In Situ Grown Oriented Polyaniline Nanowires Array for Efficient Cathode of Co(III)/Co(II) Mediated Dye-Sensitized Solar Cell

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Experimental

Materials and Reagents: $LiClO_4$ and 4-tertbutylpyridine (TBP) were obtained from Acros. Aniline, Ammonium persulfate, ammonium hexafluorophosphate, 2, 2'-bipyridyl, Cobalt chloride hexahydrate, Nitrosonium fluoroborate were purchased from J&K Chemical Ltd, China, and used as received. Organic solvents used in this work were purified using the standard process. The organic dye (**Figure S1**) was prepared according to our previous method.[1] Transparent conductive glass (F-doped SnO_2, FTO, 10 Ω/square, transmittance of 80%, Nippon Sheet Glass Co., Japan) was used as the substrate for the fabrication of TiO_2 thin film electrode. The syntheses of the oriented PANI nanowires are described as follows.

We fixed the ratio of the reactants of [AN]/[APS] as 1.5 and kept this constant throughout the experiments. Firstly, different initial concentration of aniline was dissolved in 1M HCl solution. Then, a certain amount of Ammonium persulfate (APS) was added under vigorous strring, followed by immersing a piece of well-cleaned FTO glass in the solution. After being kept at ice bath (0-5 °C) for 24h, the FTO glass was taken out and rinsed with deionized water. Finally, the PANI/FTO was redoped in 1 M HCl over night, then rinsed and dried at 80 °C in vacuum for 30 min. The precipitates in the solution were also collected and treated the same way for XRD and ATR-FTIR characterization. The Pt electrode was prepared by depositing a thin layer of Pt on FTO using thermal decomposition method. The drop-casted PANI film was prepared by depositing suspension of 11mM aniline and 24 hr polymerization on FTO with the similar thickness as PANI nanowires obtained from of 11mM aniline and 24 hr polymerization.

Synthesis of FNE29. The organic dye **FNE29**, 2-cyano-3-[5''-(4-(diphenylamino)phenyl)-3',3'',4-tri-n-hexyl-[2,2',5',2'']terthiophene]acrylic acid, was prepared according to a previous method. The chemical structure and UV-vis absorption spectrum are shown in Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2, δ ppm): 8.32 (s, 1H), 7.29-7.31 (br, 2H), 7.17 (t, *J* = 7.2 Hz, 4H), 6.81-7.01 (m, 11H), 2.63-2.70 (m, 6H), 1.47-1.54 (m, 6H), 1.10-1.30 (m, 18H), 0.73-0.78 (m, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2, δ ppm): 153.68, 140.89, 122.79, 122.71, 122.34, 121.21, 119.61, 118.94, 118.08, 116.80, 116.70, 35.11, 33.57, 25.33, 25.31, 25.22, 25.20, 23.97, 23.77, 23.73, 23.69, 23.66, 23.64, 23.61, 23.59, 23.58, 23.29, 23.22, 22.86, 22.83, 22.77, 22.71, 22.62, 16.13, 14.69, 14.54, 14.47, 13.90, 13.86, 13.81, 11.30. HRMS (ESI, *m*/*z*): $[M-H]^-$ calcd for ($C_{52}H_{57}N_2O_2S_3$), 837.358; found, 837.359.

Synthesis of $Co(bpy)_3{}^{3+/2+}$ redox couple: The cobalt complex, $[Co(bpy)_3](PF_6)_2$, and its oxidized form (Co^{3+}) were prepared according to the reported procedure.[2] A mixture of $CoCl_2 \cdot 6H_2O$ (1.0 g, 4.12 mmol, 98% Aldrich) and 2,2'-bipyridyl (2.2 g, 13.94 mmol,) were dissolved in methanol (100 mL) and refluxed for 2 h. After the resulting solution was cooled to room temperature, ammonium hexafluorophosphate (3.4 g, 20.86 mmol) was more added to the reaction mixture. The precipitate was filtrated and the residue was dried under vacuum to obtain $[Co(bpy)_3](PF_6)_2$ (3.1 g, 92% yield) as yellow solid. Additional oxidation of $[Co(bpy)_3](PF_6)_2$

(500 mg, 0.612 mmol) was carried out by using $NOBF_4$ (107 mg, 0.916 mmol) in acetonitrile (15 mL) at room temperature for 0.5 h. After removed solvent under reduced pressure, the residue was dissolved in acetonitrile (5 mL) and NH_4PF_6 (502 mg, 3.08 mmol) was more added to the solution. The precipitate of $[Co(bpy)_3](PF_6)_3$ (530 mg) was filtrated, dried under vacuum and used without further purification.

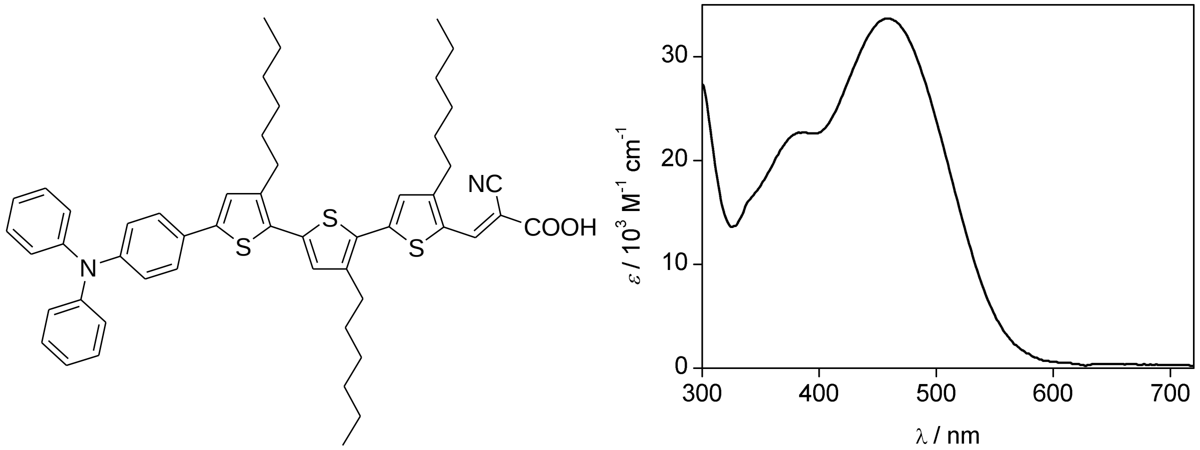

Figure S1. Chemical structure of **FNE29** dye and its UV-vis absorption spectrum in toluene

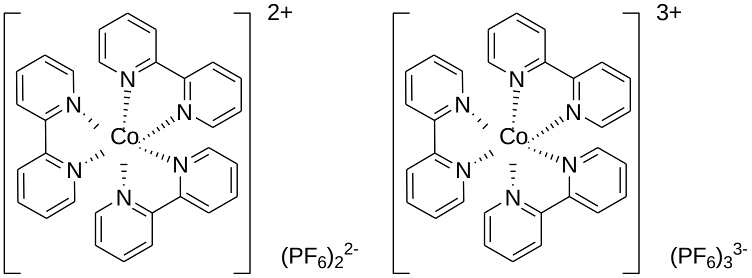

Figure S2. Chemical structures of the Co(III)/Co(II) redox couple.

Figure S3. FESEM image of the drop-casted PANI film.

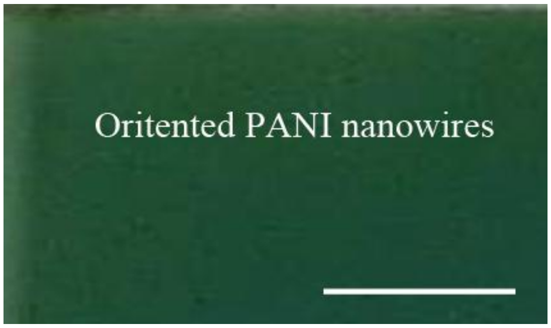

Figure S4. Digital photograph of the highly uniform oriented PANI nanowires electrode. The green color indicates that PANI is in a doping state and possesses good conductivity. Scal bar:1 cm

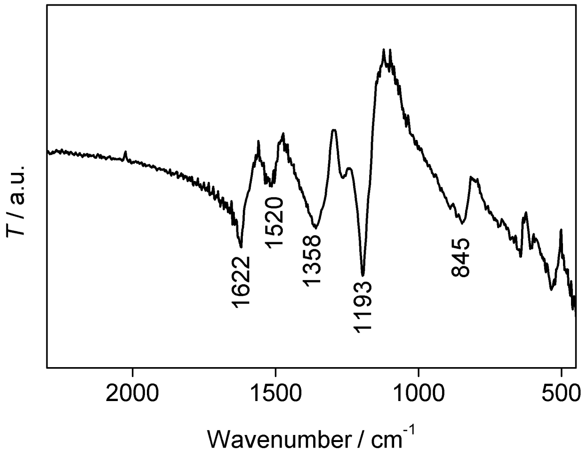

Figure S5. FTIR spectrum of the oriented PANI nanowires powder

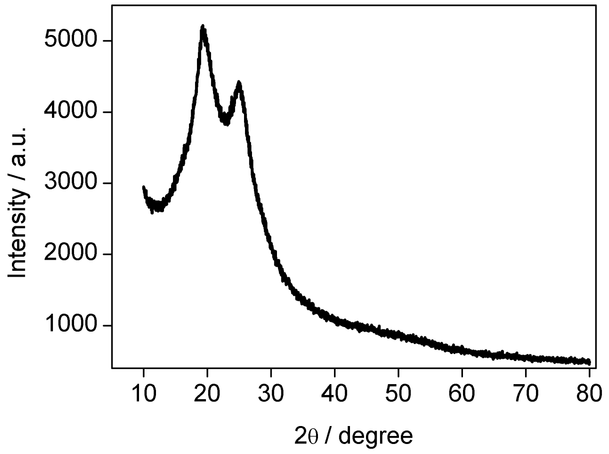

Figure S6. XRD pattern of the PANI nanowires powder obtained from initial aniline concentration of 11 mM with growth time of 24 h.

Table S1. Photovoltaic performance parameters of DSSCs based on various PANI films grown from different growth time at initial aniline concentration of 11 mM

Cathodes[a]	V_{oc}/V	J_{sc}/mA cm^{-2}	*FF*	η/%
24 h	0.78	15.09	0.70	8.24
30 h	0.77	15.07	0.69	8.01
40 h	0.78	15.00	0.68	7.96

[a] PANI cathodes were obtained from different growth time with initial aniline concentration of 11 mM. The relative deviations of photovoltaic parameters were less than 4%.

DSSC Fabrication and Photovoltaic Measurements. TiO_2 films (9 μm) composed of 6 μm nanoparticle (20 nm) layer in direct contact with the FTO (F-doped SnO_2, 15 Ω/square, transmittance of 85%, Nippon Sheet Glass Co., Japan) substrate and 3 μm light scattering particle (80% 20 nm TiO_2 + 20% 100 nm TiO_2) layer were fabricated with a screen printing method and used in this study.[3] The films were sintered at 500 ℃ for 2 h to achieve good necking of TiO_2 particles. The film thickness was measured by a surface profiler (Veeco Dektak 150, USA). The sintered films were then treated with 0.05 M $TiCl_4$ aqueous solution at 70 ℃ for 30 min followed by calcinations at 450 ℃ for 30 min. When TiO_2 electrodes were cooled down at around 120 ℃, the electrodes were dipped into the dye solutions (0.3 mM in toluene) for 24 h at room temperature for complete dye adsorption. The dye-loaded TiO_2 film as working electrode and the counter electrode (in *situ* grown oriented PANI nanowires array, drop-casted

PANI, or pyrolytic Pt on FTO) were separated by a hot-melt Surlyn film (30 μm) and sealed together by pressing them under heat. Electrolyte was composed of 0.22 M $[Co(bpy)_3](PF_6)_2$, 0.05 M $[Co(bpy)_3](PF_6)_3$, 0.1 M $LiClO_4$, and 0.2 M 4-tertbutylpyridine in acetonitrile was injected into the interspace between the working and counter electrodes from the two holes predrilled on the back of the counter electrode. Finally, the two holes were sealed with a Surlyn film covered with a thin glass slide under heat. The working performance of DSSC was tested by recording the current density-voltage curves with a Keithley 2400 Source Meter (Oriel) under illumination of simulated AM 1.5 solar light coming from an AAA solar simulator (Newport-94043A) equipped with a Xe lamp (450 W) and an AM1.5G filter. The light intensity was calibrated using a standard Si solar cell (Newport 91150). A black mask with aperture area of 0.2304 cm^2 was used during measurement to avoid stray light.

Characterizations. FTIR was performed on Nexus 470 FT-IR spectrometer (American Nicolet Company). XRD patterns was measured on a X-ray powder diffractometer (D8 Advance, Bruker, Germany) with Cu Kα radiation (λ = 0.154 nm). CV and EIS of symmetrical dummy cells were measured with an electrochemical workstation (Zahner XPOT, Germany). In these dummy cells, a thin layer of redox electrolyte solution used for DSSCs is sandwiched between two identical electrodes to be tested as cathodes of DSSCs. The EIS spectra were scanned in a frequency range of 0.01-106 Hz at room temperature. The applied bias and ac amplitude were set at open-circuit condition and 10 mV, respectively.

References

1. Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, *Chem. Mater.*, **2008**, *20*, 3993-4003.

2. S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, *J. Am. Chem. Soc.*, **2010**, *132*, 16714–16724.

3. Z.-S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, *Coord. Chem. Rev.* **2004**, *248*, 1381-1389.