

Nanobelt-Carbon Nanotube Cross-Junction Solar Cells

Enzheng Shi,¹ Jingqi Nie,² Xiaojun Qin,³ Zhongjun Li,⁴ Luhui Zhang,¹ Zhen Li,⁵ Peixu Li,⁵ Yi Jia,⁵ Chunyan Ji,¹ Jinquan Wei,⁵ Kunlin Wang,⁵ Hongwei Zhu,⁵ Dehai Wu,⁵ Yan Li,³ Ying Fang,⁴ Weizhong Qian,² Fei Wei,² Anyuan Cao.^{1*}

¹ Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China

² Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China

³ Beijing National Laboratory for Molecular Sciences, National Laboratory of Rare Earth Material Chemistry and Application, Key Laboratory for the Physics and Chemistry of Nanodevices, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

⁴ National Center for Nanoscience and Technology, 11 Beiyitiao Street, Zhongguancun, Beijing 100190, P. R. China

⁵ Key Laboratory for Advanced Materials Processing Technology and Department of Mechanical Engineering, Tsinghua University, Beijing 100084, P. R. China

Supporting Information:

- 1. Experimental materials and methods.**
- 2. Figure S1. Electronic property assignment of the double-walled CNT in Figure 2.**
- 3. Figure S2. Band diagram of metallic CNT- CdSe and semiconducting CNT- CdSe cross-junctions.**
- 4. Figure S3. Raman spectra and AFM images of the two CNTs in Figure 4a.**
- 5. Figure S4. AFM images and Raman spectra of the 8 CNTs in Figure 5.**

1. Experimental

Synthesis of long horizontal CNTs. The substrate was a 4-inch Si wafer (p-type, 100 crystalline structure, 0.05~ 0.20 Ω -cm, 400 μm in thickness) with 300 nm oxide. We cut the substrate into rectangle sheets that were 3-8 cm long and 0.6~1 cm wide and washed them by sonication in acetone, ethanol, de-ionized water for 5 min in sequence. Then the substrate was dried in air at 200 $^{\circ}\text{C}$ and ready for catalyst deposition. A 0.03 M ethanol solution of FeCl_3 was dropped onto one edge of the Si sheet to form a catalyst source region (1 mm wide). The catalyst-loaded Si substrate was placed into a 1.5 m long quartz tube (30 mm in diameter) furnace. The catalyst source region was placed near the gas entrance and the long Si sheet was directed toward the gas flow. The substrate was heated at 900 $^{\circ}\text{C}$ for 20 min in a hydrogen atmosphere to decompose and reduce the catalyst precursor into Fe nanoparticles. When the temperature was increased to 1000 $^{\circ}\text{C}$, a mixture of CH_4 and H_2 (30 sccm CH_4 and 60 sccm H_2) was fed into the reactor for 20-40 min. Then the growth was terminated by switching off the reactant gas and the furnace was cooled down to room temperature.

Synthesis of CdSe nanobelts. The CVD process was carried out in a tube furnace with a one inch-diameter quartz tube. About 13 mg source powder (CdSe, 10 μm size, 99.99%, Aldrich) was placed in an alumina boat and then loaded into the center of the furnace. Slices of Si wafer (with 300 nm oxide) coated with 5 nm Au films through thermal evaporation were used as the growth substrate. The substrate was placed in the downstream of the CdSe source, with a distance of about 15 cm. The quartz tube was flushed by Ar flow at a rate of 200 sccm for 5 minutes to remove air before heated. After that, the furnace was heated to 780- 800 $^{\circ}\text{C}$ in 20 minutes. During the growth process, Ar gas was flowing at a constant rate of 200 sccm through the quartz tube. The growth period was typically 2 hours. After reaction, mm-long CdSe nanobelts were grown on the Si substrate.

Characterization methods. The morphology and structure of CNTs, CdSe nanobelts and solar cell devices were characterized by SEM (Hitachi S4800), optical microscope (Olympus BX51M), and AFM scanning (Dimension 3100). Raman measurements on individual CNTs were performed under ambient conditions using a 633 nm (1.96 eV) and a 532 nm (2.33 eV) laser on a Jobin-Yvon HR800 Spectrometer. Solar cell tests were carried out by Keithley 2635A and a solar simulator (Newport Thermo Oriel 91195A-1000) under AM 1.5G condition at an illumination intensity of 75-100 mW/cm², calibrated by a standard Si solar cell (91150V).

Fabrication of CdSe-CNT cross-junction solar cells. The fabrication of solar cells involves 4 steps, as shown in Figure 1a. First, we located the as-grown horizontal long CNTs on the Si substrate by SEM characterization at low acceleration voltage (1.5 kV). Then, a piece of CdSe nanobelt was transferred onto the marked position close to the CNTs on Si surface. We maintained a perpendicular arrangement between the nanobelt and CNT in order to form a cross-junction. This could be done by manual manipulation using a sharp needle to directly pick up a single nanobelt due to its macroscopic size. After that, one droplet of ethanol was delivered to the CdSe-CNT interface to collapse the nanobelt onto the CNT by ethanol evaporation. This significantly improved the contact between the CNT and CdSe nanobelt. Finally, to make the solar cell, one side of the CNT was wired as the positive and the nanobelt as the negative electrode by silver paste and silver wire. To make solar cell arrays on a single CdSe nanobelt, Si substrates with multiple parallel as-grown CNTs were selected and went through the same fabrication process.

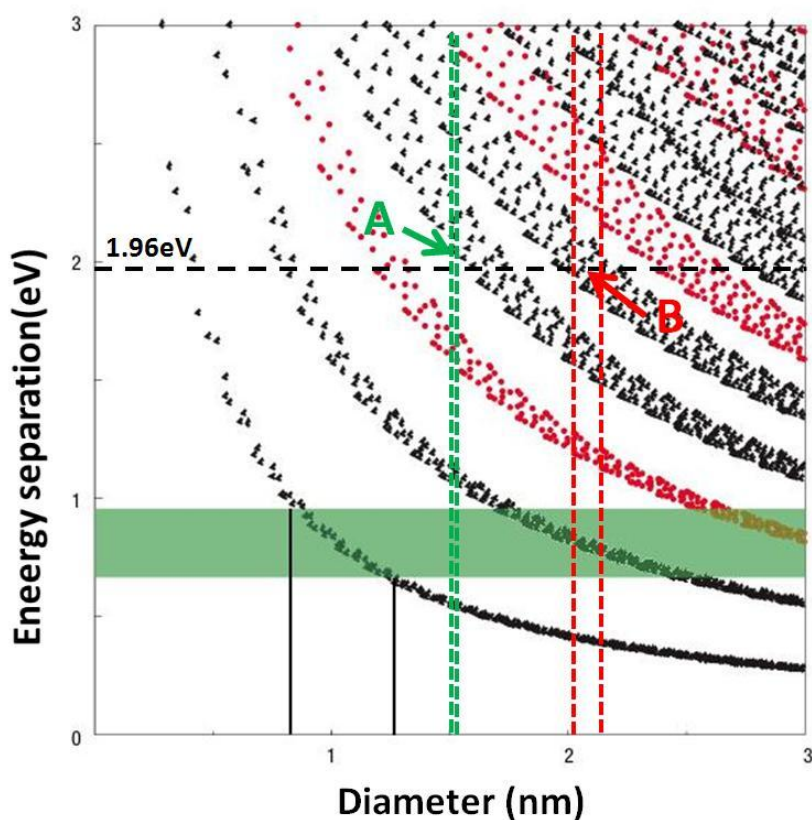


Figure S1. Electronic property assignment of the double-walled CNT in Figure 2. Based on the electronic transition energy corresponding to 633 nm wavelength ($E_{ii} = 1.96$ eV) and diameters of the 2 tubes speculated from Raman spectra, two dots, marked as A and B, with an uncertain range are drawn in the Kataura plot. In the Kataura plot, the black and red dots represent semiconducting and metallic type of nanotubes, respectively.

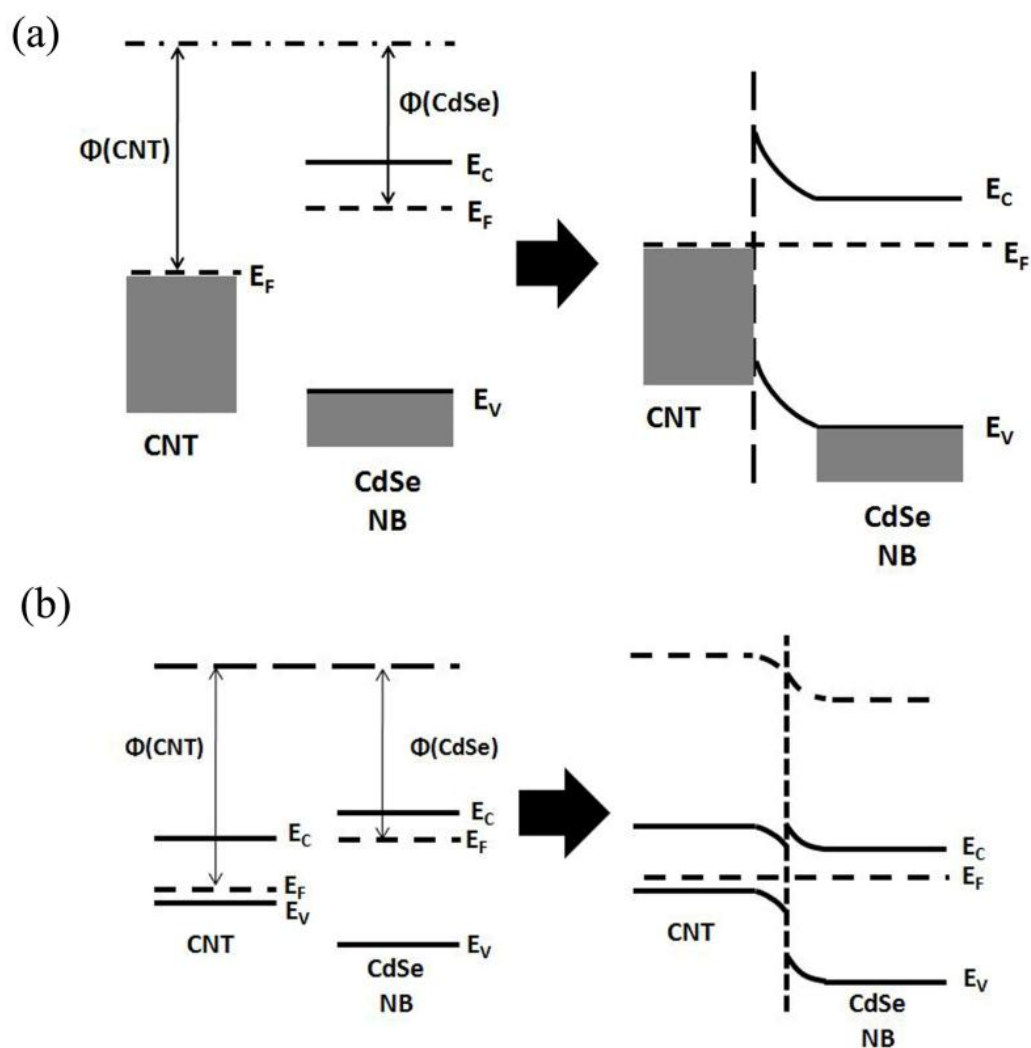


Figure S2. Band diagrams formed at the cross-junction between a CdSe nanobelt with (a) a metallic CNT, and (b) a semiconducting CNT, respectively.

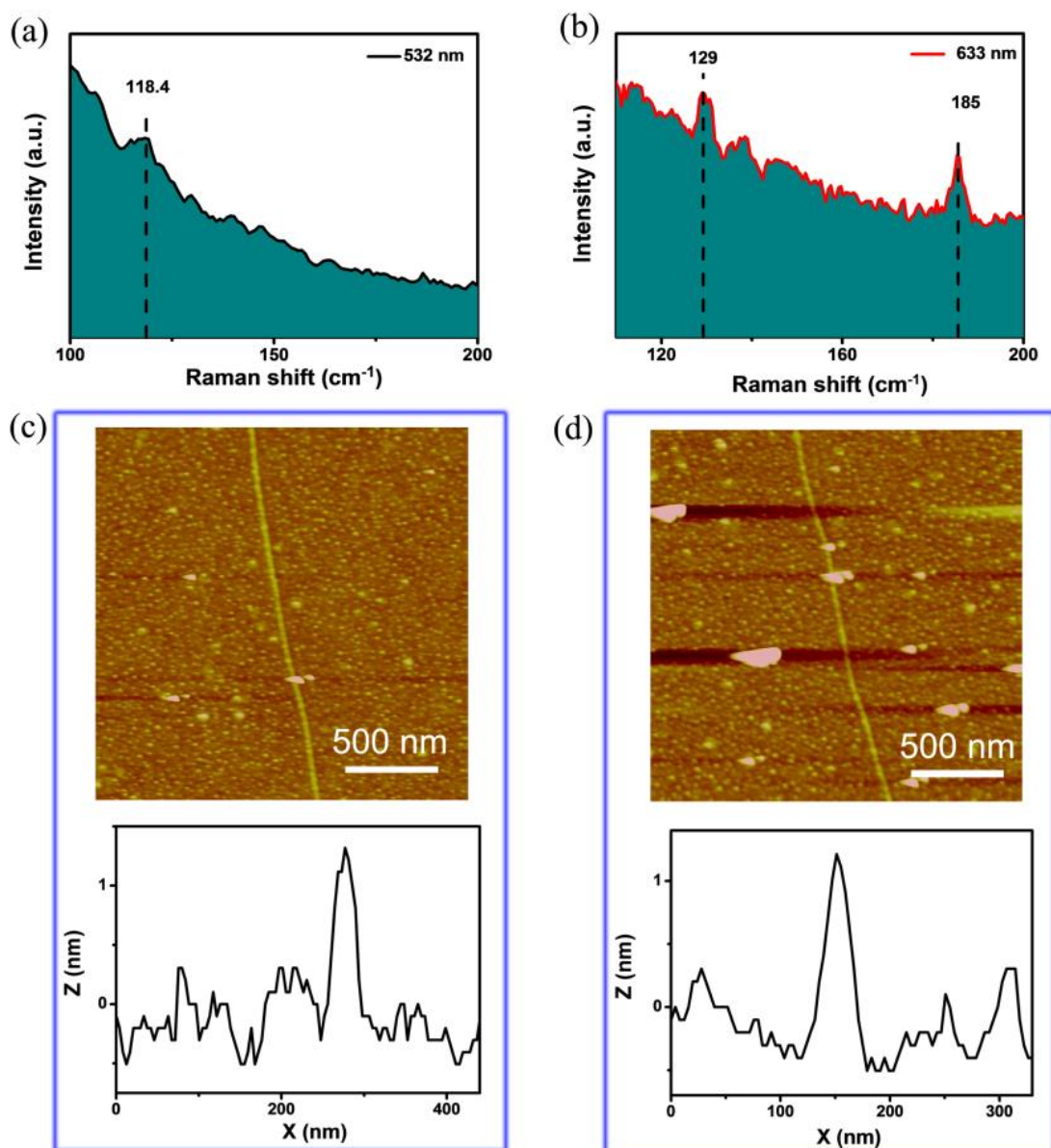


Figure S3. Raman spectra and AFM images of the 2 CNTs in Figure 4a. (a) RBM spectrum of the upper CNT recorded at excitation wavelength of 532 nm, showing a peak at 118.4 cm^{-1} , which corresponds to a diameter around 2.1-2.2 nm. (b) RBM spectra of the lower CNT recorded at excitation wavelength of 633 nm, showing 2 peaks at 129 cm^{-1} and 185 cm^{-1} , which correspond to diameters of around 1.3 nm and 1.95 nm. (c) AFM image of the upper CNT. From the height distribution of the tube, we find the diameter of this CNT is about 1.9 nm, which is consistent with the value speculated from RBM peak in (a). (d) AFM image of the lower CNT. The height distribution is consistent with the diameter value estimated from RBM peak in (b). Given the difference between two tube diameters based on RBM peaks in (b) and the uniform morphology along the length, the lower CNT is probably a double-walled tube.

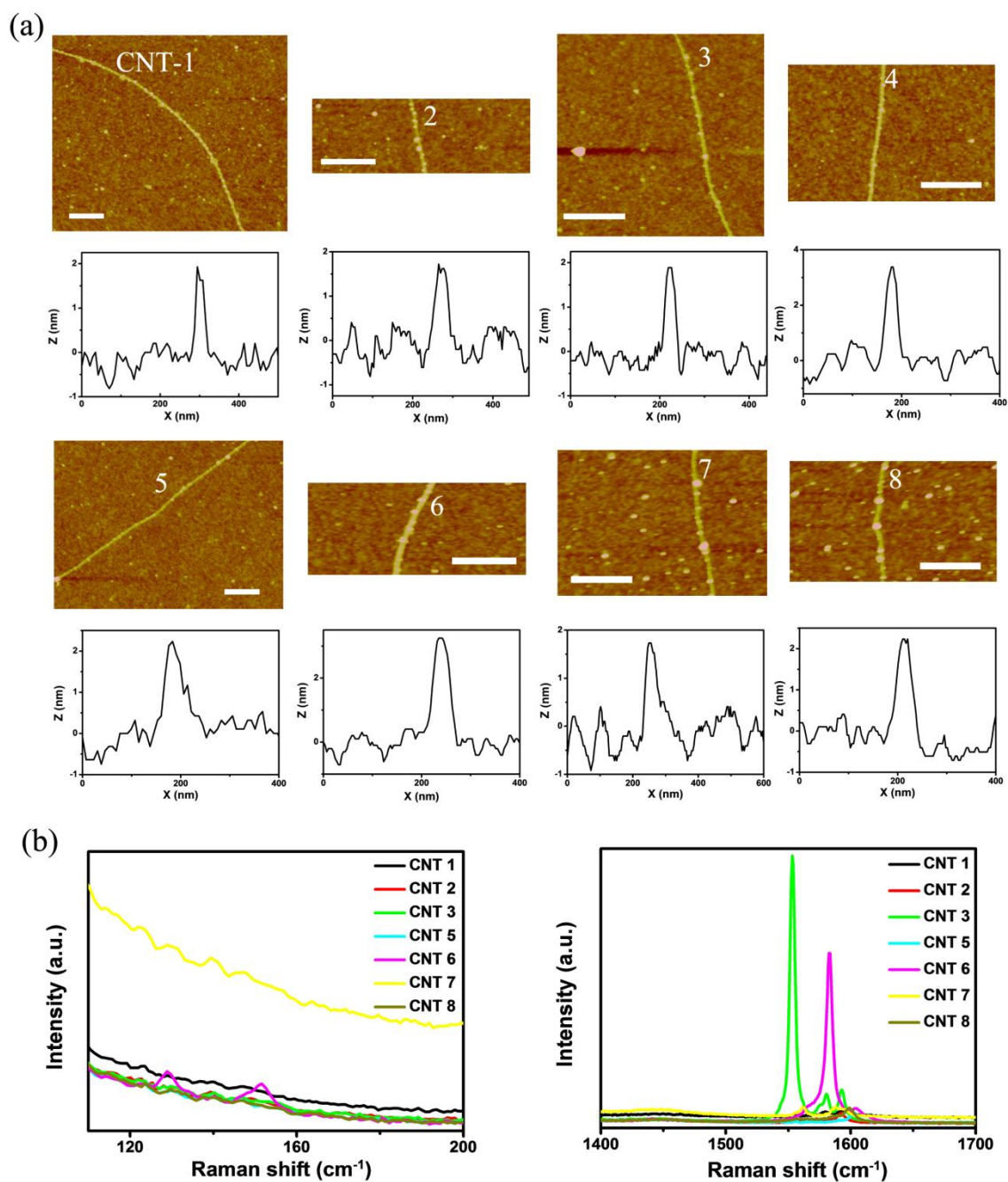


Figure S4. (a) AFM images and (b) Raman spectra (excitation 532 nm) of the 8 CNTs in Figure 5 in the main text. Scale bars in the 8 AFM images in (a) are all 500 nm. As the 4th CNT can not be excited under 532 nm, 633 nm, or 785 nm laser, its Raman signal is not listed here.