Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

High Efficiency Organic-Si Hybrid Solar Cells with One-dimensional CdS Interlayer

Zhangbo Lu, Guozhi Hou, Yu Zhu, Jiaming Chen, Jun Xu*, Kunji Chen

National Laboratory of Solid State Microstructures/School of Electronics Science and Engineering/Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, 210093, P. R. China

*Corresponding Email: junxu@nju.edu.cn

Note 1

*Contact resistivity test***:** To evaluate the electrical contact characteristic of the TiN/CdS rear contact, the Cox-Strack method is used to extract the contact resistivity, which involves a series of resistance measurements with different diameter front contacts, as shown in **Fig. 2a.** TiN/CdS films were deposited on Si substrates through a shadow mask, which is engraved with the array of dots with the diameters of 1, 2, 3, 4, 5 and 6 mm. Finally, Al is employed as the rear electrode on the Si substrates. Based on the above, a series of resistance measurements are taken between the array of different diameter front contacts and the full - area rear contact. The total resistance (R_T) can be written as

$$R_T = \frac{\rho}{d\pi} tan^{-1} \frac{4}{d/t} + \frac{4\rho_c}{\pi d^2} + R_0$$

where ρ is the resistivity of the TiN film, d is the diameter of the front circular contact, t is the total thickness of the TiN/CdS film, ρ_c is the specific contact resistance, and R_0 is the residual resistance caused by n-Si/Al contact. The total resistance consists of three parts: 1) the resistivity of the TiN/CdS film (the first term on right-hand side); 2) the specific contact resistance at Si/TiN/CdS contact (the second term on the right-hand side); 3) the residual resistance of rear n-Si/Al contact. Normally, the resistivity of the TiN/CdS layer and R_0 can be negligible, so we can extract the ρ_c by fitting the total resistance with the different diameters.

Note 2

KPFM Measurement: KPFM measurement was performed in a commercial multimode atomic force microscopy (AFM, Bruker Nanoscope 3D) system under clean dry ambient atmosphere, based on an amplitude modulation (AM) dual-pass technique. In the first pass, the tip (Pt-Ir coated, Bruker SCM-PIT type) scanned the sample in tapping mode to acquire the topography information; then in the second pass, the tip lifted a distance (15 nm in our experiment) above the sample surface and was applied to a DC/AC mixture voltage at the same time. The AC voltage (V_{AC}=500 mV in our experiment) excited at the cantilever resonant frequency drove the tip oscillating, while the DC voltage (V_{DC}) was adjusted by the Kelvin feedback system to minimize the tip oscillation amplitude and was output as the KPFM signal. The configuration of our KPFM measurement and the sample structure are schematically shown in **Fig. S5**.

Note 3

Cyclic Voltammetry measurement: For all the electrochemical tests, a three-electrode system was used to conduct the electrochemical measurements at an electrochemical workstation (CHI 660E). The CdS NWs (2.0 mg) was dispersed in 1 ml ethanol solution with 10 μl 5 wt% Nafion by stirring for half an hour to form a uniform dispersion. The working electrode was fabricated by casting 10 μl CdS NW dispersion onto a glassy carbon electrode (GCE) (diameter: 5 mm, area: 0.196 cm^2). A Pt wire and Ag/Ag^+ (Ag wires with 0.1 M $AgNO_3$ in acetonitrile) were used as counter electrode and reference electrode, respectively. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) dissolved in acetonitrile was employed as the supporting electrolyte. The scan rate was set at 50 mV/s. The HOMO and LUMO energy levels can be calculated from the onset oxidation potential (E^{ox}) and onset reduction potential (E^{red}), respectively, according to the following equations:

$$E_{HOMO} = -(E^{ox}+4.71)\ \text{eV} \quad (2)$$

$$E_{LUMO} = -(E^{red}+4.71)\ \text{eV} \quad (3)$$

$$E_{LUMO} = E_{HOMO} + E_g \quad (4)$$

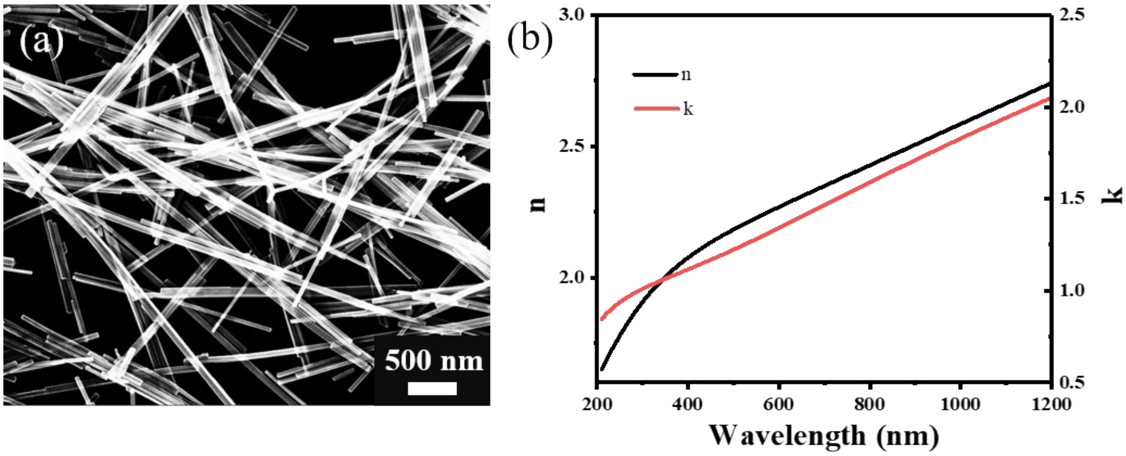

Fig. S1. (a) SEM image of CdS nanowires spin-coated on the back of silicon wafer, (b) Refractive index (*n*) and absorption coefficient (*k*) curves of the TiN film.

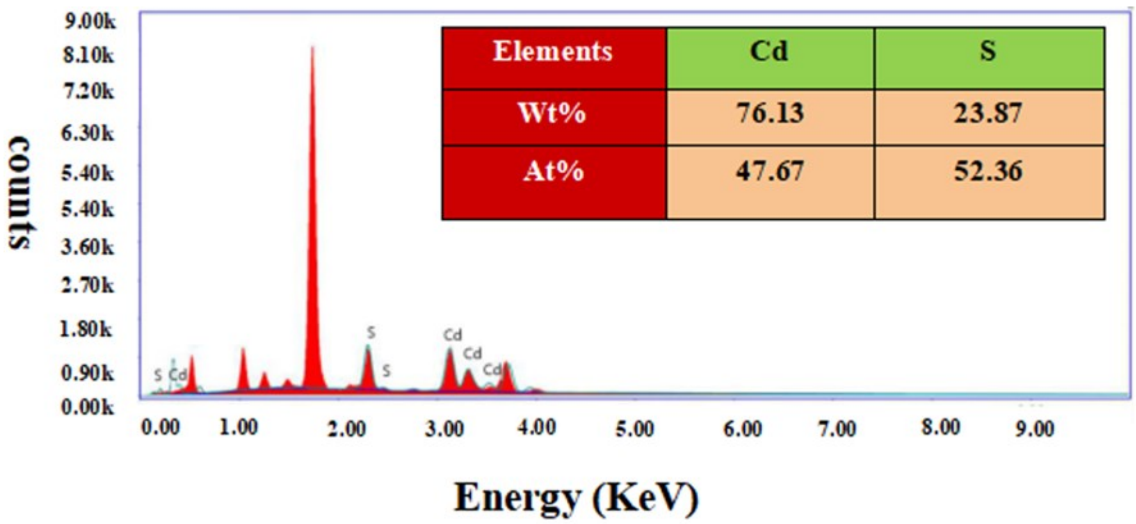

Fig. S2. Energy dispersive spectra taken from the CdS nanowires.

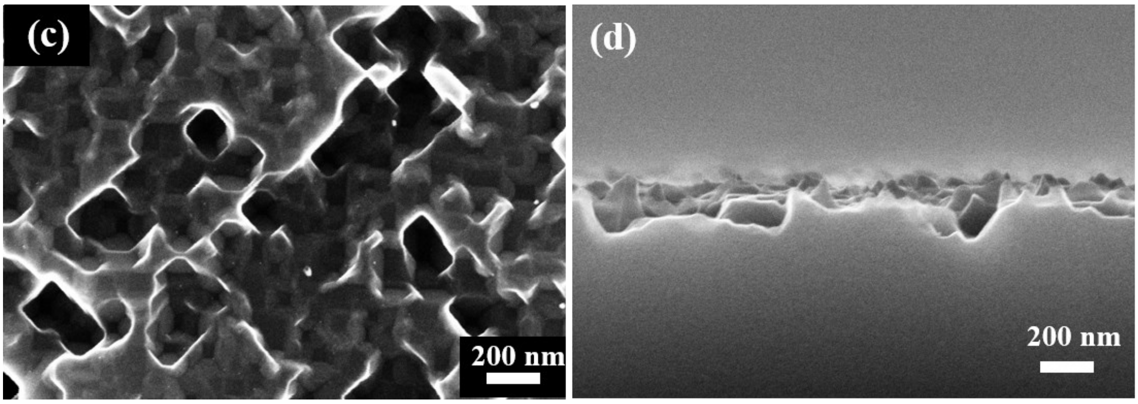

Fig. S3. SEM image of nanostructured Si obtained by TMAH modified Si nanowires

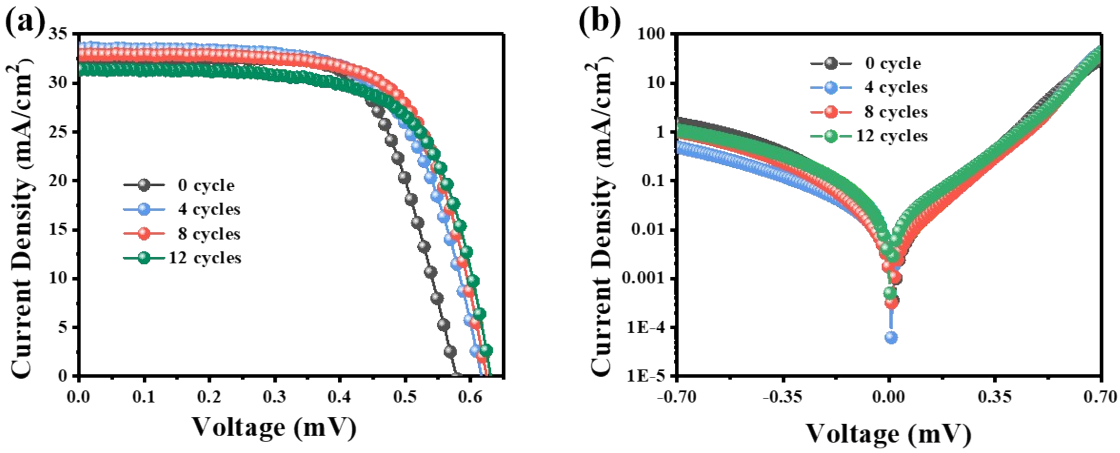

Fig. S4. (a) Photocurrent *J–V* curves, and (b) dark *J–V* curves of PEDOT:PSS/Si solar cells based on the CdS nanowire layer by spin-coating different cycles.

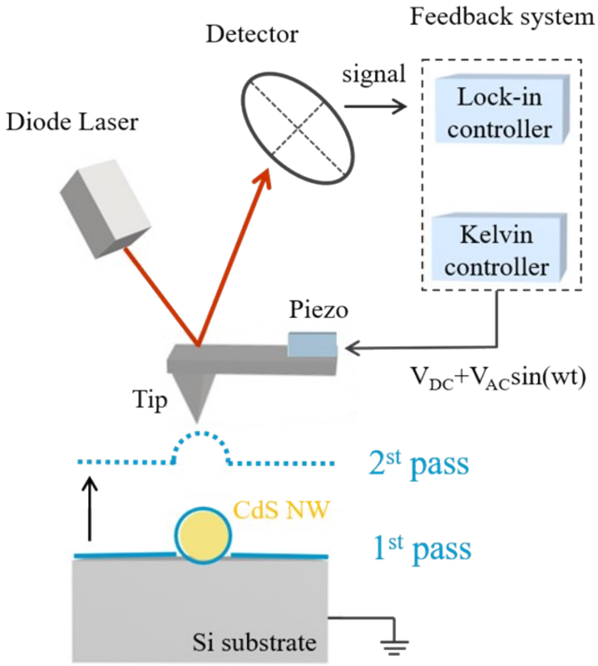

Fig. S5. The sample structure and configuration of dual-pass AM mode KPFM measurement. During the second-pass scan, a DC and AC mixed voltage is applied to the tip, and the Kelvin feedback system minimizes the tip oscillation and outputs V_{DC} as KPFM signal.

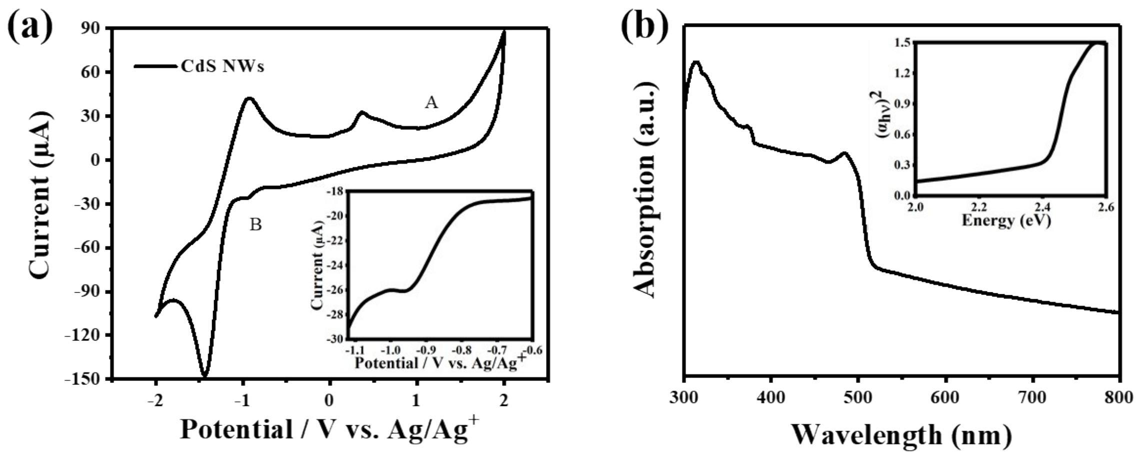

Fig. S6. (a) cyclic voltammetry of CdS nanowires in acetonitrile solution (The inset is a partial enlarged view of area B). (b) UV/Vis absorption spectrum of CdS NWs (The inset is the fitted optical band gap diagram).

Table S1. Photovoltaic performance of PEDOT:PSS/Si solar cells based on the CdS nanowire layer by spin-coating different cycles.

Spin-coating cycles	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0	578	32.57	68.12	12.83
4	617	33.53	65.02	13.45
8	625	32.92	68.26	14.04
12	630	31.38	67.59	13.36

Table S2. Summary of diode ideality factor (n), reverse saturation current density (I_0), and barrier height (φ_B) which is obtained by dark J-V curves based on different rear electrodes fabricated under the same conditions.

Contact Type	n	I_0 (A)	Φ_B (eV)	R_s ($\Omega\cdot cm^2$)
Al	1.82	7.37×10^{-7}	0.78	10.42
TiN/Al	1.69	3.99×10^{-7}	0.80	7.96
TiN/CdS NWs/Al	1.63	1.37×10^{-8}	0.89	4.86

Table S3. Optical and electrochemical properties of CdS NWs.

ETL	E^{ox} (V)	E^{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
CdS NWs	1.55	-0.80	-6.26	3.91	2.35