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Investigation of Sn^{4+}-distribution and photocatalytic performance of Sn^{4+}/TiO_2 hollow fiber nanomaterials

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Experimental section

Chemicals

All of the reagents and solvents including tetrabutyl titanate ($Ti(OC_4H_9)_4$), tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), anhydrous alcohol (C_2H_5OH), and methylene blue (MB) were purchased commercially and analytically pure. Cotton fiber (CFs) were used as the templates.

Preparation of Sn^{4+}-doped TiO_2 fibers

Sn^{4+}-doped TiO_2 fibers were prepared through a novel and smart template-assisted two-step (dipping/adsorbing-calcining) method. In order to reflect the role of the distribution state of doped Sn^{4+} ions in improving the photocatalytic performance of TiO_2, a series of Sn^{4+}-doped TiO_2 fibers with well-distribution and different amount (0.00~0.07 mol%) of Sn^{4+} ions were firstly prepared (named as Sn^{4+}/TiO_2-A) for determining an optimal Sn^{4+}-doping amount (0.03 mol% in this study) by the degradation of MB. Then another series of 0.03 mol% Sn^{4+}-doped TiO_2 fibers with different Sn^{4+}-distribution states (surface → interface →……→ bulk) were prepared (named as Sn^{4+}/TiO_2-B) for further investigating the influence of Sn^{4+}-distribution state on photocatalytic performance of TiO_2.

Preparation of Sn^{4+}/TiO_2-A

Typical preparation process of Sn^{4+}/TiO_2-A samples is described as follows: firstly, 1.2000 g CFs were dipped into a $(Ti(OC_4H_9)_4 + SnCl_4)$/EtOH solution for 0.5 h to adsorb Ti^{4+} and Sn^{4+} ions on the surface of CFs. Then, the adsorbed (Ti^{4+} and Sn^{4+}) CFs was naturally dried at room temperature to obtain a precursor, named as (Ti^{4+}+Sn^{4+})/CFs. Secondly, the (Ti^{4+}+Sn^{4+})/CFs precursor was calcined under air atmosphere at 600 ^oC for 2 h to remove CFs templates through its combustion and boost the conversion of adsorbed Ti^{4+} to TiO_2 and entrance of Sn^{4+} ions into TiO_2 lattice. By changing the mole content of Sn^{4+} to Ti^{4+} ions (0.00 to 0.07 mol%) in the solution of $(Ti(OC_4H_9)_4 + SnCl_4)$/EtOH, a series of samples with hollow fiber structure and well-distribution of Sn^{4+} ions were prepared, which were denoted as Sn^{4+}/TiO_2-A-0.00, 0.01, 0.03, 0.05, 0.07. Their photocatalytic results showed that the activity of the Sn^{4+}/TiO_2-

A-0.03% sample was the highest. So under doping 0.03% Sn^{4+}, another series of Sn^{4+}/TiO_2 samples with different distribution states of doped Sn^{4+} would be prepared and used to further investigate the influence of Sn^{4+}-distribution state on photocatalytic performance of TiO_2.

Preparation of Sn^{4+}/TiO_2-B

Another series of 0.03 mol%~Sn^{4+}/TiO_2 samples with different Sn^{4+}-distribution states/depths were prepared by repeating the above-described template-assisted two-step method for twice.

TiO_2 fibers were firstly prepared *via* the two-step method. It was importantly mentioned that the calcining time "*x*" at the second calcination step varied from 20 to100 mins. As-obtained hollow fibers were named as TiO_2-*x* (*x* = 20, 40, 50, 60, 100 mins)

A series of Sn^{4+}/TiO_2-B fibers materials were prepared from TiO_2-*x* by using the two-step method once more. 0.5000 g of as-prepared TiO_2-*x* were dipped in 10 mL $SnCl_4$/EtOH solution (the mole content of Sn^{4+} to Ti^{4+} ions: 0.03 mol%) for 1 h to adsorb Sn^{4+} ions on the surface of TiO_2-*x* nanofibers and then the adsorbed Sn^{4+} TiO_2-*x* fibers naturally dried and were calcined at 600 ^oC for another time "*y*", varying from 100 to 20 mins (keeping $x + y = 2$ h), to prepare another series of 0.03 mol% Sn^{4+}/TiO_2. The as-prepared samples were successively labeled as Sn^{4+}/TiO_2-B-*y*/*x*: 20/100, 40/80, 50/70, 60/60, 100/20. During this calcining process, the adsorbed Sn^{4+} ions on the surface of TiO_2 fibers heat-diffused into TiO_2 lattice and the diffusing/entering depth varied with the calcining time ***y***. So in the series 0.03 mol% Sn^{4+}/TiO_2-B, Sn^{4+}-distribution depth/state changed with the variation of the calcining time *y*.

Characterization

X-ray diffraction (XRD; D/Max-2400, Japan, with Cu Kr radiation (λ=1.5418A) operating at 40 kV and 100 mA) was used to identify the phase structure of the samples, the morphologies of the samples were observed by field emission scanning electron microscopy (FESEM; JEOL, JSM-6701F, Japan) and transmission electron microscopy (TEM; JEOL, JEM-2010, Japan). Inductively Coupled Plasma Optical Emission

Spectrometer (ICP-OES) was used to determine the content of doped Sn^{4+} ion. X-ray photoelectron spectroscopy (XPS) was operated on an AXIS SUPRA Versaprobe system. Ultraviolet-visible (UV-Vis) spectroscopy (UV-3600plus, Japan) was used to examine the UV-Vis absorption performance. Electrochemical impedance spectroscopy and Cyclic voltammetry (CV) were tested on the electrochemical station (CHI 660E, Chenhua).

Photocatalytic test

Photocatalytic experiments were performed on a XPA-7 (G8) photocatalytic reactor (Xujiang, Nanjing, China), described in the reference. 10 mg/L MB solution was used as simulation pollutant. Photocatalytic degradation reaction of MB was carried out in the tubes with 300 W high pressure Hg lamp and 10 cm light distance. 40 mg of the catalyst was added in 40 mL of MB solution. Before irradiation, the suspension system was maintained in dark for 0.5 h to establish adsorption-desorption equilibrium. Then, turning on the lamp, at a certain interval, 5 mL of suspension was separated by centrifugation to remove the powder. The absorbance value of the supernatant solution was measured at 664 nm (λ_{max} of MB solution) and used to calculate the concentration (C_t) of MB solution at reaction time t. The first-order kinetic degradation constant k_1 of MB solution on the samples were used to evaluate their photocatalytic activity and calculated by the formulas: $\ln C_0/C_t = k_1 t$, in which C_0 and C_t are the concentration values of MB solution at the initial time $t = 0$ and reaction time t.

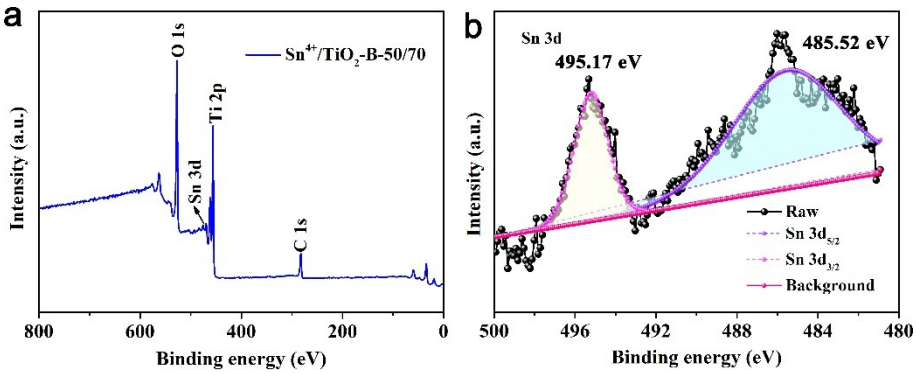
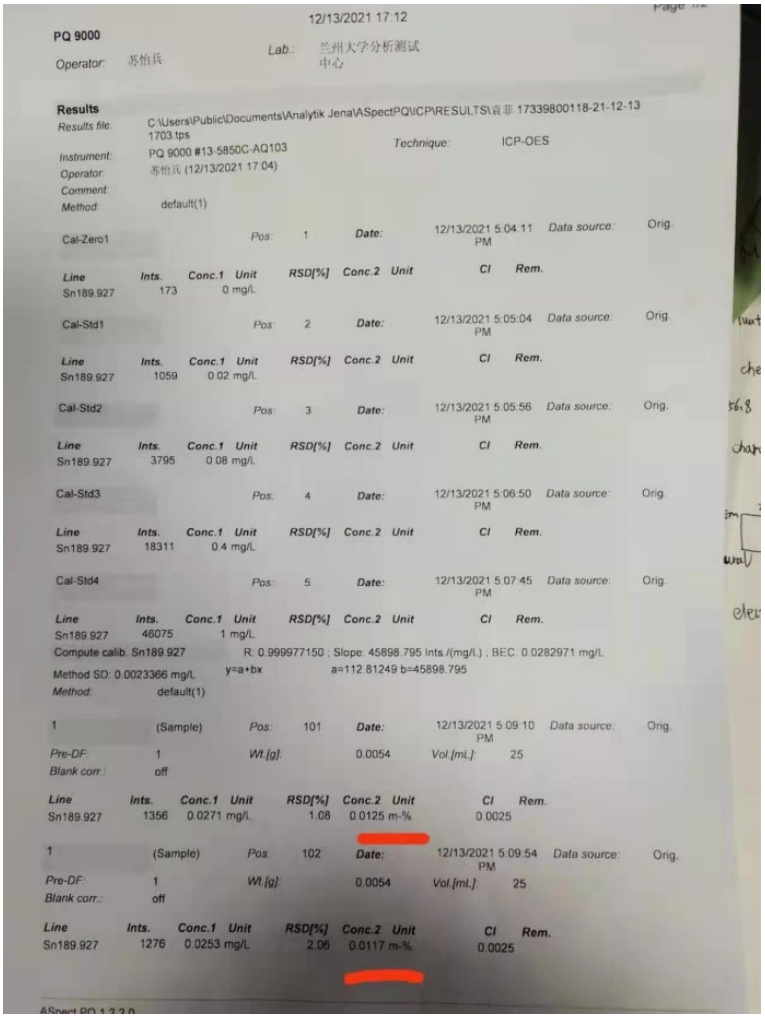


Figure S1. (a) Full spectrum, and (B) high-resolution XPS spectrum of Sn 3*d* for Sn^{4+}/TiO_2-B-50/70.



12/13/2021 17:12

PQ 9000

Operator: 苏怡兵 Lab.: 兰州大学分析测试中心

Results

Results file: C:\Users\Public\Documents\Analytik Jena\ASpectPQ\ICP\RESULTS\袁菲 17339800118-21-12-13 1703.tps

Instrument: PQ 9000 #13-5850C-AQ103 Technique: ICP-OES

Operator: 苏怡兵 (12/13/2021 17:04)

Comment:

Method: default(1)

Cal-Zero1			Pos: 1	Date: 12/13/2021 5:04:11 PM		Data source: Orig.				
Line	Ints.	Conc.1	Unit	RSD[%]	Conc.2	Unit	CI	Rem.		
Sn189.927	173	0	mg/L							
Cal-Std1			Pos: 2	Date: 12/13/2021 5:05:04 PM		Data source: Orig.				
Line	Ints.	Conc.1	Unit	RSD[%]	Conc.2	Unit	CI	Rem.		
Sn189.927	1059	0.02	mg/L							
Cal-Std2			Pos: 3	Date: 12/13/2021 5:05:56 PM		Data source: Orig.				
Line	Ints.	Conc.1	Unit	RSD[%]	Conc.2	Unit	CI	Rem.		
Sn189.927	3795	0.08	mg/L							
Cal-Std3			Pos: 4	Date: 12/13/2021 5:06:50 PM		Data source: Orig.				
Line	Ints.	Conc.1	Unit	RSD[%]	Conc.2	Unit	CI	Rem.		
Sn189.927	18311	0.4	mg/L							
Cal-Std4			Pos: 5	Date: 12/13/2021 5:07:45 PM		Data source: Orig.				
Line	Ints.	Conc.1	Unit	RSD[%]	Conc.2	Unit	CI	Rem.		
Sn189.927	46075	1	mg/L							

Compute calib. Sn189.927 R: 0.999977150 ; Slope: 45898.795 Ints./(mg/L) ; BEC: 0.0282971 mg/L

Method SD: 0.0023366 mg/L y=a+bx a=112.81249 b=45898.795

Method: default(1)

1	(Sample)		Pos: 101	Date: 12/13/2021 5:09:10 PM		Data source: Orig.				
Pre-DF:	1		Wt.[g]:	0.0054		Vol.[mL]:	25			
Blank corr.:	off									
Line	Ints.	Conc.1	Unit	RSD[%]	Conc.2	Unit	CI	Rem.		
Sn189.927	1356	0.0271	mg/L	1.08	0.0125	m-%	0.0025			
1	(Sample)		Pos: 102	Date: 12/13/2021 5:09:54 PM		Data source: Orig.				
Pre-DF:	1		Wt.[g]:	0.0054		Vol.[mL]:	25			
Blank corr.:	off									
Line	Ints.	Conc.1	Unit	RSD[%]	Conc.2	Unit	CI	Rem.		
Sn189.927	1276	0.0253	mg/L	2.06	0.0117	m-%	0.0025			

Figure S2. ICP-OES result for optimal Sn^{4+}/TiO_2-B-50/70 sample.

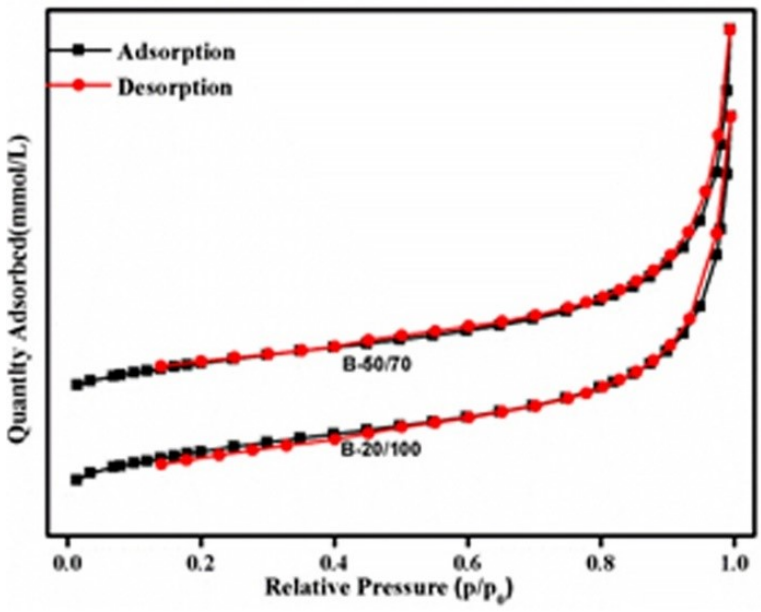


Figure S3. N_2 adsorption-desorption isotherms of Sn^{4+}/TiO_2-B-20/100 and -50/70 samples.

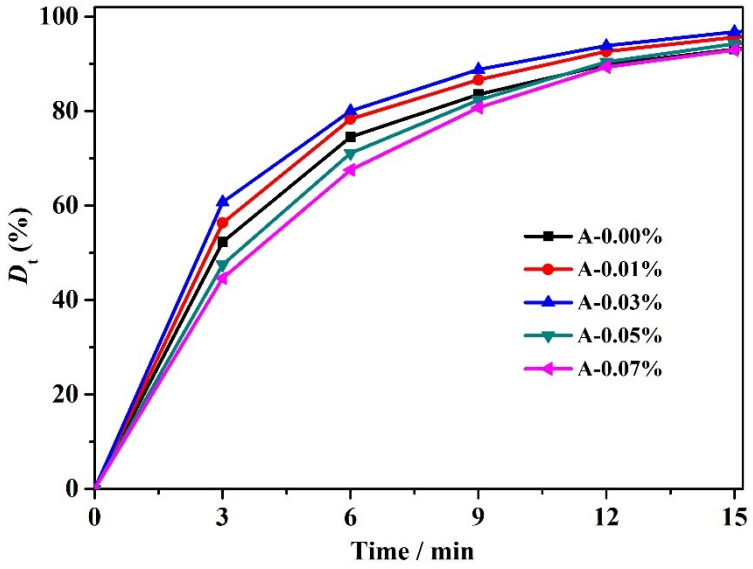


Figure S4. $D_t \sim t$ curves of MB solution on the Sn^{4+}/TiO_2-A samples.

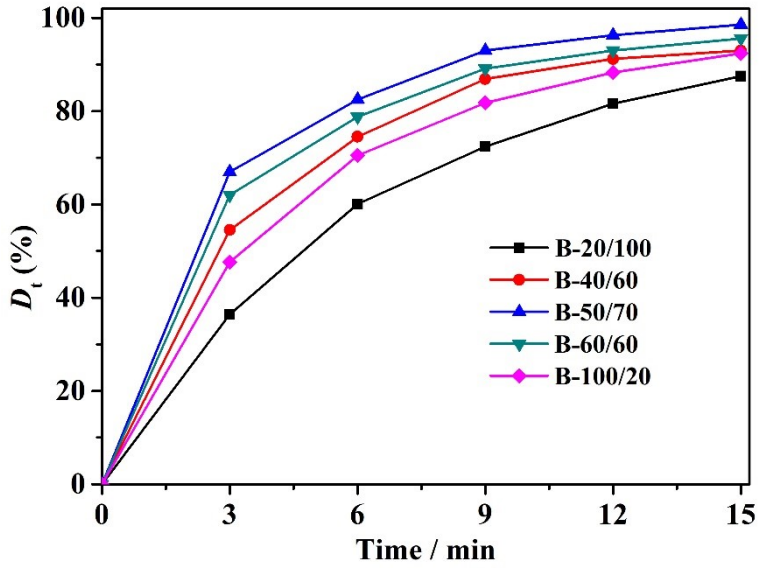


Figure S5. $D_t \sim t$ curves of MB solution on the Sn^{4+}/TiO_2-B samples.

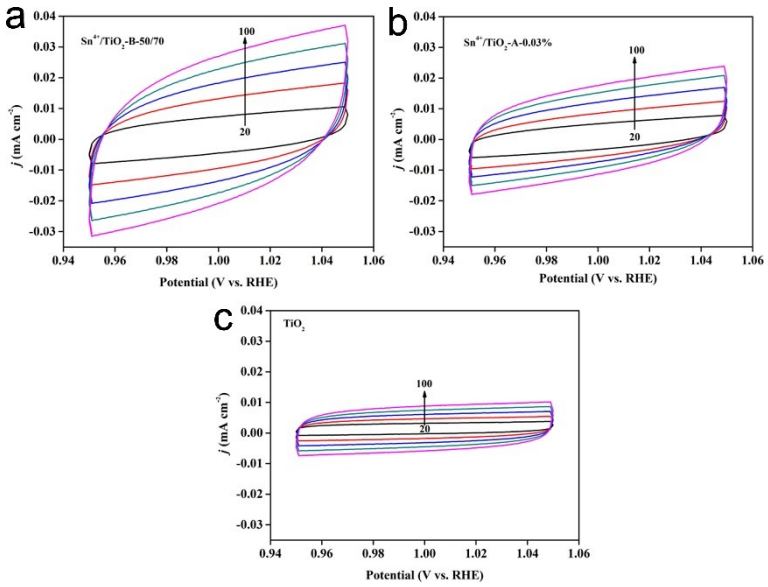


Figure S6. Cyclic voltammograms of (a) Sn^{4+}/TiO_2-B-50/70, (b) Sn^{4+}/TiO_2-A-0.03%, and (c) TiO_2 with various scan rates in 1.0 M KOH solution.

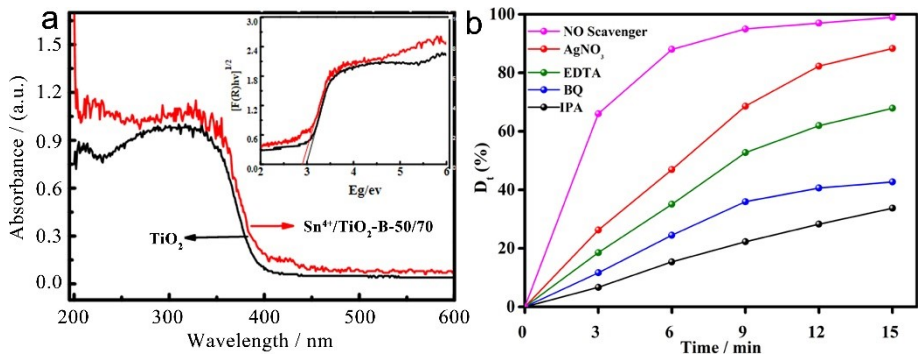


Figure S7. (a) UV-vis spectra of TiO_2 and Sn^{4+}/TiO_2-B~50/70 samples (Inset: energy band structure of TiO_2 and Sn^{4+}/TiO_2-B~50/70 samples); (b) $D_t \sim t$ curves of MB solution on the Sn^{4+}/TiO_2-B-50/70 under the presence of different scavengers.

Table S1. Comparison of Sn^{4+}/TiO_2-B-50/70 sample with reported results in the literature.

Catalyst	Dye	Degradation efficiency (%)	Time (min)	Kinetic constant (min^{-1})	Ref.
Sn^{4+}/TiO_2-B-50/70	Methyl blue	98.6	15	0.295	**This work**
HfO_2/TiO_2 spherical nanoparticles	Methyl blue	90	10	--	*Mater. Lett.*, 2018, **231**, 225
Fluorinated TiO_2 (0.63% F)	Orange 4	80	80	0.035	*Sep. Purif. Technol.*, 2013, **108**, 51
1%-Ni doped TiO_2	Remazol Black 5	95.6	100	--	*RSC Adv.*, 2015, **5**, 88266
6%-Ag-TiO_2	Methyl blue	97	120	0.0221	*Green Process. Synth.*, 2019, **8**, 659
TiO_2/MgO nanocomposite	Methyl orange	83.2	90	0.0319	*Environ. Technol.*, 2021, **42**, 2278
MoS_2-TiO_2@PAN membrane	Methyl blue	97.73	180	--	*Mater. Sci. Eng. B*, 2021, **169**, 115179
TiO_2/PSEM composite	Rhodamine B	94	80	--	*J. Inorg. Organomet. Polym. Mater.*, 2020, **30**, 2805