

Supporting Information

Facile fabrication of TiO₂-based Composites with Tunable Properties and Improved Performance through a General and Controllable Method

*Yong Yu, Zi-Ming Zhou, Wei Wen, 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)

Experimental section

1. Chemicals

The reagents used for the synthesis of composites were commercially available reagents. Zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), tetraethyl orthosilicate, ammonia, tetrabutyl titanate, ethanol, acetic acid, methyl orange (MO), and sulfuric acid were purchased from Sigma-Aldrich and carbon nanotubes (CNTs) were purchased from Shenzhen Nanotech Port Limited Company. All the chemicals were used as received without further purification.

2. Synthesis of ZrO_2

Appropriate amounts of zirconyl chloride octahydrate was added into deionized water and stirred until forming transparent solution. Ammonia was gradually dropped into the solution until the pH value was adjusted to 10 at room temperature. The collected precipitate was washed thoroughly, and then dried at 120 °C overnight. The dried powder was calcined at 650 °C for 2 h in air.

3. Synthesis of SiO_2

20 ml of tetraethyl orthosilicate was added into the mixture with 250 ml of ethanol and 20 ml of ammonia, followed by vigorous stirring for 24 h. The precipitates were washed with alcohol, and then dried at 120 °C for 24 h.

4. Synthesis of core-shell composites

The esterification of acetic acid with ethanol (molar ratio = 1:1) and hydrolysis of TiO_2 precursor was carried out in a round-bottom flask at 25 °C with core particles (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 conditions after dried at 110 °C overnight.

5. Photocatalysis Measurement

MO solution (40 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 light at room temperature. The decrease in absorbance of characteristic peaks of MO was measured after various reaction conditions using UV-vis absorbance spectroscopy.

6. Characterization

The morphologies of all samples, before and after coating, were observed by field-emission scanning electron microscope (SEM, JSM-6700F, JEOL, Japan). The structures of all samples were characterized with the aid of transmission electron microscope (TEM, Tecnai G20, JEOL, Japan) and High resolution transmission electron microscope (HRTEM, JEM-2010FEF, JEOL, Japan). TEM EDX was used for the chemical analysis of samples, before and after coating. 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 DRS and Fluorescence spectra were recorded with UV-vis spectrometer (WV-2550, Shimadzu, Japan) and Fluorescence Spectrometer (FP-6500, Jasco, Japan). The CNTs content of composite was measured by a thermal analyzer (Diamond TG/DTA, PerkinElmer, United States).

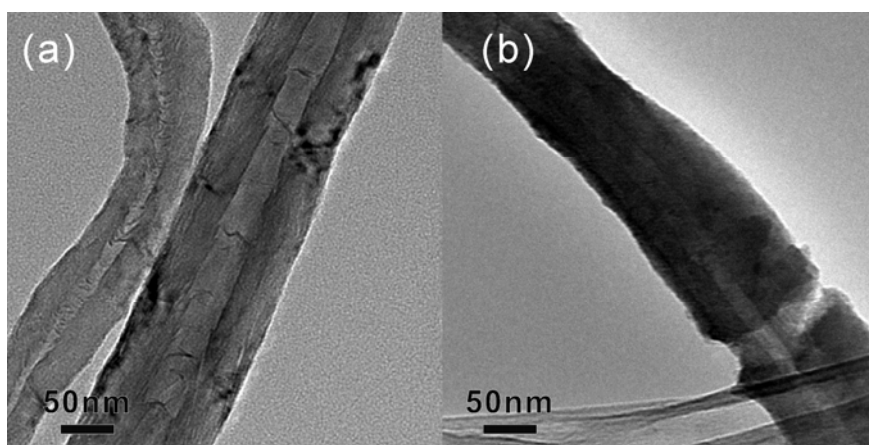


Figure S1. TEM images of pristine CNTs (a) and CNTs@TiO₂ (b).

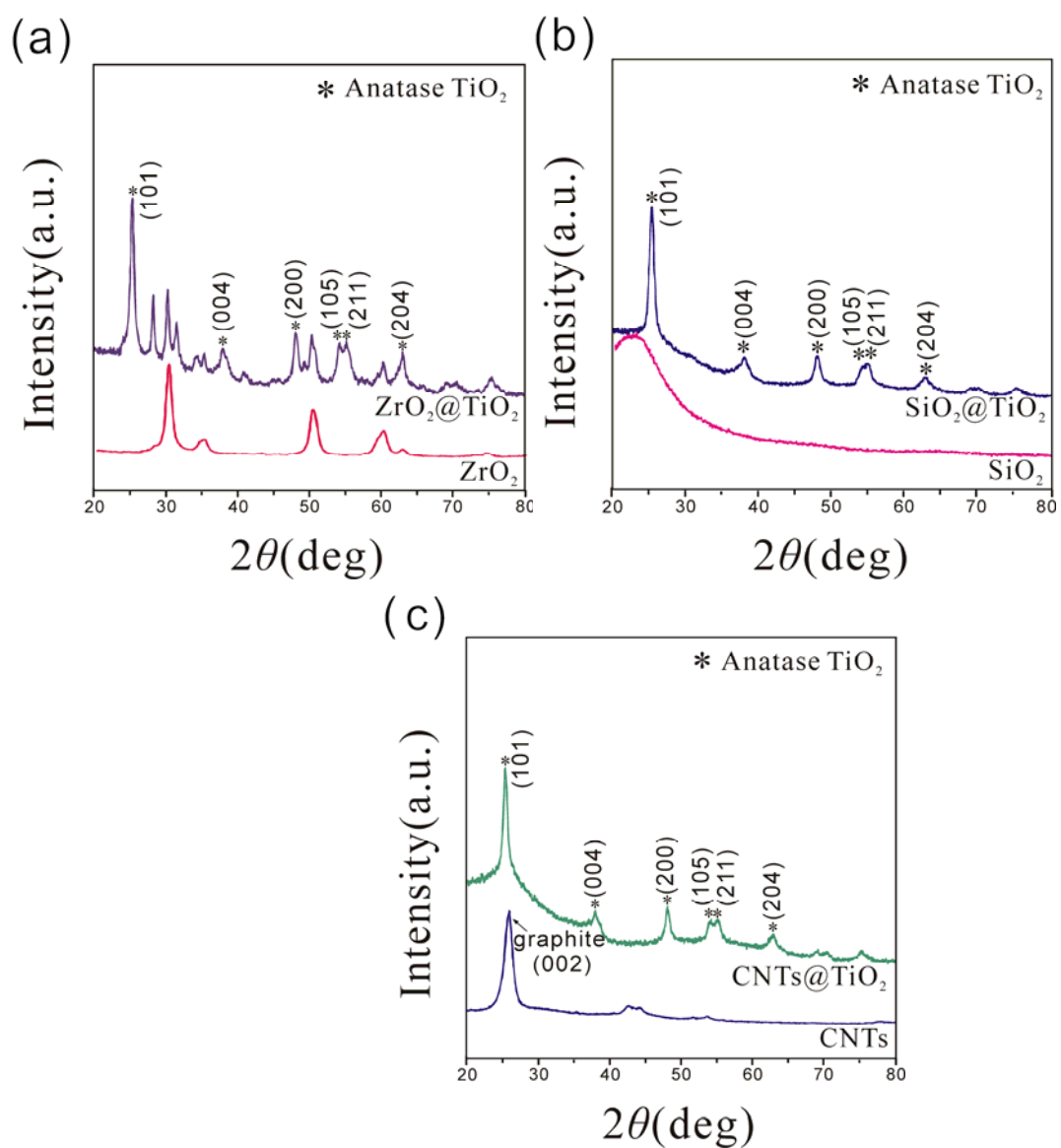


Figure S2. XRD patterns of ZrO₂@TiO₂ (a), SiO₂@TiO₂ (b), and CNTs@TiO₂ (c).

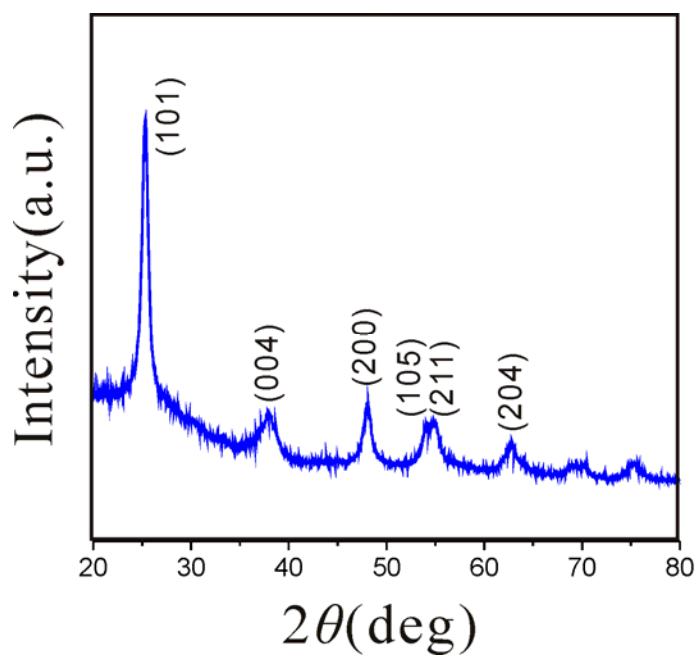


Figure S3. XRD pattern of TiO₂ NPs.

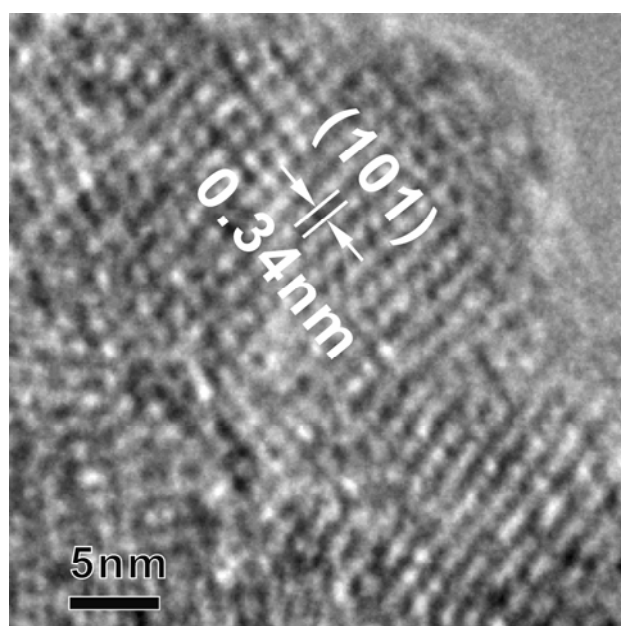


Figure S4. HR-TEM image of TiO₂ NPs.

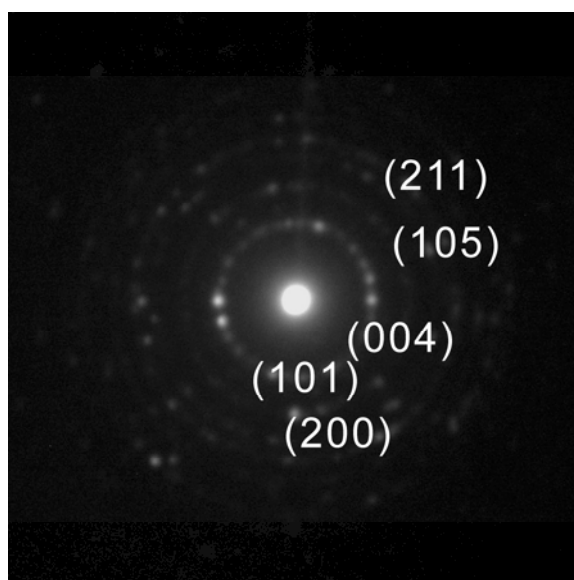


Figure S5. SAED pattern of TiO₂ NPs.

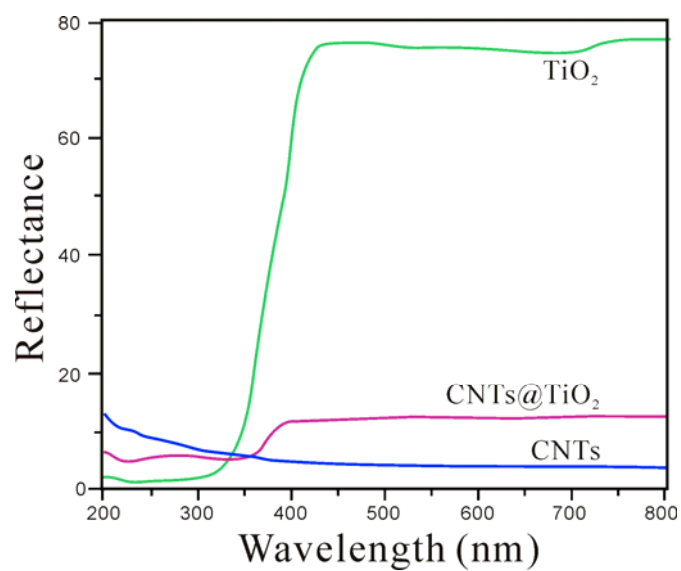


Figure S6. UV-vis absorption spectra of CNTs, CNTs@TiO₂, and TiO₂.