SYNTHESIS OF Co DOPING SrMoO₄ FOR ENHANCED PHOTOCATALYTIC PERFORMANCE VIA HYDROTHERMAL METHOD

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Visible-light-driven photocatalyst Co-doped SrMoO₄ was successfully synthesized by a facile hydrothermal preparation. The results showed that Co doping has no effect on the crystal structure of SrMoO₄ but plays an important role on the morphology. The photocatalytic measurements indicated that Co doping can effectively enhance the photocatalytic activities of the SrMoO₄ which were evaluated by the degradation of methyl blue (MB) under visible light irradiation. And the 5% Co-doped SrMoO₄ shows the optimal photocatalytic performance. The enhancement of photocatalytic activity is attributed to narrower band gap and the lower recombination ratio of photo-induced electron-hole pairs with Co doping.

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1. Introduction

Scheelite-structured compounds molybdates in the AMoO₄ (A=Ba, Sr or Ca) family have been attracting considerable attention in recent years owing to their attractive properties, as well as their versatile potential applications [1-6]. SrMoO₄ crystallize in this so-called scheelite structure, which belong to the tetragonal space group I41/a. The structure consists of two fundamental SrMoO₄ units, Sr and Mo have S4 point symmetry site. Each Mo is surrounded by four oxygens and forms a tetrahedron, and these tetrahedra are linked by the Sr-O bonds. On the other hand, each Sr is surrounded by eight oxygens and forms octahedral.

SrMoO₄ is regarded as one semiconductor material with wide band gap (4.0eV) and can only absorb UV light (λ<387nm) [7]. To maximum the use of sunlight and enhance the photocatalytic activity of SrMoO₄, many methods have been developed. For example, we adopted thermal decomposition of metal-organic salt in the organic solvent to obtain the lowest energy band 2.71eV till now. The UV-absorbance spectrum suggest that larger absorption of the SrMoO₄ samples is located in the visible light region including UV light region. As a result, nearly 100% degradation efficiency for methyl blue in 120 minutes is obtained by the photocatalytic measurement [8]. Stirring speed in the hydrothermal preparation also can enhance the SrMoO₄ photocatalytic activity [9].

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As we know, for a photocatalyst with wide band gap, the doping with a foreign element is a good way to enhance the photocatalytic activity. For example, the M doping (M=Ag, Co and Ni) into BiVO₄ can suppress the photogenerated electrons and holes and enhance the photocatalytic decomposition of organic compounds [10]. With Cr³⁺ ions doping into TiO₂ and SrTiO₃, the photocurrent of semiconductor increase, and the photocatalytic decomposition of organic compounds is enhanced [11]. Based on the above ideas, in the present work, Co/SrMoO₄ catalysts were synthesized by a facile hydrothermal process. The band structure of SrMoO₄ was previously suggested to be composed of Mo⁴⁺ and hybridization of O²⁻ and Sr⁶s. When Co²⁺ is doped into SrMoO₄ lattice, because the size mismatch between Co²⁺ is smaller for Mo⁶⁺ than for Sr²⁺, it is more likely that Co²⁺ enters Mo⁶⁺ sites. And the photocatalytic experiments suggested that the introduction of Co into SrMoO₄ is helpful for the photodegradation enhancement of methyl blue (MB). With Co doping, intermediary energy level is introduced and the band gap becomes smaller, as a result, the recombination rate of photo-induced electrons decreases and the lifetime of carriers is prolonged. Correspondingly, the photocatalytic activity is improved.

2. Experimental

Stoichiometric amounts of Sr(NO₃)₂, Co(NO₃)₃, (NH₄)₆Mo₇O₂₄ and NaOH were separately dissolved in the deionized water with stirring for 20 min using a magnetic stirrer. Then, the Sr(NO₃)₂ and (NH₄)₆Mo₇O₂₄ were mixed with continuous stirring. The NaOH solution was added to adjust pH values. Finally, the mixture was placed in a 1000 ml hastelloy autoclave (Parr 4577) and reacted at 120 ºC for 6 h. After the autoclave was cooled to room temperature naturally, the products were separated by centrifugation, washed with ethanol and deionized water several times, and subsequently dried at 80 ºC to obtain the final samples. The obtained samples, with different Co doping content (0, 0.01, 0.03, 0.05, 0.07, 0.09 and 0.11, as referred as Co--00, Co--001, Co--003, Co--005, Co--007, Co--009 and Co--011, respectively.

The crystal structures of the products were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (dx-2000 SSC) with Cu Kα radiation (λ=1.5418 Å) over a scanning range of 10-80° with a step of 0.02°. Using an X-ray photoelectron spectrometer (XPS, Elcalab 250 Xi, American), the valence states of ions were also tested. Scanning electron microscopy (SEM, S-4800, Hitachi) was used to observe the morphology and microstructure. UV-vis absorbance spectra detection was also performed by using a Japan Shimazdu UV-3600 (Japan) using BaSO₄ as a reference. The excitation and emission spectra were measured on a FL fluorescence spectrophotometer (F-4500, Hitachi).

The photocatalytic activity of Co/SrMoO₄ samples was evaluated by the degradation of methyl blue (MB) under a 350 W Xe lamp light. In each experiment, 200 mg of the photocatalyst was added to 80 ml of MB solution (10 mg/L) in one test tube. Before illumination, the suspensions were magnetically stirred in the dark for 1 h to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst and MB solution. And then, the solution under magnetic stirring was exposed to Xe lamp light irradiation. At given interval time, the test tubes were sampled and then centrifuged to remove the photocatalyst particles.
3. Results and discussions

3.1. XRD analysis

Due to the Co doping does not change the XRD patterns of SrMoO$_4$, for simplicity, the results are not provided for all samples. Herein, we provide the XRD patterns for pure SrMoO$_4$ (Co--00), 5\% Co-doped SrMoO$_4$ (Co--005) and 11\% Co-doped SrMoO$_4$ (Co--011) samples, as shown in Fig. 1. The sharp and well-defined peaks suggest that these samples have well crystallization and no other impurities were detected. The observed pattern indicates that all of the prepared SrMoO$_4$ samples have pure scheelite tetragonal structure (I41/a space group), corresponding to the JCPDS 850586 [8]. The diffraction peaks of as-prepared samples correspond to the (101), (112), (004), (200), (211), (204), (220), (116), (303), (224), (400), (316), and (404) planes, as shown in Fig. 1. The XRD result implies that Co was doped into the SrMoO$_4$ lattice and this Co doping does not change the lattice structure of SrMoO$_4$ during the crystallization process.

![Fig. 1. XRD pattern for pure SrMoO$_4$ (Co--00), 5\% Co-doped SrMoO$_4$ (Co--005) and 11\% Co-doped SrMoO$_4$ (Co--011) samples.](image)

Fig. 2 presents the crystal structure of SrMoO$_4$. In this structure, each central Mo atom is surrounded by four equivalent O atoms, constituting one MoO$_4^{2-}$ tetrahedral symmetry configuration. And each divalent metal atom shares corners with eight adjacent O atoms in MoO$_4^{2-}$ tetrahedron [12]. The lattice parameters for the above five samples are calculated according to

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2},$$

where $2d\sin\theta = n\lambda$, $a$ and $c$ are the lattice parameters, $\theta$ is the diffraction angle, $\lambda$ is the wavelength of the Cu Ka irradiation, and (h k l) are the crystal plane indexes. The calculated lattice parameters are presented in Table 1. It is found that the lattice parameters of these samples vary with Co doping. The standard values of these lattice constants are 5.39 Å and 12.02 Å for SrMoO$_4$. These variations of the lattice parameters indicate that the distortions may be introduced in the SrMoO$_4$ lattice. However, it can be seen that the lattice parameter changes slightly with Cr doping content, which may be ascribed to the similar lattice parameter between Co (r=0.69Å) and Mo (r=0.59Å), as discussed below.
Table 1. The lattice parameter values for all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co--00</th>
<th>Co--001</th>
<th>Co--003</th>
<th>Co--005</th>
<th>Co--007</th>
<th>Co--009</th>
<th>Co--011</th>
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<td>a (Å)</td>
<td>5.3834</td>
<td>5.3866</td>
<td>5.3782</td>
<td>5.3794</td>
<td>5.3785</td>
<td>5.3774</td>
<td>5.3800</td>
</tr>
</tbody>
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3.2. XPS study

XPS spectra for pure SrMoO$_4$ (Co--00) and 5\% Co-doping SrMoO$_4$ (Co--005) samples were measured and the results are presented. Fig. 3(a) provide the survey XPS spectra, and the obvious peaks corresponding to Sr 3d, Mo 4p, Mo 3d, Mo 3p, and O1s can be observed in both samples. The observed binding peaks of C 1s is at 283.28 eV which originates from carbon in the instrument. In addition, a weak peak of Co appears at about 788.42 eV in the 5\% Co-doping SrMoO$_4$. Figure 3(b)-(d) provide the high-solution XPS spectrum of Mo, O and Co element. In Figure 3(b), these peaks centered at 235.15(235.21) eV and 232.02(232.13) eV can be assigned to Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ [13]. In Fig. 3(c), the peaks at binding energies of 530.06 eV for pure SrMoO$_4$, and 530.15 eV for the 5\% Co-doped SrMoO$_4$ correspond to the O 1s. To further indentify the chemical state of Co, the Co 2p high resolution XPS spectrum of 5\% Co-doped SrMoO$_4$ is shown in Fig. 3(d). And the binding energies of 797.00 eV and 780.93 eV correspond to the Co 2p1/2 and Co 2p3/2, respectively. It suggests that the Co element existed in form of Co$^{3+}$ in our sample [14]. As discussed before, due to the radius of Co$^{3+}$ (0.69 Å) was much smaller than Sr$^{2+}$ (1.18Å), but almost similar than the radius of the Mo$^{6+}$(0.59 Å), it is reasonable to conclude that the doping Co$^{3+}$ maybe replace some Mo$^{6+}$ in the internal lattice structure of SrMoO$_4$. 
3.3. SEM analysis

Fig. 4 presents the SEM profiles for all samples (Co--001--a, Co--003--b, Co--005--c, Co--007--d). Till now, a number of preparation methods have been adopted to synthesis SrMoO$_4$ compound, such as co-precipitation reaction [15], microwave radiation [16], electrochemical process [17], hydrothermal [18], and sol–gel methods [19]. And various morphological SrMoO$_4$, such as flower-like sphere, spindle rod, peanut, dumbbell, hierarchical nanosheets, nanowires, nanoplates have been obtained [20,21]. Our SEM microphology result indicate that our samples are composed of a large quantity of anisotropic microcrystals with octahedron-like and decagonal-like morphology. In addition, these octahedron and decagonal structure tend to be faceted and aligned by “docking” processes, creating an extended morphology as shown in Fig.4. In addition, for No-doping sample SrMoO$_4$, the spindle-like crystals are observed (not shown here) in previous report. Obviously, the Co introduction into SrMoO$_4$ have effected morphology heavily [22].

Fig. 3. Survey (a), Mo 3d (b), O1s (c) XPS spectra for Co--00 and Co--005 samples, (d) Co 2p XPS spectra for Co--005 sample.
3.4. Optical properties

Fig. 5 provides the UV-visible absorption spectra of the Co--00, Co--001, Co--003, Co--005, Co--007, Co--009, Co--011 products. There exists one strong and broad absorption in the UV region (200-400nm), which is attributed to the charge transfer from the oxygen (2p) electrons that move into the central molybdenum atom inside the [MoO$_4$]$^{2-}$ ion. In addition, a hump ranging from 500 to 650nm can be observed with Co doping as shown in Fig. 5, and the reason is unclear. The optical band gap energy ($E_g$) is also calculated by the method proposed by Wood and Tauc [23]. The optical band gap is associated with the absorbance and the photo energy by the following equation: $a h \nu = A (h \nu - E_g)^n$, where $a$, $h$, $\nu$, $E_g$ and $A$ are absorption coefficient, Planck constant, photon frequency, photonic energy gap and a constant, respectively. $n$ is a constant associated with the different types of electronic transitions ($n$=1/2, 2, 3/2, or 3 for directly allowed, indirectly allowed, directly forbidden, and indirectly forbidden transitions, respectively). According to Lacomba-Perales et al [24], the molybdates with scheelite-type tetragonal structure present one directly allowed electronic transition. Thus, in our work, the $n$=1/2 value was adopted as the standard in above equation. For $n$=1/2, the energy gap $E_g$ values are able to be determined by extrapolating the linear portion of the plot ($a h \nu)^2$ vs $h \nu$ to zero absorbance. Accordingly, the calculated energy gaps of Co--00, Co--001, Co--003, Co--005, Co--007, Co--009, Co--011 samples are 4.16, 4.10, 3.97, 3.77, 3.79, 4.00 and 4.08 eV, respectively. Our calculated $E_g$ value for Co--00 sample is close to the previous data [25]. Obviously, $E_g$ value decreases and then increases with Co doping. When Mo$_6^{6+}$ ion is substituted by Co$_2^{2+}$, the intermediate levels within the band gap is introduced. Compared with pure SrMoO$_4$, the narrower band gap of Co-doped SrMoO$_4$ can decrease the recombination rate of photogenerated electron-hole pairs and enhance the photocatalytic activities, as discussed below.
3.5. Photocatalytic properties

The photocatalytic activities of as-prepared Co-doped SrMoO$_4$ samples were evaluated by the degradation of dyes MB under visible-light irradiation at room temperature. Fig. 6 shows the temporal evolution of MB solution absorption spectra under visible light irradiation for 9\% Co doping SrMoO$_4$ sample (Co--009). It can be found that, for MB solution, the intensity of the absorption peak positioned at 654nm is decreased gradually with the increase of irradiation time.

![Absorption spectra of MB with irradiation time over Co--009 sample.](image)

Fig. 6. Absorption spectra of MB with irradiation time over Co--009 sample.

Fig. 7 presents the variation of MB concentration (C/C$_0$) with irradiation time over these photocatalysts prepared with different Co doping content. The photodegradation rate of MB over pure SrMoO$_4$ (Co--00) was 64.8\% after irradiation for 120min under the same conditions. With Co-doping in SrMoO$_4$, the photodegradation rates of MB reached 64.8\%, 73.1\%, 81.6\%, 90.8\%, 85.7\%, 77.2\%, and 67.9\% after irradiation for 120min for Co--00, Co--001, Co--003, Co--005, Co--007, Co--009, and Co--011 sample, respectively. Obviously, the photocatalytic activity of SrMoO$_4$ was effected by Co doping, and Co doping is helpful to enhance the photodegradation of MB resolution. In particularly, when the Co doping concentration increased from 0 to 5\%, the photocatalytic activity increased, and 5\% Co-doped SrMoO$_4$ (Co--005) showed the best degradation performance, 90.8\% MB was degraded in 120min. When the doping content was over 5\%, the photocatalytic activity decreases, but still better than that of pure SrMoO$_4$. Our current experimental investigation clearly suggests that Co-doping is helpful to improve the photocatalytic properties of SrMoO$_4$. Furthermore, there is an optical Co doping amount of the
SrMoO$_4$ in terms of MB photocatalytic degradation efficiency.

![Graph showing the degradation rates of MB under visible light irradiation for all Co-doped SrMoO$_4$ samples.](image)

*Fig. 7. The degradation rates of MB under visible light irradiation the presence for all Co-doped SrMoO$_4$ samples.*

As we known, one proper band gap is very important to one perfect photocatalyst, because it provides energetic electron, separates photo-generated charge efficiently, and inhibits the photo-corrosion process largely [26,27]. The smaller band gap is also necessary to allow for efficient absorption overlap with the solar spectrum. This is very obligatory for the photocatalyst to effectively utilize the solar energy [28,29]. The UV-vis spectrum result also indicates, the band gaps of our obtained samples become lower with Co doping. Therefore, it is reasonable to conclude that the higher photocatalytic properties of these Co-doped samples may be related to the lower band gap.

When Co-SrMoO$_4$ photocatalyst is activated under irradiation, the electrons(e$^-$) in the valence band (VB) are stimulated to the conduction band (CB), with the same amount of holes (h$^+$) left in the VB. The electrons of the VB will be caught by O$_2$ adsorbed on the surface of Co-doped SrMoO$_4$ acting as active sites to produce ·O$_2^-$ superoxide radicals. Meanwhile, the photogenerated holes of the VB can react with H$_2$O and OH$^-$ to generate ·OH hydroxyl radicals as strong oxidizing agents. At the same time, when Co element is doped into SrMoO$_4$, the energy level may be formed in the middle of VB and CB. The electrons could be captured by trapping sites Co$^{2+}$ ions, which is also helpful for separation efficiency of photo-generated charge carriers. And with increasing Co doping content, more and more electrons and holes participate in the photocatalytic process, as a result, higher photodegradation rate for MB is achieved. However, when the amount of Co doping is higher than its optimum amount of doping, excessive Co$^{3+}$ ions may be the center of electron-hole pair recombination, thus, the photocatalytic activity is lowered for Co--007, Co-009 and Co--011 samples. A plausible electron transfer and degradation mechanism of MB over SrMoO$_4$ is tentatively proposed, as displayed in Fig. 8.
Fig. 8. Schematic diagram of charge carrier transfer process and possible photocatalytic mechanism of Co-SrMoO$_4$ nanoparticles.

The electrons in the CB react with the absorbed O$_2$ in the surface of SrMoO$_4$ and produce superoxide anion radicals (•O$_2^-$). Simultaneously, the VB holes remaining on the VB react with H$_2$O/OH$^-$ to generate hydroxyl radical species (•OH). The •O$_2^-$ and •OH could oxidize the dye molecule of MB to CO$_2$, H$_2$O, and other micromolecules. The Co doping reduces the recombination of photo-induced electrons and holes and prolong the lifetime of the electron pairs, as a result, the photocatalytic activity is enhanced due to Co doping.

4. Conclusion

In the current research, Co-doped SrMoO$_4$ samples are successfully synthesized by hydrothermal method. The structural, microphology, and photocatalytic properties have also systematically probed. XRD patterns reveal the crystal structure does not change. The UV-vis absorption analysis of our samples exhibits Eg value decreases from 4.16 to 3.77 eV with Co doping, which is associated with the presence of intermediary energy levels within the band gap. The photo-degradation efficiency of the as-prepared samples is also investigated by degradating of MB under visible light irradiation.

The experimental results indicate that Co doping enhances photocatalytic activity, and 5% Co-doped SrMoO$_4$ shows the optimal photocatalytic performance in the degradation of MB. The enhancement of photocatalytic activity is attributed to the smaller band gap and the introduction of intermediary energy levels, which decreases the recombination rate of photo-induced electrons and holes and prolongs the lifetime of carriers with Co doping. As a result, the photocatalytic activity is improved.

Acknowledgments

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References