

- **Synopsis of Research – Prof. Golan's Nanomaterials Research Group**

Aim of Research:

*The aim of our research is to identify and to understand the chemical and physical interactions and interfacial processes that govern the formation of thin films and two- and three- dimensional assemblies of ordered nanoparticle systems. This includes the direct deposition of semiconductor thin films on single crystal substrates and on ultrathin (Langmuir) organic film templates, as well as surfactant controlled chemical deposition of nanoparticles of different shape and composition onto solid supports (from solution or from the air-water interface using the Langmuir Blodgett technique) for forming ordered super-crystalline films (see Y.J. Min, M. Akbulut, K. Kristiansen, Y. Golan, J. Israelachvili, "Role of Interparticle and External Forces in Nanoparticle Assembly", *Nature Materials* 7 (2008) 527).*

Characterization techniques include advanced electron microscopy, electron and x-ray diffraction techniques, plus a variety of optical techniques (photo- and cathodoluminescence, optical absorbance, multiple beam interferometry). Surface force measurements (friction and adhesion) are performed in collaboration with Prof. J. Israelachvili at UCSB. We use various synchrotron radiation techniques for structural characterization, including grazing incidence x-ray diffraction (GIXD), grazing incidence small angle scattering (GI-SAXS) and X-ray absorption spectroscopies (EXAFS and XANES).

Short description of major research projects:

1. Ordered 2D and 3D arrays of surfactant coated nanowires and nanorods [Students: Alexander Rabkin, Alexander Pekin]. Funding: ISF

Uniform nanoparticles of ZnS, ZnSe, PbS and CdS are synthesized by thermal decomposition of single precursor xanthate salts in molten alkylamine surfactant. The nanoparticles are studied under confinement in 2D (Langmuir trough) and in 3D using a surface forces apparatus (SFA). The conditions (and subsequent surfactant-semiconductor interactions) for shape (sphere, rod and wire), size and crystallographic phase -controlled nanoparticle formation are studied. In particular, we study the ordering of monodisperse nanoparticles into super-crystalline arrays with emphasis on the role of the structure of the surfactant (primary amines such as octadecylamine, ODA). The structure and orientation of the superstructures are studied and correlated with the polarization dependent optical properties. A large number of experimental techniques are used, including TEM, π -A isotherms, DSC, TGA, optical absorbance and emission (PL) measurements, in-house powder and thin film XRD (including temperature resolved XRD), synchrotron GIXD, GI-SAXS and EXAFS (ESRF), ^{67}Zn and ^{13}C SS-NMR and SFA. Figures 1(a,b) respectively show TEM and HRTEM images of arrays of ODA-coated ZnS nanorods. The nanoparticles self-assemble into a layered superstructure with a super-crystalline order which is directly templated by the surfactant: the *hierarchical structure* starts from the wurtzite structure of the ZnS mineral cores (Fig. 1c), follows to the 2D in-plane structure of the surfactant molecules adsorbed onto the ZnS facets, then to the resulting composite bilayer/nanorod structures (Fig. 1d) packed in sheets that are stacked in a smectic-like structure (ms. submitted). A major breakthrough in this project was made when we showed that spontaneous reaction of ODA with ambient CO_2 and reversible formation of octadecylammonium-octadecylcarbamate (OAO) molecular pairs strongly affects the resulting nanoparticles and explains severe irreproducibility problems encountered by many groups working in this field (N. Belman, J.N. Israelachvili, Y. Li, C.R. Safinia, J. Bernstein and Y. Golan, "Reaction of Alkylamine Surfactants with Carbon Dioxide: Relevance to Nanocrystal Synthesis" *Nano Lett.* 9 (2009) 2088). Furthermore, this allowed us to isolate the pure phases of ODA and OAO and to determine their temperature-dependent phase behavior. For the first time, the structures of the

alkylamines and their corresponding alkylammonium-alkylcarbamates were determined and reported in detail for chain lengths of C14, C16 and C18, as summarized in Table 1 below. The directional thermal expansion of alkylammonium-alkylcarbamates was determined from temperature resolved powder X-ray diffraction (*N. Belman, J.N. Israelachvili, Y. Li, C.R. Safinia, J. Bernstein and Y. Golan, "The Temperature-Dependent Structure of Alkylamines and their corresponding Alkylammonium-Alkylcarbamates" J. Amer. Chem. Soc. 131 (2009) 9107*). More recent work highlighted the formation of highly oriented arrays of nano-PbS on well-defined sheets of alkylamine surfactant bilayers (*A. Rabkin, N. Belman, J.N. Israelachvili and Y. Golan, "Directed Co-Assembly of Oriented PbS Nanoparticles and Monocrystalline Sheets of Alkylamine Surfactant", Langmuir 28 (2012) 15119*).

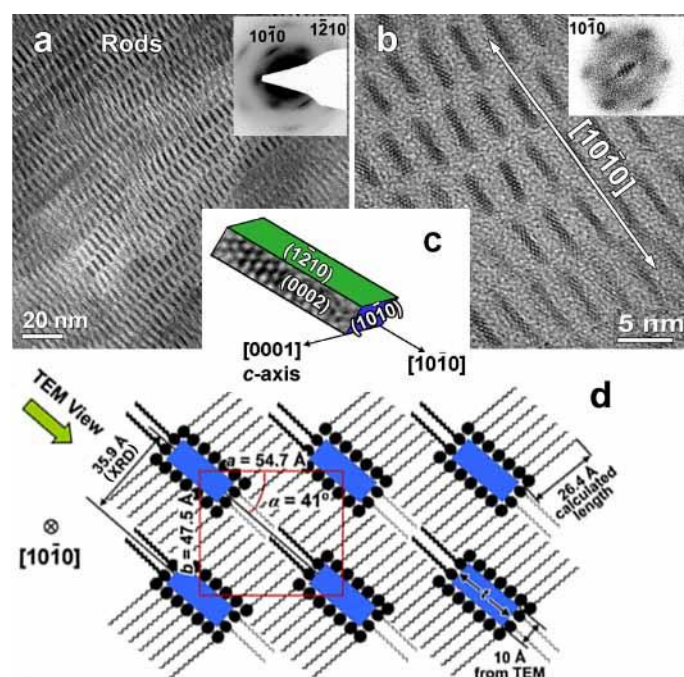


Figure 1: (a) TEM image showing an array of ultranarrow ZnS nanorods coated with octadecylamine surfactant molecules (Inset: corresponding electron diffraction pattern). (b) HRTEM lattice image and corresponding FFT pattern. (c) Results of crystallographic analysis showing the planes and directions of the wurtzite structure of the rods. (d) Packing model based on powder XRD, TEM, GIXD and GISAXS analyses. The rods are viewed edge-on from the $[10.0]$ direction, while the green arrow denotes the top view direction as viewed by TEM.

Table 1. Orthorhombic unit cell dimensions for the pure alkylamines and for the room temperature and high temperature phases of alkylammonium - alkylcarbamates derived from temperature-resolved powder XRD measurements.

	alkylamine (AA)			alkylammonium-alkylcarbamate (AAAC) room temperature (RT)			AAAC high temperature (HT)		
	a [Å]	b [Å]	c [Å]	a [Å]	b [Å]	c [Å]	a [Å]	b [Å]	c [Å]
C14	5.60	7.35	36.03	7.75	9.66	42.06	6.46	8.85	39.38
C16	5.60	7.35	40.53	7.75	9.66	47.17	6.46	8.85	44.23
C18	5.60	7.35	45.16	7.75	9.66	52.31	6.46	8.85	48.75

2. Chemical solution deposition of thin semiconductor films with controlled morphologies – fundamental studies and applications [Researchers and Students: Dr Sucheta Sengupta, Tsofnat Ganigar-Safrani, Moshiel Biton, Keren Petel, Zvi Templeman]. Funding: FTA, Vatav.

Chemical solution deposition is employed for obtaining high quality nanocrystalline PbSe thin films on GaAs and Si with a wide range of microstructures *from nanocrystalline to monocrystalline films*. The optical, electrical and interfacial properties of these films are studied in detail. More recently, this technique has been extended for growth of PbS films. Notably, monocrystalline films of PbSe and PbS with a well-defined orientation relationship with the substrate were successfully deposited using this technique, as demonstrated in Fig. 2.

These films were recently shown to exhibit prominent multiple exciton generation (MEG) both for PbSe and for PbS. Interestingly, the MEG behavior in our chemically deposited materials was not limited only to nanocrystalline films but rather observed also in monocrystalline films [J.J.H. Pijpers, R. Ulbricht, K.J. Tielrooij, A. Osherov, Y. Golan, C. Delerue, G. Allan and M. Bonn,

“Assessment of Carrier Multiplication efficiency in bulk PbSe and PbS”, *Nature Physics* **5** (2009) 811].

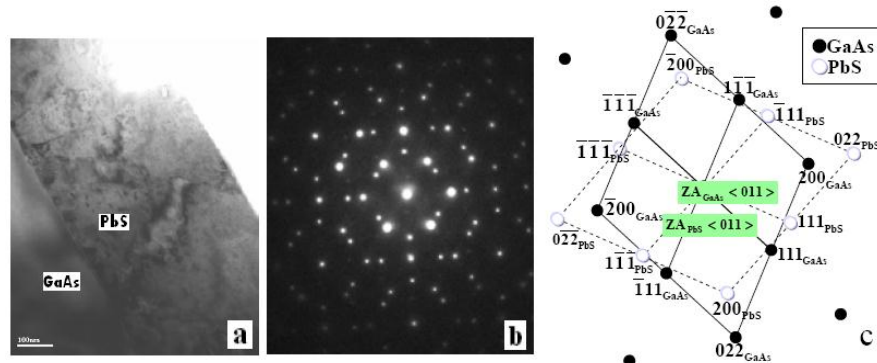


Figure 2. ‘Chemical epitaxy’ of PbS on GaAs. (a,b) Cross-sectional TEM and electron diffraction of a chemically deposited monocrystalline film. (c) Indexing of the diffraction pattern, indicating a well-defined (100)GaAs|| (011) PbS ; $[011]$ GaAs|| $[0-11]$ PbS orientation relationship. We have recently published a comprehensive review on Chemical Epitaxy of Semiconductor Thin Films: A. Osherov and Y. Golan, “Epitaxial Chemical Bath Deposition”, *MRS Bulletin* **35** (2010) 790.

Hybrid photonic crystals composed of chemically deposited semiconductor nanocrystals within micropatterned Si matrices are being fabricated in collaboration with Prof. Amir Sa’ar at the Hebrew University. We have demonstrated resonative emission in these hybrid materials, in which the emission wavelength of the chemically deposited nanoparticles is tuned to match the periodic structure of the photonic crystal (Figure 3). Tuning of the emission wavelength of the nanoparticles is achieved in various ways, including control over particle size (quantum size effects), the composition of the nanoparticles (notably solid solutions), surface treatments and temperature-dependent emission experiments at cryostatic conditions.

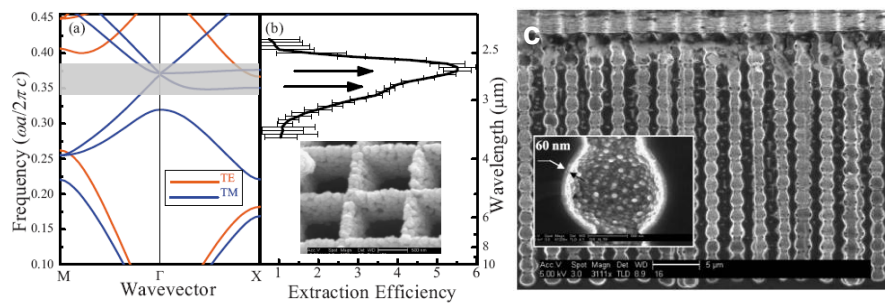


Figure 3: (a) The calculated photonic band structure and (b) the measured extraction efficiency for the 2D composite PC (top view SEM image of the composite PC is shown in the inset). Blue lines are related to TM modes while red lines are related to TE modes. The shaded area in (a) indicates the frequency range of slow-light modes and their correlation with the extraction peaks, marked by arrows in (b). (c) SEM cross-section view of a 3D macroporous silicon composite PC. The inset shows a magnified image of a PC unit cell with a thin film of chemically deposited spherical PbS nanocrystals, about 60 nm in thickness and covering the pore walls. (*Appl. Phys. Lett.* **93** (2008) 073111).

3. Semiconductor nanocrystals on polydiacetylene Langmuir film templates [Student: Alexander Upcher; project in collaboration with A. Berman and N.G. Lemcoff, BGU] Currently funded by Mafat (Israeli Defense Grant) and ARO.

Recent progress has been made in the elucidation of the structure of the different phases (crystalline monomer phase, blue phase, red phase) of polydiacetylene Langmuir films using *in-situ* synchrotron grazing angle x-ray diffraction (GIXD) and *ex-situ* TEM. Current research is underway in order to take advantage of the progress gained in the above-mentioned studies in order to fabricate combinatorial chemical/optical sensors by using *tailor-designed* modified Langmuir film templates. We also study the use of well-defined polydiacetylene films as templates for oriented nucleation of semiconductor nanocrystals such as CdS, ZnS, PbS and evaluation of the optical and electrical characteristics of these novel organic-inorganic hybrid materials.