Supporting Information

Charge Separation and Photocurrent Polarity-Switching at CdS Quantum Dots Assembly in Polyelectrolyte Interfaced with Hole Scavengers

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The supporting information contains:

1. TEM image of (PDDA/Q-CdS)$_4$ by dip SA (Fig. S1)
2. I-t curves under illumination in sulfide at 100 mV and -600 mV (Fig. S2)
3. I-V curve under illumination in sulfide at a thin electrodeposited CdS film (Fig. S3)
4. I-V curve under illumination in sulfide showing the photocurrent onset (Fig. S4)
5. CV curves under illumination in sulfide showing forward and reverse scans (Fig. S5)
6. Photocurrent density vs. wavelength at different multilayers in sulfide(Figure S6)
7. Anodic and cathodic photocurrents vs. the number of bilayers (Figure S7)
8. Scheme showing various competing processes in the film (Scheme S1).
9. I-V curve under illumination in NaOH following scans in sulfide (Figure S8)

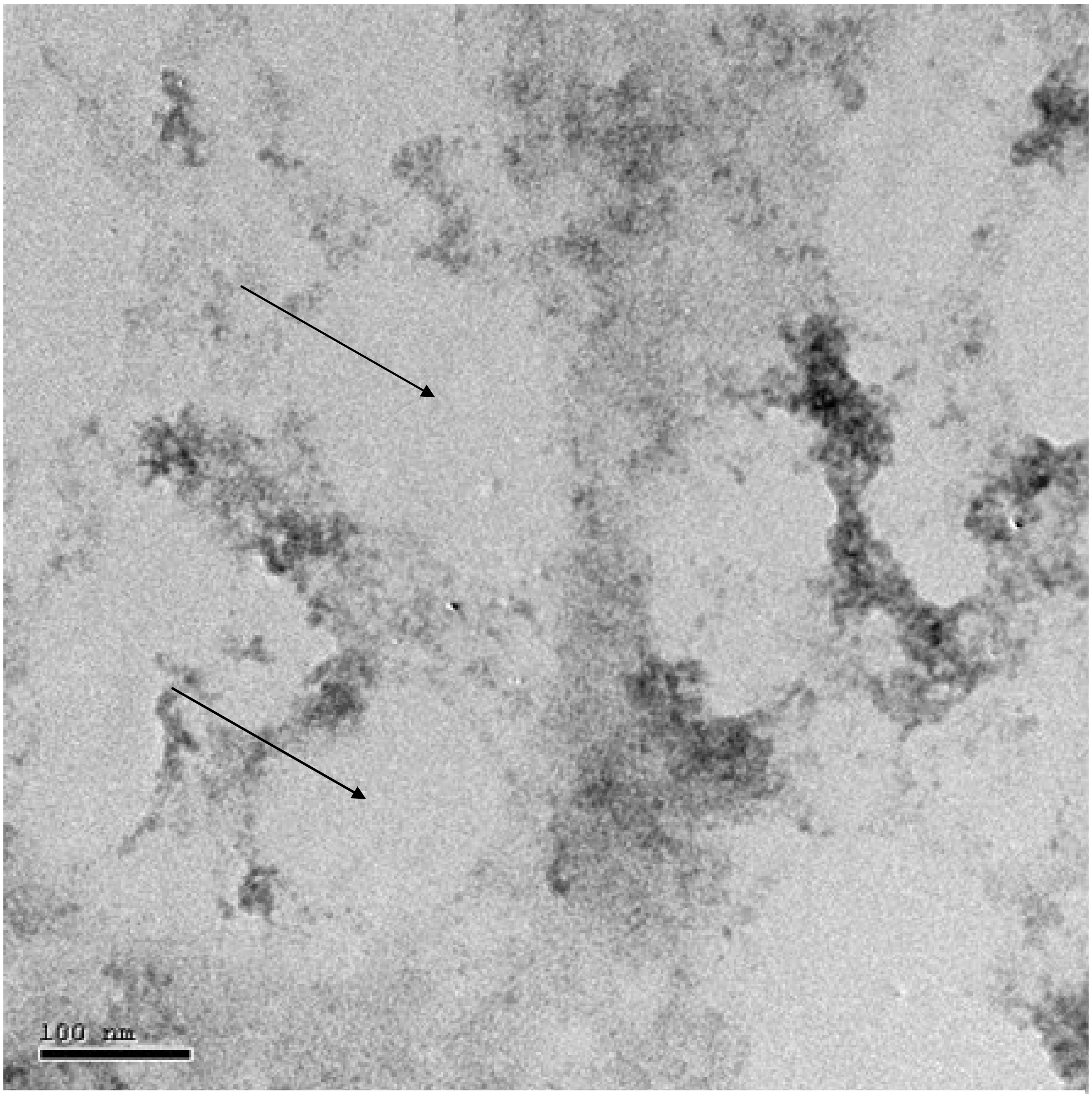


Figure S1. TEM image of (PDDA/Q-CdS)$_4$ assembled by dip SA method directly on SiO$_x$-coated Cu grid. Scale bar is 100 nm. Arrows show areas where NPs were not observed at higher magnification.

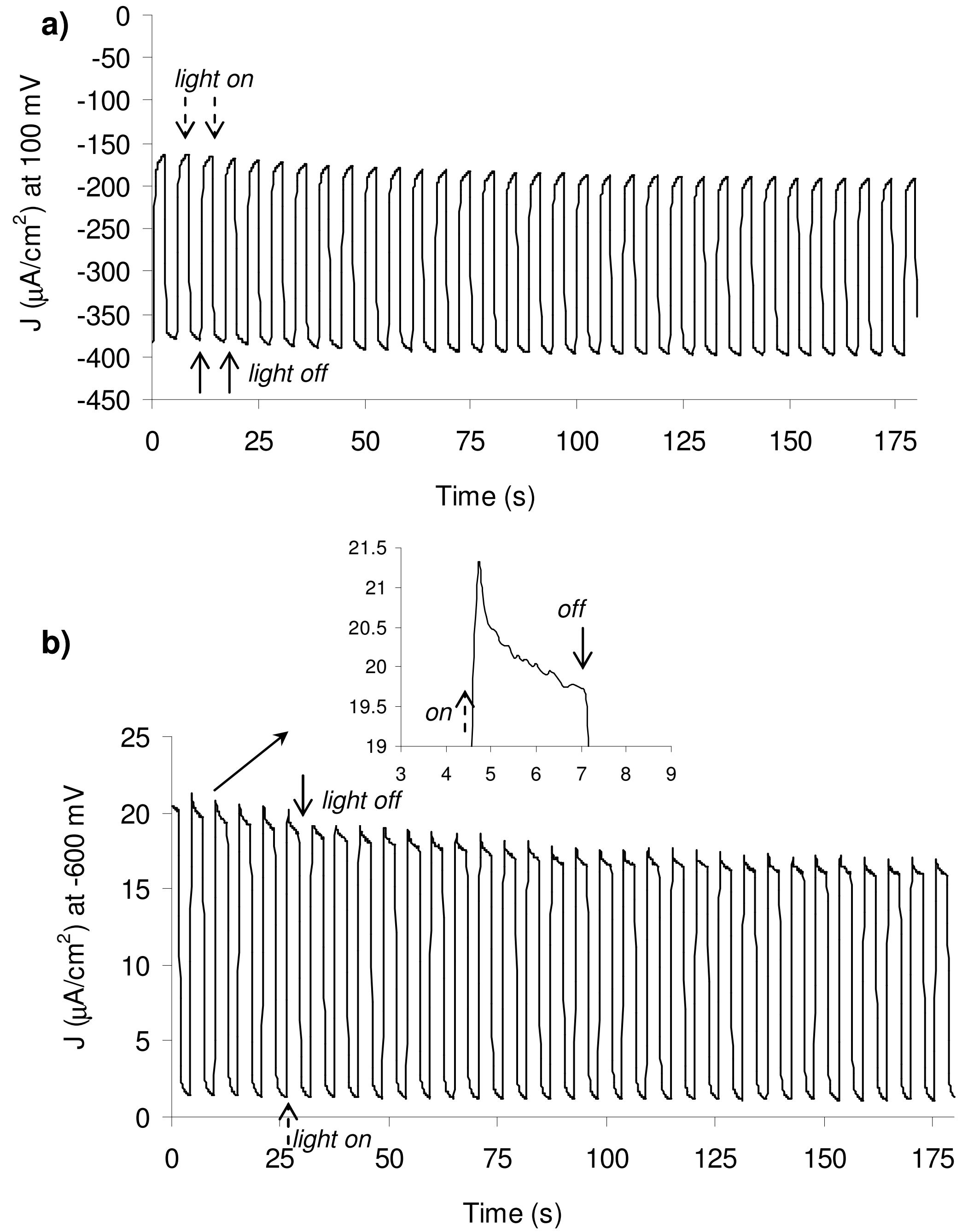


Figure S2. Amperometric curves acquired under chopped-illumination at (PDDA/Q-CdS)$_4$ (by dip-spin SA) in deoxygenated 0.1 M Na_2S/0.2M NaOH, at an applied potential of 100 mV (a) and –600 mV (b) vs. Ag/AgCl.

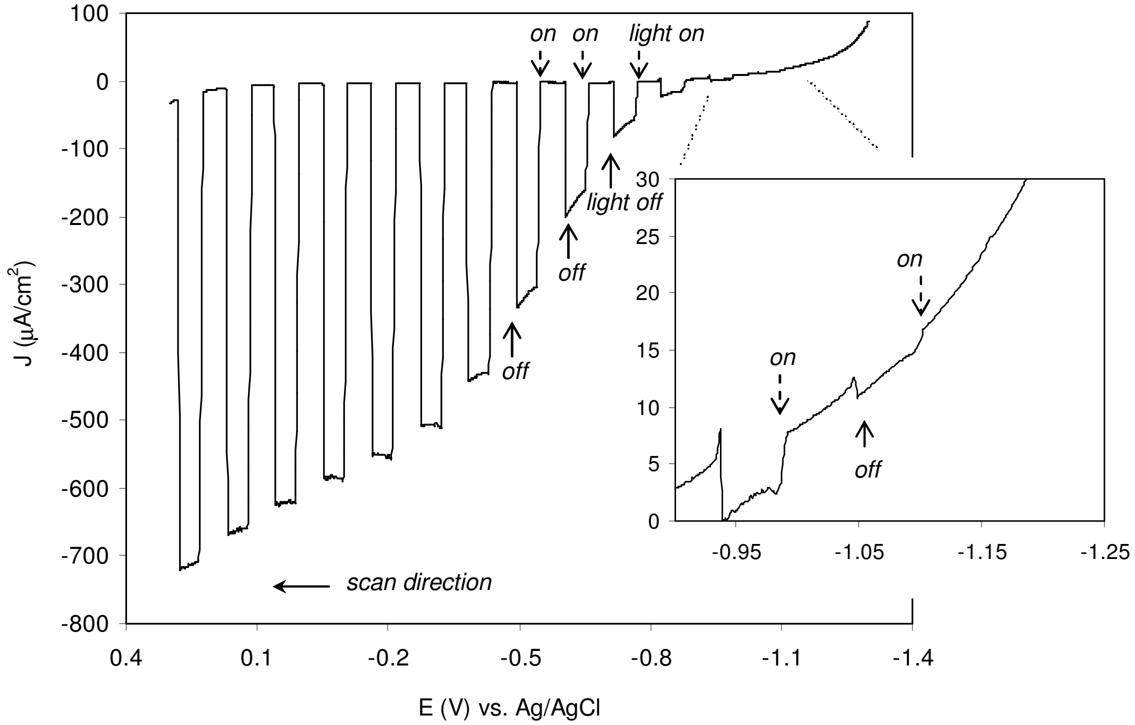


Figure S3. Photocurrent-voltage plot under chopped-illumination at an electrodeposited thin CdS film (thickness ~ 75 nm) in deoxygenated 0.1 M Na_2S/0.2 M NaOH solution (pH = 12.6). Scan rate is 20 mV/s. (Potential scan from negative to positive).

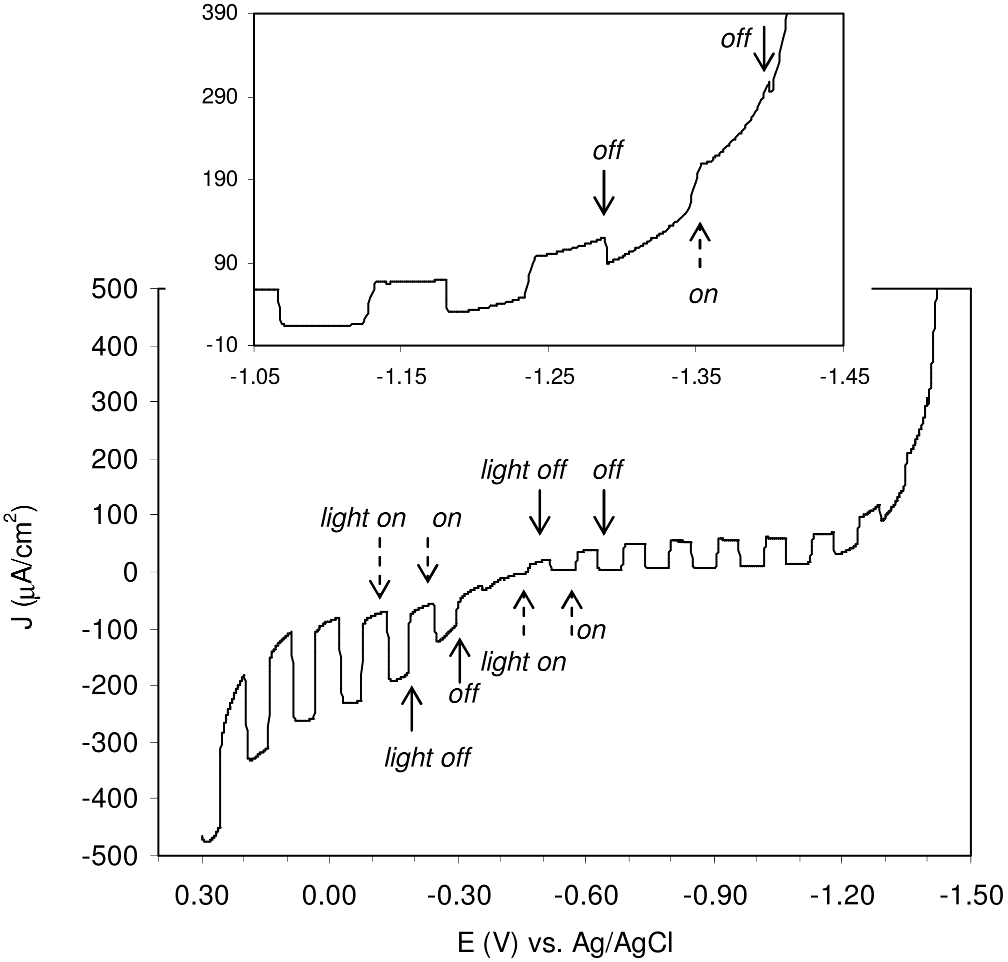


Figure S4. Photocurrent-voltage plot under *chopped*-illumination at (PDDA/Q-CdS)$_4$ film (by dip-spin SA) in deoxygenated 0.1 M Na$_2$S/0.2 M NaOH solution (pH = 12.6) showing the photocurrent onset at ~ –1.4 V. Scan rate is 20 mV/s.

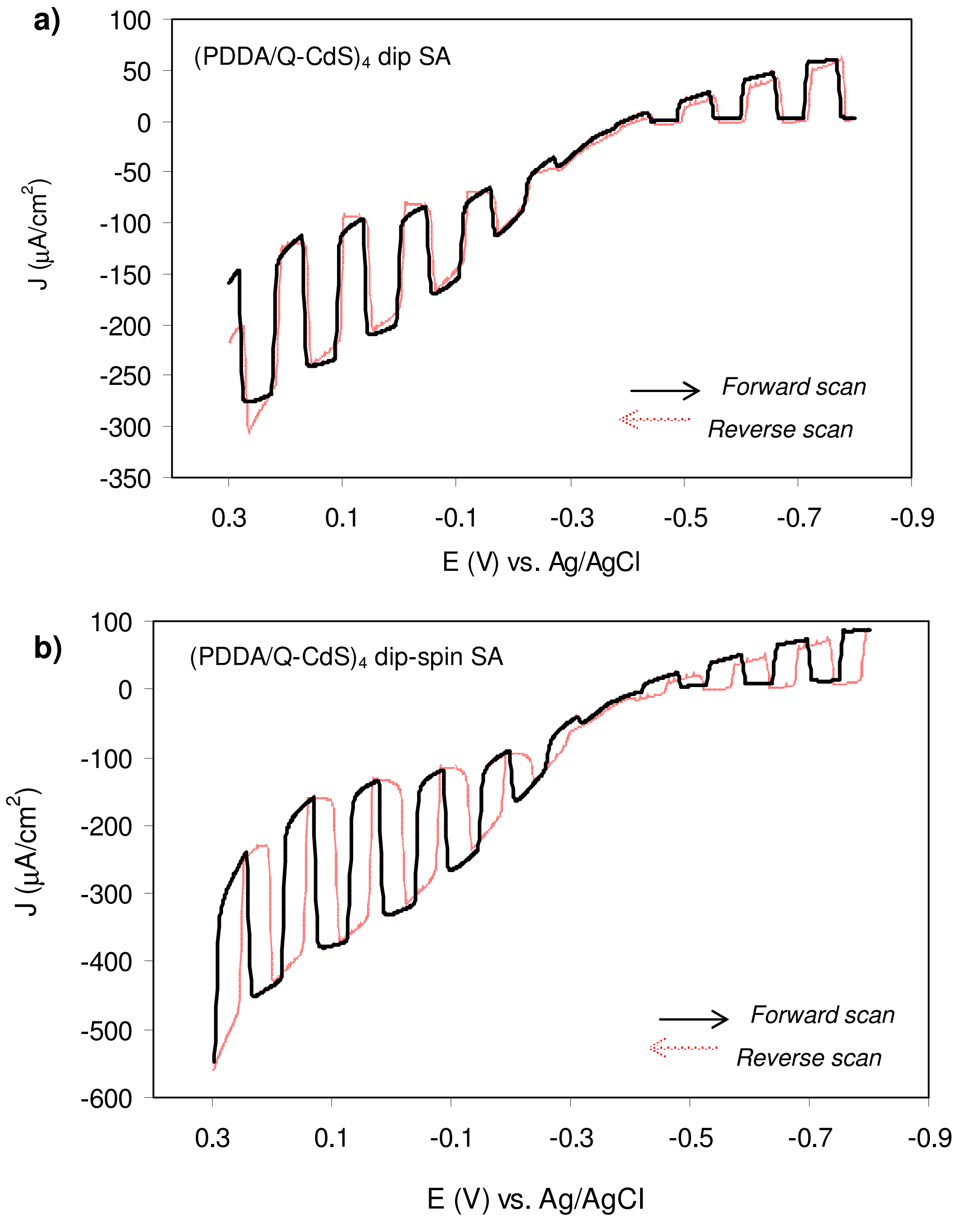


Figure S5. Forward (positive to negative) and reverse photocurrent-voltage plots under *chopped*-illumination at (PDDA/Q-CdS)$_4$ films by dip SA (a) or dip-spin SA (b) in deoxygenated 0.1 M Na$_2$S/0.2 M NaOH solution (pH = 12.6). Scan rate is 20 mV/s.

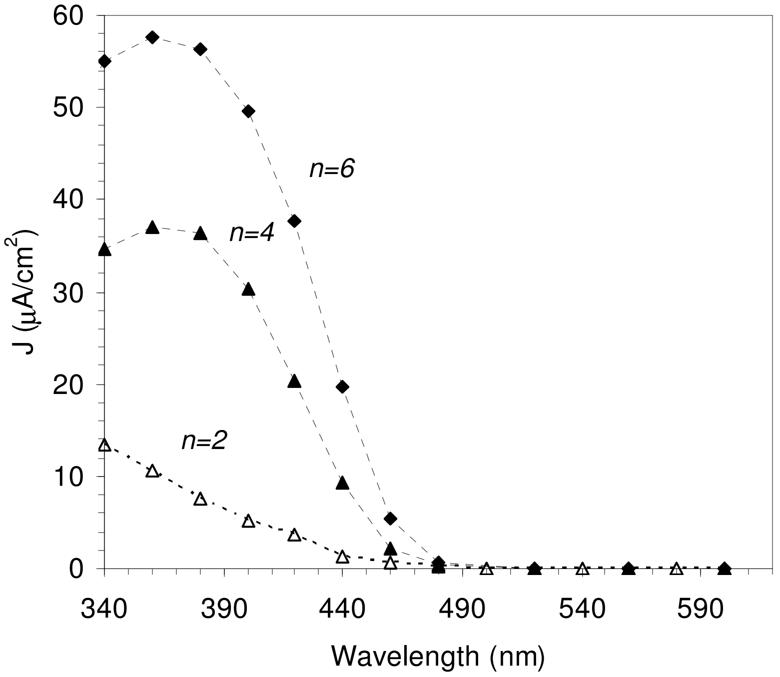


Figure S6. Photocurrent density vs. wavelength at (PDDA/Q-CdS)$_n$ films by dip-spin SA, *n* = 2, 4, 6, in deoxygenated 0.1 M Na_2S/0.2 M NaOH. The %IPCE is shown in Figure 3a.

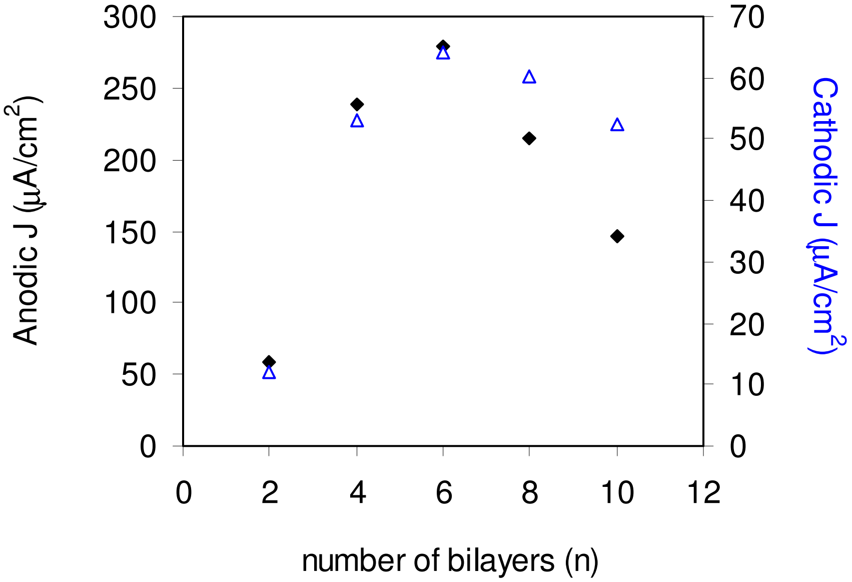
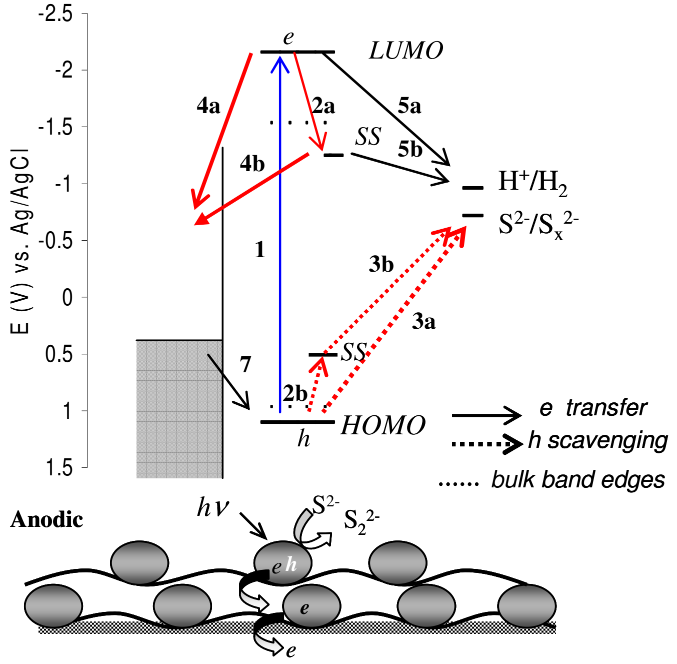


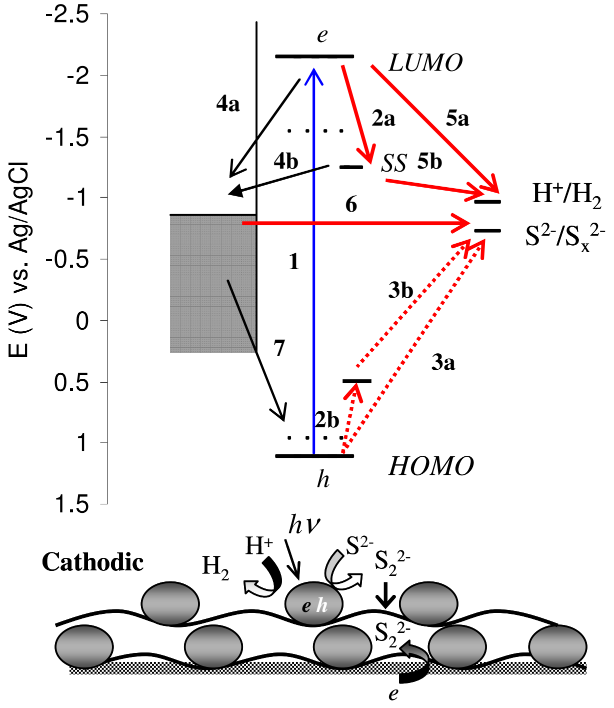
Figure S7. Anodic and cathodic photocurrents vs. the number of bilayers (*n*) measured from I-V plots in Figure 4 at 75-110 mV, and –630 - – 665 mV, respectively.

Scheme S-1. Sketches showing the main charge transfer processes at ITO/(PDDA/Q-CdS)$_n$/0.1 M Na_2S, 0.2 M NaOH leading to anodic (A) or cathodic photocurrent (B). Bold red arrows indicate the predominant processes leading to charge separation in each case. The redox potentials of solution species and the HOMO and LUMO approximated by the EMM for 3.6 nm CdS particle are shown. The processes and their numbering are described in Appendix A.

Scheme S-1A



Scheme S-1B



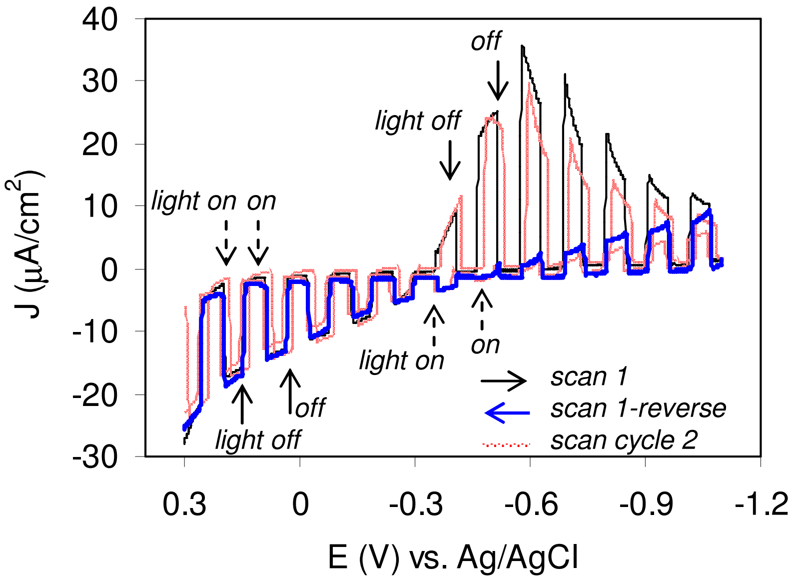


Figure S8. I-V plots under chopped-illumination in deoxygenated 0.2 M NaOH solution at (PDDA/Q-CdS)$_4$ film prepared by dip-spin SA after I-V scans under illumination between 0.4 and –0.8 V in deoxygenated 0.1 M Na_2S/0.2M NaOH. The first 2 consecutive I-V cycles are shown , and the arrows showing the on-off cycles are for the first forward scan. Scan rate is 20 mV/s.

Discussion of photoelectrochemical behavior following scans in sulfide. We investigated the effect of sulfide or any resulting surface change on the generation of a bidirectional photocurrent by studying the I-V characteristics in NaOH after a potential scan in sulfide. Figure S7 shows consecutive I-V scans at a (PDDA/Q-CdS)$_4$ film (dip-spin SA) in 0.2 M NaOH following potential scan between 0.4 and –0.8 V under illumination in sulfide. Such a film history (denoted here sulfide-treatment) resulted in a bidirectional photocurrent, absent in NaOH prior to the sulfide treatment (*cf.* Figure 2b), with cathodic photocurrents featured in a peak negative of –0.35 V and a switching potential (–0.3 to –0.35 V) close to the potential in sulfide. This indicates that a sulfur species, whether on the QD surface or in the films, is involved in leading to a cathodic photocurrent. If this history causes adsorption (presence) of a species that introduces energy levels within the gap capable of accepting photogenerated holes (hole-trap, e.g., S^{2-} or $S^{-\cdot}$ sites), a cathodic photocurrent can flow if photogenerated hole-capturing takes place to this level followed by electron transfer from the electrode to react with the trapped holes (photo-oxidized species) at suitable reducing potentials in a similar process to (5). The proposed nature of the state related to a sulfur species is supported by the similar values of the potential of zero-current in sulfide and at the sulfide-treated film. The peak-shape and lower cathodic photocurrents on the reverse scan indicate a maximum rate possibly due to state density depletion (possibly by desorption), while a second scan similar to the first indicates replenishing of these states at anodic potential. The results here also constitute evidence of involvement of solution S^{2-} in photocurrent generation in sulfide solutions since the I-V characteristics in 0.1 M Na_2S differed in several respects from the behavior in NaOH following the sulfide-treatment. Anodic and cathodic photocurrents (negative of – 0.65 V) were considerably higher in sulfide solution, and cathodic photocurrents did not feature a peak-shape nor decreased on the reverse scan, which indicates the involvement of S^{2-}(aq) in charge separation leading to cathodic photocurrent as proposed in the presented model.