

## Electronic Supplementary Information (ESI)

### One-pot, water-phase approach to high-quality graphene/TiO<sub>2</sub> composite nanosheets

#### EXPERIMENTAL SECTION

**Chemicals.** Graphite and Titanium (IV) chloride (20% in 3% hydrochloric acid) were purchased from Alfa Aesar. Poly(N-vinyl-2-pyrrolidone) (PVP · K30, molecular weight =30 000-40 000) was purchased from the Shanghai Chemical Factory (Shanghai, China). Unless otherwise stated, other reagents were of analytical grade and were used as received. All aqueous solutions were prepared with ultrapure water (>18 MΩ) from a Milli-Q Plus system (Millipore).

**Preparation of graphene oxide (GO).** The graphite oxide was synthesized from natural graphite powder based on modified Hummers method.<sup>1</sup> Then, exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion for 40 min (1000W, 20% amplitude). Finally, a homogeneous GO aqueous dispersion (0.5 mg/mL) was obtained and used for further characterizations and the chemical reduction.

**Synthesis of graphene/TiO<sub>2</sub> composites nanosheets (GTCN).** In a typical preparation of GTNS, 50 mL of GO (0.25 mg/mL) and 150 mg PVP were mixed together, followed by stirring for more than 0.5 h. Then, a 0.6 mL portion of TiCl<sub>3</sub> aqueous solution was added into as-prepared GO dispersions while stirring. The mixture was stirred for 60 min at 95 °C. Finally, the resulting stable black dispersion was centrifuged and washed with water. Then, the obtained GTCN was redispersed in water before further use. In control experiments, the GTCN was prepared under 25 or 60 °C with the same post-treatment as mentioned above. For comparison, TiO<sub>2</sub> colloid was synthesized under the same condition without GO.

**Preparation of TiO<sub>2</sub> and GTCN modified photoanodes.** Firstly, indium-tin-oxide electrode ITO ( $2 \times 1 \text{ cm}^2$ ) was cleaned by sonicating sequentially for 20 min each in

acetone, 10% KOH in ethanol, and distilled water. After washing and N<sub>2</sub> drying, TiO<sub>2</sub> and GTCN modified photoanodes were prepared by drop-coating the same sufficient quantity of TiO<sub>2</sub> colloid or GTCN (50 uL, 0.62 mg/mL) to completely cover the ITO surface, followed by drying under infrared lamp

**Characterization:**

Infrared spectra were collected on a VERTEX 70 Fourier transform infrared (FTIR) spectrometer (Bruker). UV-vis detection was carried out on a Cary 50 UV-vis-NIR spectrophotometer (Varian, U.S.A.). AFM was conducted with a SPI3800N microscope (Seiko Instruments, Inc.). TEM images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. Thermogravimetric analyze (TGA) of sample was performed on a Pyris Diamond TG/DTA Thermogravimetric Analyzer (Perkin-Elmer Thermal Analysis). Sample was heated under nitrogen atmosphere from room temperature to 900 at 5 °C min<sup>-1</sup>. Raman spectra were obtained on a J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident laser light. X-ray diffraction (XRD) spectra were obtained using a D8 ADVANCE (Germany) using Cu K (1.5406 Å) radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB MK II X-ray photoelectron spectrometer. Photocurrent experiments were performed with a CHI 832 electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wire as counter electrode, and the TiO<sub>2</sub> and GTCN modified ITO electrode as a photoanode. A 190 mW UV lamp with central wavelength of 365 nm is used as light source.

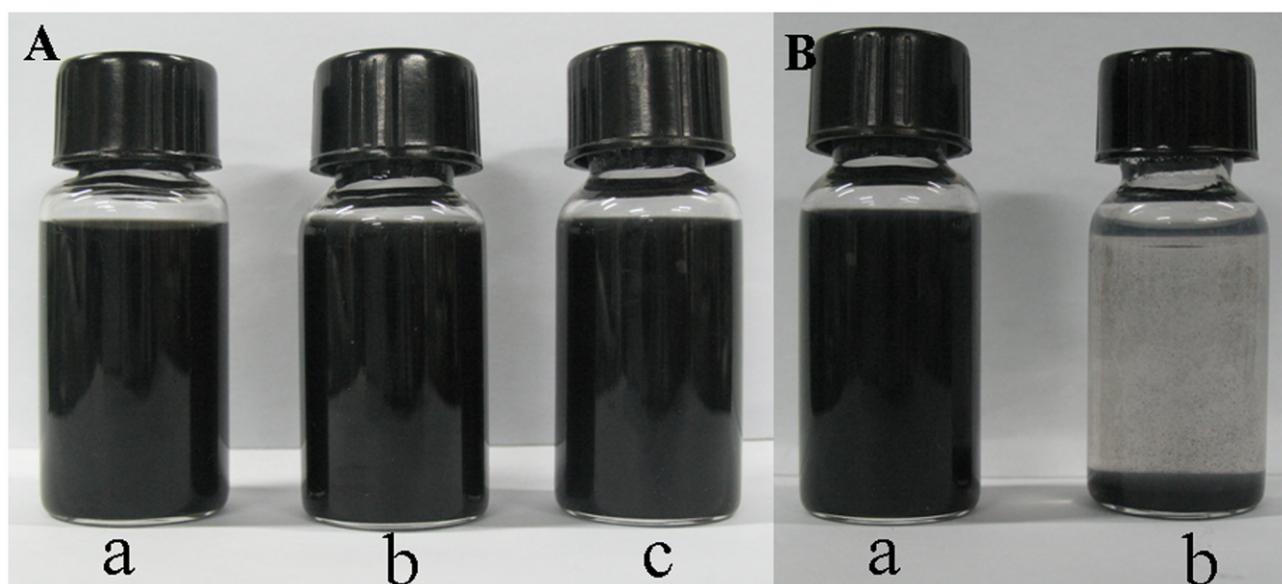


Fig. S1 (A) Photographs of aqueous dispersions of as-synthesized GTCN at 25 °C (vial a), 60 °C (vial b) and 95 °C (vial c). (B) Photographs of the obtained GTCN in the presence (vial a) and absence (vial b) of PVP.

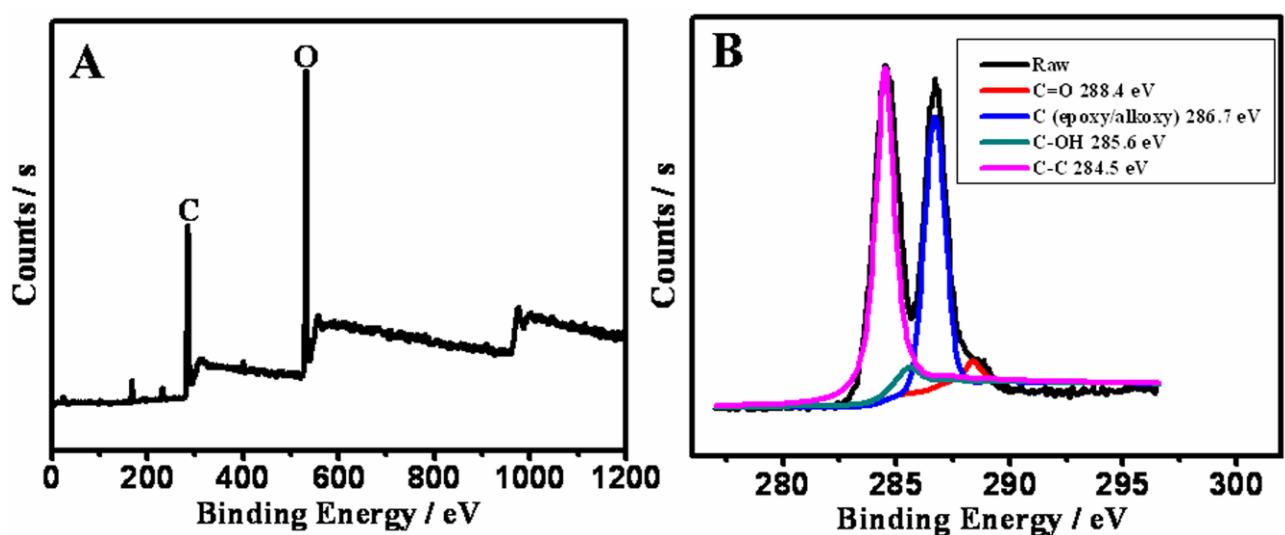


Fig. S2 The full-scale XPS spectra (A) and higher resolution curves of C1s (B) of GO.

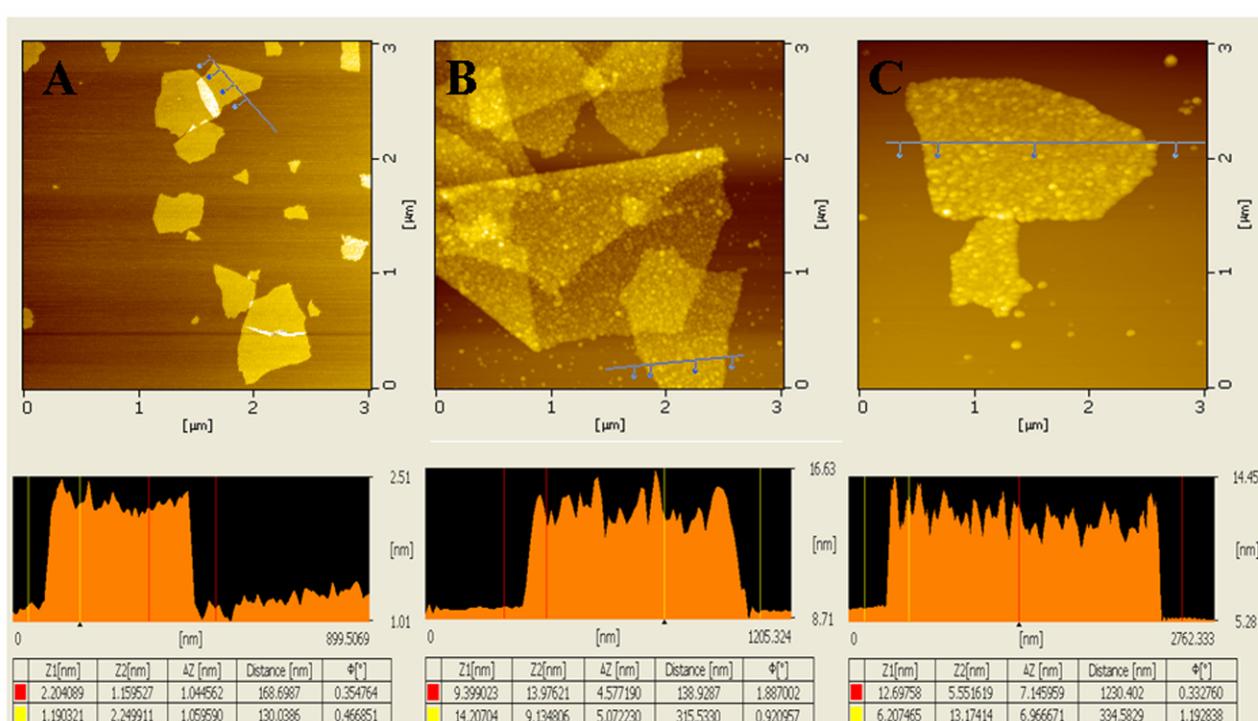


Fig. S3 The typical AFM images and corresponding height profiles along the lines shown in AFM images of as-prepared GTCN at 25 °C (A), 60 °C (B) and 95 °C (C).

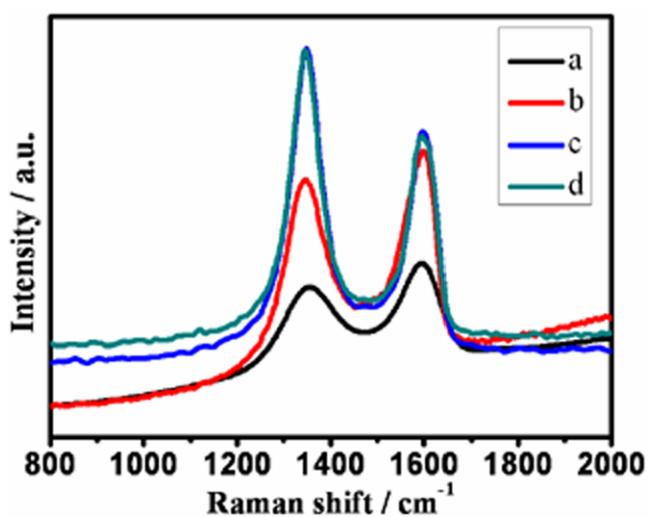


Fig. S4 Raman spectra of GO (a) and the GTCN obtained at 25 °C (b), 60 °C (c) and 95 °C (d).

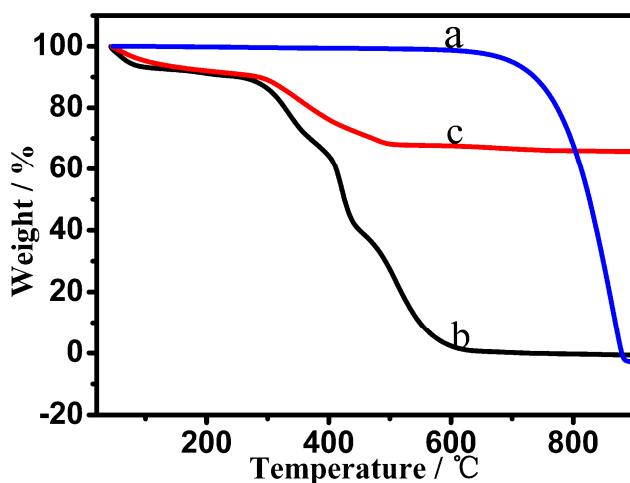


Fig. S5 TGA curves of graphite (a), PVP (b), and GTCN (c) under air atmosphere from room temperature to 900 at  $5\text{ }^{\circ}\text{C min}^{-1}$ .

The  $\text{TiO}_2$  content of the nanocomposite was accurately measured by TGA under air atmosphere from room temperature to 900 at  $5\text{ }^{\circ}\text{C min}^{-1}$  (Fig. S5c). For comparison, TGA measurements were also carried out for pristine graphite and PVP. It was shown that nearly 100 wt % loss in air atmosphere at 900 °C for the pristine graphite and PVP (Fig. S5a, b), which was much higher than that of the GTCN (34.23 wt %) and the  $\text{TiO}_2$  content of the GTCN is about 65.77 % according to the results above.

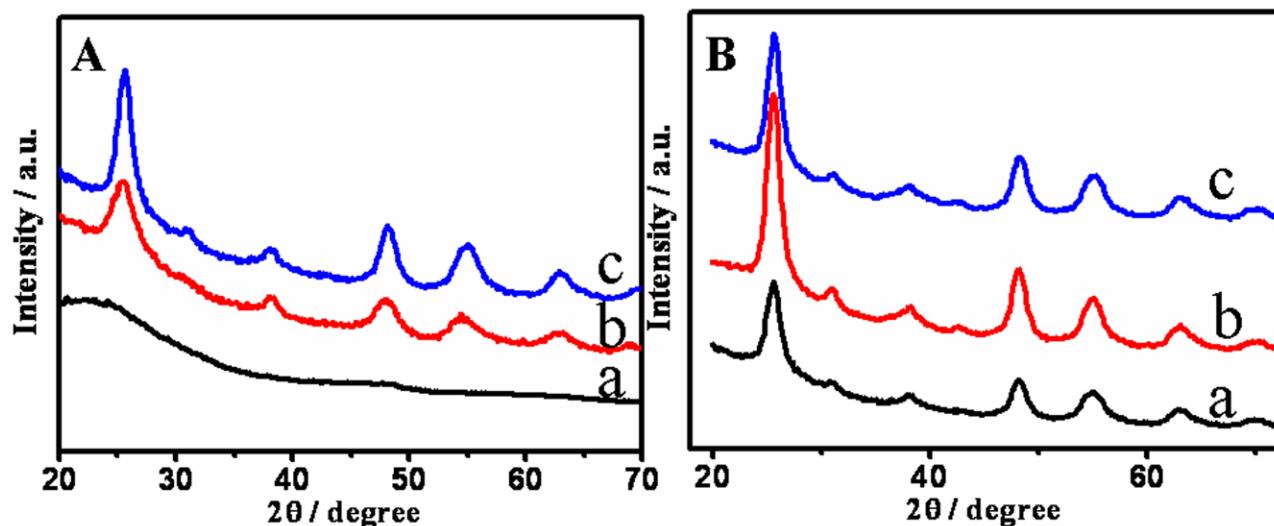


Fig. S6 (A) XRD patterns of as-synthesized GTCN at 25 °C (a), 60 °C (b) and 95 °C (c). (B) XRD patterns of GTCN prepared for 1 (a), 5 (b), and 24 (c) h.

## References

1. Li, Y. G.; Wu, Y. Y., *J. Am. Chem. Soc.* 2009, **131**, 5851.