One-Pot Preparation of FeSe-WSe₂ Composite and the Performance of Photo Fenton to Degradation Methylene Blue

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Summary: FeSe-WSe₂ composite photocatalyst was synthesized by a facile one-pot hydrothermal reaction with WSe₂, sodium selenite (Na₂SeO₃), hydrazine hydrate (N₂H₄·H₂O), hydrochloric acid (HCl), and Ferric chloride (FeCl₃). Different ratios of FeSe-WSe₂ composite photocatalysts were synthesized according to different Fe content, and FeSe-WSe₂ was characterized by XRD, SEM, UV-vis DRS and XPS. At the same time, the photocatalytic performance and catalytic mechanism of the composite photocatalyst were explored through the degradation of methylene blue (MB) by the composite. The experimental results show that under the best experimental conditions, the 37at% (Atomic ratio) FeSe-WSe₂ composite has the best removal effect on MB solution, and the removal rate reaches 99.8%. This shows that there is a synergistic effect of photocatalysis and Fenton reaction, which greatly improves the degradation ability of pollutants of FeSe-WSe₂. Since the degradation of pollutants by photo Fenton is carried out under neutral conditions, it is more conducive to future applications in actual production.

Keywords: Tungsten selenide; Iron selenide; Photo-Fenton; Photocatalyst; Methylene blue.

Introduction

The particularity of the advanced oxidation process (AOP) is mainly based on the hydroxyl radical (·OH) generated by redox, which has a high potential (2.80 V) and can degrade various refractory organic pollutants [1-4]. Because of its rapid formation and high degradation efficiency, the Fenton process has received widespread attention [1, 5-7]. However, the Fenton homogeneous process is not only affected by pH value but also limited by ferric hydroxide sludge [8-10].

To expand the application of Fenton reagents, the process of heterogeneous Fenton was developed. This is because organic compounds will be fully mineralized at ambient temperature[11]. Therefore, researchers have done a lot of research on the preparation and application of Fenton materials [12-19]. Among them, Photo-Fenton is an effective way to treat wastewater [20-24]. In the past few decades, the study of the heterogeneous Fenton process of the decomposition of organic pollutants under ultraviolet light has attracted widespread attention[25]. However, the practical application of the UV-based photo-Fenton method is limited because UV only accounts for 3%-5% of solar energy. Therefore, compared to artificial ultraviolet rays, the method of using solar light to catalyze the decomposition of organic pollutants may be very economical. Therefore, the development of optical Fenton catalyst plays an important role in actual production [26].

Visible light driving needs to be considered with the sensitivity of the catalyst to visible light and its light absorption ability. The efficient and stable photocatalyst is one of the necessary conditions for the further development and application of Fenton technology [27-29]. Some metal oxides had been researched and developed as visible light photocatalysts. The photocatalytic activity of the photocatalyst is attributed to the ability of the photocatalyst to generate electron-hole pairs determines [30, 31]. To improve the performance of...
the catalyst, the researchers increased the number of active sites and doped additional transition metal atoms into the metal catalyst to stimulate electrocatalytic activity. For example, doping other atoms on graphene gives the composite material of huge surface area, high conductivity, and unique structure.

Transition metal-carbon disulfide (TMD) is currently one of the more desirable co-catalysts because of its greater chemical stability, faster charge migration, and efficient light absorption characteristics. In this regard, tungsten diselenide has attracted a lot of attention from researchers due to its special point and transport properties and superior electrical conductivity [32]. In the meantime, fluorescent nano-semiconductors made from iron-sulphur-based compounds nanomaterials have unique optical and electrical properties that also promote their application in bio-imaging and solar energy conversion [33]. Iron diselenide has narrow band gap energy and good conductivity, so it occupies a great advantage in industrial production [34].

In this paper, a new type of photocatalyst FeSe-WSe2 was synthesized by a one-pot thermal method. Under visible light, the photo-Fenton reaction was carried out to degrade MB to explore the performance of the photocatalyst.

Experimental

Chemicals

Tungsten selenide (WSe2) was brought from Macklin; Methylene blue (MB) and Ferric chloride (FeCl3) were brought from China Shanghai Aladdin Chemical Reagent Co., Ltd. Sodium selenite (Na2SeO3) and ethanolamine were bought from Sinopharm Chemical Reagent Co., Ltd. Hydrazine Hydrate(N2H4·H2O) was purchased from Tianjin Sanhe Fine Chemical Co., Ltd.

Preparation of FeSe-WSe2

Take 0.16 g FeCl3 and 0.11 g WSe2 to 6mL water, and stirred for 30 min, then added 0.45g sodium selenite (Na2SeO3), 24 mL ethanolamine, and 8.5 mL hydrazine hydrate to the dispersed solution. The solution was reacted for 24 hours in a high-temperature oven at 140 °C. The sample is sealed and stored after washing and filtering.

Photocatalysis and photo-Fenton catalysis experiments

The light source in the photodegradation process is a xenon lamp with a wavelength greater than 420 nm. Disperse 0.05 g sample into 50 mL MB (20 mg/L) solution. Stir for 0.5 h under dark conditions to reach adsorption equilibrium. After the adsorption equilibrium, turn on the light source for photoreaction. Take a sample every 10 minutes to measure the absorbance. Then, calculate the MB concentration and removal rate according to the standard curve formula. Experiments are conducted by changing the ratio of the complex, the Fe to H2O2, and the pH.

Repeat cycle experiment

Under the 420 nm light irradiation, the stability and reusability of the photocatalyst were studied through five repeated cycles of photo-Fenton reaction in MB.

Characterization

The microstructure and element distribution of catalyst were characterized by scanning electron microscope (SEM, JSM-6700F). X-ray photoelectron spectroscopy (XPS Thermo ESCALAB Xi) was used to characterize the atomic state of the complex. X-ray diffraction analyzer (XRD, D/MAX-2500/PC, Japanese Physics) is used for sample crystal characterization.

Results and Discussion

Material characterization

It can be seen from the scanning electron micrograph of FeSe in Fig. 1(a) that FeSe is in the form of small particles of uniform size, agglomerated together, and the small particles are uniform and the same in size. And Fig. 1(a) does not contain other morphological substances, which shows that the FeSe sample prepared in the experiment has good purity and good quality. In Fig. 1(b), it can be seen that many small particles growing on the columnar WSe2 column. The appearance and shape of this small particle are consistent with Fig. 1(a). At the same time, the element distribution characterization of the composite material was carried out to further indicate the distribution state of each element in the synthesized sample. Fig. 1(c)(d) and (e) is the distribution diagram of the elements corresponding to Fe, W, and Se in the composite. From the figure, it can be seen that the distribution of each element is dense and uniform. The EDS spectrum (f) of FeSe-WSe2 also shows the presence of various elements.
Fig. 1: SEM of FeSe(a), FeSe-WSe_2(b), elemental mapping images of Fe(c), W(d), Se(e) and EDS of FeSe-WSe_2

Table-1: The content of each atom in FeSe-WSe_2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative atomic mass</th>
<th>Quality(%)</th>
<th>Atomic ratio(%)</th>
</tr>
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<tr>
<td>Fe</td>
<td>55.8</td>
<td>11.7</td>
<td>36.6</td>
</tr>
<tr>
<td>W</td>
<td>183.8</td>
<td>38.6</td>
<td>8.9</td>
</tr>
<tr>
<td>Se</td>
<td>78.9</td>
<td>49.7</td>
<td>54.5</td>
</tr>
<tr>
<td>total</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2: XPS diagram of the complex (a). Atomic energy spectrum of Fe 2p (b), Se 3d (c), and W 4f (d) in the FeSe-WSe₂ composite.

Table 1 is the comparison of the content of each element of the composite. The above electron microscopy and element characterization all show that the synthesized composite sample is uniform and free of other impurities.

XPS was used to characterize the composite to determine the atomic composition and morphology of the FeSe-WSe₂ surface. Fig. 2(a) can see the existence of the five elements and their corresponding peak positions. Among them, carbon and oxygen atoms are the backgrounds of the process of testing samples, so the carbon and oxygen atom summits appear in the full spectrum. Fig. 2(b) is the electron energy spectrum of the iron atom. The peak positions at 711.1 eV and 724.5 eV are attributed to the peaks of Fe 2p₃/₂ and Fe 2p₁/₂. 711.1 eV is belong to the original structure of the iron species, which belongs to the selenium iron ore lattice and the iron species with a higher oxidation state. The peak at 718.8 eV is derived from the binding energy of Fe(II) and Se atoms. The peak at 731.8 eV is attributed to the satellite peak of Fe 2p₁/₂ [34, 35]. Fig. 2(c) is the electron energy spectrum of the Se atom. The peak at 55.2 eV and 55.9 eV may be Se 3d₅/₂ and Se 3d₃/₂, which indicate the existence of FeSe and WSe₂. It is seen in Fig. 2(d) that the peak positions of 32.4 eV and 34.6 eV correspond to W 4f₇/₂ and W 4f₅/₂. Through the electron energy spectrum analysis of all the above atoms, it can clearly show the existing state of the atoms in the complex, and it is consistent with the literature report.
Fig. 3: XRD pattern of WSe$_2$, FeSe, FeSe-WSe$_2$.

Fig. 3 is the X-ray diffraction comparison diagram of WSe$_2$, FeSe, and FeSe-WSe$_2$. Major characteristic peaks of WSe$_2$ and the corresponding crystal planes can be seen in the figure. The angles and corresponding crystal planes in the figure are the standard PDF card (JCPDS#38-1388) of WSe$_2$ that is consistent. It can be seen from the figure that the angles of FeSe at 24.1°, 29.8°, 41.2°, 45.5°, 52.5°, 55.1°, 62.3°, 68.8° correspond to (100) (101) (102) (110) (200) (201) (202) (104) plane. This is consistent with the main peak position shown on the standard card (JCPDS#65-9125). This indicates that the prepared sample is FeSe. In addition, there are fewer spurious peaks and sharp peaks, indicating that the purity of the prepared sample is good. And from the XRD diagram of the FeSe-WSe$_2$ composite, the characteristic peaks of WSe$_2$ and FeSe are all present in the composite FeSe-WSe$_2$, and the angle corresponding to the characteristic band can be seen in the figure. Although the WSe$_2$ peak in the composite is relatively weak due to the low content of WSe$_2$, the corresponding WSe$_2$ peak position in the composite can still be seen. This shows that the synthesized sample is indeed FeSe-WSe$_2$.

The absorbance of the sample shows the absorption range of FeSe, WSe$_2$, and FeSe-WSe$_2$ by UV-vis spectrophotometer. As shown in Fig. 4(a): the absorption peak of FeSe and WSe$_2$ decreases sharply at 600-680 nm, and the light absorption capacity is weakened. FeSe-WSe$_2$ compensates for the light absorption range from 700 nm to 800 nm and increases the light absorption range. For crystalline semiconductors, the band gap can be estimated according to the Kubelka Munk equation. In Fig. 4(b), the estimated band gaps of FeSe, WSe$_2$ and FeSe-WSe$_2$ are approximately 2.6 eV, 1.3 eV and 1.2 eV. This is relatively similar to the band gap of FeSe reported in the relevant literature to be around 3.0 eV, and to the band gaps of 1.6 eV (monolayer) and 1.2 eV (multilayer) for WSe$_2$ in different morphologies, etc[36-39]. The band gap energy of composite materials is smaller than that of a single substance. When exposed to light, electrons are excited to produce electronic transitions. The results show that the composite catalytic material has a broader absorption base in the visible region and has better visible light absorption capacity. And it greatly improves the absorption and utilisation of solar energy, leading to an increase in the degradation efficiency of organic matter.
Properties of FeSe-WSe\textsubscript{2} nanocomposites

Under the same conditions, the ratio of Fe content (at\%) and the ratio of Fe to H\textsubscript{2}O\textsubscript{2} in the composite were investigated by photocatalytic experiments. The removal rate of 37at\% FeSe-WSe\textsubscript{2} is much higher and reaches 99.8\% (see in Fig. 5a), which would attribute to the increases in Fe, the higher efficiency of the photo-Fenton reaction. When the proportion of Fe in FeSe-WSe\textsubscript{2} was more than 37\%, the MB removal rate decreased. The reason is that a high concentration of Fe cannot fully participate in the optical photo-Fenton. At the same time, the influence of H\textsubscript{2}O\textsubscript{2} on the effect of MB degradation in the Fenton reaction was also carried out. With the increases in H\textsubscript{2}O\textsubscript{2} content, the effect of the photo-Fenton reaction to degrade MB gradually increased (see in Fig. 5b). When the ratio of H\textsubscript{2}O\textsubscript{2} and Fe is 1:70, the optical Fenton effect is the best.

Generally, the Fenton reaction has a better redox degradation effect within a suitable pH range. Under the conditions of pH = 4, 7, and 10, respectively, the same concentration of MB was degraded for exploration. As shown in Fig. 5(c), the removal rates of MB at pH = 4 and 10 are 91.7\% and 64.6\%, respectively. When pH = 7, the composite has the best removal effect on MB. Compared with acidic or alkaline conditions, neutral conditions have a better removal effect and are more convenient for practical applications. Through five repeated cycles of the composite degrading MB experiment, to show the stability and repeatability of the FeSe-WSe\textsubscript{2} composite photocatalyst. As shown in Fig. 5(d), with the increase in the number of photocatalytic experiments, the photocatalytic degradation efficiency of the composites stabilized above 85\%. This shows that the FeSe-WSe\textsubscript{2} composite material has excellent stability. Repeated use of photocatalysts reduces the waste of samples and preparation materials and saves resources for sustainable development.
TiO$_2$, FeSe, WSe$_2$, and FeSe-WSe$_2$ were used to degrade the MB for comparison photocatalytic performance under the same conditions. The degradation effect was shown in Fig. 6(a). The adsorption of FeSe or WSe$_2$ is weak, and the adsorption capacity of the composite material FeSe-WSe$_2$ is improved. The overall photocatalytic effect of TiO$_2$ and WSe$_2$ is weak, and the degradation efficiency of MB is only 42.2% and 17.7%. The removal efficiency of FeSe and FeSe-WSe$_2$ is 82.0% and 99.8%. The adsorption ability and photocatalytic reaction of the composite material were all improved. Fig. 6(b) shows the photodegradation kinetics of different substances on MB. The photodegradation rate of FeSe-WSe$_2$ composite material is 0.06918 min$^{-1}$, which is significantly higher than the reaction rate of WSe$_2$, FeSe, and TiO$_2$.

By comparing with the published optical Fenton article, the superiority of the material performance of this article is further explained. As shown in Table 2, the degradation experimental conditions and removal rate of different substances on MB were also compared. The FeSe-WSe$_2$ has certain advantages in terms of the concentration, reaction time, and dosage of MB degradation.

The mechanism of FeSe-WSe$_2$ degradation of MB was also deduced. At present, in numerous literature reports, FeSe is called an effective promoter [44, 45], and Fe$^{2+}$ in the composite undergoes high-valent oxidation reactions. The two reaction processes are carried out simultaneously with efficient speed of degradation of pollutants. The conduction band and valence band are calculated according to the following equations: $E_{CB} = \chi - E_e - 0.5E_g$ and $E_{VB} = E_{CB} + E_g$, where $E_{CB}$ is the CB edge potential, $\chi$ is the electronegativity of the semiconductor, $E_e$ is the energy of the free electron on the hydrogen scale (~4.5 eV), $E_g$ is the band gap and $E_{VB}$ is the VB edge potential[46].

Fig. 6: Comparison of different substances on MB (Mass ratio of Fe 37% at, Fe to H$_2$O$_2$ ratio 1:70, catalyst dosage 0.05 g, MB initial concentration $6.0 \times 10^{-5}$ mol/L, pH=7) (a) and kinetics of different catalysts on MB(b).

<table>
<thead>
<tr>
<th>Material</th>
<th>Light region</th>
<th>MB concentration (mg/L)</th>
<th>Volume (mL)</th>
<th>Dosing amount (g)</th>
<th>reaction time (min)</th>
<th>Removal rate (%)</th>
<th>Reference</th>
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<tr>
<td>Mn$_3$O$_4$@ZnO/ACFs</td>
<td>visible</td>
<td>5</td>
<td>80</td>
<td>0.025</td>
<td>150</td>
<td>close to 100</td>
<td>[40]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/Bi$_2$O$_3$</td>
<td>visible</td>
<td>10</td>
<td>100</td>
<td>0.1</td>
<td>80</td>
<td>98</td>
<td>[41]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/CuO</td>
<td>visible</td>
<td>10</td>
<td>50</td>
<td>0.05</td>
<td>120</td>
<td>94</td>
<td>[42]</td>
</tr>
<tr>
<td>FeOOH/Bi$_2$WO$_4$</td>
<td>visible</td>
<td>12</td>
<td>20</td>
<td>0.02</td>
<td>48</td>
<td>98</td>
<td>[43]</td>
</tr>
<tr>
<td>FeSe-WSe$_2$</td>
<td>visible</td>
<td>20</td>
<td>50</td>
<td>0.05</td>
<td>90</td>
<td>99.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 2 Compare the removal effect of other photo-Fenton reactions on MB.
As shown in Fig. 7, the conduction band (CB) and valence band (VB) of FeSe are 0.91 eV and 1.69 eV, and the conduction band (CB) and valence band (VB) of WSe₂ are 0.24 eV and 1.54 eV, which can be calculated from the equation in the previous paragraph. Under visible light, electrons in FeSe are excited from the valence band (VB) to transition to the conduction band (CB) and continue to migrate to the surface of the promoter WSe₂. The photogenerated electrons (e⁻) on WSe₂ react with O₂ to generate O₂⁻, and the electron holes (h⁺) are transferred from the VB of WSe₂ to the VB of FeSe. The h⁺ on the surface of FeSe reacts with adsorbed water and hydroxide to generate ·OH. FeSe particles can reduce the electron-hole recombination rate in WSe₂, and act as a promoter to greatly improve the photocatalytic activity of WSe₂ [45]. At the same time, during the photocatalytic reaction, Fe²⁺ and H₂O₂ in FeSe-WSe₂ undergo advanced oxidation reactions: first, Fe²⁺ reacts with hydrogen peroxide to form Fe³⁺, ·OH, and OH⁻. Secondly, Fe³⁺ is reduced to Fe²⁺ H₂O, and ·OH under a light. Finally, ·OH and MB redox and degrade pollutants. The above two reactions proceed simultaneously and cooperate, which greatly improves the effect of FeSe-WSe₂ in degrading pollutants [47-49]. The removal rate of pollutants is much higher than that of a single substance, and the reaction rate of the entire photocatalytic process is improved.

Conclusions

The FeSe-WSe₂ heterostructure can be carried out in the composite to obtain long service life and higher separation efficiency. At the same time, the Fe²⁺ in the composite undergoes advanced oxidation reactions, and the two reactions cooperate to accelerate the rate of degradation of pollutants. This makes the 37at%FeSe-WSe₂ composite photocatalyst have high efficiency and excellent photocatalytic performance.

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Declaration of Interest Statement

The authors declare that they have no conflict of interest.

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