ENGINEERING PARTICLE/ROD NANO-HYBRIDS USING SEED-MEDIATED CRYSTALLIZATION

Guangzhao Mao, **Ruomiao Wang**

Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202, U.S.A.

Introduction

Low-dimensional materials such as quantum dots and nanoparticles (0-D), nanorods, nanowires, nanotubes (1-D), nanoplates, and monolayers (2-D) are of particular interests for both fundamental researches and industrial applications since they are effective building blocks in the construction of nano-devices. Organic-inorganic hybrids and nanocomposites are attractive materials for electronic, optical, and biosensing applications because they combine and enhance the functions belonging to different materials groups. Nano-hybrids have added advantages of high surface to volume ratio and size-dependent properties associated with each functional component. Nature creates organic–inorganic hybrid materials via the biomineralization process, and many research groups have adopted the biomimetic approach for the creation of functional hybrid materials.

Nano-component integration, i.e. the interconnection of different nano-components, is recognized as essential step for the manufacture of nano-devices. Although significant progress has been made with respect to the synthesis and characterization of individual nanocrystals, scalable manufacture of nano-devices remains a major challenge. We pursue nano-component integration by using inorganic nanoparticles as seeds to nucleate and grow organic nanorod crystals from solution. Our previous work has shown that the epitaxial tendency of eicosanoic acid crystallization on graphite is disrupted by the presence of cadmium selenide nanoparticles capped by mercaptoundecanoic acid (MUA-CdSe) and the nanoparticles in turn promote the nucleation of eicosanoic acid nanorods.[1-3] This paper describes seed-mediated nucleation of fatty acid homologous series.

Experimental

Materials

Octadecanoic acid ($C_{18}A$, Fluka, ≥ 99.5%), eicosanoic acid ($C_{20}A$, Sigma, ≥ 99%), docosanoic acid ($C_{22}A$, Aldrich, 99%), tetracosanoic acid ($C_{24}A$, Fluka, ≥ 99.0%), hexacosanoic acid ($C_{26}A$), and triacontanoic acid ($C_{30}A$, Sigma, ≥ 95%) were used as received. Solvents used were methanol (Mallinckrodt Chemicals, 100%), ethanol (Pharmco, 100%), 1-propanol (Fisher Scientific, 100%), and 2-propanol (Mallinckrodt Chemicals, 100%). Highly oriented pyrolytic graphite (HOPG, Mikromasch, ZYB grade) was hand-cleaved just before film preparation with an adhesive tape until a smooth surface was obtained. The synthesis of MUA-CdSe nanoparticles is adapted from Peng et al,[4] and the thiol capping procedure follows a modified procedure in a previous literature.[5]

Film preparation

The freshly made solutions of the fatty acids with concentration range adjusted between 5×10^{-5} and 4×10^{-4} M depending on the solubility were used in spin coating in order to deposit a smooth single layer of the fatty acid on HOPG. 1×10^{-4} L of the solution was used in each spin coating. The spin rate was 3,000 rpm and the spin time was 1 min. To study the effect of nanoparticles on the crystallization of fatty acids, mixed solutions containing both the fatty acid and the nanoparticle were prepared. The nanoparticle concentration in the mixed solution was maintained at 1×10^{-4} M (atomic Cd) while the fatty acid concentration was maintained at $0.5–4 \times 10^{-4}$ M.

Characterization

The spin coated thin film nanostructure was imaged by Dimension 3100 Atomic Force Microscopy (AFM) in the tapping mode in ambient air. The height, amplitude, and phase images were obtained using silicon tapping tips (nanoScience Instruments, VistaProbes T300) with resonance frequency of 300 kHz and tip radius less than 10 nm. Height images were plane-fit in the fast scan direction with no additional filtering operation. The periodic pattern of the fatty acid films was studied by the 2-D fast Fourier transform (2D FFT) command while the dimensions of individual nanoparticles nanorods were analyzed by the sectional height analysis command. (Nanoscope 5.30r3sr3).

In the absence of nanoparticles, the fatty acid homologous series form nano-stripes on HOPG. Figure 1 gives an example of the stripe pattern formed by $C_{20}A$ with a periodicity of 5.6 nm. Fatty acids adsorb on HOPG with their long axis parallel to the graphite surface along the $<11\bar{2}0>$ crystallographic direction to give rise to the stripe pattern. The periodicity increases with increasing fatty acid chain length and is equal to twice the molecular chain length. The only exception is $C_{30}A$, which displays both the double and single molecular chain length patterns.

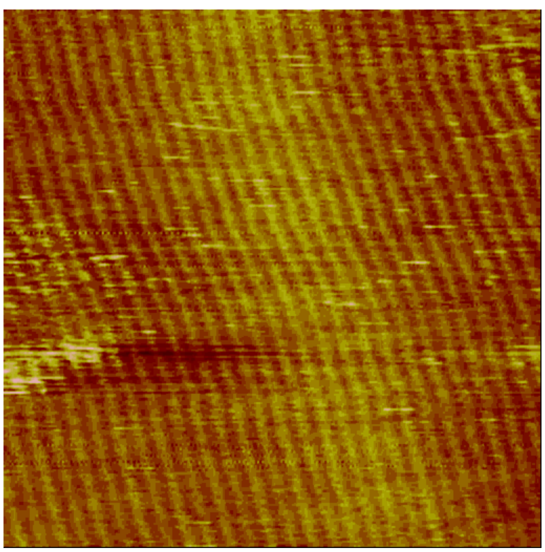

Fig. 1 Nano-stripes formed by spin coating $C_{20}A$ on HOPG. The scan size of the AFM image is 150 nm.

In the presence of MUA-CdSe nanoparticles, the stripe pattern is disturbed. Nanorods attached to nanoparticles were observed in the case of $C_{18}A$, $C_{20}A$, and $C_{22}A$. Figure 2 shows the seed-mediated growth of $C_{20}A$ on MUA-CdSe nanoparticles. On the other hand, MUA-CdSe nanoparticles are ineffective in nucleating nanorods of longer fatty acid chains ($C_{22-30}A$). The stripe pattern is more resistant against nanoparticle disturbance in the case of the longer chains.

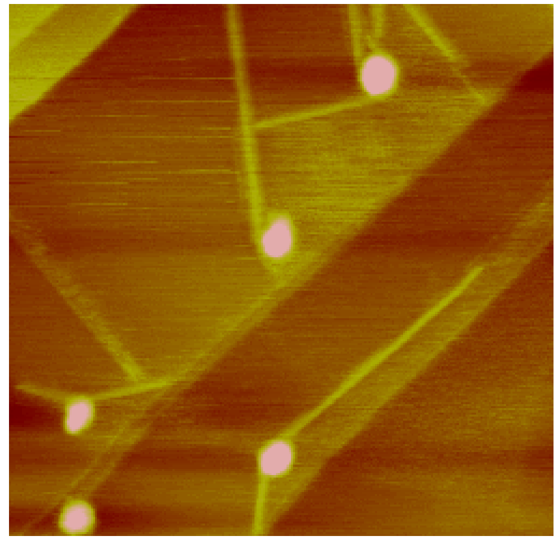

Fig. 2 $C_{20}A$ nanorods nucleated on MUA-CdSe nanoparticles. The scan size of the AFM height image is 500 nm.

Conclusion

Nanoscale hybrid structures containing inorganic nanoparticles and organic crystalline nanorods have been created by the seed-mediated nucleation mechanism. The nucleation capability of nanoparticle seeds decreases with increasing molecular size. The solution-based, room-temperature approach will facilitate divergent combinatorial and scalable chemistry for the construction of branched nano-objects.

References

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