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Synthesis of Palladium Metal Nanoparticles in the Bicontinuous Cubic Phase of Glycerol Monooleate

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Various lipid–water systems, such as vesicles[1] and microemulsions,[2] have been used to produce and stabilize nanoscale metal particles. These particles have potential applications in catalysis, micro- and nanoelectronics, magnetic recording, and optics depending on the metal and on the size and distribution of the formed particles. In this communication, we demonstrate for the first time the possibility of utilizing the bicontinuous cubic-phase structure of a lipid–water system to produce controlled-size metal nanoparticles with minimal polydispersity. The results show that the narrow aqueous channels of the bicontinuous cubic phase constrain the size of the metal particles, and therefore the cubic phase could provide a viable matrix for the synthesis of nanoscale materials.

We have utilized a polyol-type process to reduce the palladium ions to metallic palladium. The polyol process as it was originally implemented involved reduction of metal salts in neat ethylene glycol solution, on heating to about 200 °C.[3] Since then, there have been several applications of this polyol process[4] where the metal ion is intercalated in montmorillonite and reduced by refluxing the insoluble intercalated solid in neat ethylene glycol at 195 °C. Formation of palladium crystallites in montmorillonite also has been achieved under milder conditions (0 °C) in the presence of methanol.[5]

Glycerol monooleate (GMO) is an uncharged lipid with a single unsaturated fatty acid tail attached to a glycerol head group. It exhibits bicontinuous cubic phases, in which the lipid bilayer creates a three-dimensionally periodic network of aqueous channels, whose size can be controlled.[6] The head group of GMO, being a glycerol derivative, can take part in a polyol-type reaction with the metal salts (the primary hydroxyl group at the α-position can also independently reduce the salt) to form small metal particles. This, when combined with the possibility that such a reaction can be carried out at room temperature in the confined aqueous channels of the cubic phase, provides a very attractive situation for synthesizing metal nanoparticles whose size can be well controlled.

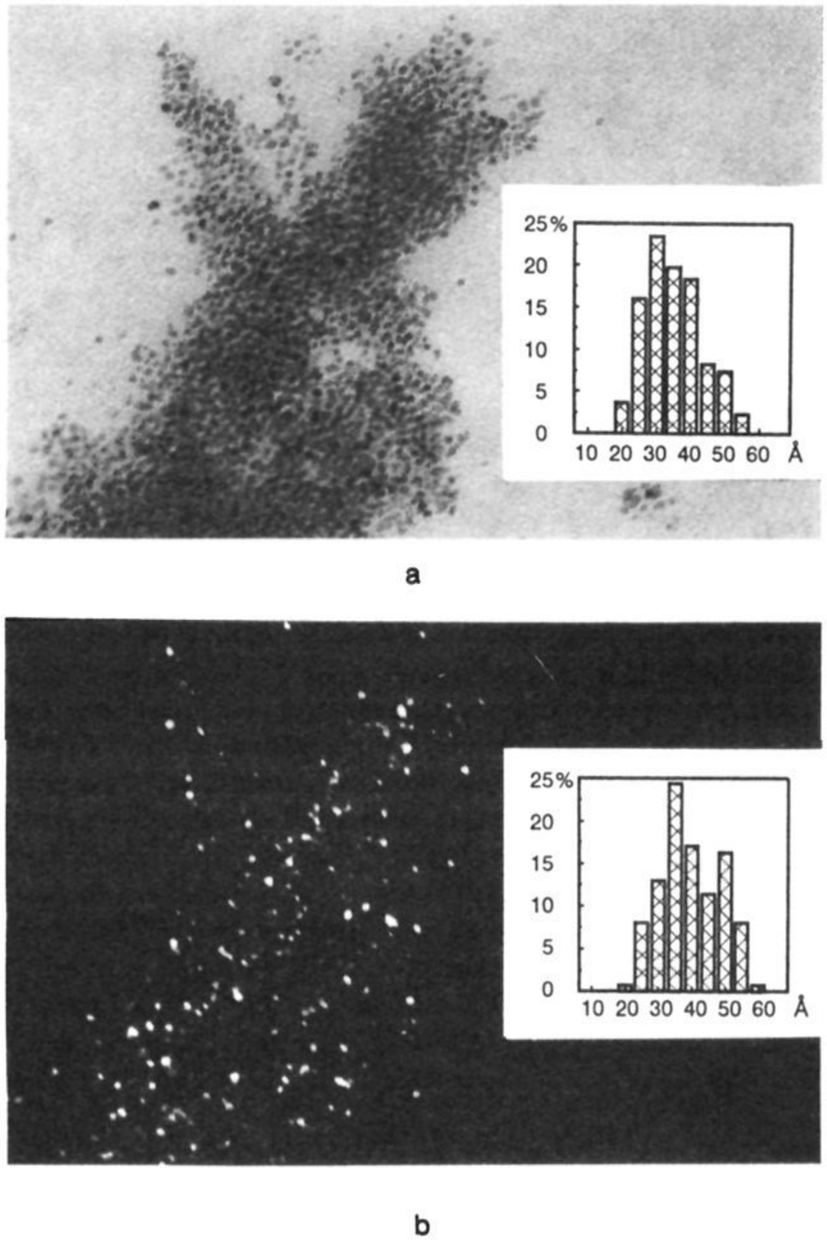

Figure 1. TEM micrographs of Pd particles formed in 70 wt % GMO sample. (a) Bright field image. (b) Dark field image of the same region showing the crystallites that contributed to the diffraction pattern. Magnification = 250 000×. Also shown as insets are histograms showing the particle and crystallite size distribution, respectively.

GMO was hydrated with sodium tetrachloropalladate solution at room temperature (20–25 °C) followed by centrifugation at 3000 rpm to ensure that the sample was homogeneous. It was then allowed to equilibrate for a period of at least 24 h, during which time the hydroxyl groups in the head group of GMO reduce the tetrachloropalladate salt to metallic palladium. The presence of metallic palladium particles imparts a black coloration to the gel. Although samples containing various amounts of lipid were prepared and studied, in this communication we will only discuss results from samples containing 70 and 60 wt % GMO. Various sodium tetrachloropalladate concentrations between 5 and 50 mM[7] were studied. The formed particle size was independent of salt concentration. In this communication we will only discuss results for the 10 mM case.

After the reaction, the lipid was separated by lyophilizing the black gel and extracting it in chloroform, leaving out the palladium particles. Fourier transform infrared (FTIR) spectra of the lipid before and after reaction were then measured using a Perkin-Elmer 1725X FTIR spectrometer. Comparison of the two spectra reveals three important features: (i) a considerable decrease in intensity of the 1300–1200-cm^{-1} vibrations associated with the –CHOH and –CH_2OH groups, (ii) a concomitant increase in the symmetric and antisymmetric stretching modes of the C—H bond (3000–2800 cm^{-1}) associated with a –CHO group, and (iii) an increase in the intensity of the C═O stretch at 1800 cm^{-1}. These changes in the FTIR spectra of the lipid, after reaction with chloropalladate solution, suggest a partial oxidation of the primary

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(1) Ferrar, W. T.; O'Brien, D. F.; Warshawsky, A.; Voycheck, C. L. *J. Am. Chem. Soc.* **1988**, *110*, 288–289. Liu, H.; Graff, G. L.; Sarikaya, M.; Aksay, I. A. *Proc. Mater. Res. Soc. Symp.* **1991**, *218*, 115–119. Kurihara, K.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6152–6153. Tricot, Y.; Fendler, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 2475–2476.

(2) Kurihara, K.; Kizling, J.; Stenius, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 2574–2579.

(3) Fievet, F.; Lagier, J. P. Blin, B.; Beaudon, B.; Figlarz, M. *Solid State Ionics* **1989**, *32/33*, 198–205. Fievet, F.; Lagier, J. P.; Figlarz, M. *Mater. Res. Bull.* **1989**, *14*, 29–34.

(4) Malla, P. B.; Ravindranathan, P.; Komarneni, S.; Roy, R. *Nature* **1991**, *351*, 355–357. Malla, P. B.; Ravindranathan, P.; Komarneni, S.; Breval, E.; Roy, R. *J. Mater. Chem.* **1992**, 2, 559–565.

(5) Crocker, M.; Buglass, J. G.; Herold, R. H. M. *Chem. Mater.* **1993**, *5*, 105–109.

(6) Hyde, S. T.; Andersson, S.; Ericsson, B.; Larsson, K. *Z. Kristallogr.* **1984**, *168*, 213–219. Larsson, K. *J. Phys. Chem.* **1989**, *93*, 7304–7314. Mariani, P.; Luzzati, V.; Delacroix, H. *J. Mol. Biol.* **1988**, *204*, 165–189. Lutton, E. S. *J. Am. Oil Chem. Soc.* **1965**, *42*, 1068–1070.

(7) No particles formed for concentrations less than 5 mM.

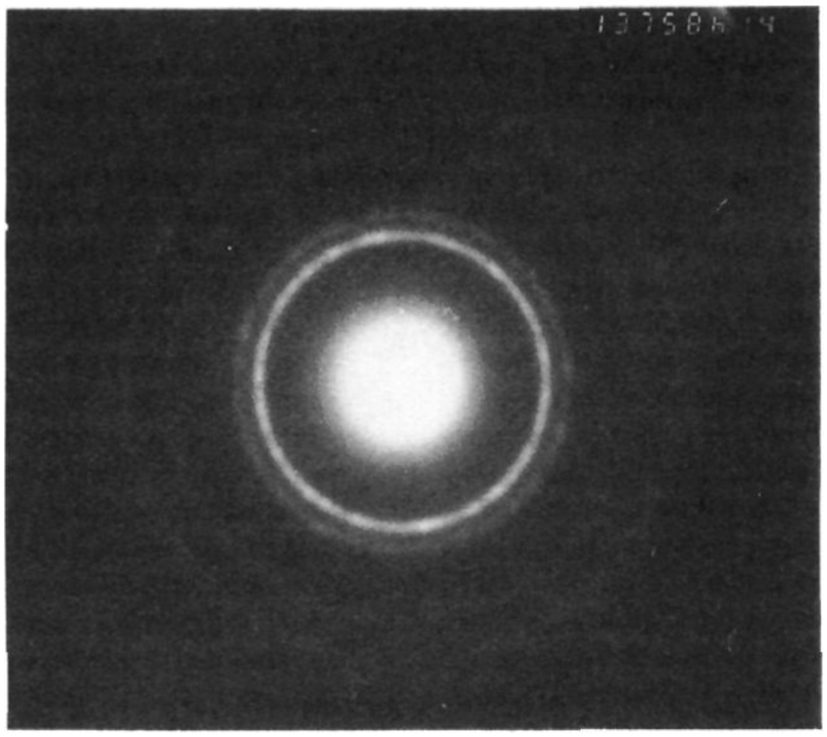

Figure 2. Selective area electron diffraction from the Pd particles. The spacings index to the fcc lattice of metallic Pd.

–CH_2OH group in GMO to an aldehyde (–CHO) by the chloropalladate salt.

Small-angle X-ray diffraction studies (SAXS) were performed both at the National Synchrotron Light Source at Brookhaven National Laboratory and, using a Rigaku RU-400 X-ray generator, at Naval Research Laboratory on the lipid samples after oxidation with 10 mM chloropalladate solution. The data show that the symmetry and the unit cell sizes of the cubic phases are unaltered (within the experimental accuracy) on the addition of the salt. The 70 and 60% samples exhibit gyroid (with a unit cell of 133 Å) and double diamond cubic phases (unit cell of 96 Å), respectively; the corresponding unit cell sizes in the absence of the salt are 128 and 99 Å. Wide-angle X-ray data showed a diffraction peak centered at $2\theta = 40°$ (d spacing of 2.25 Å) corresponding to the (111) plane of metallic palladium.

The samples for transmission electron microscopy (TEM) were prepared by smearing the lipid phase on carbon-coated copper TEM grids. The grids were then washed with methanol to remove the lipid[8] and air-dried. The TEM studies were carried out on a JEOL 200 CX microscope operated at 200 kV and on an Hitachi H-900 UHR microscope operated at 300 kV. The morphology and particle size were revealed by bright field imaging (Figure 1a), and the structure information was obtained by selected area electron diffraction. Dark field imaging (Figure 1b) was used to determine the crystallite size of palladium particles. Electron diffraction (Figure 2) of all samples showed polycrystalline ring patterns. The indexing of the diffraction rings conforms to an fcc structure, and the spacings correspond to elemental palladium with a unit cell of 3.9 Å. This is also confirmed by high-resolution TEM, which clearly shows the (111) lattice of the palladium crystallites. The bright and dark field images were used to measure the particle and crystallite size distribution, respectively, using the Image Pro analysis software. At least 200 particles per sample were used for the size evaluation, and the resulting histograms are shown as insets in Figures 1a and 1b. The mean particle size in the 70% sample was calculated to be 33.4 Å, with a standard deviation of 8.6 Å. The corresponding mean crystallite size was evaluated to be 37.1 Å, with a standard deviation of 9.1 Å. The slightly larger value for the crystallite size could be due to the differences in the regions over which bright and dark field images were analyzed. However, the fact that the crystallite size is approximately the same as the particle size indicates that the particles are monocrystalline. This was also confirmed by lattice images, which showed a single set of (111) planes. However, high-resolution electron microscopy studies show the presence of some amorphous particles also.

An analysis of the size distribution in a 60% sample shows the mean particle size to be 48.6 Å, with a standard deviation of 15.8 Å. Thus, the particles are larger in samples with a higher water/lipid ratio. This result is not surprising since a higher water content would imply a larger aqueous pore and hence a larger volume available for the metal particle to grow. In fact, the diameters of the aqueous pores (which can be calculated from the X-ray diffraction data) for the 70 and 60% samples were found to be 39 and 50 Å, respectively. These values are nominally greater than the corresponding particle sizes, which are 33.4 and 48.6 Å, indicating that the narrow aqueous pores of the cubic phase constrain the size of the formed palladium particles.[9] The presence of particles larger than the pore size (those larger than 40 Å in Figure 1a) appears to be due to the clustering of two particles. This is supported by the larger aspect ratio (1.8) measured for these particles. Currently, we are testing the constraint imposed by the cubic nanopores on the size of the palladium particles over a wider range of the pore size. We are also extending this simple process to synthesize other metal particles.

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[8] Control experiment in which the grids were not washed with methanol shows no change in particle size, morphology, or structure on washing. The images, however, are hazy due to the larger sample thickness. In situ growth of particles in thin cubic-phase samples on a TEM grid is being tried to see if the geometrical regularity of the cubic phase induces spatial ordering of the nanocrystallites.

[9] In contrast, no well-defined particles were observed in the lamellar phase, although the chloropalladate salt was reduced. These results will be presented in a more detailed paper.