Self-Assembling Peptidomimetic Monolayer Nucleates Oriented CdS Nanocrystals

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Appropriate organic matrices can control the size, shape, and morphology of inorganic crystals, leading to functional composite materials. The inorganic crystals composing biominerals are precisely orchestrated[1] by the organic matrix; this kind of control is desired in synthetic composite materials. Recent reports outline the successful syntheses of bio-inspired materials.[2] Herein, we introduce a peptidomimetic matrix that folds and self-assembles into a two-dimensional (2D) β-sheet monolayer at an air−water interface, nucleating the {01.0} face of CdS nanocrystals. The enhanced properties of nanocrystals have led to several reports focused on the control of particle size via organic templates;[2c,3−5] however, none of these involve peptidomimetic monolayers that can be designed and easily synthesized.

Amphiphilic peptidomimetics **A** and **B** (Figure 1) contain a 4-(2′-aminoethyl)-6-dibenzofuranpropanoic acid residue (**1**) which nucleates β-hairpin folding.[6a] These hairpins typically self-assemble into β-sheet fibrils.[6b] Incorporation of hydrophobic α-amino acid residues such as *N*-butyl glutamide at every other position allows peptidomimetics **A** and **B** to dissolve in $CHCl_3$/HFIP and self-assemble into a 2D β-sheet monolayer at an air−water interface, with the hydrophilic side chains projecting into the H_2O.[6c] The hydrophilic surfaces of the amphiphilic peptidomimetic **A** (acidic) and **B** (basic) monolayers differ, allowing an evaluation of the functional group requirements for CdS nanocrystalline growth.

Peptidomimetic monolayers were characterized by a Langmuir−Blodgett trough and spectroscopy (Figure 2).[7] The peptidomimetics appear to fold into a β-hairpin that self-assembles into a stable monolayer on a 10 mM $CdCl_2$ aqueous subphase (265 Å^2/molecule) as discerned from pressure−area isotherms. The FT-IR amide I band at 1620 cm^{-1} and the far-UV CD minimum at 215 nm are characteristics of assembled β-sheet structures.[8]

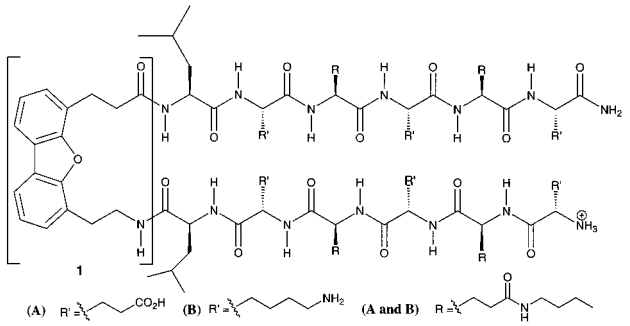

Figure 1. Primary structure of peptidomimetics **A** and **B**.

Transmission electron microscopy (TEM), atomic force microscopy (AFM), and optical spectroscopy revealed differences in CdS crystal size and orientation for crystallites nucleated on peptidomimetic **A**, relative to those formed in solution or on peptidomimetic **B**. Peptidomimetic **A** spontaneously forms a monolayer in a recrystallization dish by self-assembly and nucleates CdS crystal growth, limiting the crystals to ∼25−50 Å in width and length, Figure 3.[9] Electron diffraction studies of the CdS crystallites nucleated on peptidomimetic **A** confirm that they represent the wurtzite lattice structure (Figure 3a), as discerned by the ring patterns corresponding to {10.1}, {10.3}, {20.2}, {20.4}, and {20.5} reflections. All crystallites had their ⟨120⟩ axis normal to the peptidomimetic monolayer, implying that growth occurred from the {01.0} basal plane. HR-TEM studies of the CdS crystallites show patches of lattice fringes that are ∼27−54 Å in diameter (70% in the 36−45 Å range) with an experimental *d* spacing of 3.26 Å, closely representing the *d* spacing of the {10.1} planes in CdS, Figure 3b. The CdS crystals are all oriented roughly in the same direction on the monolayer, strongly suggesting long-range order in the peptidomimetic **A** monolayer. AFM studies demonstrate that the CdS crystals on peptidomimetic **A** are 80 Å in height and small in size (∼25−50 Å), consistent with the TEM data. CdS crystals formed at the air−aqueous interface in the absence of peptidomimetic (up to 2 mm in diameter) or those nucleated with the basic peptidomimetic **B** monolayer (>60 Å in diameter) were heterogeneous in size, nonoriented, and too thick to be analyzed confidently by AFM.

Consideration of the peptidomimetic monolayer organization and the {01.0} plane of the CdS crystals suggests a lattice match and epitaxial growth (Figure 4) that may explain the approximate 27−54 Å size of the nanocrystals. While complete assessment of the packing of the peptidomimetic monolayer is difficult, we have demonstrated that it adopts an intermolecular β-sheet structure at the surface (Figure 2), implying a 4.75 Å average β-strand-strand separation and a 6.9 Å distance separating alternating C_α atoms in each β-strand. A model for our peptido-

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(7) A known concentration of peptidomimetic dissolved in HFIP ($\epsilon = 17797$ L mol^{-1} cm^{-1}, $\lambda = 282$) was used to make a 4×10^{-5} M solution in $CHCl_3$: HFIP (9:1) employed for monolayer formation on an aqueous subphase (1×10^{-2} M $CdCl_2$). Monolayers were transferred to either a CaF_2 or quartz substrate by the vertical lifting technique.

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(9) A 40% excess of peptidomimetic in solution[7] was spread on a clean 1×10^{-2} M $CdCl_2$ subphase to give a coverage of 265 Å^2/molecule (∼200 Å^2 molecule from modeling) in a circular trough. H_2S gas in a 3 cm^3 syringe equipped with a needle was placed above the monolayer to diffuse and initiate mineralization. CdS particles were transferred by the horizontal lifting technique to a carbon coated 200-mesh copper grid (TEM) or a mica substrate (AFM).

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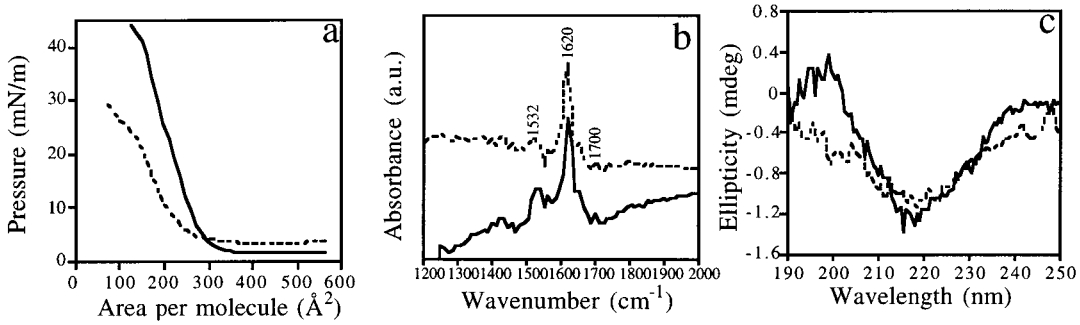

Figure 2. (a) Pressure−area isotherm of peptidomimetics **A** (——) and **B** (- - -) on a 1×10^{-2} M $CdCl_2$ subphase. (b) Transmission FT-IR spectra of peptidomimetic monolayers **A** (——) and **B** (- - -) on CaF_2. (c) Far-UV CD spectra of peptidomimetic monolayers **A** (——) and **B** (- - -) on quartz.

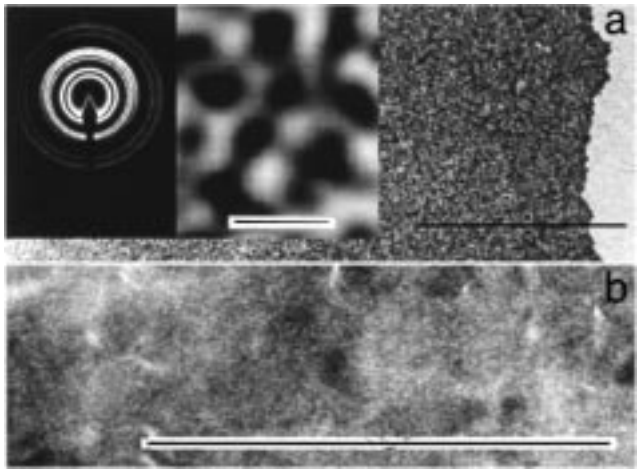

Figure 3. (a) Transmission electron micrograph of CdS nanocrystals on a peptidomimetic **A** monolayer (scale bar is 500 nm). The right inset is a magnified view showing dispersed particles that are largely uniform in diameter (scale bar is 15 nm). The left inset represents the electron diffraction (ED) pattern of CdS particle on monolayer **A**. (b) High-resolution TEM image of the nucleated CdS nanocrystal showing the lattice fringes (scale bar is 40 nm).

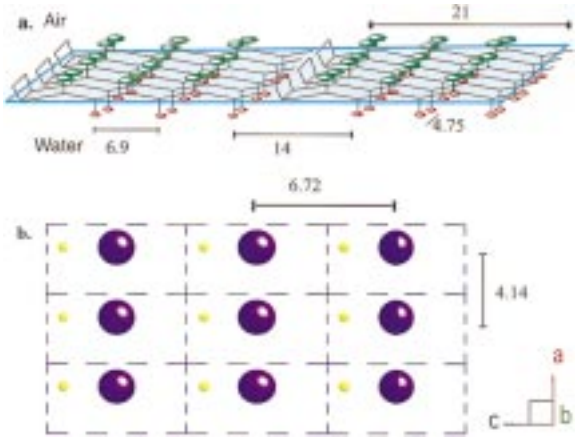

Figure 4. (a) Model of the 2D β-sheet assembly of peptidomimetic **A** or **B** at the air−water interface. Hydrophilic groups (Glu or Lys) are represented in red, hydrophobic groups in green. The rectangles represent residue **1**, and the zigzag lines in black denote the polypeptide backbone. β-Sheet formation is stabilized both by intra- and intermolecular hydrogen bonding, whereas, the head-to-tail assembly is presumably mediated by van der Waals forces. The β-strand separation and the alternating $C_\alpha-C_\alpha$ distances are indicated. (b) The cadmium cation (purple) and sulfur anion (yellow) arrangements in the {01.0} plane of CdS (sizes not to scale) in the wurtzite structure.

mimetic is shown in Figure 4a, representing a side view where the hydrophilic (e.g., Glu) and hydrophobic side chains are shown in red and green, respectively. For the {01.0} nucleation face (Figure 4b) there is a good match between the Cd−Cd distance of 6.72 Å in the ⟨001⟩ direction and the glutamic acid $C_\alpha-C_\alpha$ atom separation distance of 6.9 Å (∼3% mismatch) within a single β-strand. An explanation for the size control observed in the ⟨001⟩ (c) direction comes from the 14 Å separation between the proximal glutamic acid residues on successive head-to-tail assembled peptidomimetic molecules (Figure 4a). A 14 Å separation is much greater than the 6.72 Å separation required for lattice match; hence, crystal growth in the ⟨001⟩ direction appears to be controlled by strand length. The Cd layers in the "b" direction are staggered by 3.36 Å; hence, the projection of the crystal in the ⟨001⟩ direction is ∼20 Å in length, the minimum crystal length observed by TEM.

Lattice match in the ⟨100⟩ CdS (a) direction is less optimal with a 4.14 Å Cd−Cd distance and a 4.75 Å β-strand−strand separation (∼13% mismatch). Preliminary modeling studies suggest that conformational freedom within the monolayer allows the side chains on at least three and possibly as many as five neighboring β-strands to move close enough to accommodate the 4.14 Å Cd−Cd separation. However, beyond five strands (20 Å), epitaxial growth seems unlikely, whereas it is conceivable that electrostatic interactions between the peripheral carboxylates could stabilize the addition of a few layers of Cd ions to the crystal along the ⟨100⟩ direction, yielding the larger crystals observed (∼50 Å). This may also be the means by which crystals elongate in the *c* dimension.

Blue shifts in the UV−vis absorption threshold indicate a decrease in CdS particle size (increased band gap), resulting from the quantum size effect.[10] The absorption threshold for CdS particles nucleated on peptidomimetic (**A**) is 495 nm (2.5 eV band gap vs 2.4 for bulk CdS), whereas CdS particles nucleated on peptidomimetic **B** and CdS crystals grown on an aqueous surface exhibit edge transitions at 530 and 510 nm, consistent with their larger sizes.

In summary, an easily synthesized peptidomimetic assembles into a 2D monolayer at an air−water interface and nucleates the formation of CdS nanocrystallites via the {01.0}face. The degree of lattice matching appears to play a major role in controlling the face nucleated and the crystallite size.

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Supporting Information Available: UV spectra, AFM image, and bar graph of CdS particle size distribution on peptidomimetic **A** by HR-TEM (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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