

Nanostructure control of graphene-composited TiO₂ by a one-step solvothermal approach for high performance dye-sensitized solar cells†

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Experimental section

Graphene-TiO₂ composites were synthesized using natural graphite (Aldrich, synthetic, <20 micro) and titanium isopropoxide (TIP, 97%, Sigma-Aldrich) as the starting materials. To obtain well-exfoliated graphene oxide (GO) sheets and avoid their aggregation during the drying process, GO aqueous suspension was first prepared *via* modified hummers' method¹ and then dried through freeze drying approach. Subsequently, 10 mg of GO were resuspended in 30 ml of organic solvents by sonication for 30 min. The solvents for STG, USTG and NRTG were ethanol (EtOH, absolute for analysis, Merck), benzyl alcohol (BzOH, 99.8%, Sigma-Aldrich) and EtOH (1:2 in volume), and acetic acid (AcOH, 99.8% Sigma-Aldrich) and BzOH (3:17 in volume), respectively. 1 ml of TIP was then dropwise into GO dispersion under stirring. Through sonication for 1 h, organic titanium molecules uniformly grafted on the GO sheets by chemisorption.² The reduction of GO and crystallization of TiO₂ were achieved simultaneously through one-step solvothermal reactions. Reaction conditions were 180 °C for 24 h, 150 °C for 12 h and 150 °C for 12 h, for STG, USTG and NRTG, respectively. The resulting composites were collected by filtration, rinsed by ethanol to remove the free TiO₂ particles and dried under vacuum. To facilitate comparison, pure 12 nm spherical TiO₂, 2 nm ultra-small TiO₂ and TiO₂ nanorods were prepared in a similar manner but without the addition of GO. These control samples were labelled as STG-Ctr, USTG-Ctr and NRTG-Ctr, respectively. The electrodes were prepared by doctor-blade technique using above materials on fluorine-doped tin oxide (FTO) glass and calcined at 450 °C in air for different time. The thickness

and active area of electrode films were controlled at $\sim 6 \mu\text{m}$ and 0.2 cm^2 , respectively. The as-prepared electrodes were sensitized by immersing in ethanol solution, containing 0.4 mM N719 dye (Solaronix) for 20h. These sensitized photoanode were sandwiched with platinum-coated FTO counter electrodes and sealed using a $\sim 20 \mu\text{m}$ thick polypropylene spacer between two electrodes. The liquid iodide electrolyte (Iodolyte AN-50, Solaronix) was injected into the internal space of cells through reserved channels, which were also sealed after injections.

The morphology and thickness of the obtained GO were evaluated by atomic force microscopy (AFM, Asylum Research, MFP 3D). The morphologies of three composite nanosheets were investigated using transmission electron microscopy (TEM, JEOL-2010 microscopes) at 300 kV. The phases of graphene-TiO₂ composites were identified by X-ray diffraction (XRD) analysis using Bruker D8 X-ray diffractometer with Cu K α radiation as the X-ray source ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were obtained using a Renishaw inVia Raman microscope with excitation wavelength at 514.5 nm in a backscattering configuration. The surface morphologies of electrodes were observed using field emission scanning electron microscopy (FESEM, JEOL JSM-6700F), which was also used for EDX tests to determine the concentration of graphene in different electrodes. The specific surface area and pore volume were measured with a commercial pore and surface analyzer (Quantachrome Adsorb-1) and calculated using the Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) methods. The *J-V* characteristics of DSSCs with different electrodes were measured by an electrochemical analyzer (Keithley 2420 SourceMeter) under solar simulator illumination (ABET Technologies Sun 2000 Solar Simulator, $100\text{mW}/\text{cm}^2$, AM 1.5G spectrum). The IPCE were conducted using Newport lamp ($100\text{mW}/\text{cm}^2$) and light filters as monochromatic light source and Si photovoltaic cell as reference. The EIS were performed using PARSTAT 2273 Advanced Electrochemical system (Princeton Applied Research) with frequency range from 0.1 Hz to 100 kHz.

Supplementary results

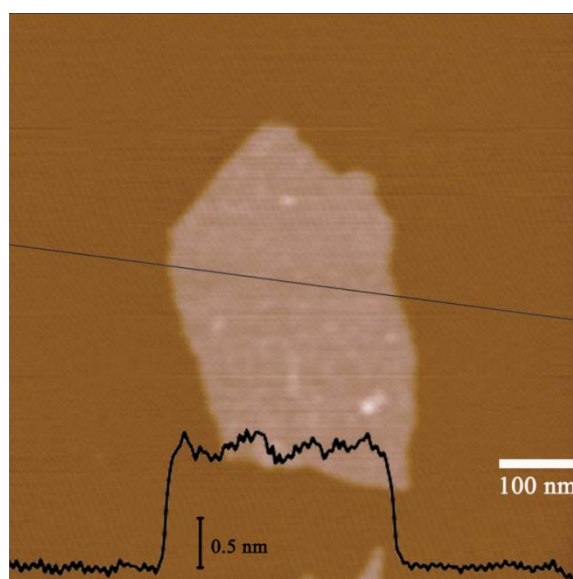


Fig. S1 AFM image of a GO nanosheet with a height profile taken along the straight line shown.

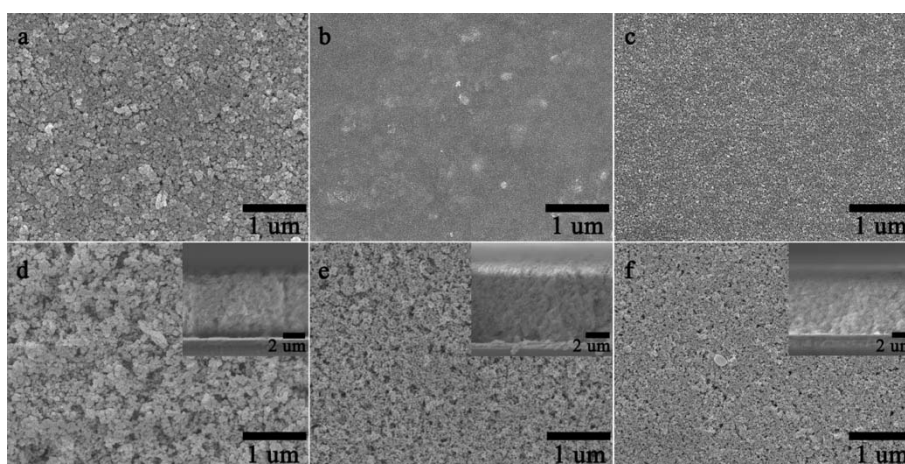


Fig. S2 SEM images of electrodes prepared using (a) STG-Ctr, (b) USTG-Ctr, (c) NRTG-Ctr, (d) STG, (e) USTG and (f) NRTG. The insets are the cross sectional SEM images of corresponding electrodes.

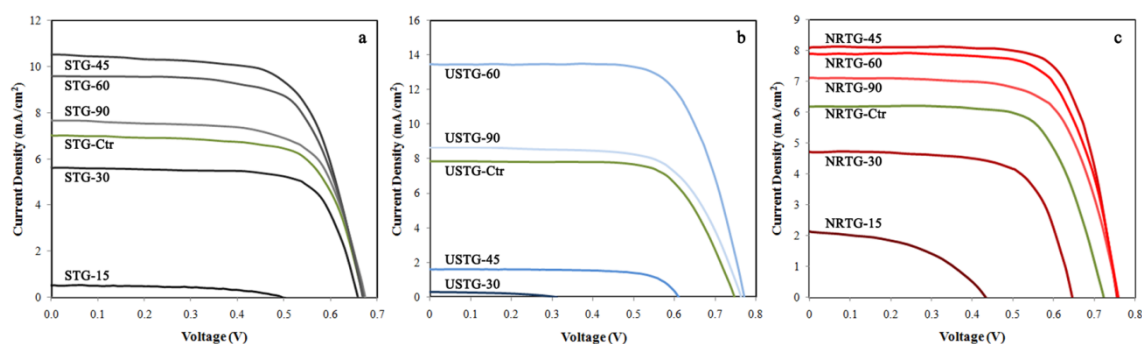


Fig. S3 *J-V* characteristics of DSSCs with different electrodes prepared using (a) STG and STG-Ctr, (b) USTG and USTG-Ctr, and (c) NRTG and NRTG-Ctr, during the optimizations.

Table S1 Parameters for solar cells based on the different electrodes

	Concentration [‡]	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	η (%)
STG-Ctr	0	0.67	7.02	68.8	3.23
STG-15	0.0332	0.50	0.54	53.8	0.14
STG-30	0.0198	0.65	5.63	73.7	2.71
STG-45	0.0110	0.67	10.5	66.6	4.68
STG-60	0.0089	0.67	9.59	68.5	4.39
STG-90	0.0074	0.67	7.66	68.7	3.52
USTG-Ctr	0	0.74	7.85	70.3	4.09
USTG-30	0.0406	0.30	0.27	44.3	0.04
USTG-45	0.0268	0.61	1.58	71.7	0.69
USTG-60	0.0133	0.77	13.5	69.9	7.25
USTG-90	0.0107	0.76	8.67	67.0	4.42
NRTG-Ctr	0	0.72	6.18	70.3	3.13
NRTG-15	0.0308	0.41	2.14	48.9	0.43
NRTG-30	0.0194	0.64	4.70	69.1	2.09
NRTG-45	0.0123	0.75	8.11	73.2	4.48
NRTG-60	0.0102	0.75	7.88	69.6	4.18
NRTG-90	0.0092	0.75	7.10	69.1	3.69
P25	0	0.67	6.20	68.8	2.85

[‡] Concentration is the weight ratio of carbon determined using EDX.

Table S2 Specific surface area and pore volume of different electrode films

	STG-Ctr	USTG-Ctr	NRTG-Ctr	STG-45	USTG-60	NRTG-45
S _{BET} (m ² /g)	104.3	123.3	100.8	132.2	167.2	130.6
Pore volume (cm ³ /g)	0.481	0.403	0.455	0.622	0.603	0.540

Table S3 Parameters of equivalent circuits fitted from EIS measurements of four cells

	P25	STG-45	USTG-60	NRTG-45
C ₁ (F/m ²)	3.493	4.392	6.482	2.367
R ₃ (Ω)	24.83	12.9	10.62	16.21

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339; C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song and C. M. Li, *Angew. Chem. Int. Ed.*, 2010, **49**, 3014.
2. Y. B. Tang, C. S. Lee, J. Xu, Z. T. Liu, Z. H. Chen, Z. B. He, Y. L. Cao, G. D. Yuan, H. S. Song, L. M. Chen, L. B. Luo, H. M. Cheng, W. J. Zhang, I. Bello and S. T. Lee, *Acs Nano*, 2010, **4**, 3482.