

Opto-electronic properties of hybrid inorganic/organic systems: Challenges for first-principles theories

Prof. Dr. Claudia Ambrosch-Draxl
Humboldt-Universität zu Berlin, Institut für Physik

Despite weak intermolecular bonding and molecule-substrate interaction, the opto-electronic properties of organic/inorganic hybrid systems crucially depend on alignment, conformation, and packing of the molecules as well as on details of the substrate. For example, surface corrugations and order/disorder affect the orientation of molecules within a monolayer or thin film. This, in turn, is correlated with charge transfer, band alignment at the interface, and electronic transport. The orientation together with the anisotropic nature of the molecules then determines whether the material efficiently emits visible light. The packing, finally, governs the electron-hole interaction in excitation processes. All this is scientifically puzzling, but also decisive for the function of devices.

Insight from a theoretical viewpoint is a must for deeper understanding. Density-functional theory, although tremendously successful for describing the properties of many materials, can badly fail here as non-local exchange and/or correlation effects are essential at all levels: in the bonding in terms of van der Waals interactions, in the electronic structure in terms of level alignment and band gaps, and in the optical spectra in terms of exciton formation. New concepts need to be developed incorporating these many-body effects. Computational feasibility of the most sophisticated methods is another issue. Organic semiconductors are certainly a challenge from both perspectives.

Selected examples will illustrate what we can learn from first-principles studies about inorganic/organic interfaces. I will address molecular alignment, film morphology, and molecule-substrate interaction and their role in the opto-electronic properties.

Controlling the energy levels at organic/inorganic semiconductor heterojunctions with molecular interlayers

Prof. Dr. Norbert Koch
Humboldt-Universität zu Berlin, Institut für Physik

Raphael Schlesinger¹, Stefanie Winkler², Johannes Frisch¹, Jens Niederhausen¹, Antje Vollmer², Yong Xu³, Patrick Rinke³, Sylke Blumstengel¹,
Fritz Henneberger¹, Matthias Scheffler³, Norbert Koch¹

¹ Humboldt-Universität zu Berlin, Institut für Physik, 12489 Berlin, Germany

² Helmholtz-Zentrum Berlin - BESSY II, 12489 Berlin, Germany

³ Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany

Combining conjugated organic with inorganic semiconductors opens up new possibilities of optoelectronic device function and efficiency by utilizing the advantages of each material's class. Being able to control the alignment of the frontier energy levels of hybrid inorganic/organic systems is essential to control their function, e.g., to achieve energy or charge transfer across the interface. Employing molecular acceptor interlayers to tune the work function of a metal and thus the energy level alignment between the metal Fermi-level and the energy levels of organic semiconductors is already established.

We now extend this concept for surfaces of ZnO by using the strong molecular acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), as evidenced by photoelectron spectroscopy and theoretical modeling. The work function of bare Zn-terminated surfaces, which were found to be predominantly hydrogen terminated in ultrahigh vacuum, was typically 3.6 eV. One monolayer (ML) of F4TCNQ on the ZnO surfaces induced a considerable work function increase by up to 1.5 eV for ZnO(000-1) and 3 eV for ZnO(0001). In contrast to the inorganic-to-organic electron transfer found for F4TCNQ on metal surfaces, density functional theory modeling suggests a different mechanism to explain the work function increase when ZnO is the inorganic component. An intramolecular charge rearrangement of F4TCNQ is suggested to give rise to the work function increase instead. The energy level alignment of organic semiconductors adsorbed on top of acceptor-modified ZnO is shown to be controlled *via* the induced work function changes.