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Charge Separation in Type II Tunneling Multilayered Structures of CdTe and CdSe Nanocrystals Directly Proven by Surface Photovoltage Spectroscopy

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Nanotechnology has a significant potential for both reducing the cost of photovoltaic devices and improving their power conversion efficiencies. Colloidal semiconductor nanocrystals (NCs) possess unique properties determined by the confinement of charge carriers within a restricted volume.[1,2] Recent years have seen an increasing amount of publications focusing on the use of semiconductor NCs as components of photovoltaic devices.[3−14] With respect to photovoltaic applications, NCs offer high extinction coefficients, and their band gap can be easily tuned through the visible and near-infrared spectral range by controlling their size and shape, thus providing an excellent tool for nanoscale design of light absorbing materials. A combination of the two semiconductor materials CdTe and CdSe offers favorable conditions for the charge separation of photoexcited charge carriers at the interface due to the type **II** alignment of their conduction and valence bands[15] (Figure 1a). An all-inorganic solar cell based on sintered layers of CdTe and CdSe nanorods showed a remarkable value of the power conversion efficiency of 2.9% for a nonoptimized heterostructure.[5] In our previous photoluminescence quenching study,[16] we provided strong indirect evidence for efficient charge separation at the CdTe/CdSe interface of type **II** layer-by-layer (LbL) deposited structures, in spite of the presence of an $\sim$1 nm thin polymer layer between the NCs. In this communication, we unambiguously prove the charge separation and diffusion in LbL assembled multilayered structures of CdTe and CdSe NCs by surface photovoltage (SPV) spectroscopy.

SPV spectroscopy is a powerful tool to characterize charge transfer at the nanoscale.[17] To obtain a surface photovoltage signal two consecutive processes are needed: (i) light absorption inducing excess charge carriers in the analyzed sample and (ii) charge separation that produces a net electric field and consequently an induced photovoltage. The SPV signal is proportional to the amount of charges Q times the charge separation d: $\text{SPV} \approx Qd$.[18] Excitons which are formed far away from the charge separating interface have to approach it to become dissociated; subsequent diffusion of the separated charges enhances the net separation distance d and thus the SPV signal. Transient SPV measurements allow us to analyze the buildup of the SPV signal for different types of layered structures giving insight into the diffusion processes of the separated charge carriers.

A scheme summarizing these processes and illustrating the experimental arrangement of the SPV detection of fields induced by separation of photoexcited charge carriers in multilayered structures of CdTe and CdSe NCs is shown in Figure 1b. SPV measurements were carried out in a capacitor arrangement[19] using a thin mica spacer ($\sim$30 μm) as an isolating layer between one electrode and the sample (Figure 1b) and a high impedance 500 MHz buffer similar to ref 20. The photon flux of the excitation lamp[21] of our SPV spectrometer, with an excitation intensity at 550 nm on the order of 10 W/m^2, is shown as a dashed line in Figure 2a. SPV spectra were taken with a lock-in amplifier. Due to retardation effects by slow buildup of the SPV signal and its long decay, we display both the in-phase signals (indexed with x) and quadrature signals (indexed with y), which are 90°-phase shifted signals displayed negative if they originate from the retardation of a positive signal.[20] SPV transients were measured on a logarithmic time scale with a pulsed laser as the excitation source.[22] All samples were measured in vacuum.

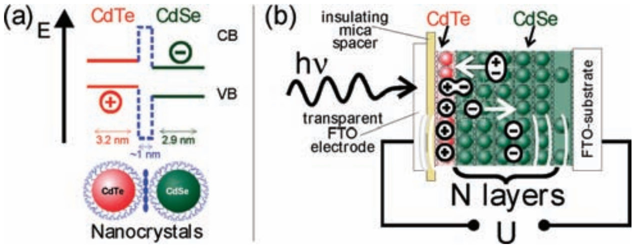

Figure 1. (a) Type II band alignment of CdTe and CdSe NCs. Conduction band (CB) and valence band (VB) levels are shown. (b) Scheme of the surface photovoltage (SPV) setup applied for the measurements on multilayered sample of CdTe and CdSe NCs. Excitons are created upon light excitation, which diffuse through the structure and may reach and become separated at the type II CdTe/CdSe interface. The random diffusion of separated charges creates an electric field measured as the SPV signal U by two transparent outer FTO electrodes in a capacitor arrangement.

The CdTe (3.2 nm diameter) and CdSe (2.9 nm diameter) NCs used in this work were water-soluble particles capped by the short-chain thiol ligand thioglycolic acid; they have been synthesized and size-fractionized as reported in refs 23 and 24, respectively. The LbL assembled samples were deposited on FTO substrates[25] by alternation of negatively charged NCs[26] with positively charged polyelectrolyte PDDA,[27] resulting in densely packed films with an rms roughness slightly above the NC diameter[28] and an average surface-to-surface distance between NCs in adjacent layers of $\sim$1 nm.[29] Absorption spectra of LbL assembled films of CdTe-only NCs and CdSe-only NCs are shown in Figure 2a. In some samples, denoted by **S** for a "spacer" in further discussion, a triple polymer layer consisting of PDDA/PSS/PDDA[27] has been deposited between

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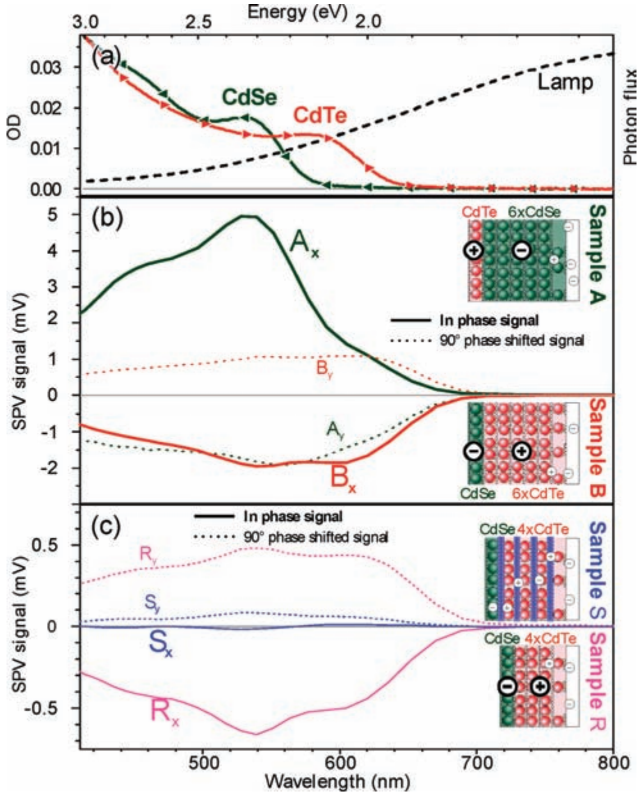

Figure 2. (a) Optical density of LbL deposited structures consisting of 3 CdTe or 3 CdSe NC layers on both sides of a glass substrate (solid lines). Photon flux of monochromated excitation lamp used for SPV measurements (dashed line). (b) SPV spectra of sample **A** consisting of 6 layers of CdSe NCs deposited on FTO substrate with a single layer of CdTe NCs on top and sample **B** consisting of 6 layers of CdTe NCs on FTO substrate with a single layer of CdSe NCs on top. (c) SPV spectra of samples **S** and **R**, both with 4 layers of CdTe NCs deposited on FTO substrate and 1 layer of CdSe NCs on top. Interlayer spacing increased from ~1 nm in the reference sample **R** to ~2 nm in the "spacer" sample **S** by use of a triple layer of PDDA/PSS/PDDA between subsequent NC layers. SPV signals shown in phase with excitation (solid lines: A_x, B_x, S_x, R_x) and 90° phase shifted signals (dashed lines: A_y, B_y, S_y, R_y).

NC layers, increasing the average distance between the adjacent NC layers to ~2 nm. All multilayer films started and ended with a PDDA layer; schemes of the samples studied in this work are presented as insets in the respective figures. The first deposited layer of NCs is typically not complete.[30]

Figure 2b shows SPV spectra of two LbL assembled CdTe/CdSe NC samples: sample **A** consisting of 6 layers of CdSe NCs deposited on the FTO substrate followed by a single layer of CdTe NCs on top, and sample **B** which consists of 6 layers of CdTe NCs on the FTO substrate with a single layer of CdSe NCs on top. NC layers in both samples are separated by a single layer of PDDA. The most important result is the inversion of sign of the SPV signal from curve A_x to B_x and from curve A_y to B_y, which is determined by changing the order of CdTe and CdSe layers in samples **A** and **B**. This is a direct proof of the directionality of charge separation at the CdTe/CdSe NCs interface as illustrated in the correspondent insets (Figure 2b). Holes are collected in CdTe NC layers and electrons in the CdSe NCs, as it is expected for the type II band alignment of these two materials. A constant lock-in phase (i.e., linear scaling of in-phase and 90°-phase shifted signals) indicates that the same charge separation processes are dominant throughout the whole wavelength range.

There is a clear contribution from different materials (CdTe and CdSe) evidenced from the correlation of SPV signals (Figure 2b) with the absorption spectra of NCs (Figure 2a). Sample **A** shows a strong SPV signal at 2.3 eV corresponding to the first absorption peak of 6 layers of CdSe NCs. A weak shoulder can be distinguished around 2.0 eV which originates from the single layer of CdTe NCs. The same two SPV signals appear for sample **B**, with a more pronounced CdTe NC peak resulting from the 6 CdTe NC layers, and a smaller CdSe NC peak superimposed on the high energy tail of the CdTe signal, originating from the single CdSe NC layer. This demonstrates that both excitation of CdSe NCs and excitation of CdTe NCs result in charge separation at the type II interface. The SPV signal originating from 6 CdSe NC layers in sample **A** is 2.5 times stronger than the SPV signal from 6 CdTe NC layers in sample **B** (Figure 2b), showing that CdSe NCs contribute more strongly to the SPV signal than the CdTe NCs, even though the excitation flux is weaker at the first absorption peak of CdSe NCs. This indicates a higher charge separation potential of CdSe NCs in our type II structures.

Figure 2c shows SPV signals for another set of samples, **S** and **R**, both with 4 layers of CdTe NCs deposited on an FTO substrate and 1 layer of CdSe NCs on top. The difference between these samples is that the use of a triple layer of PDDA/PSS/PDDA between subsequent NC layers increases the interlayer spacing from ~1 nm in the reference sample **R** to ~2 nm in the "spacer" sample **S** (insets in Figure 2c), which should lead to suppression of charge separation by tunneling through the multilayered structure for sample **S**. This is indeed clearly seen in Figure 2c: both the in-phase SPV signal S_x and the 90°-phase shifted signal S_y are very weak in comparison to the signals R_x and R_y. This excludes intralayer contributions to the charge separation and proves that the SPV signal originates from charge transfer by tunneling between the adjacent NC layers.

Comparison of the SPV signals from sample **B** with 6 CdTe NC layers (Figure 2b) and sample **R** with 4 CdTe NC (Figure 2c) reveals a strong difference in the SPV amplitude (peak maximum at 1.9 mV for B_x and 0.7 mV for R_x). The fact that the SPV signal increases by a factor of ~2.7 while the number of layers is changed by a factor of 1.5 demonstrates that (i) excitons generated in all layers contribute to the SPV signal and result in a larger total charge Q, implying random exciton diffusion toward the interface, and (ii) after separation the charge carriers diffuse away from the interface, enhancing the charge separation distance d.

The nonzero 90°-phase shifted signals A_y, B_y, S_y, R_y (Figure 2b and 2c) point to retardation effects[20] in our structures, which have been studied in more detail by conducting transient SPV measurements. Figure 3 presents SPV transients of structures with different numbers of CdSe or CdTe NC layers (as indicated in the respective frames) to give more insight into diffusion processes. Structures with several CdSe NC layers deposited on FTO substrates and 1 CdTe NC layer on top show a positive transient SPV signal (Figure 3a), while structures with several CdTe NC layers and 1 layer of CdSe NC on top exhibit a negative signal (Figure 3b). Reference structures of 3 layers of CdSe NCs only (Figure 3a) or CdTe NCs only (Figure 3b) on FTO substrates both show positive SPV signals, most probably originating from the charge separation at the type II interface between NC and FTO.[31] This observation further supports our interpretation of the negative sign of the SPV signal from structures with several CdTe NC layers in contact with 1 CdSe NC layer (Figures 2b, 2c and 3b) as evidence of charge separation at the type II interface between CdTe and CdSe NCs, highlighting the dramatic effect that only one monolayer of a different NC has in the behavior of the whole structure.

The SPV transients in Figure 3 are displayed on a logarithmic time scale, over several orders of magnitude. The data show an

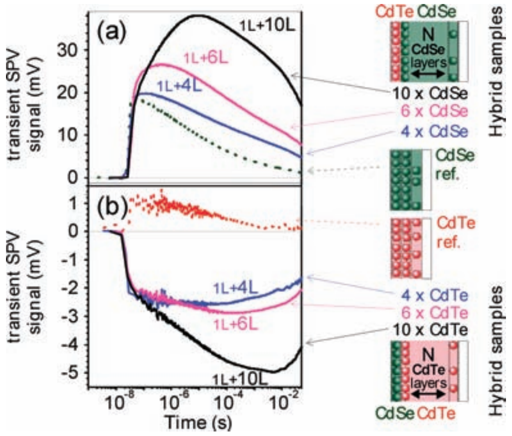

Figure 3. SPV transients of LbL deposited structures with varying number of CdSe or CdTe layers plotted on a logarithmic time scale: (a) one layer of CdTe NCs on top, number of CdSe NC layers varied (blue, 4 layers; pink, 6 layers; black, 10 layers); (b) one layer of CdSe NC on top, number of CdTe NC layers varied (blue, 4 layers; pink, 6 layers; black, 10 layers). SPV transients of reference samples made of 3 layers of CdSe NCs on FTO as well as 3 layers of CdTe NCs on FTO shown by dashed lines. Onset of the laser pulse shifted to 16 ns on both graphs.

increase in the rise time of the SPV signal as well as of the SPV amplitude as the number of layers increases. We consider the buildup of the SPV signal according to the scheme presented in Figure 1b. Excitons are formed upon excitation by a light pulse of 5 ns and diffuse through the multilayer structure toward the charge separating CdTe/CdSe interface. The exciton diffusion must occur within less than 4 ns as the characteristic photoluminescence decay times in layered CdTe or CdSe NC structures are well below this value.[30] After the separation of charges at the type II interface an SPV signal appears. Previously we estimated the time constant of charge separation in LbL assembled CdTe/CdSe NC structures to be on the order of 1 ns.[15] This means that the creation of separated charges will take no longer than 10 ns, which is the time resolution of our setup, as all excitons will have decayed by that time. As the SPV signal is proportional to the number of separated charges Q and their average distance d, any further increase of SPV transients which we observe in Figure 3 can therefore only be due to random diffusion of charges increasing the average separation distance d. Figure 3a presents a faster buildup of the SPV signals compared to the hybrid samples of Figure 3b. Taken into account the results on the polarity discussed above, we can conclude that electrons in CdSe NC structures diffuse quicker than holes in layered CdTe NCs. A lower hole mobility compared to electrons is expected for NC structures.[32]

In conclusion, we have used surface photovoltage spectroscopy to unambiguously demonstrate the directionality of charge separation in multilayered type II aligned tunneling structures of CdTe and CdSe NCs separated by a polymer spacer. Holes accumulate in CdTe NC layers, and electrons in CdSe NC layers. An increase of the thickness of the polymer spacer strongly decreases the separation efficiency. Transient SPV spectra provide evidence for diffusion of separated charges over several layers of the same kind of NCs. These findings are of importance for the use of layered type II aligned NC structures in photovoltaic applications.

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(21) Excitation source: chopped light (∼3 Hz) of a 150 W halogen lamp connected to a prism monochromator (spectral width <30 meV). The SPV spectra taken were not corrected for changing excitation flux.
(22) SPV transients measured with a 300 MHz oscilloscope (Compu-Scope 14200 (GAGE), 100 Ms/s sampling rate) with readout on logarithmical timescale (measurement window 10 ns to 100 ms). Excitation source: pulsed dye laser at 442.8 nm wavelength (pulse length 5 ns, excitation intensity at the sample 0.2 mJ/cm^2, repetition rate 1 Hz).
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(25) FTO substrate of 400 nm thick fluorine doped tin oxide layer on glass (FTO). Before the assembly these FTO substrates were given a negative surface charge by cleaning in a 1:1:3 solution of NH_3(25%)/H_2O_2(∼30%)/H_2O at 70°C for 60 min.
(26) Stock solution of 0.2−0.3 mM.
(27) Positive charged PDDA, poly(diallyldimethylammonium chloride); negative charged PSS, polystyrenesulfonate; PDDA and PSS each as 1 mg/mL in 0.5 M NaCl solutions.
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