaves will not break or weaken bonds within molecules; (ii) the intensity of electric and magnetic fields cannot cause the shift of any chemical reaction equilibrium. However, many experiments with microwave heating reveal results different from those obtained with conventional heating.[27–30] Thus, many developments are bound to occur and enhance the advantages associated with microwave heating.

In a recent communication,[31] we applied microwave techniques to the synthesis of nanoscopic metal colloids, showing that PVP-stabilized colloidal platinum clusters can be obtained by microwave heating with ethylene glycol as a reductant. The dimensions of the platinum colloids were 2–4 nm, with a narrow size distribution, depending on the preparation conditions. In this paper, we give a detailed description of the synthesis of other PVP-stabilized precious colloidal metal clusters by microwave heating, emphasizing their characterization by UV–visible absorption spectrometry, TEM, XPS and XRD.

Experimental

Materials and instruments

Poly(*N*-vinyl-2-pyrrolidone) (PVP, av. MW 40 000) was obtained from Fluka. Other analytical reagents were supplied by Beijing Chemical Corporation.

Ultraviolet–visible absorption spectral measurements were carried out with a Unicam SP1750 UV–visible spectrophotometer. Transmission electron microscopy (TEM) was undertaken with a Hitachi-9000 NAR apparatus. Particle diameters were measured from enlarged photographs. Particle size distribution histograms were obtained on the basis of measurements from about 300 particles. X-Ray photoelectron spectra (XPS) were recorded on an ESCALAB 22Oi-XL (VG, Inc.) photoelectron spectrometer using Mg-Kα radiation under a vacuum of 2×10^{-8} Pa. All binding energy values were referred to carbon ($C_{1s}=284.6$ eV). Specimens were prepared *via* immobilization of metallic colloids on SiO_2.[32] X-Ray powder diffraction (XRD) measurements were made with a Rigaku D/Max-3B diffractometer employing Cu-Kα radiation.

In order to synthesize polymer-stabilized metal clusters using a low boiling point alcohol as the reductant, a domestic microwave oven (2450 MHz, Galanz WP750) was modified. A water-cooled condenser outside the microwave oven cavity was connected by a glass joint to a glass round-bottomed flask set inside. A Teflon stirrer was set in the flask and was driven by a motor.

Preparation of PVP-stabilized colloidal metal clusters

The preparation was carried out with the modified microwave oven. 0.1110 g PVP (1.0×10^{-3} mol in terms of monomeric units) and one of the following metal precursors (containing 2.0×10^{-5} mol precious metal): $H_2PtCl_6\cdot6H_2O$, $H_2IrCl_6\cdot6H_2O$, $PdCl_2$ (before use, converted into $H_2PdCl_4\cdot nH_2O$ by treatment with concentrated hydrochloric acid), $HAuCl_4\cdot3H_2O$ or $RhCl_3\cdot3H_2O$ were dissolved in a mixed solvent composed of 10 mL methanol and 9.2 mL distilled water in a 50 mL reaction container. Then, 0.8 mL of an aqueous solution of NaOH (0.2 M) was added dropwise with vigorous stirring. After microwave irradiation, PVP-stabilized colloidal metal clusters were obtained.

DOI: 10.1039/b002232m

In the case of ruthenium nanoclusters, polyol reduction was performed. $RuCl_3 \cdot 3H_2O$ (2×10^{-5} mol) was mixed with 0.044 g PVP in 20 mL ethylene glycol. The mixture was stirred and heated as mentioned above, whereupon a dark brown colloidal ruthenium cluster was obtained. For TEM examination, the colloidal metal dispersion was removed from the ethylene glycol by using acetone as a precipitation agent and the solid residue redispersed in methanol.

Temperature measurement of microwave-irradiated system

The temperature of materials heated by microwave irradiation cannot be determined by using thermometers or thermocouples, since metals distort the microwave field in their vicinity. Recently, a number of different methods have been developed for temperature measurement of materials in microwave ovens, including gas thermometers,[33] thermochromic liquid crystal techniques,[34] fiber-optic techniques,[35] *etc*. These measurement methods are complicated and expensive, but in the present work a simple method was used. The temperature of the microwave-irradiated mixture was measured by a gradual determination method as follows: a mixture of $H_2PtCl_6 \cdot 6H_2O$ and PVP with 20 mL ethylene glycol in a 50 mL beaker was heated for a given time (*e.g.* 10 s) in the microwave oven. The microwave irradiation was turned off and a thermometer immediately placed into the heated sample to get an approximate temperature value. Then the thermometer was heated to this temperature in advance and put rapidly into another piece of the same sample that had also been heated for 10 s so that another temperature value was obtained. Repeating this process, we can obtain a much more precise temperature value for the microwave-irradiated solution. As for the temperature determination of the samples heated by a conventional oil-bath, the thermometer was put directly into the heated samples.

Results and discussion

Determination of temperature during the preparation of colloidal platinum clusters

Fig. 1 shows temperature profiles of the PVP–H_2PtCl_6–ethylene glycol solution used for platinum colloid preparation for different heating times with microwave irradiation (with full power output, 750 W) and in an oil-bath (800 W). For the solution irradiated by microwaves, the temperature increases linearly and abruptly (Fig. 1a). After 25 s, the colour of the solution changed from pale yellow to dark brown, indicating the formation of metal clusters; after about 30 s of irradiation, the solution began to boil and the temperature reached 175 °C. It is well known that the interaction of dielectric materials with microwaves leads to what is generally described as dielectric heating.[36] Thus, ethylene glycol, a polar solvent, has high microwave susceptibility, which manifests itself in the rapid temperature increase. For the same solution heated in an oil-bath, the temperature changed slowly initially (Fig. 1b), probably on account of the large thermal capacity of the oil. After 2 min heating, the temperature increased nearly linearly, but it took about 10 min for the formation of the metal colloid and the solution needed 11 min heating in the oil-bath to reach 175 °C. Therefore, the microwave heating rate was about twenty times faster than that of oil-bath, demonstrating that microwave heating can greatly shorten the formation time of metal colloids.

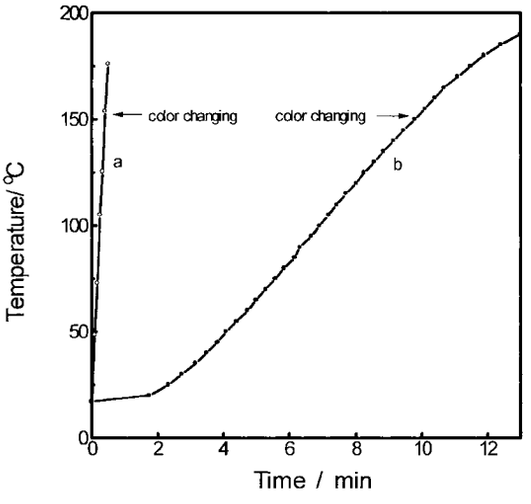

Fig. 1 Time–temperature profiles for a PVP–H_2PtCl_6–ethylene glycol solution heated by microwaves (a) and an oil-bath (b).

Formation of PVP-stabilized colloidal platinum clusters characterized by ultraviolet–visible absorption spectra

UV–visible absorption spectrophotometry is a convenient technique for monitoring the progress of metal colloid formation[37,38] based on the corresponding UV absorption spectra of the species present in the liquid medium. A PVP–H_2PtCl_6–methanol–water solution exposed to microwave irradiation (750 W) was sampled at different times and then the samples were characterized by UV absorption spectrophotometry (Fig. 2). As can be seen from Fig. 2, $PtCl_6^{2-}$ shows an absorption peak at 260 nm, the intensity of this peak decreasing with increasing irradiation time. After about fifteen minutes, the absorption peak disappeared completely, which indicated that $PtCl_6^{2-}$ was entirely reduced to Pt^0. As the irradiation time was prolonged, the optical density increased due to the plasma absorption of the platinum clusters.[38] After 26 min heating, no further change was observed. It should be noted that the evolution of the UV absorption spectrum of the PVP-stabilized colloidal platinum dispersion obtained by microwave heating is similar to that of the spectrum of the sample heated by the oil-bath.[39] The only difference is in the rate at which the absorption peaks of the species changed. The whole process, including reduction of the platinum precursor and formation of the platinum clusters, was faster with microwave heating than with oil-bath heating.

PVP-stabilized nanometal clusters

A number of different colloidal metal clusters were synthesized by microwave heating; they were stable for several months. Table 1 lists various parameters of PVP-stabilized noble metal clusters prepared by microwave and conventional oil-bath heating, for comparison. A TEM photograph and the size

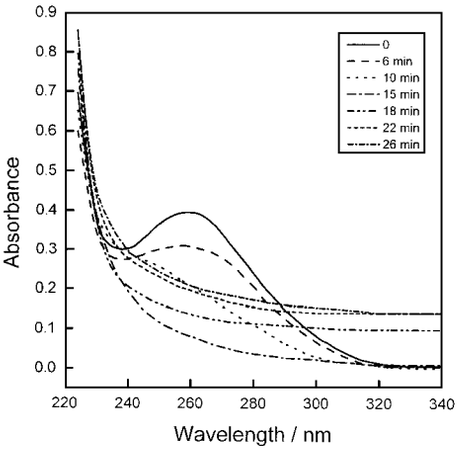

Fig. 2 Ultraviolet absorption spectra during the formation of platinum clusters in the PVP–H_2PtCl_6–methanol–water system after different irradiation times.

Table 1 Synthesis conditions for and dimensions of PVP-stabilized nanoscale colloidal precious metal clusters

Sample no.	Metal colloid	Reductant	NaOH[a]	Time[b]/min	Average diameter, d/nm		Standard deviation, σ/nm		Relative standard deviation, σ/d	
					Microwave heating	Oil-bath heating	Microwave heating	Oil-bath heating	Microwave heating	Oil-bath heating
1	Pt	Methanol	8	12	1.0	1.1	0.24	0.30	0.24	0.27
2	Pt	Methanol	0	20	2.0	2.7	0.37	0.68	0.18	0.25
3	Ir	Methanol	8	0.3	1.1	1.2	0.19	0.26	0.17	0.22
4	Pd	Methanol	0	0.5	1.3	2.7	0.27	0.64	0.21	0.24
5	Rh	Methanol	0	13	1.7	2.2	0.33	0.60	0.19	0.27
6	Au	Methanol	8	0.5	7.6	7.4	1.45	2.02	0.19	0.27
7	Pt	Ethylene glycol	8	0.4	1.2	1.1	0.24	0.31	0.20	0.28
8	Pt[c]	Ethylene glycol	8	0.4	2.0	1.8	0.32	0.55	0.16	0.31

[a]The molar ratio of NaOH to Pt. [b]Time for the formation of colloidal metal clusters synthesized by microwave heating. [c]Without stirring.

distribution histogram of platinum clusters synthesized by microwave heating are shown in Fig. 3. Standard deviations (σ) were calculated from the distribution of colloidal metal particle sizes. Relative standard deviation (σ/d) is a useful parameter for measuring the dispersity of colloidal particles with different sizes. From Table 1, it can be seen that the noble metal clusters synthesized by microwave heating have smaller relative standard deviations than those prepared by conventional oil-bath heating, implying a better dispersity. Thus, it can be concluded that microwave heating gives more uniform clusters. As is also evident from Table 1, the difference in size of metal clusters synthesed by microwave and oil-bath heating is most obvious for the systems without NaOH (no. 2, 4 and 5), the average diameters of metal clusters were smaller with microwave heating. As is well known, the size of colloidal metal particles depends on the speed of reduction of the metal precursor.[38–40] For the systems without NaOH, in which the reduction of the metal precursor is relatively hard, temperature determination and UV absorption spectra indicate that microwaves provide fast heating and, thus, accelerate the reduction of the metal precursor and the nucleation of the metal cluster. Therefore, rapid microwave heating leads to smaller particle sizes. In the solutions containing NaOH, the reduction of the metal precursor is greatly accelerated and microwave heating has little influence on the particle sizes of the metal colloids. No. 7 and 8 in Table 1 show data for Pt clusters prepared with and without stirring. With stirring, smaller particles result, probably because more nuclei are formed.[31,41]

Microwaves are electromagnetic waves, which contain electric and magnetic field components. The force derived from these changes direction rapidly, which causes heat because the assembly of molecules cannot respond to it instantaneously, creating friction and manifesting itself as heat. When microwaves are incident perpendicular to the surface of a material, their intensity decreases progressively inside the sample in the direction of incidence as the microwave energy gets progressively dissipated. But for most materials, D (the distance in the direction of penetration at which the incident power is reduced to half its initial value) is quite large and, therefore, the power dissipation is fairly uniform throughout the material as long as the sample is not too large. The formation of uniform colloidal particles demands a uniform growth environment, and homogeneous microwave heating affords this. With microwave irradiation of liquid samples, temperature and concentration gradients can be avoided, providing a uniform environment for nucleation. However, when using a household microwave oven as the microwave source, the power density is not homogeneous everywhere within the oven cavity.

From Fig. 1, it can be seen that the temperature at which the solution changes colour is about 150 °C whether heated by microwaves or in an oil-bath, although the formation rates of the metal clusters were different. What is more, the UV absorption spectra in Fig. 2 show that the rate of disappearance of metal precursor and formation of metal clusters in the solution is similar for both microwave and conventional heating. It seems that the mechanism of formation for metal colloids under microwave irradiation is similar to that which operates with oil-bath heating. Thus, we conclude that the role of microwave irradiation is mainly thermal. The advantage of microwave irradiation for the formation of uniform colloidal metal dispersions with small particle sizes is, therefore, the uniform and fast nature of the heating.

Preparation of PVP-stabilized colloidal ruthenium dispersions

Diverse methods have been reported for preparing ruthenium clusters.[42] Although the redox potential of Ru^{3+} to Ru^0 is

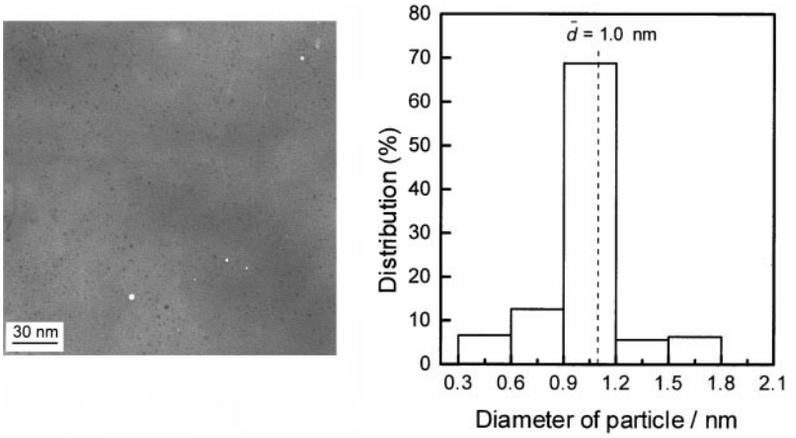

Fig. 3 TEM photograph (left) and the corresponding particle size distribution histogram (right) of PVP-stabilized platinum clusters (no. 1 in Table 1).

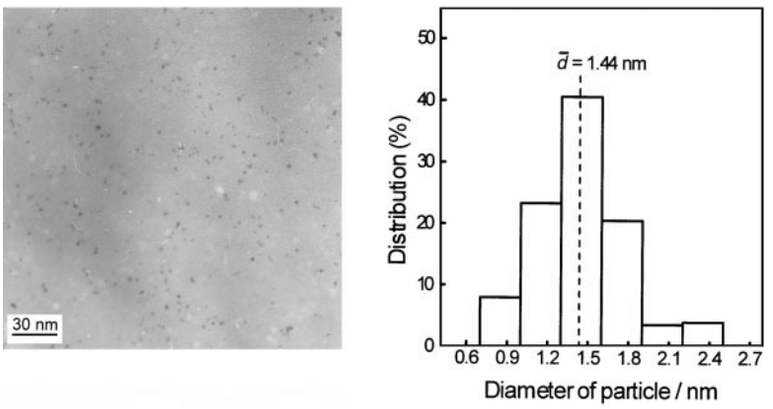

Fig. 4 TEM photograph (left) and the corresponding particle size distribution histogram (right) of PVP-stabilized ruthenium cluster.

relatively high, ruthenium clusters cannot be obtained by simply refluxing $RuCl_3$–alcohol–water solutions.[42c,43] Recently, Miyazaki *et al.*[44] reported that a colloidal dispersion of ruthenium can be prepared by the polyol method. However, the colloids prepared in this way were not stable, significant agglomeration even taking place during the course of the preparation. In contrast, with microwave heating, a stable ruthenium cluster ($d=1.44$, $\sigma=0.33$ nm) was successfully prepared by using PVP as a stabilizer and ethylene glycol as a reductant. A TEM photograph and the corresponding particle size distribution histogram of the colloid are shown in Fig. 4.

To confirm the formation of metallic ruthenium clusters, XPS was used to determine the oxidation state of ruthenium (Fig. 5). The binding energy of Ru $3d_{5/2}$ (279.9 eV, Fig. 5a) in the clusters was consistent with that for bulk ruthenium metal.[45] Furthermore, the binding energy of Ru $3p_{3/2}$ and Ru $3p_{1/2}$ (461.7 eV and 483.8 eV, Fig. 5b) confirmed this conclusion. In addition, the X-ray diffraction (XRD) pattern of the ruthenium clusters (Fig. 6) shows a single broad "peak" (because of the small size of the colloidal metal clusters). The diffraction angle of the peak is $2\theta=42.8°$, which is consistent with the d value (2.11 Å) of ruthenium metal.[46] Using the Scherrer formula, we found the crystal size of the ruthenium clusters to be about 1.4 nm, which is perfectly in accord with the TEM results.

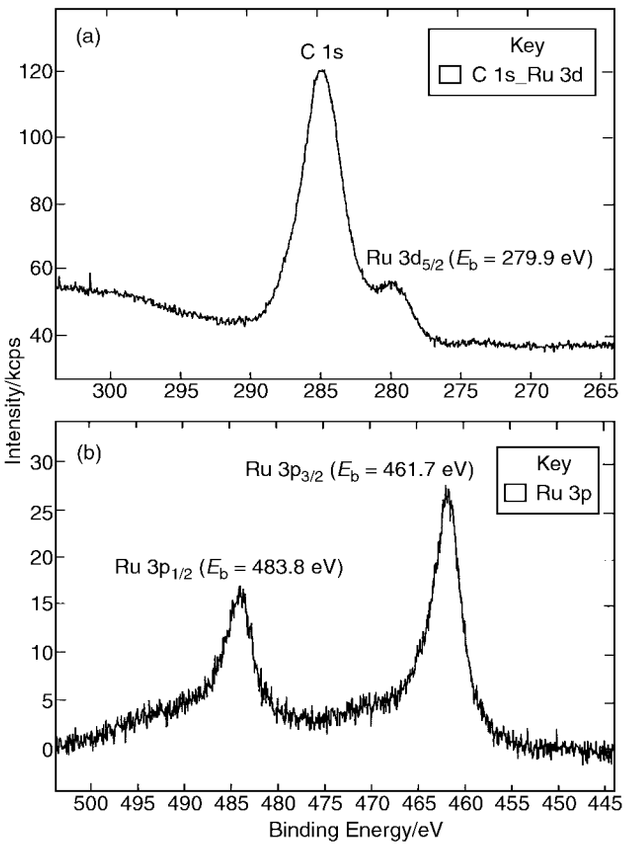

Fig. 5 XPS spectrograms for the ruthenium clusters: C 1s and Ru $3d_{5/2}$ (a), Ru $3p_{1/2}$ and Ru $3p_{3/2}$ (b).

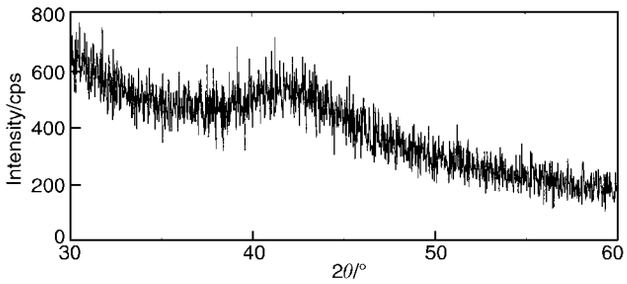

Fig. 6 X-Ray diffractogram for the ruthenium clusters.

Conclusion

Microwave heating provides an effective method for synthesis of PVP-stabilized nanometal clusters of small size and uniform dispersity in a short irradiation time because of its homogeneous and fast heating characteristics. Stable colloidal ruthenium clusters without boron have been synthesized with ethylene glycol as the reductant. It has been confirmed that the advantage of microwave heating is mainly thermal.

Acknowledgements

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

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