Salt-assisted solution combustion synthesis of ZnFe$_2$O$_4$ nanoparticles and photocatalytic activity with TiO$_2$ (P25) as nanocomposite

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Well-dispersed zinc ferrite (ZnFe$_2$O$_4$) nanoparticles were successfully prepared by a novel salt-assisted solution combustion process. The effects of types and amounts of the added salt on the properties of the products were investigated by XRD, SEM, and BET nitrogen adsorption techniques. The results indicated that the introduction of salt into reaction system facilitate the formation of well-dispersed spinel zinc ferrite and increase specific surface area of the resultant from 7.14 to 88.34 m$^2$·g$^{-1}$ when KCl/M ratio is 2/3. A visible-light-active ZnFe$_2$O$_4$/TiO$_2$ photocatalyst was prepared by physically grinding the ZnFe$_2$O$_4$ nanoparticles with TiO$_2$ (P25) at ambient temperature, and it exhibited excellent photocatalytic activity for the mineralization of rhodamine B. With increasing of ZnFe$_2$O$_4$ amount from 0 to 3 wt%, the activity of ZnFe$_2$O$_4$/TiO$_2$ composite increased. The maximum photocactivity is observed when the amount of ZnFe$_2$O$_4$ is 3 wt% and more than 97% of rhodamine B disappears after 4 h visible-light irradiation.

Key-words : Salt-assisted solution combustion synthesis, ZnFe$_2$O$_4$, Nanoparticles, Photocatalytic activity

1. Introduction

Spinel-structured ferrite and related compounds have been one of the most attractive and interesting mixed oxides due to their innovative use in advanced technologies. These oxides have been used as functional material in many fields due to their unique physicochemical properties. As an important member of spinel-structured ferrite family, ZnFe$_2$O$_4$ has been intensively investigated owing to its fascinating magnetic and electromagnetic properties, and their potential applications in various fields, such as magnetic applications,1) anode materials for lithium ion batteries,2) gas sensors,3) semiconductor photocatalysts,4) and absorbent materials.5)

With the increasingly serious environmental pollution, photocatalysis is considered as a promising method for solving environment problems, especially for the removal of organic contaminants with sunlight. TiO$_2$ powder is currently believed to be the most promising known semiconductor material. However, titania is a wide band gap semiconductor and can only absorb about 5% of sunlight in the ultraviolet region. ZnFe$_2$O$_4$ is a narrow band gap semiconductor (1.9 eV) that has a potential application in the conversion of visible light.6) However, ZnFe$_2$O$_4$ cannot be used directly in the photocatalytic degradation of organic pollutants due to the lower valence band potential and poor property in photoelectric conversion.7) TiO$_2$ shows relatively high reactivity and chemical stability under ultraviolet light, while zinc ferrite is sensitive to visible light. So the coupling of these two semiconductors may become a new type of composite having high utility of sunlight and high photocatalytic activity.

Up to now, various approaches have been applied to fabricate ZnFe$_2$O$_4$, such as coprecipitation, sol-gel, hydrothermal and solvothermal method, thermal decomposition, microwave irradiation, combustion method.8)–11) Among the various routes, solution combustion synthesis has been regarded as one of effective and economic approaches owing to its convenient processing, simple experimental setup, significant saving in time and energy, and homogeneous products.12) Solution combustion synthesis is based on the intense redox reaction between oxidant—the desired metal nitrates and reductant—various organic compounds with nitrogen content, which releases large amount of heat in an instant and results in a drastic temperature increase of the reaction system, yielding the product with specific phase and morphology.13) Many attempts have been made to investigate the influence of synthesis condition upon the combustion process, like the type of fuel,14) the influence of fuel-to-oxidant ratio,15) the role of pH16) and the effect of various aids, and to optimize the preparation conditions.17) However, conventional solution combustion synthesis of well-dispersed nanocrystalline oxide particles faces two difficulties of inhibiting particulate agglomeration and promoting phase formation.18)

In this paper, we develop a salt-assisted solution combustion synthesis (SSCS) to prepare ZnFe$_2$O$_4$ nanoparticles and found that the types and amounts of the added salt have obvious effects on the formation of the desired phase.

2. Experimental section

2.1 Preparation of ZnFe$_2$O$_4$ nanoparticles

All reagents were of analytical grade and used without further purification. In a typical synthesis, initially, 1.25 mmol of Zn(NO$_3$)$_2$·6H$_2$O and 2.5 mmol of Fe(NO$_3$)$_3$·9H$_2$O (with molar ratio of Zn/Fe = 1:2.) were dissolved in 25 ml aqueous solution of L-$\,$-$\,$-$\,$-alanine (Ala, C$_3$H$_7$NO$_2$) under magnetic stirring. The molar ratio of Ala/NO$_3$$^-1$ is 1/6. Secondly, salt was added to the above solution. The resultant solution was transferred into a ceramic crucible and then placed in a muffle furnace at 573 K. The solution bubbled up and auto-ignited with the rapid evolution of a
large volume of gases. In order to remove salt, the as-synthesized powder was boiled in deionized water, filtered and washed with deionized water and ethanol. Finally, the product was dried in an oven at 353 K for 2 h. For comparison, ZnFe₂O₄ nanoparticles were prepared by the conventional combustion synthesis.

### 2.2 Characterization

The crystalline phases of the samples were identified by X-ray diffraction (XRD, Siemens D-5000) with a graphite monochromator and Cu Kα1 radiation (λ = 0.15405 nm) irradiation. The crystallite size was determined based on the XRD patterns using the Sherrer’s equation: 

\[
D = \frac{0.9\lambda}{B\cos \theta}
\]

The morphologies were observed with a scanning electron microscope (SEM, JEOL JSM-6330F, Japan). The specific surface areas of the samples were measured by using N₂ adsorption at 77K (Tristar 3000). The diffuse reflectance UV–vis (DR-UV–vis) spectra of the samples were recorded using a varian (Cary 5000) spectrophotometer equipped with an integrating sphere accessory. Barium sulphate was used as reference for the reflectance spectra.

### 2.3 Photocatalytic activity measurement

The photocatalytic activity was evaluated by the photodegradation of rhodamine B (RhB) in aqueous solution. A 175 W metal halide lamp was used as the light source, which emits both UV and visible-light over a wide wavelength. To limit the irradiation wavelength, the light beam was passed through a filter to cutoff wavelengths shorter than 400 nm. The initial concentration of RhB in a quartz reaction vessel was fixed at 10 mg/L and the photocatalyst loading was 1 g/L. The nanocomposite photocatalyst ZnFe₂O₄/P25 was prepared by physical grinding of the respective powders in a mortar for less than 30 min. Prior to illumination, the suspension was magnetically stirred in the dark for 30 min to establish the adsorption–desorption equilibrium at room temperature. During irradiation, stirring was maintained to keep the mixture in suspension. At regular intervals, samples were taken from the suspension. The liquid was analyzed by UV–visible spectrophotometer (TU1801, PGENERAL) after the solid photocatalyst were removed by centrifuge.

### 3. Results and discussion

#### 3.1 XRD and BET analyses of ZnFe₂O₄ nanoparticles

According to the principle of propellant chemistry, it is assumed that in the case of alanine-nitrate combustion, primarily N₂, CO₂, and H₂O are evolved as the gaseous products, the salt-assisted redox combustion reaction can be expressed as follows:

\[
\text{Zn(NO₃)₂ · 6H₂O + 2Fe(NO₃)₃ · 9H₂O} + \psi\text{C₃H₇NO₂ + nSalt} = \text{ZnFe₂O₄ + (4 + \psi/2)N₂ + 3ψCO₂} + (24 + 7ψ/2)H₂O + nSalt
\]

The stoichiometric fuel-to-oxidizer ratio (Ala/NO₃⁻)= 1/3. In our experiment, the molar ratio of Ala/NO₃⁻ used is 1/6 (fuel-lean condition).

**Figure 1** shows the XRD patterns of ZnFe₂O₄ prepared by SSSCS as a function of the amount of KCl. It can be seen that when the Ala/NO₃⁻ is 1/6, in the absence of salt, all the reflections agree well with those of pure cubic phase of zinc ferrite according to the reported data (JCPDS Card No. 79-1150), where the diffraction peaks at 2θ values of 30.1, 35.2, 42.8, 52.9, 56.5, and 67.8° can be ascribed to the reflection of (220), (311), (400), (422), (511), and (440) planes of the spinel ZnFe₂O₄, respectively. It is very significant that the introduction of KCl in the solution combustion synthesis results in a drastic decrease of diffraction peak intensity. With increasing the value of KCl/M ratio from 0 to 1, the ZnFe₂O₄ crystalline phase is evident, while the diffraction peaks gradually widen and weaken. This can be attributed to temperature decrease in reaction system due to the increasing KCl addition. However, further increasing KCl/M leads to a mixture of amorphous phase and formation of impurity phase [Fig. 1(g)]. When KCl/M and ZnFe₂O₄ phase, a limit, the auto-propagating combustion reaction cannot occur.

Introduction of NaCl in the solution combustion synthesis, the XRD patterns of the samples are depicted in **Fig. 2**. It can be seen that variation of diffraction peaks is similar to the case of KCl. It is apparent that increasing NaCl/M from 0 to 1 results in a drastic decrease in the crystalline ratio. However, introduction of CuCl₂ in the CSCS process, the prepared samples are dominantly amorphous phase.

The influences of different salts on the characteristics of ZnFe₂O₄ samples prepared via the SSSCS process are summarized in **Table 1**.
The CSCS process can obtain the ZnFe$_2$O$_4$ nanopowders with higher investigation, the introduction of the equal molar KCl into the temperature which assists crystal growth. Among the salts chosen for crystalline size could be attributed to a decrease in surface area than the introduction of the equal molar NaCl produces. Table 1 shows that the different salts in the SSCS process have a distinct influence on such characteristics of ZnFe$_2$O$_4$ as surface area and crystallite size, which may be dependent on the diverse properties of salts such as solubility, melting point, heat capacity, et al.\textsuperscript{22})

Thermal stability of ZnFe$_2$O$_4$ prepared by KCl-assisted combustion synthesis was investigated and Table 1 presents the crystallite sizes and BET surface areas of samples calcined at different temperatures for 2 h. It can be seen that both heat treatment and higher calcination temperature promote the formation of spinel structure and accelerate the growth of crystallite size. After calcined at 973 K for 2 h, the sample prepared by KCl-assisted combustion synthesis retained a high surface area of 24.76 m$^2$/g, while as-synthesized ZnFe$_2$O$_4$ without salt-assisted only had a surface area of 7.14 m$^2$/g.

**3.2 SEM of ZnFe$_2$O$_4$ nanoparticles**

The morphology of the prepared samples was determined by SEM and is shown in Fig. 3. These images reveal remarkable changes in microstructures, regarding grain size, porosity and particle distribution by changing KCl/M ratio. Figure 3 reveals that the typical morphology of the particles obtained in the solution combustion synthesis, foamy agglomerated particles with a wide distribution and presence of large voids in its structure. The formation of these features is attributed to the large volume of gas evolved during combustion. In contrast, the introduction of salt (KCl, NaCl) into the redox mixture solution breaks up the ZnFe$_2$O$_4$ agglomerates and leads to a great improvement in dispersing state and an obvious reduction in particle size.

**3.3 UV–vis diffuse reflection spectra of ZnFe$_2$O$_4$ nanoparticles and ZnFe$_2$O$_4$/TiO$_2$ nanocomposite**

Figure 4 shows the diffuse reflection spectra of TiO$_2$, ZnFe$_2$O$_4$/TiO$_2$ and ZnFe$_2$O$_4$ prepared by SSCS (KCl/M = 2/3). It can be seen that the TiO$_2$ [Fig. 4(a)] presents a strong reflectance in visible region, while single ZnFe$_2$O$_4$ nanoparticles [Fig. 4(f)] exhibit a weak reflectance for visible light. The reflectance curves of ZnFe$_2$O$_4$/TiO$_2$ nanocomposites are between those of pure TiO$_2$ and pure ZnFe$_2$O$_4$ and display reflectance characteristics of the component P25 in UV region and ZnFe$_2$O$_4$ in visible region. The increase of ZnFe$_2$O$_4$ amount results in a dramatic decrease of the reflectance in the visible range of 400–700 nm, which proves that, upon addition of ZnFe$_2$O$_4$ nanoparticles to TiO$_2$, the absorption of the composite powders in the visible spectrum range increases significantly in comparison with that of the undoped TiO$_2$. The obvious large red shift of the nanocomposites is considered to be due to the mixing effect of band gaps and the interface effect of ZnFe$_2$O$_4$/TiO$_2$ composite.\textsuperscript{23)}

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### Table 1. Effect of salt type and salt/M ratio on the properties of ZnFe$_2$O$_4$ prepared at Ala/NO$_3^-$ = 1/6

<table>
<thead>
<tr>
<th>Salt</th>
<th>Molar ratio</th>
<th>Annealed temperature (K)</th>
<th>BET surface area (m$^2$/g)</th>
<th>Crystallite size (nm)</th>
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<tr>
<td>KCl</td>
<td>0</td>
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<td>7.14</td>
<td>23.5</td>
</tr>
<tr>
<td>KCl</td>
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<td>—</td>
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<td>—</td>
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<td>9.7</td>
</tr>
<tr>
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<td>—</td>
<td>88.34</td>
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</tr>
<tr>
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<td>—</td>
<td>48.65</td>
<td>13.4</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
<td>NaCl</td>
<td>3/3</td>
<td>1273</td>
<td>7.48</td>
<td>30.5</td>
</tr>
</tbody>
</table>

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Fig. 3. SEM photographs of as-synthesized powders with various KCl/M ratios: (a) KCl/M = 0, (b) KCl/M = 1/3, (c) KCl/M = 1/2, (d) KCl/M = 2/3.

Fig. 4. UV–vis diffuse reflection spectra of ZnFe$_2$O$_4$–TiO$_2$ photocatalysts: (a) TiO$_2$, (b) 1.5% ZnFe$_2$O$_4$–TiO$_2$, (c) 3% ZnFe$_2$O$_4$–TiO$_2$, (d) 6% ZnFe$_2$O$_4$–TiO$_2$, (e) 10% ZnFe$_2$O$_4$–TiO$_2$, (f) ZnFe$_2$O$_4$. 

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3.4 Photocatalytic activity

To reveal the effect of the ZnFe$_2$O$_4$ nanoparticles on the photocatalytic properties of titania, photocatalytic degradation of rhodamine B solution under visible light irradiation ($\lambda > 400$ nm) was examined with pure TiO$_2$, ZnFe$_2$O$_4$, and ZnFe$_2$O$_4$/TiO$_2$ composite. As shown in Fig. 5, RhB is hardly degraded in the absence of photocatalysts. Curve g shows that ZnFe$_2$O$_4$ has a little photocatalytic activity under visible light irradiation, despite single ZnFe$_2$O$_4$ having a good absorption of visible light. The degradation of rhodamine B on pure TiO$_2$ under visible light irradiation is attributed to the photobleaching process, in which dye molecule acting as photosensitizer. It is apparent that the introduction of ZnFe$_2$O$_4$ can surely promote the photocatalytic activity of P25 under visible light irradiation. With increasing of ZnFe$_2$O$_4$ amount from 0 to 3\%, the activity of ZnFe$_2$O$_4$/TiO$_2$ composite increased. The maximum photocactivity is observed when the amount of ZnFe$_2$O$_4$ is 3\% and more than 97\% of rhodamine B disappears after 4 h visible-light irradiation. This may be the reason that a coupled semiconductor system is formed between ZnFe$_2$O$_4$ and TiO$_2$, as the visible light-absorbing semiconductor part having a relatively narrow band gap (1.9 eV) and titanium oxide, as the wide band gap portion.

It is agreed upon that the initial concentration of organic pollutants on the photodegradation rate can be described well by Langmuir–Hinshewood kinetic model, which has been widely used in liquid- and gas-phase photocatalysis.\(^{20,27}\)

$$\frac{dC}{dt} = \frac{kKC}{1 + KC}$$

At diluted substrate concentrations, Eq. (1) can be simplified as follow: $r = \frac{dC}{dt} = k_{app}C$. In the integrated form of: $k_{app}t = \ln C_0/C$, where $C_0$ is the initial concentration of RhB solution, $k_{app}$ represents apparent rate constant. Thus, the apparent rate constants of catalysts with various ZnFe$_2$O$_4$ contents were calculated and shown in Fig. 6. It can be seen that the photocactivity of catalysts was remarkably enhanced by the introduction of ZnFe$_2$O$_4$. The apparent rate constant $k$ for 3\% ZnFe$_2$O$_4$/TiO$_2$ composition is 0.910 h$^{-1}$, a value much higher than that of the pure P25 (0.254 h$^{-1}$), and the higher or lower amount of ZnFe$_2$O$_4$ results in diminishing the $k$ value of ZnFe$_2$O$_4$/TiO$_2$ composition.

4. Conclusions

Well-dispersed zinc ferrite (ZnFe$_2$O$_4$) nanoparticles were successfully prepared via the facile introduction of salt in the solution combustion synthesis. It was found that the instant salt precipitation in situ inhibits the formation of hard agglomerates and results in drastic increase in surface area. The largest specific BET surface area of zinc ferrite nanoparticles by SSCS is 88.34 m$^2$/g. A visible-light-active ZnFe$_2$O$_4$/TiO$_2$ photocatalyst can be prepared by grinding ZnFe$_2$O$_4$ nanoparticles and TiO$_2$ (P25) in a mortar without any surface modification or high-energy milling. The photocatalytic experiment for the degradation of RhB indicates that the highest activity under visible light irradiation, when the amount of ZnFe$_2$O$_4$ is 3 wt\%.

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References