Photothermal synergic catalytic degradation of the gaseous organic pollutant isopropanol in oxygen vacancies utilizing ZnFe₂O₄

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Abstract
ZnFe₂O₄ is an environmentally friendly semiconductor material which has potential applications in catalytic organic pollutant degradation. Here, we demonstrate the synthesis of ZnFe₂O₄ and its photothermal catalytic application. The obtained ZnFe₂O₄ prepared by using the sol-gel method has a large specific surface area which reaches 56.4 m²/g. Electron paramagnetic resonance, X-ray photoelectron spectra, and photoabsorption results indicate that ZnFe₂O₄ has plentiful oxygen vacancies. When evaluated by the degradation of the gaseous organic pollutant isopropanol, oxygen-vacancy-rich ZnFe₂O₄ presents a high and stable thermal catalytic performance, while driven by high-intensity light. In addition, a distinct improvement is observed. Moreover, a synergic photothermal catalytic mechanism of isopropanol degradation on ZnFe₂O₄ is proposed.

Keywords
ZnFe₂O₄, photothermal catalysis, oxygen vacancies, isopropanol degradation

Introduction
Catalytic technology has significant prospects in environmental purification, especially for the degradation of toxic organic chemicals. Recently, much attention has been paid to catalytic technology, including photocatalysis,¹ thermal catalysis,² and photo electrocatalytic degradation.³ Among them, photocatalytic pollutant removal, which utilizes photo-generated electrons and holes to degrade organic pollutants at room temperature, is a hot research field and has been studied intensively.⁴ Semiconductor photocatalysts have stable chemical properties, are low-cost, and have high recycling rates; however, researchers still face challenges that need to be solved. One challenge is due to the rapid combination of photo-generated electrons and holes in a redox reaction, the quantum efficiencies of most photocatalysts are low.⁵ Another challenge is that during the process of catalytic reaction, refractory intermediates are sometimes deposited, which hinders the adsorption of reactants on photocatalytically active sites.⁶

As is known, when the catalyst is irradiated by light, some light energy is converted into photo-generated electron-holes, and other light energy transfers into heat to increase the temperature of samples.⁷,⁸ The high temperature, that is, thermal energy, usually cannot be utilized for photocatalysts to produce photo-generated photons and holes for photocatalytic reactions. To make better use of solar energy, a feasible method is combining photocatalysis and low temperature thermal catalysis, which shows some advantages: photothermal catalysis can maximize the utilization of solar energy and thermal energy, and it has excellent durability for thermal catalytic oxidation with the low energy consumption of photocatalytic oxidation.⁹ Moreover, a synergic photothermal catalyst can generate hot carriers to take part in redox reactions or convert photon energy into heat to accelerate the reaction rate.¹⁰⁻¹² Although photothermal synergic

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catalysis is an effective strategy, reported photothermal catalysts are rare. ZnFe$_2$O$_4$ is a type of ferrite with a spinel structure and is also known as a soft magnetic material, an antibacterial agent and as a photocatalyst. It is cheap, non-toxic, environmentally friendly, and has high chemical stability. ZnFe$_2$O$_4$ has a narrow bandgap of about 1.9 eV, which means that it can utilize sunlight energy efficiently. Li et al. have prepared ZnFe$_2$O$_4$ nanotube arrays to degrade 4-chlorophenol in solution, with the photocatalytic degradation rate of 4-chlorophenol being 100%. Dhiman et al. studied the effects of different ZnFe$_2$O$_4$ nanostructures, with the results showing that nanorods have the best photocatalytic activity for dye degradation. Wu et al. successfully prepared well-organized porous hierarchical ZnFe$_2$O$_4$ nanostructures and studied their solar light-driven photocatalytic performance for methylene blue (MB) degradation. Oliveira et al. synthesized ZnFe$_2$O$_4$ photocatalysts by the combustion reaction in solution. ZnFe$_2$O$_4$ exhibited good photocatalytic response to the degradation of the dyes at 400 °C, and photoinduced electron-hole pairs can react directly with the dye as well as interact with O$_2$ and H$_2$O forming oxidizing radicals during the catalytic process.

Until now, many researchers have focused on the photocatalytic performance of ZnFe$_2$O$_4$; however, only a few reports have considered the photothermal catalytic properties of ZnFe$_2$O$_4$. It has been reported that oxygen vacancies can significantly improve the thermal catalytic performance of a catalyst, because oxygen vacancies can change the phase of the material (such as electrical conductivity and material energy band structure) and the surface (surface composition, molecular adsorption, etc.) properties, which increases the thermal catalytic performance greatly. Therefore, endowing ZnFe$_2$O$_4$ with thermal catalytic properties by introducing oxygen vacancies should improve the performance of catalyst when driven by solar light.

In this work, we demonstrate the synthesis of ZnFe$_2$O$_4$ and its performance in photothermal catalytic degradation of the gaseous organic pollutant isopropanol (IPA). A large specific surface area and oxygen-vacancy-rich ZnFe$_2$O$_4$ with photothermal catalytic performance has been obtained. Also, defective ZnFe$_2$O$_4$ exhibits a synergic improvement of the photothermal catalytic degradation of IPA. We believe this study will promote applications of ZnFe$_2$O$_4$ in air purification.

**Results and discussion**

**Thermogravimetry–differential scanning calorimetry analysis**

The conversion of precursors of ZnFe$_2$O$_4$ was investigated by thermogravimetry–differential scanning calorimetry (TG–DSC). As shown in Figure 1, from 23 °C to 200 °C, the rate of weight loss is about 11.15%, which is due to water release from the hybrid of organic and inorganic materials. From 200 °C to 400 °C, a rapid weight loss of up to 50.91% might be due to decomposition of the organic component of polyethylene glycol and the detachment of neutral water molecules existing in the crystal material lattice. An obvious and intense exothermic peak from 300 °C to 400 °C corresponds to the decomposition of the organic component of polyethylene glycol in the DSC curve. From 400 °C to 1000 °C, the weight loss rate is only 4.06%, indicating that the precursor had completely been converted into highly stable and crystalline ZnFe$_2$O$_4$. The optimum temperature for the synthesis of spinel ZnFe$_2$O$_4$ was 400 °C.

**X-ray diffraction analysis**

The obtained ZnFe$_2$O$_4$ powder samples were characterized by X-ray diffraction (XRD; Figure 2). All diffraction patterns could be indexed to cubic spinel ZnFe$_2$O$_4$ (JCPDS, No. 22-1012). When the calcination temperature reached 400 °C, no impurity appeared because a high calcination temperature is beneficial to the diffusion of ions and accelerates the growth of ZnFe$_2$O$_4$ crystals. According to Scherrer’s formula, calculated from the half-width of the (311) peak, the average crystal size is 18.3, 22.1, 51.2, and 85.3 nm for ZnFe$_2$O$_4$-400, ZnFe$_2$O$_4$-500, ZnFe$_2$O$_4$-600, and ZnFe$_2$O$_4$-700, respectively. A large average crystal size indicates that the crystals of ZnFe$_2$O$_4$ grow well and that less boundaries or defects exist.

**Scanning electron microscopy analysis**

The morphology of the sample was observed by scanning electron microscopy (SEM). As shown in Figure 3, ZnFe$_2$O$_4$-400 is an agglomeration of irregular particles. There are many pores between the particles. With an increase in calcination temperature, the grain size of the nanoparticles becomes larger, which is consistent with the results of XRD. When the calcination temperature exceeds 700 °C, the grains reach about 100 nm. Figure 4 shows the element mapping and confirms the existence of Zn, Fe, and O and they are well-dispersed in ZnFe$_2$O$_4$.

**X-ray photoelectron spectra analysis**

To study the chemical composition and element valence of ZnFe$_2$O$_4$, X-ray photoelectron spectra (XPS) analysis was performed. The survey spectra shown in Figure 5(a)
suggest ZnFe₂O₄ is mainly composed of Zn, Fe, and O elements. Figure 5(b) shows the O 1s spectrum which can be divided into three peaks located at 529.6, 530.3, and 531.56 eV, respectively. The peak at 529.6 eV corresponds to the lattice oxygen O²⁻ in ZnFe₂O₄, including Zn-O and Fe-O, and the peak at 530.3 eV is from oxygen vacancies. The peak at 531.56 eV is adsorbed oxygen from the water molecules. The formation mechanism of oxygen vacancies has been reported in several literatures. By using solution combustion synthesis with nitrate precursors, oxygen vacancy generation occurs because the reaction conditions result in oxygen being expelled from the reaction vessel. By comparing three peaks of oxygen element, we found that the oxygen vacancies are appreciable. In Figure 5(c), the Zn high-resolution XPS spectrum, the peaks at 1020.92 and 1043.9 eV can be assigned to Zn 2p3/2 and Zn 2p1/2, confirming the presence of Zn²⁺. From Figure 5(d), the peak at 724.8 eV can be assigned to Fe 2p 1/2, and the peak of Fe 2p 3/2 can be divided into two peaks at 711.17 and 713.7 eV, while those at 711.17 and 713.7 eV corresponding to the existence of Fe³⁺. Based on the above analyses, it can be seen that there are numerous oxygen vacancies existing on the surface of the obtained ZnFe₂O₄.

N₂ adsorption and desorption analysis

The specific surface areas and pore volumes of the ZnFe₂O₄ samples were studied. As shown in Figure 6, there is a hysteresis loop constructed by type-IV isotherms, implying that a porous structure exists. The pore size distribution is shown in the inset in Figure 6. All the samples present a wide pore size distribution, indicating that the pores are mainly formed by the agglomeration of nanoparticles. The specific surface areas of ZnFe₂O₄-400, ZnFe₂O₄-500, ZnFe₂O₄-600, and ZnFe₂O₄-700 are 56.4, 33.2, 14.4, and 8.2 m²g⁻¹, respectively. With an increase in calcination temperature, the specific surface area of samples decreased; this phenomenon is caused by crystal growth leading to a reduction of the porosity.

Ultraviolet-visible diffuse reflectance spectra and electron paramagnetic resonance analysis

The ultraviolet (UV)-visible diffuse reflectance spectra (DRS; Figure 7) show that the obtained ZnFe₂O₄ samples have a broad spectrum of light absorption until to 650 nm. With an increase in calcination temperature, the absorption...
Figure 4. Element mapping of ZnFe₂O₄-400.

Figure 5. (a) XPS survey spectra, and (b) O 1s, (c) Zn 2p, and (d) Fe 2p spectra of ZnFe₂O₄.
edge of ZnFe₂O₄ blueshifts due to a decrease in the number of oxygen vacancies. Furthermore, the oxygen vacancies are also determined from the electron paramagnetic resonance (EPR) spectra. EPR was carried out at ambient temperature to evaluate the defects in samples, and the EPR spectra are shown in Figure 8. According to the formula $g = \frac{\hbar}{\beta H}$, the EPR spectra show a single broad signal with a $g$ value of around 2.0076, indicating that there are unpaired electrons and oxygen vacancies in ZnFe₂O₄. The EPR signal intensity of ZnFe₂O₄-400 is higher than that of ZnFe₂O₄-600, indicating that ZnFe₂O₄-400 has more oxygen vacancies. A high calcination temperature leads to a reduced number of oxygen vacancies in ZnFe₂O₄, which is consistent with the UV-DRS results.

**Thermal and photothermal catalytic performance**

The catalytic performance under irradiation of Xe light was evaluated. As shown in Figure 9, the conversion rate increases with the time elapsed. After 120 min of the catalytic reaction, the conversion rates of IPA were 85.45%, 81.39%, 32.77%, and 4.98% for ZnFe₂O₄-400, ZnFe₂O₄-500, ZnFe₂O₄-600, and ZnFe₂O₄-700, respectively. Because the light irradiation not only generated electron-hole pairs and plenty of heat, under our experimental conditions, the temperature of the samples under 300 W Xe light irradiation can reach 140 °C. In order to investigate the influence of thermal energy on the catalytic performance, the thermal catalytic capacity of ZnFe₂O₄ was studied by placing the catalytic reactor in a 140 °C oven without light irradiation. To eliminate the possibility of IPA self-degradation, a blank experiment without ZnFe₂O₄ was carried out. No degradation of IPA occurred spontaneously at 140 °C, so, it is believed that the degradation of IPA occurs due to the catalyst. As shown in Figure 10, over a 120 min catalytic reaction, the conversion rate of IPA tends to saturation and are 30.45%, 26.67%, 22.34%, and 1.33% for ZnFe₂O₄-400, ZnFe₂O₄-500, ZnFe₂O₄-600, and ZnFe₂O₄-700, respectively. Compared with the thermal performance, the photothermal catalytic activity increases greatly, suggesting a synergistic enhancement of light and heat.

In both photothermal and thermal catalytic reactions, ZnFe₂O₄-400 exhibits the highest activity among all the samples, which are 23.42 and 17.16 times higher than ZnFe₂O₄-700, respectively, and the catalytic activities reduced on raising the calcination temperature. According to the specific surface area results, EPR studies, and UV-vis analysis, the higher calcination temperature can reduce the specific surface area and oxygen vacancy concentration. As is known, a large specific surface area can provide more active sites for catalytic reactions, and the surface oxygen vacancies also play a vital role in absorbing and activating O₂ during the degradation of gaseous organic chemicals.

**Thermal and photothermal catalytic mechanisms**

On the defective surface, the thermal catalytic oxidation of the IPA is believed to conform to the Langmuir–Hinshelwood
mechanism. The oxygen vacancies can act as the active sites for absorbing O$_2$ to form active oxygen species O$_2^-$ because the chemisorption energy is low on the sites of surface oxygen vacancies; the next step is the reaction of gaseous organic reactants with adsorbed reactive oxygen species. High concentrations of oxygen vacancies are beneficial for carrying out catalytic reaction. For the photothermal catalytic oxidation under light irradiation, due to the high temperature generated by light energy, a thermal catalytic reaction based on the mechanism would work. Meanwhile, ZnFe$_2$O$_4$ produces a large amount of photo-generated electrons and holes to initiate a photocatalytic reaction. The surface chemisorbed O$_2$ can capture electrons to produce superoxide (O$_2^-$) and/or peroxide (O$_2^2$) species (equation 1). Also, a small amount of O$_2^-$ can be further converted into ·OH through a series of transformations (equations 2 and 3) and can be activated into numerous oxidative species. When IPA adsors on the surface of ZnFe$_2$O$_4$, the active oxygen species then oxidize the adsorbed IPA to acetone (equation 4). Finally, the acetone and H$_2$O molecules are desorbed from the surface

$$\begin{align*}
    O_2 + e^- (ZnFe_2O_4) & \rightarrow O_2^- \\
    2 \cdot O_2^- + 2H_2O & \rightarrow 2OH^- + H_2O_2 + O_2 \\
    H_2O_2 + e^- & \rightarrow \cdot OH + OH^- \\
    \cdot O_2^- + \cdot OH + IPA & \rightarrow \text{acetone} + H_2O
\end{align*} \tag{1-4}$$

The role of oxygen vacancy in catalysis

Since ZnFe$_2$O$_4$ is a typical n-type semiconductor, the formation of oxygen vacancies causes the redistribution of excess electrons in its adjacent atoms, which is to produce an electron donor level below the ZnFe$_2$O$_4$ conduction band. The density functional theory (DFT) method was utilized to calculate the total density of states, observed from the DFT calculations.

$$\begin{align*}
    O_2 + e^- (ZnFe_2O_4) & \rightarrow O_2^- \\
    2 \cdot O_2^- + 2H_2O & \rightarrow 2OH^- + H_2O_2 + O_2 \\
    H_2O_2 + e^- & \rightarrow \cdot OH + OH^- \\
    \cdot O_2^- + \cdot OH + IPA & \rightarrow \text{acetone} + H_2O
\end{align*} \tag{1-4}$$

Conclusion

ZnFe$_2$O$_4$ with oxygen vacancies are obtained via a soft-chemistry method. The obtained ZnFe$_2$O$_4$ samples exhibit high performance in the photothermal catalytic degradation of the gaseous organic pollutant IPA. ZnFe$_2$O$_4$-400 has a larger specific surface area and numerous oxygen vacancies, which are the reasons for its high photothermal catalytic performance. It combines the advantages of photocatalysis and thermal catalysis. In the process of photothermal catalytic degradation, oxygen vacancies on the surface of ZnFe$_2$O$_4$ facilitate the reaction being carried out as well as electron and hole separation. This study shows ZnFe$_2$O$_4$ is a potential material for organic matter degradation.

Experimental details

The synthesis of ZnFe$_2$O$_4$ powder

Ferric nitrate nonahydrate (4.03 g) and zinc acetate dihydrate (1.1 g) were dissolved in deionized water (100 mL) and stirred for 0.5 h. The resulting solution was treated with polyethylene glycol (2 g) and stirred for another 0.5
The solution was placed in an oven at 120 °C for 24 h. Finally, the obtained dry gel was calcined at 400 °C, 500 °C, 600 °C, and 700 °C for 2 h each with a heating rate of 3 °C/min in a muffle furnace. According to the different calcination temperatures, the obtained samples were named ZnFe$_2$O$_4$-400, ZnFe$_2$O$_4$-500, ZnFe$_2$O$_4$-600, and ZnFe$_2$O$_4$-700.

**Characterization**

X-ray diffraction (XRD) patterns of the powders were recorded at room temperature using a Bruker D8 Advance X-ray diffractometer. A scanning electron microscope (SEM) was used to characterize the morphology of the obtained products (S4800, Hitachi). EPR spectroscopy was accomplished using a CW-EPR Bruker EIXSYS spectrometer. The UV-vis diffuse reflection spectra were obtained for dry-pressed disk samples using a Scan UV-vis spectrophotometer (UV-vis DRS UV-2450, Shimadzu). N$_2$ adsorption was measured at 77 K on an Autosorb-1 (Quantachrome Instruments). Thermogravimetry-differential scanning calorimetry (TG-DSC) was carried out (Netzsch STA449) in a flow of air (20 mL/min) at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos XSAM 800 X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos XSAM 800 X-ray photoelectron spectroscopy equipped with Mg-Kα radiation source operated at 200 W and all the binding energies were calibrated as the (C 1s) peak at 284.6 eV.

**Theoretical calculation**

The electronic structure of the material was calculated by using the Vienna ab initio Simulation Package (VASP). ZnFe$_2$O$_4$ was calculated based on DFT. The projector-augmented wave method (PAW) was used in the calculations. The exchange-correlation energy used the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) functional. The plane wave cutoff was set to 600 eV, and the Gaussian smearing width was limited to 0.05 eV. The 5.0 $\times$ 5.0 $\times$ 5.0 Monkhorst–Pack scheme was used for sampling of the Brillouin zone. ZnFe$_2$O$_4$ nanostructures were optimized until the Hellmann–Feynman forces were less than 0.01 eV/Å and the energy cutoff was converged within 1.0 $\times$ 10$^{-5}$ eV. Spin polarization was applied in the calculations.

**Data availability statements**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Declaration of conflicting interests**

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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