A novel preparation of Ag-doped TiO$_2$ nanofibers with enhanced stability of photocatalytic activity

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Experimental

Materials and methods

(1) TiO$_2$ 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/TiO$_2$ membrane was calcined at 520 $^\circ$C for 4 hours in the rate of 2 $^\circ$C min$^{-1}$.

(2) Pure TiO$_2$ fibers were put in 0.001M AgNO$_3$ solution, then, irradiated with ultraviolet light for 5 minutes.

(3) TiO$_2$ fibers treated by photocatalytic reduction process of silver were put into autoclave containing 0.1M C$_6$H$_{12}$N$_4$ (HMTA) and 0.01M, 0.03M, 0.05M AgNO$_3$ respectively. The hydrothermal reaction was carried out at 90 $^\circ$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–TiO$_2$ 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 TiO$_2$ fibers and Ag/TiO$_2$ fibers) were reused five times and the change of the RhB absorbance was used to monitor the extent of the reaction.
The simultaneous TG and DTA curves of composite PVP/TiO\textsubscript{2} fibers could be divided into three aspects and the weight loss ratio was about 73% until the TG curve shows no change at 520\textdegree C. Therefore, the obtained non-woven film was calcined to form the TiO\textsubscript{2} fibrous film at 520\textdegree C.

As we can see from the picture, there are some particles doping on the surface of TiO\textsubscript{2} fiber.

Figure S3: UV light photocatalytic activity of the Ag/TiO\textsubscript{2} heterostructure (Ag\textsuperscript{+}, 0.01M)
During the process of degradation for RhB, there is no obvious shift of $\lambda$ max in the photocatalysis process. Photogenerated electrons would transfer to the Ag particles, leading the holes on the surface of TiO$_2$ fibers. With the opposed assistance provided by the repulsion between the cationic RhB molecule and the positively charged TiO$_2$ surface, RhB would adsorb on the surface slightly by oxygen atoms in the carboxylate group. The holes on the surface of TiO$_2$ fibers react with H$_2$O 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 $\lambda$ max of Rhodamine B does not have obvious shift during the photocatalysis process.

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