An Essay of Taleb's Mokari Ph.D thesis

In my thesis, we succeed to develop new composite of nanocrystals with semiconductor–semiconductor, semiconductor-insulator and semiconductor-metal interfaces in the same particles.

Formation of semiconductor- semiconductor interface *(Chemistry of Materials 2003)*[1]

A method for the synthesis of CdSe/ZnS core/shell nanorods is reported. In the first step rods are grown, and in a second step a shell of ZnS is overgrown at moderate temperatures in a mixture of trioctylphosphine-oxide and hexadecylamine. Structural and chemical characterization using transmission electron microscopy, X-ray diffraction, and energy dispersive X-ray spectroscopy were performed providing direct evidence for shell growth. The emission quantum yield significantly increases by over 1 order of magnitude for the core/shell nanorods compared to the original rods because of the improved surface passivation. Rods with lengths up to 30 nm were investigated, and in this size regime the maximal achievable QY showed little dependence on length and strong dependence on rod diameter, with increased QY in smaller diameters. Color tunability is available via tuning of the rod diameter. The stability against photooxidation was significantly improved in core/shell nanorods compared with rods coated by organic ligands. This work was published in ***Chemistry of Materials 2004***.

Formation of semiconductor- insulator interface *(chemistry of Materials (2005)*[2]

A general method for entrapment of hydrophobically coated nanocrystals in micrometer and submicrometer composite silica spheres, nano@micro, was developed. The method employs two starting solutionsshydrophobic solvent containing the sol-gel precursor, a polymer, and the nanocrystals, and an emulsifying hydrophilic phase which catalyzes the sol-gel process. The use of a hydrophobic polymer, polystyrene, serves to encapsulate the nanocrystals inside the spheres while maintaining many of their original properties. The obtained nano@micro spheres were characterized structurally by transmission electron microscopy and scanning electron microscopy, chemically by energy dispersive X-ray spectroscopy, and optically by ensemble and single-particle fluorescence spectroscopy. It is possible to control the size of the microspheres from the 100 nm scale to the micrometer scale, with good monodispersivity and with good separation between the microspheres. The method is demonstrated for encapsulating a wide variety of Nanocrystals, primarily semiconductors covering different spectral bands, and of different shapes including spheres and rods. The semiconductor nanocrystals impart widely tunable emission to the microspheres. A similar encapsulation technique was also applied to thiol-coated Au particles. The technique is generally applicable to other hydrophobic nanocrystal systems of magnetic, oxide, and other materials. (please see our paper in ***Chemistry of Materials 2005.***

Formation of Semiconductor- Metal interface[3,4,5,6]

1) Formation of symmetric Semiconductor-Metals Hetrostructure (*Science 2004*)

We show the anisotropic selective growth of gold tips onto semiconductor (CdSe) nanorods and tetrapods, there results were reported in ***Science 2004***. The size of the gold tips can be controlled by the concentration of the starting materials. The new nanostructures display modified optical properties caused by the strong coupling between the gold and semiconductor parts. The gold tips show increased conductivity as well as selective chemical affinity for forming self assembled chains of rods. Such gold-tipped nanostructures provide natural contact points for self-assembly and for electrical devices and can solve the difficult problem of contacting colloidal nanorods and Tetrapods to the external world. We prepared CdSe rods and tetrapods of different dimensions by high-temperature pyrolysis of suitable precursors in a coordinating solvent containing a mixture of trioctylphosphineoxide and phosphonic acids. We dissolved AuCl3 in toluene with the addition of dodecyldimethylammonium bromide (DDAB) and dodecylamine. For growth of Au tips, we mixed this solution at room temperature with a toluene solution of the colloidalgrown CdSe nanorods or tetrapods. After the reaction, the quantum rods were precipitated by addition of methanol and separated by centrifugation. The purified product could then be redissolved in toluene for further study.

We studied the interface between the semiconductor and the metals using Scanning Tunneling Microscopy (STM). The results show a coupling between the two materials and evolution from semiconductor to metal as the tip scans from the middle of the rod (CdSe body) to the edge (gold tip), these results were published in Physical Review Letter 2005[7]

2) Formation of Asymmetric Semiconductor-Metals Hetrostructure (*Nature Materials 2005)*

A challenging problem is the formation and control of asymmetric metal–semiconductor heterostructures. In this work *(Nature Materials 2006)* we focus on the detailed understanding of the growth process leading to the formation of symmetric or asymmetric heterostructures. Surprisingly, we find that one-sided growth of a gold tip on a semiconductor quantum dot or rod is preceded by two-sided growth. Experimental analysis and theoretical modeling show that a ripening process drives gold from one end to the other, transforming the NDBs to NBTs. Ripening is therefore occurring effectively on the nanostructure itself, leading to a phase-segregated structure and thus extending the realm of ripening phenomena and their importance in nanostructures.

3) Diffusion of gold in InAs nanocrystals *(Angew. Chemi. Int. Ed. 2006)*

Trying to expand our procedure to other semiconductor materials reveals a completely different behavior. We try to grow gold on InAs nanocrystals with different shapes. In this case, Au diffuses into the InAs particles leading to a Au core coated by an amorphous shell. This behavior is in contrast with that observed for the reaction of Au with CdSe nanoparticles where gold grows in patches on the surface (or on the apexes of rods), and at high concentrations transforms to one patch (or one side for rods) through a ripening process.

To conclude, we succeed to develop new nano hetrostructures with different interfaces and composition. Three interfaces were obtained including Semiconductor-Semiconductor, Semiconductor-Insulator and semiconductor-Metal interface. All the results published on the top journal including, Science, Nature material, Chemistry materials, Angew Chemi, Int. Ed., PRL and other highly cited journals.

An enormous of works was done based on my new materials including optical, spectroscopy and physical characterization. In each one of these works I was involved and take an essential part. We succeed to publish up to 30 papers in different fields and also in highly cited journals.

References

1. Mokari, T.; Banin, U. ***Chem. Mater***. **2003**, 15, 3955

2. Mokari, T., Sertchook, H.; Aharoni, A.; Avnir, D.; Banin, U. ***Chem. Mater. 2005***, 17, 251

3. Mokari, T.; Rothenberg, E.; Popov, I.; Costi, T.; Banin, U. ***Science*** **2004**, 304, 1787.

4. Mokari, T, Sztrum, C. G.; Salant, A.; Rabani E.; Banin U. ***Nature Materials, 2005*** 4, 855

5. Mokari**,** T.; Aharoni, A.; Popov, I.; and Banin U. .***Angew. Chemi. Int. Ed***. **2006**, 45, 8001

6. Mokari, T. R. Costi., Sztrum, C. Rabani, E, Banin, U. ***phys. stat. sol. (b), 2006*** 1–7.

7. Stienr, D.; Mokari, T.; Banin, U.; Millo, O. ***Phys. Rev. Lett.*** **2005,** 95, 056805,