Sulfurization synthesis and photocatalytic activity of oxysulfide La$_3$NbS$_2$O$_5$

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Abstract: The oxysulfide La$_3$NbS$_2$O$_5$ was synthesized by sulfurization using H$_2$S and characterized by X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (DRS) and field emission scanning electron microscopy (FE-SEM). The relationship between the sulfurization conditions and the photocatalytic activities for H$_2$ evolution was investigated. Sulfurization method allowed for synthesis of La$_3$NbS$_2$O$_5$ at much lower temperatures and significantly shortened reaction time of 1 h compared with conventional solid-state techniques. The particle morphologies were regular platelike with sizes of 0.1–0.6 μm and smooth surfaces. The highest activity for H$_2$ evolution was obtained at 1073 K for 1 h, which was about 1.83 times that of La$_3$NbS$_2$O$_5$ prepared by solid-state method.

Key words: sulfurization method; H$_2$ evolution; La$_3$NbS$_2$O$_5$; photocatalysis; visible light

1 Introduction

Since the discovery of photoelectric splitting of water on TiO$_2$ electrodes by FUJISHIMA and HONDA in 1972 [1], the photocatalytic water splitting using solar energy and semiconductors to generate clean energy hydrogen has attracted increasing attention [2–7]. A large number of photocatalysts consisting of metal ions with d$^0$ and d$^{10}$ electron configurations have been developed for photocatalytic H$_2$ and O$_2$ evolution from water to date [8–12]. However, these photocatalysts are not active under visible light. Therefore, the development of photocatalysts with visible-light response would be valuable for application to H$_2$ production using solar energy. Metal oxysulfides are candidates for visible-light responsive photocatalysts, and promising results have been reported for Sm$_2$Ti$_2$S$_2$O$_5$ [13,14], La$_5$GaS$_5$O [15], La$_2$O$_2$S$_2$ [16], ZnS$_{1−x}$−$x$O$_x$(OH)$_y$ [17]. Recently, oxysulfide La$_3$NbS$_2$O$_5$ with large particle size has been synthesized by a solid-state reaction method [18], and its photocatalytic activity is very low [19]. Solid-state synthetic procedures provide relatively limited or no control over particle sizes or morphologies. By contrast, sulfurization synthetic methods have shown the ability to control the crystal growth of metal oxysulfides particles [20]. Further, it has been demonstrated that surface morphology as well as particle size are significant factors in photocatalytic activity [21], and the use of fine particles with good crystallinity is favorable for photocatalysis [22]. Thus, sulfurization synthetic methods are appropriate for probing the effects of particle morphologies and sizes on their photocatalytic activities, and which will lead to new insights on the origins of their photocatalytic activities.

In this work, the sulfurization synthesis of oxysulfide La$_3$NbS$_2$O$_5$ was investigated. Measurements of their photocatalytic activities for H$_2$ evolution were performed in a 0.01 mol/L Na$_2$S–Na$_2$SO$_3$ solution, and the relationship between the sulfurization conditions and the photocatalytic activities for H$_2$ evolution was investigated, along with a comparison of the photocatalytic activity of the new material with that of the products obtained from the solid-state methods.

2 Experimental

2.1 Synthesis of La$_3$NbS$_2$O$_5$

Powder samples of La$_3$NbO$_7$ were prepared by a polymerized complex (PC) method using NbCl$_5$ and La(NO$_3$)$_3$·6H$_2$O as starting materials [23]. Methanol was
employed as solvents, and anhydrous citric acid and ethylene glycol were employed as a complexing agent to immobilize Nb and La ions. After polymerization of a mixture containing stoichiometric amounts of La and Nb (La/Nb=3:1) according to the method in Ref. [24], La$_3$NbO$_7$ was obtained by calcination at 773 K in air. This La$_3$NbO$_7$ is referred to as the oxide precursor. The oxide precursors (0.5 g) were placed in quartz carrier and then were placed in tubular furnace. Powder samples of La$_3$Nb$_2$O$_7$ were prepared from the oxide precursors by calcination under flowing H$_2$S (flow rate of 10 mL/min) at various temperatures for various time. The solid-state preparation of La$_3$Nb$_2$O$_7$ followed the reported procedures [18].

2.2 Characterization of catalysts

The crystal structure of prepared samples was analyzed by the powder X-ray diffraction (D/Max 2500 VB+, Japan) with Cu K$_\alpha$ radiation ($\lambda$=0.154056 nm). The particle microstructures and approximate sizes of prepared samples were determined by FE-SEM (Sirion 200, Philips, Netherlands).

Surface area of prepared samples was measured on a surface area analyzer (Autosorb/monosorb, Quantachrome, America) by N$_2$ absorption at 77 K using the Brunauer Emmett Teller (BET) method. The DRS of prepared samples was obtained using a UV–Vis scanning spectrophotometer (TU-1901, Beijing-Purkinje, China) at room temperature, and was converted from reflectance to absorbance by the Kubelka–Munk method.

2.3 Photocatalytic testing

Reactions were carried out in an inner-irradiation quartz reaction vessel connected to a glass closed gas circulation system. The powder catalyst (1 g) was dispersed and suspended in a 0.01 mol/L Na$_2$S–Na$_2$SO$_3$ solution (570 mL) under magnetic stirring. The cocatalyst Pt (1.0%, mass fraction) was loaded by impregnation from H$_2$PtCl$_6$ followed by reduction in H$_2$ at 473 K for 2 h. The reactant solution was evacuated several times to remove air completely prior to irradiation using a 250 W high-pressure Xe arc lamp. For visible irradiation ($\lambda$$\geq$ 400 nm), a sodium nitrite (NaNO$_2$) aqueous solution (2 mol/L) was inserted in the light path used to block ultraviolet (UV) light. The gases evolved in the reaction were analyzed by gas chromatography (Shimadsu GC-8A, Japan, Ar carrier). The number of photons reaching the solution was measured with a Si photodiode. The apparent quantum efficiencies were calculated using the equation: $Q=(AR/I)\times100\%$, where $A$, $R$, and $I$ are coefficients based on the reactions (H$_2$ evolution, 2), the H$_2$ evolution rate (molecules h$^{-1}$), and the rate of absorption of incident photons (7.2×10$^{21}$ photons h$^{-1}$ at 400 nm$\leq$$\lambda$$\leq$600 nm based on the total photon number reaching the reaction solution).

3 Results and discussion

Figure 1 shows the XRD patterns of La$_3$NbS$_2$O$_7$ prepared by sulfurization method at 1123 K for different sulfurization time. For comparison, Fig. 1 also shows the XRD patterns of La$_3$NbS$_2$O$_7$ prepared at 1273 K for 9 d by the solid-state method. Diffraction peaks corresponding to La$_3$NbS$_2$O$_7$ appeared for the sample sulfurized after 0.5 h. After 1 h sulfurization, the diffraction peaks of La$_3$NbO$_7$ disappeared. At sulfurization time for 1 or 2 h, a single phase of La$_3$NbS$_2$O$_7$ was obtained. Thus, the sulfurization method allows for very quick synthesis of La$_3$NbS$_2$O$_7$ compared with the solid-state method, which took up to 9 d. Figure 2 shows the XRD patterns of La$_3$NbS$_2$O$_7$ obtained at various sulfurization temperatures for 1 h. The power XRD analysis showed that La$_3$NbS$_2$O$_7$ calcined at 1073 K or above was a single phase. In the case of the samples

![Fig. 1 XRD patterns of La$_3$NbS$_2$O$_7$ prepared at 1123 K for different sulfurization time and at 1273 K for 9 d by a solid-state method](image1)

![Fig. 2 XRD patterns of La$_3$NbS$_2$O$_7$ obtained at various sulfurization temperatures](image2)
calcined at 1023 K, most of the peaks in XRD patterns were attributed to La₃NbS₂O₅, but relatively weak peaks due to La₃NbO₇ were also observed. With increasing temperature from 1023 to 1173 K, the major peaks became narrower and their intensity increased.

Table 1 lists the crystallite size and BET area of La₃NbS₂O₅ sulfurization samples with sulfurization temperature and time. The crystallite sizes of La₃NbS₂O₅ samples were determined by the Scherrer equation, using the (105) reflection of La₃NbS₂O₅ for calculation. The BET area of La₃NbS₂O₅ samples was measured on a surface area analyzer by N₂ absorption at 77 K using the BET method. With sulfurization temperature from 1023 to 1173 K, the crystallite size of La₃NbS₂O₅ increased gradually, and the BET area of La₃NbS₂O₅ decreased gradually. The crystallite size of La₃NbS₂O₅ prepared at 1123 K for 0.5 h was estimated to be about 57.3 nm, and continued to grow with sulfurization time. The BET area of La₃NbS₂O₅ prepared at 1123 K for 0.5 h was estimated to be about 6.67 m²/g, and continued to decrease with sulfurization times. For comparison, Table 1 also shows the crystallite size and BET area of the solid-state preparation of La₃NbS₂O₅ samples. Because of calcination at high temperatures over a long period, the crystallite size of La₃NbS₂O₅ prepared by solid-state method was larger than that of La₃NbS₂O₅ prepared by sulfurization method, while the BET area of La₃NbS₂O₅ prepared by solid-state method was significantly less than that of La₃NbS₂O₅ prepared by sulfurization method.

Table 1 Crystallite size and BET area of La₃NbS₂O₅ samples

<table>
<thead>
<tr>
<th>Catalyst sample (LNSO(T-h)(a))</th>
<th>Crystallite size/nm</th>
<th>BET area/(m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNSO(1023-1)</td>
<td>51.5</td>
<td>9.32</td>
</tr>
<tr>
<td>LNSO(1073-1)</td>
<td>55.2</td>
<td>7.04</td>
</tr>
<tr>
<td>LNSO(1123-0.5)</td>
<td>57.3</td>
<td>6.67</td>
</tr>
<tr>
<td>LNSO(1123-1)</td>
<td>58.8</td>
<td>6.35</td>
</tr>
<tr>
<td>LNSO(1123-2)</td>
<td>60.5</td>
<td>6.02</td>
</tr>
<tr>
<td>LNSO(1173-1)</td>
<td>62.6</td>
<td>5.81</td>
</tr>
<tr>
<td>LNSO(SSR)b</td>
<td>92.7</td>
<td>0.65</td>
</tr>
</tbody>
</table>

(a) La₃NbS₂O₅ sample calcined at a certain temperature for a certain sulfurization time, e.g. LNSO(1023-1) denotes La₃NbS₂O₅ sample calcined at 1023 K for 1 h; (b) La₃NbS₂O₅ sample prepared by solid-state method

Figure 3 shows SEM images of La₃NbS₂O₅ prepared by the solid-state and sulfurization methods. In the case of La₃NbS₂O₅ prepared by the solid-state methods, irregular block-like particles with sizes of 1–3 μm as well as a lot of smaller size particles were observed. In the case of La₃NbS₂O₅ prepared by the
sulfurization methods, platelike particles with smooth surfaces were obtained, and their particle sizes were 0.1−0.6 μm. The difference in the particle size between those calculated by the Scherrer equation and those observed by SEM suggests that the particles observed by SEM are the polycrystalline particles. It was found that the morphology of La₃NbS₂O₅ prepared by sulfurization methods was relatively constant, and independent of sulfurization temperature. This similar phenomenon had also been reported for Sm₂Ti₂S₄O₅ [14].

The optical properties of photocatalytic materials were very important because they dictated the number of photons absorbed by the system. Figure 4 shows the DRS of La₃NbS₂O₅ prepared under varying sulfurization conditions and a solid-state procedure. It was found that all of La₃NbS₂O₅ showed obvious absorption in the visible light range (>400 nm) irrespective of the preparation conditions. The optical absorptions of La₃NbS₂O₅ prepared by sulfurization method were slightly attenuated with increasing sulfurization time and temperature, and were obviously higher than that of La₃NbS₂O₅ prepared by the solid-state method. Using the formula \( E_g/eV=1240/\lambda_g \), where \( \lambda_g \) (nm) was extrapolated from the linear rise in the absorption curve, the band gaps of the sulfurization synthesized La₃NbS₂O₅ were calculated to be in the range of 2.13−2.17 eV, and the band gap of the solid-state synthesized La₃NbS₂O₅ was calculated to be about 2.26 eV.

![Fig. 4 DRS of La₃NbS₂O₅ prepared under varying sulfurization conditions and solid-state procedure](image)

In order to test the effects of the sulfurization synthesis conditions on its photocatalytic activity, each sample was tested for photocatalytic H₂ evolution in an inner-irradiation quartz reaction vessel in a 0.01 mol/L Na₂S−Na₂SO₃ solution. Table 2 shows the rate of H₂ evolution of La₃NbS₂O₅ prepared under varying sulfurization conditions and a solid-state procedure. The highest activity of H₂ evolution (11×10⁻⁶ mol/h) was obtained for the sample prepared at 1073 K for 1 h by sulfurization method, which was about 1.83 times that obtained by the solid-state method due to larger surface area (see Table 1) and higher optical absorption (see Fig. 4). The quantum efficiency for H₂ evolution was about 0.092% for the La₃NbS₂O₅ sample prepared at 1073 K for 1 h. In contrast, the quantum efficiencies of H₂ evolutions for La₃NbS₂O₅ (SSR) were estimated to be about 0.05%. The photocatalytic activity of La₃NbS₂O₅ prepared at 1023 K for 0.5 h was lower than that of the sample prepared at 1123 K for 0.5 h due to lower crystallinity (see Table 1), and the photocatalytic activity of La₃NbS₂O₅ prepared at 1073K for 1 h due to lower crystallinity and impurity La₃NbO₇. Also, the photocatalytic activity of La₃NbS₂O₅ prepared at 1123 K for 0.5 h was lower than that of the sample prepared at 1123 K for 1 h due to lower crystallinity and impurity La₃NbO₇, and the photocatalytic activity of La₃NbS₂O₅ prepared at 1123 K for 2 h was lower than that of the sample prepared at 1123 K for 1 h due to particle growth. The photocatalytic activity decreased with increasing sulfurization temperature from 1073 to 1173 K. Because crystal structures of La₃NbS₂O₅ prepared by different sulfurization temperatures were uniform, and morphology of La₃NbS₂O₅ prepared by different sulfurization temperatures was relatively constant. Particle growth and slightly attenuated optical absorptions with increasing sulfurization temperature were considered to be responsible for the reduced photocatalytic activities. Thus, it was all-important to control the sulfurization conditions which had an important influence on photocatalytic activity of oxysulfide La₃NbS₂O₅.

**Table 2 Rate of H₂ evolution of La₃NbS₂O₅ prepared under varying sulfurization conditions and solid-state procedure**

<table>
<thead>
<tr>
<th>Catalyst sample</th>
<th>Rate of H₂ evolution/(10⁻⁶ mol·h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNSO(1023-1)</td>
<td>3</td>
</tr>
<tr>
<td>LNSO(1073-1)</td>
<td>11</td>
</tr>
<tr>
<td>LNSO(1123-0.5)</td>
<td>7</td>
</tr>
<tr>
<td>LNSO(1123-1)</td>
<td>10</td>
</tr>
<tr>
<td>LNSO(1123-2)</td>
<td>8</td>
</tr>
<tr>
<td>LNSO(1173-1)</td>
<td>5</td>
</tr>
<tr>
<td>LNSO(SSR)</td>
<td>6</td>
</tr>
</tbody>
</table>

**4 Conclusions**

1) The oxysulfide La₃NbS₂O₅ was synthesized by sulfurization method at much lower temperatures and
significantly shortened reaction times of 1.0 h compared to conventional solid-state techniques.

2) With increasing sulfurization temperature and time, the crystallite size of La$_2$NbS$_2$O$_5$ increased gradually, and the BET area of La$_2$NbS$_2$O$_5$ decreased gradually. The optical band gaps of sulfurization synthetic La$_2$NbS$_2$O$_5$ were 2.13–2.17 eV, which were less than that (2.26 eV) of La$_2$NbS$_2$O$_5$ prepared by conventional solid-state techniques.

3) Photocatalytic activities of sulfurization synthetic La$_2$NbS$_2$O$_5$ in a 0.01 mol/L Na$_x$S$_2$–Na$_2$SO$_3$ solution were $3 \times 10^{-6}$–$11 \times 10^{-6}$ mol/h, and the maximum rate was about 1.83 times that of La$_2$NbS$_2$O$_5$ prepared by solid-state method.

References


硫氧化物 La$_3$NbS$_2$O$_5$ 的硫化合成及其光催化活性

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摘 要: 采用 H$_2$S 硫化的方法合成硫氧化物 La$_3$NbS$_2$O$_5$, 并通过 X 射线衍射(XRD)、紫外−可见漫反射(DRS)、场发射扫描电镜(FE-SEM)等技术对其进行表征和分析，研究硫化条件与光催化分解水产氢活性的关系。结果表明：与传统固相法比较，硫化法使 La$_3$NbS$_2$O$_5$ 在更低的温度和更短的反应时间(1 h)合成；合成的 La$_3$NbS$_2$O$_5$ 粒子呈规则的盘子状，粒径为 0.1−0.6 μm，粒子表面光滑；在 1073 K 硫化 1 h 制得的 La$_3$NbS$_2$O$_5$ 具有极高的产氢活性，大 约为固相法制得 La$_3$NbS$_2$O$_5$ 的产氢活性的 1.83 倍。

关键词: 硫化法；产氢；La$_3$NbS$_2$O$_5$；光催化；可见光

(Edited by Chao WANG)