Measurement and validation of PbS nanocrystal energy levels

D. M. N. M. Dissanayake,^{a)} T. Lutz, R. J. Curry, and S. R. P. Silva

Advanced Technology Institute, Faculty of Engineering and Physical Sciences, University of Surrey, Surrey GU27XH, United Kingdom

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Cyclic voltammetry was used to measure PbS nanocrystal (PbS-NC) energy levels. Accuracy of these measurements was justified by electron transfer experiments, with well known fullerene derivatives, which included photoluminescence quenching experiments and current density-voltage measurements of hybrid photovoltaic devices. It is believed that these energy level measurements, carried out on PbS-NCs under ambient conditions, would provide valuable information for the design and fabrication of optimized hybrid nanoelectronic devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.2964203]

Narrow bandgap colloidal semiconductor nanocrystals (NCs) are actively researched for their size depended optical properties and solution processibility.^{1,2} NCs can be incorporated with organic semiconductors to fabricate low cost, flexible, and large area optoelectronics and photonic hybrid devices.^{3,4} A fundamental drawback in the design of hybrids is the accurate understanding of energy level positions, which govern charge transfer at NC-organic interfaces. Mostly, NC band diagrams reported in literature for hybrid devices are obtained by calculations, based on bulk ionization potential (IP) and electron affinity (EA).¹ Direct measurement of the IP, using photoemission spectroscopic techniques, has been reported for PbS-NCs.³ However, a major problem encountered in such studies was the detrimental effect caused by the passivating organic ligands, capping the NCs, on photoemission measurements and subsequent analysis. Insulating organic ligands caused charge buildup on the substrates as well as screened NCs from exposure to ultraviolet photons, severely affecting the accuracy of the measurements. Consequently, these NCs were annealed in ultra-high vacuum to overcome such problems and the calculated energy levels showed reasonable agreement to the device performance. However, these annealing techniques were reported to alter the surface (bulk) condition as well as the stoichiometry of the NCs from its condition present at device fabrication.³ Therefore, less invasive techniques such as electrochemistry have to be employed for measurement of these NC energy levels. Kucur *et al.* reported IP and EA values for different size CdSe NCs using cyclicvoltammetry.⁵ Furthermore, differential pulse voltammetry, which demonstrate greater sensitivity than cyclicvoltammetry, has been used previously for determining the subtle changes of the NC energy levels, with different ligands, proving the versatility of electrochemical techniques.⁶ In this paper, we utilize a technique of electrochemistry to investigate the energy levels of PbS-NCs and probe the accuracy of the obtained values by charge transfer experiments. Current density-voltage (*JV*) characteristics of hybrid photovoltaic (PV) devices fabricated using C₆₀ and soluble C₆₀ derivative of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), and photoluminescence (PL) quenching experiments were used for determining the electron transfer (ET) from PbS-NCs

justifying the energy band diagrams obtained. This work provides crucial information about PbS-NC energy levels for the design and fabrication of optimized hybrid optoelectronic devices.

PbS-NCs with rocksalt crystalline structure were synthesized according to a method reported by Hines and Scholes.⁷ Approximate size of these PbS-NCs was calculated as 3.8 nm by applying the absorption onset value to theoretical models documented elsewhere.⁸ All chemicals were analytical grade reagents and were purchased from Sigma Aldrich and used as received. As-synthesized capping oleic acid ligands were exchanged for shorter butylamine ligands² and PbS-NCs were dissolved in anhydrous toluene (70 mg/ml). Electrochemical measurements were carried out using an Autolab PGSTAT12 potentiostat/galvanostat. The PbS-NC solution was drop casted and dried on top of 1 cm² area Pt electrode for measurements. 0.1M tetrabutylammonium-hexafluorophosphate (TBAPF₆) dissolved in acetonitrile (HPLC grade) was used as the electrolyte solution. A homemade Ag/AgCl electrode, calibrated against ferrocene [0.5 mM in acetonitrile:TBAPF₆ (0.1M)] solution, was used as the reference electrode. Cyclicvoltammetry sweeps were carried out at 50 mV/s, starting from negative to positive bias, with the electrochemical cell purged with nitrogen for 10 min prior to each measurement. Hybrid PVs were fabricated by spin coating PbS-NC solutions (70 mg/ml) on poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) coated indium tin oxide substrates to obtain uniform film thickness of 100 nm. 30 nm C₆₀ (99.99%, American Dye Source) was sublimated on PbS-NC film and afterwards a 10 nm bathocuproine (BCP) and 50 nm Al top contact deposited to fabricate 10 mm² PVs. Similarly, a film of PCBM (20 mg/ml in CHCl₃) (99.9%, Solenne) was spin coated at 700 rpm (60 s) on predeposited PbS-NCs and subsequently capped by a BCP and Al top contact to fabricated PbS-NC:PCBM device. *JV* characteristics of the devices were obtained using an Oriel solar simulator at AM1.5G simulated solar irradiation. PL experiments were carried out on PbS-NC:C₆₀ and PbS-NC:PCBM bilayer thin film samples to study effects of PL quenching resulting from ET from PbS-NCs to the fullerene derivatives. An Ar ion laser operating at 351 nm (150 mW) UV was used for the PL experiments.

Cyclicvoltammogram taken of PbS-NCs deposited on a Pt electrode is shown in Fig. 1 with voltage taken relative to

^{a)}Electronic mail: m.dissanayake@surrey.ac.uk.

FIG. 1. Cyclic voltammogram graph of PbS-NC film deposited on the working electrode in acetonitrile+0.1M TBAPF₆ scanned at 50 mV/s. Inset shows the voltammograms of 5 mM of butylamine (solid line) and a baseline taken (dotted line) on acetonitrile+0.1M TBAPF₆ pristine solution.

the reference electrode. Distinct peaks E_{p1} and E_{p2} of the voltammogram are seen at 1.08 and -0.06 V in the forward and reverse cycles, respectively. Both E_{p1} and E_{p2} can clearly be distinguished from baseline, shown by the dotted line in inset Fig. 1, thus can be attributed to the Faradic processes occurring in the PbS-NC sample. To clearly separate the redox reactions taking place in the butylamine ligands from PbS-NC reactions, a reference voltammogram was carried out on the ligands (solid line in the Fig. 1 inset). A redox peak (E_{pbuta}) of the butylamine voltammogram seen at 2.37 V can be clearly separated from the E_{p1} and E_{p2} seen for the PbS-NC sample. Hence, it can be concluded that the E_{p1} and E_{p2} corresponds to the oxidation and reduction reactions respectively of the PbS-NCs only. Using above measurements, IP of the PbS-NCs was calculated using the onset potential (E_{ons}) and reference electrode potential against the vacuum level (I_{RE}), according to Eq. (1).^{5,9,10}

$$IP = -(E_{ons} + I_{RE})[eV]. \quad (1)$$

I_{RE} was obtained as 4.48 eV by calibration against the oxidation potential of ferrocene (Ref. 11) (0.5 mM in acetonitrile+0.1M TBAPF₆). Therefore the IP is calculated as 5.2 eV for PbS-NCs using E_{ons} value 0.75 V measured from Fig. 1. As previously reported, onset reductions potentials were not seen to provide accurate values for the EA of NCs and therefore not used in this study.⁵ Alternatively, EA is obtained by subtracting the optical bandgap (1.2 eV), obtained from PbS-NC optical absorption onset (Fig. 2), from the calculated IP value. Therefore, the EA value for the PbS-NCs used for this study is taken as (4.0 eV). It should be noted that the size distribution of the PbS-NCs sample ($\sim 10\%$), derived from the full width at half maximum (0.186 eV) of the PL spectra given in Fig. 2, introduces an error to the EA value ($< \pm 0.1$ eV) calculated above. Quantification of the error introduced by PbS-NCs size distribution on the derivation of the IP value is non trivial and therefore differed for a more detailed study.

Using the IP and EA obtained above, energy diagrams can be proposed as schematically, as shown in inset Fig. 2, between PbS-NCs and C₆₀ (PCBM) donor-acceptor hybrids. C₆₀ and PCBM are very well characterized electron acceptors, extensively used in organic PVs. Since the EA, 4.5 eV

FIG. 2. Absorbance (black square) and PL (white square) of PbS-NCs spin coated on quartz. Inset shows the energy diagrams between bilayer systems of PbS-NCs and the fullerene derivatives.

(3.7 eV), and IP, 6.2 eV (6.1 eV), of C₆₀ (Ref. 12) (PCBM) (Ref. 13) are well known, they can be used effectively as references in charge transfer experiments. Observing the above band diagram, it is possible to infer the rate of ET between PbS-NCs and C₆₀ (PCBM) layers. ET from PbS-NCs to C₆₀ is seen to be more energetically favorable as compared to ET from PbS-NCs to PCBM. Under flat band condition there exist a 0.3 eV energy barrier between the NCs and PCBM obstructing the ET.

To probe qualitatively the ET between PbS-NCs and C₆₀ (PCBM) and justify the band diagrams obtained above, PL experiments were carried out. Ultrafast charge transfer at a donor-acceptor interface is known to significantly quench radiative recombination of the donor and, therefore, is a widely used technique in molecular electronics.¹⁴ Bilayer PbS-NC: C₆₀ (PCBM) films were excited and the PbS-NC PL was observed. As seen from Fig. 3, PbS-NC PL is significantly quenched in the presence of C₆₀ proving efficient ET consistent with the above hypothesis. Approximately two orders greater PL intensity is observed between PbS-NC:PCBM bilayer as compared to PbS-NC:C₆₀ indicating greater radiative recombination, attributed to reduced ET from PbS-NCs to PCBM. As shown in Fig. 3, single layer of PCBM did not demonstrate PL at the wavelength range similar to

FIG. 3. PL intensities of PbS-NC:PCBM (white squares), PbS-NC:C₆₀ (black squares), and PCBM only (white circles) excited using 351 nm Ar ion laser.

FIG. 4. *JV* characteristics of PbS-NC:C₆₀ (black squares), C₆₀ single layer (white squares), PbS-NC:PCBM (black circles) and PCBM single layer (white circles) devices.

PbS-NC:PCBM sample, further confirming above observations.

To confirm accuracy of the energy level calculations and results obtained from PL quenching, hybrid PVs were fabricated using PbS-NC and the fullerene (derivatives) used above (Fig. 4). The PbS-NC:C₆₀ device shows larger short circuit current density (J_{sc}) as compared to the reference C₆₀ single layer device. This increase of J_{sc} is attributed to the increased photon harvesting of PbS-NCs together with the increased exciton dissociation at the heterojunction. Therefore, it can be concluded that reasonably efficient ET exist between the PbS-NCs and C₆₀. Conversely, the J_{sc} of PbS-NC:PCBM is nearly an order of magnitude lower than the J_{sc} of PCBM single layer device clearly attributed to poor ET at PbS-NC:PCBM heterojunction as compared to the PbS-NC:C₆₀. The PbS-NC layer can also absorb a significant amount of light going through to the PCBM, subsequently reducing the number of photons harvested in the PCBM layer. Overall, the decreased ET reduces net current generated though the PbS-NC:PCBM device compared to PCBM single layer device. Furthermore, PbS-NC:C₆₀ shows greater than two orders of magnitude larger J_{sc} as compared to PbS-NC:PCBM agreeing with the PL quenching data shown in Fig. 3. Therefore, both PL quenching experiments and the *JV* characteristics of PbS-NCs and C₆₀ (PCBM) favorably justifies the band diagram obtained from cyclic voltammetry measurements discussed above. It can also be postulated that

majority of charge transfer occurs from band-edge energy levels as opposed to the higher energy levels. This has important implication for hybrid device fabrication using NCs in general. For example, promising NC based PVs proposed in literature assume hot electron injection from higher energy levels from the NCs to acceptors. Clearly such hot electron injection was not seen to manifest in the device architectures studied here.

In conclusion, cyclic voltammetry was used to measure the EA and IP of PbS-NCs in ambient conditions. The accuracy of these measurements was justified by ET experiments with well characterized acceptor materials [C₆₀ (PCBM)], which included PL quenching experiments and *JV* measurements of hybrid PVs. It is believed that these energy levels measurements obtained and verified, using the techniques described above, would provide valuable information for the design and fabrication of optimized hybrid nanoelectron devices in the future.

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