

Electronic supplementary information (ESI) for

**Nanocables Composed of Anatase Nanofibers Wrapped in UV-Light  
Reduced Graphene Oxide and Their Enhancement of Photoinduced  
Electron Transfer in Photoanodes**

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**Experimental**

Figure S1. (A) XRD patterns, (B) FTIR spectrum and (C) TGA curve of (a) raw graphite, (b) GO, (c) TiO<sub>2</sub> nanofibers and (d) RGO/TiO<sub>2</sub> nanocables.

Figure S2. TEM images of anatase TiO<sub>2</sub> nanofibers at different magnifications.

Figure S3. (A) TEM image and (B) TGA curve of a GO/TiO<sub>2</sub> nanocable prepared by magnetic stirring in the dark for 20 h in an identical suspension to the trials exposed to UV irradiation and finally washed with water 6 times.

Figure S4. (A, B) TEM and (C) HRTEM image of RGO/TiO<sub>2</sub> prepared by a chemical reduction method.

Figure S5. Ti 2p high resolution XPS spectra of (a) TiO<sub>2</sub> nanofibers and (b) RGO/TiO<sub>2</sub> nanocables.

Figure S6. (A) *C 1s* high resolution XPS and (B) Raman spectra of the residual reduced graphene oxide in the suspension.

Figure S7. (A) HRTEM, (B) *C 1s* high resolution XPS and (C) Raman spectra of the RGO/TiO<sub>2</sub> nanocables (like the sample in Figure 1C) calcined under a constant argon flow at 450 °C for 30 min.

Figure S8. The photocurrent response of the photoanodes without (black) and with (red) different amounts of RGO/TiO<sub>2</sub> nanocables under UV-irradiation in a 10 mM NaNO<sub>3</sub> electrolyte: (A) 10 wt%, (B) 15 wt%, and (C) 20 wt%.

## Experimental

### 1. Chemical and materials

Graphite powder (99.95%, 325 mesh), titanium tetraisopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , 97%) and  $\text{TiO}_2$  nanoparticle (P25, 20% rutile and 80% anatase, average size of  $\sim 20$  nm) were purchased from Alfa Aesar, Sigma-Aldrich and Degussa respectively. Sodium chloride (NaCl), potassium permanganate ( $\text{KMnO}_4$ , 98%), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%), hydrochloride (HCl, 37%), poly(vinyl pyrrolidone) (PVP,  $M_w \approx 1.3 \times 10^6$ ), acetic acid ( $\text{CH}_3\text{COOH}$ , glacial), hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , 80%), sodium nitrate ( $\text{NaNO}_3$ ), potassium ferricyanide(III) ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ , 99%), potassium ferrocyanide ( $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , 99%) and potassium chloride (KCl) were all obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

### 2. Synthesis of graphene oxide (GO) sheets

GO sheets were synthesized using a modified Hummer's method.<sup>S1</sup> 1 g of graphite was ground with 0.05 g of NaCl for 10 min and then washed with water to remove the NaCl. 23 mL of  $\text{H}_2\text{SO}_4$  (98%) was added and the solution was stirred for 22 h at room temperature. 6 g of  $\text{KMnO}_4$  was added slowly and the temperature was carefully kept below 20 °C using an ice bath. Afterwards, it was stirred at 40 °C for 30 min, then 90 °C for 45 min. The temperature was increased to 105 °C after adding 46 mL of distilled water. 25 min later, the reaction was ended by adding 140 mL of distilled water and 10 mL of 30%  $\text{H}_2\text{O}_2$  solution. The as-prepared graphite oxide product was bright yellow, purified by washing with 5% HCl and finally dialyzed with distilled water for 3 days. A given volume of the product was dried at 40 °C in a vacuum and was carefully weighed. With this data, the GO concentration could be calculated. The purified GO colloid was further diluted to 0.8 g/L with distilled water and was ultrasonicated for 30 min.

### 3. Electrospinning of $\text{TiO}_2$ nanofibers

The  $\text{TiO}_2$  nanofibers were prepared by electrospinning a solution containing 2.5 mL of titanium tetraisopropoxide, 3.0 mL of acetic acid, 0.3 g of PVP and 4.5 mL of ethanol at a voltage of 16.5 kV and a flow rate of 0.3 mL/h.<sup>S2</sup> The as-spun nanofibers were kept in air overnight and then calcined in air at 510 °C for 4.5 h. 1.6 mg of the  $\text{TiO}_2$  nanofibers was dispersed in 2 mL of ethanol followed by 10 min of ultrasonication and magnetic stirring overnight, yielding a 0.8 g/L suspension.

#### 4. UV-light reduced graphene oxide/TiO<sub>2</sub> (RGO/TiO<sub>2</sub>) nanocables

2 mL of aqueous GO colloid (conc. of 0.8 g/L or other indicated value) was added to 2 mL of TiO<sub>2</sub> suspension (0.8 g/L) followed by 2 min of ultrasonication, which ensured a homogeneous suspension. The yellow suspension was then irradiated under UV-light for 20 h with constant magnetic stirring. We chose a UV lamp (254 nm and 365 nm, 6W, GL-9406, Kylin-Bell Lab Instruments Co., Ltd.) as a mild UV-light source to reduce the GO sheets. The as-prepared RGO/TiO<sub>2</sub> nanocables were then washed with distilled water at least six times to remove residual RGO left in suspension.

#### 5. Evaluation of electron transport in photoanodes

5% (wt%) of RGO/TiO<sub>2</sub> was mixed with P25 and the mixture was dispersed in ethanol with mild ultrasonication, yielding a concentration of 5 g/L. The photoanodes were carefully prepared by drop-casting 15  $\mu$ L of the above suspension on a clean fluorine-doped tin oxide (FTO) conductive glass surface and then calcinating the sample under a constant argon flow at 450 °C for 30 min. The active surface area was controlled to 0.25 cm<sup>2</sup> using Scotch tape as a spacer. The photoanodes were irradiated with a 6 W UV lamp with a wavelength of 365 nm. Photogenerated current was recorded with a CHI 660B (CH Instrument, Chenhua Co., Shanghai, China) using the traditional three electrode system. The photoanode was used as the working electrode with a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The electrolyte was a 10 mM solution of aqueous NaNO<sub>3</sub>. The electrochemical impedance spectra (EIS) were measured using a Zahner IM6ex impedance analyzer (Germany) in the frequency range of 0.1 Hz to 1M Hz at the open-circuit voltage. We used the same conventional three electrode cells, but 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>](1:1) in 0.1 M aqueous KCl was used as an electrolyte.

#### 6. Characterizations

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were collected using a Tecnai G2 T20 (FEI) operated at 200 kV. Atomic force microscopy (AFM) images were measured with a MFP-3D-SA (Asylum Research) in tapping mode in air. All samples were dispersed in distilled water or ethanol and drop cast onto honey copper grids (for TEM) or a silicon wafer (for AFM). The crystal structure information was obtained with X-ray diffraction (Bruker, D8 advance using Cu-K $\alpha$  radiation,  $\lambda=1.5406$  Å). Fourier transform infrared (FTIR) spectra were recorded on a NICOLET 5700

spectrometer. Thermogravimetric analysis (TGA) was conducted using a SDT Q600 under N<sub>2</sub> flow and heated at a rate of 10 °C/min. The carbon concentrations were determined using an elemental analyzer (Elementar Vario MICRO, German). Zeta-potential of the TiO<sub>2</sub> and GO was measured by dynamic light scattering (Nano ZS, ZE N3600, Malvern Instruments, Ltd.). X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific K-Alpha using monochromatic Al K $\alpha$  radiation. Raman spectra were recorded on a Jobin Yvon LabRAM HR800 micro-Raman spectrometer with a 514 nm laser.

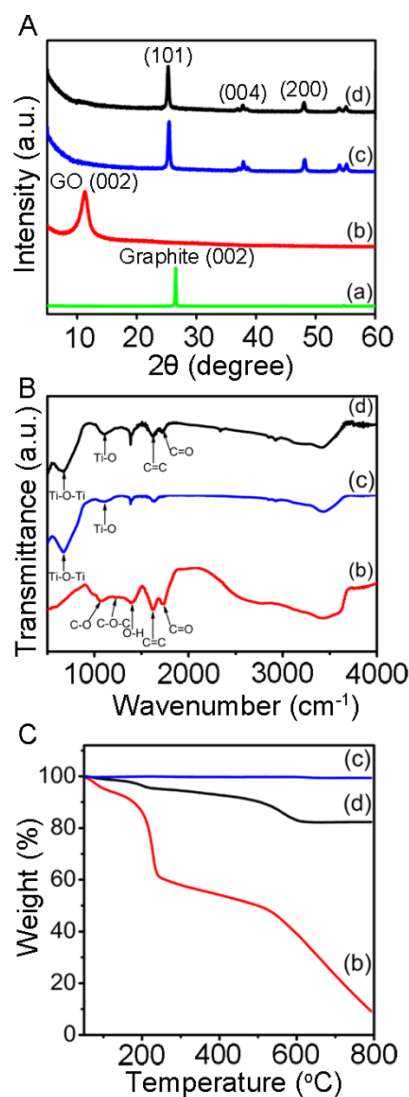


Figure S1. (A) XRD patterns, (B) FTIR spectrum and (C) TGA curve of (a) raw graphite, (b) GO, (c) TiO<sub>2</sub> nanofiber and (d) RGO/TiO<sub>2</sub> nanocables. On the basis of these results, the GO sheets have been functionalized with epoxy and hydroxyl groups by the modified Hummer's method. The oxidation of raw graphite also results in an interlayer spacing (*d*-spacing) increase from 3.4 Å to 7.8 Å, estimated from the (002) peak in the XRD patterns at 2θ of 26.5° and 11.4°, respectively. After UV-light reduction, the GO sheets transferred to RGO with significantly less oxygen-containing groups and the RGO successfully wrapped around the TiO<sub>2</sub> nanofibers.

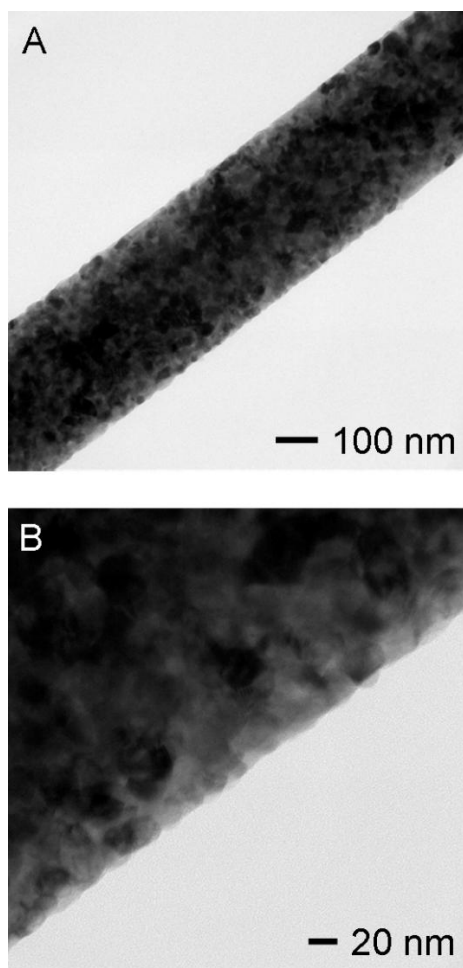


Figure S2. TEM images of anatase TiO<sub>2</sub> nanofibers at different magnifications.

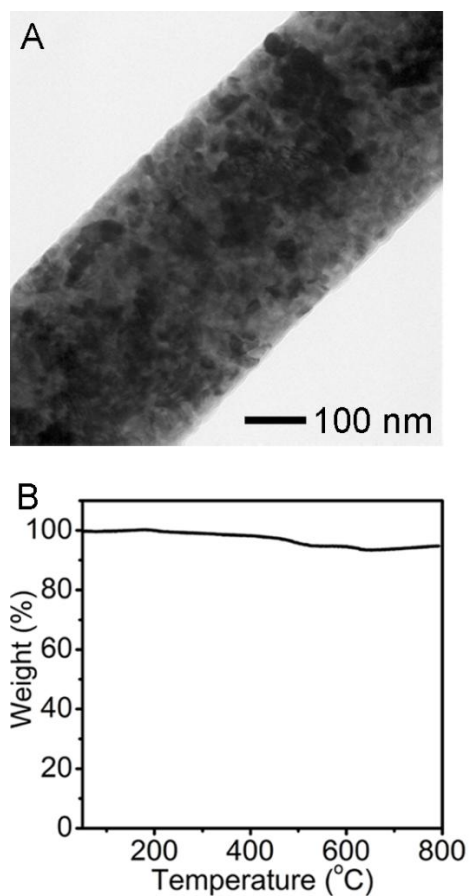


Figure S3. (A) TEM image and (B) TGA curve of a GO/TiO<sub>2</sub> nanocable prepared by magnetic stirring in the dark for 20 h in an identical suspension to the trials exposed to UV irradiation. The solution was washed with water 6 times.



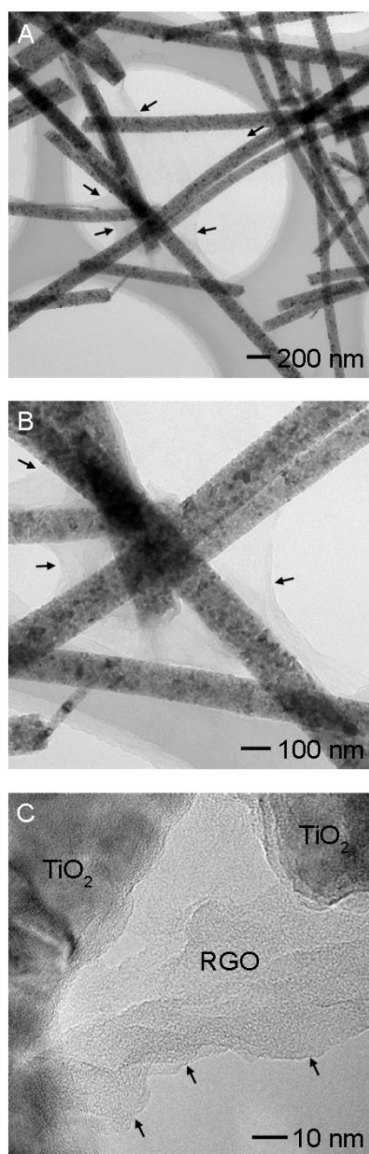


Figure S4. (A, B)TEM and (C) HRTEM image of RGO/TiO<sub>2</sub> prepared by a chemical reduction method. The suspension, identical to the solution exposed to UV-light irradiation in Figure 1C, was heated at 95 °C for 1 h with 5 μL of N<sub>2</sub>H<sub>4</sub> in a sealed vial as the suspension's color changed to grey and finally black. The as-prepared black RGO/TiO<sub>2</sub> products aggregated in the solution and settled at the bottom of the vial after the reaction. The RGO preferred to wrap around the TiO<sub>2</sub> nanofibers, similar to the ones reduced by UV-light. The black arrows indicate the edges of the RGO sheets, which wrapped several neighboring TiO<sub>2</sub> nanofibers as shown in all three images.

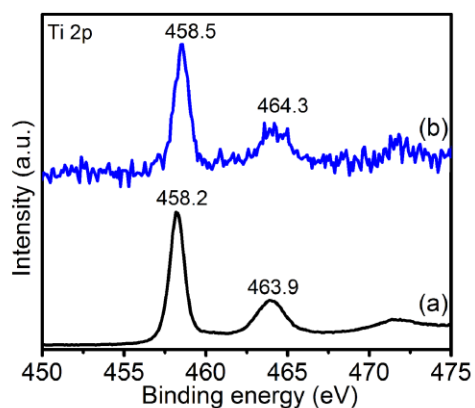


Figure S5. Ti 2*p* high resolution XPS spectra of (a) TiO<sub>2</sub> nanofibers and (b) RGO/TiO<sub>2</sub> nanocables. The peaks can be attributed to Ti 2*p*<sub>3/2</sub>, Ti 2*p*<sub>1/2</sub> and their satellite peaks with typical characteristic Ti<sup>4+</sup> binding energies. Any Ti-C bonds would be visible in the spectrum with non-vanishing features such as a peak or shoulder in the vicinity of 455 eV.<sup>S3</sup> The absence of such peaks confirms the absence of Ti-C bonding in the RGO/TiO<sub>2</sub> nanocables.

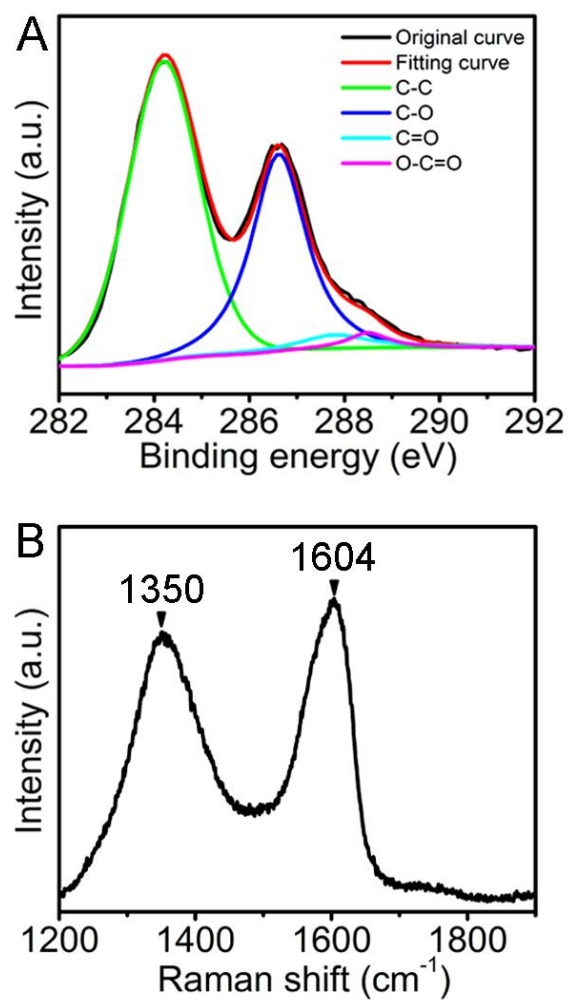


Figure S6. (A) C 1s high resolution XPS and (B) Raman spectra of the residual reduced graphene oxide in the suspension.

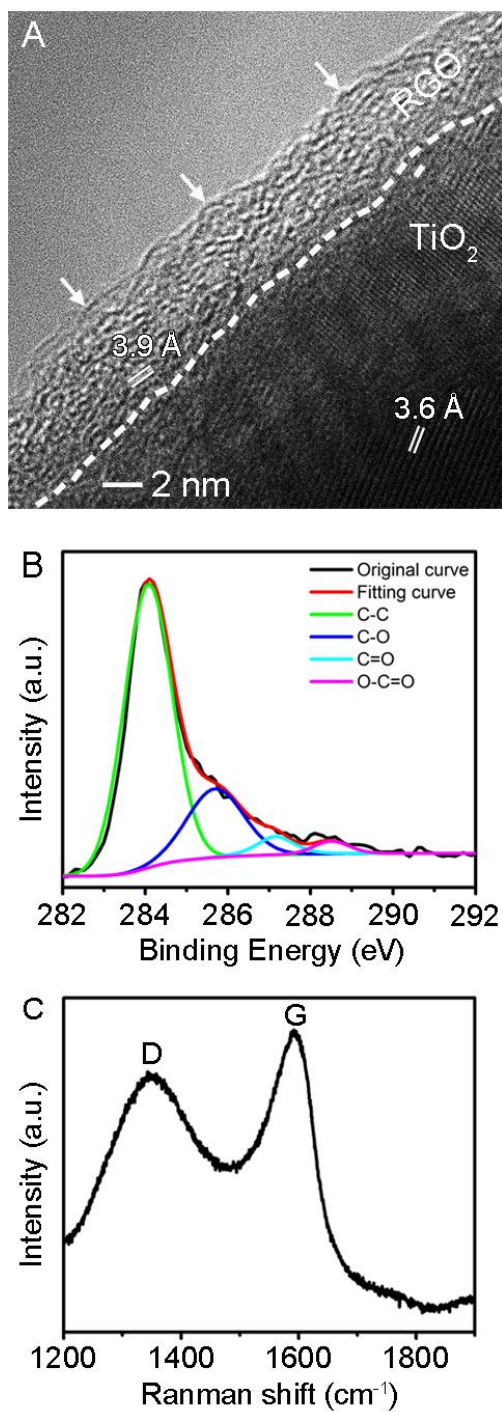


Figure S7. (A) HRTEM, (B) C *1s* high resolution XPS and (C) Raman spectra of the RGO/TiO<sub>2</sub> nanocables (identical to those in Figure 1C) calcined under a constant argon flow at 450 °C for 30 min.

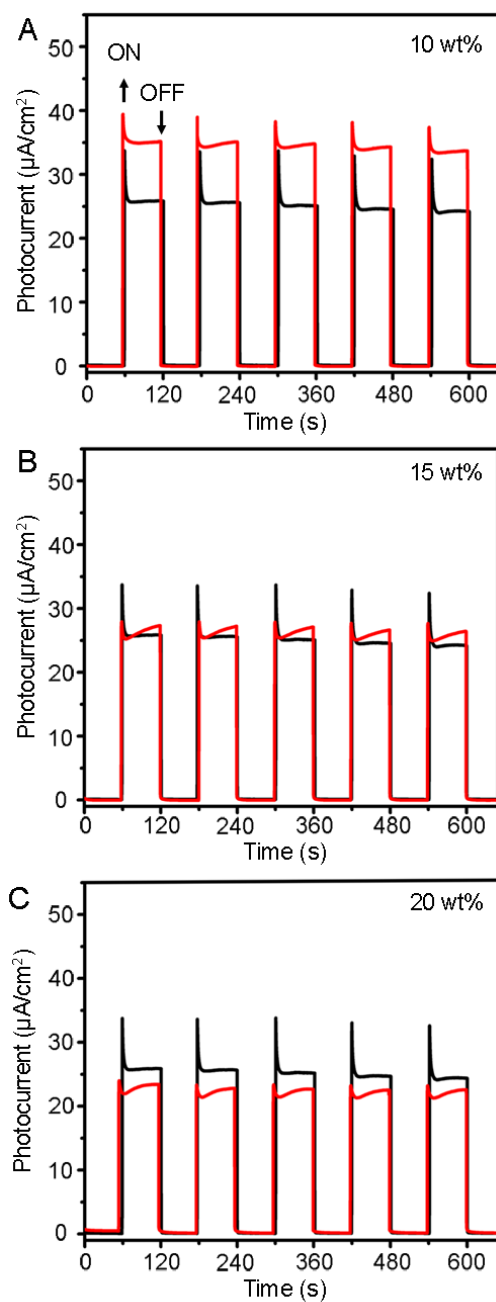


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## References

- S1. Z. Liu, J. T. Robinson, X. Sun and H. Dai, *J. Am. Chem. Soc.*, 2008, **130**, 10876-10877.
- S2. D. Li and Y. Xia, *Nano Lett.*, 2003, **3**, 555-560.
- S3. X. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science*, 2011, **331**, 746-750.