

Facile Synthesis of Carbon Nanotube-Inorganic Hybrid Materials with Improved Photoactivity

Yong Yu, Jun Chen, Zi-Ming Zhou, and Yuan-Di Zhao*

Britton Chance Center for Biomedical Photonics at Wuhan National Laboratory for Optoelectronics – Hubei Bioinformatics & Molecular Imaging Key Laboratory, Department of Biomedical Engineering, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

**Corresponding authors: Tel: 0086-27-87792235; zydi@mail.hust.edu.cn*

1. EXPERIMENTAL SECTION

1.1 Chemicals

The reagents used for the synthesis of CNTs@TiO₂ were commercially available reagents. Tetrabutyl titanate (AR, 97%), ethanol (AR, 99%), acetic acid (AR, 99%), and sulfuric acid (AR, 99%) were purchased from Sigma-Aldrich. Multi-wall Carbon nanotubes with the diameter of 40~60 nm were purchased from Shenzhen Nanotech Port Limited Company. All the chemicals were used as received without further purification. Deionized water was used in all experiments.

1.2 CNTs treatment

In a typical acid treatment, 1g pristine CNTs was sonicated in 10 mL mixed solution of concentrated sulfuric acid and nitric acid with a volume ratio of 3:1 with an ultrasonic bath for 5 minutes. The suspension was then refluxed under magnetic stirring at 120 °C for 20 minutes. After that, the suspension was cooled naturally to room temperature and centrifuged. The resulting wet powder was thoroughly washed with distilled water until the pH of the filtered solution was about 7. Finally, the wet powder was kept in a dessicator under vacuum after dried at 80 °C for 24 h.

1.3 Synthesis of CNTs@TiO₂ composite

The esterification of acetic acid with ethanol (molar ratio = 1:1) and hydrolysis of TiO₂ precursor was carried out in a round-bottom flask at 25 °C with CNTs (1 g), sulfuric acid (0.3 g), and tetrabutyl titanate (5 g) under moderate stirring after ultrasonic treatment. The collected precipitate was washed thoroughly with anhydrous ethanol and finally calcined with controlled temperatures under argon protection after

dried at 110 °C overnight.

1.4 Photocatalysis Measurement

MO solution (20 mg/L) was prepared in water, and 20 mL of the solution was transferred to quartz cuvettes. Control catalysts were placed in the cuvettes filled with MO solution. The quartz cuvettes were then exposed to UV or visible light (halogen-tungsten lamp with light filter to cut off the light below 410 nm) at room temperature. The decrease in absorbance of characteristic peaks of MO was measured after various reaction conditions using UV-vis absorbance spectroscopy.

1.5 Characterization

The morphologies of all samples were observed by field-emission scanning electron microscope (SEM, JSM-6700F, JEOL, Japan). SEM EDX was used for the chemical analysis of samples. The composition of samples were measured by a powder X-ray diffractometer (XRD, D8 ADVANCE, Bruker, Germany) with Cu KR irradiation ($\lambda=0.15418$ nm). UV-vis absorption spectra were recorded with UV-vis spectrometer (WV-2550, Shimadzu, Japan). FTIR and Raman spectra were recorded between 300-3000 cm^{-1} with FTIR-Raman spectrometer (VERTEX 70, Bruker, Germany), and the laser wavelength was 1064 nm.

2. Results

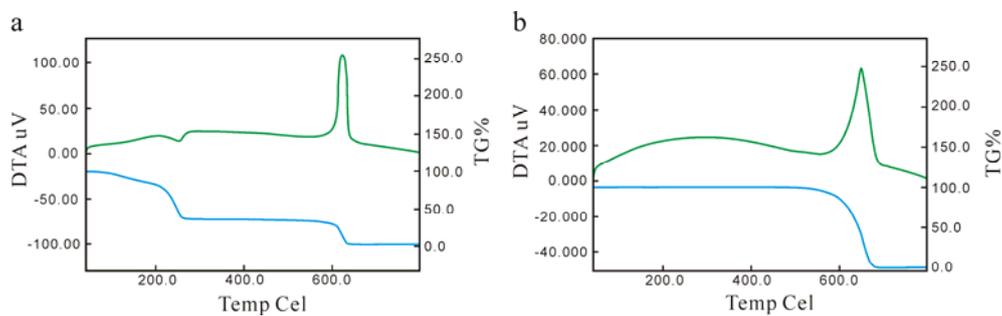


Figure S1. TGA-DSC curves of CNTs before (a) and after (b) oxidation.

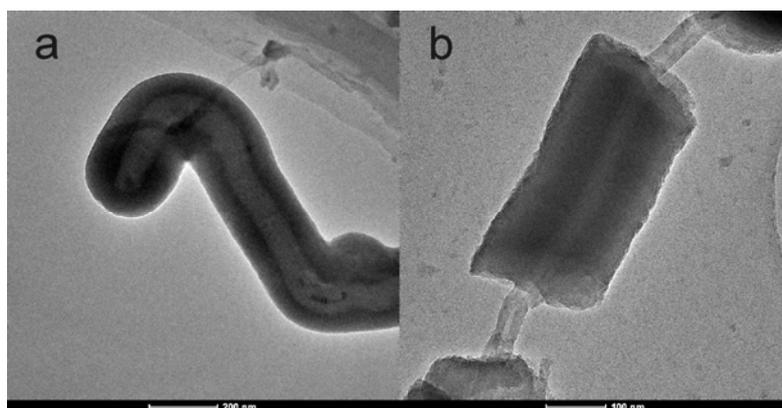


Figure S2. High magnification TEM images of the end (a) and middle (b) of core-shell CNTs@TiO₂.