

A novel preparation of Ag-doped TiO₂ nanofibers with enhanced stability of photocatalytic activity

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Experimental

Materials and methods

- (1) TiO₂ nanofibers were fabricated by electrospinning technique. The sol-gel was mixed with 5.00 g of tetrabutyl titanate (Ti(OBu)₄ 97%, Sigma Aldrich), 23 mL of methyl alcohol (99.5%, Beijing chemical works), 0.3 mL of acetic acid (99.5%, Beijing chemical works) and 1.40g polyvinylpyrrolidone (PVP, Mw ~ 1 300 000, Sigma Aldrich). All chemicals used in this study were analytical grade and were used without further purification. The feeding rate of the solution in the syringe was controlled at 1.0 mL h⁻¹. The voltage applied to the syringe was 12Kv and the distance from the tip to the collector was 15cm. The as-spinning PVP/TiO₂ membrane was calcined at 520 °C for 4 hours in the rate of 2°C min⁻¹.
- (2) Pure TiO₂ fibers were put in 0.001M AgNO₃ solution, then, irradiated with ultraviolet light for 5 minutes.
- (3) TiO₂ fibers treated by photocatalytic reduction process of silver were put into autoclave containing 0.1M C₆H₁₂N₄ (HMTA) and 0.01M, 0.03M, 0.05M AgNO₃ respectively. The hydrothermal reaction was carried out at 90°C for 10 hours. The as-prepared products were easily collected and then washed with deionized water.

Characterization

The X-ray diffraction (XRD) patterns of the samples were measured using a D/MAX 2250 V diffractometer (Rigaku, Japan), using Cu Ka ($\lambda = 0.15418$ nm) radiation under 40 kv, 30 mA and scanning over the range of 20° ~80°. The morphologies and microstructures of the as-prepared samples were characterized by scanning electron microscopy (SEM, SHIMADZU X-550) and transmission electron microscopy (TEM, Tecnai G2). The as-spun PVP-TiO₂ composite nanofibers were subjected to thermogravimetry differential thermal analysis (TG-DTA, HCT-3). UV-vis absorption spectra were recorded using a UV-vis spectrophotometer (Hitachi U-3010).

Photocatalytic experiments

The selective photocatalytic decomposition of Rhodamine B (Rh B) was conducted in an aqueous solution containing the photocatalyst at ambient temperature. The glass reactor with condensing equipment was illuminated by a wideband lamp bulb (125 W Philips TL/05) with a predominant wavelength of 365 nm. Experimental details were as follows: 0.1g as-prepared sample was placed in 250ml beaker including 100ml RhB (10mg L⁻¹). The mixed aqueous solution with the photocatalyst added was allowed to reach an adsorption-desorption equilibrium primarily before irradiation in the dark for 2h. Then, an aliquot (3 mL) of the solution was taken at 15 minutes intervals during the experiment and tested using UV-vis spectrophotometer. Each catalytic experiment lasted for a total of one hour. After every assay, the analyzed aliquot was poured immediately back into the glass reactor to ensure a roughly equivalent volume of solution. The samples (pure TiO₂ fibers and Ag/TiO₂ fibers) were reused five times and the change of the RhB absorbance was used to monitor the extent of the reaction.

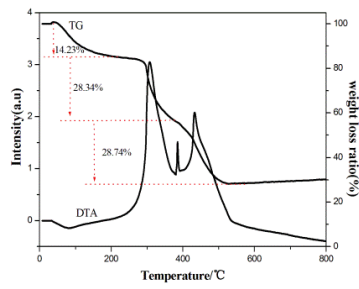


Figure S1: Thermogravimetry-differential thermal analysis (TG-DTA) curves of PVP-TiO₂.

The simultaneous TG and DTA curves of composite PVP/TiO₂ fibers could be divided into three aspects and the weight loss ratio was about 73% until the TG curve shows no change at 520°C. Therefore, the obtained non-woven film was calcined to form the TiO₂ fibrous film at 520°C.

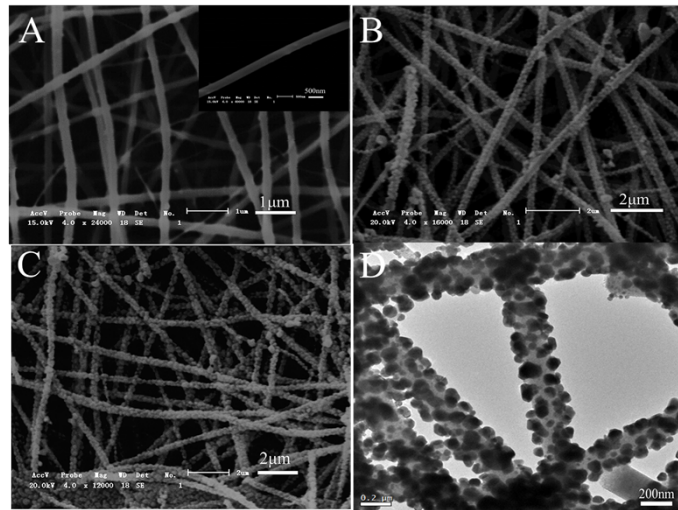


Figure S2: A SEM of TiO₂ fibers after illumination by UV light in Ag⁺ solution (inset was single fiber); B-C Ag/TiO₂ fibers (0.03M and 0.05M AgNO₃ in hydrothermal process respectively); D the TEM image of high densities Ag on surface of TiO₂ fibers.

As we can see from the picture, there are some particles doping on the surface of TiO₂ fiber.

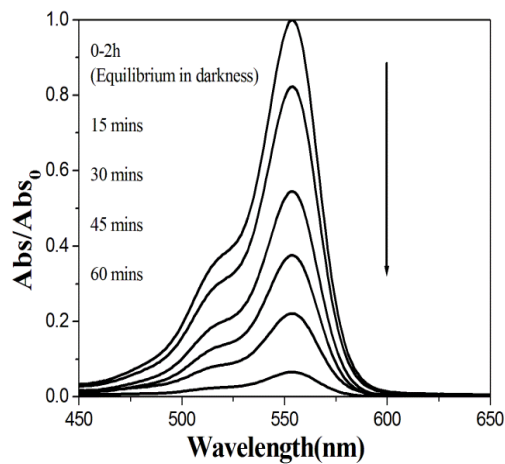


Figure S3: UV light photocatalytic activity of the Ag/TiO₂ heterostructure (Ag⁺, 0.01M)

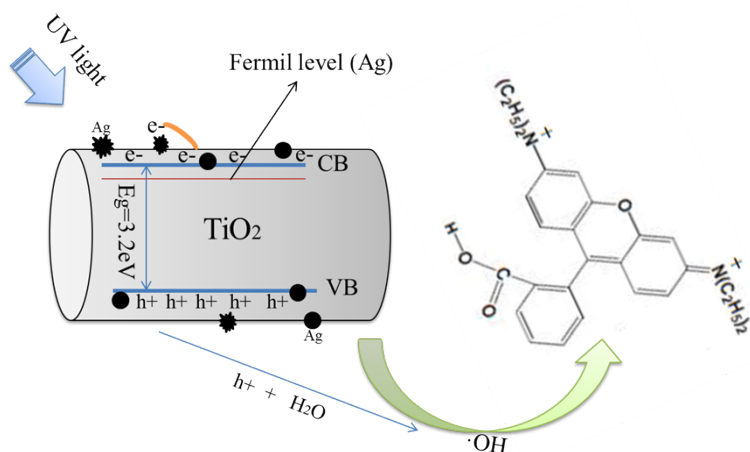


Figure S4: The mechanism of photocatalytic reactions on the semiconductor photocatalyst for degradation of RhB

During the process of degradation for RhB, there is no obvious shift of λ_{max} in the photocatalysis process. Photogenerated electrons would transfer to the Ag particles, leading the holes on the surface of TiO₂ fibers. With the opposed assistance provided by the repulsion between the cationic RhB molecule and the positively charged TiO₂ surface, RhB would adsorb on the surface slightly by oxygen atoms in the carboxylate group. The holes on the surface of TiO₂ fibers react with H₂O and produce the radical species ($\cdot OH$), but it would not attack the diethylamino groups. With the increase of $\cdot OH$, it will diffuse into the bulk solution and attack the chromophoric structure, causing to the cycloreversion of RhB. So it seems the λ_{max} of Rhodamine B does not have obvious shift during the photocatalysis process.