

Supplementary Information

A novel composite of TiO₂ nanotubes with remarkably high efficiency for hydrogen production in solar-driven water splitting

Caixian Zhao ^{†,‡}, Hean Luo^{*†}, Feng Chen ^{†,‡}, Ping Zhang^{*‡}, Lanhua Yi [§] and Kuiyi You [†]

[†] School of Chemical Engineering, Xiangtan University, Xiangtan, 411105, China. Fax: +86 731 58298267; Tel: +86 731 58293545; E-mail: hluo@xtu.edu.cn

[‡] School of Civil Engineering and Mechanics, Xiangtan University, Xiangtan, 411105, China. Fax: +86 731 58293240; Tel: +86 731 58292247; E-mail: zhangp@xtu.edu.cn

[§] Department of Chemistry, Xiangtan University, Xiangtan, 411105, China.

The supplementary information includes:

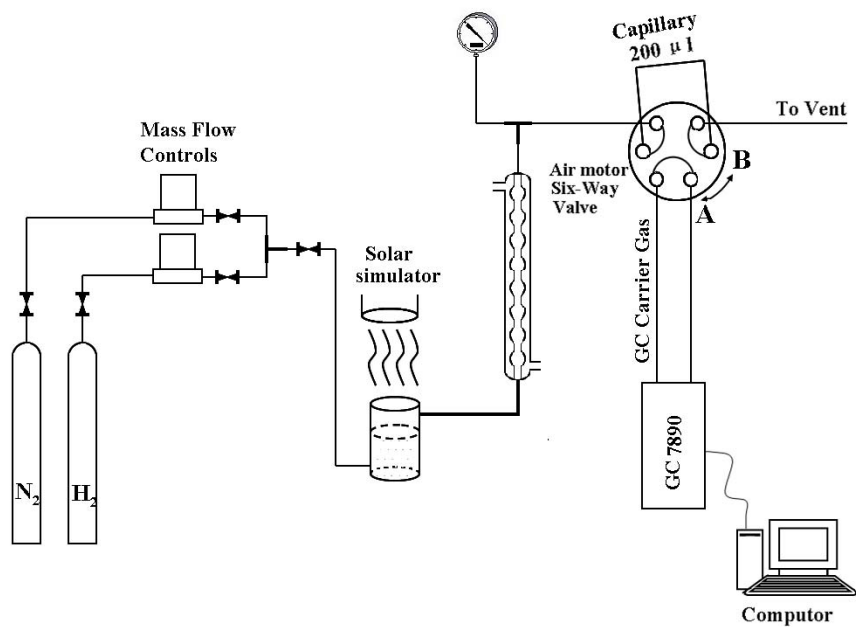
Scheme S1

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. N_2 was used as a carrier gas in all the tests.

Figure S1

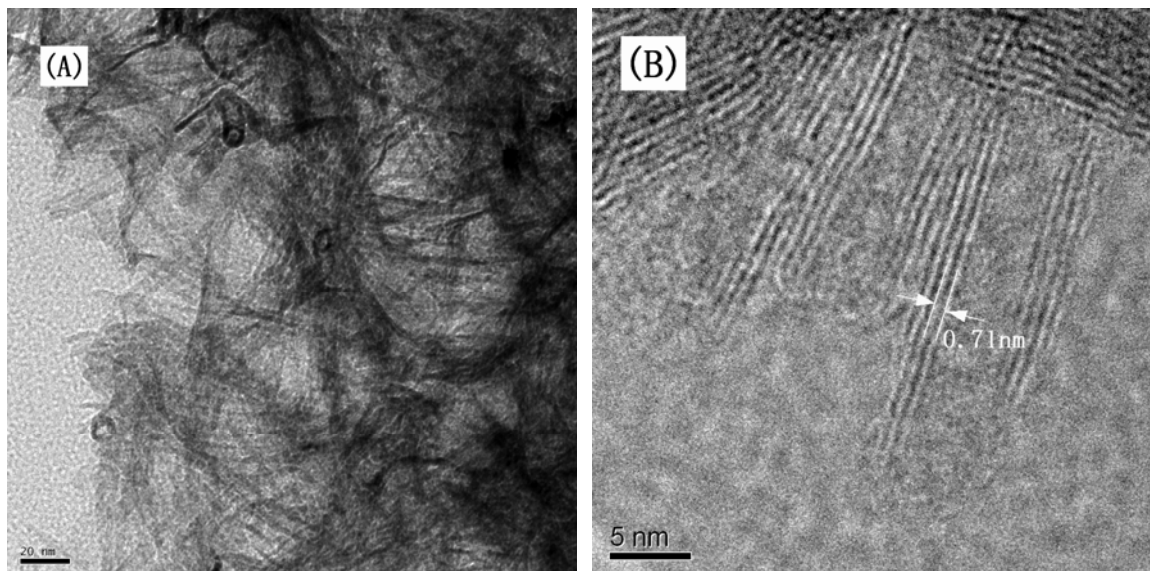


Fig. S1 TEM (A) and HRTEM (B) images of TNT-350B.

Figure S2

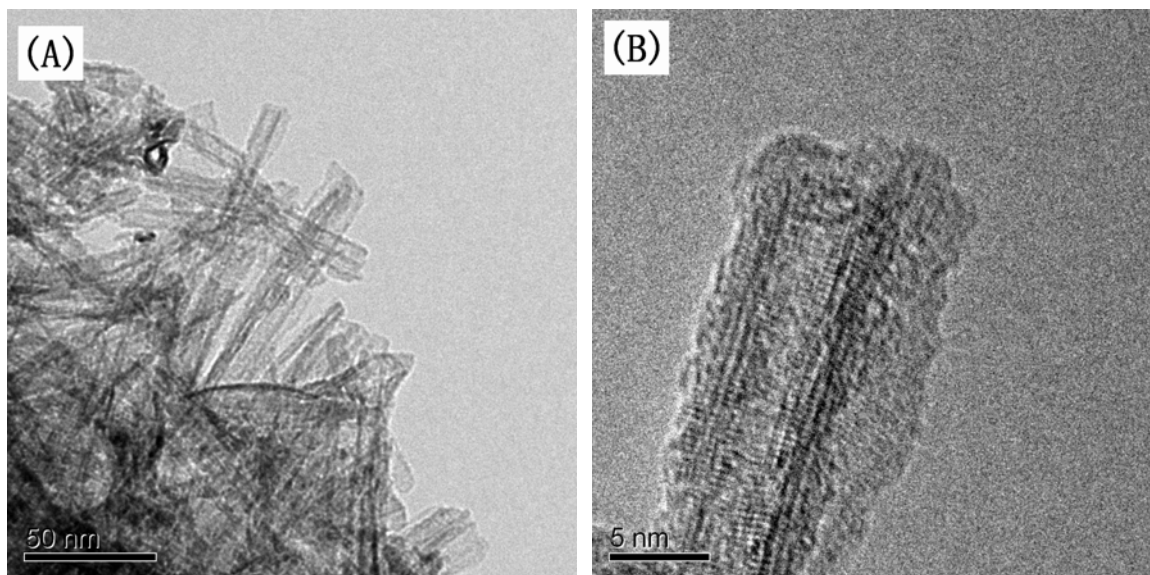


Fig. S2 TEM (A) and HRTEM (B) images of TiO_2 /polymer complex.

Figure S3

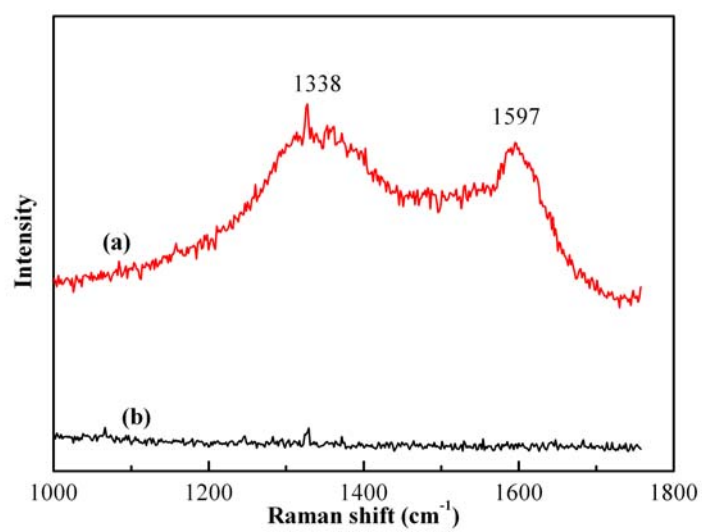


Fig. S3 Raman spectra of (a) CTCNT-700 and (b) TNT-350. Two bands at about 1338 cm^{-1} (D-band) and 1597 cm^{-1} (G-band) for the graphitized structures were observed, confirming the carbon with graphitic nature in the CTCNT-700 composite.

Figure S4

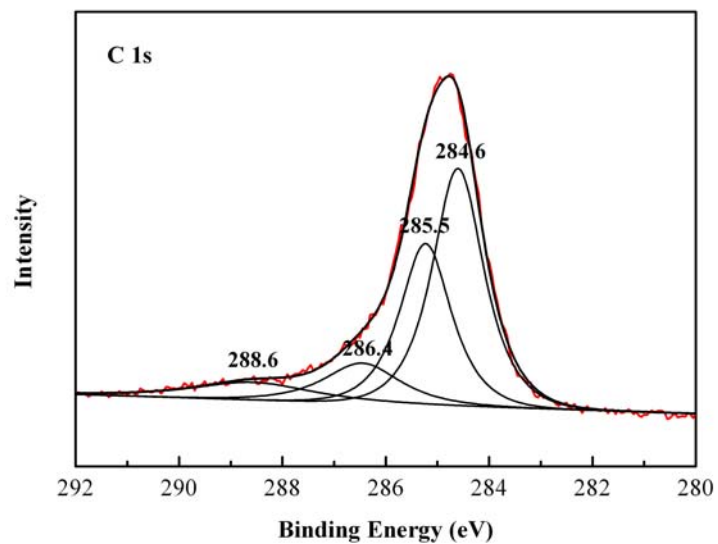


Fig. S4 The high-resolution XPS spectra of C 1s regions for CTCNT-700. The signal for C 1s can be well fitted with four contributions. The peak around 284.6 eV is associated with the adventitious elemental carbon. The main contribution around 285.5 eV possesses the same binding energy as that of graphite 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^{1,2}, respectively.

Figure S5

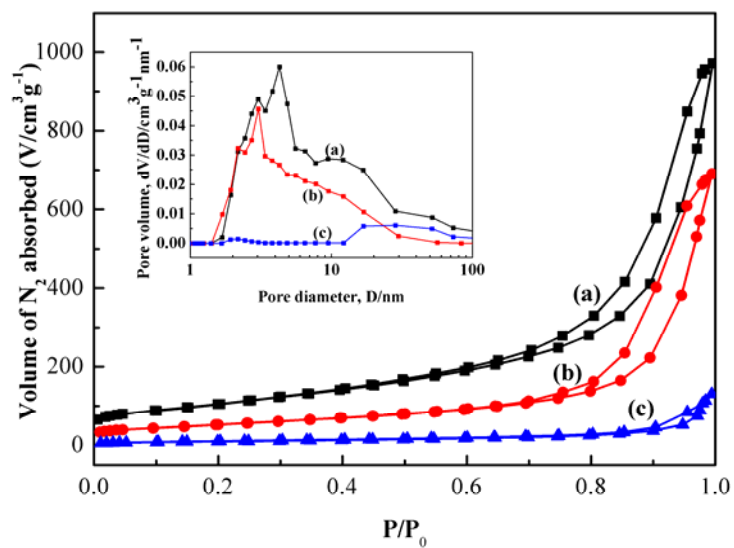


Fig. S5 Nitrogen adsorption-desorption isotherms of (a) TNT-350, (b) CTCNT-700 and (c) TNT-700. The inset figure shows the corresponding pore size distribution curves.

Figure S6

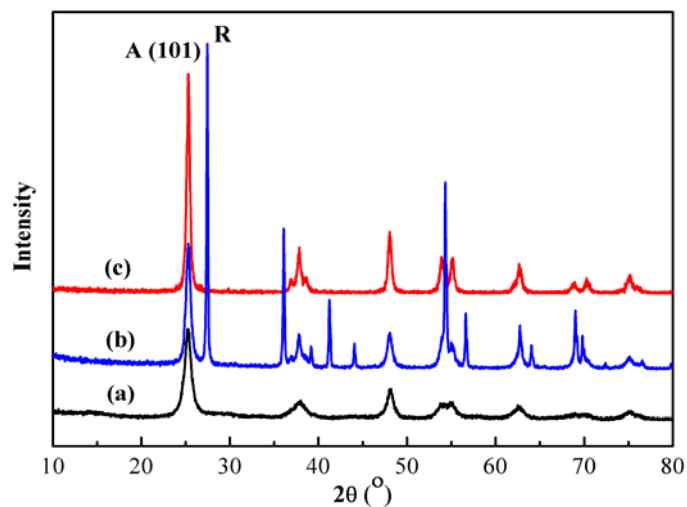


Fig. S6 XRD patterns of (a) TNT-350, (b) TNT-700, and (c) CTCNT-700. The XRD patterns illustrates that both CTCNT-700 and TNT-350 are composed of only anatase TiO_2 . Their diffraction peaks at 2θ values of 25.3° , 37.9° , 48.15° , 54.01° and 55.3° can be indexed to (101), (004), (200), (105), and (211) crystal planes of anatase TiO_2 (JCPDS 21-1272) respectively, while TNT-700 has characteristic diffraction peaks at 27.4° , 36.1° and 41.2° , which attributed to the (110), (101), and (111) faces of rutile TiO_2 . These results indicate that the introduction of carbon layer for CTCNT could suppress the transform of anatase TiO_2 to rutile TiO_2 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 TiO_2 at 25.3° .

Figure S7

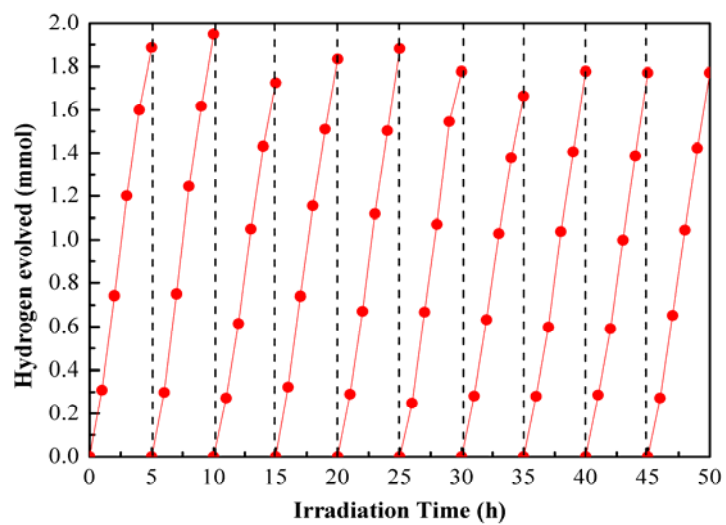


Fig. S7 Time course of hydrogen generation by solar photocatalytic water splitting with 0.01 g of CTCNT-700 in a vacuum system. The hydrogen generation rate is about $36.0 \pm 0.15 \text{ mmol} \cdot \text{hour}^{-1} \cdot \text{g}^{-1}$, which confirms results of the continuous measurement.

Figure S8

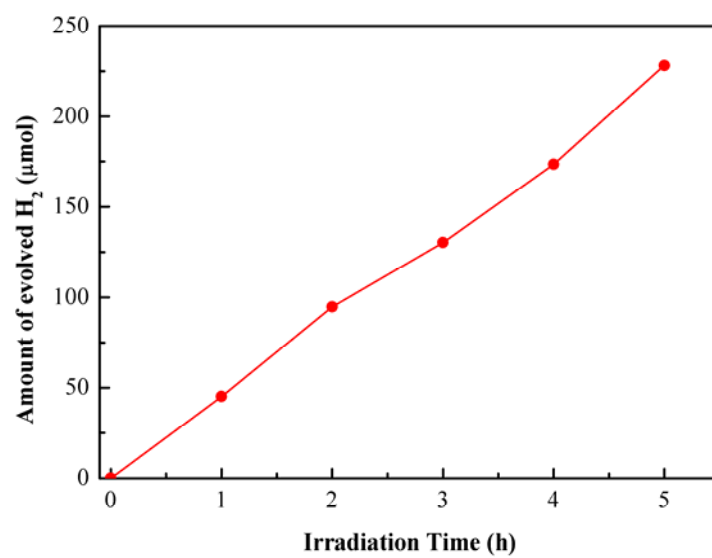


Fig. S8 Time course of hydrogen generation with 0.03 g of CTCNT-700 under visible light illumination. During 5 hours irradiation, the hydrogen evolution is about 228 μmol, which corresponds to 1.52 mmol·hour⁻¹·g⁻¹.

Reference

1. A. Choukourov, A. Grinevich O. Polonskyi, J.I Hanus, J. Kousal, D. Slavinska and H. Biederman, *J. Phys. Chem. B*, 2009, **113**, 2984-2989.
2. E. M. Rochafellow, X. W. Fang, B. G. Trewyn, K. Schmidt-Rohr and W. S. Jenks. *Chem. Mater.*, 2009, **21**, 1187-1197.