Aerogel-like Three-dimensional Gold Nanoparticle Network via Sublimation of Volatile Organic Crystals Decorated with Gold Nanoparticles

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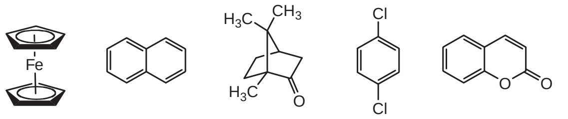
We demonstrate novel strategy to create the three-dimensional networks of the gold nanoparticle from organic crystals decorated by the gold nanoparticles via slow removal of the crystals by sublimation.

Utilities of organic crystals as interfaces have attracted growing interest to prepare novel functional composite materials with metal nanoparticles. Moore and co-workers reported inorganic microcrystals coated by gold nanoparticles to develop a new method for the composite materials by crystal lattice mediated self-assemblies (CLAMS).[1] More recently, we demonstrated that the specific crystal faces of the micro- and millimeter hexagonal crystals of l-cystine were decorated by the gold nanoparticles.[2] Thus, as one of the potential applications of the crystals decorated gold nanoparticles, we attempted to construct the three-dimensional (3D) interconnected network structures consisting of the gold nanoparticles from them.[3,4] Our approach was removal of the substrate crystals by sublimation after coating by the gold nanoparticles. Gentle removal of the organic crystal should develop in situ the 3D network of the nanoparticles from the two-dimensional (2D) ones on the crystal surfaces. To our best knowledge, this is the first report to describe preparation of 3D network structures via sublimation to yield aerogel-like matter that have potential applications such as catalysis, sensors, and nanometer electrochemical device components.[5]

Ferrocene (**1**) was used as the first candidate of organic crystals as volatile substrates (Scheme 1). The prismatic orange crystals of **1** were prepared by recrystallization from decane. Then, they were immersed in the solution of the various gold nanoparticles for 2 h. In the case of the cationic gold nanoparticles (average diameter; 13.5 nm) modified by 2-aminoethanethiol,[6] the crystals were slightly colorized with purple, after washing by dipping in distilled water repeatedly. However, the solutions of other commercially available citrate-modified gold nanoparticles (BB international, average diameter; 19.9 nm) provided no apparent color changes of the crystal faces. Moreover, by contrast with the selective decoration of the l-cystine crystals,[2] all the surfaces of **1** were colorized, which could be confirmed by naked eyes. Thus, the adhesion to the hydrophobic crystal surfaces of **1** was attributed not to electrostatic interaction between the crystals and nanoparticles but to nonspecific deposition of 2-aminoethanethiol-modified gold nanoparticles that had higher aggregation abilities.[6] This was also confirmed by successful deposition of the 2-aminoethanthiol-modified gold nanoparticles onto hydrophobic HOPG under the same protocol. Other gold nanoparticles did not deposit on both the crystal surfaces of **1** and HOPG.



1 2 3 4 5

Scheme 1. Molecular structures of volatile organic crystals.

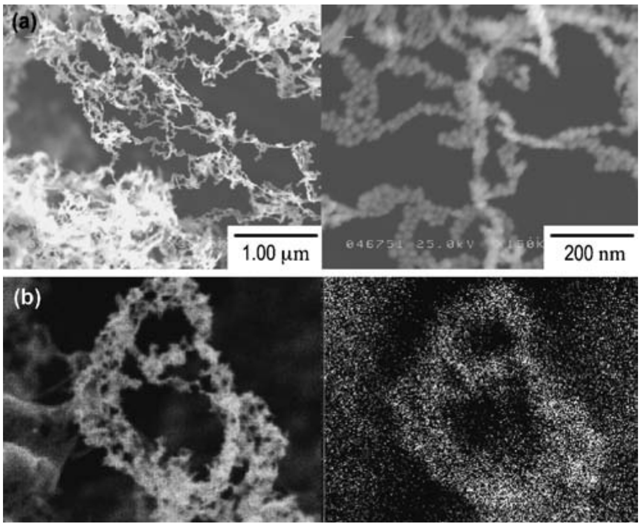


Figure 1. (a) SEM images of the fibrous gold nanoparticles created from **1**. (b) SEM image (left) and Au elemental mapping (right) of fibrous gold nanoparticles created from **1**.

Then, they were placed on a SEM grid and evacuated in vacuum (1 mmHg) for 6 h at room temperature. On SEM images, as shown in Figure 1, a fibrous network structure was observed. The network was constructed mostly by single fibers or bundles of a few fibers. The length of the fibers was more than one hundred micrometers. The single fiber was composed of one-dimensional (1D) interconnected nanoparticles with the diameters of ca. 20 nm. This size of the particles was consistent with those of the starting gold nanoparticles. TEM observations also indicated formation of necklace-like 1D assemblies of nanoparticles. In order to clarify the composition of the fibrous network, we examined the network in the rectangle zone by EDX analysis. The peaks observed in the elemental analysis spectrum were assigned as gold for 2.120 keV and carbon for 0.277 keV. No peaks from iron (6.403, 7.057, and 7.110 keV) were detected at all. Consequently, one can conclude that the resulting fibrous structure was composed of mainly from gold and carbon, and the crystals of ferrocene (**1**) were completely removed from the composite materials with the gold nanoparticles. Moreover, the

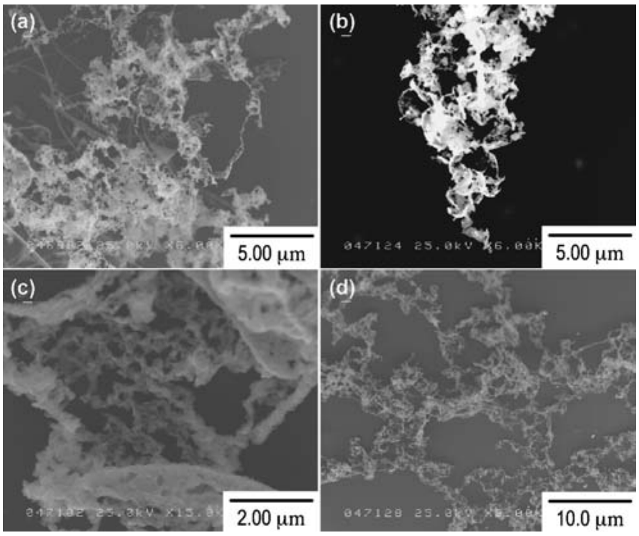


Figure 2. SEM images of the fibrous gold nanoparticles from (a) **2**, (b) **3**, (c) **4**, and (d) **5**.

element mapping also indicated that the fibrous network structures were composed of carbon and gold. It is clear, therefore, that 3D network structures of gold nanoparticles were prepared by the coating onto the ferrocene single crystals followed by sublimation of the substrate crystals.

In order to clarify generality of this method, we tried to use the following volatile crystals; naphthalene (**2**), camphor (**3**), 1,4-dichlorobenzene (**4**), and coumarin (**5**). All these compounds were decorated only by the 2-aminoethanethiol-modified gold nanoparticles, when they were immersed under the same conditions. After removal of the organic crystals in vacuum, the fibrous network was observed by SEM as shown in Figure 2. They all had the similar network structures. In the case of coumarin, the fibers had the larger diameters due to bundles of the 1D arrays of the gold nanoparticles, and the bundled fibers were extended longer than others. The slight change in the network structures was caused by the difference of the shapes and the sizes of the substrate crystals and amount of the gold nanoparticles onto the crystal faces.

Finally, the proposed scheme for formation of the gold nanoparticles 3D network is discussed. The first step is the decoration of the crystal surfaces by the gold nanoparticles as the 2D aggregate of the gold nanoparticles. Since several attempts to observe the surfaces of the intermediate decorated crystals by SEM were found to be unsuccessful owing to relatively rapid sublimation of the substrate crystals, we cannot discuss the structures of the aggregated gold nanoparticles on the substrate crystals, either the 2D network that observed on other substrates by capillary force during drying processes or randomly distributed discrete small aggregates similar to the surface of the l-cystine crystals decorated by gold nanoparticles reported previously. Then, the organic substrates are gently removed by sublimation. Shrinkage of the substrate accompanies cross-linking of the 2D networks on each face or development of 3D network by assemblying the nanoparticles on the surface, due to the capillary force between the gold nanoparticles and the substrate crystal. The resulting supramolecular structure is quite similar to the microstructures of the aerogels of the metal and semimetal oxide prepared by freeze-drying or supercritical drying.[2–4] Our attempts by freeze-drying of aqueous gold nanoparticle solutions failed to prepare the similar 3D network, because rapid deposition of the gold nanoparticles into black, large, closely packed aggregates was observed by cooling. Thus, the easy operation under the mild condition without any special equipment is advantage of our process to prepare the aerogel-like fibrous network structures interconnecting metal nanoparticles. Various other micro- and nanoparticles should be applicable to decoration of the volatile organic crystals.

In conclusion, we here report the preparation of the novel 3D fibrous network consisting of gold nanoparticles by decoration of volatile organic crystals and removal of the substrate crystals by sublimation. The resulting 3D network features 1D arrays of the bulk nanoparticles, and they should access to fabricate 3D networks of nanowires.[5] Applications of this method to other nanoparticles provide us to create new three-dimensional networks consisting of interconnetcted networks of nanometer-scale solid building blocks, by controlling the surface of the organic crystals are under current investigation.

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