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Article

Zn-doping mediated formation of oxygen vacancies in SnO₂ with unique electronic structure for efficient and stable photocatalytic toluene degradation

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ABSTRACT

To optimize the electronic structure of photocatalyst, a facile one-step approach is developed for the simultaneous realization of Zn-doping and surface oxygen vacancies (SOVs) formation on SnO₂. The Zn-doped SnO₂ with abundant SOVs exhibits efficient and stable performance for photocatalytic degradation of toluene under both low and high relative humidity. Experimental and theoretical calculations results show that the synergistic effects of Zn-doping and SOVs on SnO₂ can considerably boost the charge transfer and separation efficiency. Utilizing the *in situ* DRIFTS and theoretical calculations methods, it is revealed that the benzene ring of toluene is opened at benzoic acid on the SnO₂ surface and selectively at benzaldehyde on the Zn-doped SnO₂ surface. This implies that Zn-doped SnO₂ photocatalysts shorten the pathway of toluene degradation, and toxic intermediates can be significantly inhibited. This work could provide a promising and sustainable route for safe and efficient removal of aromatic VOCs with photocatalytic technology.

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1. Introduction

Volatile organic compounds (VOCs) emitted from interior furniture and industrial activities are typical air pollutants that pose a serious threat to the environmental and human well-being [1]. Conventional technologies, including membrane

separation, incineration, adsorption, and biodegradation, have been applied to remove VOCs [2]. Nevertheless, there are some potential drawbacks to these methods, such as inefficient removal, high energy cost, or secondary contamination [3]. Photocatalytic oxidation provides a mild technology for the complete mineralization of VOCs to H₂O and CO₂ [4,5]. It has signif-

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icant potential to be an alternative to current air handling technologies. However, the widely used TiO_2 -based photocatalysts for degradation of VOCs still suffer from low photocatalytic conversion rate and rapid deactivation, especially for the aromatic hydrocarbons [6,7]. Therefore, it is imperative to exploit novel photocatalysts to degrade VOCs with persistent stability for the practical application.

Recently, SnO_2 has received more and more attention for its non-toxic, reliable stability, and excellent photoelectric performance [8,9], making the SnO_2 exhibit broad application prospects in photodetectors [10], gas sensors [11], dye-sensitized solar cells [12], lithium rechargeable batteries [13], and photocatalysis [14], etc. Besides, recent studies have further reported that SnO_2 is sensitive to multiple noxious gases with promising utilization prospects in gas detectors [15,16]. However, only a minority of research has investigated the potentiality of SnO_2 as photocatalysts ascribed to its wide bandgap ($E_g = 3.6$ eV) and high electron-hole pairs recombination rate, which limit its photocatalytic application [17]. In order to increase the photocatalytic efficiency, doping of metal ions and non-metal ions [18,19], surface sensitization of noble metals [20], co-doping [21,22], hybridization with carbon materials [23,24], and other methods are proposed.

Transition metal ion doping often attempts to delay the rapid recombination of e^-h^+ pairs by providing a defective state [25–27]. The defect sites can trap photogenerated electrons or holes, thereby inhibiting recombination and facilitating interfacial charge transfer. Compared to other metal elements, the SnO_2 lattice can be easily doped with Zn ions, since the Zn^{2+} and Sn^{4+} ions have a similar ionic radius of 0.73 and 0.71 Å, respectively. Replacing Sn^{4+} ions with Zn^{2+} ions would lead to surface modification, forming more oxygen vacancies to compensate for the positive charge. Most importantly, many research results have verified that the presence of SOVs not only generates the defect level but also promotes a large number of localized electrons accumulated in oxygen vacancies [28–30]. The surface oxygen vacancies (SOVs) are natural active sites for enhanced chemisorption of O_2 and H_2O [31–33]. The synergistic SOVs and Zn-doping construction on SnO_2 can remarkably compensate for the drawback of a single exogenous ion doping or oxygen vacancy generation [34–37]. For example, ultrathin TiO_2 nanosheets rich in oxygen vacancies were reported by Zhao *et al.* [38] using a simple copper-doping strategy, and these photocatalysts exhibited significant performance in photocatalytic reduction of N_2 to NH_3 . Nevertheless, to our knowledge, the synergistic effects of simultaneous Zn-doping and SOVs construction on the electronic structure of SnO_2 and their influence on the photocatalytic VOCs degradation have not been revealed.

A hydrothermal approach was developed to realize the Zn-doping mediated formation of SOVs on SnO_2 in one single process in this work. It is observed that Zn-doped SnO_2 with abundant SOVs exhibits very predominant performance for the degradation of toluene in air, far exceeding that of commercial P25 photocatalyst. The synergistic effects of simultaneous Zn-doping and SOVs construction on the electronic structure of SnO_2 are investigated deeply. In addition, in the process of

photocatalytic degradation of toluene, some toxic intermediates such as epoxy compounds, polyols, peroxides, and aromatic oxides are produced [39]. In order to investigate the differences between the ring-opening mechanisms of Zn-doped SnO_2 and pure SnO_2 , the ring-opening efficiencies and reaction paths of the ring-opening intermediates are provided on the basis of the theoretical calculations and *in situ* DRIFTS. Through this work, novel insights can be gained into the construction of novel photocatalysts via metal doping and formation of SOVs for safe and efficient removal of air pollutants.

2. Experimental

2.1. Synthesis of photocatalysts

A hydrothermal approach was used to synthesize Zn-doped SnO_2 samples. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (10 mmol) and NaOH (50 mmol) were dissolved in 50 mL of deionized water, respectively, and then stirred for 20 min. Before the mixing of two solutions, the different molar mass of ZnCl_2 (mol Zn/mol Sn = 10, 25, 30) was used as the source of zinc incorporated into the SnCl_4 solution. Stirred the mixture for 30 min and then dropped 50 mL of ethanol solution. Subsequently, the resulting mixture was poured into the Teflon-lined stainless autoclave and kept at 180 °C for 24 h. The products were collected by centrifugation and repeatedly washed with ultra-pure water and then absolute ethanol. Finally, the products were dried at 60 °C. The obtained SnO_2 with different zinc content is recorded as X-Zn- SnO_2 (X = 1, 2, 3). The pure SnO_2 was also synthesized in the same way without adding a zinc source.

2.2. Characterization

Following those characterizations, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-vis reflectance spectrometry spectrum (UV-vis DRS) and electron spin resonance (ESR) measurements were used to analyze the as-obtained catalysts. Different characterizations are described in detail in Supplementary Material.

2.3. Theoretical calculations

Density functional theory (DFT) calculations were performed with the “Vienna ab initio simulation package” (VASP 5.4.1). A plane-wave basis set with cutoff energy 400 eV was employed to ensure accurate results. K points in the Brillouin zone was sampled with a $3 \times 3 \times 1$ Monkhorst Pack grid. The Perdew-Burke-Ernzerhof (PBE) exchange correlation functional was conducted to model SnO_2 and Zn^{2+} doped SnO_2 with oxygen vacancy. The geometrical relaxation was performed until the residual force was not more than 0.03 eV/Å, then electronic properties were carried out. The model construction process and schematic (Figs. S(1,2)) are given in the form of Supplementary Material.

2.4. *In situ* DRIFTS study on the photocatalytic toluene

oxidation process

Continuous *in situ* DRIFTS system was performed using a Tensor II FT-IR spectrometer (Bruker) setup with an in-situ diffuse reflectance cell (Harrick). The experimental conditions were given in the form of Supplementary Material.

2.5. Evaluation of UV-light photocatalytic activity

The photocatalytic activity of the catalysts was performed in a home-made rectangular aluminum reactor with an online photoacoustic multi-gas analyzer (GASERA ONE, USA). At first, a 0.40 g prepared sample was evenly dispersed in four frosted glasses (40 mm × 100 mm) with a small amount of ethanol. Then the glasses were dried at 60 °C until dry. The coated glass was put into the reactor (340 mL, 200 mm × 100 mm × 17 mm). The initial concentration of the continuous stream of toluene was diluted to about 45 ppm with two separated air streams (wet air and dry air). The two relative humidity (RH) levels (50% and 100%) in the reactor chamber are achieved via flow controllers. The Supplementary Material gives the efficiency calculations and reaction conditions for photocatalytic toluene.

3. Results and discussion

3.1. Materials and structures

The crystalline structure and phase purity are firstly investigated by XRD. The XRD pattern (Fig. 1(a)) could correspond to the tetragonal phase SnO₂ (JCPDS No. 41–1445). The crystalline characteristic peaks of ZnO, Zn₂SnO₄, ZnSnO₃, and other impurities are not seen in the pattern. Besides, the angle of diffraction peaks did not deviate after the Zn-doping, which may be attributed to the reason that the radius of the Zn²⁺ ions (0.73 Å) is close to that of the Sn⁴⁺ ions (0.71 Å). In addition, the decreased degree of crystallinity can be observed with increasing Zn dopant concentration, attributing to the potential formation of the defect. The EPR spectra (Fig. 1(b)) show an EPR signal at $g = 2.002$, corresponding to oxygen vacancies [40]. The pure SnO₂ shows only a weak EPR signal, suggesting the existence of intrinsic SOVs. However, the signal intensity of Zn-SnO₂ was almost 2-fold enhanced compared to that of pure SnO₂, indicating an elevated concentration of SOVs. An energy level below the CB can be produced by SOVs, thus enhancing light absorption and reduced e⁻-h⁺ pairs recombination [41].

Fig. 1. (a) XRD pattern of SnO₂ and X-Zn-SnO₂; (b) EPR spectra of SnO₂ and 2-Zn-SnO₂.

Moreover, the broadening of the peak width manifests that the crystalline size of SnO₂ nanoparticles is decreased [38].

Fig. S3 shows the SEM morphology of the samples. The size of average particles for SnO₂ sample is 160–200 nm, while 2-Zn-SnO₂ nanoparticles are composed of fine spherical nanoparticles in a smaller size range of 12–14 nm (Fig. S4). The samples size follows the sequence: 3-Zn-SnO₂ < 2-Zn-SnO₂ < 1-Zn-SnO₂ << SnO₂. The particle size of Zn-doped SnO₂ was significantly reduced since the Zn-doping can effectively inhibit the crystal growth and phase transition of SnO₂ nanoparticles, resulting in increased content of SOVs [42]. The decrease in size is conducive to increasing its specific surface area (Table S1) and improving its active adsorption sites [43]. Fig. 2 shows the TEM and HRTEM results for SnO₂ (Figs. 2(a,b)) and Zn-doped SnO₂ (Figs. 2(c,d)). The micrographs also demonstrate that the formed nanoparticles are homogeneous, and aggregate to form large-sized aggregates with good dispersion. Moreover, the pure SnO₂ exhibits nanoparticles with clear crystal lattices and edges, while the edges of the 2-Zn-SnO₂ nanoparticles show a disordered state, indicating that the surface structure of the 2-Zn-SnO₂ sample is disrupted and may form SOVs [44–48]. Both SnO₂ and 2-Zn-SnO₂ have lattice fringes of 0.335 nm and are attributed to (110) facets. The even distribution of Sn, O, and Zn in the nanoparticles is confirmed by the EDX element mapping of 2-Zn-SnO₂ samples (Figs. 2(e–g)), suggesting the incorporation of Zn ions into SnO₂ successfully.

The chemical states of undoped and doped system nanoparticles were explored via XPS analysis. The survey scan (Fig. 3(a)) displays the 2-Zn-SnO₂ is mainly composed of Sn, O, Zn, and C. The binding energies of the Sn element are 486.5 and 495.0 eV (Fig. 3(b)), assigned to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively [49]. Of these, the former has a relatively lower value, attributing to the fact that SOVs reduce the binding energy of Sn [50]. The spectrum of O 1s in the Zn-doped SnO₂ sample (Fig. 3(c)) shows an additional shoulder compared with the pure SnO₂. The coordination of oxygen in Sn-O-Sn at 530.5 eV decreases in value with the presence of SOVs [51], the other peak at 531.7 eV corresponds to the coordination of Sn-O-Zn [52]. The binding energies at 1021.6 and 1044.7 eV correspond to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively, in the Zn 2p spectrum (Fig.

Fig. 2. TEM and HRTEM images of SnO₂ (a,b) and 2-Zn-SnO₂ (c,d); EDX elemental mappings of Sn (e), O (f), and Zn (g).

Fig. 3. XPS spectra of SnO₂ and 2-Zn-SnO₂ survey (a), Sn 3d (b), O 1s (c), and Zn 2p (d).

3(d)) [49]. Apparently, Zn²⁺ ions are doped into the SnO₂ lattice and SOVs are generated simultaneously.

3.2. Optical properties and band structure

Photocatalytic activity is directly affected by efficient light absorption and charge separation [53]. The light absorption properties of Zn-doped SnO₂ and undoped samples were investigated by UV-vis (Fig. 4(a)). Notably, the absorption edges of the Zn-doped SnO₂ sample red shifted from 320 to 375 nm under the synergistic effects of Zn-doping and SOVs [54]. Fig. 4(a) (inset) shows the bandgap values of 3.65 and 3.32 eV for pure SnO₂ and Zn-doped SnO₂, respectively. The lower bandgap

suggests that Zn-doping and the formation of SOVs have a substantial influence on narrowing the bandgap of SnO₂. The narrowed bandgap allows SnO₂ to enhance light absorption and has a superior photocatalytic activity against toluene degradation in UV light.

3.3. Photocatalytic performance, ROS generation, and transformation

The efficiency of photocatalytic degradation toluene over pure SnO₂ and Zn-doped SnO₂ samples was evaluated under UV light (360 nm) irradiation. Fig. 4(b) shows that all the Zn-doped SnO₂ samples exhibit enhanced photocatalytic efficiency, which

Fig. 4. (a) The UV-Vis DRS spectra and the estimated plot of $(\alpha h\nu)^{1/2}$ vs. photon energy (inset) of SnO₂ and 2-Zn-SnO₂ samples; (b) UV light photocatalytic toluene removal (RH = 50%) on SnO₂ and X-Zn-SnO₂ samples; cycling tests for 2-Zn-SnO₂, SnO₂ and P25 at RH = 50% (c) and RH = 100% (d).

is superior to that of pure SnO₂. It demonstrates that doping with Zn²⁺ ions is a valuable approach for promoting the photocatalytic activity of SnO₂. Furthermore, the photocatalytic performance of 2-Zn-SnO₂ was tested for 35 min, and the maximum degradation rate of toluene reached 77.5% (RH = 50%). However, the photocatalytic performance of 3-Zn-SnO₂ is inferior to that of 2-Zn-SnO₂ due to its weak light-harvesting capability and high electron-hole pairs recombination efficiency. From Fig. 4(a), it can be seen that the light absorption intensity of 3-Zn-SnO₂ is weaker than that of 2-Zn-SnO₂. Fig. S5(a) shows that 3-Zn-SnO₂ exhibits a higher electron-hole pairs recombination efficiency. Figs. 4(c,d) show the performance of different photocatalysts at two RH levels for recycled runs (50% and 100%), respectively. The 2-Zn-SnO₂ photocatalyst remains extremely stable degradation efficiency at RH = 50% even after the fourth run, and outperforms RH = 100% owing to the competitive adsorption of H₂O under high RH. Pure SnO₂ also shows stable performance, but the degradation efficiency was not as efficient as 2-Zn-SnO₂. In addition, the degradation of toluene in a blank experiment without a photocatalyst was 9.60%, as shown in Fig. S5(b), which may be due to the toluene oxidation by generated ozone under UV light irradiation [55]. However, P25, as a commercial catalyst, fleetly lost its catalytic activity after four cycle tests. Those results imply that 2-Zn-SnO₂ is an efficient and stable photocatalyst. Doping of SnO₂ with Zn²⁺ significantly improves the efficiency of toluene degradation, and the main reasons for this enhanced activity are the doping of Zn²⁺ and the formation of SOVs.

The premise of heterogeneous catalysis is to fully promote the adsorption of reactants to guarantee the following photocatalytic reaction proceeds. The SOVs can provide unsaturated sites and promote adsorption and activation of the species in the reaction. The generation and transformation of reactive oxygen species (ROS: •O₂[−], ¹O₂, and •OH) on SnO₂ and 2-Zn-SnO₂ were further investigated. The electron-trapping

ESR spectra are shown in Fig. 5(a), showing the rapid depletion of electron sacrificial agent in 2-Zn-SnO₂ under light conditions. The results reveal that more electrons are generated on 2-Zn-SnO₂, which is in favor of upgrading the photocatalytic activity. As expected, 2-Zn-SnO₂ produced more •O₂[−] (O₂ + e[−] → •O₂[−]) than SnO₂ and P25 (Fig. 5(b)), intimately related to the fact that the separated photogenerated electrons readily associate with O₂ to produce more •O₂[−] under UV light. Meanwhile, the amount of •OH (OH[−] + h⁺ → •OH) produced by 2-Zn-SnO₂ significantly exceeds that produced by SnO₂ and P25 (Fig. 5(c)), due to the increased charge separation and H₂O molecules activation. Obviously, the ¹O₂ yielded by the •O₂[−] + h⁺ → ¹O₂ pathway is stronger than those of pure SnO₂ and P25. These improvements in radical production are owing to the synergistic effects of SOVs and Zn-doping on SnO₂ to significantly improve photogenerated charge transfer and separation efficiency.

The chemisorption and activation mechanisms of SOVs enhanced O₂ and H₂O were simulated by DFT calculations. The structure of the adsorbed O₂ and H₂O molecules were first optimized for SnO₂ and Zn-doped SnO₂, respectively (Figs. 6(a–d)). Intuitively, the O–O bond length of O₂ is enlarged, and the O–H–O bond angle of the H₂O molecule decreases compared to the pure SnO₂. Furthermore, both O₂ and H₂O molecules possess higher adsorption energy (*E*_{ads}) on the Zn-doped SnO₂ surface than that of SnO₂. At the same time, the electron localization function (ELF) diagrams (Figs. 6(e–h)) also show that O₂ and H₂O are more likely to form electron transfer channels with atoms on the X-Zn-SnO₂ surface, which facilitates the transfer of electrons. The total charge (Δ*q*) values of −0.56 and −0.85 e for O₂ correspond to the undoped and Zn-doped SnO₂ samples, respectively. Δ*q* is expressed as a negative value when electrons are transferred to the adsorbed O₂. The more negative value of Δ*q* is, the more electrons could be accepted by the adsorbed O₂. Those consequences imply that the presence

Fig. 5. ESR spin-trapping for electrons (a), superoxide radicals (b), hydroxyl radicals (c), and singlet oxygen (d).

Fig. 6. Optimized O_2 and H_2O adsorption on SnO_2 (a,c) and X-Zn-SnO_2 (b,d): charge accumulation is in blue and depletion in yellow; electron localization function (e–h).

of SOVs weakens the O–O and H–O bonds, thereby promoting the activation of O_2 and H_2O to oxidize toluene.

For SnO_2 , a shallow donor state below the CB can be formed by Zn^{2+} dopants [56]. Moreover, removing an O atom from the surface will cause one or two electrons to be trapped in the oxygen vacancy site. These trapped electrons can also generate donor states below the CB [57,58]. These donor states can directly affect the electronic structure of SnO_2 by overlapping the CB, thereby narrowing the bandgap and shifting the Fermi level of SnO_2 towards higher energy [59]. The higher Fermi level can effectively facilitate the separation and transfer of photogenerated charges. Besides, the SOVs can serve not only as photo-generated charges traps but also as adsorption sites. The SOVs can enhance the adsorption of oxygen, water, and toluene. As a result, the carriers can react rapidly with these adsorbates, thus preventing the recombination of charges and increasing the generation of active radicals. In general, all mentioned above revealed that the synergistic effects of SOVs and

Zn -doping could potentially improve the photogenerated charges transfer and separation efficiency, which are the critical factors to improve the photocatalytic degradation performance of toluene.

3.4. *In situ* DRIFTS investigation on the mechanisms of photocatalytic toluene oxidation

In the photocatalytic degradation of toluene, the ring-opening process is a key step in determining the rate. The adsorption and activation of toluene molecular are the critical steps before the ring-opening. The value of -0.63 and -0.54 eV are the adsorption energy of toluene on Zn -doped SnO_2 and SnO_2 , respectively (Figs. S6(a,b)). The ELF diagrams (Figs. S6(c,d)) demonstrate that the adsorbed toluene molecule is more likely to form electron channels with the Zn -doped SnO_2 surface, which is conducive to electron transport. The Δq values of $+0.002$ and $+0.011$ e for toluene correspond to SnO_2 and Zn -doped SnO_2 samples, respectively. Δq is expressed as a positive value when electrons are donated to the electron-deficient field. Thus, the more positive of the Δq is, the easier of the toluene molecules are oxidized to a higher valence, which further facilitating the conduct of photocatalytic oxidation. The oxidation route of toluene before ring-opening is as follows: toluene $\rightarrow$ benzyl alcohol $\rightarrow$ benzaldehyde $\rightarrow$ benzoic acid.

The *in situ* DRIFTS monitoring of intermediates and products during toluene oxidation was carried out. Table S2 lists the assignments of the IR bands. Under the dark conditions, it can be observed that many new bands show up after 20 min of the toluene injection (Figs. 7(a,c)). On the SnO_2 surface, the spectral band at 3635 cm^{-1} is benzyl alcohol and 1357 cm^{-1} is benzaldehyde. The band at 1628 cm^{-1} is due to the adsorbed OH groups. For 2-Zn-SnO_2 , an increase in intermediates was observed, including benzyl alcohol (3631 cm^{-1}), benzaldehyde

Fig. 7. *In situ* DRIFTS spectra of toluene adsorption and reaction process on SnO_2 (a,b) and 2-Zn-SnO_2 (c,d); species evolution of benzyl alcohol, benzaldehyde, and benzoic acid during the adsorption (e) and reaction process (f).

(1454 and 1298 cm^{-1}), and benzoic acid (1493 cm^{-1}). The bands of 3028 and 1357 cm^{-1} are attributed to the benzene ring, indicating that it cannot be opened in the absence of light. Furthermore, the normalized species evolution results (Fig. 7(e)) based on IR spectra in time sequence showed that the accumulation of benzyl alcohol and benzaldehyde on 2-Zn-SnO₂ was significantly higher than that of SnO₂.

Figs. 7(b,d) show the *in situ* DRIFTS spectra of photocatalytic toluene oxidation of undoped and doped SnO₂ surfaces under UV irradiation, respectively. The peaks of toluene and benzyl alcohol in the reaction process of 2-Zn-SnO₂ and SnO₂ were decreased compared with the adsorption process, which indicated that they were converted to benzaldehyde (1699, 1608, 1393, 1216, 1693, 1599, and 1304 cm^{-1}) and benzoic acid (1504 and 1401 cm^{-1}). From the normalized species evolution (Fig. 7(f)) of the reaction, it can be seen that benzoic acid was oxidized from toluene and accumulated on the surface of SnO₂. The unsaturated long-chain enol gradually broke off after benzene ring opening and were eventually oxidized to CO₂ and H₂O. However, on the surface of Zn-doped SnO₂, the benzyl alcohol consumption was evident, and the benzaldehyde accumulation was significant. In addition, benzoic acid did not change significantly over time, and this experiment confirmed that the ring-opening process on Zn-doped SnO₂ primarily begins with benzaldehyde. The results above indicate that the benzene ring is likely to open on the SnO₂ surface at benzoic acid and selectively at benzaldehyde on the Zn-doped SnO₂ surface, thereby shortening the degradation pathway of toluene and significantly suppressing the intermediates. The normalized absorbance of the final mineralized product CO₂ over time is a visual indication of the degradation efficiency. The diagram in Fig. S7 shows that more CO₂ is produced on the surface of 2-Zn-SnO₂ than that of SnO₂, which not only confirms that Zn-doping and creation of oxygen vacancies substantially inhibit the production of toxic intermediates, but also indicates that toluene can be made to degrade more efficiently.

The DFT calculations revealed the potential mechanism of the difference in reaction selectivity between the Zn-doped SnO₂ and SnO₂. Fig. 8 showed that the adsorption energy of the

Fig. 9. Photocatalytic toluene degradation process on the surface of SnO₂ photocatalyst with Zn-doping and SOVs.

Zn-doped SnO₂ to that aromatic-ring containing species increased obviously in contrast to SnO₂, indicating that the charge transfer between the adsorbents and Zn-doped SnO₂ promoted the oxidation of benzyl. In particular, the Eads pattern of benzaldehyde and benzoic acid is reversed between the Zn-doped SnO₂ and SnO₂, which may manifest that benzaldehyde is more favorable converted on SnO₂ and decomposed on Zn-doped SnO₂, thus effectively shortening the degradation path of toluene [5]. The photocatalytic toluene degradation process on the surface of SnO₂ photocatalyst with Zn-doping and SOVs are illustrated in Fig. 9.

4. Conclusions

We have implemented the simultaneous Zn-doping and SOVs generation on SnO₂ using a simple one-step method. These Zn-doped SnO₂ nanoparticles with abundant SOVs exhibited efficient and stable performance for the photocatalytic degradation of toluene under both low and high RH conditions. The donor states of Zn-doping and SOVs can overlap the CB and thus directly affect the electronic structure of SnO₂, thereby

Fig. 8. Calculated reactants and intermediates adsorption on the surface of SnO₂ (a–c) and Zn-doped SnO₂ (d–f).

Graphical Abstract

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Zn-doping mediated formation of oxygen vacancies in SnO₂ with unique electronic structure for efficient and stable photocatalytic toluene degradation

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The synergistic effects of Zn-doping and surface oxygen vacancies on SnO₂ can boost the charge transfer and reactants activation, shorten the pathway of toluene degradation, and significantly inhibit the toxic intermediates formation.

narrowing the bandgap and shifting the Fermi level of SnO₂ toward high energy level. The SOVs can act as adsorption sites to facilitate the chemisorption of H₂O and O₂. The synergistic effects of SOVs and Zn-doping on SnO₂ can dramatically boost the charge separation and transfer efficiency, which remarkably improved the activity of toluene degradation. Moreover, the benzene ring is likely to be opened on the SnO₂ surface at benzoic acid, whereas on the Zn-doped SnO₂ surface, the benzene ring is selectively opened at benzaldehyde. Hence, the degradation pathway of toluene is shortened, and toxic intermediates can be significantly inhibited. Some new insights and awareness can be offered through this work on the construction of novel photocatalysts via combining metal doping and the oxygen vacancies generation for safe and efficient removal of air pollutants.

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Electronic supporting information

Supporting information is available in the online version of this article.

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具有独特电子结构的锌掺杂SnO₂介导形成氧空位实现高效稳定的光催化降解甲苯

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摘要: 室内家具和工业生产排放的挥发性有机化合物(VOCs)是典型的空气污染物, 对环境和人类健康造成严重威胁。然而, 目前广泛应用的二氧化钛(P25)光催化剂在降解VOCs, 尤其是降解芳香烃的过程中, 存在光催化转化率低, 失活快等问题。因此, 开发具有高效和稳定性的新型光催化剂来降解VOCs, 并将其实际应用是重要的科学问题。SnO₂是一种稳定无毒的半导体光催化剂, 但电子和空穴的复合率较高。掺杂过渡金属离子后可以提供缺陷态来抑制催化剂电子空穴对的快速复合, 促进界面电荷转移。相比其他金属离子, Zn²⁺与Sn⁴⁺的离子半径非常相近, 因此Zn²⁺会很容易掺杂到SnO₂晶格中。并且用Zn²⁺取代Sn⁴⁺会形成表面修饰, 即形成更多的氧空位(SOVs)来补偿正电荷。氧空位的存在不仅会产生缺陷能级, 而且还可以促进大量局域电子的累积。SnO₂上氧空位和Zn掺杂结构的协同作用可以弥补单一的外源离子掺杂或产生氧空位的不足。因此, 本文采用一种简便的一步法合成催化剂Zn-SnO₂, 即在SnO₂上同时实现Zn掺杂和形成SOVs, 利用两者对SnO₂

的协同作用提高电荷转移和分离效率,使其在低或高相对湿度条件下均表现出高效、稳定的光催化降解甲苯性能。

采用低温固态电子顺磁共振(EPR)检测了催化剂中的氧空位,在纯 SnO_2 中仅检测到弱的EPR信号,而 Zn-SnO_2 上的EPR信号非常强,表明 Zn^{2+} 的掺杂诱导产生了大量的氧空位。扫描电镜和透射电镜结果表明,掺杂 Zn^{2+} 可以有效抑制 SnO_2 纳米粒子的晶体生长和相变,使得掺杂 Zn^{2+} 的 SnO_2 粒子的粒径显著减小,从而导致SOVs含量增加,此外粒径的减小有利于增大其比表面积,增加活性吸附位点。紫外可见漫反射结果表明, Zn-SnO_2 拓宽了光吸收范围,这归因于锌掺杂和氧空位的协同作用。在紫外光照射下, Zn-SnO_2 的光催化降解甲苯性能优于纯 SnO_2 和P25,降解率达到77.5%。ESR光谱结果表明, Zn-SnO_2 上的电子自旋共振信号强度均强于纯 SnO_2 和P25,说明 Zn-SnO_2 具有较好的氧化能力,也与DFT计算 O_2 和 H_2O 的吸附能结果相吻合,表明了锌掺杂和SOVs对 SnO_2 的协同作用可以显著提高电荷转移和分离效率。最后,通过原位红外光谱和DFT计算方法对甲苯降解的机理进行了研究。结果表明,甲苯的苯环在纯 SnO_2 表面倾向于在苯甲酸阶段打开,在 Zn-SnO_2 表面更倾向于在苯甲醛阶段选择性地开环。可见, Zn-SnO_2 光催化剂缩短了甲苯的降解路径,并能显著抑制中间毒副产物产生。综上,本工作提供了一种安全、高效和可持续的降解VOCs的光催化剂。

关键词: 光催化; 锌掺杂; 表面氧空穴; 甲苯; 原位红外光谱

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