1622 *Chem. Mater.* **2000,** *12,* 1622−1627

Preparation of Tractable Platinum, Rhodium, and Ruthenium Nanoclusters with Small Particle Size in Organic Media

Yuan Wang,* Jiawen Ren, Kai Deng, Linlin Gui, and Youqi Tang

State Key Laboratory for Structural Chemistry of Unstable and Stable Species,
Institute of Physical Chemistry, Peking University, Beijing 100871, China

Received January 31, 2000. Revised Manuscript Received April 4, 2000

In the absence of any usual protective agent, stable platinum, rhodium, and ruthenium metal nanoclusters with small particle size in organic media are effectively prepared by heating corresponding metal hydroxide colloids in ethylene glycol containing NaOH for the first time. The average diameters of the Pt, Rh, and Ru nanoclusters determined by means of transmission electron microscopy are in a range from 1 to 2 nm. The particle size distribution in each colloidal solution is sharp, within 2 nm wide. Studies on the preparation conditions and some properties of the "unprotected" Pt metal nanoclusters have been carried out. By adjusting pH, it is convenient to separate the Pt nanocluster as a precipitate from glycol solvent, and the precipitated Pt nanoclusters can easily be "dissolved" in many organic solvents to form transparent Pt nanocluster solutions with high concentration in the absence of usual protective agents. The "unprotected" Pt nanoclusters can also be easily transformed to various protected Pt nanoclusters with the same Pt cores and can be extracted into toluene by forming PPh_3-modified Pt clusters.

Introduction

The preparation and properties of narrowly distributed nanoscopic metal colloids or metal nanoclusters have been intensively studied because of the intense scientific interest in exploring the properties of small metal particles, and because of anticipation in new technological applications.[1] They can be used as quantum dots for understanding the quantum size effect and designing new optic and electric materials.[2,3] The transition metal nanoclusters also serve as a bridge between homogeneous and heterogeneous catalysts and provide new opportunities for catalysis.[4] They are not only active and selective catalysts for various organic reactions such as hydrogenation[5] and hydration,[6] but also active catalysts for visible light-induced hydrogen evolution.[7] Generally speaking, transition metal nanoclusters with small particle size (1−3 nm) have high catalytic activity, good light transparency, and obvious size-dependent properties.

To prepare stable noble metal colloids with small particle size (1−3 nm) and narrow size distribution, protective agents such as surfactants, polymers, or organic ligands were usually used. On the other hand, a dilute aqueous colloidal solution of small Pt nanocluster (Pt < 100 ppm) stabilized by adsorbed $[PtCl_6]^{2-}$ and citrate has been prepared.[1c] The previous strategies for the preparation of small metal nanoclusters have been greatly promoting the development of metal colloid or nanocluster chemistry.[1] However a stable, "unprotected" small metal nanocluster in organic media with a reasonable metal concentration should be of great help for research in the active and prospective field of metal nanocluster chemistry.

Some results of the preparation of nanoscopic metal colloids in organic media without traditional protective agents have been reported,[8−10] the products can be called "unprotected" metal colloids. "Unprotected" metal colloids do not mean that the metal nanoparticles are truly bare. In fact, they are stabilized by solvents or

---

* Corresponding author. Telephone: +86-10-62758575. E-mail: wangy@ipc.pku.edu.cn.

(1) For example: (a) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709. (b) Schmid, G., Ed. *Clusters and Colloids;* VCH: Weinheim, 1994; and references therein. (c) Furlong, D.; Launikons, A.; Sasse W. *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 751. (d) Chen, C.; Serizawa, T.; Akashi, M. *Chem. Mater.* **1999**, *11*, 1381. (e) Le Bars, J.; Specht, U.; Bradley, J. S.; Blackmond, D. *Langmuir* **1999**, *15*, 7621. (f) Goia, D.; Matijevic, E. *Colloids and Surfaces A:* **1999**, *146*, 139.

(2) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 101.

(3) (a) Chen, S.; Ingram, R.; Hostetler, M.; Pietron, J.; Murray, R.; Schaaff, T.; Khoury, J.; Alvarez, M.; Whetten, R. *Science* **1998**, *280*, 2098. (b) Elghanian, R.; Storhoff, J.; Mucic, R.; Letsinger, R.; Mirkin, C. *Science* **1997**, *277*, 1078. (c) Andres, R. P.; Bielefeld, J.; Henderson, J.; Janes, D.; Kolagunta, V.; Kubiak, C.; Mahoney, W.; Osifchin, R. *Science* **1996**, *273*, 1690.

(4) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(5) (a) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (b) Toshima, N.; Kuriyama, M.; Yonezawa, Y.; Kushihashi, K.; Asakura, K. *J. Phys. Chem.* **1991**, *95*, 7448. (c) Bonnemann, H.; Braun, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1992. (d) Zuo, X.; Liu, H.; Liu, M. *Terahedron Lett.* **1998**, *39*, 1941.

(6) Toshima, N.; Wang, Y. *Langmuir* **1994**, *10*, 4574.

(7) Toshima, N.; Kuriyama, M.; Yamada, Y.; Hirai, H. *Chem. Lett.* **1981**, *1981*, 193. Duonghong, D.; Norgarello, E.; Gratzel, M. *J. Am. Chem. Soc.* **1981,** *103*, 4685. Kurihara, K.; Kizling, J.; Stenius, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1983,** *105*, 2574.

(8) Curtis, A.; Duff, D.; Edwards, P.; Jefferson, D.; Johnson, B.; Kirkland, A.; Wallace, A. *J. Phys. Chem.* **1988**, *92*, 2270.

(9) Cardenas-Trivino, G.; Klabunde, K.; Brock, D., E. *Langmuir* **1987**, *3*, 986.

(10) (a) Esumi, K.; Tano, T.; Meguro, K. *Langmuir* **1989**, *5*, 268. (b) Tano, T.; Esumi, K.; Meguro, K. *J. Colloid Interface Sci.* **1989**, *133*, 530.

10.1021/cm0000853 CCC: $19.00

simple anions adsorbed on them, or by both. Curtis[8] and co-workers prepared an "unprotected" copper colloid in methanol by the reduction of copper(II) salts with hydrazine hydrate. The copper colloidal particles have a mean diameter of 13.3 nm. Klabunde[9] and co-workers prepared stable Pd colloids with average diameters of 6−8 nm in acetone or propanol by using the atom clustering process. These Pd colloidal particles are "living" in the sense that they can be used to produce metal film. Esumi[10] reported the preparation of stable palladium colloids with average Pd particle sizes of 8−10 nm from the thermal decomposition of palladium complexes in methyl isobutyl ketone. To our knowledge, reports on the chemical preparation of stable "unprotected" Pt, Rh, and Ru metal nanoclusters with particle sizes less than 3 nm in organic media have so far been scarce.

In this paper, we report an effective preparation method for the stable "unprotected" Pt, Ru, and Rh metal nanoclusters with small particle size and narrow size distribution in organic solvents for the first time. The resultant "unprotected" Pt nanocluster in ethylene glycol (glycol) can easily be separated from the solvent as a precipitate that is "soluble" in many kinds of organic solvents. Moreover, these metal nanoclusters have a valuable advantage that many polymers or organic ligands can easily modify them to form various protected metal nanoclusters with the same metal core.

Experimental Section

Materials. Hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, 99%) was purchased from Beijing Hongke Chemical Products Co. and used as received. $RhCl_3{\cdot}3H_2O$ and $RuCl_3{\cdot}6H_2O$ were supplied by N.E. Chemcat Co. Polyoxyethylene(20) stearyl ether ($C_{18}H_{37}(OCH_2CH_2)_{20}OH$ (POSE)) and Poly(*N*-vinyl-2-pyrrolidone) (PVP) (average molecule weight 50 000) were purchased from Aldrich Co. Organic solvents and the other chemicals were of an AR grade and were used as received.

Transmission Electron Microscopy Measurements. Transmission electron microscopy (TEM) photographs were taken on a JEM 200CX electron microscope operated at 120 kV with a magnification of 100 000×. High-resolution transmission electron microscopy photographs were taken on a Hitachi H-9000 electron microscopy operated at 300 kV with a magnification of 400 000×. Samples for the TEM measurements were prepared by placing a drop of the metal nanocluster solution, appropriately diluted, on a copper grid coated by a polymer or carbon film. Excess solution was removed by adsorbent paper. The average diameter of the metal particles was determined from the diameters of 300 nanoparticles found in an arbitrarily chosen area in enlarged microphotographs by using a magnifier with a magnifying power of 10.

X-ray Diffraction Measurements. Samples for X-ray diffraction (XRD) measurements were prepared by adding dilute HCl acid into the Pt metal nanocluster solutions to precipitate the metal nanoclusters. The precipitates were dried under vacuum. X-ray diffraction patterns were recorded by a Dmax-2000 diffractometer (Rigaku Co.).

X-ray Photoelectron Spectroscopy Measurement. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA LAB-5 (VG Co.). Samples were prepared by precipitating the Pt nanocluster in the colloidal solution with diluted HCl acid. The precipitated Pt nanocluster was washed by dissolving in acetone and precipitating with diluted HCl acid for several times before completely drying under a vacuum. The sample was put on an indium film covered on a Ni sample set, and the In 3d core levels signals were used as an internal standard.

Preparation of "Unprotected" Platinum Nanoclusters. All operations were carried out under inert atmosphere (Ar or N_2). In a typical preparation, a glycol solution of NaOH (50 mL, 0.5 M) was added into a glycol solution of $H_2PtCl_6{\cdot}6H_2O$ (1.0 g, 1.93 mmol in 50 mL) with stirring to obtain a transparent yellow platinum hydroxide or oxide colloidal solution which was then heated at 160 °C for 3 h, with an Ar flow passing through the reaction system to take away water and organic byproducts. A transparent dark-brown homogeneous colloidal solution of the Pt metal nanocluster (Pt: 3.76 g/L glycol, 19.3 mmol/L) was obtained without any precipitate. The obtained Pt nanocluster solution is very stable, no precipitate was observed after standing for several months.

Preparation of "Unprotected" Rhodium and Ruthenium Nanoclusters. Stable, transparent, dark-brown, homogeneous colloidal solutions of rhodium and ruthenium metal nanoclusters without any precipitate were successfully prepared by using a procedure similar to that described above. A total of 5 mL aqueous solution of $RhCl_3{\cdot}3H_2O$ (79.0 mg, 0.30 mmol) or $RuCl_3{\cdot}6H_2O$ (95.0 mg, 0.30 mmol) was added into 100 mL of glycol. Then 5 mL of aqueous solution of NaOH (0.5 M) was added with stirring. The other preparation conditions were the same as those described above.

Stable, transparent, dark-brown, homogeneous glycol solutions of rhodium and ruthenium metal nanoclusters with a metal concentration higher than 5 g/L can also be prepared by the similar method.

Preparation of PPh_3 Modified Pt Nanoclusters by Using the "Unprotected" Pt Nanoclusters as Building Blocks. In a typical experiment, 5 mL of a toluene solution of PPh_3 (3.81 mmol/L) was mixed with 20 mL of a glycol solution of the Pt nanocluster (1.90 mmol/L)(PPh_3/Pt ratio: 0.50) followed by adding 15 mL of ethanol into the mixture to form a homogeneous, red-brown Pt nanocluster solution. After stirring for 10 min, 50 mL water was added into the obtained Pt nanocluster solution. A liquid in two phases was obtained. PPh_3-modified Pt nanoclusters then stayed in the upper red organic solution leaving a colorless aqueous solution in the bottom. Washing the organic nanocluster solution with water three times and drying it with NaCl give rise to a brown Pt nanocluster toluene solution, suggesting that the Pt nanocluster has been completely captured by PPh_3 through a coordination action to the surface Pt atoms of the Pt nanoclusters.

Results and Discussion

Preparation of "Unprotected" Noble Metal Nanolusters Having Small Particle Size. Metal nanoclusters are usually prepared by chemically or physically forming metal atoms in solutions followed by an aggregation process of the metal atoms in the presence or absence of protective agents such as polymers, surfactants, or strong coordination ligands. In the presence of protective agents, not only are the formed metal nanoparticles stabilized but also the clustering processes are influenced by the protective agents.[11] In the absence of protective agent, however, to effectively prepare a stable "unprotected" metal nanocluster with small particle size and narrow size distribution in organic media, a suitable solvent and an effective method for controlling the metal particle size have to be used. The reduction method, using polyol for the preparation of fine powders of Cu, Ni, Co, and some noble metals with micro size from metal hydroxides, had been studied by Figlarz and co-workers.[12] We had succeeded in setting

---

[11] (a) Hirai, H.; Nakao, Y.; Toshima, N. *J. Macromol. Sci., Chem.* **1979**, *A13*, 727. (b) Ahmadi, T.; Wang, Z.; Green, T.; Henglein, A.; El−Sayed, M. *Science* **1996**, *272*, 1924.

[12] (a) Fievet F.; Lagier, J. P.; Blin B.; Beaudoin B.; Figlarz M. *Solid State Ionics* **1988**, *32−33*, 198. Fievet F.; Lagier, J. P.; Figlarz, M. *MRS Bull.* **1989**, *14*, 29.

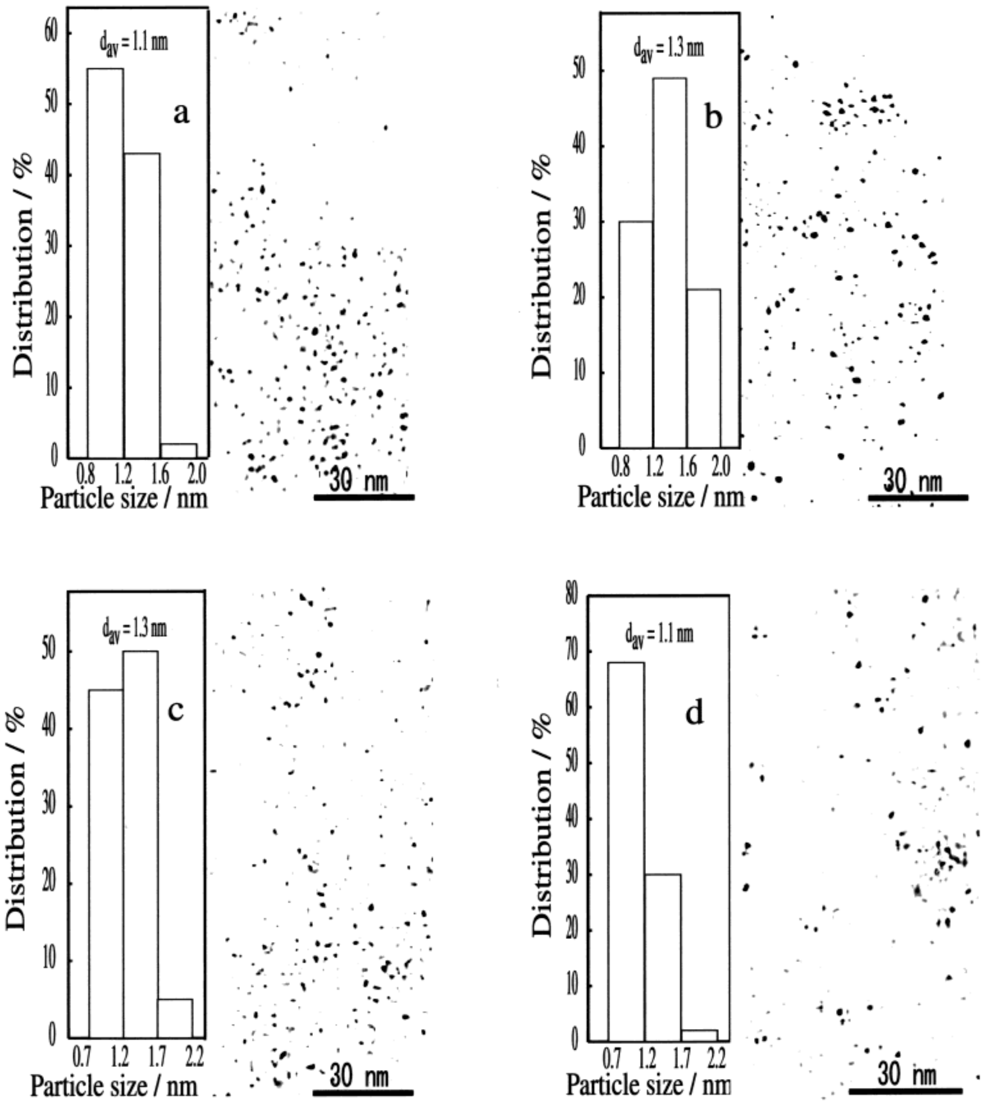

Figure 1. TEM photographs and size distributions of the platinum, rhodium, and ruthenium nanoclusters in glycol: (a) Pt nanocluster (0.37 g Pt/L); (b) Pt nanocluster (3.7 g Pt/L); (c) Rh nanocluster (0.31 g/L); and (d) Ru nanocluster (0.32 g/L).

up a method for the preparation of polymer-protected Cu/Pd and Cu/Pt alloy nanocluster catalysts by reducing the corresponding hydroxide precursors with a modified polyol process.[6] In this work, ethylene glycol was used as the organic solvent in the preparation of the "unprotected" metal nanoclusters and metal hydroxide colloidal particles were preformed before the reduction process.

The present preparation procedure of the "unprotected" noble metal nanoclusters can be expressed as follows:

$$H_2PtCl_6 \xrightarrow[\text{(2) 160 °C, } N_2 \text{ flow}]{\text{(1) NaOH, pH > 12 in glycol}} \text{“unprotected” Pt nanocluster}$$

By heating a glycol solution or glycol/water mixture containing Pt, Rh, or Ru hydroxide or oxide colloids and NaOH at 160 °C for 3 h, a transparent colloidal solution of the metal nanoclusters was obtained without any precipitate. The metal colloids are very stable, no precipitation was observed after standing for at least several months. The pH value of the starting Pt hydroxide colloidal solution is very important for obtaining the present stable "unprotected" Pt nanocluster in glycol. If it is less than about 12, instead of a metal colloidal solution, a precipitate was obtained during the heating process as we have reported before.[6] However, the obtained Pt nanocluster in glycol is very stable when the pH was adjusted to a value higher than 7.

Figure 1 shows the TEM photographs and size distributions of the unprotected Pt, Rh, and Ru nanoclusters in glycol. The average particle size of the Rh nanocluster is 1.3 nm with a size distribution of 0.7 to 2.2 nm, while that of the Ru nanocluster is 1.1 nm with a size distribution also from 0.7 to 2.2 nm. The narrowly distributed Pt nanoclusters (0.37−10 g Pt/L) have an average diameter of 1−2 nm.

Influence of Metal Concentration on the Size of Pt Nanocluster. The average particle sizes of the Pt nanoclusters prepared by the present method are slightly dependent on the concentration of H_2PtCl_6 in the starting glycol solution, which is quite different from the usual cases for the chemical preparation of "unprotected" metal colloids. For example, Esumi[10] reported the influence of metal concentration on the metal particle size in the preparation of organopalladium sols by thermal decomposition of palladium acetate in meth-

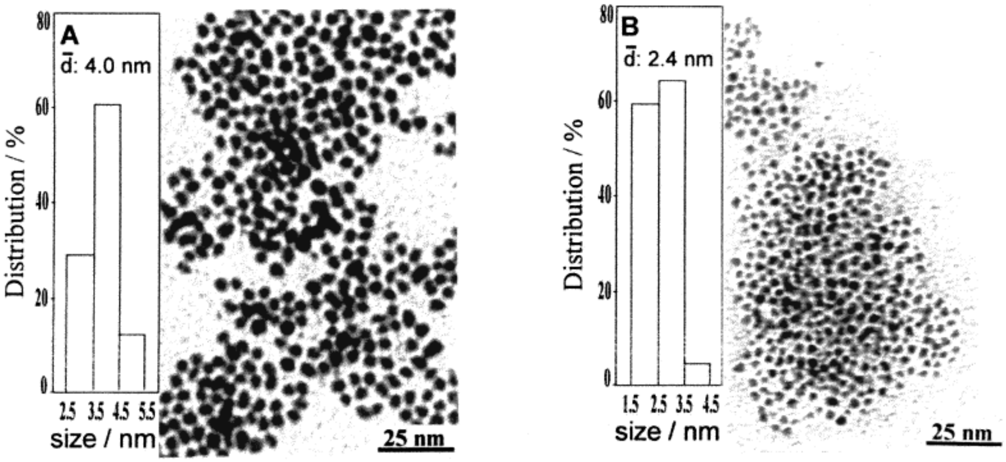

Figure 2. TEM photographs of the platinum hydroxide colloid in glycol/water (10/1) and the Pt cluster derived from reduction of the Pt hydroxide colloid: (A) platinum hydroxide colloid and (B) Pt nanocluster (0.37 g/L Pt).

yl isobutyl ketone. When the Pd concentration is about 0.1 mmol/L, the average Pd particle size is about 8 nm, while when the Pd concentration increases to 1 mmol/L, the average Pd particle size changes to be ∼140 nm. However in the present system, an “unprotected” Pt nanocluster prepared in a H_2PtCl_6 concentration of 51 mmol/L has an average diameter of 1.3 nm, which is only slightly larger than that of the Pt nanocluster prepared in a H_2PtCl_6 concentration of 0.37 mmol/L ($d_{av} = 1.1$ nm). This result shows that the present method is very effective for preparing “unprotected” Pt metal nanoclusters having small particle size and narrowly size distribution. The reason that small “unprotected” metal nanoclusters can be obtained in a high metal concentration in this work is partially due to the formation of small and narrowly distributed metal hydroxides colloidal particles before the reduction process in the preparation.

Influence of Solvent in the Preparation on the Particle Size of the Pt Nanocluster. The solvent used in the preparation experiments has important influence on the particle size of the obtained Pt nanocluster. When the starting mixture contains 10% of water, the particle size of the obtained Pt nanocluster (0.37 g Pt/L) increases obviously. Figure 2 shows the TEM photograph of the platinum hydroxide or oxide colloidal particles in glycol/water (10/1) and the Pt nanocluster derived from reduction of the Pt hydroxide colloid. The narrowly distributed platinum hydroxide colloidal particles have an average particle size of 4.0 nm. The Pt nanocluster has an average diameter of 2.4 nm (Figure 2B), which is larger than that of the Pt nanocluter prepared at the same Pt concentration without addition of water in the starting mixture (1.1 nm, Figure 1a). These results suggest that the particle size of the “unprotected” Pt nanocluster can be controlled to some extent by changing the preparation conditions.

Separation and Redispersion of the “Unprotected” Pt Nanoclusters. The “unprotected” platinum nanoclusters in glycol prepared in this work can be conveniently separated as a black precipitate by adding a dilute aqueous solution of HCl to adjust pH of the Pt nanocluster solution to a value lower than 4. The precipitated Pt nanocluster collected by centrifugation can be “dissolved” in many organic solvents, such as alcohol, ketone, THF, DMF, and DMSO, giving rise to different transparent colloidal solutions of the “unprotected” Pt nanoclusters. However, the precipitated Pt nanoclusters are not soluble in toluene or water. The Pt nanocluster “dissolved” in some ketone sovents was found to be very stable. For example, the Pt nanocluster in cyclohexanone or cyclopentanone does not form any precipitate after standing for at least several months. Stable cyclohexanone or cyclopentanone solutions of the Pt nanoclusters ($d_{av} = 1-2$ nm) with a Pt concentration higher than 200 g/L can be easily obtained by dissolving the precipitated Pt nanoclusters in the solvents. Figure 3 shows the TEM photograph and size distribution of a Pt nanocluster in cyclopentanone. It can be seen from Figure 3 that no obvious aggregation of the Pt nanoparticles occurs during the transferring process.

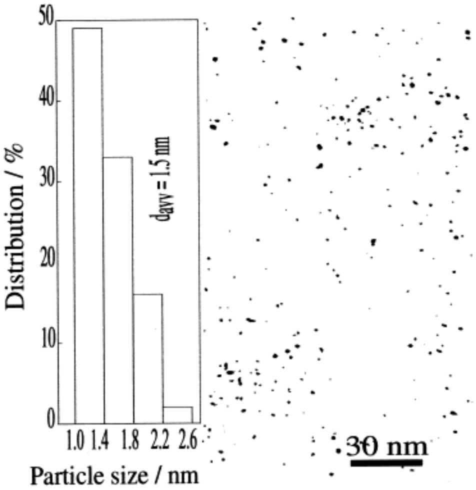

Figure 3. TEM image of a Pt nanocluster in cyclopentanone prepared by dissolving a precipitate Pt nanocluster in the solvent.

These properties may provide a convenient way to the fabrication of various composite functional materials containing small Pt nanoclusters and are helpful to studies on the stabilizing mechanism for the “unprotected” metal nanoclusters in different solvents.

Characterization of the Metal Nanoclusters. X-ray diffraction (XRD) measurements were carried out on the precipitated Pt nanocluster (prepared in a concentration of 3.7 g/L Pt) (Figure 4). The diffraction

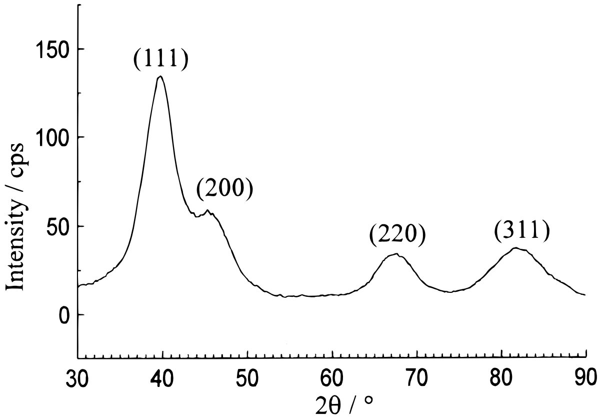

Figure 4. X-ray diffraction pattern of the precipitated Pt nanocluster (3.7 g/L).

lines of (111) (0.2269 nm), (200) (0.1971 nm), (220) (0.1388 nm), and (311) (0.1178 nm) of metallic Pt can be clearly observed in the diffraction pattern of the Pt nanocluster, proving that the Pt nanocluster has a fcc crystal structure.[13] The average Pt particle size calculated from the half width of the diffraction line (111) is ∼2 nm, which agrees well with the TEM results. The larger particles in the Pt nanocluster (although the amount is small) should dominate the contribution to the diffraction signals.

X-ray photoelectron spectroscopic (XPS) analyses were carried out on a dried Pt nanocluster (dried Pt, 3.7 g/L) sample. Before drying, the Pt nanocluster was washed by precipitating in dilute HCl acid and “dissolving” in acetone for several times to remove glycol and other impurities. The spectrum of the dried Pt nanocluster is quite similar to that of pure Pt metal, signals from O 1s and Cl 2p levels cannot be detected in the expanded spectra. The binding energies of Pt $4f_{7/2}$ and $4f_{5/2}$ of the dried Pt nanoclusters have a value of 70.9 and 74.2 eV, respectively. The XPS results prove that the Pt nanocluster has a valence state of metallic Pt,[14] ruling out the possibility that there exists platinum oxide in the Pt nanocluster surface. XPS spectroscopy measurements were also carried out for a dried Rh nanocluster and a dried Ru nanocluster. The Rh $3d_{5/2}$ and Ru $3d_{5/2}$ binding energies of Rh and Ru in the corresponding metal nanoclusters have a value of 307.1 and 280.0 eV, respectively, indicating that both Rh and Ru in the metal nanoclusters are in a metallic state.

For understanding the high stability of the prepared “unprotected” metal nanoclusters, GC-MS measurements were carried out on a glycol solution of the Pt nanocluster containing NaOH to analyze the volatile species in the Pt nanocluster solution that may affect the stability of the Pt nanocluster. The sample for the GC-MS measurement was prepared as follows: The Pt nanocluster in glycol was precipitated by adding dilute HCl acid, the precipitated Pt nanocluster collected by centrifugation was washed by dissolving in ethanol and precipitating with dilute HCl acid for several times. The obtained precipitated Pt nanocluster was finally “dissolved” in glycol containing NaOH to give rise to a very stable Pt colloidal solution as the original Pt nanocluster solution. In the GC-MS measurements operated at different conditions (inlet temperature: 300 °C), no other organic compound except the added solvents, i.e., glycol and small amount ethanol, can be detected.

Element analyses were carried out on the dried Pt nanocluster. The sample was washed by the method mentioned above before drying under vacuum. The composition of C in the dried Pt nanoparticles is less than 0.8%. The characterization results mentioned above suggest that in the present Pt nanocluster glycol solution, it is glycol and the simple anion OH^- adsorbed on the Pt nanocluster surface that make the metal particles separate from each other so well, preventing the Pt nanocluster from aggregating even at high temperature.

Preparation of Some Functional Pt Nanocluster Products by Using the “Unprotected” Pt Nanoclusters as Building Blocks. The species adsorbed on the present “unprotected” metal nanoclusters, i.e., glycol and the simple anion, can easily be removed or replaced by various coordination ligands or protective agents. This character makes the “unprotected” Pt nanocluster very interesting as a building block material to prepare various nanoscopic Pt clusters with the same Pt core size and different modifying or protective shells as well as matrix materials.

After adding an aqueous solution of polyoxyethylene-(20) stearyl ether ($C_{18}H_{37}(OCH_2CH_2)_{20}OH$ (POSE)) to the original Pt nanocluster solution (POSE/Pt mole ratio is 5), the Pt nanocluster was transformed to a surfactant-protected metal nanocluster with the same Pt particle size, which is stable in a wide range of pH. TEM results did not show the change in particle size or aggregation of the Pt nanocluster.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) protected noble metal nanoclusters have been intensively studied in many research groups and exhibit excellent stability and catalytic properties for many organic reactions. The PVP-protected metal nanocluster catalysts are usually prepared by refluxing an alcohol solution of the corresponding metal compounds in the presence of PVP, a method set up by Hirai, Toshima and co-workers. To prepare small metal nanoclusters (1−2 nm) with narrow size distribution, a molar ratio of PVP (as monomeric unit) to the metal higher than 40 have to be used.[11a] In this work, we have succeeded in preparing some PVP-protected noble metal nanoclusters with a high metal/PVP ratio.

The procedure for the preparation of a PVP-protected platinum nanocluster in this work is as follows: The “unprotected” platinum nanocluster in glycol (6 mL, 3.7 g/L, 0.11 mmol Pt, $d_{av} = 1.3$ nm) was precipitated by adding HCl acid (1 M). The black precipitate obtained by centrifugation was “dissolved” in ethanol (4 mL) to obtain a transparent, dark-brown colloidal solution. The platinum nanocuster in ethanol is not very stable and will precipitate after standing for several hours. After 2 mL of an ethanol solution containing 4.4 mg PVP (0.039 mmol as monomeric unit) was added to the above colloidal solution with stirring, a very stable PVP protected platinum nanoclusters (PVP monomeric unit/

---

(13) McClune, W. F. *Powder Diffraction File Alphabetical Index Inorganic Phase*; JCPDS: Swarthmore, PA, 1980.

(14) *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seach, M., Eds.; John Wiley & Sons: New York, 1983.

Figure 5. The TEM image of a PVP-protected Pt nanocluster with a high Pt/PVP ratio (monomeric unit of PVP/Pt mole ratio: 0.35) prepared in this work, the average diameter of the PVP-protected Pt nanocluster is 1.5 nm.

Pt molar ratio = 0.35) "solution" was obtained. TEM results (Figure 5) revealed that no aggregation occurs during this process. Dried PVP-protected Pt nanoclusters with high Pt/PVP ratio (Pt% > 80%, $d_{av} = 1-2$ nm) can be obtained by removing solvent under vacuum, which are "soluble" in water or alcohol.

From these results, we can conclude that to stabilize Pt nanoclusters with small particle size, a high PVP/Pt ratio as usually used is not necessary. A small amount of PVP (PVP monomeric unit/Pt ratio higher than 0.35) is enough to prevent the small Pt nanocluster ($d_{av} =$ 1.5 nm) from aggregating in water or ethanol. The reason that the Hirai and Toshima's preparation method needs a large amount of PVP for preparing small metal nanoclusters is that PVP plays other important roles in addition to preventing the small metal nanoclusters from aggregating in their preparation process, i.e., coordination of PVP to metal ions, controlling the reduction speed of metal ions and influencing the clustering process of metal atoms.[11a]

Transferring the "Unprotected" Pt Nanoclusters into Toluene by Forming PPh_3 Coordinated Pt Nanoclusters. Schmid and co-worker[1a,b] have prepared many metal nanoclusters with definite or near definite numbers of metal atoms and protective ligands, such as $Au_{55}(PPh_3)_{12}Cl_6$ and $Pt_{55}(PPh_3)_{12}Cl_6$, which have been considered as Q-particles having invaluable advantages.[2] On the other hand, Liu and Toshima[15] have reported that adding a large amount of PPh_3 to a PVP-protected Pt metal nanocluster solution (the molar ratio of PPh_3 to Pt is 15) cannot directly transfer the Pt colloidal particles into toluene, but forms a flocculate of Pt colloids. The flocculate can be "dissolved" in butanol or butanol−toluene (1/9 v/v) mixed solution but not in pure toluene, implying that PVP may still remain in the flocculate.

The "unprotected" Pt nanocluster (3.7 g Pt/L for example) in glycol prepared in this work can be easily transformed to a PPh_3-modified Pt nanocluster by adding a small amount of PPh_3 to the Pt nanocluster solution (PPh_3/Pt molar ratio is 0.5). The obtained PPh_3-modified Pt nanocluster can be extracted into toluene, forming a toluene solution of the PPh_3-modified Pt nanocluster. TEM measurements revealed that no aggregation occurs during this coordination capturing−transforming process. The lattice fringes crossing the whole Pt nanoparticle of the PPh_3-modified Pt nanocluster were observed in the high-resolution TEM measurements. The fact that a small amount of PPh_3 is enough for transferring the nanoclusters into toluene in this experiment can be understood since the species adsorbed on the Pt nanocluster in glycol can easily be replaced by PPh_3, and the resultant PPh_3-modified Pt nanocluster does not contain other protective agents such as PVP that is insoluble in toluene.

Conclusion

We report in this paper a new effective method for the preparation of "unprotected" Pt, Rh, and Ru nanoclusters with small particle size in organic media. The "unprotected" Pt nanoclusters with different particle size can be prepared by changing the preparation conditions. The high stability of the present "unprotected" metal nanoclusters was explained by the stabilizing effects of the adsorbed solvent and simple anions. "Unprotected" Pt nanoclusters in cyclohexanone or cyclopentanone were found to be very stable and a Pt nanocluster ($d_{av} = 1-2$ nm) cyclohexanone solution with a metal concentration higher than 200 g Pt/L has been successfully prepared. It has been revealed that a small amount of PVP (Pt/PVP mass ratio ~5) is enough to prevent Pt nanoclusters with small particle size from aggregating. The "unprotected" metal nanoclusters dissolved in different organic solvents obtained in this work provide new opportunities for preparing many new functional materials containing the corresponding metal nanoclusters. For example, they can be used to fabricate composite films of polymers or inorganic metal oxides and small metal nanoclusters with high metal loading, metal nanocluster catalysts with demanding particle size, and surface-modifying species.

Acknowledgment. The authors express their sincere thanks to Professor Hui-zhong Huang at our institute and to Ms. Xiu-zhen Gai at the TEM Laboratory of Peking University for their help in the XPS and TEM measurements, respectively. This work was partially supported by a special Grant-in-Aid (project 29925308) from the National Natural Science Foundation of China and a Grant-in-Aid (no. 99000) from the Education Ministry of China.

CM0000853

---

[15] Liu, H.; Toshima, N. *J. Chem. Soc., Chem. Commun.* **1992**, 1095.