Particle−Rod Hybrids: Growth of Arachidic Acid Molecular Rods from Capped Cadmium Selenide Nanoparticles

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Organic−inorganic hybrids form the basis of biomineralization[1] and are attractive materials for electronic, optical, and biosensing applications because they combine and sometimes enhance the functionalities of different material groups. For example, junctions between self-assembled monolayers and metal nanoparticles allow the study of single electron-transfer processes,[2] room-temperature light-emitting diodes (LEDs) are created by the incorporation of a dye molecule within a perovskite framework,[3] and attachment of oligonucleotides to gold nanoparticles triggers the self-assembly of DNA/nanoparticle arrays for biosensing and DNA sequencing.[4] The drive toward device miniaturization demands that functional units such as nanoparticles and nanorods be connected in a predefined manner. Therefore, in addition to the synthesis of nanoparticles[5] and nanorods,[6] an emerging focus is on connecting and assembling the various nano-units. Existing methods deal largely with inorganic materials.[7] This communication describes a spin-coating method to nucleate organic molecular rods of uniform size from an inorganic nanoparticle at a solid surface.

Long chain alkane derivatives, such as arachidic acid (AA), form a 2-D crystalline stripe phase on highly oriented pyrolytic graphite (HOPG).[8] This molecular pattern has been used to control the deposition and aggregation of simple organic molecules and macromolecules[9] as well as the synthesis of metal sulfide molecular rod arrays.[10] In an attempt to immobilize and align nanoparticles on the AA pattern, it is found that the nanoparticles of cadmium selenide capped by mercaptoundecanoic acid (MUA−CdSe) nucleate single crystalline rods of AA with a cross section of a single unit cell.

AFM images of the AA film spin coated from its 2-propanol solution display the stripe phase with a film thickness of 0.4 nm and a bilayer periodicity of 5.6 nm.[10] Spin coating of the MUA−CdSe 2-propanol solution yields only a few particles trapped at the HOPG defect lines. However, when a film is spin coated from a mixed 2-propanol solution of AA and MUA−CdSe, the particle−rod hybrid structure spontaneously forms (Figure 1). The particle heights range from 3.5 to 30 nm. TEM of capped and uncapped CdSe nanoparticles suggests that the small particles are discrete particles, whereas the larger particles are aggregates formed upon MUA photooxidation[11] (Supporting Information). The rods have identical height (0.95 ± 0.09 nm) and width (5.39 ± 0.05 nm) but a wide length distribution (50−250 nm). The number of rods per particle varies with the molar ratio of MUA to CdSe. When MUA/CdSe = 0.38:1, the average number of rods per particle is 1.9 (Figure 1A), while an average of 2.8 rods emanate from each particle when MUA/CdSe = 0.50:1 (Figure 1B). Unlike the AA
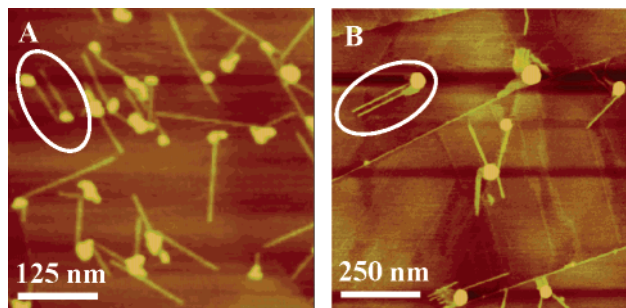
Figure 1. AFM height images of samples spin coated from a 0.1 mM AA, 0.1 mM MUA−CdSe 2-propanol solution on HOPG. (A) MUA/CdSe = 0.38:1, Z-range = 5 nm. (B) MUA/CdSe = 0.50:1, Z-range = 8 nm. Examples of parallel rod pairs are circled in the images.
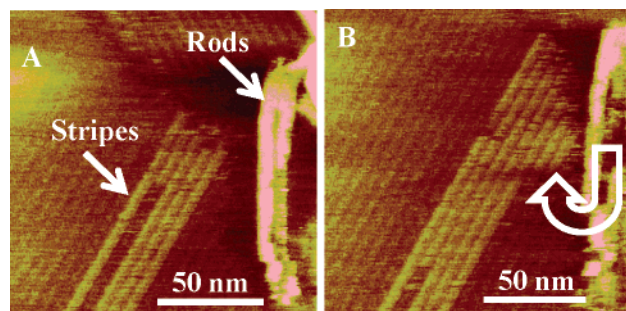

Figure 2. AFM height images of two consecutive scans (A and B) of the same area of a sample spin coated from a 0.1 mM AA and 0.1 mM MUA−CdSe (MUA/CdSe = 0.50:1) 2-propanol solution on HOPG. Z-range = 1.2 nm. In this case, the rod and stripe have a mutual orientation angle of 28°. The nanoparticle connected to the twin rods is to the upper right, just outside the image.

stripe phase, which always exhibits the three-fold symmetry of HOPG, the rods radiating from the particles display random orientations.[10] An analysis of multiple images indicates that a high percentage (∼40%) of rods are parallel to each other with a center-to-center separation of approximately 18 nm. Identical rods can also be induced at the defect sites of HOPG in the same film (Supporting Information), although no such rods are found at similar HOPG defects in the spin-coated film of pure AA.

The particle−rod structure forms on top of the AA stripe phase and not directly on top of HOPG as shown in Figure 2A. Figure 2B shows that some molecules are transferred from the rods to the AA stripe phase on the left by the scanning tip in a subsequent scan of the same area, from which it is concluded that the rods are also made of the AA molecules. The total length of the new stripe portion is 280 nm (two new stripes plus the extension of the existing stripes), and approximately 140 nm of the molecular rod is lost. This suggests that the rod consists of twice the number of AA molecules as the stripe of the same length.
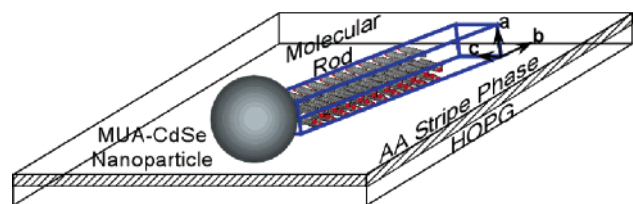
Figure 3. Schematic illustration of the molecular packing structure of the AA rod in relation to the MUA−CdSe nanoparticle and the 2-D solid surface. The stearic acid C-form crystal structure is used instead of AA. The carbon atoms are in gray, and the oxygen atoms are in red. The hydrogen atoms are omitted.

The height and width of the rods are consistent with the unit cell lengths along the *a* and *c* axes, respectively, of the C-form fatty acid crystal structure with four molecules per unit cell.[12,13] The C-form is kinetically favored over the more stable B-form.[14] Thus, the rods are formed by AA unit cells attaching to each other along the *b* direction during crystallization. Figure 3 shows the crystalline packing structure of the molecular rod in relation to the nanoparticle and the solid surface. The alkyl chain zigzag plane is parallel to the particle−rod interface but perpendicular to the substrate, unlike the underlying AA stripe phase, where the alkyl chain zigzag plane is parallel to the HOPG basal plane.[8b] This provides further evidence that the molecular rods are nucleated directly from the nanoparticle and not from the 2-D plane.

Upon solvent evaporation during spin coating, AA precipitates first to self-assemble into the ordered stripe phase due to its low solubility and 1-D epitaxial interaction with the HOPG lattice. The AA monolayer immobilizes the MUA−CdSe nanoparticles, which likely trap a small amount of liquid by defect pinning of the three-phase line during the last stage of solvent evaporation.[15] Upon continued evaporation, heterogeneous nucleation induced by the nanoparticles results in the 1-D growth of the AA crystal. However, it is unclear whether rod formation is due to the presence of a highly curved surface[16] or as a result of the strong undercooling conditions of the spin coating, which also favors unidirectional growth perpendicular to the growing interface.[17] This will be addressed in future experiments by varying the supersaturation or temperature conditions during crystallization. The intermolecular forces between alkyl chains favor the parallel attachment of the zigzag chain plane of AA to the interface.[17b] This communication shows that the nanoparticles serve as nanoseeds in nucleating crystalline rods of AA of the smallest possible size, in which the cross-sectional areas are defined by one unit cell.

The role of the MUA capping agent in particle−rod formation is unclear. Presumably, the intermolecular forces between MUA and the solvent are important for the liquid pinning because without MUA, CdSe nanoparticles are not dispersible and therefore not wettable by the solvent. The mutual interactions between MUA and AA (either hydrogen bonding at their terminal carboxylate groups or nonpolar interactions between the respective alkyl chains) allow the CdSe particles to be immobilized on the substrate and may also be responsible for the heterogeneous nucleation of the AA rods. Indeed, the HOPG defect lines only nucleate AA molecular rods in films prepared from joint MUA−CdSe and AA solutions. Since MUA binds reversibly to the CdSe nanoparticle, it is presumed that some concentration of free MUA is available

in solution, which may subsequently bind to the HOPG surface and nucleate AA rods. Efforts are underway to examine nanoparticles with other capping agents and on solid surfaces other than HOPG.

This communication reports a simple method to nucleate organic crystalline rods from inorganic nanoparticles by spin coating. The solution-based process potentially allows the precise tuning of the wetting profile of the solution on the surface-attached nanoparticle, which provides the reservoir for the growth of the single crystalline rods. The results suggest that nanoparticles can be regarded as nanoseeds for the nucleation of guest crystals. It should be possible to further functionalize the AA rods by electrostatic complexation with metal ions[10] or organic ions.[9] It should also be possible to combine the simple spin-coating method with patterning techniques to make hybrid thin films where various molecular links can be made among ordered nanoparticle arrays.

Supporting Information Available: Experimental procedures and relevant AFM and TEM images (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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