

Progress Report for SI-785: Oriented nucleation of CdS and PbS nanoparticles at conjugated polymer interfaces

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We hereby report the current status of an ongoing project for which initial results have been collected on a previous experimental session (17/2 to 24/2/02).

The purpose of the project was to gain control over the crystallization of semiconductor nanoparticles on the air-solution interface under a crystalline polymer monolayer. Grazing incidence diffraction from the monolayer and the incipient crystallites elucidate the cooperative structural adaptation of the combined system during nucleation and crystallization.

We use polymerizable long-chain acids with diacetylene functionality as a precursor for the monolayer. The compound, 10,12-pentacosadiynoic acid (C-25) is spread on a Langmuir trough from chloroform solution on pure water, compressed and UV polymerized ($\lambda=254\text{nm}$). The formed monolayer is a linear polyconjugated molecule (polydiacetylene, PDA), made of rigid chains that are organized in parallel in 2-D crystalline domains that are 2-50 μm in size. This crystalline surface has been shown to be an effective template for crystallization of calcite (CaCO_3)¹ and cadmium sulfide (CdS)². In a typical experiment, the water subphase is slowly replaced by dilute CdCl_2 , and then a small amount of H_2S is infused into the gas-tight chamber in which the trough is situated. In a series of experiments that are reported here, grazing incidence diffraction data were collected in real-time from the PDA films on water, after subphase substitution and after the CdS crystallites have formed at the polymer interface following exposure to hydrogen sulfide.

At least 8 major reflections were observed from the films ranging from $d=3.0\text{\AA}$ to $d=7.9\text{\AA}$.

Table 1: Summary of the main observed reflections

Refl #	2θ	γ	d_{xy}	q_{xy}	q_z	$Q_{(total)}$	D (\AA)	Comments
1	18	16.8	4.966	1.265	1.182	1.731	3.630	High γ angle reflection on water and low Cd conc.
2	19.7	0	4.541	1.383	0	1.383	4.543	
3	20.5	0	4.366	1.439	0	1.439	4.368	} Close reflections.
4	22.5	2.5	3.982	1.577	0.165	1.583	3.968	
4a	22.8	0	3.930	1.598	0	1.598	3.932	
5	19.9	9.5	4.495	1.396	0.670	1.549	4.055	High γ angle refl. of high Cd conc. Instead of #2 (split peaks)
6				0.84	1.9	2.077	3.024	Very high γ angle of high Cd conc. Instead of refl. #1 (sharp double arc)
7				1.46	1.17	1.871	3.358	Discrete reflection from $(00.2)_{\text{CdS}}$
8	11	2.5	8.105	0.774	0.176	0.794	7.906	First order of refl. #4 (?) (on Si substrate)

The reflection data indicate that the PDA structures on water subphase is similar to that on low concentration of CdCl_2 (0.5mM and 1 mM) and the films do not undergo significant structural changes when water is replaced with CdCl_2 solution.

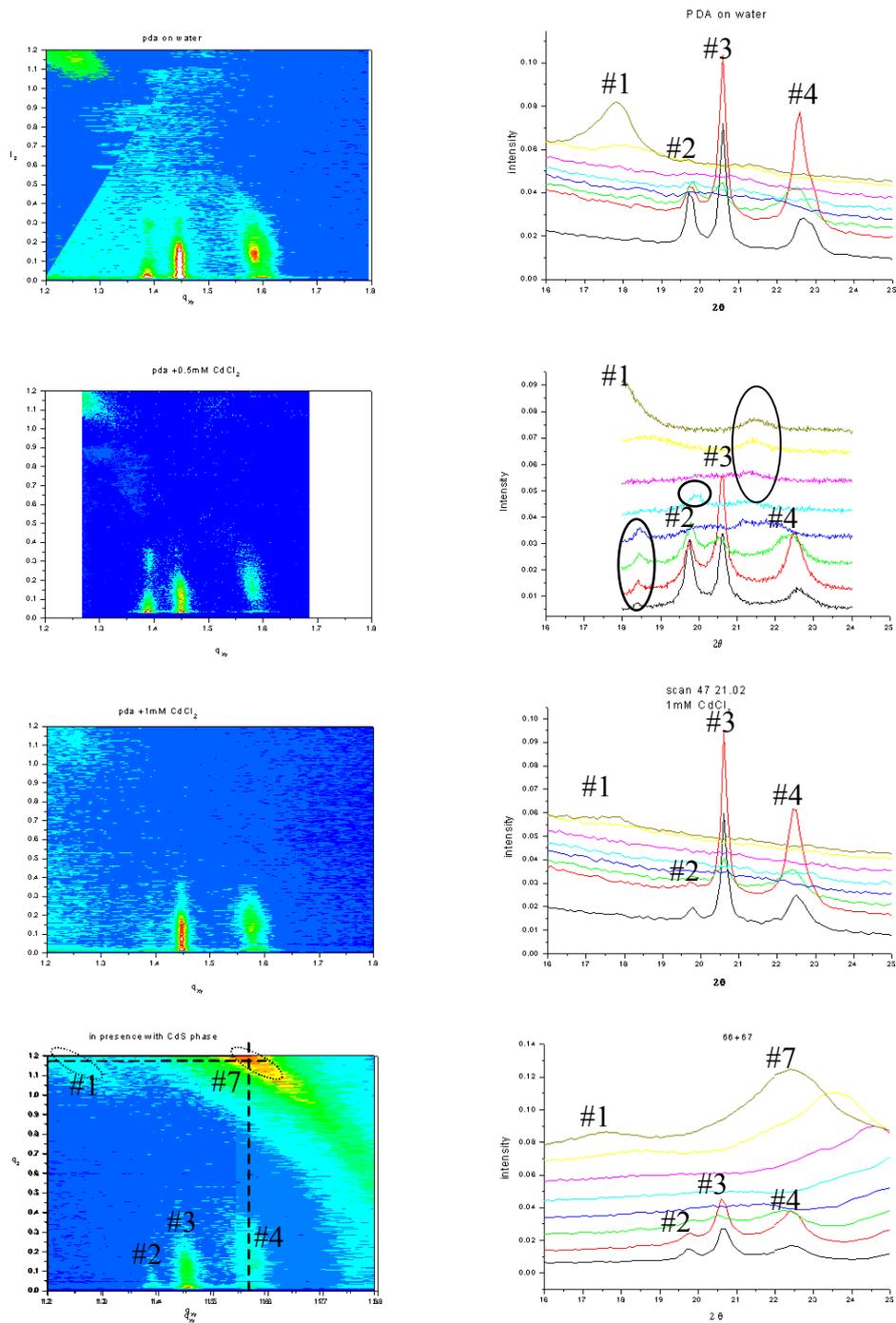


Figure 1: Diffraction maps (left) and sequences of diffraction traces each integrated over 100 channels of detector's PSD (right) of the GIXD data collected from PDA film on water (A), 0.5 mM (B) and 1.0 mM CdCl₂ solutions. (C); GIXD diffraction from the PDA film after deposition of CdS (D). The reflections are numbered as in table 1. For the most part, these reflections appear in all these diffractograms, with the exception of 3 additional reflections in (B). In (D) reflection #7 is $\langle 00.2 \rangle_{\text{CdS}}$. Its projections on the q_{xy} and q_z axes coincides with reflections from PDA, implying a mechanism for the observed uniform alignment.

However, subphase concentration of 2.4 mM CdCl_2 does indeed affect the PDA structure and significant shifts in several reflection positions are observed. These include the disappearance of the high q_z reflection (refl. #1) and its possible reappearance at even higher vertical angle as a narrow double arc (refl. #6). Also, one of the characteristic reflections at $2\text{-theta}=19.8$ degrees (refl #2), probably has shifted to higher q_z value and split into at least 3 sharp reflections. (refl.#5). Reflections #3 and #4 remained unchanged. This suggests that the PDA film on high cadmium subphase concentration (2.4mM) becomes more crystalline and dense with some inclined planes (figure2).

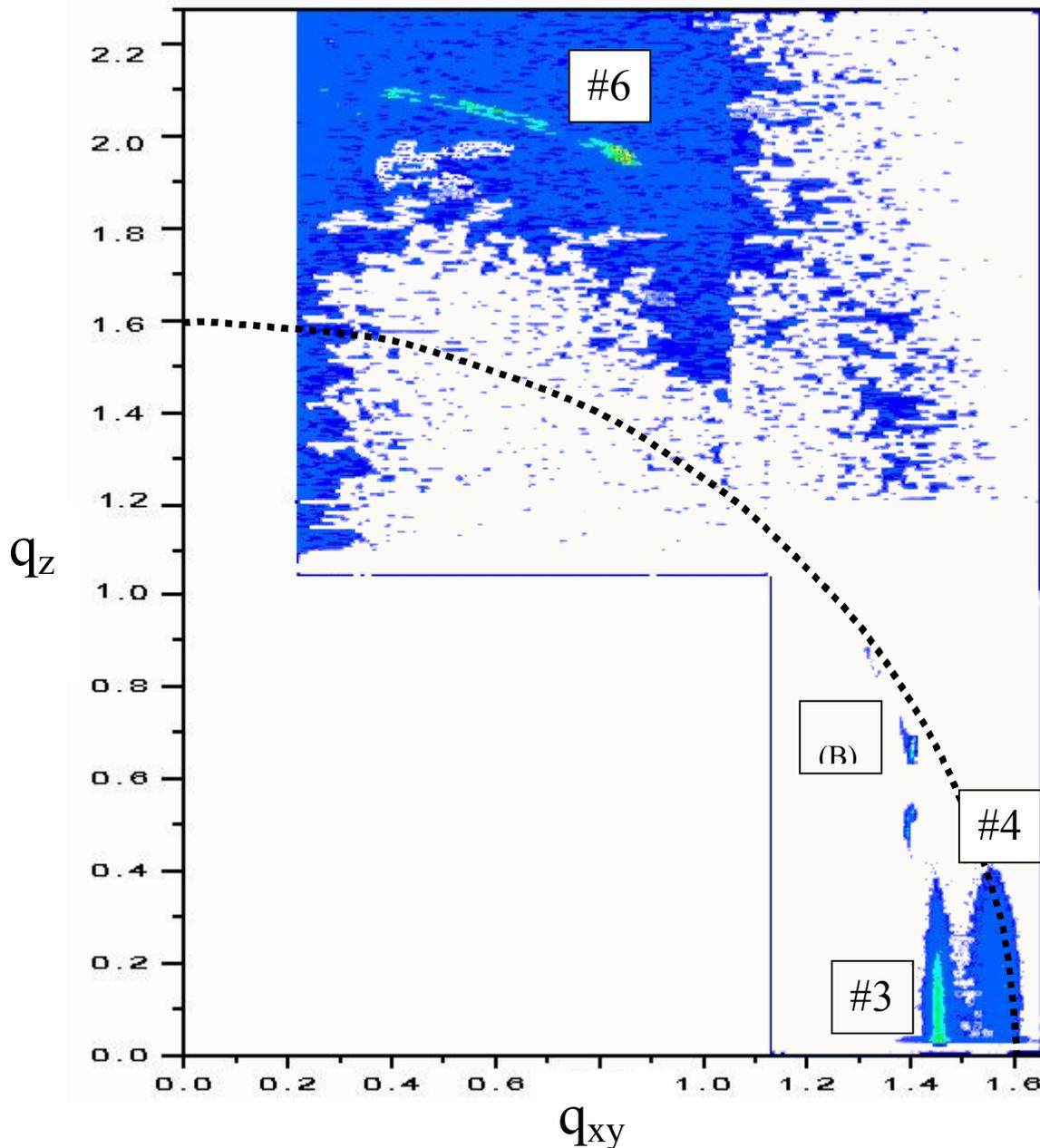


Figure 2: Combined GIXD diffractogram of low and high g scans of PDA film on 2.4 mM CdCl_2 subphase. The film was compressed and polymerized on water and subphase was replaced. The dashed arc follows $q_{\text{total}}=1.6$ and is an aid to the eye.

The main differences between PDA films on water and on dilute cadmium subphase ($C \leq 1.0 \text{ mM Cd}^{++}$) are manifested in variations in the reflections relative intensity, which suggest minor film reconstructions. A possible small, gradual shift in peak #4 position suggest a gradual change in the film, although more measurements are required in order to allow for a more conclusive description of this important feature.

Diffraction data that was collected after exposure of the PDA film to H_2S , and precipitation of CdS crystallites indicate that the crystallization is indeed oriented. The CdS structure is identified as hexagonal (wurtzite) structure by comparison the *jcpds* database. It is observed that most of the reflections from the mineral do not indicate particular orientation and appear as uniform intensity arcs (rings). However, the $(00.2)_{\text{CdS}}$ ($d=3.36 \text{ \AA}$) reflection (#7) is restricted with narrow spread at $q_z=1.1-1.2$ ($\gamma=16^\circ \pm 1^\circ$); $q_{xy}=1.55 \pm 0.1$. The projections of this reflection on the q_{xy} and q_z axes nearly coincide with two PDA reflections: #4 and #1, respectively. (figure 3)

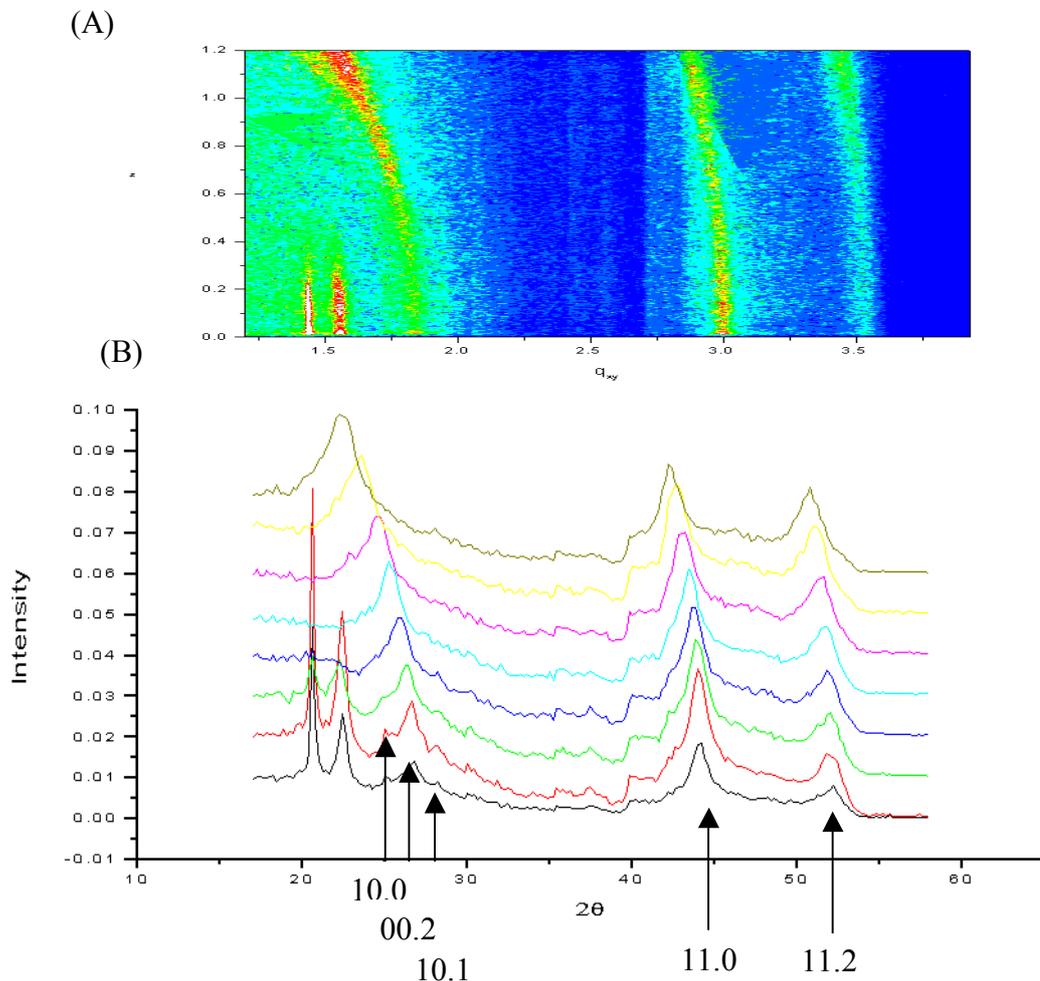


Figure 3: GIXD diffractogram from PDA film after CdS deposition. Reflections from the film and the crystallites are depicted. Note the intense (00.2) basal plane reflection at $q_z=1.15$, in comparison to the uniform ring structure of the other CdS reflections. (A) Diffraction map. (B) Diffraction traces integrated over 100 channels of the PSD. Miller indices for the wurtzite (hexagonal) structure are indicated.

It appears that the alignment of CdS crystallites on PDA film originates from the good match between the two structures as follows. The $(00.2)_{\text{CdS}}$ planes are inclined with respect to the PDA plane at about 16° , a similar inclination as one of the PDA off-axis planes. Moreover, the projection of these planes on the interface plane nearly coincides with the spacing of a second PDA reflection. These prominent structural features are likely to induce the CdS orientation on the PDA templates.

It is hypothesized that the manner by which the alignment of CdS crystallites on PDA interface takes place involve these two effects. It is not clear at this stage if the combined effect is a requirement for this effect to occur, and it is a coincidence that is unique for the PDA/CdS system, or only one of the matches between these heterostructures is sufficient for such a unique alignment to take place.

This understanding of the way in which the two different structures are co-aligned is corroborated with different observations. Electron diffraction study indicated uniaxial orientation of the CdS crystallites on PDA substrate, with the $\text{CdS}_{(220)}$ aligned perpendicular to the polymer chain direction. The second observation is the morphological evidence from AFM indicating uniform elongated crystal habit ($l=50\text{-}75\text{nm}$; $w=20\text{-}30\text{nm}$ $h= 2\text{-}5 \text{ nm}$) and coalignment at a nearly fixed angle of $45^\circ \pm 3^\circ$ between the crystallite long direction and the polymer chain (figure 4)

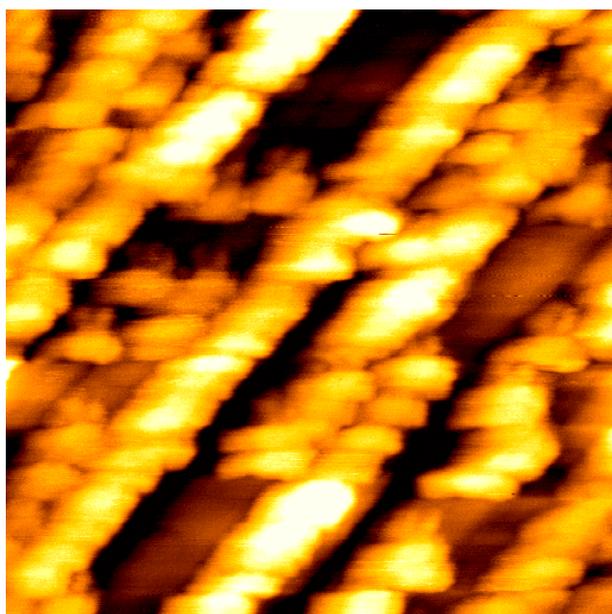


Figure 4: AFM micrograph depicting the coalignment of the spindle-like CdS crystallites diagonally with respect to the PDA template.

In order to better understand the combined mechanism of epitaxy at the organic-inorganic interfaces, we hereby propose to carry out further experiments which should allow us to separate the effects of tilt and mismatch are required.

In this proposal, we request for beam time on Troika beamline 10B in order to continue this exciting project in two directions: (i) obtain better crystallographic data of the PDA film in order to assign indices to the collected reflections. This will allow establishing the correspondence with specific directions in the PDA film. (ii) We will attempt to address the hypothesis presented before, namely that two independent conditions are required for the alignment to take place: inclination of a prominent set

of planes in the monolayer; and (partial) lattice match between periodicity on the PDA film and the projection of a certain crystallographic direction onto the film plane. We will address this question by replacing the cadmium ions with ions of different atomic and ionic radii. Preliminary experiments in which the Cd^{2+} were replaced by Pb^{2+} cations in the very same system showed that much larger PbS crystallites were obtained which maintained the same uniaxial orientation of $\langle 110 \rangle_{\text{PbS}}$ parallel to the linear direction of the polymer support (figure 5). This is most probably due to the less efficient packing of the PDA film in presence of the significantly larger Pb^{2+} ions.

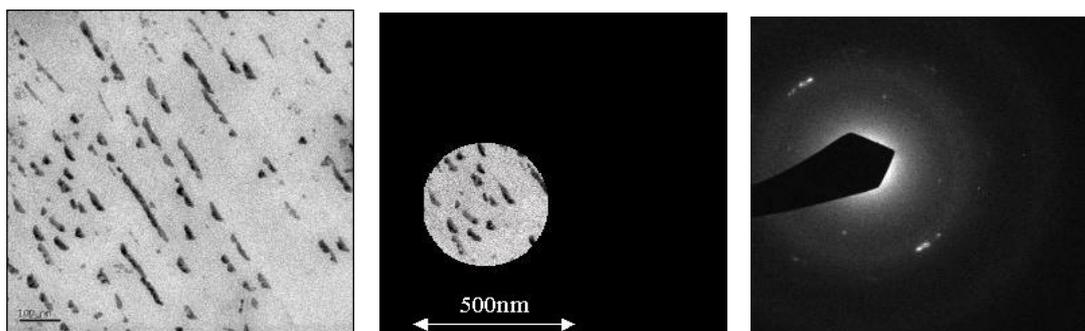


Figure 5: PbS crystallites grown in situ on PDA film at the air-solution interface. This set of TEM micrograph and selected area electron diffraction demonstrate the uniform crystallographic alignment of the triangular shaped crystallites with respect to the PDA. The crystals are nucleated along the polymer with 220 planes perpendicular to the polymer chains. The middle image represents the size of the area selected for diffraction. It is important to note that while the electron diffraction pattern on the left shows the lone uniaxial alignment mentioned above, other patterns showed correspondence to well-defined CdS zone axes such as e.g. $\langle 111 \rangle$ and $\langle 112 \rangle$ which conform to the uniaxial alignment restriction described above.

In the next experimental stage we will attempt to tailor specific features, like the orientation of PbS crystallites on Cd-PDA substrate, as a demonstration of the possibility to manipulate particle orientation and size by the control of the PDA packing in the presence on Cd^{2+} or other ions. The experimental scheme will be first to form the PDA film on water, followed by subphase replacement with cadmium ions and then by lead ions. The final step will be the deposition of PbS. Diffraction data will be collected at every step in order to monitor the structural evolution of the film and the crystallographic orientation of the incipient crystallites.

References

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