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Charge extraction from colloidal inorganic nanocrystals

Szendrei, Krisztina

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Summary

Currently, silicon and other highly crystalline semiconductors surmount today's information technology and photovoltaic industry. These semiconductors are generally epitaxially grown or thermally evaporated on rigid substrates resulting in high production costs. Therefore, a considerable amount of research has been done on finding solution processable materials, since they could provide compatibility with flexible substrates in combination with low temperature processing and reduced manufacturing costs. There has been significant progress in using solution processable organic semiconductors, since they could fulfill these requirements. On the other hand, their application is mostly limited to wavelengths shorter than $1\mu\text{m}$ due to the lack of infrared energy capture.

Semiconductor nanocrystals (NCs), also called quantum dots, can overcome this limitation. Thanks to the quantum confinement, their broad absorption and narrow emission are tunable over a wide wavelength range from the ultraviolet to the near-infrared depending on the size and chemical composition. The discovery of NCs can be dated back to almost 30 years ago. Since then, NC synthesis research has remarkably improved, allowing for precise control over the chemical composition, size, shape and surface properties today. For most of the applications the key issue is to control the surface chemistry of the NCs, since they are generally synthesized with an organic molecular shell around them. The role of this molecular shell is twofold: i) to provide good solubility and colloidal stability and ii) to passivate surface dangling bonds to prevent nonradiative recombinations at surface sites. The major drawback is that these molecules are electrical insulators. Therefore modifying the surrounding medium of the NCs is unavoidable for electronic applications. Several strategies have so far been presented to obtain charge extraction from the NCs, including integrating semiconducting NCs with insulating ligands into semiconducting polymer-based matrices and attachment of electroactive end-functionalized polymers or small molecules.

In this thesis, we introduce some of the alternative routes to facilitate charge extraction from PbS NCs and their application in hybrid photodetectors and inorganic solar cells.

Efficient and stable photoconducting materials with sensitivity in a broad spectral range are indispensable for both PD and solar cell applications. Organic/inorganic hybrid systems composed of colloidal NCs and fullerene derivatives are excellent candidates for both applications due to their improved stability in ambient conditions, the possibility of an extremely broad and tunable spectral response and cheap processing method. Chapter 2 focuses on the fabrication and study of organic/inorganic PDs composed of [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) and PbS NCs. The morphology of the active layer is characterized by different microscopy techniques. Efficient photoinduced

electron transfer from the NCs to the fullerenes is evidenced by time resolved photoluminescence spectroscopy on thin films as a proof of the efficient NC sensitization. The devices show a responsivity of up to 0.32 AW^{-1} and a detectivity of 2.5×10^{10} Jones at 1200 nm, which is comparable to that of commercial PDs.

In chapter 3 we present an alternative way for surface modification of PbS and CdSe NCs in solution. The chapter is devoted to investigate the successful binding of a fullerene derivative, namely 3,4-dihexyloxyphenyl- C_{61} -butyric-acid (dPCBA) to PbS and CdSe nanocrystals. This molecule is an excellent candidate to serve as electroactive ligand for NCs, since it has similar structure and properties to its famous sibling PCBM (phenyl- C_{61} -butyric-acid-methyl-ester), which is widely used as electron acceptor in bulk heterojunction photovoltaic devices. Via ligand design, the electronic properties can be tuned with direct effects on the conduction and optical activity of the NC thin films. The surface modification phenomenon was followed by steady-state and time-resolved photoluminescence (PL) experiments, since the PL quenching can serve as good indicator for NC-ligand interaction. The dramatic PL quenching in the case of both NCs indicates the effective coordination of dPCBA to the NC surface. The electrically active nature of the new complexes is proven by current-voltage (*IV*) measurements on thin films of the NC-dPCBA complexes. The comparison of the relative energy levels of the conduction and valence bands of the NCs and the HOMO-LUMO (highest occupied-lowest unoccupied molecular orbital, respectively) levels of dPCBA provides more information to understand the quenching mechanism and supports the idea of photoinduced carrier transfer from NCs to dPCBA molecules.

Photovoltaic devices based on solution-processable colloidal inorganic nanocrystals (NCs) have recently received increasing attention thanks to the unique optical and electrical properties of the NCs. Until now, the presence of the insulating molecular shell around the NCs was considered to be the major drawback preventing their use in electronics and optoelectronics. Recently, several methods have been developed to replace long insulating molecules such as oleic acid (OA) by shorter and conductive ligands such as ethanedithiol (EDT) or benzenedithiol (BDT) after thin film deposition. These methods are based on layer-by-layer (LBL) post deposition ligand exchange, which can reduce inter-particle spacing and increase the electronic coupling between NCs. The post deposition ligand exchange method enabled the fabrication of more conductive films and their utilization as active layer in optoelectronic devices. In chapter 4, we report on the fabrication of efficient PbS solar cells, showing PCEs approaching 4%. The effect of 2 different NCs' size on the performance and key parameters of the devices are discussed together with peculiar features of the device functioning. The successful ligand exchange is evidenced by Fourier Transform Infrared Spectroscopy (FTIR). Besides the standard characterization of the devices, a simple physical model is used to get deeper insights in the working mechanism and limiting factors of our

solar cells. The results prove that the devices are not under space charge limitation, since the photocurrent depends linearly on the light intensity. In addition, we show that the device performance is influenced by charge trapping and the degree of this effect depends on the size of the NCs.

Finally, chapter 5 explores the origin of temperature dependence of electrical and optical properties of NC thin films. We demonstrate that the overall effect of the temperature on the device efficiency originates from the temperature dependence of V_{oc} and J_{sc} while the FF remains approximately constant. The optical properties of PbS thin films before and after benzenedithiol (BDT) treatment exhibit very distinct behavior. Both the optical density (OD) and PL are red-shifted after the ligand exchange and additional red-shift occurs, when the temperature is reduced from 293K. The temperature variation of the energy gap can be explained by considering the unique thermal expansion of the NCs' bandgap with temperature. In addition, the PL spectra of BDT treated PbS NCs becomes much more complex: the PL is quenched and extra emission peaks appear at lower temperatures. The quenching indicates the presence of nonradiative pathways at lower temperatures which can be ascribed to defect states emerging due to surface modification. Moreover, Gaussian analysis suggests the appearance of intrinsic and surface related defect states which could serve as radiative and nonradiative channels for recombination of the charge carriers.

Consequently, the electronic applications of NCs strongly depend on the nature of the surface ligands and the interaction between the NCs and the ligands. Therefore, significant effort is required to design novel ligand molecules enabling charge transport between adjacent NCs without introducing surface dangling bonds and trap states. It is quite unlikely that NCs would gain ground on crystalline semiconductors in the near future; however, they might compete with organic electronics and amorphous silicon.