Fabricant and characterization of SrWO₄ and novel silver-doped SrWO₄ using co-precipitation method: Their photocatalytic performances for methyl orange degradation

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ABSTRACT

A simple co-presipitation method has been developed to synthesize SrWO₄ and Ag°-SrWO₄ micro/nanostructures with different morphologies, including platelet-, star- and flower-like, in the presence of Na(B(C₆H₅)) as surfactant. The formation of platelet-, star- and flower-like shapes of particulate system was examined by electron microscopy technique. The products were characterized by X-ray diffraction, scanning electron microscope, UV-vis absorption, energy dispersive X-ray and fourier transform infrared spectra. The scheelite type tetragonal structure of all the synthesized compounds was revealed by powder X-ray diffraction analysis. The influence of surfactant concentration (sodium tetraphenylborate as new surfactants) on the size and morphology of products was investigated. Finally, a good photocatalytic activity was first discovered of the Ag°-SrWO₄ microcrystals for the degradation of methyl orange dye after 100 min under UV-vis light. Hence, from the present investigation it was observed that the doping of Ag in SrWO₄ will yield a new kind of multifunctional material for fabricating electronic devices.

INTRODUCTION

Alkaline earth metal tungstates with a formula of AWO₄ (A = Ca, Sr, Ba), as a member of Scheelitte-type metal tungstates, have attracted extensive interests because of their potential applications in various fields, such as optoelectronic industry, solid-state laser system, scintillator, photocatalysis, light emitting diodes (LEDs), and energy storage materials [1-8]. Strontium tungstate (SrWO₄), among various AWO₄ materials, belonging to a body-centered tetragonal system with WO₄²⁻ molecular ions loosely bound to Sr²⁺ cations, has attracted a great deal of attention in recent years because of their excellent physical properties [9]. In the structure of WO₄²⁻, a WO₄²⁻ anion with short W–O bond lengths consists of a central highly charged W ion without d electrons surrounded by four oxygen ions in a tetrahedral arrangement.

Over the years, many different routes were developed to obtain the SrWO₄ nanostructures, for example: co-precipitation [10], electrochemical [11, 12], biomimetic system of a supported liquid membrane [13], sonochemical [14], hydrothermal process [15], solvothermal-mediated micro emulsion method [16], microwave-hydrothermal [17] and cyclic-microwave [18]. The low electrical conductivity, and high recombination rate of photogenerated electron-hole pair in SrWO₄ nanostructures impede their practical applications [18]. In order to resolve these problems can
be used from deposition method of metallic nanoparticles (such as silver nanoparticle). In particular, Ag doped samples explicitly used for photocatalytic applications. The Ag nanoparticles have the unique physical and chemical properties, which are different from those of the bulk metal [19-21]. Their properties are attributed to intra-band quantum excitations of the conduction electrons [22-24], mimicking the interactions of light on metal surface via the photoelectric absorption and compton scattering.

Researchers have prepared graphene and metal ion-based hybrids, such as graphene-SrWO₄, Yb-SrWO₄, Ag⁺-CdMoO₄, Eu³⁺-SrWO₄ and Ag⁺-NiTiO₃ [6,15,22,31,24]. However, there is no record found for the Ag-doped SrWO₄ synthesized by co-precipitation method and evaluation of its photocatalytic activity for the degradation of organic pollutants under UV light, as far as our best knowledge. Herein, we will report a facile co-precipitation method for the synthesis of Ag⁺-SrWO₄ nanocomposite as photocatalyst material to achieve improved photocatalytic activity. Besides, the effect of Sr²⁺/surfactant ratio on the morphology and particle size of SrWO₄ nanostructures and Ag⁺-SrWO₄ nanocomposite was investigated. Furthermore, the as-synthesized SrWO₄ and Ag⁺-SrWO₄ was used as an efficient photocatalyst for the photocatalytic degradation of methyl orange (MO) dye within 100 min.

MATERIALS AND METHODS

Synthesis of SrWO₄ nanostructures

The SrWO₄ nanostructures were synthesized by a new simplistic co-precipitation method. In a typical synthesis procedure, 1 mmol of Na₃WO₄ was dissolved in the Na(B(C₆H₅)) (as surfactants)/H₂O (hot water, typically 70 °C) mixture with the different ratios 1:0.5, 1:0.75, 1:1, 1:1.25 and 1:1.5. Afterwards, 1 mmol of Sr(NO₃)₂ was dissolved slowly into 50 ml hot solution (50 °C) under magnetic stirring. Then, the resultant solution was heated at 70 °C for 15 min under magnetic stirring, and the obtained precipitation was dried at 70 °C for 1 h. Table 1 shows the samples preparation conditions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sr/Surfactant ratio</th>
<th>Doping agent</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:0.5</td>
<td>-</td>
<td>SrWO₄</td>
</tr>
<tr>
<td>2</td>
<td>1:0.75</td>
<td>-</td>
<td>SrWO₄</td>
</tr>
<tr>
<td>3</td>
<td>1:1</td>
<td>-</td>
<td>SrWO₄</td>
</tr>
<tr>
<td>4</td>
<td>1:1.25</td>
<td>-</td>
<td>SrWO₄</td>
</tr>
<tr>
<td>5</td>
<td>1:1.5</td>
<td>-</td>
<td>SrWO₄</td>
</tr>
<tr>
<td>6</td>
<td>1:1.5</td>
<td>Ag</td>
<td>Ag⁺-SrWO₄</td>
</tr>
</tbody>
</table>

Table 1. Reaction conditions for preparation of products.

Fig. 1. XRD patterns of: (a) SrWO₄ nanostructure (sample No. 5), and (b) Ag⁺-SrWO₄ nanocomposite.
Synthesis of Ag°-SrWO₄ nanocomposite

The Ag°-SrWO₄ nanocomposite was prepared as follows: at first, the as-prepared SrWO₄ nanoparticles from last past step were dissolved in the mixture of 50 ml of water and 1.8 g sodium tetraphenylborate (Sr²⁺/Na(B(C₆H₅)) ratio = 1:1.5) and then, the reaction mixture was stirred for 10 min to become homogenous. Subsequently, AgNO₃ solution was added to the above mixture under magnetic stirrer for 20 min at 70 °C. Then, the obtained gray powder was annealed at 500 °C for 1 h. At the end, the Ag°-SrWO₄ nanocomposite was obtained.

Photocatalytic experimental

The Photocatalytic activities of the SrWO₄ nanostructure and Ag°-SrWO₄ nanocomposite dissolved in water were measured by the decomposition of organic dye methyl orange (MO) under UV light illumination. In this case, 25 mg (5 ppm) of catalyst powder was added to 25 ml of dye aqueous solution at room temperature and then magnetically stirred in dark for 20 min before the irradiation to get absorption–desorption equilibrium between the photocatalyst and dye. The dye degradation percentage was calculated as:

\[
\text{Degradation rate (\%) = } \left(1 - \frac{A_t}{A_0}\right) \times 100
\]

where \(A\) and \(A_0\) are the obtained absorbance value of the dye solution at \(t\) and 0 min by a UV–vis spectrometer, respectively.

Materials and characterization

Sodium tetraphenylborate (Na(B(C₆H₅))), strontium...
nitrate trihydrate and silver nitrate were applied without additional purification. The XRD patterns of the products were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray (EDX). Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets.

RESULTS AND DISCUSSIONS

The XRD patterns of samples No. 5 and 6 synthesized by co-precipitation method were shown in Fig. 1. In this figure, the diffraction peaks with the (101), (112), (004), (200), (204), (220), (116) and (312) crystal plane of scheelite type tetragonal structure SrWO4 [JCPDS code 85-0587] show the as-synthesized pure SrWO4 nanostructures. The XRD pattern of Ag⁺-SrWO4 nanocomposite is similar with pure SrWO4 except for absorption intensity and precise position. In Fig. 1b, the diffraction peaks at 2θ = 38.017°, 45.342° and 65.649° are related to the Ag doped in the SrWO4 structure. In the XRD patterns of samples No. 5 and 6, only the tetragonal SrWO4 phase were observed, that confirms the incorporation of the dopant Ag⁺ ion into the SrWO4 matrix.

A large volume of research has been performed to evaluate the effects of surfactants and capping agents on the morphology and particles size of nanomaterials [25–30]. Figs. 2(a-c) and 3(a and b) show the SEM images of SrWO4 samples synthesized in aqueous solution using different Sr/surfactant ratios (1:0.5, 1:0.75, 1:1, 1:1.25 and 1:1.5, respectively). As shown in these figures, with the increasing of the surfactant concentration and decreasing of reaction speed between ions, the Sr²⁺ ions react with the WO₄²⁻ ions regularly, and product the SrWO4 nanostructures with small particle size. At first, when the surfactant concentration is low, the products connected together as flower-like microcrystal structures (Fig. 2a-c), then with the increasing of Sr/surfactant ratio to 1:1.5 (Fig. 3b), the amount of flower-like structures decreased and the platelet-like SrWO4 structures are produced. These structures have high surface/volume ratio, thus show better photocatalytic activity. Also, Fig. 3b displays a star-like SrWO4 microcrystal formed by two rice-like SrWO4 microcrystals. Fig. 4 shows a schematic representation of the synthesis and growth process of SrWO4 microcrystals synthesized by co-precipitation method in the presence of Na(B(C₆H₅)₃) as surfactant. The mineralization
process of SrWO₄ crystallites in aqueous solution can be divided into two steps: the initial nucleating step and the subsequent crystal growth process. In the subsequent stage, the crystal growth step is mainly a kinetically controlled process that finally can create small-size plate crystals with an evolution process.

Fig. 5 shows SEM image of Ag°-SrWO₄ nanocomposite synthesized using Sr/surfactant ratio of 1:1.5. As shown in this figure, with doping of silver nanoparticles into SrWO₄ structures, the Ag nanoparticles on the surface of rice- and star-like SrWO₄ crystals were formed. These nanoparticles increase the surface area of as-synthesized structures and, as a result, the photocatalytic activity is increased.

The FTIR spectra, in order to determine the chemical structure of the SrWO₄ nanostructure and Ag doped SrWO₄ in 400-4000 cm⁻¹ range are given in Fig. 6(a and b). The characteristic band at 825 cm⁻¹ is due to the stretching mode of O–W–O in the WO₄ tetrahedra, whereas the weak band around 489 cm⁻¹ is characterized by the W–O stretching vibration [31, 32]. The bands centered at 3461 cm⁻¹ and 1642 cm⁻¹ can be ascribed to O–H band stretching vibration and O–H bending vibration resulting from crystal water, respectively. Compared with pure SrWO₄, the adsorption peak of WO₄²⁻ in Ag°-SrWO₄ recedes, and the positions of some spectral peaks of Ag°-SrWO₄ show slight shift, indicating the chemical interaction between Ag and SrWO₄. The stretching and flexion mode of the Sr–O and Ag is below the 150 cm⁻¹ and 400 cm⁻¹, respectively, which is beyond the recorded range [33].

EDS analysis, is an analytical technique used for the elemental analysis or chemical characterization of a sample, also, can be used to estimate their...
relative abundance. Fig. 7 shows the EDS analysis of samples No. 1-6. The EDS analysis confirms the presence of Sr, W, and O elements (Fig. 7a-f) and demonstrates the availability of least amount of Ag in doped sample (Fig. 7f). Furthermore, it was also observed that the concentration of Na(B(C6H5)) as surfactant influences on the atomic percentage of elements. With the increasing of Sr/Surfactant ratio to 1:1.5 (Fig. 7e), the weight percentage of Sr, W and O elements reaches to 26.12, 54.79 and 19.08%, respectively, that these values are close to stoichiometric values.

Fig. 8 displays the UV-vis diffuse reflectance spectrum (DRS) of the SrWO4 samples. The DRS spectrum depicts that the product exhibited a typical optical absorption behavior of a wide-band-gap semiconducting oxide, having an intense absorption band with a steep edge [34]. The band gap of SrWO4 (sample no. 5) calculated from the main absorption edge of the profile is about 4.25 eV, which is suitable for photocatalytic water splitting under UV light irradiation.

In the photocatalytic activity studies under UV excitation, MO solution was used as organic dye and its results are given in Fig. 9. The Figs. 9a and b show the photocatalyst activity of the SrWO4 nanostructures and Ag-SrWO4 nanocomposite, respectively. The photocatalytic degradation of methyl orange (MO) in the presence of Ag-SrWO4 nanocomposite was very much higher compared
Fig. 8. UV-vis diffuse reflectance spectra of sample No. 5.

Fig. 9. (a and b) Photocatalytic activities of samples No. 5 and 6, respectively and (c) reaction mechanism of methyl orange photodegradation under UV light irradiation.

It is well known that the photocatalytic activity of photocatalyst mainly results from the photo-induced electrons and holes. During UV-irradiation for 100 min, SrWO$_4$ nanostructures show 52.2% decomposition (Fig. 9a), while the Ag$^\circ$-SrWO$_4$ nanocomposite shows 92.03% decomposition (Fig. 9b). Based on above experiments, a proposed mechanism for photocatalytic degradation of methyl orange by Ag$^\circ$-SrWO$_4$ under UV light irradiation is shown in Fig. 8c. The valence band of SrWO$_4$ consists of the hybrid orbitals of O2p as well as Sr5s and the conduction band consists of Mo4d orbital and the band gap energies between them is

to SrWO$_4$ nanostructures [35].
about 4.25 eV. Ag nanoparticles on the SrWO₄ surface, act as electron traps and enhance the electron–hole pair separation. Then the electrons on Ag nanoparticles could be transferred to the adsorbed molecular oxygen to produce super oxide free radicals (O₂⁻•) and then converted to active •OH. Similarly, holes formed on the valence band of SrWO₄ are responsible for the oxidation of dye molecules leading to the formation of various degraded products. The degradation mechanism for the Ag•SrWO₄ can be given as:

\[
\text{SrWO₄} + \text{hv} \rightarrow \text{SrWO₄} (e^-) + \text{SrWO₄} (h^+) \tag{1}
\]

\[
\text{Ag}^+ + \text{SrWO₄} (e^-) \rightarrow \text{Ag} (e^-) + \text{SrWO₄} \tag{2}
\]

\[
\text{Ag} (e^-) + \text{O}_2 \rightarrow \text{Ag}^- + \text{O}_2^- \ (\text{electron transfer}) \tag{3}
\]

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{•OOH} \tag{4}
\]

\[
\text{•OOH} + \text{H}^+ + \text{SrWO₄} (e^-) \rightarrow \text{H}_2\text{O}_2 \tag{5}
\]

\[
\text{H}_2\text{O}_2 + \text{SrWO₄} (e^-) \rightarrow \text{•OH} + \text{OH}^- \tag{6}
\]

\[
\text{SrWO₄} (h^+) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{•OH} \tag{7}
\]

\[
\text{SrWO₄} (h^+) + \text{OH}^- \rightarrow \text{•OH} \tag{8}
\]

\[
\text{O}_2^- + \text{MO} \rightarrow \text{degraded product} + \text{O}_2 \tag{9}
\]

\[
\text{•OH} + \text{MO} \rightarrow \text{degraded product} + \text{H}_2\text{O} \tag{10}
\]

Thus, the separation of the charge carriers was attributed to such trapping by Ag dopant in SrWO₄. Subsequently, enhanced the yield of •OH quantities in the degradation of methyl orange, which further improved the photocatalytic activity of Ag•SrWO₄.

**CONCLUSIONS**

In summary, SrWO₄ and Ag•SrWO₄ microcrystals were successfully synthesized by co-precipitation method at 70°C for the first time. We considered the effect of surfactant concentration on the size and morphology of products. The SEM images indicated that the microcrystals, resulting in the growth of superstructures with rice, star- and flower-like shapes, were formed via self-assembly of small nanocrystals. The products were characterized by XRD, DRS, EDS, SEM and FT-IR. The Ag doped SrWO₄ presents enhanced photocatalytic activity compared to pure SrWO₄ from 52.2 to 92.03% in 100 min under UV light irradiation.

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**CONFLICT OF INTEREST**

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

**REFERENCES**

10. Zhao X, Cheung TLY, Zhang X, Ng DHL, Yu J. Facile Preparation of Strontium Tungstate and Tungsten Trioxide Hollow Spheres. Journal of the American Ceramic Society. 2006;0(0):060623005134010-???
12. Cui C, Bi J, Gao D. Room temperature synthesis of crystallized luminescent SrWO₄ films by an adjustable galvanic cell