PbS nanocrystal based photovoltaics for infrared imaging and solar cells

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The size-tunable band gap energies of PbS nanocrystals corresponding to wavelengths between 900 nm and 2000 nm can be ideally matched to the optimum band gap energies proposed for single- and multi junction solar cells with maximized sun harvesting properties. Furthermore, the high photosensitivity of PbS nanocrystal films with manipulated ligand shells has been demonstrated by Sargents group, reporting record detectivity of photoconducting devices operating at room temperatureⁱ. While for photoconducting devices it is sufficient to achieve carrier mobility for one carrier type, photovoltaic devices require after photoexcitation and charge separation a balanced transport of electrons and holes, making the development of photodiodes more demanding than those of purely photoconductors. In organic bulk heterojunction solar cells the desired ambipolar transport is obtained by combining an electron acceptor (usually a fullerene derivative) with a photosensitive conjugated polymer acting also as hole conductor, resulting in high external quantum efficiencies of these devices under sun light irradiation. In contrast, the combination of colloidal PbS nanocrystals with fullerene derivatives operates very well in photoconduction,ⁱⁱ but poorly in photovoltaic mode. The latter is caused by the small hole conductivity through the nanocrystal film, which is hampered by the presence of the bulky nanocrystal ligand shell. Furthermore, the photoconductivity in PbS nanocrystal/fullerene derivatives strongly depends on the nanocrystal size, due to the closely matching of the fullerene derivative LUMO (lowest unoccupied molecular orbital) and the lowest unoccupied states in the PbS nanocrystals.ⁱⁱⁱ Usually the highest photoresponse is observed for the smallest nanocrystal size.

To obtain photovoltaic response from colloidal PbS nanocrystals we make use of a ternary blend, containing the conjugated polymer poly(3hexylthiophene) (P3HT), [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), and the PbS-QDs with a weight ratio of 1:1:4.^{iv} This blend forms the photoactive layer within a diode structure with Poly(3,4-ethylenedioxy thiophene) :

poly(styrenesulfonate) (PEDOT:PSS) interlayers used to improve the electrical contact to the structured indium tin oxide (ITO) bottom contacts and with Aluminium top contacts. With these diodes external quantum efficiencies up to 51% have been achieved and nanocrystal based flat-panel imagers have been demonstrated, by integrating the solution-processed infrared photodiodes on top of amorphous silicon active matrix (a-Si AM) backplanes. The ambipolar transport in the ternary blend is proven by measurements in thin film transistor geometry, evidencing the hole transport in the conjugated polymer and the electron transport in the fullerene, while the photosensitivity is clearly given by the inserted PbS nanocrystals.

Temperature dependent experiments reveal the high sensitivity of the photoresponse on the energy level alignment between the Nanocrystals and the fullerene derivative, resulting in quenching of the photoresponse at low temperatures for 5.2 nm nanocrystals in size.^v With smaller nanocrystals the optimum operation temperature is found between room temperature and 72 °C, making these photodiodes promising for various applications.

While the high external quantum efficiency of the photodiodes is obtained under reverse bias, making these devices to efficient infrared-detectors, their performance without bias or in short circuit, so as a solar cell, is rather poor. Thus we have tested also a second concept towards photodiodes, which is based again on the ligand manipulation of the PbS nanocrystal shell.^{vi} These devices contain a purely PbS nanocrystal film as photosensitive material and a treatment with benzenedithiol (BDT) is applied multiply times during film deposition in order to exchange the original insulating ligands by bidentate ligands and to crosslink neighboring nanocrystals. The photosensitive films device active layer with a thickness of 140 nm was prepared between an ITO anode and a 1 nm LiF/100 nm Al cathode. The devices with an active area of 4 mm² operate as efficient solar cells, exhibiting under AM1.5 illumination a power conversion efficiency close to 4% and fill factors of 60%. These results exceed all previously reported literature values, making these devices promising for future improvements and applications.

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