Composite Materials

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Anisotropic Decoration of Gold Nanoparticles onto Specific Crystal Faces of Organic Single Crystals**

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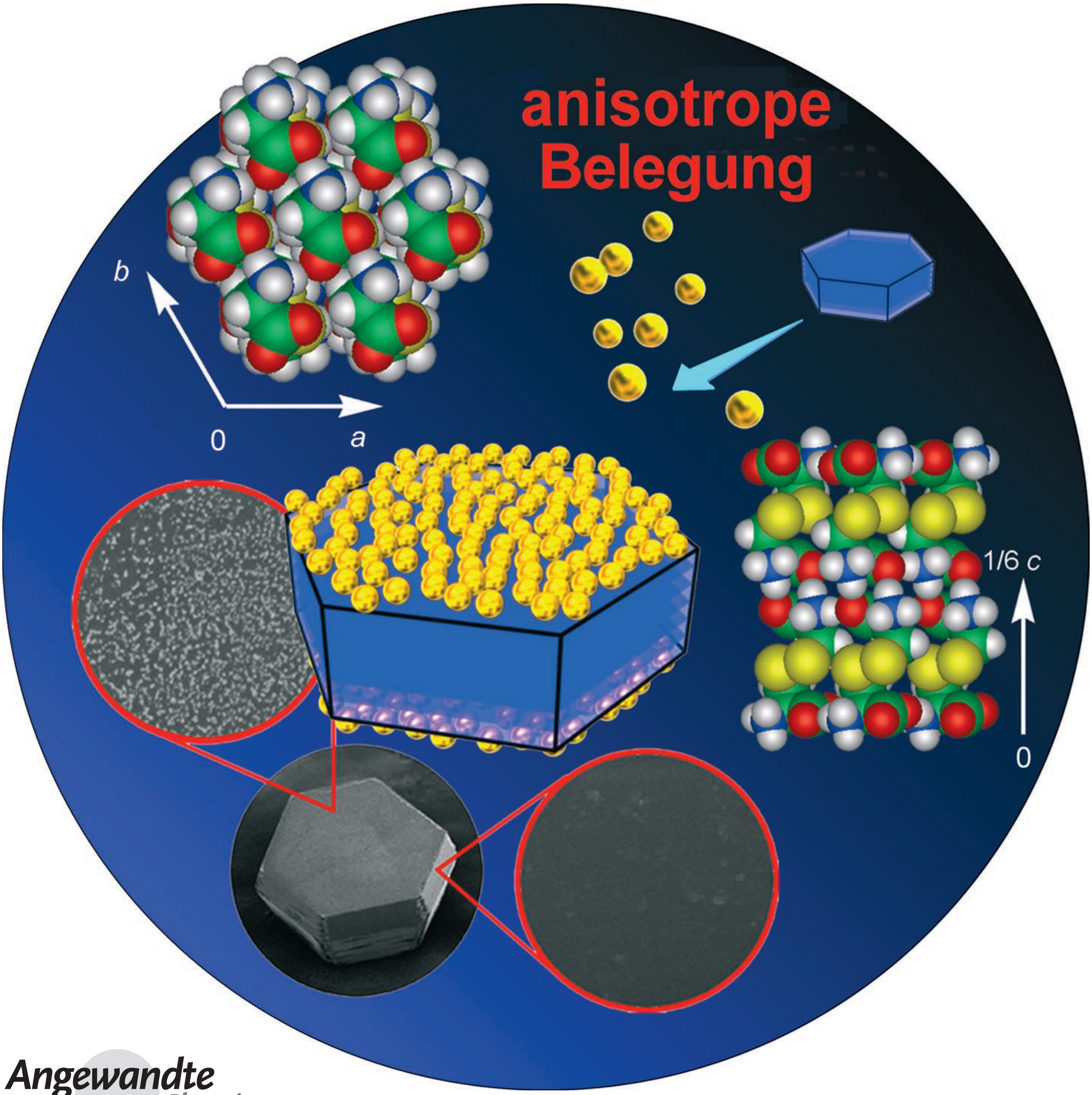

Anisotropy, various polyhedral shapes with well-defined faces, and a wide range of sizes from nano- to millimeter are characteristic features of organic single crystals. The anisotropy is attributed to the anisotropic packing of organic molecules in the crystalline state, and each face has different surface properties. Therefore, organic single crystals should play a key role in making multicomponent composites through their face-selective association with other materials. Anisotropic adhesion of organic single crystals by other organic molecules is the first step toward the preparation of such composites and has been studied mainly from the viewpoint of crystal growth and dissolution.[1] More recently, face-selective dyeing of inorganic single crystals by dye molecules in solution has been documented[2] and controlled aggregation of inorganic mesocrystals has been discussed for the formation of inorganic superstructures as models of biomineralization.[3–5]

Gold nanoparticles are a fascinating material as a result of their unique optical (plasmon band), electronic, catalytic, and supramolecular properties, as well as their wide applications for nanotechnology and biotechnology.[6] Composite materials with one- or two-dimensional arrays of gold nanoparticles have attracted considerable interest in a bottom-up approach for nanometer-sized devices. They are generally prepared by treatment of gold nanoparticles with inorganic substrates,[7] polymer surfaces,[8] and single atomic monolayers,[9] as examples. However, utility of organic single crystals remains in its infancy.[10] Only recently, Moore and co-workers reported inorganic microcrystals coated with gold nanoparticles developed by crystal-lattice-mediated self-assembly (CLAMS).[11] In this composite material, the whole surfaces were covered by gold nanoparticles as a result of the isotropic nature of the inorganic crystals. Therefore, anisotropic coating of gold nanoparticles onto the selective faces has not yet been reported. Here we demonstrate the first example of a composite crystalline material of organic single crystals with gold nanoparticles and anisotropic face-selective adhesion of gold nanoparticles onto the crystal faces of the organic crystals.

Single-crystal transparent hexagonal prisms of L-cystine (**1**; Figure 1) were immersed in a solution of gold nanoparticles at room temperature by both a batch method and a mounted method. After two hours, the crystals were stained purple although their hexahedral shape remained unchanged. After washing with water, composite crystals of L-cystine decorated with gold nanoparticles were obtained by both methods. Under the microscope, all the surfaces of the crystals appeared slightly rough and a few small hexagonal crystals were deposited on the hexagonal faces. The two hexagonal faces of the hexagonal prism were stained purple and all the six rectangular side surfaces remained colorless. This result was confirmed by the absorption spectra, which were dependent on the crystal surfaces. As shown in Figure 2, the absorption spectrum from the direction perpendicular to the hexagonal face revealed an absorption maximum around 700 nm assignable to the surface plasmon band of the aggregated gold nanoparticles,[12] whereas that from the parallel direction displayed no apparent absorption maximum. The anisotropy of the absorption spectra was attributed to the adhesion of the gold nanoparticles. This result indicates that the gold nanoparticles were deposited selectively on the hexagonal faces of **1**.

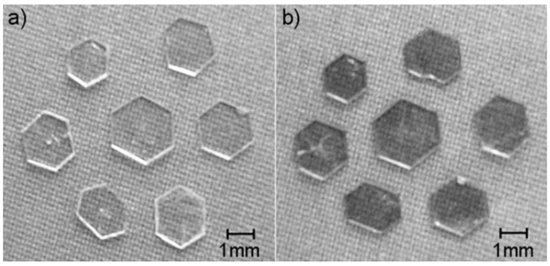

Figure 1. Hexagonal single crystals of L-cystine (**1**) before (a) and after (b) immersion in a solution of gold nanoparticles.

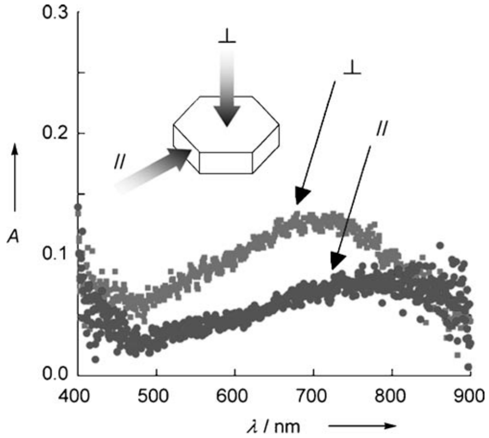

Figure 2. UV/Vis absorption spectra of a single crystal of **1** decorated with gold nanoparticles, showing the absorption perpendicular (⊥) and parallel (∥) to the hexagonal face.

To investigate the face-selective decoration of the gold nanoparticles by electron microscopy, we carried out the decorating experiments on micrometer-sized crystals. The smaller crystals were prepared by a similar method and were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 3 shows the SEM images of the hexagonal micrometer-sized single crystals, which

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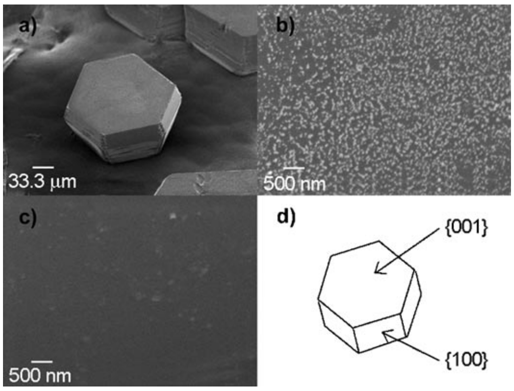

Figure 3. SEM images of a) the hexagonal crystals decorated by gold nanoparticles, b) the {001} face, and c) the {100} face. d) A drawing of the orientation of the crystallographic axes deduced from X-ray crystallographic studies.

revealed well-defined shapes with sharp edges. The crystal faces could be easily assigned by the similar shape of the micrometer-sized crystals to those of the millimeter-sized crystals. Interestingly, deposition of the nanoparticles was observed only on the hexagonal surfaces while the rectangular faces remained smooth. The diameters of the nanoparticles were the same magnitude as those of the added gold nanoparticles. Moreover, the AFM image (Figure 4) of the hexagonal faces illustrated aggregation of the smaller nanoparticles on the hexagonal surface. X-ray photoelectron spectroscopy (XPS) data of the single crystals indicated the presence of Au(4f) on the colored crystals of **1**. These results indicate that the hexagonal faces were selectively decorated with gold nanoparticles. The side rectangular faces were intact even in the solution of gold nanoparticles.

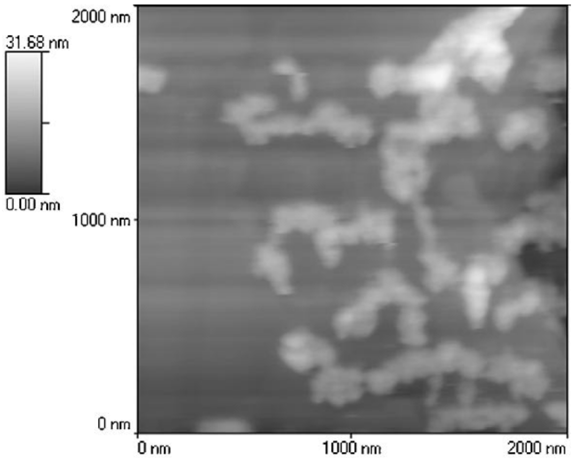

Figure 4. AFM image of the {001} face of the hexagonal crystal decorated by gold nanoparticles.

The cell parameters and the Miller indices of the crystal faces of the hexagonal single crystals were determined by X-ray diffraction studies. The hexagonal crystals revealed the same cell parameters as those of the previously reported example.[13] The hexagonal faces were assigned to the crystallographic {001} or $\{00\bar{1}\}$ faces and the rectangular faces were assigned to {100} and {010} faces, and so on. This result indicates that the gold nanoparticles selectively interacted with the {001} and $\{00\bar{1}\}$ faces. The molecular packing diagrams of **1** are shown in Figure 5.[13] In the crystal structure, the molecules **1** are arranged in layered structures by the two-dimensional hydrogen-bonding network between primary ammonium cations and carboxylate anions. The hydrogen-bonding network runs parallel to the hexagonal faces, and the zwitterionic groups are exposed on the surface of the {001} or $\{00\bar{1}\}$ hexagonal faces. They have the potential to interact with gold nanoparticles by an electrostatic interaction. On the other hand, the rectangular faces are constructed by the alternative stacking of the hydrophobic disulfide layers and the hydrophilic zwitterionic layers, with a periodic distance of about 9 Å. Therefore, the gold nanoparticles were attached selectively on the surfaces of the {001} and $\{00\bar{1}\}$ faces as a result of the higher density of polar residues on the hexagonal faces than on the rectangular ones.

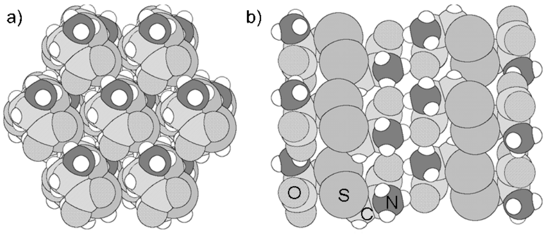

Figure 5. Crystal packing diagram[11] of the hexagonal form of **1**: a) the {001} face viewed from the crystallographic *c* axis and b) the {100} face viewed from the crystallographic *a* axis. H atoms are shown as small white spheres.

In conclusion, we prepared a composite crystalline material containing gold nanoparticles and organic crystals of L-cystine (**1**). The anisotropic decoration that arises as a result of different functional groups on the crystal faces should lead to further decoration of other materials by other intermolecular interactions, which might induce anisotropic aggregation of the single crystals by the attractive or repulsive interaction between the uncoated or coated faces.[3] As the surfaces of organic single crystals should be more varied than those of inorganic ones and partially controllable by recent advances in the crystal engineering of organic molecules,[14] a wide variety of composite materials may be prepared by organic crystals as a nucleus. Moreover, the wide variations in the shapes and sizes of the organic crystals should provide various polyhedral composite materials decorated by nanoparticles.[11] Details of the anisotropic adhesion onto the {001} or $\{00\bar{1}\}$ faces and screening of multicomponent composite materials from organic crystals and nanoparticles are currently under investigation.

Experimental Section

Materials: Single crystals of L-cystine (**1**) were prepared by recrystallization from 0.5% hydrochloric acid solution. Single-crystal transparent hexagonal prisms of **1** were deposited from the solution by cooling to room temperature. The sizes of the single crystals were in the range of a few micrometers to 2 mm in length.

General procedure of the batch method: Several single crystals of **1** were immersed in a solution of gold nanoparticles (1.0 mL, diameter 20 Å; BB International) at room temperature. After immersion for two hours, the crystals were collected by filtration or isolated using forceps and washed with water.

General procedure of the mounted method: A single crystal of **1** was mounted in a glass capillary such that the hexagonal faces were parallel to the side walls of the capillary. Then the capillary containing the mounted crystal was placed in a solution of the gold nanoparticles such that the hexagonal faces were vertical, eliminating the effect of gravity, and immersed for two hours. The mounted crystal was then taken out from the solution and washed with water.

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