ZnWO4 nanoparticle photocatalyst has been prepared by annealing treatment of hydrothermal sample, and the high photocatalytic activity was explored. The crystalline of ZnWO4 photocatalysts were improved as the increase of annealing temperature and time. It was found that ZnWO4 nanoparticle catalysts exhibited a high photocatalytic activity, not only in the decomposition of formaldehyde in gaseous, but also in the degradation of RhB in water. The highest photocatalytic activity both appeared at 450 °C for 1 h due to good crystallization and high surface area. The photocatalytic activity of ZnWO4 was a little higher than that of P-25 (Degussa) in gaseous and lower than that of P-25 (Degussa) in aqueous. The main reason is that the dispersion of ZnWO4 powders in aqueous is not good due to its high density. The surface area, crystal size, dispersion and crystalline are important factors, which influence the photocatalytic activities of ZnWO4 catalysts.

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Keywords: ZnWO4; Photocatalytic activity; Dispersion; Annealing

1. Introduction

A great deal of effort has been devoted in recent years to developing heterogeneous photocatalysts with high activities for environmental applications such as air purification, water disinfection, hazardous waste remediation, and water purification [1–3]. The research of various oxide semiconductor photocatalysts are mainly based on Ti [4–6], Nb [7], Ta [2,8–9], and In [10]. It has also been reported that, for compounds consisting of sixth group element, some polytungstates are homogenous photocatalysts for H2 evolution from an aqueous solution containing an electron donor [11]. However, there are only a few reports about W-based heterogeneous photocatalysts, Na2W12O41 [12], Bi2W2O9 [12], (NaBi)0.5WO4 [13], AgInW2O8 [14], Bi2WO6 [15], besides WO3 [16]. These W-based photocatalysts can produce not only H2 but also O2 from an aqueous solution containing sacrificial reagents. Recently, we also have reported that the Bi2WO6 is a good photocatalyst for photodegradation of organic compounds under visible light irradiation [17,18]. These results suggest the possibilities that some W-based photocatalysts with the activity for environmental applications may be developed.

ZnWO4 is one of the families of metal tungstates that have a high application potential in various fields, such as photoluminescence, microwave applications, optical fibers, scintillator materials, humidity sensors, magnetic properties, and catalysis [19]. Its unique combination of physical and chemical properties, in terms of molecular and electronic versatility, reactivity, and stability, make us have reason to consider it may be a promising candidate for the photo-degradation of chemical contaminants.

In the past decade, nanosized ZnWO4 has been prepared by several different processes such as Czochralski method, sintering of WO3 and ZnO or ZnCO3 powders, and synthesis by the polymerized complex method and hydrothermal reaction over extensive period [19–21]. According to up-to-date literature, ZnWO4 powder photocatalyst was prepared by a simple hydrothermal method at 180 °C for 2 h, and then annealed at different temperatures and times. In this work, the crystallization process and optical properties of ZnWO4 have been investigated. Furthermore, the effects of physical properties, such as surface area, crystallinity and dispersion, on the photocatalytic activity of ZnWO4 were discussed in detail firstly.
2. Experimental

2.1. Synthesis

ZnWO₄ nanoparticles were synthesized through combining hydrothermal process and annealing treatment. All chemicals used were analytic grade reagents without further purification. Ten millimoles of Zn(NO₃)₂·6H₂O and equal molar Na₂WO₄·2H₂O were put into a beaker. Then, 30 mL of distilled water was added to the beaker and magnetically stirred to form a homogeneous solution at room temperature. The resulting precursor suspension was transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 2h, without shaking or stirring, then allowed to cool naturally to room temperature. The products were filtered off, washed several times with distilled water, and dried at 100 °C for 4h, subsequently, different fractions were annealed for 1h at 400, 450, 500, and 550 °C, or annealed at 450 °C for 0.5, 1, 2, 4, and 8h, respectively.

2.2. Characterization

The products were characterized by characterized by powder X-ray diffraction (XRD) on Bruker D8-advance X-ray diffractometer at 40 kV and 40 mA for monochromatized Cu Kα (λ = 1.5418 Å) radiation. Morphologies and structures of the prepared samples were further examined with transmission electron microscopy (TEM) by a JEM 1010 electron microscope operated at an accelerating voltage of 100kV. BET surface area was determined by ASAP 2010 V5.02H. The absorbed gas was nitrogen. UV–vis diffuse reflectance spectrums (DRS) of the samples were measured by using Hitachi U-3010 UV–vis spectrophotometer. The photoluminescence emission spectra (PL) of ZnWO₄ powders were performed on Perkin-Elmer LS55 luminescence spectrometer.

2.3. Photocatalytic test

Photocatalytic activities of ZnWO₄ nanoparticles were evaluated by degradation of rhodamine-B (RhB) and gaseous formaldehyde under ultraviolet light irradiation of 11 W low-pressure lamp with 254 nm, respectively. The average light intensity was 1.5 mW/cm². The radiant flux was measured with a power meter from Institute of Electric Light Source (Beijing). RhB solutions (200 mL, 10⁻⁵ mol L⁻¹) containing 0.1 g of ZnWO₄ nanoparticles were put in a glass beaker. Before the light was turned on, the solution was first ultrasonicated for 10 min, and then stirred for 10 min to ensure equilibrium between the catalyst. Three milliliters of sample solution were taken at given time intervals and separated through centrifugation (4000 rpm, 10 min). The supernatants were analyzed by recording variations of the absorption band maximum (553 nm) in the UV–vis spectra of RhB using a U-3010 spectrophotometer (Hitachi).

The photocatalytic activity experiments on ZnWO₄ powders for oxidation decomposition of formaldehyde in air were performed at ambient temperature using a sealed reactor. The photo-reactor used was a 250 mL cylindrical quartz vessel, which consisted of an inlet, an outlet and a sample port. The photocatalysts were prepared by coating an aqueous suspension of ZnWO₄ powders onto a 2 m stainless-steel column (GDX-403) at 100 °C.

The photocatalytic activity of the samples can be quantitatively by comparing the removal efficiency of formaldehyde (R (%)). R (%) was calculated according to the following equation [22]:

\[ R(\%) = \frac{[\text{gas}]_0 - [\text{gas}]_f}{[\text{gas}]_0} \times 100\% \]  

where \([\text{gas}]_0\) and \([\text{gas}]_f\) represent the initial equilibrium concentration and reaction concentration of formaldehyde, respectively.

3. Results and discussion

3.1. Control of crystalline and size

The crystalline structures of synthesized samples were characterized by XRD. Figs. 1 and 2 showed the influence of the annealing temperature and time on crystalline of ZnWO₄ photocatalysts, respectively. In Fig. 1, with increasing of temperature, the XRD patterns became perfect and the intensities increased...
The effects of annealing temperature (1 h) on crystal size and BET surface area

Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>19.57</td>
<td>19.98</td>
<td>24.83</td>
<td>27.43</td>
</tr>
<tr>
<td>Crystal size (nm)</td>
<td>20.55</td>
<td>24.83</td>
<td>25.38</td>
<td>32.36</td>
</tr>
<tr>
<td>BET surface areas (m²/g)</td>
<td>23.63</td>
<td>22.08</td>
<td>20.05</td>
<td>17.88</td>
</tr>
</tbody>
</table>

can be seen from Table 1 that the crystal size of ZnWO₄ powders increases from 19.57 to 46.83 nm as the annealing temperature increases from 400 to 550°C. In Table 2, the crystal sizes of ZnWO₄ increase from 20.55 to 32.90 nm with extension of annealing time. However, comparison between the temperature series and time series shows that such a tendency is apparently affected by annealing temperature.

BET surface areas are also shown in Tables 1 and 2. With the increase of annealing temperature and extension of annealing time, the surface area of ZnWO₄ powder decreases. From Table 1, the surface areas of ZnWO₄ powders decrease from 44.71 to 3.5 m²/g as the annealing temperature increases, which demonstrates that a decrease of surface area with annealing temperature is mainly due to the growth of crystal size of ZnWO₄ powders. It also can be found that the influence of annealing time on surface area is in Table 2. When annealing time was prolonged, the surface area of ZnWO₄ changed little, indicating that the annealing time had less effect on the surface area of ZnWO₄ powders.

In this work, homogeneous morphology ZnWO₄ nanoparticles were synthesized, on the scale of 20–100 nm. TEM micrographs of ZnWO₄ nanoparticles are shown in Figs. 3 and 4. These micrographs demonstrate that the size of primary particles of the samples is quite uniform and in accord with the results obtained by means of the Scherrer equation. Fig. 3 shows the morphology and grain size of ZnWO₄ varied with the change of temperature. When the temperature became higher, the morphology of ZnWO₄ is homogeneous and the grain sizes of ZnWO₄ grow larger. A certain amount of amorphous phase in this powder was shown in the precursor, which was proved in Fig. 3(a). The grain sizes are small (about 20–30 nm), when the annealing temperature was below 500°C. However, when the annealing temperature increased to 550°C, the particles grow up to 100–200 nm, of which crystallinity looks to become better, being consistent with sharpening of diffraction lines of X-rays in Fig. 1. However, the grain sizes of the sample were much larger compared with the crystal sizes of the same sample (Table 1). These results illuminate that some particles interconnected with each other and interfused to the bigger particles.

Fig. 4 revealed the influence of the annealing time on the grain size of ZnWO₄. It is shown that the grain sizes are in the range of 20–30 nm. The grain sizes of the powders become a little larger when annealing time was prolonged. But the changes are not conspicuous. These figures suggest that annealing temperature take a much more important role than annealing time on the grain size of ZnWO₄. These results are similar to the influence of temperature and time on the crystallization process,
crystal size and surface areas of ZnWO₄ particles (Figs. 1 and 2, Tables 1 and 2).

3.2. Optical properties

Annealing treatment obviously affects light absorption characteristics of ZnWO₄ shown in Fig. 5. All optical absorption spectra shapes of the nanoparticles were almost the same. ZnWO₄ presented the optical absorption threshold at 380 nm that correspond to the band gap energy of 3.26 eV. The absorption spectra of the annealing ZnWO₄ samples show a lower intensity in the UV–vis range, which was due to the decrease of the absorption of the defect. That is to say, annealing treatment improve the crystalline defect. The as-prepared ZnWO₄ shows three transition bands at 305, 260 and 220 nm that correspond to the transition energy of 4.06, 4.76 and 5.63 eV, respectively. According to the research of Nedilko and Hizhnyi [23], these transitions can be identified in the tungstate group.

For a crystalline semiconductor, it was shown that the optical absorption near the band edge follows the equation: [24]

\[ a = A \left( \frac{h\nu - E_g}{h\nu} \right)^{n/2} \]

where \( a \), \( \nu \), \( E_g \), and \( A \) are absorption coefficient, light frequency, band gap, and a constant, respectively. Among them, \( n \) decides the characteristics of the transition in a semiconductor. By using this equation, the values of \( n \) for ZnWO₄ was 1, this means that the optical transition for ZnWO₄ is directly allowed. For W-based semiconductors, it was already found that excitons are formed due to the transitions into the tungstate W₅d states hybridized with O₂p and possess a very strong tendency for self-trapping [25]. Free electrons and holes can be created due to the transitions into cationic states. An active photocatalyst for the decomposition of the organic compounds must have a VB with strong oxidizing ability and photogenerated holes with high mobility. The hybridized VB of ZnWO₄ has shown strong ability to photocatalytic degradation of the organic pollutants in the work described herein. Therefore, the photocatalyst with a strong oxidizing potential could be expected.

The optical properties of these nanoparticles are being studied. The photoluminescence (PL) emission and excitation spectra of the samples were shown in Fig. 6(a) and (b). It can be clearly seen that ZnWO₄ powder obtained at 500 °C for 1 h, display a strong blue emission peak centered at about 460 nm at room temperature (Fig. 6(a)). Within the range of temperature at 400–500 °C, the position of the emission peaks of the product remained almost unchanged. The absolute luminescence intensity increased with increasing annealing temperature, implying the larger grains had a much improved luminescence intensity. The very weak PL intensity of the precursor is due to the fact that the product contained poor crystalline ZnWO₄ nanoparticles.

ZnWO₄ nanoparticles exhibited a blue emission band in the range of 400–540 nm, centered around 460 nm when excited 285 nm, which agrees well with previously reported for bulk
ZnWO$_4$ in the literature [26]. The spectral characteristics of ZnWO$_4$ were also very similar to those of the other scheelite tungstate crystals (MWO$_4$, M = Pb, Ca, Ba) [27]. The emission band shape might be explained by charge transfer transitions between the O$_{2p}$ orbital and empty orbits of the central W$_{6d}$ ions in the [WO$_6^{2-}$] complex [28]. The strong luminescence intensity indicates the good crystallinity, since the optical property of the ZnWO$_4$ powders is comparable with that of the previously reported ZnWO$_4$ [29] thin films that were annealed at high temperature.

### 3.3. Photocatalytic activity

The formaldehyde and Rhodamine-B degradation over these photocatalysts under UV light irradiation was investigated. Figs. 7–9 show the results of formaldehyde and Rhodamine-B degradation in the presence of representative samples obtained according to various annealing temperatures and times, respectively.

Fig. 7 represents the photocatalytic decomposition of formaldehyde over ZnWO$_4$ obtained at different annealing temperatures and times. The results in Fig. 7(a) demonstrated that the photocatalytic activity is strongly dependent on the annealing temperature. It can be seen that precursor shows weak photocatalytic activity with formaldehyde removal efficiency of 60%. This may be due to the fact that, although ZnWO$_4$ powder precursor has a smaller particle size and larger surface area, it shows a low crystallization. With an increase of annealing temperature, the photocatalytic activity of ZnWO$_4$ increased due to the enhancement of ZnWO$_4$ crystallization. At 450 °C, the photocatalyst reaches the highest photocatalytic activity with
formaldehyde removal efficiency of 95.2% in 25 min. However, with further increasing annealing temperature, the formaldehyde removal efficiency decreases from 95.2 to 76.8%. Those annealing above 450 °C have lower photocatalytic activities because of the decreased surface area and the increased crystallite size. Namely, the larger the particle and grain size grow, the longer distance the electron–hole pairs have to migrate. Moreover, for the decomposition of gas-phase compounds, the absorption of gas molecules on to the photocatalyst surface will be a major rate-determining step, which is due to the surface area. On the other hand, the decomposition of organic molecules, which have already been absorbed on the surface, is not a critical step. The major factor here is the decomposition of the absorbed organic molecules, which is due to crystallinity. Thus, the photocatalytic activity reaches a maximum at annealing temperature of 450 °C.

Ohtani et al. [30] have proposed a model of the photocatalytic mechanism. In their model, a high activity of photocatalyst should satisfy two requirements: large surface area for absorbing substrates and high crystallinity to reduce photo-excited electron–hole recombination rate. In general, the crystallinity
increases with annealing temperature while surface area does decrease. When ZnWO₄ powders are annealed at low temperature, a certain amount of amorphous ZnWO₄ still exists and acts as a site of photo-excited electron–hole recombination, which is adverse to the photocatalytic activity of ZnWO₄. Annealing can increase the crystallization of ZnWO₄, which means that the content of amorphous ZnWO₄ decrease and the photo-excited electron–hole recombination depress; and thus, the photocatalytic activity of ZnWO₄ increase. Therefore, annealing exhibits an advantageous effect to the photocatalytic activity of ZnWO₄ at low temperature. Although ZnWO₄ powders annealed at high temperature have well crystallinity, their surface areas are low. This explains why the photocatalytic activity of ZnWO₄ powders reaches a maximum at 450 °C in this study.

Fig. 7(b) shows the relationship of between the annealing time and photocatalytic activity. According to the trend of curve change, it is found that the photocatalytic activity is slightly dependent on the annealing time. With extension of annealing time, the photocatalytic activity of ZnWO₄ nanoparticles increases, reaches a maximum at 1 h, and then decreases when annealing time exceeds 1 h. This can be explained by the photocatalytic mechanism above. ZnWO₄ powder annealed for 0.5 h has not a good crystallinity though it has a large surface area; those annealed for more than 1 h have better crystallinity but lower surface area. Therefore, the photocatalytic activities are lower than the annealed for 1 h.

In summary, the annealing temperature and time are key factors strongly to influence the photocatalytic activity and, in particular, the highest value obtained with the samples annealed at 450 °C for 1 h. The photocatalytic activity of P-25 was about three times higher than that of the best sample prepared in present study on the degradation of RhB in aqueous, which can be explained that P-25 had a better dispersion and higher absorption capacity than others. However, in gaseous formaldehyde degradation process, the photocatalytic activities of ZnWO₄ are better than the rhodamine-B degradation process. The most imaginable reason is that the influence of dispersion was eliminated in gas formaldehyde degradation process. It is found that the dispersion of ZnWO₄ powder decreased in rhodamine-B aqueous with the increase of grains size, this can be explained why the P-25 had better photocatalytic activity than ZnWO₄ powder in aqueous. Furthermore, photocatalysts always were applied with film form. This result demonstrated that nanosized ZnWO₄ may be a promising photocatalyst for the photodegradation of chemical contaminants.

4. Conclusion

ZnWO₄ photocatalyst exhibited a high activity for the formaldehyde decomposition and RhB degradation. The sample prepared at 450 °C for 1 h showed the highest photocatalytic activity due to good crystallization and high BET surface area.
area. The dispersion of photocatalyst in solution is an important factor that influences the photocatalytic activity. Furthermore, this work provides some insight into the design of new promising photocatalysts for the degradation of organic contaminants.

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References