Communication

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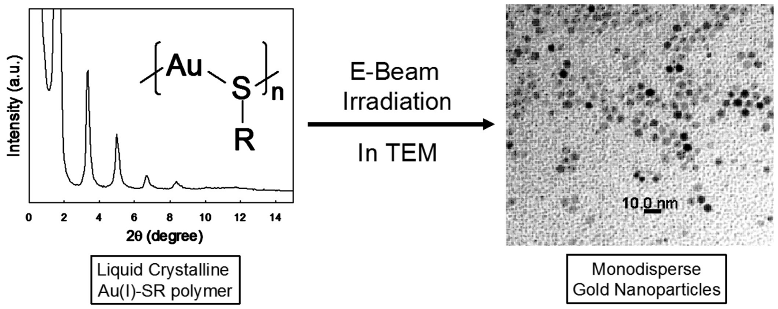

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Synthesis of Gold Nanoparticles from Gold(I)−Alkanethiolate Complexes with Supramolecular Structures through Electron Beam Irradiation in TEM

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It is well-known that the physicochemical properties of gold nanoparticles are highly related to their sizes and size distributions.[1] Therefore, the ability to synthesize nanoparticles in a size-controlled manner has been one of the main goals of materials science over the past decade due to their possible applications in electronic and optical devices.[1] One of the most successful synthetic methods allowing for precise control of the size was achieved by Schaaff et al.[2] through a modification of the well-known Brust method.[3] They reported that gold nanoparticles with an extremely narrow size distribution could be prepared through the reductive decomposition of polymeric Au(I)−SRs, which are made by the reaction of the gold salt and alkanethiol prior to the reduction step, although to the best of our knowledge the structure and chemical properties of the Au(I)−SRs have not been clearly elucidated.

Recently, we found that a gold polymer, Au(I)−SC$_{18}$ (C$_{18}$ = −C$_{18}$H$_{37}$), prepared from the well-known chemical reaction of $\mathrm{LiAuCl_4 + 3\ RSH \rightarrow Au(I){-}SR + RS{-}SR + 3\ HCl + LiCl}$,[2b,4] shows mesomorphic behavior and luminescent properties upon UV irradiation. Furthermore, when the Au(I)−SC$_{18}$ polymer was irradiated by an electron beam in a transmission electron microscope (TEM), highly monodisperse gold nanoparticles were obtained.

The Au(I)−SC$_{18}$ polymer was prepared simply by mixing a gold salt (LiAuCl$_4$, 0.1 mmol) with an excess amount of octadecanethiol (C$_{18}$H$_{37}$SH, 1.0 mmol) in THF (5 mL). When the mixture was stirred for 24 h, the yellowish color of LiAuCl$_4$ totally disappeared, and the Au(I)−SC$_{18}$ polymer was obtained as a white, solid precipitate. The chemical structure of Au(I)−SC$_{18}$ was confirmed from the solid-state ^{13}C NMR and FT-IR experiments (see Supporting Information). Additionally the elemental analysis and thermal gravimetric analysis results showed that the stoichiometry corresponds to one octadecane-thiolate group per gold atom within experimental error.[5]

The X-ray diffraction (XRD) curve of the powdery Au(I)−SC$_{18}$ at room temperature shows a series of ordered reflections that can be assigned to the (0*k*0) ($k = 1-7$) planes in a small angle region (Figure 1a), indicating that the sample has a highly ordered layer structure. In the wide angle region, two reflections were observed at *d*-spacings of 3.45 and 3.95 Å, respectively, while their intensities were very small. The layer *d*-spacing of Au(I)−SC$_{18}$ (49.0 Å) is about twice the calculated length of a fully extended octadecanethiolate group (25.3 Å). Therefore, Au(I)−SC$_{18}$ would be expected to have a bilayer structure. Similar layer structures have been found for other polymeric metal complexes, such as RNCAu(I)−SPh[6] and Ag(I)−SRs.[7] In the DSC curve of the Au(I)−SC$_{18}$ polymer, a sharp endotherm was observed at 157 °C ($\Delta H = 116$ J/g) (Figure 1b). Above the endotherm, Au(I)−SC$_{18}$ was determined to be isotropic from the XRD experiments. On heating the powdery Au(I)−SC$_{18}$ from room temperature, the ordered small-angle and wide-angle reflections were maintained until 157 °C, at which point both the small angle peaks and the wide-angle peaks disappeared. When Au(I)−SC$_{18}$ in the isotropic state was cooled at 5 °C/min, a grainy texture of bi-refringent domains was observed from about 157 °C using polarized optical microscopy. It is well-known that highly viscose polymer melts can prevent the formation of the normal texture for their mesomorphic phases.[8] In addition to this result, both the mechanically soft nature of the sample and the broad wide-angle X-ray reflections (see Supporting Information) from room temperature to the isotropic temperature also indicate that Au(I)−SR$_{18}$ has mesomorphic phases. The two wide angle reflections below the isotropic temperature possibly represent the Au- - -Au distances corresponding to aurophilic interactions, which in turn cause the luminescence of Au(I)−SC$_{18}$ upon UV irradiation (Figure 1c). Bachman et al. also reported the luminescence property of Au(I)−phenylthiolate (Au(I)−SPh) prepared from PhSNa and EtNCAuCl.[6] In the case of Au(I)−SC$_{18}$, as the temperature increases, the intensity of the luminescence decreases, only to disappear completely when the sample is heated above the isotropic temperature. Therefore, the luminescent property of Au(I)−SC$_{18}$ is observed only in the LC state. Detailed studies on the luminescence property of Au(I)−SC$_{18}$ are currently under way.

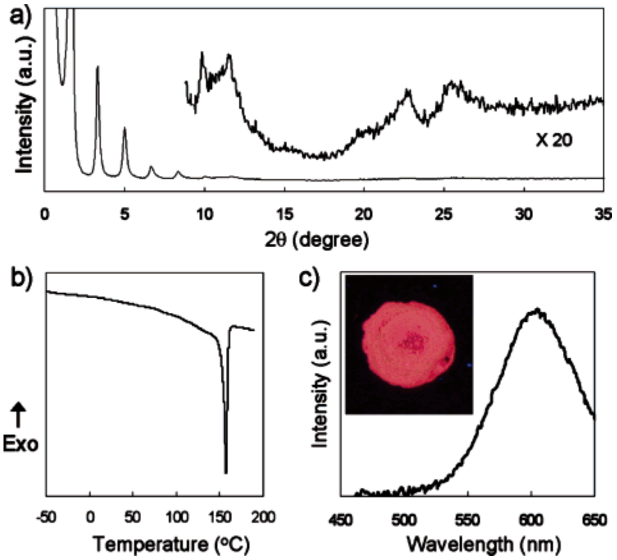

Figure 1. (a) The XRD pattern of Au(I)−SC$_{18}$ at room temperature. (b) The DSC curve of Au(I)−SC$_{18}$ on a heating scan at 5 °C/min. (c) Emission spectrum of powder Au(I)−SC$_{18}$ sample with $\lambda_{ex} = 350$ nm. (Inset) Photograph of the luminescence of Au(I)−SC$_{18}$ placed on a slide glass when photoirradiated with a UV lamp (>350 nm).

We performed TEM experiments (JEOL JEM-3000F, 300 keV) for Au(I)−SC$_{18}$ to observe the ordered structure of the sample, because normally the ordered phase of a block copolymer can be observed by TEM. For the sample preparation for TEM, the powdery Au(I)−SC$_{18}$ was dispersed in THF, and a droplet of the solution was dropped onto a carbon-coated copper grid. When Au-

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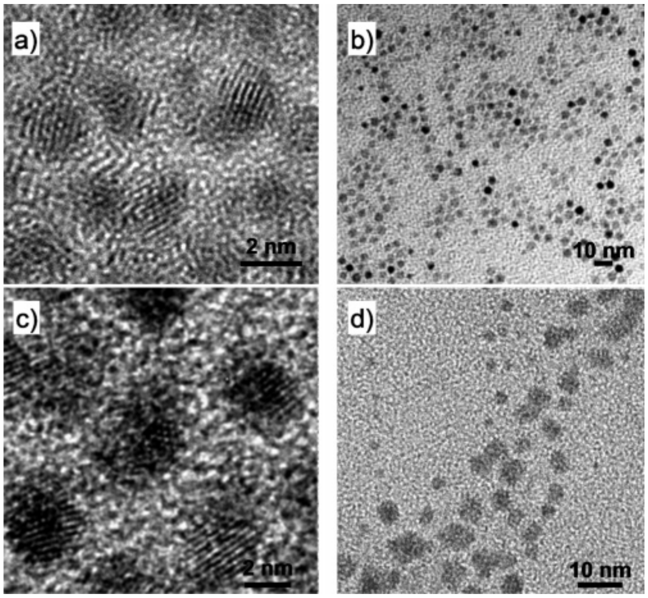

Figure 2. (a) High-resolution TEM images of gold nanoparticles formed from Au(I)$-$SC$_{18}$ by electron beam irradiation in TEM of 300 keV (JEM-3000F). The characteristic lattice fringes (lattice spacing = 2.5 Å) of the fcc crystal structure of gold are clearly shown. TEM images of gold nanoparticles formed (b) from Au(I)$-$SC$_{18}$ by electron beam irradiation in TEM of 80 keV (JEM-1010), (c) from Au(I)$-$SC$_6$ in TEM of 300 keV, and (d) from Au(I)$-$SC$_2$ in TEM of 300 keV.

(I)$-$SC$_{18}$ was irradiated by the electron beam in the TEM, to our interest, spherical nanoparticles with an average diameter of 1.9 nm (±0.3 nm) were observed (Figure 2a). The spherical shapes of the gold nanoparticles are not clearly seen in these TEM images probably due to the three-dimensionally assembled structure of the gold nanoparticles, as reported by others.[9]

We found that the size of the gold nanoparticles can be controlled by adjusting the accelerating voltage of the electron beam in the TEM. For example, the average sizes of the gold nanoparticles formed in the TEM of 80 keV (JEOL JEM-1010) and 200 keV (JEOL JEM-200CX) were 5.0 nm (±1.1 nm) (Figure 2b) and 2.0 nm (±0.5 nm), respectively. It may be that the higher the energy of the electron beam, the larger the number of nucleation sites,[10] thereby allowing nanoparticles with smaller sizes to be obtained. We also found that the size of the gold nanoparticles increases as the length of the alkyl group decreases. For example, when Au(I)$-$SC$_6$, Au(I)$-$SC$_{10}$, and Au(I)$-$SC$_{14}$, which all have highly ordered bilayer structures, were irradiated by the electron beam (300 keV) in the TEM, gold nanoparticles with diameters of 2.9 ± 0.6 nm (Figure 2c), 2.3 ± 0.3 nm, and 2.1 ± 0.4 nm, respectively, were obtained. One possible explanation for this is that, in the Au(I)$-$SRs with the longer alkyl groups, as the volume ratio of the metallic moiety decreases, the crystal growth rate (which is related to the diffusion of the gold atoms) decreases, thereby causing smaller gold nanoparticles to be formed. In addition, the highly ordered structure of the Au(I)$-$SR is found to be one of the key factors involved in the formation of the monodisperse nanoparticles. The longer the alkyl group, the higher the positional ordering the Au(I) atoms, which in turn probably influences the uniform growth of the gold nanocrystals. When Au(I)$-$SC$_2$, which was found to have a much less ordered structure (only a weak (010) reflection was observed from the XRD pattern), was irradiated with the electron beam, a mixture of gold nanocrystals with various sizes and irregular shapes were obtained (Figure 2d). Currently, we are working on the reduction of Au(I)$-$SRs using an electron beam accelerator of high capacity with different energy values (0.3 to tens of MeV) to perform the controlled-synthesis of a large quantity of gold nanoparticles with a monodisperse size distribution using this solvent-free process.

In conclusion, the one-pot fabrication of thiol-stabilized monodisperse gold nanoparticles was achieved through the electron beam irradiation of Au(I)$-$SRs with highly ordered supramolecular structures. The Au(I)$-$SRs were synthesized simply by mixing LiAuCl$_4$ and alkanethiols in THF. Au(I)$-$SRs were found to be mesomorphic and showed luminescent behavior upon UV irradiation. The novel luminescent properties and LC behavior of the Au(I)$-$SRs with various alkyl groups and various functional groups are also being studied. The results will be reported shortly.

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Supporting Information Available: Detailed synthetic procedures, EDX and NMR spectra, POM and TEM images, XRD spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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