Supplementary Information

A novel composite of TiO$_2$ nanotubes with remarkably high efficiency for hydrogen production in solar-driven water splitting

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The supplementary information includes:

Scheme S1

Figure S1-S8

**Movie S1:** Hydrogen evolution over 90 mg of CTCNT photocatalyst in ethanol aqueous solution irradiated under a 300 W Xe lamp (PerkinElmer Co. Inc., light intensity was about 130 mW/cm²).

**Movie S2:** Hydrogen evolution over 90 mg of CTCNT photocatalyst in ethanol aqueous solution irradiated under natural sunlight on 4/26/2012 12:30 PM in the Xiantang University campus, located at 27°53′19.54″ N, 112°52′00.36″ E, Hunan province, People’s Republic of China.
Scheme S1

Scheme S1 Schematic illustration of the water splitting reaction apparatus, including the online gas detection system via the gas chromatography. N₂ was used as a carrier gas in all the tests.
Figure S1

Fig. S1 TEM (A) and HRTEM (B) images of TNT-350B.
Fig. S2 TEM (A) and HRTEM (B) images of TiO$_2$/polymer complex.
Figure S3

Fig. S3 Raman spectra of (a) CTCNT-700 and (b) TNT-350. Two bands at about 1338 cm$^{-1}$ (D-band) and 1597 cm$^{-1}$ (G-band) for the graphitized structures were observed, confirming the carbon with graphitic nature in the CTCNT-700 composite.
Fig. S4 The high-resolution XPS spectra of C 1s regions for CTCNT-700. The signal for C 1s can be well fitted with four contributions. The peak around 284.6 eV is associated with the adventitious elemental carbon. The main contribution around 285.5 eV possesses the same binding energy as that of graphite intercalation compound, which could be assigned to graphitic carbon. The third and the fourth peaks at binding energy of 286.4 and 288.6 eV can be attributed to C-O and C=O bonds, respectively.
Nitrogen adsorption-desorption isotherms of (a) TNT-350, (b) CTCNT-700 and (c) TNT-700. The inset figure shows the corresponding pore size distribution curves.

Fig. S5 Nitrogen adsorption-desorption isotherms of (a) TNT-350, (b) CTCNT-700 and (c) TNT-700. The inset figure shows the corresponding pore size distribution curves.
Fig. S6 XRD patterns of (a) TNT-350, (b) TNT-700, and (c) CTCNT-700. The XRD patterns illustrate that both CTCNT-700 and TNT-350 are composed of only anatase TiO₂. Their diffraction peaks at 2θ values of 25.3°, 37.9°, 48.15°, 54.01°, and 55.3° can be indexed to (101), (004), (200), (105), and (211) crystal planes of anatase TiO₂ (JCPDS 21-1272) respectively, while TNT-700 has characteristic diffraction peaks at 27.4°, 36.1°, and 41.2°, which are attributed to the (110), (101), and (111) faces of rutile TiO₂. These results indicate that the introduction of carbon layer for CTCNT could suppress the transformation of anatase TiO₂ to rutile TiO₂ at high temperature. Notably, no typical diffraction peaks belonging to carbon are observed in CTCNT-700, which may be caused by which characteristic peak at 24.5° is shielded by the main peak of anatase TiO₂ at 25.3°.
Fig. S7 Time course of hydrogen generation by solar photocatalytic water splitting with 0.01 g of CTCNT-700 in a vacuum system. The hydrogen generation rate is about 36.0±0.15 mmol·hour⁻¹·g⁻¹, which confirms results of the continuous measurement.
**Figure S8**

![Graph showing time course of hydrogen generation](image-url)

**Fig. S8** Time course of hydrogen generation with 0.03 g of CTCNT-700 under visible light illumination. During 5 hours irradiation, the hydrogen evolution is about 228 μmol, which corresponds to 1.52 mmol·hour⁻¹·g⁻¹.
Reference
