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Magic Nuclearity Giant Clusters of Metal Nanocrystals Formed by Mesoscale Self-Assembly

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Magic nuclearity giant clusters formed by the mesoscale self-assembly of Pd nanocrystals of 2.5 nm diameter (nuclearity, ~ 561) have been identified by transmission electron microscopy. The clusters have discrete diameters, corresponding to those expected for magic nuclearity of 13, 55, 147, 309, 561, and 1415 and corresponding to closed shells of 1, 2, 3, 4, 5, and 7, respectively. Imaging at different tilt angles has provided confirmation of the spherical nature of these giant clusters. Giant clusters of magic nuclearity have also been found with Pd nanocrystals of ~ 3.2 nm diameter (nuclearity, ~ 1415).

Introduction

Mesoscale self-assembly of polyhedral objects is a topic of great current interest.¹ The occurrence of self-assembly in nanometric dimensions through weak forces has been well documented. Thus, cooperative assemblies of ligated metal and semiconductor nanocrystals as well as of colloidal polymer spheres appear to form through the mediation of electrostatic and capillary forces. Typical examples of mesoscale assemblies are provided by the ordering of nanocrystals of Au^{2,3} and CdSe⁴ and of polystyrene spheres.⁵ Besides ordered two-dimensional arrays, such forces have also been exploited to obtain giant nanocrystal aggregates measuring tens of nanometers,⁶ 2D rings of micrometer diameters,⁷ and dendrimeric structures of Au nanocrystals.⁸ The ability to engineer such assemblies may extend the reach of current lithographic techniques. In this context, the synthesis and programmed assembly of well-defined metal nanocrystals assumes significance.⁹ Metal nanocrystals with magic number of atoms 13, 55, 309, 561, and 1415 corresponding to 1, 2, 4, 5, and 7 closed shells, respectively, have been prepared by chemical means.^{10–13} We have obtained two-dimensional arrays of Pd₅₆₁ and Pd₁₄₁₅ nanocrystals by employing alkanethiol spacers.¹⁴ Schmid et al.^{15,16} have arranged Au₅₅ clusters on a polymer film and have isolated microcrystals of the same.

The assembly of magic nuclearity nanocrystals into giant clusters containing a magic number of initial nanocrystals has been a subject of fascination.¹⁷ Initial electrophoresis experiments of Schmidt¹⁷ with Au nanocrystals indicated the formation of (Au₁₃)₁₃ types of superclusters. Further, a high mass secondary ion peak observed also seemed to support this contention.^{18,19} Theoretical calculations based on the embedded atom method have indicated that such a growth of metal nanocrystals is indeed a possibility.²⁰ In Figure 1, is shown a schematic illustration of a (M₅₅)₅₅ giant cluster.

In our experiments with monodisperse Pd nanocrystals in a ethanol–water mixture,¹¹ we observed some giant aggregates as a result of mesoscale self-assembly. In this article, we report electron microscopic investigation of the aggregates of Pd₅₆₁ and Pd₁₄₁₅ nanocrystals. The aggregates have diameters that could be assigned to values expected of giant clusters containing

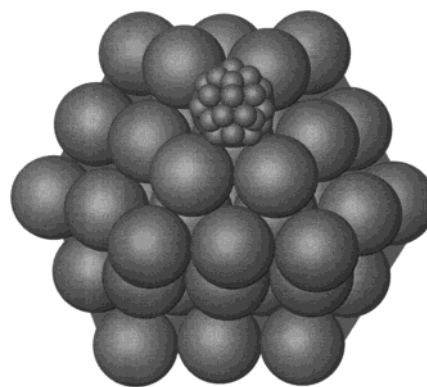


Figure 1. Schematic illustration of a (M₅₅)₅₅ giant cluster. The structure of one of the nanocrystals is shown.

a magic number of the initial nanocrystals. Thus, it has been possible to obtain giant clusters containing approximately 561 nanocrystals, each of which comprises around 561 atoms.

Experimental Section

Monodisperse Pd nanocrystals were prepared in a ethanol–water mixture in the presence of poly(vinylpyrrolidone) (PVP) following the procedure of Teranishi et al.¹² Typically, a 15 mL of a 2.0 mM aqueous solution of H₂PdCl₄ was reduced by refluxing it with a mixture of 15 mL of absolute ethanol and 25 mL of water containing 33.3 mg of PVP ($M_w \sim 40\,000$ g mol^{−1}) for ~ 3 h. The obtained sols were examined with a JEOL-3010 transmission electron microscope (TEM), operating at 300 kV. Samples for TEM were prepared by depositing a drop of the sol on a holey carbon grid and allowing it to dry slowly in air and then in a desiccator overnight.

Results and Discussion

A scan of the grid revealed the presence of a large number of uniform spherical particles. Figure 2 shows a typical TEM image of the dispersion. In addition to isolated nanocrystals, we observed pairs of particles separated by a nearly uniform distance. A few were seen as sitting on top of each other. The histogram in Figure 2 shows that the metal cores are of a uniform diameter of 2.5 nm ($\sigma = 6\%$). Furthermore, high-

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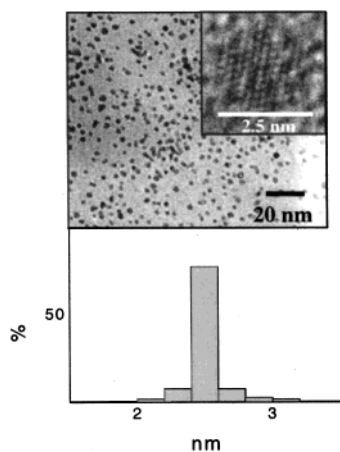


Figure 2. (a) TEM micrograph showing Pd₅₆₁ nanocrystals. The inset shows a high-resolution image of an individual nanocrystal. (b) Histogram showing the size distribution (in percentage).



Figure 3. TEM image of Pd₅₆₁ nanocrystals forming giant clusters. The numbers correspond to the proposed number of nanocrystal shells, n .

resolution TEM images (see inset of Figure 2) revealed 11 [111] lattice fringes with each nanocrystal,¹³ indicating the atomic nuclearity to be close to 561.

Besides the 2.5 nm nanocrystals, the grid also contained bigger features resembling aggregates of nanocrystals. Such aggregates were spherical and seemed to exhibit an unusual preference for a few definite sizes. In Figure 3, a typical low magnification ($\times 80\,000$) TEM image revealing the presence of giant aggregates of nanocrystals is shown. A histogram showing the frequency distribution of the observed diameters is given in Figure 4. Evidently, the giant clusters exhibit preference for specific diameters, 9.6, 15.6, 21.6, 27.7, 33.8, and 46.0 nm, with the smaller giant clusters being more abundant. To estimate the number of nanocrystals present in these aggregates, we calculated the effective volume of a nanocrystal on the basis of the distance between adjacent nanocrystals in TEM images (Figure 2). The pairs of particles were chosen carefully such that the

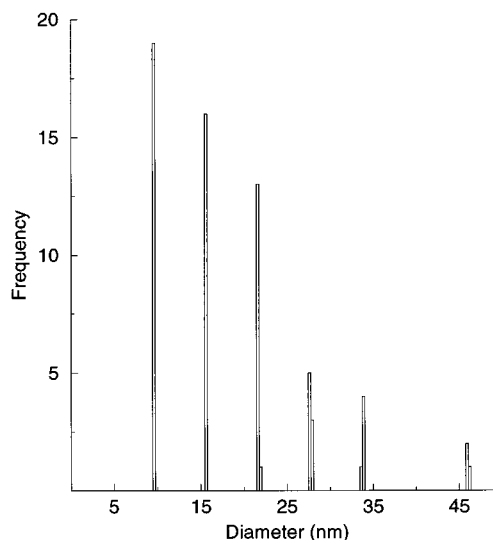


Figure 4. Histogram showing the distribution in the diameters of giant clusters.

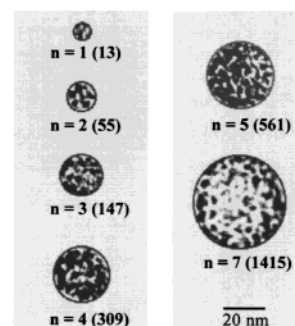


Figure 5. Giant clusters of different magic nuclearities, (Pd₅₆₁) _{n} , the circles corresponding to the diameters of the clusters calculated on the basis of the effective volume of an individual nanocrystal.

TABLE 1: Giant Clusters of Pd₅₆₁ Nanocrystals

diameters measd (nm)	no. of nanocrystals	diameters measd (nm)	no. of nanocrystals
9.6 ± 0.1	13 ± 1	27.7 ± 0.1	309 ± 34
15.6 ± 0.1	55 ± 6	33.8 ± 0.1	561 ± 61
21.6 ± 0.1	147 ± 16	46.0 ± 0.15	1415 ± 156

two metal cores were distinct. The mean value obtained from hundred such measurements was 4.1 ± 0.1 nm. This value is more suitable than the diameter of an isolated nanocrystal, the latter being 3.3 nm as estimated by STM measurements.²¹ We assume that the effective volume thus estimated takes into account the free volume in the nanocrystal aggregate. In other words, a particle pair is taken to adequately describe interactions in the bigger aggregates. In Table 1, we list the observed diameters of the giant clusters along with the estimates of the nuclearities. To our surprise, the estimated values compare closely with the magic nuclearities of 13, 55, 147, 309, 561, and 1415 corresponding to closed shells 1, 2, 3, 4, 5, and 7, respectively. In Figure 5, we have projected the calculated perimeters enclosing the different giant clusters. The close agreement between the observed and calculated diameters is indeed gratifying.

The giant aggregates obtained are distinct from the two-dimensional rings obtained by other groups.^{7,22} To establish the spherical nature of the giant clusters observed by us, they were imaged at different tilts ($\pm 17.5^\circ$) along two perpendicular axes in the focal plane. In Figure 6, we show such images obtained

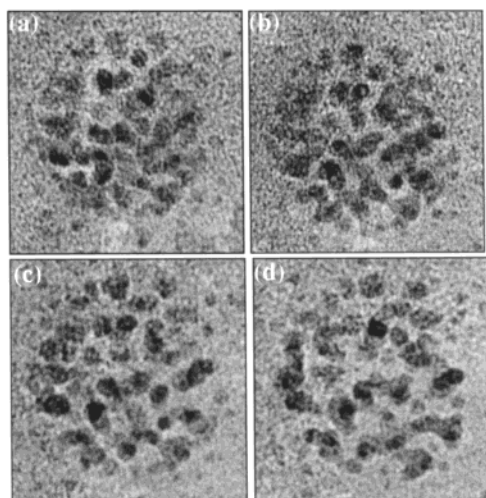


Figure 6. A $(\text{Pd}_{561})_{561}$ giant cluster imaged at various tilt angles along two perpendicular axes in the focal plane: (a) -18.7° , 1.4° ; (b) -7.3° , -1.4° ; (c) 0° , 1.4° ; (d) 12.4° , -1.4° .

with a giant cluster of nuclearity 561. The projected image appears circular over the entire tilt range of 35° , along both the directions. We observe a few individual nanocrystals to shift their positions in the image under different tilt conditions, though the exact trajectories could not be followed. A series of such tilt experiments confirmed the spherical nature of the aggregates. Furthermore, we were able to obtain lattice-resolved images of the individual Pd_{561} nanocrystals constituting the giant cluster. Such images revealed the characteristic 11 [111] lattice fringes. Attempts to image the internal structure of giant clusters were, however, not successful probably because of the interference from the polymeric ligand shell of the nanocrystals.

We have previously obtained two-dimensional arrays of metal nanocrystals by using monothiol^{2,9,14,23} and three-dimensional layered assemblies with metal and semiconductor nanocrystals by employing dithiols.²⁴ Brushlike ligands in these cases direct the assembly process along definite directions. We believe that the giant clusters discussed in this paper are a result of self-assembly in three-dimensions facilitated by the relatively passive and isotropic PVP coating around the nanocrystals. Unlike in a two-dimensional assembly, where the solvent plays an important role,²⁴ the formation of giant clusters does not seem to be influenced by the choice of the solvent. We are able to obtain the giant clusters from a wide variety of solvents such as water, ethanol, ethanol water mixtures, or other types of solvents such as ethylene glycol. In all cases, there were no significant changes in the size distribution of the obtained giant nanocrystals. These giant clusters could be reproducibly obtained over several trials starting with sols of widely differing concentrations and employing PVP of molecular mass $\sim 160,000 \text{ g mol}^{-1}$ as well.

We have made attempts to investigate the process of self-assembly of nanocrystals of a different magic nuclearity. Experiments with Pd nanocrystals of 3.2 nm diameter, corresponding to a nuclearity of 1415, have revealed the formation of giant clusters with possible nuclearities of 147 and 309, as shown in Figure 7. However, the slightly wider distribution in the pristine nanocrystal diameter (possibly due to a mixture of the 7 and 8 shell clusters¹³) seems to hinder the facile formation of uniform giant clusters. A majority of these clusters ($\sim 60\%$) display elongation along one axis. A narrow size distribution in the initial nanocrystal sol appears to be essential for the formation of the magic nuclearity giant clusters.

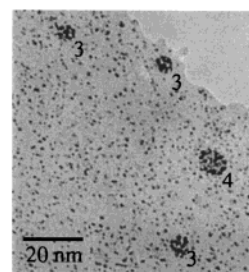


Figure 7. TEM image of giant clusters of Pd_{1415} nanocrystals. The numbers correspond to the proposed number of nanocrystal shells, n .

Conclusion

Giant clusters of Pd nanocrystals are obtained by the mesoscopic assembly of nanocrystals of uniform size. This observation provides an illustration of the principle of self-similarity. These clusters of metal nanocrystals are perhaps bound by the same laws that endow special stability to magic numbered nanocrystals.¹⁵ It would therefore appear that these laws are invariant under scaling. The giant clusters of Pd_{561} nanocrystals obtained by us are different from other types of ligand directed nanocrystal aggregates which are formed mostly due to the directional nature of the ligand shell.^{16,6}

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