锌掺杂 OV-β-Bi₂O₃可见光催化活性的提高: 能带结构的调节和电荷分离的促进

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摘要:采用溶胶-凝胶-原位碳热还原处理的方法,制备了一种含有氧空位(OV)的新型Zn掺杂β-Bi₂O₃纳米材料(OV-Zn:Bi₂O₃), 氧空位的浓度可以通过改变Zn²⁺的掺杂量进行调节。作为参照,只有氧空位没有Zn²⁺的新型β-Bi₂O₃(OV-β-Bi₂O₃)也通过类似的 方法制得。通过紫外可见漫反射光谱、X射线光电子能谱、电子顺磁共振、光致发光光谱和光电化学测试,系统研究了氧空位 和Zn²⁺掺杂对OV-Zn:Bi₂O₃降解亚甲基蓝(MB)和2,4,6-三氯苯酚(2,4,6-TCP)可见光催化活性的综合影响。结果表明,氧空位 的引入不仅可以使光吸收向长波方向拓展,而且可以促进光生载流子的分离。因此,与传统的β-Bi₂O₃相比,OV-β-Bi₂O₃对亚甲 基蓝(MB)和2,4,6-三氯苯酚(2,4,6-TCP)的降解活性显著增强。对于OV-Zn:Bi₂O₃催化剂,Zn²⁺掺杂可使光催化剂的价带边缘 向下移动,增强了光激发空穴的氧化能力,并且适量的锌掺杂也能提高光生载流子的分离效率。因此,OV-Zn:Bi₂O₃的可见光 活性优于OV-β-Bi₂O₃,而且当Zn与Bi物质的量之比为0.3时,OV-Zn:Bi₂O₃-0.3对MB和2,4,6-TCP的降解活性最高。

关键词:氧空位;锌离子掺杂;光催化;电荷分离;可见光活性 中图分类号:0614.24*1;0643.36 文献标识码:A 文章编号:1001-4861(2021)03-0541-14 DOI:10.11862/CJIC.2021.064

Enhancement of Visible-Light Catalytic Activity for Zn Doped OV-β-Bi₂O₃: Regulation of Electronic Structure and Promotion of Charge Separation

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Abstract: A novel Zn-doped β -Bi₂O₃ nanomaterial (OV-Zn:Bi₂O₃) with two crystal defects, oxygen vacancy (OV) and doped Zn²⁺, was prepared via a sol-gel method followed by *in-situ* carbon thermal reduction treatment. The concentration of OV of OV-Zn:Bi₂O₃ sample can be modulated by regulating the content of doped Zn²⁺. As a reference, the novel β -Bi₂O₃ having OV but without doped Zn²⁺ (OV- β -Bi₂O₃) was also synthesized via a similar process. The comprehensive effect of OV and doped Zn²⁺ on the visible-light-activity of OV-Zn:Bi₂O₃ for the degradation of meth-ylene blue (MB) and 2,4,6-trichlorophenol (2,4,6-TCP) was investigated by ultraviolet-visible light diffuse reflec-

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tance spectra, X-ray photoelectron spectra, electron spin resonance, photoluminescence spectrum and photoelectrochemical measurements. The results show that introduction of OV can not only drastically extend the photoabsorption into longer wavelength region but also promote the separation of photo-generated charge carriers. So, compared to traditional β -Bi₂O₃, OV- β -Bi₂O₃ demonstrated highly promoted activity for the degradation of methylene blue (MB) and 2,4,6-trichlorophenol (2,4,6-TCP). For OV-Zn: Bi₂O₃ catalysts, Znic doping can make the valence band edge of catalysts move down and the oxidation ability of photo-excited holes increase. And appropriate amount of zinc doping can also improve the separation efficiency of photogenerated carriers. In contrast to OV- β -Bi₂O₃, the visible light activity of OV-Zn: Bi₂O₃ was further improved and OV-Zn: Bi₂O₃-0.3 with a molar ratio (n_{Zn}/n_{Bi}) of 0.3 exhibited the highest activity for the degradation of MB and 2,4,6-TCP.

Keywords: oxygen vacancy; Zn2+ doping; photocatalysis; charge separation; visible light activity

0 Introduction

Over the past decades, visible-light-active Bi based compounds are recommended as a category of the hottest photocatalysts, which is because Bi³⁺ ion in the crystal lattice exhibits unique d^{10} configuration and $6s^2$ lone pair electrons. Such an electronic structure contributes to promoting the transfer of photogenerated carriers and the regulation of band gap by the orbital hybridization of Bi³⁺ with other ions^[1-2]. Among various Bi based photocatalysts, Bi₂O₃ is the simplest and foremost one, thanks to its innocuity, adjustable band gap and high oxidation power of valence band (VB) hole^[3-5]. Generally, Bi₂O₃ has five different polymorphs, *i. e.*, monoclinic α , tetragonal β , body-centered cubic γ , face-centered cubic δ and triclinic ω -phases^[6-9]. Among them, β - Bi₂O₃ usually exhibits the best visible - light activity for its smaller band gap and unique tunnel structure^[6]. However, β -Bi₂O₃ still doesn't have sufficient efficiency for the photocatalytic application due to its fast recombination of light-induced hole and electron. So, many researchers have tried to adopt various modification methods to improve the photocatalytic performance of β -Bi₂O₃ under visible light irradiation, such as doping transition metal ions^[9-11] and constructing heterojunction semiconductor^[12-14]. Impurity doping in β -Bi₂O₃ has been confirmed to be an effective strategy to improve its visible light activity. Luo et al. found that Gd-doped β -Bi₂O₃ showed much higher photocatalytic activity for the photodegradation of phenol than pure β -Bi₂O₃, since the doped Gd³⁺ ion serves as an effi-

cient scavenger to entrap photo-generated electrons thereby effectively separating photo-induced electron-hole pairs^[9]. Liang et al. reported that Fe-doped β -Bi₂O₃ photocatalyst with 4% molar fraction of Fe displayed desired photocatalytic activity, because Fe doping provides the photocatalyst with the ability to promote the migration of electron-hole pairs, thereby adding to photocatalytic activity^[10]. Besides doped ions, oxygen vacancy (OV) often was introduced into semiconductor to improve the light absorption and charge separation ability of catalyst^[15-17]. Lu et al. pointed out that the construction of oxygen vacancies on the surfaces of photocatalyst can improve the visible light absorption, target air pollutants enrichment and electron mobility^[16]. However, most of the OV-modified photocatalysts are synthesized under a harsh condition such as in a hydrogen or nitrogen atmosphere or under vacuum deoxidation condition^[16,19-20]. The OV produced by this method is unstable and easy to be filled by oxygen in air atmosphere. Therefore, it is very essential for the development of a facial and controllable method to generate stable oxygen defect photocatalysts.

In this work, we prepared Zn-doped OV- β -Bi₂O₃ nanoparticles (OV-Zn: Bi₂O₃) with two crystal defects, OV and doped Zn²⁺, via a sol-gel method followed by *in* -*situ* carbon thermal reduction treatment. The OV in OV-Zn: Bi₂O₃ samples is stable and controllable by regulating the content of doped Zn²⁺. As a reference, traditional β -Bi₂O₃ without OV and OV- β -Bi₂O₃ having OV but without doped Zn²⁺ were also synthesized. Various characterization methods were adopted to investigate the effect of OV and doped Zn^{2+} on the improvement of photocatalytic activity of OV-Zn: Bi₂O₃ series.

1 Experimental

1.1 Preparation of the catalysts

OV-Zn: Bi₂O₃ catalyst was synthesized via a simple sol-gel method followed by *in-situ* carbon thermal reduction treatment. Typically, 0.072 mol of citric acid monohydrate and 0.015 mol of Bi(NO₃)₃·5H₂O were dispersed in 30 mL of distilled water and ultrasonicated for 10 min to form a transparent sol. The as-obtained sol was stirred vigorously for 30 min while the ammonia solution of disodium ethylenediaminetetra acetate (EDTA) was slowly added to afford a new sol denoted as sol A. 1.5 mmol of Zn(CH₂COO)₂·2H₂O was dissolved in 5 mL of ammonia and stirred to form sol B. The as-obtained sol B was dropped into sol A under stirring with a water-bath (80 °C) for 1 h to afford sol C. After being cooled to room temperature, 2 mL of sol C was carbonized in an electric furnace to obtain a viscous black product at 300 °C. The viscous black product was further calcined at 400 °C for 2 h to yield a yellow powder, OV-Zn: Bi₂O₃-0.1 with a theoretical molar ratio (n_{Z_0}/n_{B_i}) of 0.1. A series of Zn-doped OV- β -Bi₂O₃ phtocatalysts with theoretical $n_{Z_{\rm P}}/n_{\rm Bi}$ of 0.3, 0.5 and 1.0 were prepared in the same manners while the amount of Zn(CH₃COO)₂·2H₂O was adjusted to be 4.5, 7.5 and 15.0 mmol. Corresponding products were labeled as OV -Zn: Bi₂O₃-0.3, OV-Zn: Bi₂O₃-0.5 and OV-Zn: Bi₂O₃-1.0, respectively. Pure $OV-\beta$ -Bi₂O₃ powder with abundant oxygen vacancies but without doped Zn²⁺ was also prepared with the same procedure in the absence of $Zn(CH_3COO)_2 \cdot 2H_2O.$

For comparison, traditional β -Bi₂O₃ powder without OV was prepared by the precipitation method^[21-22]. Briefly, 2 g of Bi(NO₃)₃·5H₂O and 0.1 g of CTAB (cetyltrimethyl ammonium bromide) were both dissolved in 20 mL of nitric acid (1 mol·L⁻¹) solution with stirring for 20 min. Then, 0.4 g of oxalic acid was added in above solution and reacted under stirring for 30 min. The white precipitate was filtered, washed and calcined at 270 °C to obtain the yellow powder, traditional β -Bi₂O₃.

1.2 Characterization

A JSM-7610F scanning electron microscope (SEM) was performed with an accelerating voltage of 15 kV to observe the morphology and microstructure of as-prepared traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn : Bi₂O₃ series. The crystal structure of the catalysts was characterized using a Bruker D8 X-ray powder diffractometer equipped with Cu K α radiation source (λ = 0.154 8 nm); the tube current was 40 mA, operating voltage was 40 kV, and the scan range was $5^{\circ} \le 2\theta \le 70^{\circ}$. A Thermo Fisher Scientific Escalab 250Xi X-ray photoelectron spectrometer (XPS, monochromatic Al Ka excitation source) was deployed to analyze the chemical states of as-prepared photocatalysts. The ultravioletvisible light diffuse reflectance spectra (UV-Vis DRS) of as-prepared photocatalysts were recorded with a PE Lambda 950 spectrometer equipped with an integrating sphere attachment. Electron spin resonance (ESR) spectra were obtained with a Bruker E500 apparatus. The measurement was conducted at room temperature in ambient air, without vacuum-pumping. The gtensors of the ESR signals were obtained by setting g of diphenyl picryl hydrazyl (DPPH, g=2.003 6) as the reference. The photoluminescence (PL) spectra of the products were obtained with a PuXi TU-1900 fluorescence spectrophotometer under the excitation at 380 nm. The photocurrent response and voltammogram (I-V) curve were measured at CHI 650E electrochemical workstation (Chenhua Instrument Company) with a three-electrode system including a modified ITO glass as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as reference. A 300 W xenon lamp with a 420 nm cutoff filter was used as a visible light source.

1.3 Evaluation of visible light photocatalytic activity

The photocatalytic activity of as-prepared photocatalysts were evaluated by the degradation of methylene blue (MB) and 2,4,6-trichlorophenol (2,4,6-TCP) in a glass cylindrical reactor under visible light irradiation (300 W xenon lamp equipped with a 420 nm cutoff filter). The reactor was surrounded by a water-cooling system so as to ensure that the photocatalytic reaction occurs at room temperature. In each experiment, 100 mg of the to-be-tested photocatalysts was suspended in 150 mL MB or 2,4,6-TCP solution, which concentrations were all 10 mg \cdot L⁻¹. Differently, the light intensity for the degradation of MB was 23 mW·cm⁻² and that for 2,4,6-TCP was 45 mW·cm⁻². Prior to illumination, the suspension was fiercely stirred in dark for 1 h until the absorption-desorption balance was achieved. During the photocatalytic reaction, 5 mL of the suspension was taken at certain time intervals to determine the concentration of MB and 2,4,6-TCP by UV-Vis spectrophotometry (TU-1810, Puxi Instrument Company, China) at the maximum absorption wavelength of 665 nm and 310 nm, respectively. The degradation rate of pollutant was calculated as $(c_0-c)/c_0 \times 100\%$, where c_0 refers to the initial concentration of pollutant after the adsorption - desorption equilibrium was reached, and cis the concentration of pollutant measured at a certain time interval during the photocatalytic reaction process.

2 Results and discussion

2.1 Crystal structure

Scheme 1 displays the schematic diagram for preparation process of traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃ series. For OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃, the critical step marked by red circle in diagram is the carbonization of EDTA-Bi complex on an electric stove. The reductive carbon produced in the carbonization process can reduce Bi^{3+} in the subsequent calcination process, resulting in the escaping of some oxygen atoms in β -Bi₂O₃ or Zn-doped Bi₂O₃ and leading to the formation of OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃.

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Fig. 1a depicts the XRD patterns of traditional β -Bi₂O₃, OV-*B*-Bi₂O₃ and OV-Zn: Bi₂O₃ series with different $n_{Z_p}/n_{\rm Bi}$. The diffraction peaks of β - Bi₂O₃, OV - β - Bi_2O_3 and OV-Zn: Bi_2O_3 series at $2\theta = 27.94^\circ$, 31.76° , 32.69°, 46.21°, 46.90°, 54.26°, 55.48° and 57.75° are indexed to the (201), (002), (220), (222), (400), (203), (421) and (402) crystal planes of tetragonal β - Bi₂O₃ (PDF No. 27-0050)^[10-11], indicating that all as-prepared catalysts possess the same crystal structure. OV-Zn: Bi₂O₃ catalysts with a n_{Zn}/n_{Bi} of 0.1~1.0, *i.e.*, OV-Zn: Bi₂O₃-0.1, OV-Zn: Bi₂O₃-0.3, OV-Zn: Bi₂O₃-0.5 and OV -Zn: Bi₂O₃-1.0, showed the same XRD patterns as traditional β -Bi₂O₃ and OV- β -Bi₂O₃ did. And all the OV-Zn: Bi₂O₃ photocatalysts did not show diffraction peaks of zinc oxide. Moreover, the enlarged XRD patterns shown in Fig.1b demonstrate that the (201) peak of the OV-Zn: Bi2O3 photocatalysts tended to slightly shift towards lower 2θ value with the increase of zinc concentration. This means that as-prepared OV-Zn: Bi₂O₃ photocatalysts do not consist of the mixtures of Bi₂O₃ and ZnO phases but Zn-doped tetragonal Bi₂O₃. It is generally recognized that there are two modes of ion doping, substitutional doping and interstitial doping. The ionic radii of Bi3+ ion and Zn2+ ion are 0.103 and



Scheme 1 Schematic illustration of preparation for traditional β-Bi₂O₃ (a), OV-β-Bi₂O₃ (b) and OV-Zn: Bi₂O₃ series (c)



Fig.1 (a) XRD patterns of as-prepared traditional β-Bi₂O₃, OV-β-Bi₂O₃ and OV-Zn:Bi₂O₃ series with different n_{Zn}/n_B;
(b) Enlarged (201) peak in the 2θ range of 26°~30° for OV-β-Bi₂O₃ and OV-Zn:Bi₂O₃ series

0.074 nm, respectively^[23]. On one hand, if the lattice sites of Bi³⁺ in Bi₂O₃ crystal are partly substituted by smaller Zn²⁺ ion, the lattice parameters of Bi₂O₃ would decrease in association with the slight shift of the XRD peaks towards higher 2θ values. This supposition, however, is not supported by the above-mentioned XRD data. On the other hand, if some Zn²⁺ ions are doped in Bi_2O_3 crystal by way of interstitial doping, the volume of Bi2O3 crystal cell would be expanded and the distance of the crystal plane (d spacing) would be increased. This supposition, indeed, is supported by relevant XRD data. Namely, according to Bragg's law, $2d\sin\theta$ = $n\lambda$, the decrease of θ refers to the increase of d; and the volume expansion of the OV-*β*-Bi₂O₃ crystal cell after Zn doping proves that Zn^{2+} ion is doped into OV- β -Bi₂O₃ crystal via interstitial doping to afford the OV-Zn

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: Bi₂O₃ photocatalysts in this work.

2.2 Morphology observation

Fig. 2 shows the SEM images of traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃ series with different Zn content. It can be seen that both OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃ series exhibited similar spherical shape and had an average size of 100 nm (Fig. 2a~2e). This indicates that the doping of zinc has little effect on the morphology of OV- β -Bi₂O₃. Compared to OV- β -Bi₂O₃, traditional β -Bi₂O₃ prepared by the precipitation method consisted of many nano-sheets with thickness of about 10 nm (Fig.2f), which was consistent with that reported in the literature^[21] and might be the reason for much larger specific surface area of 10 m² · g⁻¹ than that of OV- β -Bi₂O₃ with a value of 2 m² · g⁻¹.



Fig.2 SEM images of pure OV- β -Bi₂O₃ (a), OV-Zn:Bi₂O₃-0.1 (b), OV-Zn:Bi₂O₃-0.3 (c), OV-Zn:Bi₂O₃-0.5 (d), OV-Zn:Bi₂O₃-1.0 (e) and traditional β -Bi₂O₃ (f)

2.3 XPS analysis

The chemical states of related elements in asprepared samples were analyzed by XPS. Fig.3a shows the high-resolution XPS spectra of Bi4f in traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃-0.3. Compared to traditional β -Bi₂O₃, the Bi4f peaks of OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃-0.3 shifted to the lower binding energies, indicating that the Bi atom in both samples with OV has higher electron density (or lower chemical valence) than that in β -Bi₂O₃ due to the charge compensation. The absence of partial oxygen atoms can reduce the coordination number of Bismuth ion leading to the decrease of binding energy of Bi4f. The Zn2p_{3/2} and Zn2 $p_{1/2}$ peaks of OV-Zn: Bi₂O₃-0.3 were centered at 1 022.9 and 1 046.1 eV (Fig.3b), which means that the doped Zn is present in the form of Zn²⁺ in Zn-doped β -Bi₂O₃^[24]. Besides, as shown in Fig.3c, the O1*s* spectrum of traditional β -Bi₂O₃ was split into two peaks, I and II : peak I at 530.3 eV is assigned to the lattice oxygen in β -Bi₂O₃ crystal and peak II at 531.4 eV is ascribed to adsorbed oxygen in the form of hydroxyl group^[7,15,25-26]. Different with traditional β -Bi₂O₃, a new peak III appeared for OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃-O.3, which was situated at about 532.6 eV corresponding to the OV defect^[7,27].



Fig.3 High-resolution XPS spectra of Bi4f (a), Zn2p (b) and O1s (c) for traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃-O.3 samples

2.4 ESR analysis

ESR test was adopted to confirm the existence of oxygen vacancies in OV - β - Bi₂O₃ and OV - Zn: Bi₂O₃ series as a direct and sensitive way. As shown in Fig.4, no ESR signal could be observed for traditional β -Bi₂O₃. While there was a strong symmetric ESR peak for OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃ series both having a center at g=2.004, which is attributed to single-electron -trapped OV (V₀⁻) with a positive charge^[28-29]. For OV-Zn: Bi₂O₃ series, XRD results suggested that Zn²⁺ ion is doped into $OV - \beta - Bi_2O_3$ crystal via interstitial doping not substitution, which leads to more positive charge in semiconductor. So, with the increase of the doped Zn^{2+} content, the concentration of V_0^- decreased and the intensity of ESR signal decreased gradually. This demonstrats that the concentration of OV may be modulated by the amount of doped Zn^{2+} in $OV - Zn \colon Bi_2O_3$ series. Many studies reported that, OV can not only broaden the photoabsorption range of the catalyst but also serve as trapping center for excited electrons to improve the separation efficiency of photogenerated carriers^[16,30]. To study the trapping role of OV, many ESR spectra under laser irradiation of different catalysts will be further compared.



Fig.4 ESR spectra of traditional β-Bi₂O₃, OV-β-Bi₂O₃ and OV-Zn:Bi₂O₃ series at room temperature in air

2.5 Optical properties of as-prepared samples

It is well known that both OV and doped ions can change the optical absorption and electronic energy structure of semiconductor, which can be determined by UV-Vis DRS. Fig.5a shows the UV-Vis DRS spectra of traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃ samples with different $n_{Z\pi}/n_{Bi}$. The absorption edge of traditional β - Bi₂O₃ was approximately 460 nm. The absorption range of OV- β -Bi₂O₃ was clearly broadened, with the absorption edge extending to approximately 500 nm. For OV - β - Bi₂O₃, which has the wider light absorption range, more electron-hole pairs can be generated to participate in photocatalytic reaction under visible light irradiation. Compared with OV - β -Bi₂O₃, the absorption edge of OV-Zn: Bi₂O₃ samples gradually blue-shifted to shorter wavelength with the increase of Zn content. However, the absorption range of nearly all $OV-Zn: Bi_2O_3$ samples, except $OV-Zn: Bi_2O_3-1.0$, was still wider than that of traditional $\beta - Bi_2O_3$. The band gap can be estimated using the following equation (Eq.1):

 $(\alpha h\nu)^2 = A(h\nu - E_g)^n$ (1) Where α , ν , A and E_g are absorption coefficient, light frequency, a constant and band gap energy, respectively. The value of n is 1 for direct transition and 4 for indirect transition of semiconductor. According to the literature^[9], the value of n is 1 for β -Bi₂O₃. The band gap energies of traditional β -Bi₂O₃, OV- β -Bi₂O₃, OV-Zn : Bi₂O₃-0.1, OV-Zn: Bi₂O₃-0.3, OV- β -Bi₂O₃-0.5 and OV-Zn: Bi₂O₃-1.0 were estimated from a plot of $(\alpha h\nu)^2$ vs $h\nu$ to be 2.72, 2.40, 2.46, 2.50, 2.53 and 2.80 eV, respectively (Fig.5b).

To further investigate the effect of Zn doping on the VB position of OV-Zn: Bi_2O_3 , we adopted Eq. **2** to determine the VB edge position of pure OV- β - Bi_2O_3 and OV-Zn: Bi_2O_3 series^[31-32].

$$E_{\rm VB} = X - E_{\rm e} + 0.5 E_{\rm g}$$
 (2)

Where E_e is about 4.5 eV on the hydrogen scale; E_g is the band gap of OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃; E_{VB} is the valence band edge potential; and X is the absolute electronegativity of the solid (the X value for Bi₂O₃ was calculated to be 6.24, Supporting information). Simultaneously, the conduction band (CB) position of the samples can be obtained from $E_{CB}=E_{VB}-E_g$. As shown in Table 1, compared to OV- β -Bi₂O₃, the VB position of OV-Zn: Bi₂O₃ samples gradually moved down with the increase of n_{Zn}/n_{Bi} , which suggests that the oxidizing capacity of the photoexcited holes tends to rise with the increase of Zn content. Furthermore, the VB spectra of



Fig.5 UV-Vis DRS spectra (a) and plots of $(\alpha h \nu)^2$ vs photon energy (b) of traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃ series

traditional β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃-0.3 as the representative of OV-Zn:Bi₂O₃ series were measured by XPS. As shown in Fig.6, the VB potentials of OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃-0.3 were lower than that of traditional β -Bi₂O₃ for the narrow band gap due to the existence of OV, and the VB potential of OV-Zn: Bi₂O₃-0.3 was higher than that of OV- β -Bi₂O₃, which may imply that the photo-induced holes of OV-Zn: Bi₂O₃-0.3 possesses stronger oxidizing ability than that of OV- β -Bi₂O₃. These results are well consistent with above DRS analysis.

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Table 1Values of E_g , E_{VB} and E_{CB} for traditional
 β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn:Bi₂O₃

Catalyst	$E_{\rm g}/{\rm eV}$	$E_{\rm VB}/{\rm eV}$	$E_{\rm CB}$ / eV
β -Bi ₂ O ₃	2.72	3.10	0.38
OV - β - Bi_2O_3	2.40	2.94	0.54
OV-Zn:Bi ₂ O ₃ -0.1	2.46	2.97	0.51
OV-Zn:Bi ₂ O ₃ -0.3	2.50	2.99	0.49
OV-Zn:Bi ₂ O ₃ -0.5	2.53	3.01	0.48
OV-Zn:Bi ₂ O ₃ -1.0	2.80	3.14	0.34



Fig.6 VB XPS spectra of traditional β -Bi₂O₃ (a), OV- β -Bi₂O₃ (b) and OV-Zn:Bi₂O₃-0.3 (c) as the representative of OV-Zn:Bi₂O₃ series

2.6 Visible light photocatalytic activity

Different pollutants including MB dye and colorless phenol compound, 2, 4, 6-TCP, were employed as the substrate to evaluate the photocatalytic activity of traditional β -Bi₂O₃, OV - β -Bi₂O₃ and OV - Zn: Bi₂O₃ samples under visible light irradiation. Fig. 7a and 7b shows the photocatalytic performance of different catalysts toward MB dye degradation with the light intensity of 23 mW · cm⁻² (λ =420 nm). It can be seen that, in the absence of any photocatalyst, nearly 80% of MB was retained after 3 h of visible light irradiation. In the presence of traditional β -Bi₂O₃ and OV - β -Bi₂O₃, about 40% and 70% of MB was degraded after 4 h of visible light irradiation, respectively, which indicates that, although the specific surface area of $OV - \beta - Bi_2O_3$ was smaller than that of traditional β -Bi₂O₃, the former promotes much higher degradation rate of MB than the latter for the wider light absorption range resulted from OV. Furthermore, OV-Zn: Bi₂O₃ catalysts with different n_{Za}/n_{Bi} can more efficiently catalyze the degradation of MB under visible light irradiation as compared with OV - β -Bi₂O₃; and in particular, OV-Zn: Bi₂O₃-0.3, with a photocatalytic efficiency similar to that of OV-Zn: Bi₂O₃ -0.5, can catalyze the photodegradation of up to 91% of MB within 4 h of visible light irradiation. The linear relationship between $ln(c_0/c)$ and irradiation time for



 λ > 420 nm, the light intensities were 23 mW \cdot cm⁻² for MB and 45 mW \cdot cm⁻² for 2,4,6-TCP

Fig.7 Photocatalytic degradation of MB (a) and linear fitting for first order kinetics (b) over different catalysts under visible light irradiation; Photocatalytic degradation of 2,4,6-TCP (c) and linear fitting for first order kinetics (d) over different catalysts under visible light irradiation

MB degradation is shown in Fig. 7b. The reaction rate constant (k) and linear correlation coefficient (R^2) for different catalysts are summarized in Table 2. It can be seen that all as - prepared catalysts had an R^2 value of above 0.97, which means that the degradation of MB catalyzed by β -Bi₂O₃, OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃ series is of the first order kinetic nature. Moreover, OV-Zn: Bi₂O₃-0.3 had the highest rate constant among all the tested catalysts, which demonstrates that the optimal n_{Zn}/n_{Bi} of OV-Zn: Bi₂O₃ catalysts should be 0.3.

2,4,6-TCP, as a well-known organic pollutant in wastewater of pharmaceutical, paint and pesticide in-

Table 2Reaction rate constant (k) and correlation
coefficient (R^2) of traditional β -Bi₂O₃,
OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃ series for
photocatalytic degradation of MB under
visible light irradiation

Catalyst	R^2	k / min ⁻¹
β -Bi ₂ O ₃	0.972	0.001 91
OV - β - Bi_2O_3	0.995	0.004 98
OV-Zn:Bi ₂ O ₃ -0.1	0.979	0.005 75
OV-Zn:Bi ₂ O ₃ -0.3	0.985	0.009 71
OV-Zn:Bi ₂ O ₃ -0.5	0.995	0.009 13
OV-Zn:Bi ₂ O ₃ -1.0	0.998	0.006 21

dustries, can cause severe nervous system and respiratory disease. Fig.7c shows the photocatalytic activity of traditional *B*-Bi₂O₃, OV-*B*-Bi₂O₃ and OV-Zn: Bi₂O₃ samples toward the degradation of 2,4,6-TCP under visible light with the intensity of 45 mW \cdot cm⁻² (λ =420 nm). It can be seen that, after irradiation for 100 min, about 51% and 71% of 2,4,6-TCP was degraded by OV- β -Bi₂O₃ and OV-Zn: Bi₂O₃-0.3, respectively, while only 37% of 2, 4, 6 - TCP was removed over traditional β -Bi₂O₃ within 100 min. Mover, as illustrated in Fig.7d, the order of the reaction rate constant in the degradation of 2, 4, 6 - TCP was $k_{\text{OV-Zn} : Bi_2O_2 - 0.3} > k_{\text{OV-Zn} : Bi_2O_2 - 0.5} >$ $k_{\text{OV-Zn}: Bi_{1}O_{2}-1,0} > k_{\text{OV-Zn}: Bi_{2}O_{2}-0,1} > k_{\text{OV-B}-Bi_{1}O_{2}} > k_{B-Bi_{1}O_{2}}$, which was the same with that of the degradation of MB dye, confirming the optimal $n_{\rm Zn}/n_{\rm Bi}$ of OV-Zn: Bi₂O₃ catalysts was 0.3.

The above systematic photocatalytic experiments revealed that, compared to traditional β -Bi₂O₃, both OV - β -Bi₂O₃ and OV-Zn: Bi₂O₃ exhibited superior activity due to the introduction of OV. Moreover, the synergistic effect of OV and doped zinc ions can promote the photocatalytic activity of OV-Zn: Bi₂O₃ in the degradation of MB and 2,4,6-TCP under visible light. In terms of the practical applications of catalysts, the reusability and stability are two vital factors worth special emphasis. Therefore, cycling experiments of $OV - \beta - Bi_2O_3$ and OV - Zn: $Bi_2O_3 - 0.3$ as the representative samples were carried out to evaluate their reusability for the degradation of MB under visible light irradiation. As shown in Fig.8, after 4 cycles running, the degradation rate of MB in the presence of $OV - \beta - Bi_2O_3$ and OV - Zn: $Bi_2O_3 - 0.3$ decreased slightly. The XRD patterns of $OV - \beta - Bi_2O_3$ and $OV-Zn: Bi_2O_3-0.3$ before and after four cycles of the photocatalytic degradation of MB are compared in Fig.9. It can be seen that, after four-cycle experiments, there was not any change in the crystal structure for both samples, which demonstrates that both $OV-\beta$ -Bi₂O₃ and $OV-Zn: Bi_2O_3$ possess strong structural stability during the photocatalytic degradation of MB.



Fig.8 Plots of c/c_0 versus irradiation time over OV- β -Bi₂O₃ (a) and OV-Zn:Bi₂O₃-0.3 (c) as well as photodegradation efficiency of MB over OV- β -Bi₂O₃ (b) and OV-Zn:Bi₂O₃-0.3 (d) in different recycling runs



Fig.9 XRD patterns of OV-Zn:Bi₂O₃-0.3 (a) and OV-β-Bi₂O₃ (b) before and after four-cycling degradation of MB under visible light irradiation

2.7 Photocatalytic mechanism

To investigate the active species involved in the MB degradation over OV-Zn: Bi_2O_3 catalysts, we adopted triethanolamine (TEOA) and *tert*-butanol (TBA) as the radical scavengers for holes and hydroxyl radicals to conduct trapping experiments^[33-35]. And N_2 was also

added to remove oxygen and prevent the formation of superoxide radicals^[36]. Fig. 10 displays the photocatalytic activity of OV-Zn: Bi_2O_3 -0.3 sample for the photocatalytic degradation of MB in the presence of TEOA and TBA (their concentration in the photocatalytic system was 6 mmol·L⁻¹). It can be seen that TEOA could strongly inhibit the photocatalytic activity of OV-Zn: Bi_2O_3 -0.3, which indicates that h^+ is the main active species for the degradation of MB. And after the introduction of TBA, the photodegradation of MB was obviously suppressed, which confirms that •OH also plays an important role in the photocatalytic degradation of MB. This is consistent with DRS results. As shown in Fig. 11, although the electrons in the VB of OV-Zn: Bi_2O_3 -0.3 can be excited to the CB by visible light, the active $\cdot O_2^-$ radical cannot be generated, due to the lower potential of $O_2/ \cdot O_2^-$ (-0.33 eV (vs NHE)) than that of CB potential of OV-Zn: Bi₂O₃-0.3 (0.49 eV (vs NHE), Table 1)^[37-38]. However, the holes in VB can oxidize OH^- (or H_2O) to generate $\cdot OH$ or directly oxidize MB, due to the higher VB potential of OV-Zn: Bi₂O₃-0.3 (2.99 eV (vs NHE), Table 1) than that of OH⁻/·OH (2.40 eV (vs NHE)) and $H_2O/\cdot OH$ (2.72 eV (vs NHE))NHE))^[39-40]. These results confirm that h^+ and \cdot OH are the main active species in the photodegradation pro-



Fig.10 Effect of different scavengers on MB degradation process over OV-Zn:Bi₂O₃-0.3 catalyst

cess of MB over OV-Zn:Bi₂O₃-0.3 photocatalyst.

In order to investigate the effect of OV and doped Zn²⁺ on the improvement of photocatalytic activity, photoelectrochemical experiments were carried out to evaluate the charge carrier density and the photogenerated carrier separation efficiency of different catalysts. The density of charge carriers, which is an important parameter affecting the photocatalytic activity of catalyst, can be obtained by the following Nernst equation:

$$E_{\rm f1} - E_{\rm f2} = kT \ln(N_{\rm f1}/N_{\rm f2})/e \tag{3}$$

Herein, E_{f1} and E_{f2} is the quasi-Fermi level of sample 1 and sample 2, respectively. $N_{\rm f1}$ and $N_{\rm f2}$ is the carrier density of two samples. In addition, k, T and e are the Boltzmann constant (1.381×10⁻²³ J·K⁻¹), temperature and elementary charge (1.602×10^{-19} C). With the addition of methylviologen dichloride (MVCl₂) serving as the fast electron acceptor, the photocurrent onset potential in a voltammogram can be considered as the quasi-Fermi level of majority carriers^[15,41-43]. As shown in Fig. 12a, the photocurrent onset potentials of $OV - \beta$ - Bi_2O_3 and $OV-Zn: Bi_2O_3-0.3$ were -0.37 and -0.41 V, both of which were higher than that of traditional β - Bi_2O_3 with a value of -0.45 V. According to above Nernst equation, the carrier densities of $OV - \beta - Bi_2O_3$ and OV-Zn: Bi₂O₃-0.3 were determined as 22.5 and 4.7 times larger than that of traditional β -Bi₂O₃, respectively. This suggests that the existence of OV can largely increase the charge carrier density of semiconductor by expanding the light absorption range of catalyst. Compared to $OV-\beta$ -Bi₂O₃, although the carrier density of OV



Fig.11 Photocatalytic degradation mechanism of OV-β-Bi₂O₃ and OV-Zn:Bi₂O₃ under visible light irradiation

-Zn: Bi₂O₃-0.3 was reduced for the wider band gap, the oxidation ability of photogenerated holes was enhanced and the separation efficiency of photo-generated carriers might be increased for the electron trapping role of the doped Zn²⁺. The transient photocurrent responses of different catalysts under visible light are shown in Fig. 12b. It can be seen that, the photocurrent densities of both $OV-\beta$ -Bi₂O₃ and OV-Zn: Bi₂O₃-0.3 were much larger than that of traditional β -Bi₂O₃. It demonstrates that the efficient generation and separation of photoinduced electron-hole pairs of both $OV-\beta$ -Bi₂O₃ and OV-Zn: Bi₂O₃ arise from the OV. Moreover, the photocurrent density of OV-Zn: Bi₂O₃-0.3 was larger than that of $OV - \beta - Bi_2O_3$, suggesting that the doped Zn^{2+} may also play an important role in promoting the separation efficiency for OV-Zn: Bi₂O₃ series. Fig. 12c shows the Zn2p XPS spectra of OV-Zn: Bi₂O₃-0.3 before and after MB degradation reaction. It can be seen that, after reaction, the binding energies of $Zn2p_{1/2}$ and $Zn2p_{3/2}$ shifted to lower energy, indicating that parts of doped Zn²⁺ was reduced by trapped electron to a new chemical state with lower valence. This further confirms that moderate doped Zn²⁺ can also serve as an electron trapping cen-

ter to promote the separation of photogenerated carriers. The PL spectra of catalysts can also reflect the separation efficiency of photogenerated electron-hole pairs in semiconductor. It is well known that a stronger PL intensity represents lower separation efficiency and higher recombination rate of the photogenerated charge carriers. Fig.12d shows the PL spectra of different samples at the excitation wavelength of 380 nm. It can be seen that $I_{\beta-Bi_2O_3} > I_{OV-\beta-Bi_2O_3} > I_{OV-Zn : Bi_2O_3-1.0} > I_{OV-Zn : Bi_2O_3-0.3}$ indicating that $E_{\text{OV-Zn} : Bi_2O_2-0.3}$ (separation efficiency of $\text{OV-Zn}:\text{Bi}_2\text{O}_3-0.3) > E_{\text{OV-Zn}:\text{Bi}_2\text{O}_3-1.0} > E_{\text{OV-β-Bi}_2\text{O}_3} > E_{\beta\text{-Bi}_2\text{O}_3},$ which was consistent with transient photocurrent results of catalysts. All the above data suggest that OV and appropriate doped Zn²⁺ can promote the separation efficiency of photogenerated carriers, however, excessive zinc may also become the recombination center, reducing the catalytic activity of OV-Zn: Bi₂O₃ series.

To further study the role of OV in promoting the separation efficiency of photogenerated carriers, the ESR spectra were recorded for OV-Zn: Bi_2O_3 series under laser irradiation (λ =420 nm) in air. Fig. S1 (Supporting information) are the ESR spectra of OV-Zn:



Fig.12 (a) *I-V* curves of traditional β-Bi₂O₃, OV-β-Bi₂O₃ and OV-Zn:Bi₂O₃-0.3; (b) Photocurrent response of traditional β-Bi₂O₃, OV-β-Bi₂O₃, OV-β-Bi₂O₃-0.3 and OV-Zn:Bi₂O₃-1.0 under visible light (λ>420 nm); (c) Comparison of Zn2p XPS spectra of OV-Zn:Bi₂O₃-0.3 before and after reaction; (d) PL spectra of β-Bi₂O₃, OV-β-Bi₂O₃, OV-β-Bi₂O₃, OV-β-Bi₂O₃, OV-β-Bi₂O₃-0.3 and OV-Zn:Bi₂O₃-1.0

Bi₂O₃ series, where the dashed and solid lines correspond to the signals before and after laser irradiation, respectively. It can be seen that, the ESR signal intensity of V₀⁻ in all catalysts having OV could be increased under visible light irradiation, indicating that the OVs in OV-Zn: Bi₂O₃ series prepared in this work are very stable and there are more V_o[•] produced under visible light. It is well known that, besides V_0 , there are two other kinds of OV, two-electron-trapped OV (effective charge=0, denoted as V_0^{\times}) and no-electrontrapped OV (effective charge=+2, denoted as $V_0^{(1)}$)^[27,29], both of which do not contribute to ESR signals because of the absence of unpaired electrons. Under visible light irradiation, the electrons can be photoexcited to conduction band, leaving the holes in VB. If there are trapping electron centers, *i.e.*, V₀^{...} or trapping hole centers V_0^{\times} on the surface of catalyst, the electron of the conduction band may be trapped by surface Vo" and the hole of the VB may be captured by surface V_0^{\times} . Both kinds of OVs transformed into V₀⁺ and the signal intensity became stronger accordingly (Fig. 11). The separation efficiency of photogenerated carriers will be also improved. In other words, $\Delta h ~(\Delta h = h_{\text{light}} - h_{\text{dark}}, h_{\text{light}})$ and h_{dark} refer to the intensities of ESR signal at g=2.004 under visible light and in dark, respectively) is closely related to the separation efficiency of photogenerated carriers caused by surface OV. The dependences of Δh and the reaction constant (k) for the degradation of MB by OV-Zn: Bi₂O₃ series on the intensity of ESR signal for V₀⁻ ($h_{\text{ESR, OV}}$) are shown in Fig.13a. It can be seen that with the increase of $h_{\text{ESR, OV}}$, both of Δh and k first increased and then decreased, suggesting that excessive OV may be detrimental to the activity of catalyst. Fig.13b shows the dependences of $h_{\text{ESR, OV}}$ and k for the degradation of MB by OV-Zn: Bi₂O₃ series on n_{Zn}/n_{Bi} . It can be seen that, with the increase of doped Zn²⁺, $h_{\text{ESR, OV}}$ decreased and there was a peak of reaction constant situated at n_{Zn}/n_{Bi} =0.3 for OV-Zn: Bi₂O₃-O.3. This suggests that the concentration of OV can be modulated by the doped zinc and excessive zinc doping may also reduce the separation efficiency of photogenerated carriers.

Two kinds of OV on the surface of catalysts, $V_0^{\circ \circ}$ and $V_0^{\circ \circ}$, can serve as trapping centers of electrons and holes, respectively. And moderate doped Zn^{2+} can also act as electron capture sites to promote the separation efficiency of photogenerated carriers. Thus, the visible light activity of both OV - β -Bi₂O₃ and OV - Zn: Bi₂O₃ series can be improved. Of course, compared to OV - β -Bi₂O₃, moderate doped Zn²⁺ can result in the optimal energy level structure for OV - Zn: Bi₂O₃, and OV - Zn: Bi₂O₃-0.3 exhibited the highest activity for the degradation of MB and 2,4,6-TCP.



 $\Delta h = h_{light} - h_{dark}$; h_{light} and h_{dark} refer to the intensities of ESR signal at g=2.004 under visible light and in dark, respectively

Fig.13 (a) Dependence of Δh and reaction rate constant (*k*) for the degradation of MB by OV-Zn: Bi₂O₃ series on intensity of ESR signal for V_o⁻ (*h*_{ESR, OV}); (b) Dependence of *h*_{ESR, OV} and *k* on *n*_{Zn}/*n*_{Bi}

3 Conclusions

 $OV-\beta-Bi_2O_3$ and Zn-doped $OV-\beta-Bi_2O_3$ series (OV-Zn: Bi_2O_3) were prepared by a simple sol-gel method followed by *in-situ* carbon thermal reduction treatment.

The concentration of oxygen vacancy in $OV-Zn:Bi_2O_3$ can be modulated by the content of doped zinc. The more the content of doped Zn^{2+} is, the less the concentration of oxygen vacancy will be. The introduction of oxygen vacancy and moderate zinc can not only regulate the energy structure of OV-Zn: Bi_2O_3 , but also promote the separation efficiency of photogenerated carriers. So, the visible light activity of OV-Zn: Bi_2O_3 series was superior to that of OV- β -Bi₂O₃, and the activity of OV- β -Bi₂O₃ was better than that of traditional β -Bi₂O₃. This study offers a new method to prepare the novel visible-light-responsive catalyst with stable controllable oxygen vacancy.

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Supporting information is available at http://www.wjhxxb.cn

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