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# Quantity Synthesis of Nanosized Metal Clusters

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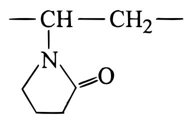
Metal colloids or clusters have recently attracted much attention by virtue of their unique physical and chemical properties. Metal clusters in the range of 1−10 nm are most important for theoretical and practical reasons.[1−3] Some of them have already displayed unusual performances in catalysis,[1−7] magnetism,[8] and electronics.[9] Much of the study has focused on finding methods to prepare nanoscale metal clusters with narrow size distribution, such as metal vapor deposition,[10] chemical reduction in liquid,[2−6,11] electrochemical synthesis,[12] and forming nanoclusters within polymers[13,14] and block copolymers.[15−18] However, all of them are only suitable for laboratory use and cannot be used to produce metal clusters in large scale, e.g., the alcoholic reduction method[2] will be unsuccessful when the volume of solution is extended to ∼2 L. Quantity synthesis is a prerequisite for industrial application of metal clusters as stated by Matijevic.[19] In this communication, we describe a method by which large quantities of nanoscale noble metal clusters are prepared in the solid state via polymer-matrix effect and the resultant clusters can be redispersed in suitable solvents, respective to the polymer stabilizers, in any concentration.

In comparison with the present procedure, reported methods based on the polymer matrix preventing cluster agglomeration to form useful devices are highly specific and their applications are strictly limited. First, it usually needs particular medium (supercritical fluid carbon dioxide[14]) or covalent organometallic compounds, such as $(COD)PtMe_2$[14] and (COD)Ag(Hfacac)[17] (COD = 1,5-cyclooctadiene, Hfacac = $[CF_3C(O)CHC(O)CF_3]^-$), to avoid phase separation. In the latter case, the organometallic precursors are chemically bound to some special monomeric units (such as pyridine[16]) of the polymers. Fréchet and co-workers[13] have put forward a “monomer as solvent” approach, which demands a fast polymerization so as to prevent aggregation of the precursor. Second, the metal clusters made by the above-mentioned ways are incorporated in the solid cross-linked polymers and cannot be redispersed in solvents. Consequently, preparation of metal clusters by these methods restrict their applications, especially in the catalysis realm.[4−7]

In a 50 mL flask, there were placed 10 mL of aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ ($5.00 \times 10^{-4}$ mol) and 10 mL of aqueous solution of poly(*N*-vinyl-2-pyrrolidone) (PVP, MW = 40 000, 2.78 g, $2.50 \times 10^{-2}$ mol as monomeric unit) to give a homogeneous orange-yellow solution. The solution was frozen quickly in liquid nitrogen in a few seconds, and then was evaporated under vacuum (freeze-drying); there was left an orange solid powder. The solid powder was treated under $H_2$ (4.0 MPa) at room temperature in an autoclave for 96 h (or at higher temperature for a shorter time). The color of the powder changed from orange to black and Pt(0) was achieved. The black solid composite can be dissolved in water, methanol, nitroethane, chloroform, etc., which made it a polymer-stabilized metal cluster in solution. Changing the molar ratio of PVP/Pt, we can obtain the PVP-stabilized platinum clusters with different sizes.

There are *N*-vinyl-2-pyrrolidone monomeric units in PVP:



Both the C=O group and N atom can interact with ions. So, in the PVP matrix, the $[PtCl_6]^{2-}$ complex ion was loosely attached to the chain of PVP, and the quick freeze in liquid nitrogen further prevented the phase separation. After the freeze-drying treatment, the platinum clusters formed within the solid PVP matrix by $H_2$ reduction. Transmission electron microscopy

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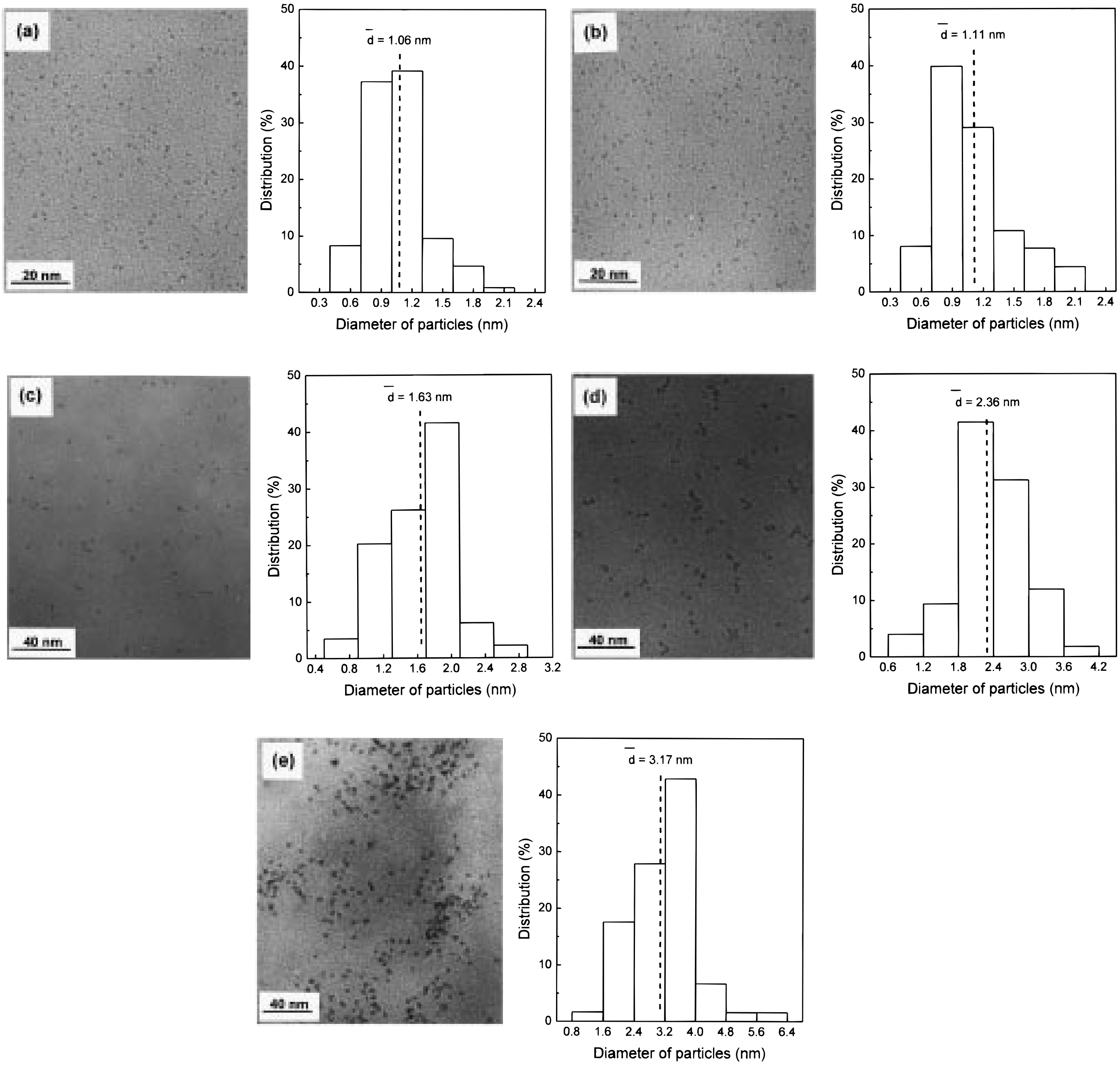

**Figure 1.** Electromicroscopic photographs (left) and the corresponding particle size histograms (right) of nanosized platinum clusters at different molar ratios of PVP/Pt (a) 100; (b) 50; (c) 25; (d) 10; (e) 2.5.

(TEM) photographs[20] showed that the average diameters of the platinum clusters were 1.06 (PVP/Pt = 100) and 1.11 nm (PVP/Pt = 50) with narrow size distributions (standard deviation $\sigma$ = 0.30 and 0.35 nm, respectively) (Figure 1 a,b). This result indicated that the higher the molar ratio of PVP/Pt, the smaller and the more uniform the size. Surely, if PVP/Pt changed from 25 to 10 and 2.5, the platinum particles varied from 1.63 to 2.36 and 3.17 ($\sigma$ = 0.42, 0.60, and 0.85 nm, respectively) (Figure 1 c–e).

The reproductive experiments gave the same results as above, as well as a certain size, by altering the molar ratio of PVP/Pt. Hence, this method provides a useful way to manufacture different sizes of metal nanoclusters in large quantity.

X-ray diffraction patterns of the PVP–$H_2PtCl_6$ system before and after $H_2$ treatment (PVP/Pt = 50) were recorded in Figure 2. There is only a dispersed peak when the metal platinum nanoparticles formed; the peak position ($2\theta = 39.7°$) is consistent with the crystal datum of the platinum phase ($d$ = 2.27 Å).[21] A dispersed peak is the particularity of metal colloidal clusters for the very small size of the particles.[3,5] Also, by the Scherrer formula, it can be calculated that the mean crystalline size of the platinum particles in PVP was about 1.0 nm from the peak width of the X-ray diffraction line. This is in accord with the TEM observation (1.11 nm for PVP/Pt = 50).

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(20) TEM photographs were taken by using a Hitachi-9000 NAR electron microscope. Specimens were prepared by placing a drop of the ethanol solution of the polymer-stabilized metal clusters upon a copper grid covered with a perforated carbon film and evaporating the solvent. The particle diameters were measured from the enlarged photographs. The particle size distribution histograms were obtained on the basis of the measurements of more than 300 particles.

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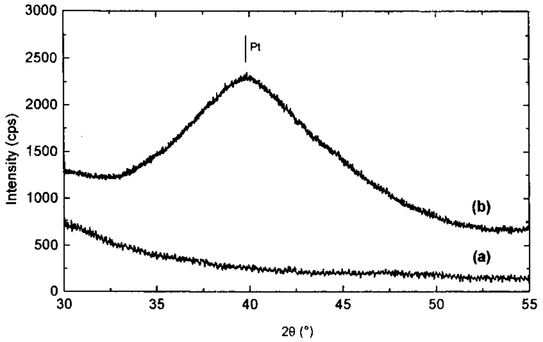

**Figure 2.** X-ray diffraction patterns of the PVP−$H_2PtCl_6$ (a) and the nanosized platinum clusters in PVP (b) at PVP/Pt = 50.

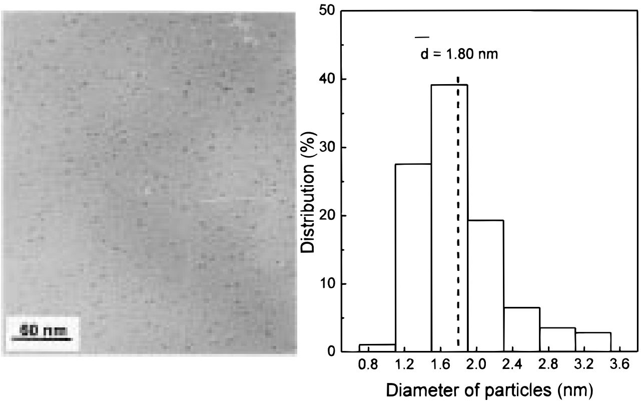

**Figure 3.** Electromicroscopic photograph (left) and the corresponding particle size histogram (right) of the nanosized rhodium cluster in PVA.

Moreover, all the HCl gas resulting from the $H_2$ treatment (eq 1) can be released quantitatively from the

$$nH_2PtCl_6 + 2nH_2 \rightarrow Pt_n + 6nHCl \qquad (1)$$

PVP−metal nanocluster composite (this was determined by acid−base titration). So, this process provides a convenient method to achieve ion-free noble metal nanoclusters. This is advantageous to the catalytic reactions in which $Cl^-$ may affect the catalysts' performance.[22]

Many polymers have been used to stabilize metal colloidal clusters in solution. Another important synthetic polymer is poly(vinyl alcohol) (PVA). Nord and co-workers[23] in their famous work have employed it as a stabilizer in noble metal colloids. As the same, large quantity of PVA-stabilized rhodium was obtained by freeze-drying−reduction ($RhCl_3 \cdot nH_2O$ and PVA dissolved in water). The TEM photograph (Figure 3) showed that the average diameter was 1.80 nm with $\sigma = 0.49$ nm.

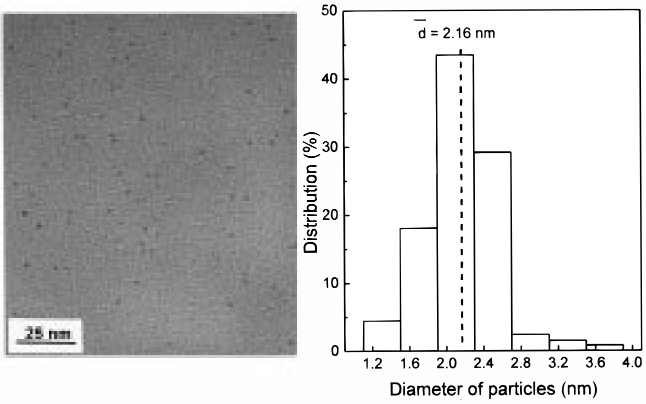

**Figure 4.** Electromicroscopic photograph (left) and the corresponding particle size histogram (right) of the nanosized platinum cluster in sodium dodecyl benzenesulfonate.

The forenamed PVP- and PVA-stabilized metal nanoclusters were made in 100 mg quantities of pure metals at one batch. However, 1 g quantities of metals were also obtained by the same procedure, and the nanoclusters had the same size and size distribution as before. Therefore, large quantities of polymer-stabilized metal nanoclusters can be easily obtained by freeze-drying the solution of metal salts and stabilizers (polymers) and then reducing with $H_2$. The reductant ($H_2$) is clean, and there are not any other unwanted residues. Moreover, the process proceeds at very low temperature. As a result, the prepared metal nanoparticles are immature in metallography, as compared to those prepared by high-temperature treatment methods. This may give the nanosized metal clusters some unusual properties in the fields of catalysis, powder metallurgy, material science, etc.

In the foregoing text, we just described the large-scale preparation of polymer-stabilized noble metal nanoclusters. However, surfactants can also be used as stabilizers by this method.[24] The TEM photograph (Figure 4) indicated that the average diameter of sodium dodecyl benzenesulfonate-stabilized platinum nanocluster was 2.16 nm with $\sigma = 0.40$ nm. The spray-drying process is efficient in getting powder from solution in several seconds. By the stabilizer-matrix effect, combined with freeze-drying or with spray-drying, one can achieve the nanoscale metal clusters stabilized by various stabilizers (e.g., polymers, surfactants, tertiary amines, substituted triphenyl phosphine dissolved in suitable solvents) in reasonably up-scaled quantities.

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[24] In a 100 mL flask, 1.74 g sodium dodecyl benzene sulfonate ($5.00 \times 10^{-3}$ mol) was dissolved in 50 mL of water. Then, 2 mL of aqueous $H_2PtCl_6$ ($1.00 \times 10^{-4}$ mol) was added and mixed. After the mixture was freeze-dried and reduced, the sodium dodecyl benzenesulfonate-stabilized platinum nanocluster in the solid state was obtained (the average diameter was 2.16 nm with $\sigma = 0.40$ nm). This nanocluster is unstable when dispersed in water and will deposit after 2 weeks standing, but it can be stored without change for a much longer time in the solid state.