Broad spectral photocurrent enhancement in Au-decorated CdSe nanowires

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SUPPLEMENTARY INFORMATION

1. Synthesis of CdSe NWs

We followed the SLS method with slight modifications. For the growth of the CdSe NWs, we adapted the recipe developed in the group of Kuno. 25 mg of cadmium oxide (CdO) (Aldrich), 2.5 g of trioctyl-phosphine oxide (TOPO, $C_{24}H_{51}OP$) (Strem Chemicals), and 0.25 ml of oleic acid ($C_{18}H_{34}O_2$) were mixed in a 25 ml three neck round bottom flask (RBF). Under continuous stirring, the mixture was kept at 100 °C until the TOPO was completely melted, followed by degassing at the same temperature under vacuum (< 100 mTorr). Under a controlled flow of Argon, the temperature in the flask was brought to 300 °C until all CdO dissolves (reaction mixture turns from red-brownish to colorless), after which the temperature was set to 250 °C. Pre-mixed solutions of bismuth chloride ($BiCl_3$) in acetone (50 µl) and trioctyl-phosphine-selenide (TOPSe) in TOP (100 µl) are then injected into the hot RBF and the reaction is immediately quenched by removal of the heating mantle. The product was washed three times by centrifugation with methanol and chloroform and finally dispersed in 4 ml of toluene. For the following processes this solution was diluted 1:9 in toluene.

2. Gold decoration of CdSe nanowires

The CdSe NWs were functionalized with Au NPs by the method of Banin et al. with slight modifications. 10 mg of gold chloride, 40 mg of dodecyl-dimethyl-ammonium-bromide ($C_{14}H_{32}BrN$), and 70 mg of dodecyl-amine ($C_{12}H_{27}N$) were first mixed in a vial on top of which 3 ml of toluene were added, yielding a change in color of the solution from bright yellow to colorless. Some tens of µl of this solution (see below) were added to an aliquot (500 µl) of the CdSe NWs, which resulted in the decoration of the CdSe NWs with Au nanoparticles.

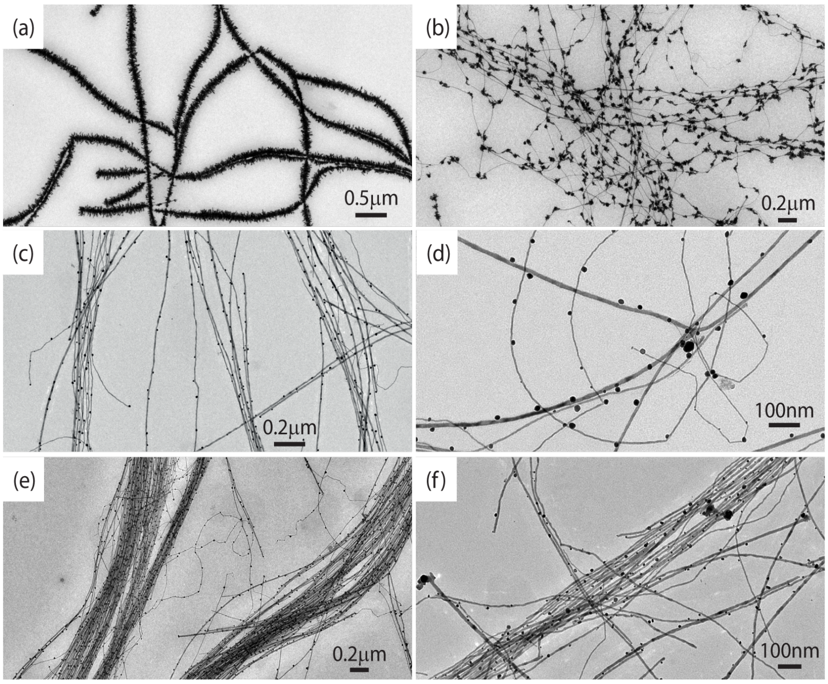

Figure S1. TEM images of Au-decorated NWs fabricated by different amounts of $AuCl_3$ solution added to 500 µl of CdSe NW solution: (a) 200 µl of 100% concentrated $AuCl_3$ solution; (b) 100 µl of

100% concentrated $AuCl_3$ solution; (c) 50 μl of 100% concentrated $AuCl_3$ solution; (d) 20 μl of 100% concentrated $AuCl_3$ solution; (e) 30 μl of 6% concentrated $AuCl_3$ solution; (f) 30 μl of 2% concentrated $AuCl_3$ solution.

3. Electrode device fabrication

Interdigitated patterns with 2 to 8 μm electrode separation, respectively, were defined by conventional photolithography on cover glass slides. Oxygen plasma cleaning (30 seconds at 100 W) was carried out to ensure the removal of residual organic resists. The interdigitated electrodes were then obtained by electron-beam evaporation of Ti/Au (5 nm/100 nm) and lift-off in acetone. Afterwards, the NWs were drop-casted onto the electrodes and, once the solvent evaporated, the device was annealed at 200 °C for 20 min in an inert atmosphere.

4. Dark and photocurrent comparison, and photocurrent spectra of as prepared Au-CdSe NWs.

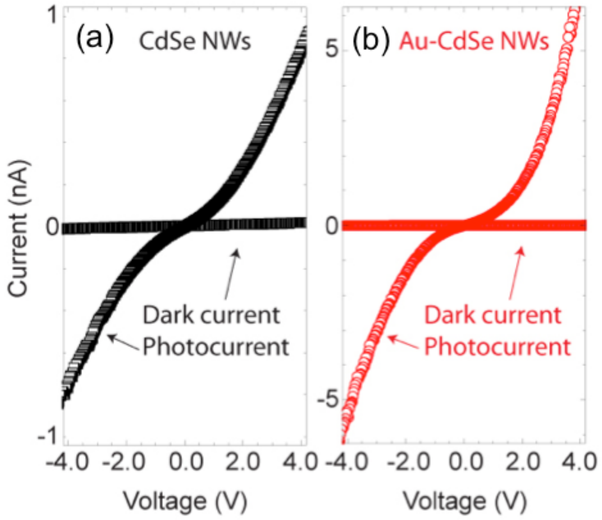

Figure S2. Photo and dark I-V curves recorded from the Au-decorated and bare CdSe NWs. (a) and (b) Dark- and photocurrent vs. applied voltage for the CdSe NWs and the "aged" Au-CdSe NWs, respectively. All data were recorded under vacuum.

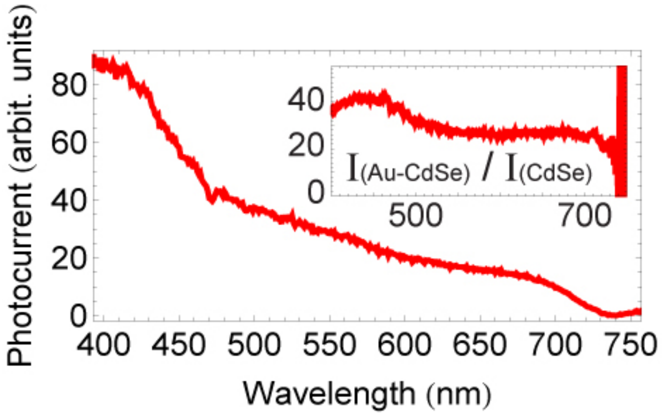

Figure S3 Photocurrent spectrum recorded from "as-prepared" Au-CdSe NWs.

5. Interdigitated electrode samples coverage with nanowires

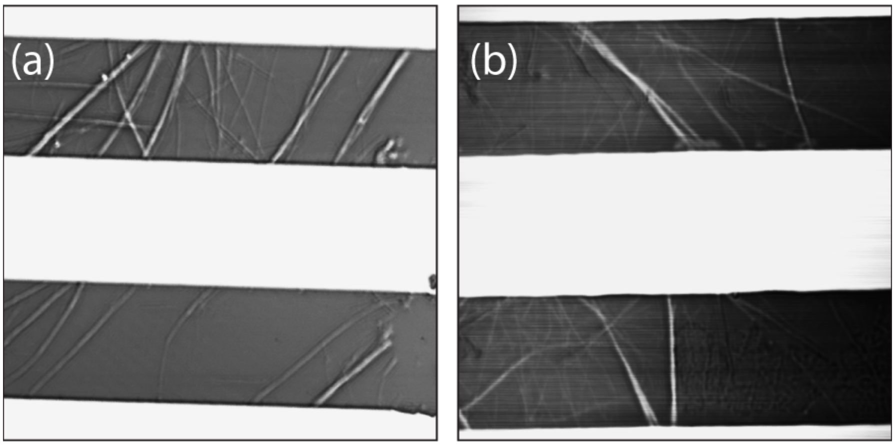

Figure S4 Typical confocal optical microscope images of electrode devices that were functionalized with (a) bare CdSe and (b) Au-decorated NWs.

6. Post deposition gold decoration of CdSe NWs

We followed the same procedure as previously described to obtain CdSe NWs devices on silicon substrates. The electrode devices were dipped for 5 s in 500 µl of 6% concentrated $AuCl_3$ solution, followed by drying with nitrogen flow and annealing at 200 °C for 20 minutes under inert atmosphere. After measuring the I-Vs characteristics, the device was imaged by scanning electron microscopy (SEM). It resulted in evenly Au-decorated CdSe NWs and a strong (hundred-fold) enhancement in photocurrent.

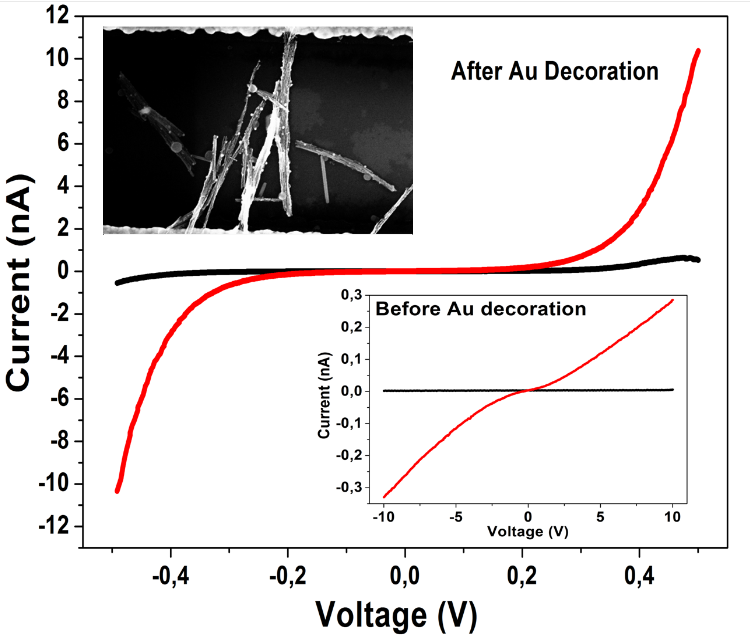

Figure S5. Dark (black) and photocurrent (red) recorded from a different CdSe NW device that was treated with AuCl solution after the NWs were deposited on the SiO_2 substrate. The upper inset shows an SEM image of the NWs at the Au electrode interface, the lower inset shows the IV data of this device before Au decoration.

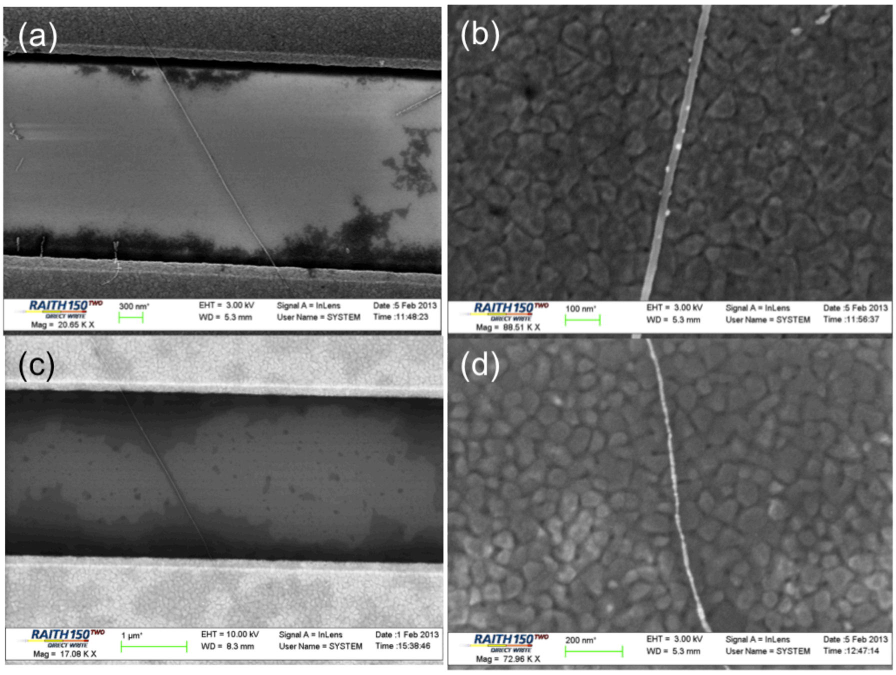

Figure S6. SEM images of Au decorated CdSe NWs on interdigitated electrodes that were fabricated on SiO_2 substrates. (a-b) Au decoration in solution, (c-d) post-deposition Au decoration.

7. SPCM maps of bare and Au decorated CdSe nanowires

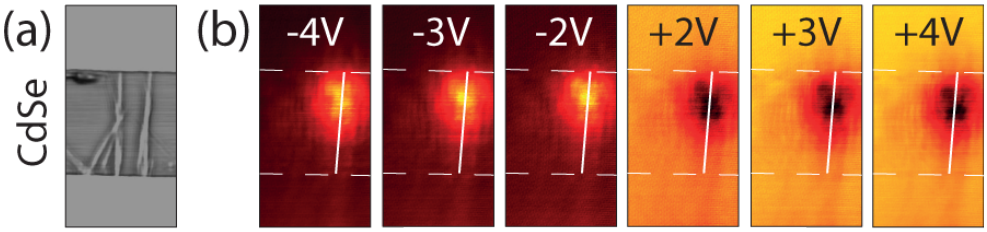

Figure S7 Optical reflection (a) and SPCM (b) measurements of the CdSe NWs on 8 µm electrode gap device.

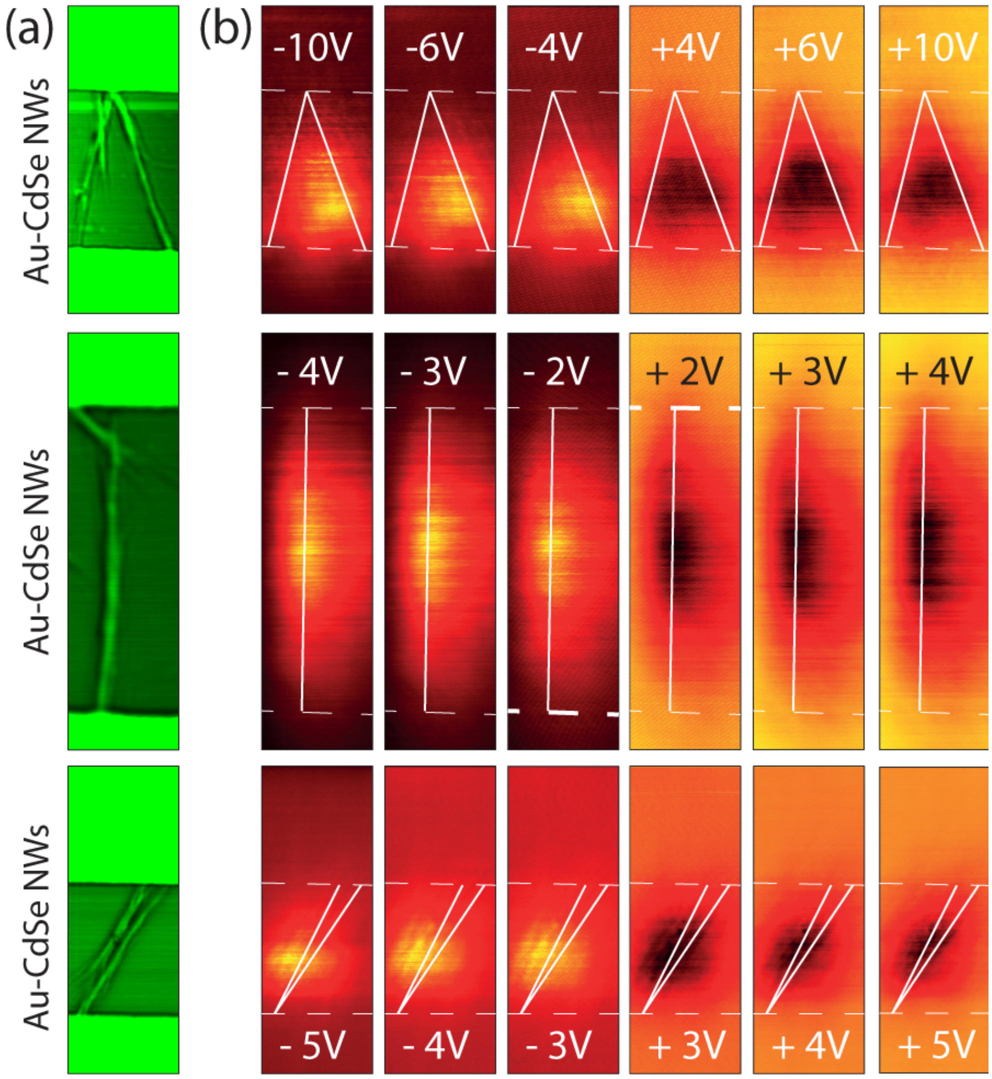

Figure S8 Optical reflection (a) and SPCM (b) measurements of the as-prepared Au-CdSe NWs on different 8 µm electrode gap devices.

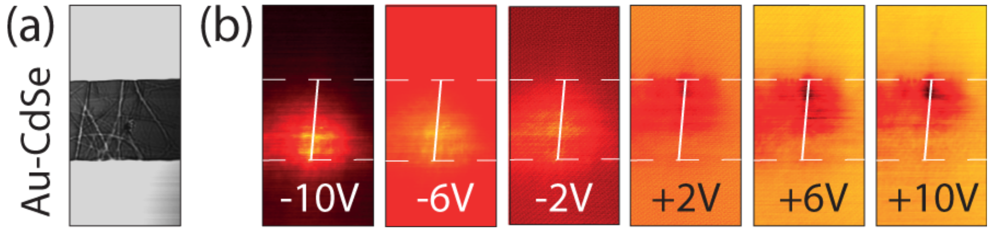

Figure S9 Optical reflection (a) and SPCM (b) measurements of the aged Au-CdSe NWs on 8 µm electrode gap device.

8. Synthesis of Au nanoparticles

Chemicals.

Gold (III) chloride ($AuCl_3$ (99%), oleylamine (70%), 1-oleic acid (90%) dodecyldimethylammonium bromide (DDAB) $[CH_3(CH_2)_9]_2N(CH3)_2Br$ (98%), were purchased from Sigma-Aldrich. Anhydrous ethanol, chloroform, toluene, and hexane were purchased from Carlo Erba reagents. All chemicals were used as received without any further treatment or purification.

Synthesis of gold nanocrystals.

In short, the gold (Au) nanocrystals were synthesized by reducing $AuCl_3$ by $NaBH_4$ in a toluene solution of DDAB, followed by the surface capping of Au nanocrystals with oleylamine (or other appropriate surfactants to render solubility in different solvents). In a typical synthesis, about 40 mg of

$AuCl_3$ and 90 mg of DDAB salts were dissolved in 30 ml of toluene in a round bottom flask, to which about 1.5 mL (of a 0.3 M sodium borohydride) solution were added dropwise carefully, and the resulted solution was stirred for about 2 hr. Then, 1.5 mL of oleylamine (surfactant) was added in drops, and the mixture was heated to 80 °C for 1 hour and then cooled to room temperature. The Au nanocrystals were washed and precipitated with ethanol. The conventional TEM image is reported in Figure S11, showing the as-prepared Au nanocrystals on a Cu TEM grid. These nanocrystals are quite stable and also amenable for further functionalization with a wide range of surfactants.

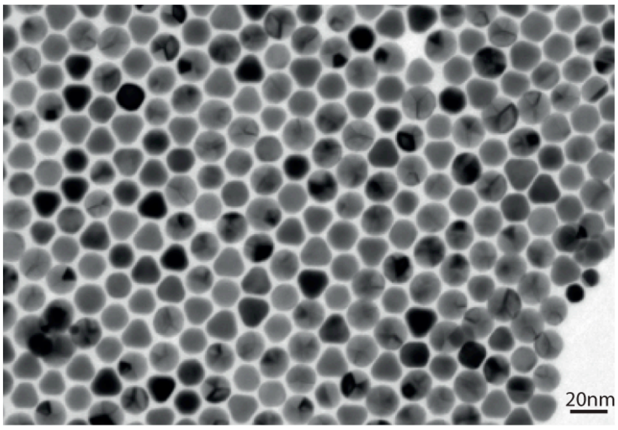

Figure S10. TEM image of the Au NPs.

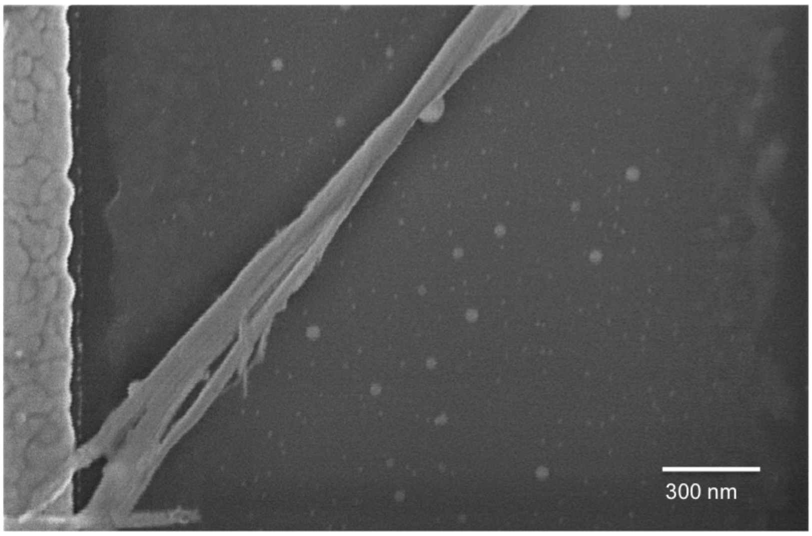

Figure S11. SEM image of CdSe NW device after the Au NPs were deposited by spin-coating from ethanol solution.

9. Photo-current voltage curve fitting with the Drndic model (ref. 28 of main text)

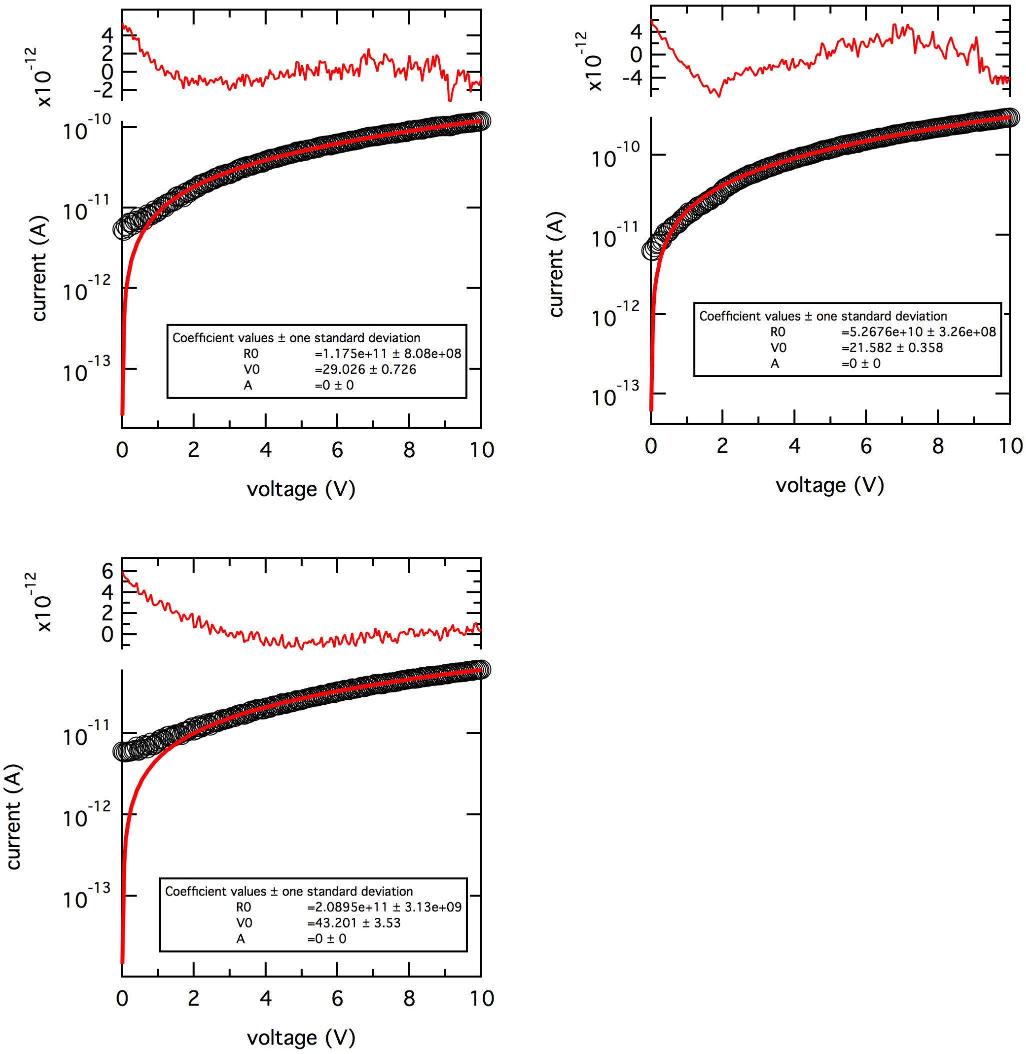

Figure S12. Fitting of the photocurrent-voltage curves recorded from bare CdSe NWs deposited on interdigitated electrodes with 8 µm separation. The fitting function is I(V) = V/R0 * exp(V/V0), as described in the text. The residuals of the fitting are plotted in the upper panels of the individual graphs.

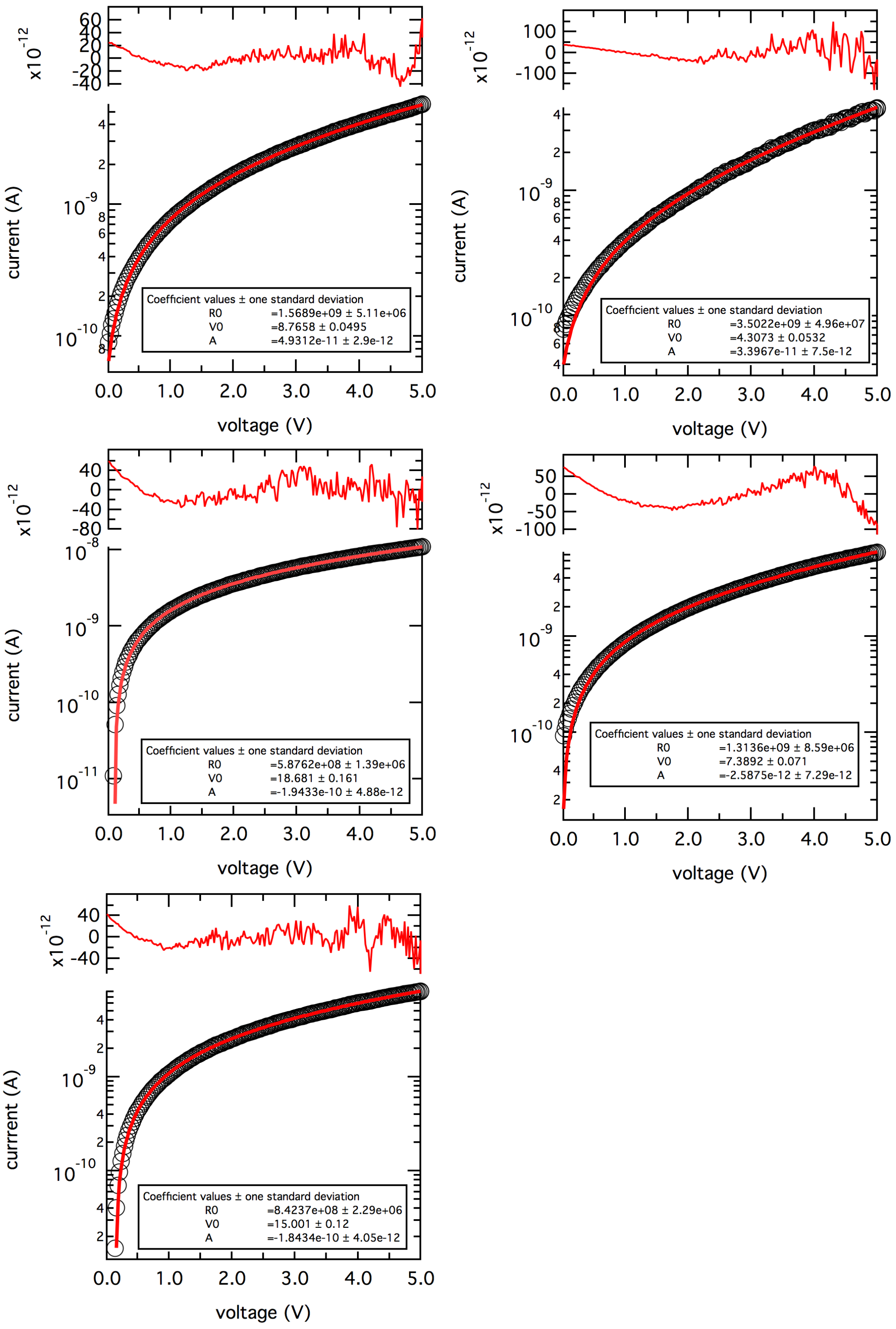

Figure S13. Fitting of the photocurrent-voltage curves recorded from Au-CdSe NWs deposited on interdigitated electrodes with 8 µm separation. The fitting function is I(V) = A + V/R0 * exp(V/V0), as described in the text, and A is a constant that compensates a small offset in current that could result from the current amplifier. The residuals of the fitting are plotted in the upper panels of the individual graphs.