

Supporting Information

Step-by-step build-up of ordered p-n heterojunctions at nanoscale for efficient light harvesting

Junfeng Yan^{ab}, Qian Ye^a, Xiuxun Han^a, Feng Zhou^{a*}

^a Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou,
730000, China; ^b Graduate School, Chinese Academy of Sciences, Beijing, 100039,
China.

Email: zhouf@lzb.ac.cn

Experimental Section

1 Reagent:

Ultrapure water used in all experiments was obtained from a NANOpure Infinity system from Barnstead/Thermolyne Corporation. 5-norbornene-2-methanol was purchased from Sigma-Aldrich (Shanghai, China). Grubbs second catalyst was used as received from Sigma-Aldrich. The Anchor Agent N-(3,4-Dihydroxyphen-ethyl) bicycle [2.2.1] hept-5-ene-2-carboxamide was synthesized according to previous report.¹ Other reagents were used as received.

2 The synthesis of 5-norbornene-2-methanol-3-thiopheneacetic acid ester

2.1 Synthesis of compound 1 and 2

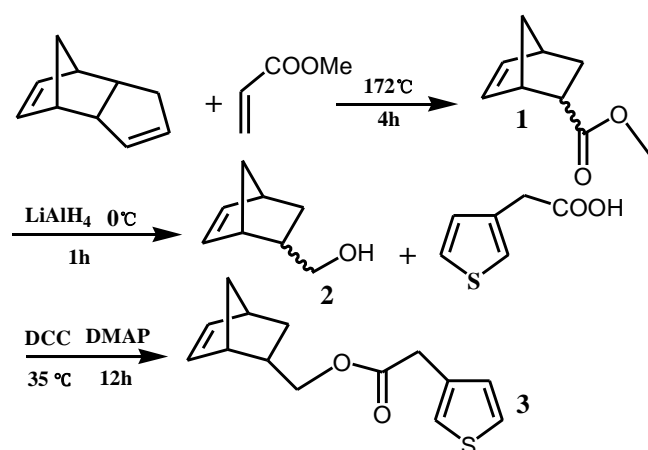
26 mL cyclopentadiene (194 mmol) and 35 mL methyl acrylate (388 mmol) were added

into a Teflon-lined autoclave of 100 mL capacity, then it was kept at 172°C for 4 hours with adding 100 mg hydroquinone as a free radical inhibitor to enable the Diels-Alder reaction worked well.² Finally, the mixture was evaporated under reduced pressure to collect a colourless liquid at 45-48°C (compound 1). ¹H-NMR (400 MHz, CDCl₃), (ppm): (mixture of exo and endo isomers) 5.89-6.17 (m, 2H, -CH=CH-), 3.67, 3.60 (s, 1.5H, 1.5H, -CH₃), 1.23-3.18 (m, 7 H, 7 aliph. Ring-H).

1g compound 1 (6.58 mmol) was charged into a flask containing 60 mL diethyl ether, then 0.249g (6.58 mmol) lithium aluminium hydride LiAlH₄ was added slowly under ice water bath and the reaction was stirred for 30 minutes. The mixture was sequentially kept at room temperature for 30 minutes, then 5 mL water was added into the mixture to stop the reaction.³ The mixture solution was extracted with diethyl ether and dried over anhydrous MgSO₄, and the solvent was evaporated under reduced pressure to give a colorless liquid which is 5-norbornene-2-methanol (compound 2). The crude product was purified by silica gel column chromatography (Petroleum ether: Ethyl acetate =5:1), ¹H-NMR (400 MHz, CDCl₃), (ppm): (mixture of exo and endo isomers) 5.95-6.15 (m, 2H, -CH=CH-), 3.22-3.72 (m, 2H, -CH₂O-), 0.50-2.93 (m, 7 H, 7 aliph. Ring-H).

2.2 Synthesis of compound 3 (5-norbornene-2-methanol-3-thiopheneacetic acid ester, denoted as NMTE) A round-bottomed flask (50 mL) was charged with 5-norbornene-2-methanol (436mg, 351mmol), 3-thiopheneacetic acid (499mg, 351mmol), dicyclohexylcarbodiimide (DCC) (820 mg, 420 mmol), 4-(dimethylamino)-pyridine (DMAP) (10 mg, 82 mmol) and 25 mL anhydrous CH₂Cl₂. The reaction mixture was stirred for 12 h at 35°C, the crude reaction product was extracted with anhydrous

CH₂Cl₂. The organic extracts was washed with water, saturated NaHCO₃ and NaCl solutions, and the solvent was evaporated under reduced pressure to give a yellow liquid. The crude product was purified by silica gel column chromatography (Petroleum ether: Ethyl acetate =10: 1) to give colorless viscous liquid. ¹H-NMR (400 MHz, CDCl₃), (ppm): (mixture of exo and endo isomers) 7.26-7.30 (m, 1H), 7.16 (s, 1H), 7.06 (d, 1H, *J* = 5.6Hz), 5.89-6.16 (m, 2H, -CH=CH-), 3.69-4.21 (m, 2H -CH₂O-), 3.68 (d, 2H, *J* = 5.6Hz, -CH₂CO-), 0.51-2.82 (*m*, 7 H, 7 aliph. Ring-H). ¹³C-NMR (100 MHz, CDCl₃), (ppm): 171.1, 137.6, 136.9, 136.1, 133.8, 132.1, 128.5, 125.7, 122.8, 69.0, 68.3, 49.3, 44.9, 43.8, 43.6, 42.2, 41.6, 37.9, 37.7, 36.0, 29.5, 28.9.



Scheme S1. The synthesis process of compound 1, compound 2 and compound 3.

3. Substrate preparation and modification

TiO₂ nanowires was synthesized from commercial P25 in a Teflonlined autoclave, as reported in our previous work.⁴ The preparation process of initiator modified TiO₂ nanowires has described previously.

4. Surface-initiated polymerization on TiO₂ nanowires

In a typical SI-ROMP, 50 mg of TiO₂ nanowires modified by anchor agent were immersed in a solution which contained 10 mg of Grubbs second catalyst in 3 mL of anhydrous dichloromethane and the mixture was stirred for 30 minutes under Ar protection. Then the product was carefully rinsed with pure dichloromethane for 3 times using centrifugation for removing the excess catalyst. The [Ru]-functionalized TiO₂ nanowires were immersed in 3 mL of freshly prepared solutions of monomers (100 mg NMTE in 3 mL dichloromethane). The reaction was performed at room temperature for 15 minutes, the resulting samples were isolated from the reaction mixture with extensively washed using centrifugation with pure dichloromethane. The polymer grafted samples were further dried under vacuum over night before further analysis.

5. Oxidation polymerization

The obtained samples in the above step was added into a flask with 20 mL chloroform under N₂ bubble, then 3-hexylthiophene (1.5 g, 8.93 mmol) was charged into the flask and FeCl₃ (2.9 g, 17.8 mmol) was slowly put in the reaction mixture. The reaction was performed for 24 h at room temperature under N₂ protection. The final product was repeatedly washed with methanol, tetrahydrofuran and diethyl ether and dried.

The polymerization of 3-thiopheneacetic acid was carried out with the similar way, 1.5g 3-thiopheneacetic acid was added into the reaction and other operation was followed as the above procedure. The polymer modified TiO₂ nanowires were immersed in 30 mL 0.5 M NaOH/MeOH for stirring 12 h and purified by repeated washing with ethanol using centrifugation. Then the sample was put into 30 mL 0.5 M Cd(Ac)₂/MeOH to exchange Cd ions and further purified by centrifugation. The polymer modified TiO₂

nanowires was put into an evacuated vial and H₂S gas was continuously injected into it for generating CdS nanoparticles, the solid/liquid reaction was performed for 12h to prepare CdS NCs/conductive polymer hybrid materials.

Using the above method, we have prepared CdS/P3THA-TiO₂ nanotubes materials.

6 Characterization

Fourier-transform infrared (FT-IR) spectroscopy were measured on a Nicolet is10 instrument (Thermo Scientific). Chemical composition information about the samples was obtained by X-ray photoelectron spectroscopy (XPS), the measurement was carried out on K-Alpha-surface Analysis (Thermon Scientific) using X-Ray Monochromatisation. Thermal stability was determined with a thermogravimetric analyzer (TGA) (Perkin-Elmer, PET) over a temperature range of 25-800 °C at a heating rate of 10°C/min under N₂ atmosphere. The morphology of these materials were investigated by transmission electron microscopy (TEM) (Hitachi model JEM-2010). The STEM and mapping images were carried out using a FEI Tecnai G2 F30 transmission electron microscope. UV-vis absorption spectra were performed using a Specord 50 spectrophotometer (Analytik Jena, Germany) at 1 cm path length.

7 Photoelectrochemical measurements

Photoelectrochemical measurements were performed in a two electrode cell, the hybrid materials on F-doped tin oxide (FTO) served as the working electrode and a Pt foil as the counter electrode. The photoelectrodes were prepared by doctor blading of hybrid paste (ethanol) on FTO with a surrounding adhesive tape as a frame. A conventional three-electrode cell was used to measure the current density vs voltage curve, including a saturated Ag/AgCl electrode (SCE) as reference electrode, a platinum counter

electrode, and hybrid materials/FTO as working electrode, which was performed on a CHI 660B electrochemical workstation (Shanghai, China). The light intensity is 150 mW/cm² under simulated sunlight and the cell area is 0.16 cm².

Results and Discussion

1 FI-IR spectrum

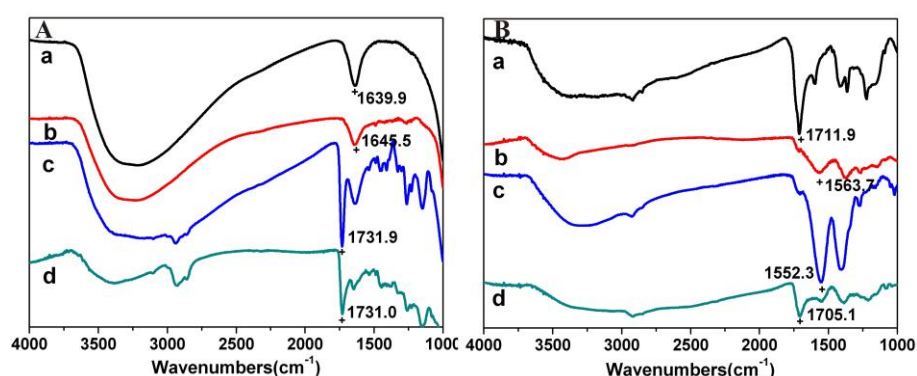


Figure S1. FR-IR spectra of A: (a) TiO₂ nanowires, (b) initiator modified TiO₂ nanowires, (c) P(NMTE)-TiO₂ nanowires, (d) P3HT-TiO₂ nanowires; B: (a) P3HTA-TiO₂ nanowires, (b) Na-P3HTA-TiO₂ nanowires (c) Cd-P3HTA-TiO₂ nanowires, (d) CdS-P3HTA-TiO₂ nanowires.

FT-IR transmission spectra are employed to confirm the grafted polymers on TiO₂ nanowires. Plain TiO₂ nanowires shows a featureless spectrum except for wide absorption peaks of absorbed water and hydroxyl groups around 3000 cm⁻¹. Typical features of the initiator modified TiO₂ nanowires exhibits absorbance peaks at 1645.5 cm⁻¹ from C=O stretch of amide carbonyl in the initiator molecules, after ROMP polymerization, that peaks appeared at 1731.9 cm⁻¹ can be concluded from C=O stretch of the ester carbonyl in the monomers. When the oxidation polymerization with FeCl₃ as the catalysis to polymerize 3-hexylthiophene monomers, the peaks at 1731.0 cm⁻¹ due

to the C=O stretch of the ester carbonyl. These characteristic bands of 1508.9, 1456 cm^{-1} (aromatic C=C stretching), 1391.2 cm^{-1} (methyl bending), 1146.4 cm^{-1} (C-S stretching) can be used to confirm the P3HT. (Fig. S1(A))

In order to further elucidate the preparation process of CdS nanocrystals/polymer hybrid structures, FT-IR transmission spectrum are carried out as shown in Fig. S1(B). The peaks of 1711.9 cm^{-1} can be ascribed to the C=O stretch of poly(3-thiopheneacetic acid) grafting, after the Na ions exchange, the asymmetric vibration of the carboxylate groups shifted to 1563.7 cm^{-1} , corresponding to the IR absorbance of ionized carboxylate. Similarly, when Cd^{2+} ions was immobilized onto polymer chains, the peaks of 1552.3 cm^{-1} corresponded to the ionized carboxylate. After reacted with H_2S gas, the peaks of 1705.1 cm^{-1} can be ascribed to the protonated carboxylic groups. From these results, after exposure to H_2S gas, Cd^{2+} ions participated in the formation of CdS nanocrystals.

2. Chemical composition analysis (XPS)

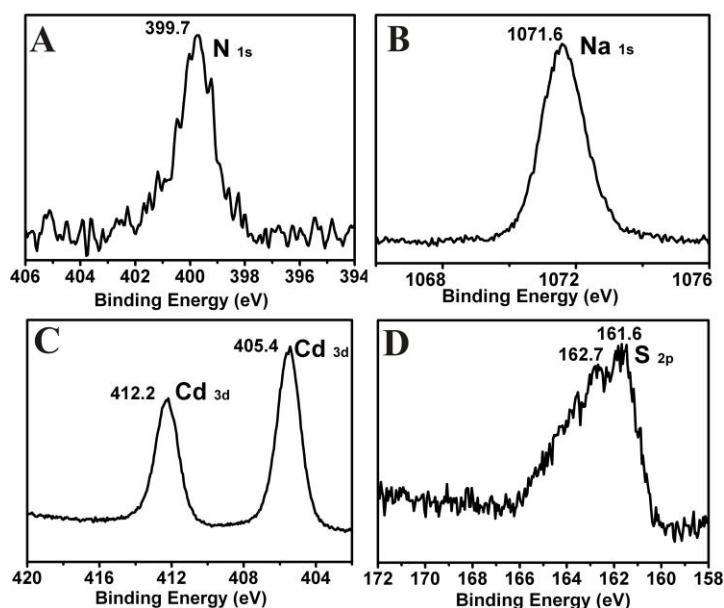


Figure S2. XPS survey spectra of N (1s) of initiator modified TiO_2 nanowires (A), Na (1s) of

Na-P3THA-TiO₂ nanowires (B), Cd (3d) of Cd-P3THA-TiO₂ nanowires and S (2p) of CdS-P3THA-TiO₂ nanowires.

The high-resolution XPS spectral analysis in Fig. S2(A) shows that the N (1s) peaks corresponding to the successful initiator anchoring. When P3THA brushes grafted onto TiO₂ nanowires, the Na (1s) peak at 1071.3 eV provide direct proof of the successful Na⁺ exchange (Fig. S2(B)), second cationic exchange was carried out in Cd²⁺ solution, in Fig. S2(C), the Cd 3d peaks appears at binding energies of 405.4 eV and 412.2 eV can confirm the successful Cd²⁺ exchange. When H₂S gas was used to generate CdS nanocrystals, the S (2p) peak at binding energies of 161.6 and 162.7 eV can be used to confirm successful CdS NCs formation in Fig. S2(D).

Sample	XPS atomic concentration (%)					
	[N]	[O]	[Ti]	[C]	[Cd]	[S]
TiO ₂ NWs	0	47.27	17.53	35.2	0	0
Initiator-TiO ₂ NWs	1.03	34.53	14.75	49.68	0	0
P(NMTE)-TiO ₂ NWs	0	24.76	5.93	66.25	0	3.05
P3THA-TiO ₂ NWs	0	17.55	0.95	76.23	0	5.27
CdS-P3THA-TiO ₂ NWs	0	16.08	0	78.32	2.46	3.14

Table 1. Surface analysis results of TiO₂ nanowires (NWs), initiator-TiO₂ NWs, P(NBTA)-TiO₂ NWs, P3THA-TiO₂ NWs, CdS-P3THA-TiO₂ NWs.

3 TEM

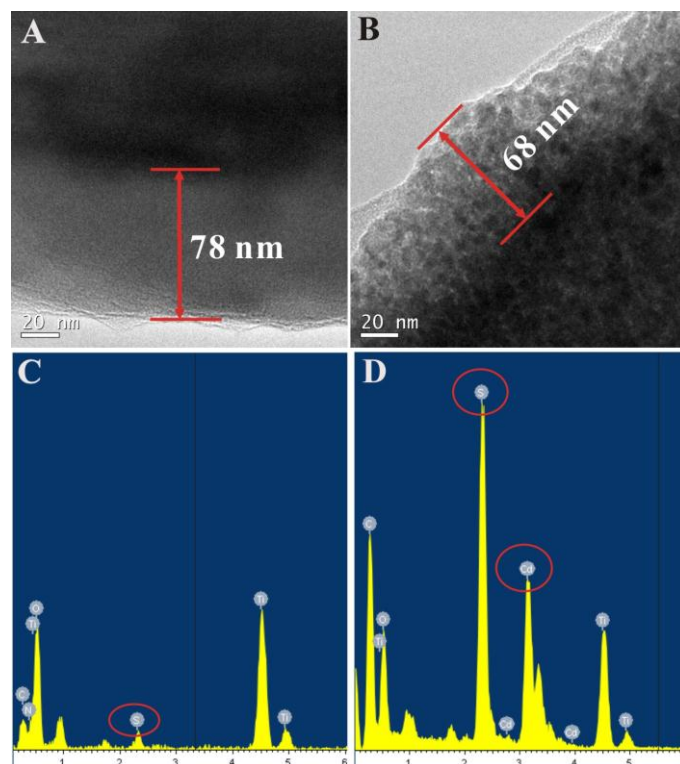


Figure S3. TEM images of (A) P3HTA-TiO₂ nanowires, (B) CdS-P3HTA-TiO₂ nanowires. Energy dispersive spectroscopy (EDS) spectra: (C) P3HTA-TiO₂ nanowires, (D) CdS-P3HTA-TiO₂ nanowires.

Fig. S3 (A) displays the TEM images of P3HTA on TiO₂ nanowires, the boundary is very clear that the polymer thickness can reach 78 nm. When CdS nanocrystals was prepared, we can see that high density nanoparticles adhered on both the polymer layer and TiO₂ nanowires, the boundary can be also easily distinguished due to the apparent color difference as shown in Fig. S3 (B). Energy dispersive spectrometer (EDS) was used to confirm the successful polymerization and CdS nanocrystals loading, Fig. S3 (C) shows that after polymerizing 3HTA monomers, the S signal appears corresponding to the S element in thiophene unit. When CdS nanocrystals formed, the S peak further increased and Cd signal appeared in Fig. S3 (D), so we can concluded that CdS nanocrystals have been formed via solid/gas reactions.

References

- 1 Q. Ye, X. Wang, S. Li and F. Zhou, *Macromolecules*, 2010, **43**, 5554-5560.
- 2 D. Huertas, M. Florscher and V. Dragojlovic, *Green Chem.*, 2009, **11**, 91-95.
- 3 W. Fischer, C. A. Grob, G. V. Sprecher, A. Waldner, *Helvetica Chimica Acta*, 1980, **63**, 928-937.
- 4 D. Wang, F. Zhou, C. Wang, W. Liu, *Microporous and Mesoporous Mater.*, 2008, **116**, 658-664.