# Supporting information for
# Si/poly-CuTAPc Coaxial Core-shell Nanowire Array as Enhanced Visible-light Pohotocatalyst for Hydrogen Production

## S1, Synthesis of CuTAPc[1]

3.5 g of Copper sulfate, 2 g of 4-nitrophthalic acid (Alfa Aesar), 0.3 g of ammonium chloride, 0.2 g of ammonium molybdate and excess urea (3 g) were finely grounded and placed in a 50 mL three-necked flask containing 10 mL of nitrobenzene. The reaction mixture was stirred at 185 °C for 3 h. The solid product was washed with alcohol until free from nitrobenzene. The product was treated twice with 20 mL of 1.0 M hydrochloric acid and 1.0 M sodium hydroxide. The chloride-free 4,9,16,23-tetranitrophthalocyaninecopper (II) was dried at 125 °C. About 1.2 g of finely grounded 4,9,16,23-tetranitrophthalocyaninecopper (II) was placed in 100 mL of water. To this slurry, 20 g of $Na_2S\cdot9H_2O$ was added and stirred at 50 °C for 5 h. The separated product was treated with 250 mL of 1.0 M hydrochloric acid and then 100 mL of 1.0 M sodium hydroxide solution, stirred for 1 h and centrifuged to separate the solid complex. The product was repeatedly treated with water, stirred and centrifuged until the material was free from sodium hydroxide and sodium chloride. The pure complex was dried in vacuum. The structure was characterized by a FTIR spectrophometer (Varian 3100 FTIR): (KBr, cm-1) 3336.8 (NH2), 1345.0, 1251.8, 1083.2 (C–N), 821.4, 863.5 (Ar), 746.1 950, 1605.6 (N–H). $^1$H NMR (400 MHz, DMSO-d6): δ= 8.39 (4H, s, Ar-H), 8.18 (d, 4H, Ar-H), 8.13 (4H, d, Ar-H). $^{13}$C NMR (100 MHz, DMSO-d6): δ ppm = 121.5, 123.2, 132.1, 134.4, 136.5, 139.1. MS[m/z] calculated for $C_{32}H_{20}N_{12}Cu$, 636; found, 634.5. Anal. Calcd for $C_{32}H_{20}N_{12}Cu$: C, 60.48; H, 3.13; N, 26.57 . Found: C, 59.81; H, 3.83; N, 24.68.

## S2, Synthesis of silicon nanowires array [2]

The commercial heavily doped n-type Si wafers(1~10Ω/cm) were washed with water and acetone and then immersed for 10 min (room temperature) in oxidant solution containing $H_2SO_4$ (97%) and $H_2O_2$ (35%) (3:1v/v) to entirely remove organics and to form a thin oxide layer. The wafers were immediately immersed into HF-$AgNO_3$ solution in sealed vessels and treatment for the designed time. The solution concentrations of HF and $AgNO_3$ were always chosen to be 5 and 0.02 mol/l, respectively. The Ag on the surface of nanowire was removed by 50% $HNO_3$.

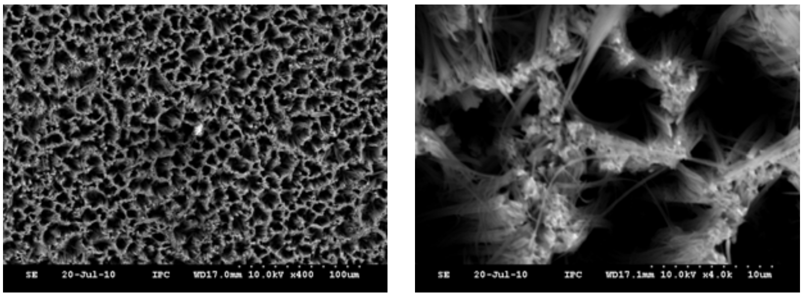

Figure S1 The SEM image of SiNWs arrays.

## S3, Schematic of the preparation of Si/poly-CuTAPc coaxial core-shell nanowire arrays electrode

The SiNWs arrays was washed several times by deionized water and then immersed into 50:1 HF solution for 10 min and then the H-terminated SiNWs arrays was washed several times by ethanol and acetone, and then was immersed in 20% $HNO_3$ solution for 15 min to ensure the surface was OH-terminated. The poly-CuTAPc film was coated on the Si nanowires' surface through electro-polymerization. A three-electrode cell was composed of a SiNWs arrays work electrode, a Pt wire counter electrode and a Saturated Calomel Electrode(SCE) reference electrode. The electrolyte containing 0.1 M TEAP (tetra-n-butyylammonium perchlorate) and 10 uM CuTAPc, $N_2$ bubbled DMSO (dimethyl sulfoxide) solution. The potential window used for cyclic voltammetric electro-polymerization of the CuTAPc onto the SiNWs electrodes was +1.0 to -0.600 V (vs SCE), at a scan rate of 100 mv/s (Figure S2). Once the electro-polymerization was completed, the work electrode was rinsed with DMSO several times to remove the CuTAPc monomer and then washed with acetone to remove the DMSO.

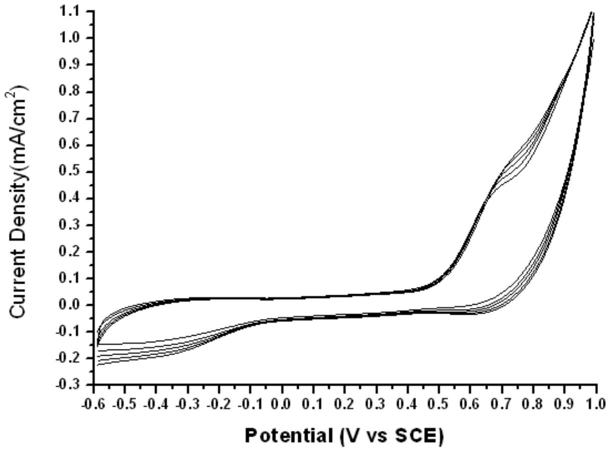

Figure S2 Repeated cyclic voltammograms recorded during the first 5 cycles of electropolymerization, scan rate, 100 mV/s; initial potential, +1.000 V; working electrode, OH-terminated n-type SiNWs arrays.

An experiment was conducted to investigate the majority of the carrier in the polymer film (Org. Lett. 2011, 13, 3146), the result was shown in figure S3: The hole-only device consisted of the following layers: p-Si (1~10 Ω/cm)/poly-CuTAPc (120 cycles)/$MoO_3$ (2nm)/Al (50 nm) and the electron-only device consisted of the following layers: n-Si (1~10 Ω/cm)/poly-CuTAPc (120 cycles)/TPBI (30 nm)/$Cs_2CO_3$ (2 nm)/Al (50 nm). The results indicated that the majority carrier of the poly-CuTAPc was the holes.

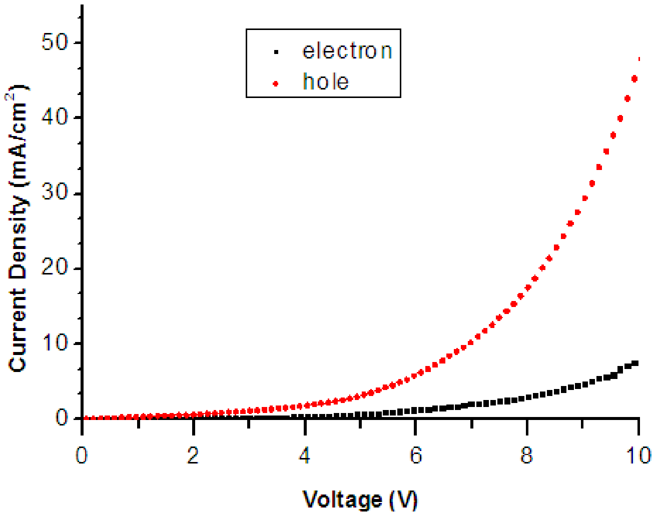

Figure S3 Current density versus voltage for the hole-only and electron-only devices of poly-CuTAPc film.

## S4, The IR of Si/poly-CuTAPc coaxial core-shell nanowires.

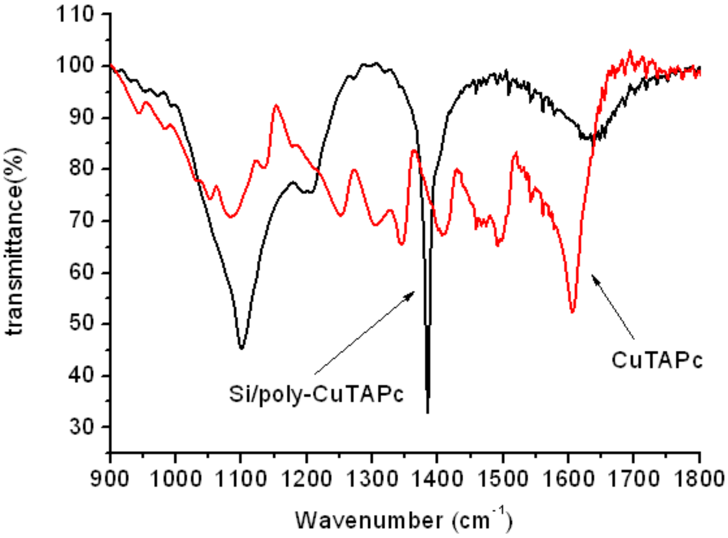

Figure S4 The IR of Si/poly-CuTAPc coaxial core-shell nanowires and CuTAPc.

The IR of Si/poly-CuTAPc coaxial core-shell nanowires and CuTAPc was measured by Varian 3100 FT-IR.

## S5, The UV-visible absorption of Si/poly-CuTAPc coaxial core-shell nanowire arrays and Si NWs arrays.

The UV-visible absorption spectra of SiNWs array, Si/poly-CuTAPc coaxial core-shell nanowire arrays were measured by Varian Carry 5000 at the range of 300 nm~1000 nm.

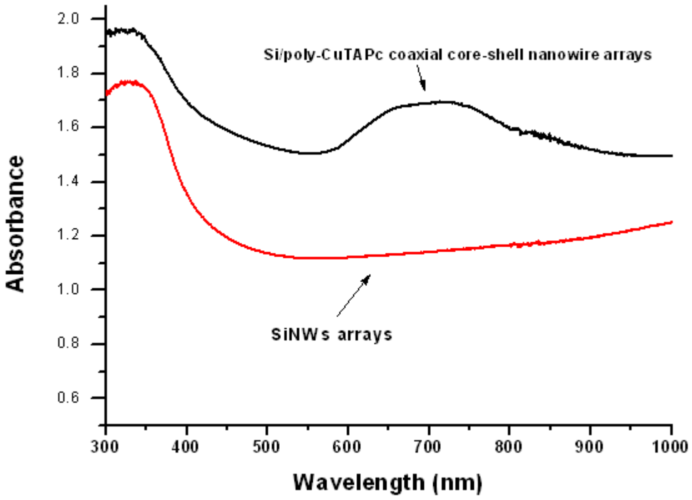

Figure S5 The UV-visible absorption of Si/poly-CuTAPc coaxial core-shell nanowire arrays and Si NWs arrays.

## S6, Photoelectrochemical Measurements:

Photo-electrochemical analysis under white light illumination was conducted using a 500 W xenon lamp as an excitation source. The intensity of the illumination near the surface of the electrode was 100 mW/cm$^2$. A CV Instruments 660A potentiostat was used to record steady-state current data. The performance of the modified and unmodified planar Si were also investigated under the same condition as figure 2, and the result was shown in figure S6. As is shown, the modified (unmodified) SiNW array showed better performance than the modified (unmodified) planar Si in our system.

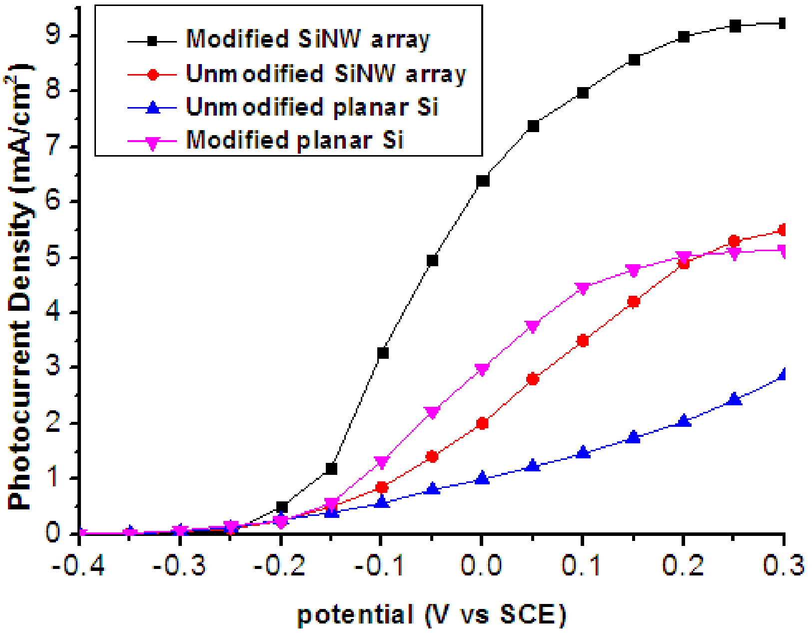

Figure S6 Photocurrent densities for modified and unmodified planar silicon and SiNW array with the same condition as figure 2.

## S7, Energy band diagram of the SiNWs/Poly-CuTAPc hetorojunction.

After polymerization, the HOMO of Poly-CuTAPc is expected higher than CuPc's HOMO (□4.7 eV) due to the formation of -N=N- bond. (*J. Phys. Chem. A* **2009**, 113, 2500-2506 )

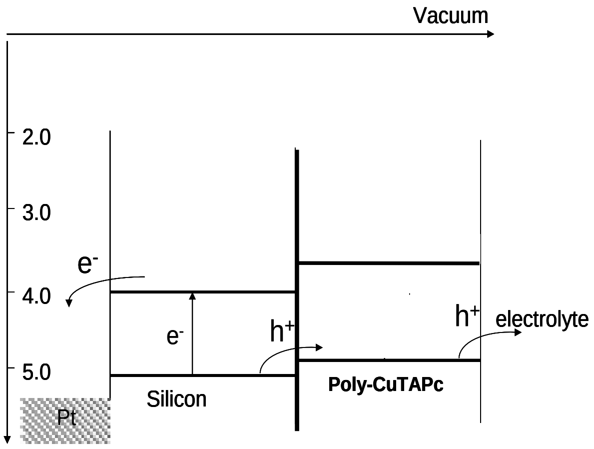

Figure S7 Energy band diagram of a SiNWs/poly-CuTAPc hetorojunction.