Preparation of Gold Nanoplates Protected by an Anionic Phospholipid

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Gold nanoplates were prepared by the photoreduction of $NaAuCl_4$ in the presence of dimyristoyl-L-α-phosphatidyl-DL-glycerol (DMPG) as a protective agent. When the DMPG concentration is appropriate, hexagonal nanoplates were formed. When the DMPG concentration was lower or higher, spherical particles were predominantly formed.

Metal nanoparticles show unique properties that are different from those of bulk metals.[1–3] Extensive efforts have been made to prepare size-controlled spherical particles.[4] Spherical gold nanoparticles show the surface plasmon absorption band at about 520 nm, shifting slightly to longer wavelengths with increasing particle size.[3] Rod-like gold nanoparticles have been prepared and show two absorption bands due to the transverse and longitudinal plasmon absorptions in the visible to near IR range.[5–8] Recently, silver nanorods,[9] nanoprisms,[10] nanodisks,[11–14] and nanoplates[15,16] have been prepared. In the case of gold, however, there are very few reports for the nanodisks[11] and planar nanoparticles.[17] We would like to report here the preparation and characterization of gold nanoplates having hexagonal or truncated triangular shape.

After nitrogen bubbling, aqueous solutions containing $NaAuCl_4$ and dimyristoyl-L-α-phosphatidyl-DL-glycerol (DMPG) were irradiated by a parallel beam from a 500 W high-pressure mercury lamp through condenser and collimator lenses (Ushio UI-502Q) with the distance between the lamp and the sample being 37 cm. The irradiation time was 2 h because preliminary experiments showed no difference in the absorption spectrum between 2 and 4 h irradiation time.

Figure 1 shows transmission electron microscope (TEM) images of nanoparticles prepared in the presence of different concentrations of DMPG with an initial $NaAuCl_4$ concentration of 0.66×10^{-3} mol dm^{-3}. When the DMPG concentration is 0.5×10^{-3} mol dm^{-3}, hexagonal and/or truncated triangular nanoplates are predominant (Figure 1a). When the DMPG concentration is 1.0×10^{-3} mol dm^{-3}, there are cavities in the plates (Figure 1b). Some of the plates are seen to be overlapped fully or partially. When the DMPG concentration is decreased below 0.5×10^{-3} mol dm^{-3}, the fraction of the hexagonal plates decreases and the fraction of agglomerated spherical particles increases. When the DMPG concentration is increased above 1×10^{-3} mol dm^{-3}, more and more cavities are formed in the plates, and finally the plates change to smaller spherical particles as seen in Figure 1c. Thus, the excess amount of DMPG prohibits the formation of the nanoplates.

Figure 2 shows TEM images and electron diffraction (ED) patterns for plates with the DMPG concentration 0.5×10^{-3} mol dm^{-3} and 1.0×10^{-3} mol dm^{-3}, respectively. The hexagonal symmetry of the ED patterns indicates that these plates, even the one having cavities, are single crystals and the

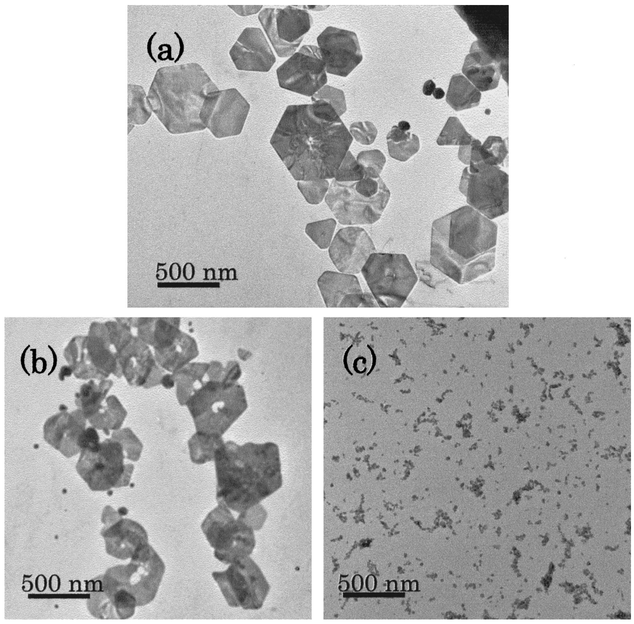

Figure 1. TEM images of the gold nanoparticles protected by DMPG. The DMPG concentrations (10^{-3} mol dm^{-3}) are (a) 0.5, (b) 1.0, and (c) 4.0.

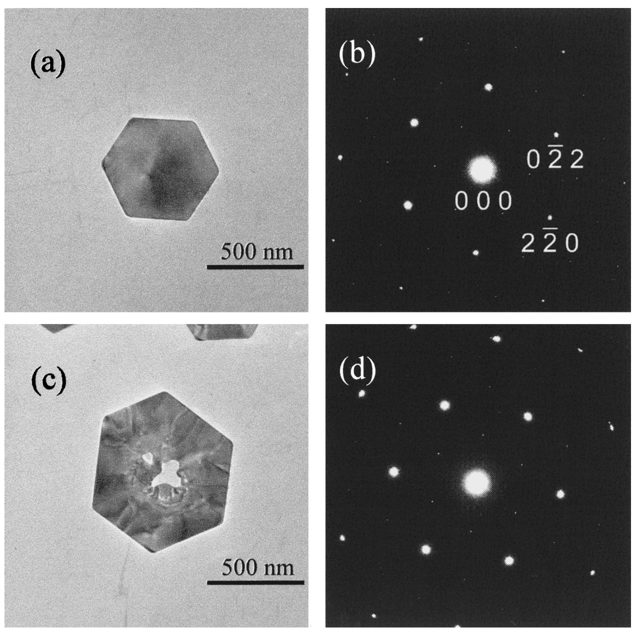

Figure 2. TEM images and ED patterns of gold nanoparticles protected by DMPG. DMPG concentrations (10^{-3} mol dm^{-3}) are (a), (b) 0.5 and (c), (d) 1.0.

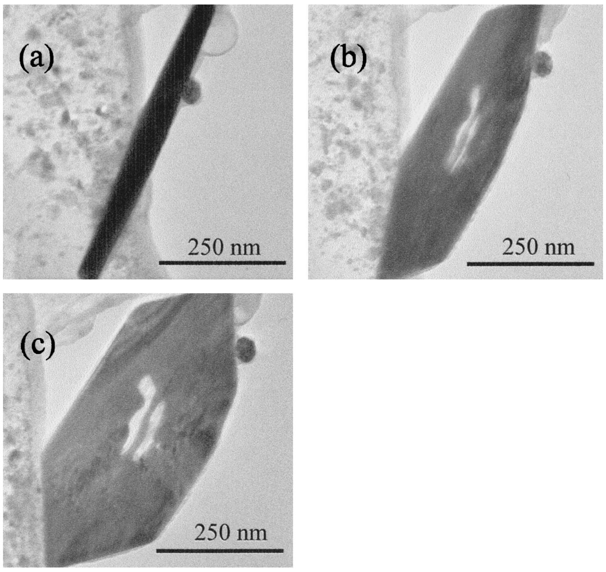

Figure 3. TEM images of a gold nanoparticle protected by DMPG (1.0×10^{-3} mol dm^{-3}) taken from different angles. The relative angles are (a) $+17.3°$, (b) $0°$, (c) $-18.1°$.

incident electron beams are perpendicular to {111} facets of the plates.

Figure 3 shows TEM images taken for a particle from different angles. From Figure 3a the thickness of the plate is found to be less than 40 nm.

The particles were heated using a Gatan model 652-Ta double tilt heating holder. The boundary of the two partially overlapping hexagonal plates disappeared at ca. 1010 °C keeping the hexagonal shape and they finally melted at 1032 °C, loosing the hexagonal shape suddenly. Considering the fact that the sample temperature could be higher than the displayed holder temperature because of the electron beam irradiation, the melting temperature is very close to that of the bulk metal gold, i.e., 1064 °C.[18] This fact indicates that the particles are quite pure.

Gold nanorods are known to be fragmented into smaller particles by laser irradiation.[19,20] These nanoplates could be another candidate for optical memory materials. Because these nanoplates are protected by a natural phospholipid, one of their potential applications is the use as a biocompatible probe or a carrier of the drug delivery system. An interesting optical property of these nanoplates is that liquid suspensions appear turbid when viewed from the incident light direction, but appear transparent when viewed from the other side of the incident light, suggesting their use for new materials such as functional glass.

Our preliminary results show that the nanoplates are not predominantly formed when the protective agent is a synthetic double chain surfactant such as sodium didodecylphosphate, sodium ditetradecylphosphate, didodecyldimethylammonium bromide, or ditetradecyldimethylammonium bromide, but are formed when the protective agent is an anionic phospholipid such as dilauroyl- or dipalmitoyl-L-α-phosphatidyl-DL-glycerol. It is not clear at this point if there is any relation between the morphology of the self-assembled amphiphile and the shape of nanoparticles formed. The results of this study show that the concentration of DMPG is an important factor to control the nanoparticle shape, but how the molecules affect the growth of different crystallographic planes differently is not clear. Further studies are underway to clarify these points and to improve the monodispersity of the plates.

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