	Experiment title: GIXD of Ordered Nanoparticle Arrays at the Air-Water Interface	**Experiment number**: SI-1157
Beamline: ID-10B	**Date of experiment**: From: 09/03/2005 to: 15/03/2005	**Date of report**: 18/10/2005
Shifts: 18	**Local contact(s):** Dr. Oleg Konovalov	***Received at ESRF:***
Applicants *Y. Golan, S. Efrima, Ben-Gurion U., Israel, J. Israelachvili, UCSB. Also participated in the experiment: *N. Belman, *S. Acharya, Ben-Gurion U., Israel.		

The aim of this experiment was to study the structural parameters of ordered arrays of uniform and monodispersed zinc sulfide (ZnS) nanorods in 2D Langmuir films. The nanorods were capped with octadecylamine (ODA) or tetradecylamine (TDA) surfactants with different lengths of carbon chains: C_{18} and C_{14}, respectively. ZnS nanorods dissolved in chloroform were spread on the water surface on a Langmuir trough and compressed to a close-packed structure. Grazing incidence small-angle x-ray scattering (GI-SAXS) measurements were performed directly at the air-water interface at different surface pressures.

From the diffraction intensity map of q_z vs. q_{xy} obtained in a GI-SAXS experiment from ZnS nanorods capped with ODA at the air-water interface at a temperature of 5ºC at zero pressure (open barriers) two fairly weak peaks at q_z=0 can be seen at Figure 1a.

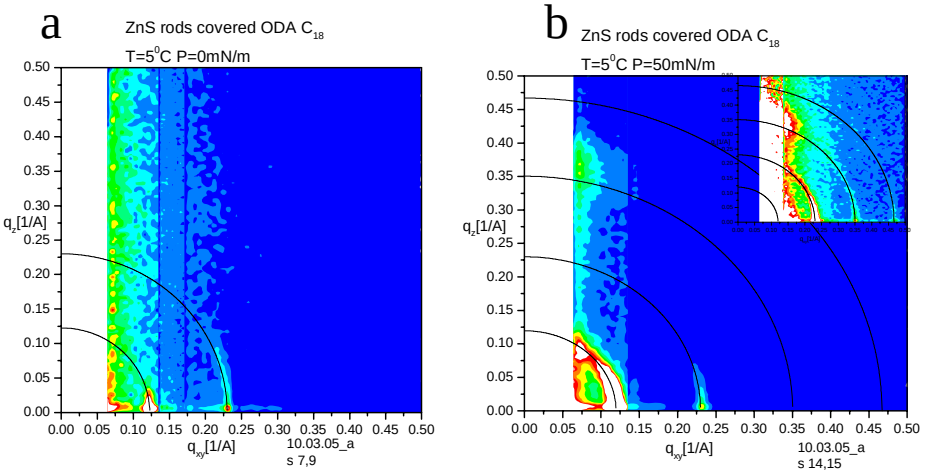

Figure 1: GI-SAXS intensity maps of q_z vs. q_{xy} obtained from ZnS nanorods capped with ODA at the air-water interface at a temperature of 5ºC (a) zero pressure and (b) compressed to P=50mN/m.

This important result indicates that the nanorods form ordered 2D islands at the air-water interface even before any compression takes place. When the nanoparticle film was compressed to a pressure of 50mN/m, the diffraction intensity map shown in Figure 1b was obtained with four peaks at q_z=0. The third and the fourth peaks can be seen in the inset in Figure 1b, in which the brightness was adjusted and optimized. Table 1 summarizes the data in real and reciprocal space. The increase in diffraction intensity and in diffraction order obtained confirmed the monodispersity of the nanoparticles and (as expected) indicates that more ordered islands are present under the beam footprint at P=50mN/m.

ZnS rods covered ODA C_{18}		q_z=0			
		q_{xy1}	q_{xy2}	q_{xy3}	q_{xy4}
P=0mN/m	q[1/A]	0.196-0.123	0.230	-	-
	d[A]	51.23-52.548	27.30	-	-
P=50mN/m	q[1/A]	0.120	0.230	0.350	0.467
	d[A]	52.54	27.31	17.93	13.45

Table 1: Summary of GI-SAXS diffraction data from the four peaks obtained from ZnS nanorods capped with ODA at the air-water interface, at zero pressure and when compressed to P=50mN/m.

The GI-SAXS intensity map of q_z vs. q_{xy} from ZnS nanorods capped with TDA (C_{14}, shorter hydrocarbon chain length) at the air-water interface, at a temperature of 5ºC at zero pressure is shown in Figure 2a. The nanoparticle film was compressed to a pressure of 50mN/m and the GI-SAXS map in Figure 2b was obtained with three peaks at q_z=0. The third peak can be seen in the inset in Figure 2b. Table 2 summarizes this data.

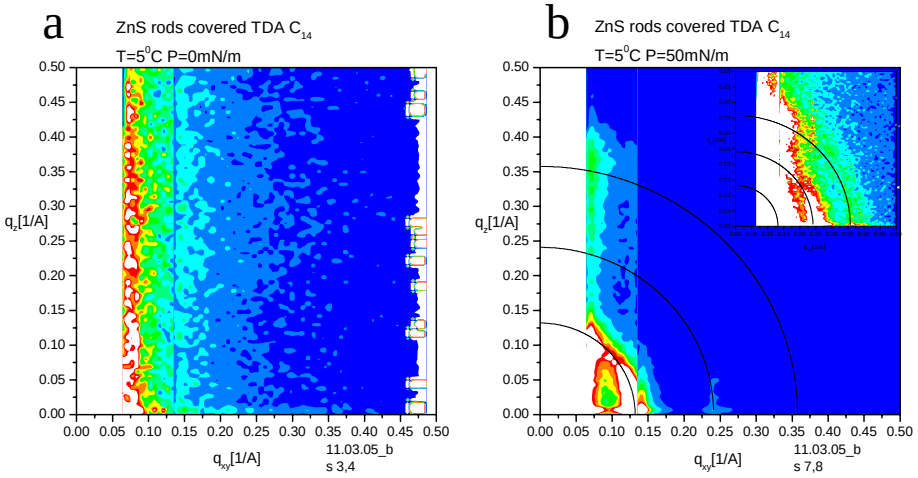

Figure 2: Diffraction intensity maps of q_z vs. q_{xy} obtained in a GI-SAXS experiment from ZnS nanorods capped with TDA at the air-water interface, at the temperature of 5ºC (a) zero pressure and (b) compressed to P=50mN/m.

ZnS rods covered TDA C_{14}		q_z=0		
		q_{xy1}	q_{xy2}	q_{xy3}
P=0mN/m	q[1/A]	-	-	-
	d[A]	-	-	-
P=50mN/m	q[1/A]	0.1319	0.241	0.358
	d[A]	47.64	26.07	17.55

Table 2: Summary of GI-SAXS diffraction data from the three peaks obtained from ZnS nanorods capped with TDA at air-water interface, at zero pressure and when compressed to P=50mN/m.

It can be clearly seen that at zero pressure ZnS nanorods coated with TDA are not structured (there are no peaks in Figure 2a), while at the same pressure ODA coated rods (shown in Figure 1a) have fairly strong peaks. Also at high pressure in the case of ODA (Figure 1b) the peaks are much sharper and stronger than for TDA-coated nanorods (Figure 2b). In both cases, the peaks become stronger at higher pressures because of the greater amount of material present in the beam footprint. The TDA (C_{14}) –coated samples are confirmed to be less uniform compared to the ODA samples, as has been established by TEM imaging we have carried out in-house at BGU (unpublished).

The distances between the nanorods are summarized in Tables 1,2. The data indicates that a smaller spacing is obtained between ODA-covered ZnS nanorods due to their shorter carbon chains. Hence, this demonstrates that the inter-rod spacing in the nanorod superlattices can be continuously tuned simply by using different hydrocarbon chain lengths.

It should be noted that the samples were extremely stable under the beam and the GI-SAXS intensity maps did not change upon multiple scans. Another important note concerns the ZnS mineral peaks that were searched for at higher angles with appropriate experimental setup, yet were not observed. This can be accounted for due to the extremely thin ZnS core that was only 1.5 nm in diameter.