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Template-Directed Synthesis: Oriented CdI_2 Prepared in a Langmuir–Blodgett Film

John K. Pike,[†] Houston Byrd,[†] Augusto A. Morrone,[‡] and
Daniel R. Talham*,[†]

Department of Chemistry and
Major Analytical Instrumentation Center
University of Florida
Gainesville, Florida 32611-2046

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The use of organized organic assemblies to direct the orientation of growing particles has current interest in the study of biomineralization[1–6] and in materials applications.[7–12] We report here the direct synthesis of an oriented inorganic extended solid within a deposited Langmuir–Blodgett (LB) film. Solid CdI_2 has been formed by the reaction of gaseous HI with an LB film of cadmium arachidate. In this preparation, the LB film acts as a template for building the inorganic solid. Electron diffraction shows that the template-formed CdI_2 is oriented exclusively with its [001] axis normal to the LB layers and, for domain sizes ranging up to several micrometers, has a preferred alignment about the [001] axis.

Floating organic monolayer films on water have been shown to induce preferred orientations in crystals grown at the film/water interface.[2–12] Crystallization of organic materials such as glycine[7–9] and inorganic materials such as $BaSO_4$,[3,4] $CaCO_3$,[2,5,6] and PbS[12] at film/water interfaces results in selected crystal morphologies and preferred crystal orientations. In these studies, mediated crystal growth occurs when there is geometric,[2–6,12] stereochemical,[7–9] or electrostatic[10] complementarity between the floating Langmuir monolayer and the nascent crystal.[2–12] Previously, deposited LB films have successfully mediated only the size of inorganic particles.[13–18] Our premise is that if oriented inorganic solids are to be grown in LB films, then the structure of the inorganic solid should complement the layered LB film structure. Cadmium iodide has a layered structure in which the bonding within the anion–metal–anion layer is ionic-covalent, while the anion–anion interaction between layers is Van der Waals in nature and easily cleaved.[19]

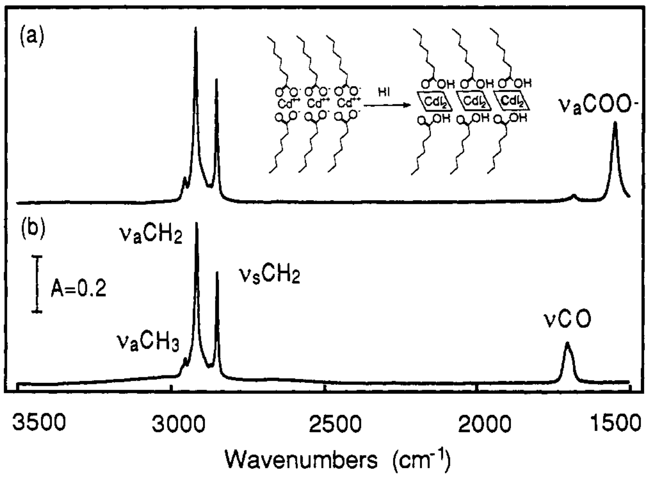

Figure 1. ATR-FTIR spectra of a 20-layer LB film of cadmium arachidate: (a) before and (b) after a 5-min exposure to HI. The cartoon depicts the reaction scheme. In spectrum b, the disappearance of the $\nu_a COO^-$ band indicates that the reaction goes to completion.

Twenty layer cadmium arachidate LB films were deposited[20] from a 20 °C subphase 4 $\times 10^{-4}$ M in Cd^{2+} at a pH of 6.2[21] onto solid supports[22] made hydrophobic by self-assembly[23] of octadecyltrichlorosilane or by LB deposition of arachidic acid ($CH_3(CH_2)_{18}COOH$). Cadmium iodide was formed within the film by first placing the deposited cadmium arachidate LB film into a glass tube sealed with a rubber septum. The 80-mL-volume tube was evacuated and backfilled with dry Ar before 5 mL of gaseous HI was slowly introduced into the sample chamber. After 5 min, the tube was purged with positive pressure of dry Ar. The reaction was followed by attenuated total reflectance FTIR (Figure 1). The $\nu_a COO^-$ band of the cadmium arachidate film appears at 1546 cm^{-1}. Upon exposure to gaseous HI, the $\nu_a COO^-$ band disappears completely and a new band appears at 1701 cm^{-1} due to the C=O stretch of the carboxylic acid, indicating that the HI has completely protonated the LB film. XPS analysis of the HI-exposed cadmium arachidate film shows a Cd:I ratio of 1:2, in agreement with the CdI2 stoichiometry.

Transmission electron microscopy (TEM) and diffraction (TED) analyses were performed on cadmium arachidate, HI-exposed cadmium arachidate, and HI-exposed arachidic acid LB films. Electron micrographs of both cadmium arachidate and HI-exposed arachidic acid films are featureless. TED of the cadmium arachidate LB film reveals the expected in-plane hexagonal symmetry[21,24,25] and a d_{100} spacing of 4.26 ± 0.06 Å. Upon exposure of the cadmium arachidate LB film to HI, bright-field TEM shows the appearance of dark crystallites. The observed particles range in size from tens of nanometers up to a few micrometers across. Some of the smaller particles have a hexagonal shape, while the larger crystallites lack well defined edges. During the TED experiment, the 200-kV electron beam was normal to the film. Bragg spots from both the organic lattice

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* Address correspondence to this author.

[†] Department of Chemistry.

[‡] Major Analytical Instrumentation Center.

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(22) The choice of substrate depends on the analysis to be performed. Substrates used were, for FTIR: 45° 50 × 10 × 3 mm^3 Si ATR crystals (Wilmad Glass Co.). For XPS: 20 × 15 × 1 mm^3 p- and n-type (100) Si (Semiconductor Processing Co.). For TEM/TED: 300 mesh Ti grids (Ted Pella) covered with *ca.* 600-Å Formvar (Aldrich) and 300-Å SiO.

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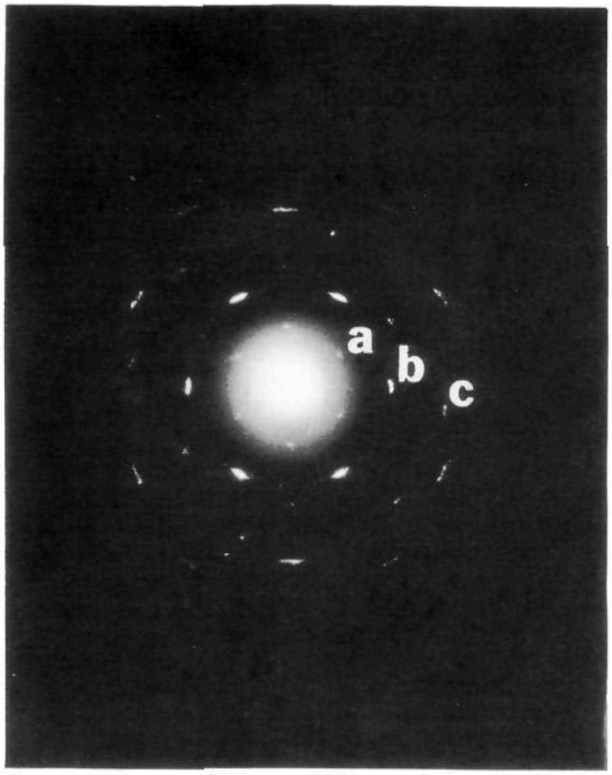

Figure 2. TED pattern of HI-exposed 20-layer cadmium arachidate LB film. The pattern corresponds to the [001] zone axis of CdI_2. Visible are several orders of the (a) {100}, (b) {110}, and (c) {120} reflections. The limiting aperture covers a 2.6-μm area.

and the inorganic lattice are seen. The organic lattice diffraction pattern quickly fades away, while that of the inorganic lattice does not change position or orientation upon extended exposure to the electron beam.[26] Figure 2 shows the TED pattern of a 20-layer cadmium arachidate LB film after exposure to HI. Analysis of the pattern reveals a clear hexagonal symmetry with an angular variance of 8° about the zone axis. Bragg spots corresponding to *d*-spacings of 2.12 ± 0.02 and 3.63 ± 0.06 Å can be assigned to the {110} and {100} reflections of CdI_2.[27] Several orders of each reflection are seen. The observed diffraction corresponds to the [001] zone axis of CdI_2, and we find that throughout the film, the CdI_2 is oriented exclusively with its [001] axis normal to the LB film basal plane. In addition, the absence of polycrystalline rings indicates that domains exist in which the CdI_2 crystallites are oriented within the LB plane. The TED pattern in Figure 2 arises from a 2.6-μm-diameter area, and dark field TEM of the same region shows that several discrete crystallites contribute to this diffraction pattern. The angular deviation of the Bragg spots shows that these CdI_2 particles are rotated by ±4° about the [001] axis. Electron diffraction of the larger, continuous particles (≥0.7 μm) yields single-crystal type diffraction patterns with sharp Bragg spots corresponding to the CdI_2 [001] zone axis. A control experiment on a solution-cast film of cadmium arachidate also produced CdI_2 particles, but no preferential orientation of these particles was observed by electron diffraction.

To account for the observed orientation of the CdI_2 particles, we can consider two mechanisms. First, the cadmium arachidate precursor film organizes the cadmium ions into an arrangement similar to that found in CdI_2 and thereby directs the growth of the inorganic lattice by facilitating diffusion parallel to the LB basal plane and limiting diffusion between planes. Such a mechanism could account for all of the CdI_2 particles growing with their [001] axes perpendicular to the LB plane. However, the observation of domains in which discrete CdI_2 particles have the same in-plane orientation suggests that some degree of lattice matching exists between the LB template and the (001) face of CdI_2 and that this lattice match is responsible for directing the oriented growth of particles. This mechanism is analogous to how oriented particles are thought to grow at solution/monolayer interfaces.[2-12] Using a shorthand based on the Wood[28] notation, a $c(\sqrt{3}/2 \times \sqrt{3}/2)30°$ relation is found for the (001) surfaces of CdI_2 and the cadmium arachidate precursor, where $2a_{\mathrm{CdI_2}} = \sqrt{3}\cdot a_{\text{cadmium arachidate}}$ (a is the unit cell constant of the parent lattice; $a_{\mathrm{CdI_2}} = 4.24$ Å and $a_{\text{cadmium arachidate}} = 4.92$ Å). This superposition of the two surface nets is very nearly commensurate, having only a 0.5% lattice mismatch.

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