

Supporting Information for

Solvothermal synthesis of well-defined TiO₂ mesoporous nanotubes with enhanced photocatalytic activity

Zhenfeng Bian^a, Jian Zhu^a, Fenglei Cao^a, Yuning Huo^a, Yunfeng Lu^{b,*}, Hexing Li^{a,*}

^a Department of Chemistry, Shanghai Normal University, Shanghai 200234, P. R. China

^b Chemical & Biomolecular Engineering Department, University of California, Los Angeles CA
90095, USA

Experimental

1. Catalyst Preparation

All chemicals in this work were of analytical grade, and used as received. Multiwall carbon nanotubes (CNTs) were provided in plentiful amounts by Shenzhen Nanotech Port Limited Company. Their outer diameters and lengths were 60–100 nm and 5–15 μm, respectively. They were treated by ultrasonic in concentrated acids (H₂SO₄/HNO₃=1v/1v) to functionalize with surface hydroxyl and carboxyl groups and remove the catalytic metals effectively. The functionalized CNTs were dried under dynamic vacuum at 100°C before the reaction.

In a typical run of synthesis, 0.1 g of CNTs was first dispersed in a clear solution containing 20 ml ethanol, 1.0 ml TiOSO₄ (Aldrich Corp (NO. 495379)), 10 ml glycerol, 10 ml ethyl ether. Then, the stable aqueous suspension was added into a 50

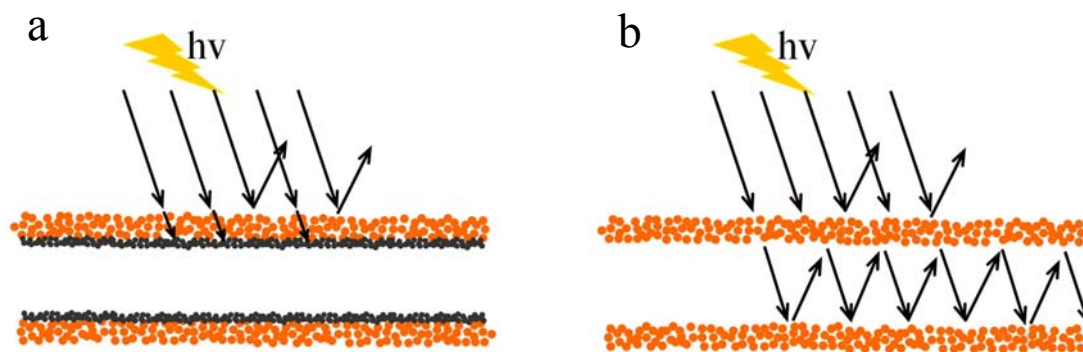
ml autoclave and kept at 110°C for 48 h. The solid products were filtered, washed thoroughly with absolute ethanol and dried under vacuum at 100°C. The as-prepared samples calcined at different temperature for 4 h to remove CNTs. For comparison, CNTs was also dispersed in deionized water which replaced the alcohol solution under the same condition.

2. Activity test

The liquid phase photodegradation of phenol was used as a probe to evaluate the catalytic performance of the TiO₂ samples and carried out at 30°C in a self-designed 200 ml reactor containing 0.050 g catalyst and 50 ml phenol aqueous solution (1mmol/L). Four 8 W lamps with characteristic wavelengths of 365 nm were used as the UV light source which were mounted at 5 cm around the solution. **Before photocatalytic reaction, TiO₂ suspension magnetically stirred for about 30 min in the dark to achieve the adsorption equilibrium.** The reaction mixture was stirred at the speed of 1000 rpm to eliminate the diffusion effects. The photocatalysis was started by irradiating the reaction mixture with UV light. After reaction for 4 h, the catalyst was separated from the solution and the phenol concentration left in the solution was analyzed by a UV spectrophotometer (UV 7504/PC) at its characteristic wavelength ($\lambda = 270$ nm), from which the degradation yield could be calculated. **UV-Vis spectroscopy, HPLC and TOC analyses demonstrated that the phenol was completely mineralized to CO₂ since no other organic products were detected under the present reaction conditions. Preliminary tests demonstrated that, in the absence of either the**

photocatalyst or the light source, only less than 3% phenol decomposed after reaction for 4 h, and thus could be neglected in comparison with degradation yield resulting from photocatalysis. The reproducibility of the photocatalytic degradation was checked by repeating the results at least three times and was found to be within acceptable limits ($\pm 5\%$).

In order to determine the catalyst durability, the photocatalyst was separated from aqueous solution after each run of reactions, followed by washing with H₂O for 3 times and drying at 100°C for 12 h under vacuum. Then, the catalyst was used in the subsequent reaction under the identical conditions.



Scheme S1. Schematic illustration of the light absorbance of the TiO₂ nanotube before (a) and after (b) removal of the CNTs template.

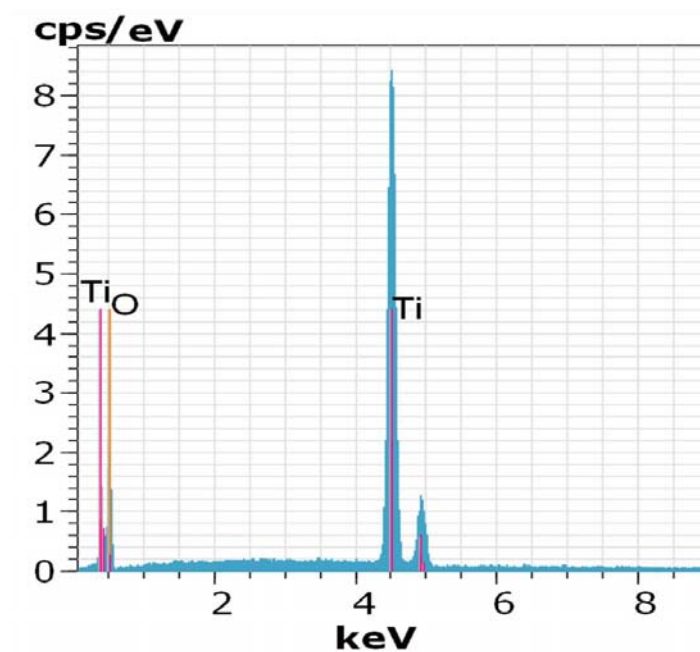


Figure S1. EDX spectrum of TiO₂ nanotubes calcined at 500°C.

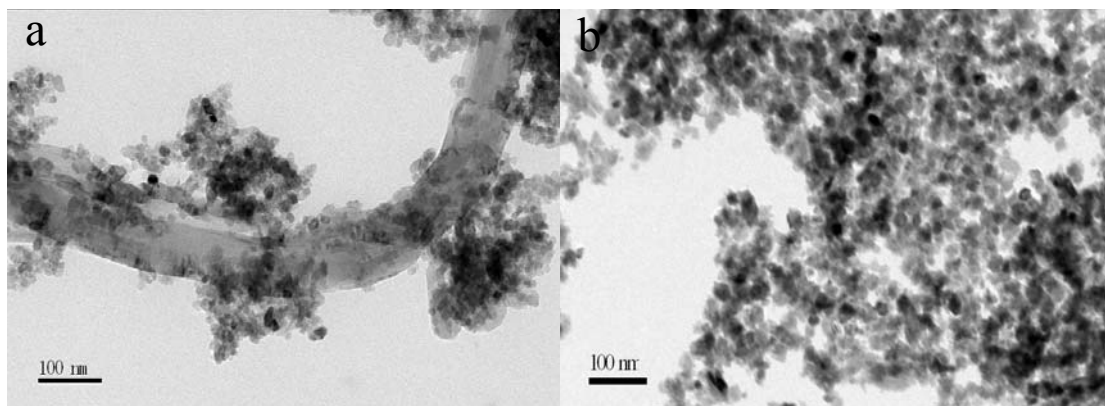


Figure S2. TEM images of (a) TiO₂/CNTs obtained by hydrothermal treatment of TiOSO₄ at 110°C for 48 h and (b) the TiO₂ sample obtained by calcination of the TiO₂/CNTs at 500 °C (T-NPs).

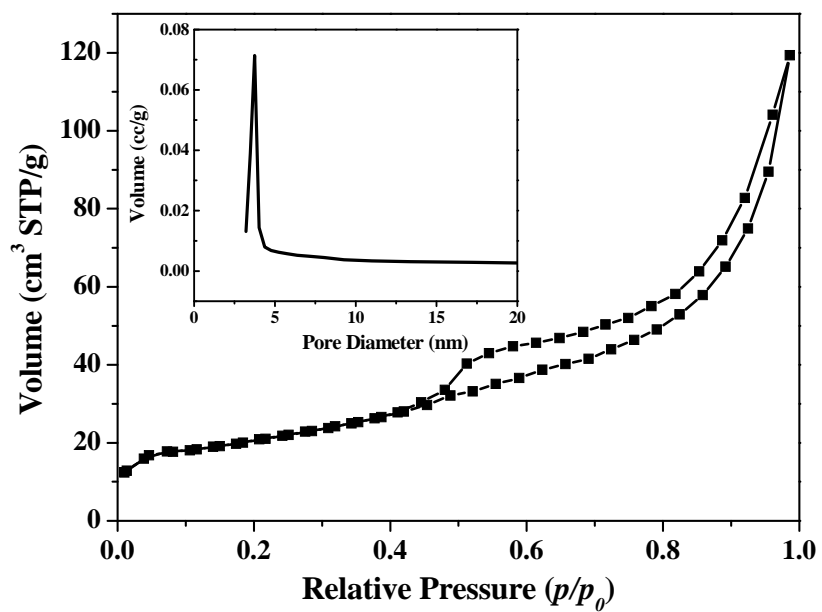


Figure S3. N₂ adsorption-desorption isotherm of the TiO₂-NTs after being calcined at 500°C. The inset is the pore size distribution.

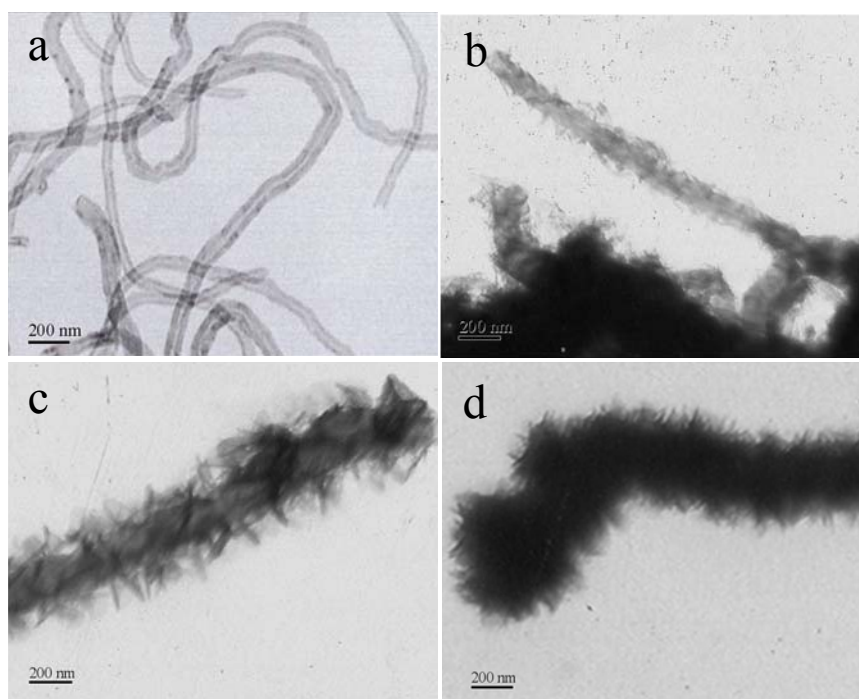


Figure S4. TEM images of the pure CNTs template (a) and the CNTs coating with TiO₂ under solvothermal conditions for (b) 1 h, (c) 48 h and (d) 144 h.

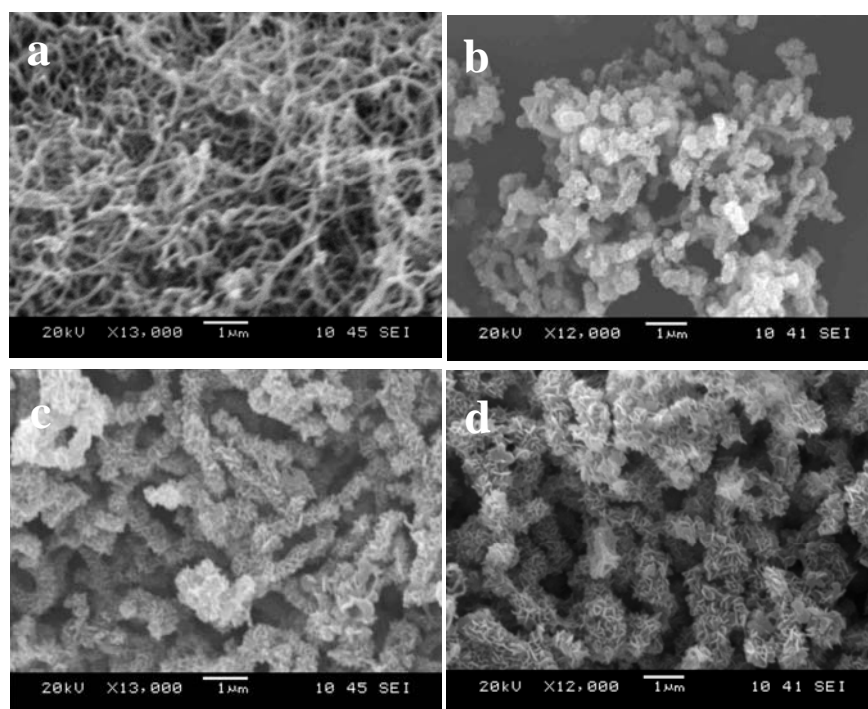


Figure S5. SEM images of the pure CNTs template (a) and the CNTs coating with TiO₂ under solvothermal conditions for (b) 1 h, (c) 48 h and (d) 144 h.

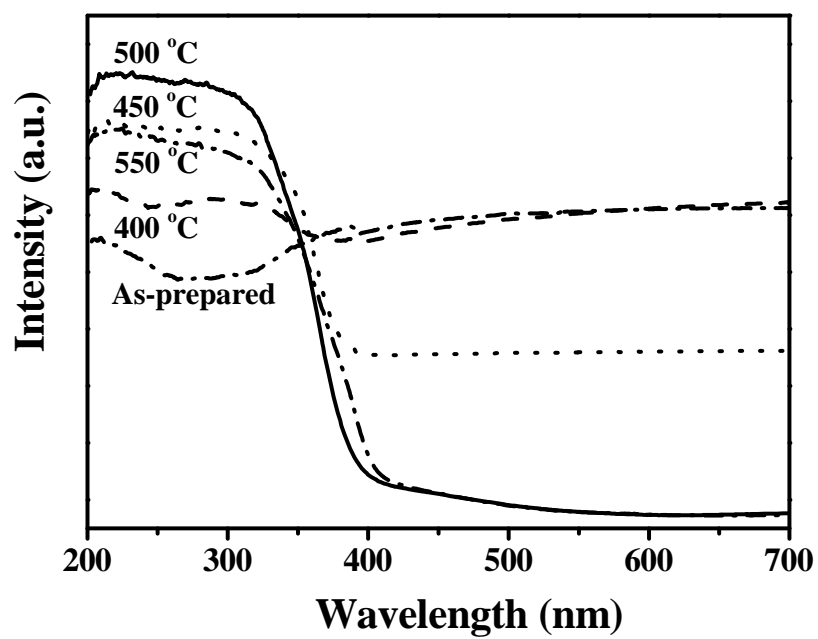


Figure S6. UV-Vis DRS spectra of CNTs/TiO₂ samples calcined at various temperatures.

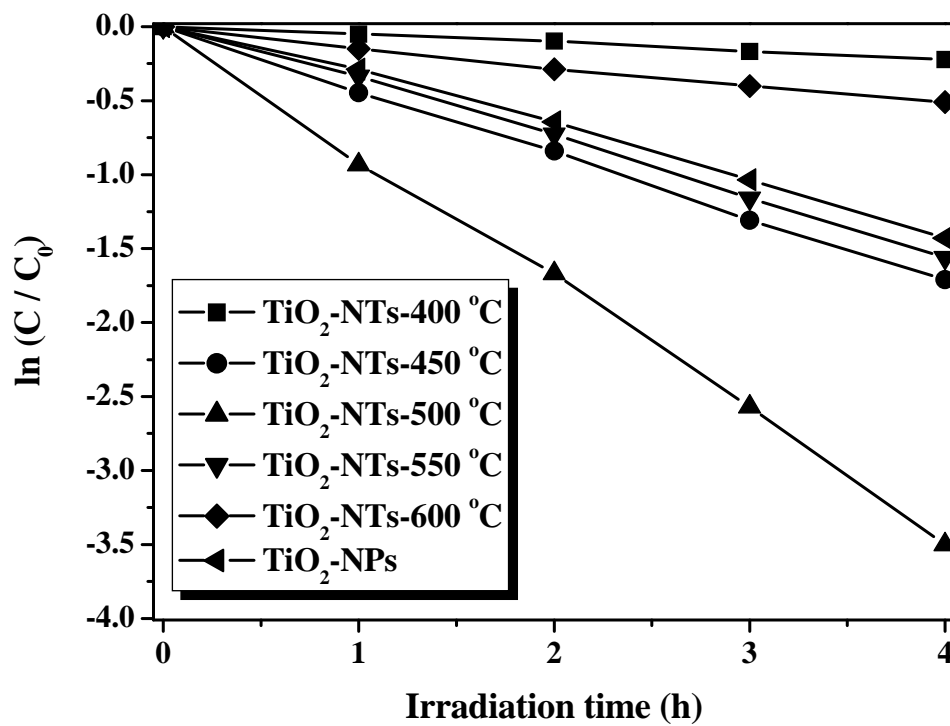


Figure S7. The dependence of $\ln(C/C_0)$ on reaction time under UV light irradiation.

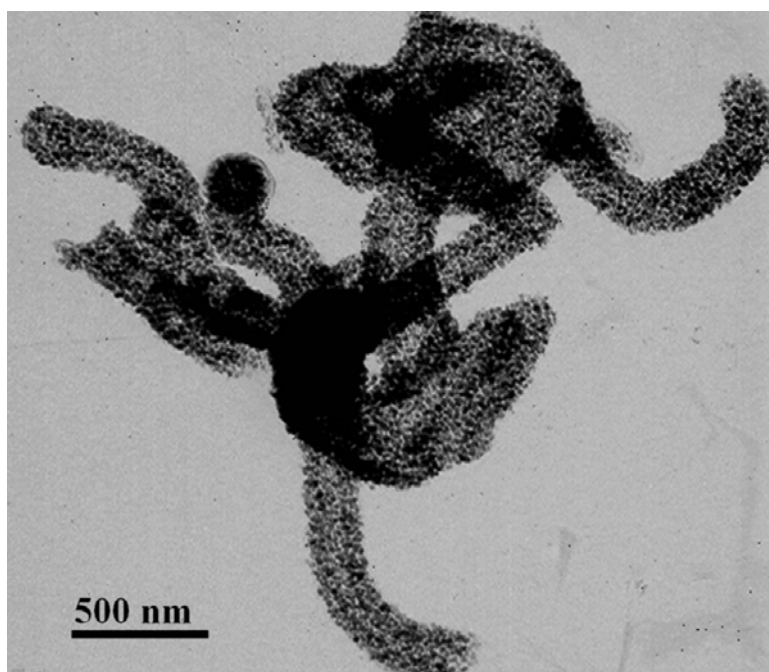


Figure S8. TEM image of TiO₂ nanotubes after being used repetitively for 8 times.