

EXPERIMENTAL SECTION

1. Experimental Materials

AAO membranes (Whatman Co. Ltd), C₂H₂, Ar, titanium isopropoxide (97+%, Alfa Aesar).

2. Construction of CNT/TiO₂ Coaxial Core-Shell Nanotube Arrays

2.1 Preparation of carbon nanotubes in AAO templates:

Porous anodic aluminum oxide membranes (Whatman, Anodisc, 200-300 nm) were placed in a tubular furnace pre-heated to 650°C in an Ar carrying gas at a flow rate of 40 sccm, with the nanochannels oriented along the flow direction. A mixture of C₂H₂ and Ar (20% C₂H₂ and 80% Ar, at a flow rate of 50 sccm) was then flown for 14 min with the temperature maintained at 650°C. Finally, the furnace was cooled down to room temperature gradually in 7 hours in an Ar flow of 40 sccm.

2.2 Preparation of CNT/TiO₂ composite nanotubes in AAO template:

Firstly, titanium isopropoxide (97+%, Alfa Aesar, USA) was stirred at room temperature for 30 min and then was heated to 55°C. Secondly, the carbon-nanotube-filled AAO membranes were immediately dipped into titanium isopropoxide and sonicated for 4 min first and then kept in still situation for 5 min. During this process, the temperature of titanium isopropoxide was maintained at 55°C. Finally, CNT-TiO₂ coaxial core-shell heterojunction arrays were obtained after the sample was baked at 300°C in the atmosphere for 2 h.

3. Characterization of the Products

Here we studied the morphology and structure by scanning electron microscopy

(SEM, JSM-6700F) and transmission electron microscopy (TEM, JEM-2100). Energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, XSAM800) were used to show the elemental composition, chemical state and existence of the target products. Brunauer-Emmett-Teller (BET, SA-3100) was used to measure the surface area of the product by physisorption of nitrogen at 77 K. In order to show the morphologies of the samples clearly, for SEM and TEM analysis, the products were extracted from the AAO templates by using NaOH solutions ($3\text{mol}\cdot\text{L}^{-1}$). UV-Vis spectroscopy was used to test the light absorption characteristic of the products. And finally a degradation experiment using MO as a target pollutant was also conducted to measure the photocatalytic properties of the products.

4. Photocatalytic Degradation of MO

The photocatalytic degradation of the sample TiO_2 , CNT, CNT/ TiO_2 in AAO templates was performed in three separated quartz reactors containing methyl orange (MO) solution ($10\text{ mg}\cdot\text{L}^{-1}$), and the pH of the solution was adjusted to 3 by using H_2SO_4 . The samples were exposed to UV light (300 W, the strongest emission at 365 nm). The size of the sample used in the photocatalytic degradation test depended on the volume of the MO solution. The value was about $1.5\text{ mL}/\text{cm}^2$. The suspension was kept in the dark for 2 h to reach the adsorption-desorption equilibrium before the irradiation process started. The change of MO concentration as a function of the absorption maximum at a wavelength of 506 nm was monitored by UV-Vis spectrometer (UV-2450) absorption. The kinetics of the degradation reaction were also investigated by the equation: $\ln(C_0/C) = kt$, where C_0 was the initial

concentration of MO, and C was the concentration during the reaction. k was the apparent rate constant, and t is the irradiation time.

Figures and captions

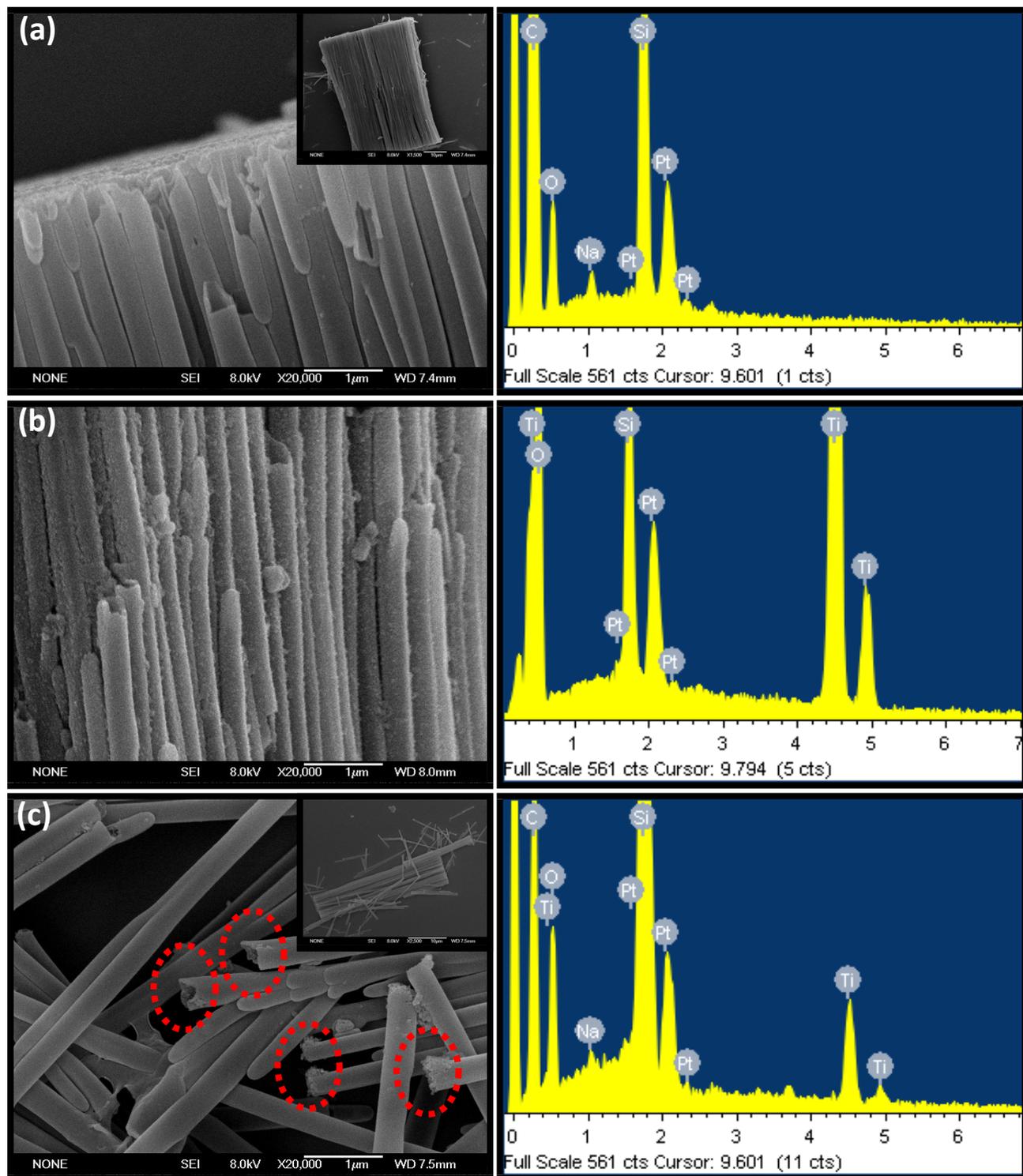


Fig. S1. SEM and EDS analyses of (a) CNTs, (b) TiO₂ nanotubes, and (c) CNT/ TiO₂ composite nanotubes.

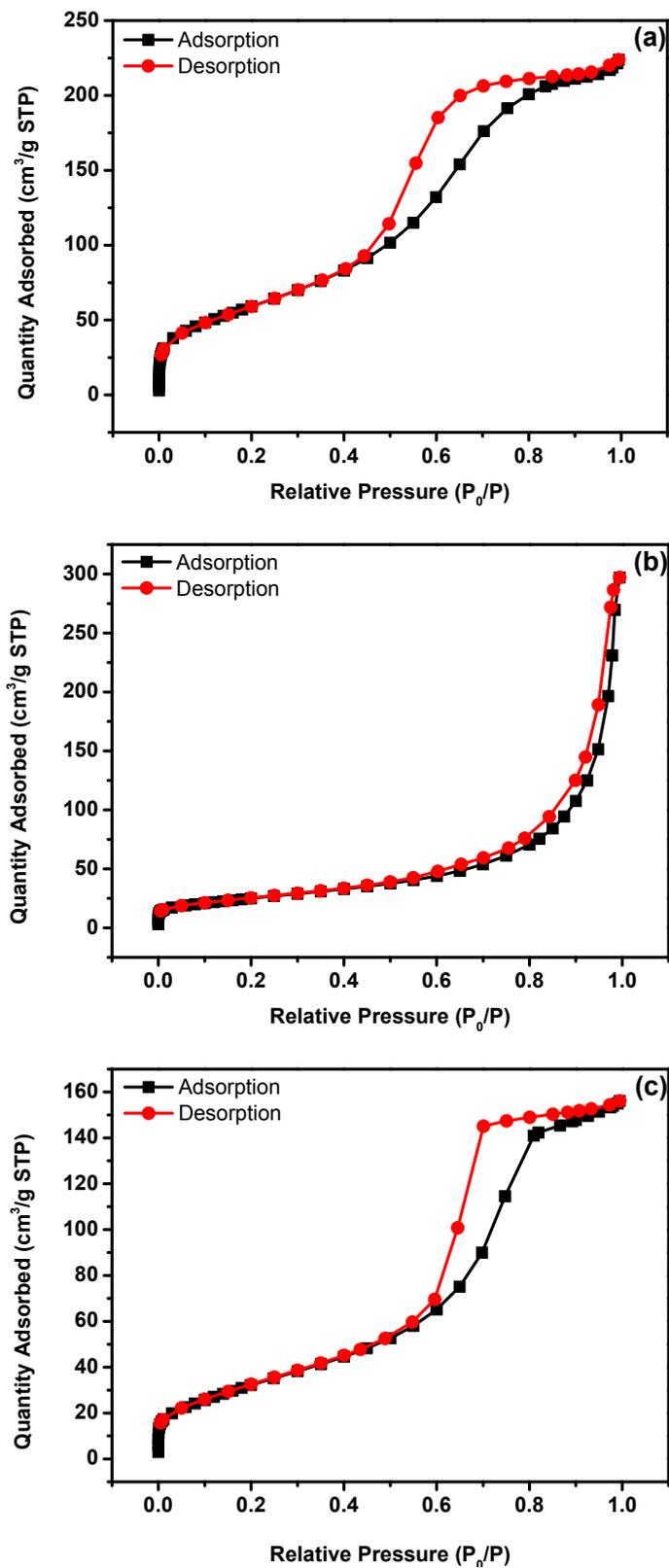


Fig. S2. Nitrogen adsorption-desorption isotherm of (a) CNTs, (b) TiO₂ nanotubes, and (c) CNT/TiO₂ composite nanotubes.

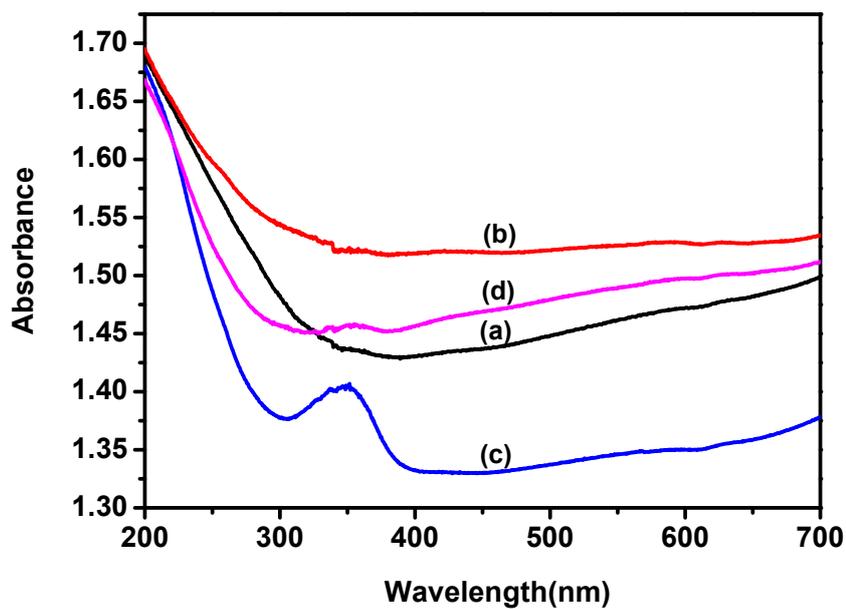


Fig. S3. UV-Vis diffuse-reflectance spectra of (a) AAO template, (b) CNTs imbedded in an AAO template, (c) TiO₂ nanotubes imbedded in an AAO template, and (d) CNT/TiO₂ composite nanotubes imbedded in an AAO template irradiated by a UV lamp.

Table 1. Surface area of CNTs, TiO₂ nanotubes, and CNT/TiO₂ composite nanotubes.

Sample	CNT	TiO ₂	CNT/TiO ₂
S _{BET} (m ² g ⁻¹)	221.6	90.6	122.5

Table 2. Apparent rate constant κ (min^{-1}) of CNTs imbedded in an AAO template, TiO_2 nanotubes imbedded in an AAO template, and CNT/ TiO_2 composite nanotubes imbedded in an AAO template.

Sample	CNT	TiO_2	CNT/ TiO_2
κ (10^{-3}min^{-1})	0.392	1.650	6.020
R^2	0.978	0.998	0.982