Electronic Supporting Information (ESI)

Sodium hypophosphite induced simultaneous P doping and hollowing process of TiO₂ spherical nanostructures with enhanced photocatalytic activity

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Experiments

1. Chemical and reagents

Titanium(IV) sulphate (Ti(SO₄)₂, 95%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium citrate dehydrate (Na₃C₆H₅O₇·2H₂O, 99%), Sodium hypophosphite (NaH₂PO₂·H₂O, 99%) and methylene blue (MB) were purchased from Aladdin industrial corporation (Shanghai, China). Sulphuric acid (H₂SO₄, 98%) was obtained from Tianjin NO. Five Chemical Reagent Factory, China. All chemicals were analytical grade and used without further purification.

2. Preparation of P-doped TiO₂ hollow spherical nanostructures

The P-doped TiO₂ hollow spherical nanostructures were prepared by a simple and facile one-step hydrothermal method. Typically, 3 mmol (0.882 g) of $Na_3C_6H_5O_7\cdot 2H_2O$, 0.5 mmol (0.106 g) of $NaH_2PO_2\cdot H_2O$ and 1 mmol (0.239 g) of Ti(SO₄)₂ were sequentially dissolved in 70 mL of H₂SO₄ solution (3.5%) to form homogeneous solutions by stirring. Subsequently, the above solution was transferred into a Teflon-lined stainless steel autoclave (100 mL) and kept at 200 °C for 24 h. When it naturally cooled down to room temperature, the sample was separated by centrifugation and washed several times with deionized water and anhydrous ethanol. Finally, the resulting product was dried at 60 °C for 12 h.

In the same manner, a series of samples were prepared by altering the P/Ti molar ratio in the precursor solution. The products prepared from P/Ti molar ratio of 0, 0.2, 0.5, 0.75 and 1.0 were denoted as undoped TiO₂, THMs-0.2P, THMs-0.5P, THMs-

0.75P and THMs-1.0P, respectively.

3. Characterization

The products were characterized by X-ray powder diffraction (XRD, BRUKER AXS GMBH D8-S4 with Cu K α radiation, k=0.1542 nm, 40 kV, 40 mA), scanning electron microscopy (SEM, Hitachi SU8010), and transmission electron microscopy (TEM, JEOL JEM-2100F). Nitrogen adsorption-desorption experiments were carried out on Quantachrome NOVA- 2000 at 77 K. Fourier transform infrared spectroscopy measurements (FTIR) were recorded on a Nicolet 6700 spectrometer with a KBr pellet. Phosphorus content was determined by X-ray fluorescence spectrometry (XRF, Rigaku ZSX Primus 2). X-ray photoelectron spectroscopy (XPS, PHI15000. PERKINELMZR) measurements were conducted using Mg K α X-ray source. UV–vis diffuse reflection spectra were recorded using U-4100 Spectrophotometer. The transient photocurrent measurement was conducted on a CHI760E electrochemical workstation. Photoluminescence (PL) emission spectra were measured by Fluorolog3 spectrofluorometer (HORIBA Jobin Yvon Inc.) under the excitation at 325 nm.

4. Photocatalytic activity test

The photocatalytic activity of P-doped TiO₂ hollow spherical nanostructures was evaluated by degradation methylene blue (MB) under simulated sunlight irradiation. In a typical procedure, 36 mg of photocatalyst was placed into the reactor containing 60 mL of MB aqueous solution (10 mg L^{-1}). The mixture was first stirred vigorously for 1h in the dark to establish adsorption-desorption equilibrium and then was exposed to light from a 500 W high-pressure Xenon lamp (Beijing Lighting Research Institute, China). At a given time interval, 3.5 mL of the suspension was extracted and then centrifuged. The supernatant was measured with the Lambada 35 UV-vis spectrophotometer by recording the characteristic absorption peak of MB at 664 nm.

To further understand the photodegradation process, the photocatalytic degradation kinetic of MB was also investigated by using Langmuir-Hinshelwood first-order reaction kinetic as expressed in the following equation [1].

$$\ln \frac{C}{C_0} = -k_{app}t$$

Where, the apparent rate constant, k_{app} , is used to evaluate the photocatalytic activity of photocatalyst. The linear relations of $\ln(C/C_0)$ versus the irradiation time for different samples are obtained.

To rule out the dye sensitization effect, phenol degradation was also carried out by adding the phenol (10 mg L^{-1}) solution with the THMs-0.5P at the same conditions described above.



Fig. S1 XRD pattern of THMs-0.5P



Fig. S2. SEM and TEM images of (a) undoped TiO₂, (b) THMs-0.2P, (c) THMs-0.75P, (d) THMs-1.0P



Fig. S3. XRD patterns of various photocatalysts

Table S1 XRF P content, crystal structure and texture structure parameters of various samples

Sample	P content	Lattice parameters		Cell volume	Crystallite	S_{1} (m ² c ⁻¹)	d ()	$\mathbf{V}(\mathbf{a},\mathbf{r},\mathbf{r},\mathbf{r},\mathbf{r},\mathbf{r})$
	(wt%)	a (Å)	c (Å)	(Å ³)	size (Å)	S_{BET} (m ² g ⁻¹)	u (nm)	v (cm ³ g ¹)
undoped TiO ₂	-	3.7824	9.5109	136.0681	193	73.64	11.9	0.214
THMs-0.2P	0.43	3.7857	9.5308	136.5909	179	75.48	12.7	0.233
THMs-0.5P	0.73	3.7856	9.5056	136.2281	153	91.52	12.7	0.265
THMs-0.75P	0.99	3.7811	9.5428	136.4307	142	90.96	11.2	0.237
THMs-1.0 P	1.01	3.7831	9.4872	135.779	141	69.02	9.8	0.167



Fig. S4 Evolution of XRD patterns of THMs-0.5P during hydrothermal reaction process



Fig. S5 (a) Morphology evolution and (b) schematical illustration of the formation mechanism of

THMs-0.5P



Fig. S6 MB adsorption on different samples in dark



Fig. S7 The kinetic linear fits of the degradation process



Fig. S8 UV-Vis absorbance spectra of phenol solution under different light irradiation times



Fig. S9 Cycling runs for photodegradation of MB over THMs-0.5P under simulated sunlight irradiation

To determine the dominant active species for MB degradation during the photocatalytic process, active species trapping experiments were conducted. Tert-Butanol (TB), benzoquinone (BQ) and disodium ethylene diamine tetraacetate (EDTA-2Na) were separately added to the photocatalytic system as scavengers of hydroxyl radical (•OH), superoxide radicals (\cdot O₂⁻) and photogenerated holes (h⁺), respectively [2, 3]. As shown in Fig. S8, the degradation efficiency presents only a slight decrease with the addition of BQ. However, an obviously inhibitory effect on the degradation process of MB occurs with the addition of TB or EDTA-2Na. Another interesting finding is that the two scavengers exhibit almost the same inhibitory effect. In view of the fact that •OH is derived from the reaction between h⁺ and surface adsorbed water or hydroxyl groups, •OH is determined as the dominant active specie in the photocatalytic reaction.



Fig. S10 Active species trapping experiments over THMs-0.5P under simulated sunlight

irradiation.

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