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Quantitative Analysis of Photons Decaying Pathways in Si Nanowires Array for High Efficient Photoelectrochemical Solar Hydrogen Generation

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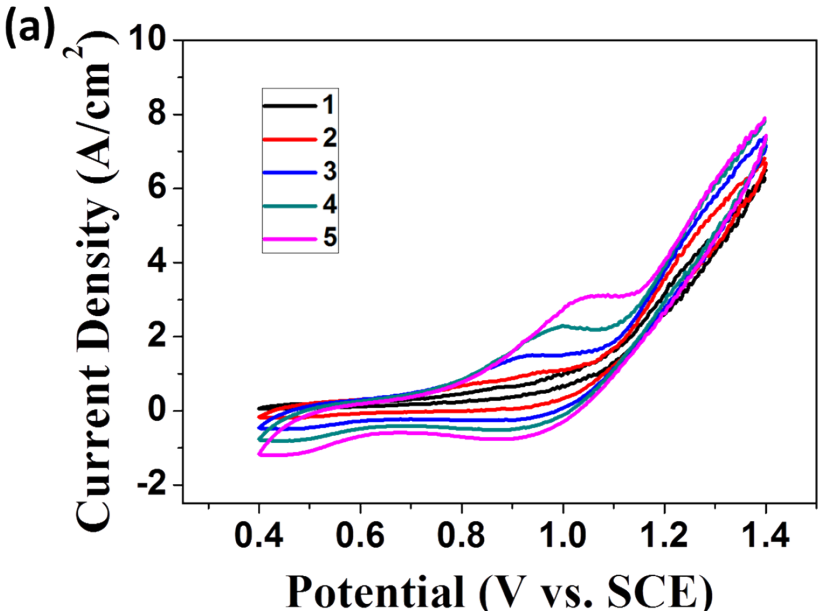
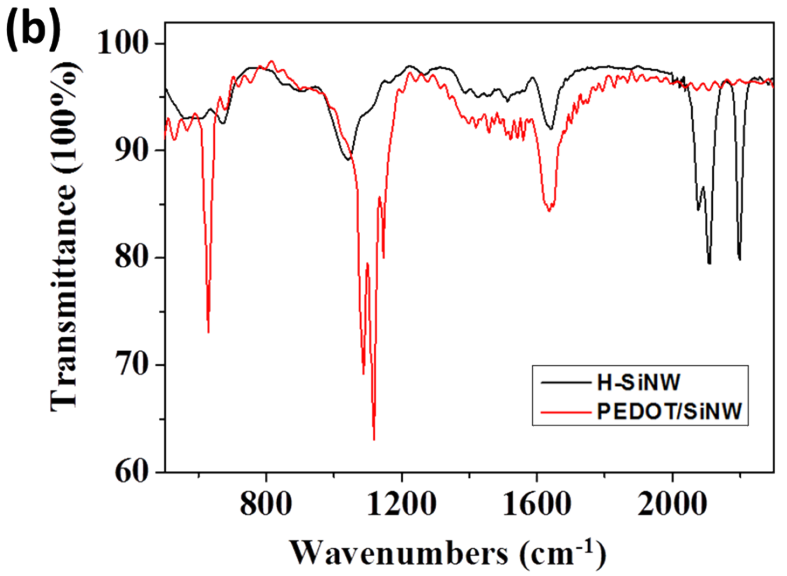
S1. Modification of SiNW arrays with PEDOT by electro-polymerization

N-type Si wafers (0.01~0.02Ω/cm) were firstly cleaned with water and ethanol, and then immersed in oxidant solution containing H_2SO_4 (97%) and H_2O_2 (35%) (V/V=3/1) for 10 mins in room temperature to remove the organics. Then, cleaned Si wafer was immersed into HF-$AgNO_3$ solution in sealed vessels to etch in 50℃ water bath for 15 mins. The concentration of HF and $AgNO_3$ in the etchant were chosen to be 5 and 0.02 mol/L, respectively. Finally, etched Si wafer was immersed into aqua fortis to remove the residual Ag particles for an hour. SiNWs arrays were immersed into 50:1 HF solution for 15 mins to make the H-terminated SiNWs arrays. After the H-SiNWs arrays were washed with ethanol and acetone, PEDOT were coated on H-SiNWs arrays via electro-polymerization. This process was performed in a three-electrode cell with 3,4-ethylenedioxythiophene (EDOT 0.01M) as the monomer in a $LiClO_4$/EtCN electrolyte. H-terminated SiNWs arrays were used as working electrode, a platinum mesh was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. During the electropolymerization process, N_2 was bubbled into the electrolyte to remove the O_2 from the reaction system. The

electropolymerization was performance in the potential window of +1.4 to 0.4 V (vs SCE) at a scan rate of 100 mV/s. When the electropolymerization was finished, PEDOT/SiNWs array was washed with EtCN for several times to remove the EDOT and then risned with ethanol to remove EtCN.

The presence of H-termination and PEDOT are confirmed by FTIR. Figure S1(b) shows the FTIR spectrum of H-SiNWs and the PEDOT modified SiNWs by Varian 3100 FT-IR. For the spectrum of H-SiNWs (black curve), the distinctive stretching modes at 2080cm^{-1}, 2110cm^{-1}, and 2180cm^{-1} all relate to Si-H surface bonds. While for PEDOT/SiNWs (red curve), the peak of 632 cm^{-1} were caused by the C-S bond vibration, and peaks centering at 1087, 1118 and 1145 cm^{-1} were assigned to ν(C-O-C) which originated from C-O-C bond stretching in the ethylene dioxy group, which confirmed the successful presence of PEDOT on SiNWs' surface. In addition, AgNPs are confirmed by SEM and HRTEM which shows their crystalline nature (Fig. 1 and S1c).





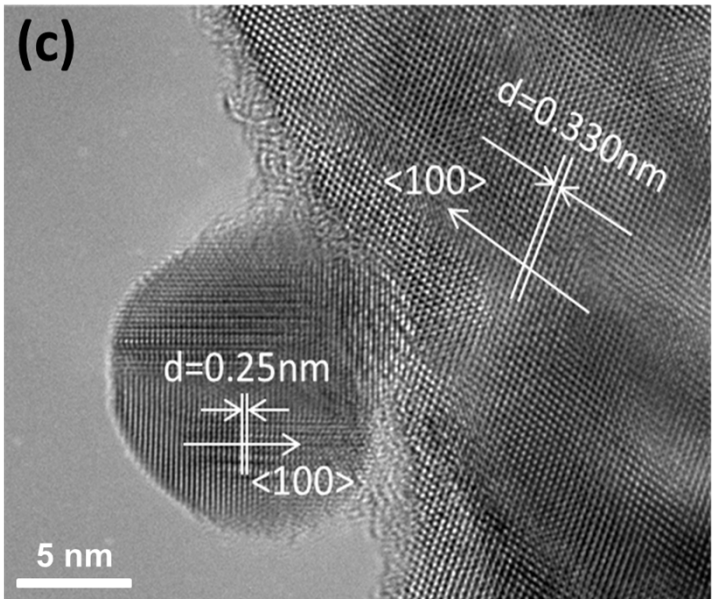


Figure S1 (a) Repeated cyclic voltammograms recorded the first 5 cycles of electro-polymerizaion, scan rate, 100mV/s; initial potential, 1.4V (vs. SCE), working electrode, H-terminated N-type SiNW arrays. (b) FTIR spectrum of PEDOT/SiNW and H-SiNW. (c) The original HRTEM image of Fig. 1d.

S2. Hydrogen production measurement of H-SiNWs array and AgNPs/PEDOT/SiNWs array

Photo-electrochemical measurement was conducted in a three-electrode system with the modified SiNWs arrays as working electrode, the platinum mesh as the counter

electrode and the SCE as the reference electrode. A 500 W xenon lamp was used as excitation source. The intensity of the illumination near the surface of the electrode was adjusted to 100 mW/cm^2 with an optical power meter. A CV Instruments 660C potentiostat was used to record steady-state current data. Photo-electrochemical measurements were carried out in a water/methanol (V/V=2/1) mixture (PH=2, adjusted with H_2SO_4) as electrolyte. The short-circuit photocurrent response of the different photoanodes were measured with three-electrode photo-electrolysis cells at zero applied potential (vs. SCE). The electrolyte was sufficiently saturated with N_2 before the measurement. H_2 generation was measured by GC analysis (14B Shimadzu) using nitrogen as carrier gas with a molecular sieve column (5 Å; 30 m×0.53 mm) and a thermal conductivity detector.

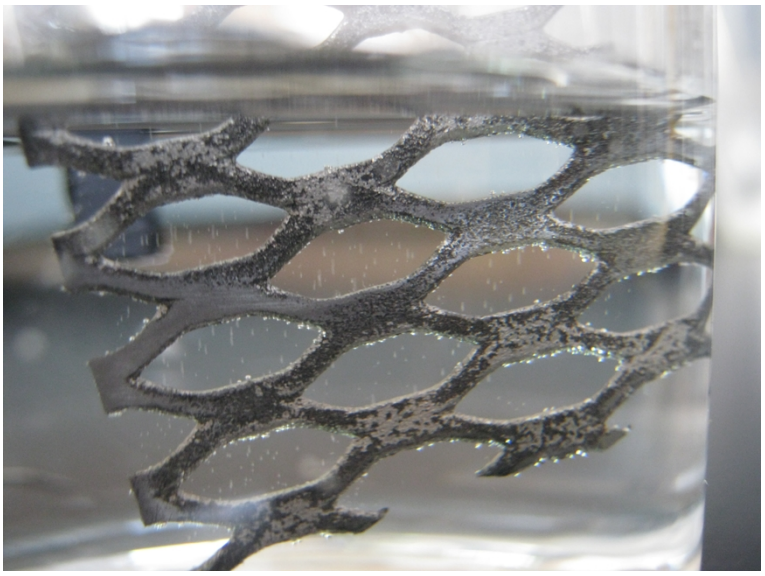


Figure S2 Photographed H_2 bubbles produced on the Pt mesh.

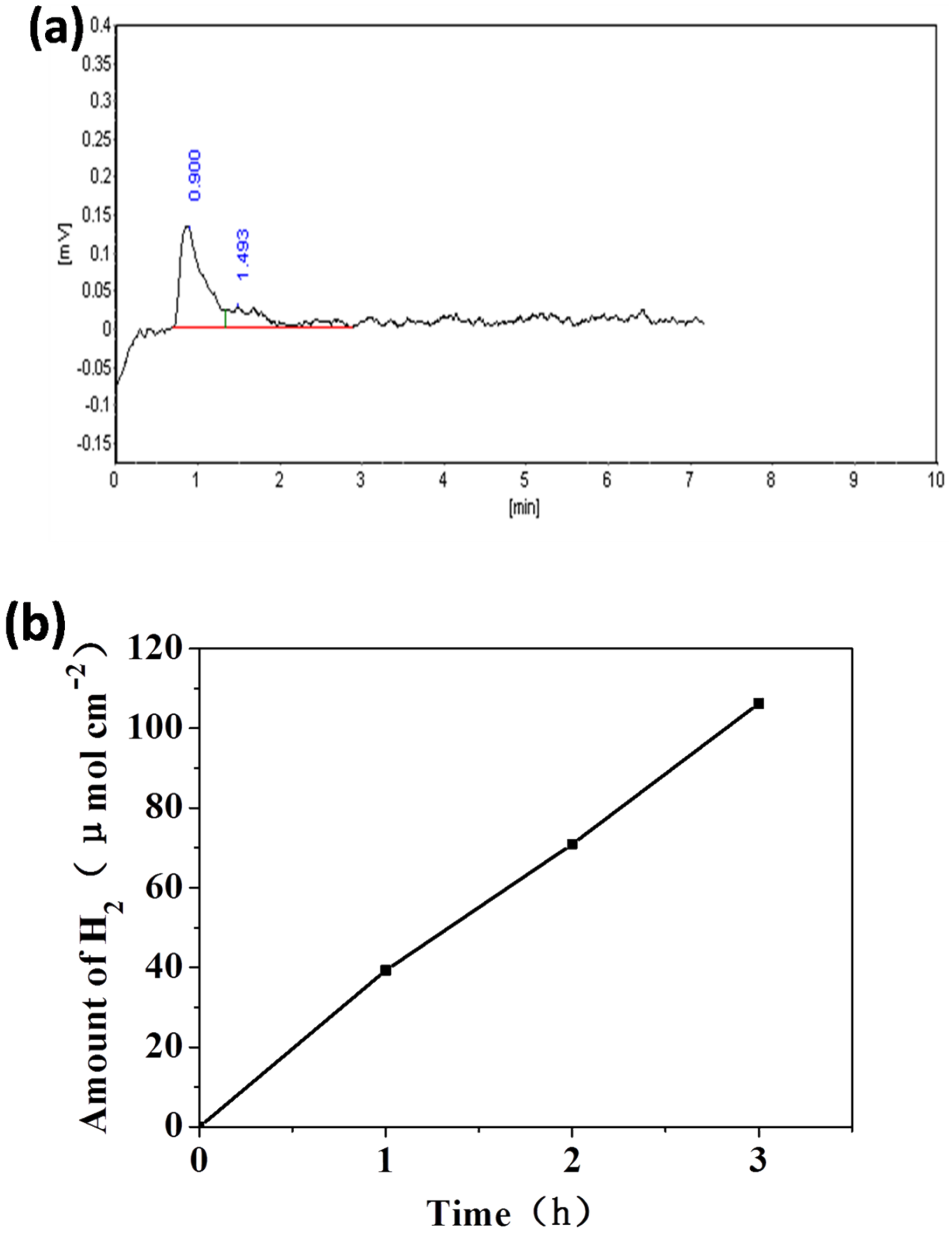
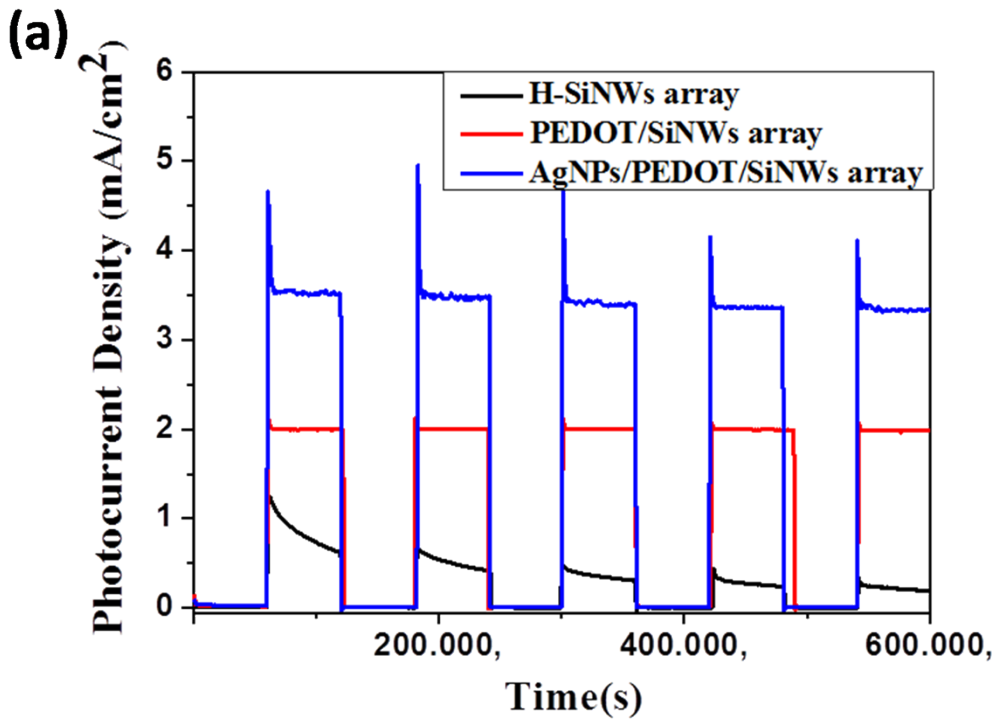


Figure S3 (a)The H_2 peak in gas chromatography. (b) Plot of hydrogen evolution calculated per cm^2 as a function of time with AgNPs/PEDOT/SiNW arrays as the photoanode and Pt mesh as the cathode.



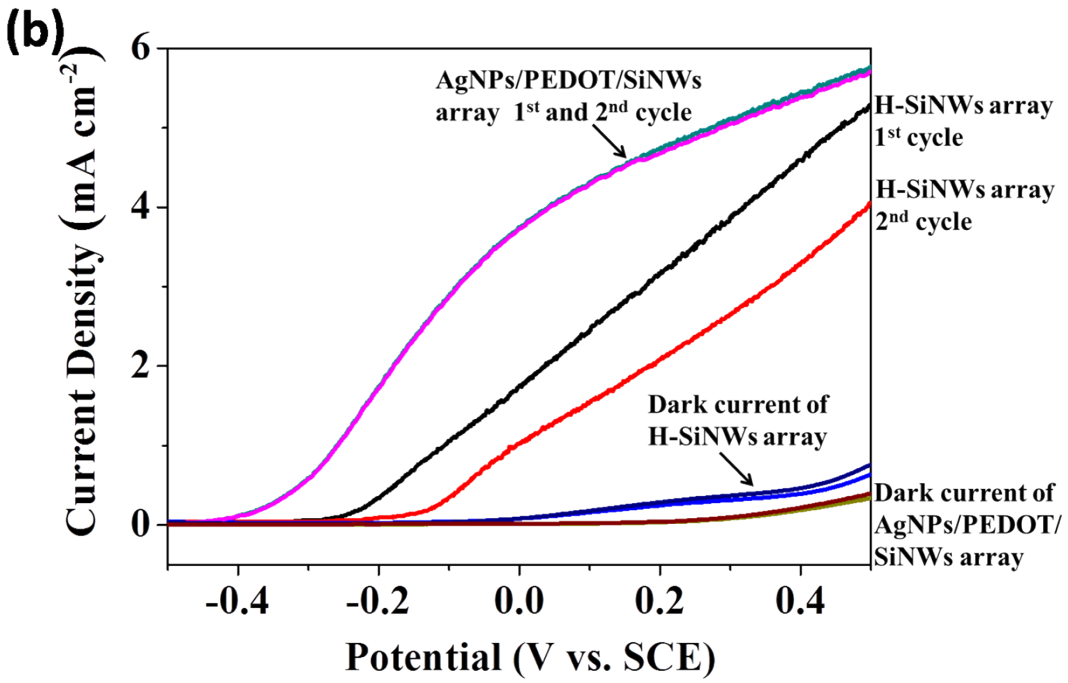


Figure S4 (a)The short-circuit photocurrent response of different photoanodes. (b) Typical current-potential characteristics of the different photoanodes in the dark and under illumination, collected at a scan rate of 50mV/s from -0.5 to +0.5(V vs. SCE).

S3. Procedure of photocatalytic degradation of RhB

Photocatalytic degradation reaction was conducted at room temperature under ambient air condition with stirring. Silicon nanowire array (cut into 0.5cm×0.5cm) with different PEDOT thickness and AgNPs loading was put into RhB aqueous solution（2μM，3mL）in a quartz cuvette. Prior to irradiation, the RhB solution and Si nanowire array were magnetically stirred in the dark for 2 hours to ensure the equilibrium of the working solution. During the experiment, the cuvette was placed about 15cm form the Xe lamp to minimize the heat effect. The light intensity reaching the photocatalyst was 100 mW cm^{-2}, as measured by a power meter. The UV-Vis absorption spectra of the solution at given intervals were recorded by removing the substrates. The solutions were analyzed by recording variations of the absorption band maximum (553 nm) of RhB using a Hitachi UV-3010 spectrophotometer. After the spectral measurements, the substrates were placed back into the solutions for further irradiation at intervals of 10 min for up to 180 min. for the examination of the stability of the photocatalyst, UV-Vis absorption spectra were also taken every 10 min. After taking absorption spectra of the solutions after 180 min of irradiation, the photocatalysts were rinsed with deionized water to fully remove the residual organic species on the substrates. The same photocatalysts were subsequently immersed into fresh RhB solution at the same concentrations for another run of experiment. The capability of degradation is presented by the ratio of RhB solutions' absorption recorded during and before illumination. In the active species capture experiments, different scavengers (9,10-Diphenylanthracene,50μM; Ethylene Diamine Tetraacetic Acid, 50μM) were adding in the solution to evaluate the contribution of singlet O_2 and holes to the degradation. The experiment procedure is the same as other photodegradtion experiments we talked above.

The evaluation for the two pathways (i.e. the excitons' dissociation pathway and the energy transfer pathway) is based on following experiments.

Firstly, $^1O_2$ is produced in the energy transfer pathway, while holes are produced in the excitons' dissociation pathway. Moreover, both $^1O_2$ and holes can trigger the bleaching of RhB under irradiating. It implies that the amount of these two species

can be calculated by considering the change of RhB concentration before and after light exposure. The calculation process is shown following.

RhB's photodegradation ratio without any scavengers is $1-(C/C_0)_{baseline}$, where C_0 and C are the concentration of RhB at the beginning and in the end of the experiment. It indicates the amount of RhB that photodegradated by ($^1O_2$□holes□other active species).

Meanwhile, RhB's photodegradation ratio with scavengers is $1-(C/C_0)_{scavenger}$. For instance, in case $^1O_2$ is captured by its scavenger, this ratio indicates the amount of RhB that photodegradated by active species in the $1-(C/C_0)_{baseline}$ expect the $^1O_2$. Thus then

$D(_{hole}) = (C/C_0)_{hole} - (C/C_0)_{baseline}$; and $D(^1_{O2}) = (C/C_0)^1_{O2} - (C/C_0)_{baseline}$

indicate the contribution of the hole and the $^1O_2$ for RhB's degradation extent. On the other hand, their generating pathway (i.e. the excitons' dissociation pathway and the energy transfer pathway) can be evaluated and compared.

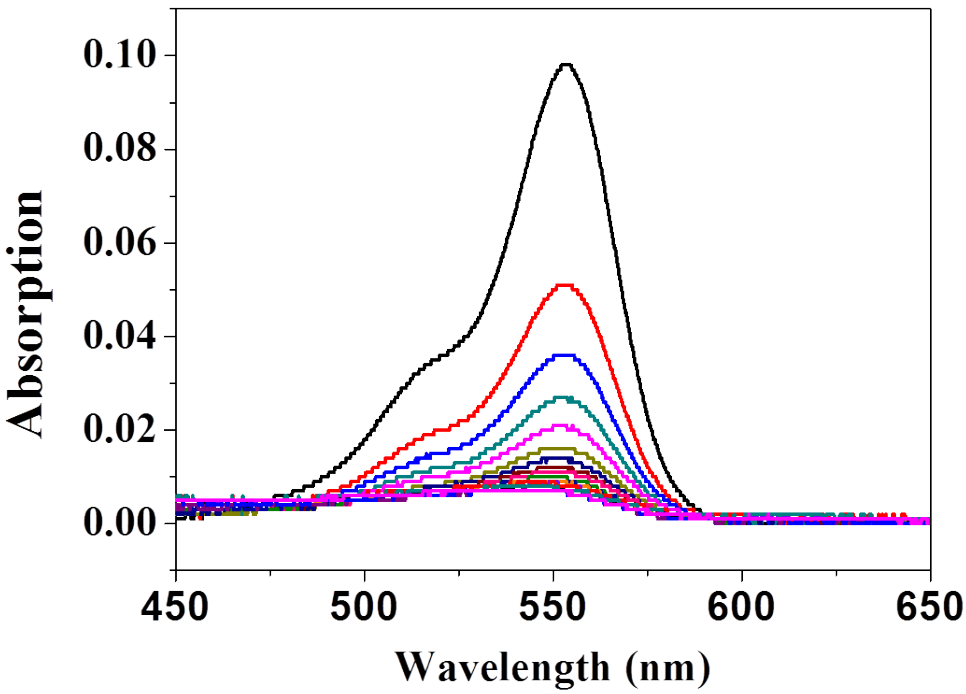


Figure S5 Typical variations of the absorption band maximum (553 nm) of RhB with SiNWs array-based photocatalysts.

S4. UV-vis absorption spectra of SiNWs array-based photocatalysts

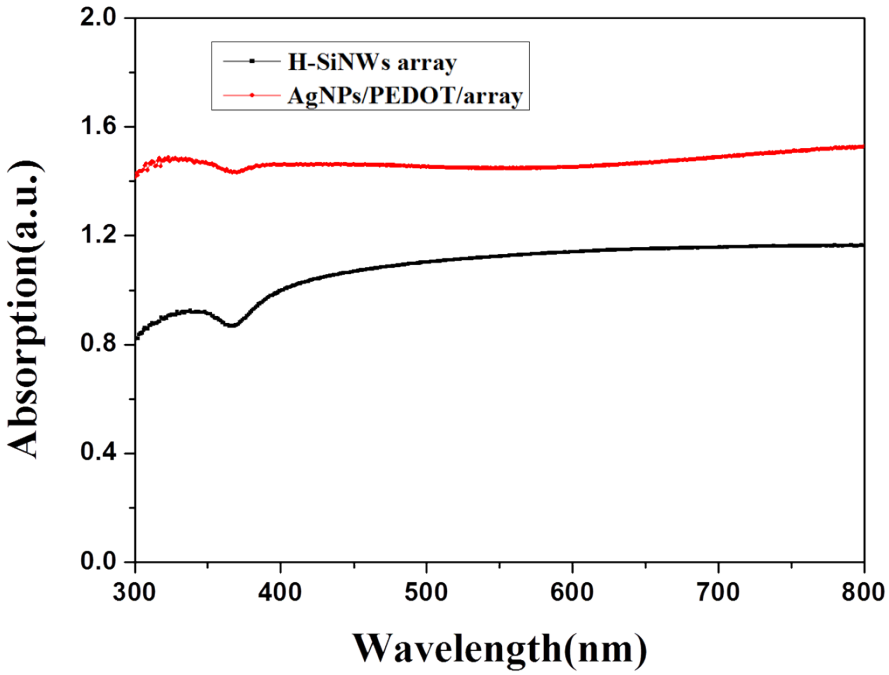


Figure S6 UV-vis absorption spectra of H-SiNWs array and AgNPs/PEDOT/ SiNWs array.

S5. Plasmonic effect of AgNPs

The plasmonic effect of metal nanoparticles has always been studied through UV-vis absorptions and IPCE performance (Nano Lett. 2013, 13, 14; Nano Lett. 2013, 13, 3817). In our previous study, we had well discussed AgNPs'plasmonic effect (ACS Appl. Mater. Interfaces, 2014, 6, 9742). In that work, UV-vis absorption spectra of SiNWs and AgNPs dispersed in ethanol andthe IPCE enhancement of AgNPs/PEDOT/SiNW arrayscompared to PEDOT/SiNW arrays had been obtained and showed in Supporting Information Fig. S7. As shown in Fig.S7a AgNPs have their maximum absorption at 430nm, which overlapped with the absorption of the SiNWs at 380–430nm. The overlap indicates that plasmonic resonance between AgNPs and SiNWs is energetically feasible. Meanwhile, the peak of IPCE enhancement appeared in the same waveband was shown in Fig. S7b. This is a strong

evidence for enhancing the photo-absorption and the photocatalytic ability through AgNPs' plasmonic effect (Nano Lett. 2013, 13, 14; Nano Lett. 2013, 13, 3817).

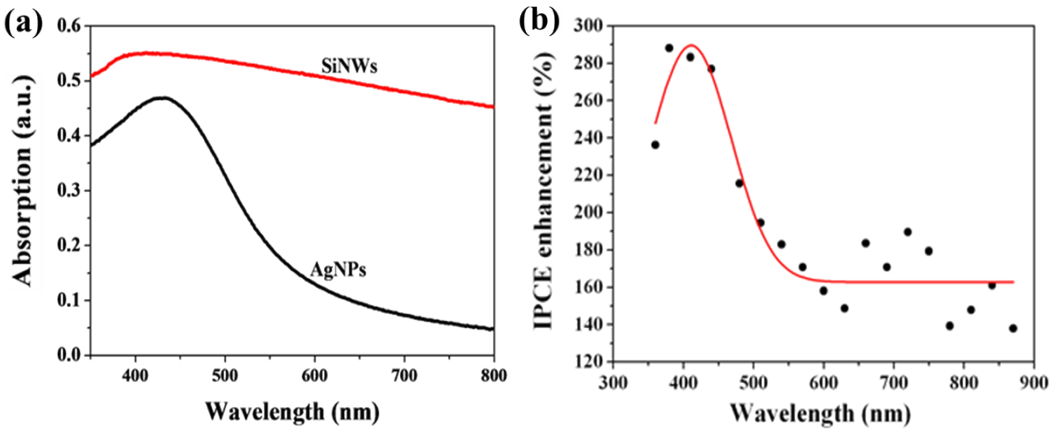


Figure S7 (a) UV-vis absorption spectra of SiNWs and AgNPsdispersed in ethanol. (b)IPCE enhancement of AgNPs/PEDOT/SiNW arrays compared to PEDOT/SiNW arrays. Copyright 2014, American Chemical Society.