Structure, Properties, and Synthesis of SnWO$_4$

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stannous tungstate   photocatalysis   photoelectrocatalysis

1. Introduction

With the rapid development of technology, energy has become a necessity for social operation, and the human consumption of non-renewable traditional energy (from sources such as oil and coal) is decreasing. The energy crisis has become an urgent problem that needs to be solved. Therefore, researchers are enthusiastically looking for alternative renewable clean energy sources. Among the many potential energy sources, solar energy has attracted significant attention due to its large reserves and reproducibility. Although solar energy exhibits a variety of excellent properties, its dispersion, instability and intermittency have led to its low utilization. Therefore, exploring efficient ways to better use solar energy is necessary for the generation of alternative power. Photocatalytic and photoelectrochemical methods show promise for degrading pollutants and generating new kinds of energy (such as hydrogen and chemical) via the use of solar energy. All the relevant reactions are completed by the photo-generated holes and electrons; thus, they follow a similar principle. Since the first report of TiO$_2$ in 1972 [1], different kinds of materials with a smaller band gap than that of TiO$_2$ (3.0–3.2 eV) have been explored [2].

One of these materials is stannous tungstate (SnWO$_4$), which is a potential catalyst due to its narrow band gap, suitable band position, and nontoxicity [3]. However, due to its low charge separation efficiency and poor stability [4], its photocatalytic and photoelectrochemical performance has not met theoretical expectations. To solve this problem, many researchers are committed to obtaining a better catalytic performance and higher solar energy efficiency by means of morphology control, doping, and multi-component compositing.

2. Structure, Properties, and Synthesis of SnWO$_4$

In the 1970s, Jeitschko and Sleight reported the crystalline structure and morphology of the low-temperature (α) and high-temperature (β) phases of stannous tungstate materials [5][6]. Orthorhombic α-SnWO$_4$ exhibits a stable structure below 670 °C, and it tends to transform into cubic β-SnWO$_4$ above 670 °C [7]. A reverse transition from the β-phase to the α-phase may occur under negative pressure, and the W is replaced by Mo [8]. In the crystal of α-SnWO$_4$, W and O form WO$_6$ octahedral structures that are interconnected in four corners, while O binds to Sn in a

regular octahedral form [5]. For β-$SnWO_4$, the W atoms of β- form WO_4^{2-} tetrahedrons with O and disperse within the crystal, whereas near the Sn atoms, O is bound to it as a twisted octahedron [6].

This difference in structure leads to different properties for the α and β phases. The W-O bond in the WO_4^{2-} tetrahedron (~1.75 Å) [5] is shorter than that in the WO_6 octahedrons (~1.80–2.15 Å) [6]. It leads to a larger crystal field-splitting energy and a higher orbital energy of W in β-$SnWO_4$. The conduction band edge of the α phase is mainly composed of a W 5d orbital, while the β phase contains an Sn 5p orbital, in addition to the W 5d orbital. The valence bands of both $SnWO_4$ are formed by hybridizing the O 2p and Sn 5s orbitals, and the Sn-O bonds are almost identical in length (~2.20–2.80 Å) [5][6]. Thus, the positions of the valence bands are similar. These characteristics result in a narrower band gap for α-$SnWO_4$ (~1.7 eV) than for β-$SnWO_4$ (~2.7 eV) [3], and α-$SnWO_4$ has a wider range of light absorption and a higher theoretical photocurrent density (~17 mA cm^{-2} [9]) than β-$SnWO_4$. In addition, the β phase is a direct band gap and the α phase is an indirect band gap [3], which leads to a higher carrier separation efficiency for the α phase than the β phase [10]. Due to the wider band gap, the photo-generated electrons (holes) of β-$SnWO_4$ show a more significant reduction (oxidation) activity. Thus, β-$SnWO_4$ was used in photocatalysis, and only α-$SnWO_4$ has been used in photoelectrochemical water splitting and sulfite oxidation. However, in addition to the excellent optical properties mentioned above, the use of stannous tungstate exhibits problems that urgently need to be solved. Since Sn is divalent and oxidizable in $SnWO_4$, it is susceptible to photocorrosion, which is attributed to stannous, and the following reaction occurs: $SnWO_4 + H_2O + 2h^+ \rightarrow SnO_2 + WO_3 + 2H^+$. Therefore, $SnWO_4$ has poor stability, which limits its performance in practical applications [4]. At the same time, a recombination of carriers occurs in the diffusion process of $SnWO_4$. Its diffusion length is short, which limits the number of photo-generated carriers that can arrive at the surface of the crystal, leading to unsatisfactory photocatalytic and photoelectrochemical performance.

Various methods have been developed to synthesize $SnWO_4$ materials, and their differences in thermodynamic stability lead to changes in the synthesis of α-$SnWO_4$ and β-$SnWO_4$. Because the α phase is a kind of crystalline phase at low temperatures, its synthesis conditions are milder. Many methods can be used to synthesize the α phase, e.g., hydrothermal methods, solid–solid reaction methods [3][11][12][13], and magnetron sputtering methods [10][14][15]. Each synthesis method has its own advantages. The hydrothermal method can be used to obtain crystals with a complete crystal phase, small particle size, and uniform distribution. A magnetron sputtering method can obtain dense and uniform high-quality thin films. The solid–solid reaction method possesses a simple process and a large output. However, the synthesis of the high-temperature crystalline β-phase is relatively harsh because it requires higher temperature conditions (which should be obtained by rapid cooling at more than 940 K). It has been reported that most β-$SnWO_4$ powders are synthesized with a high-temperature solid phase method [11][12][16][17]. β-$SnWO_4$ can also be obtained by using $NaWO_4$ as a raw material through kinetic control under more mild conditions [18]. Jan Ungelenk and Claus Feldmann synthesized β-$SnWO_4$ using a microemulsion method at low temperatures [19]. When W and O combine to form a discrete WO_4^{2-} tetrahedron in $NaWO_4$, the structure is similar to that of β-$SnWO_4$, so Na_2WO_4 is likely to be directly converted to β-$SnWO_4$. Additionally, assisted by hydrothermal [20][21] and microwave-assisted hydrothermal methods [22], α-$SnWO_4$ can also be synthesized using $NaWO_4$ and $SnCl_2$ as the precursors.

To synthesize the film for photoelectrochemical water spliting, an indirect or direct coating method can be used. In indirect coating, as-prepared SnWO$_4$ powders are drop-cast onto conductive substrates. This is an easy-to-perform method, but the performance of the photoanode is weak due to the poor charge transfer caused by bad connections between the particles. For direct coating, Moritz Kölbach et al. employed a pulsed laser-deposited method that used an α-SnWO$_4$ target formed by annealing WO$_3$ (99.99%) and SnO (99.99%) powders [23]. Bozheyev et al. reported on the use of a magnetron co-sputtering method in which Sn (99.99%) and W (99.95%) were the targets, and the deposition was performed with the existence of O$_2$ [24]. Recently, Gottesman used a new method—rapid thermal processing—to synthesize an α-SnWO$_4$ film. The technique could be used to treat a sample at higher temperatures, without destroying the glass-based F:SnO$_2$ (FTO), and a desired crystallinity with few defects was obtained [25]. Liu et al. used a chemical vapor deposition to convert WO$_3$ into α-SnWO$_4$, and the reaction is shown in Equation (1) [26]. An in situ hydrothermal conversion method was also reported, in which WO$_3$ was used as a precursor to react with Sn^{2+} in the solution [27]. The possible reactions occurring in this method are illustrated as Equations (2)–(3) [28]. As a result, the α-SnWO$_4$ film exhibits similar nanostructured array morphology to that of WO$_3$ films due to the inherited behavior (**Figure 1**) [28]. The anion in hydrothermal conversion solutions may also affect the morphology of α-SnWO$_4$ films [29].

$$4WO_3 + 3SnCl_2 \rightleftharpoons 3SnWO_4 + WCl_6 \ (1)$$

$$WO_3 + H_2O \rightleftharpoons 2H+ + WO_4^{2-} \ (2)$$

$$WO_4^{2-} + Sn^{2+} \rightleftharpoons SnWO_4 \ (3)$$
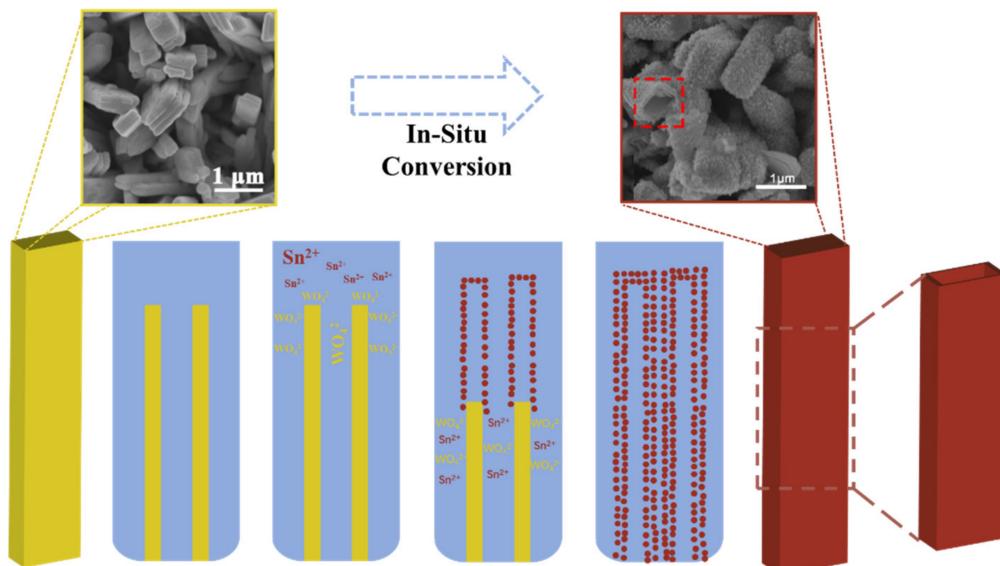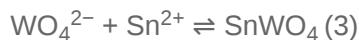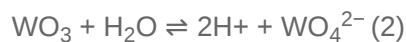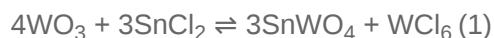
Figure 1. Schematic for in situ conversion from a rod-like WO$_3$ array to a rod-like SnWO$_4$ [28].

Generally speaking, SnWO$_4$ has good optical properties, such as a narrow band gap and a special band structure, which results in excellent application prospects for the fields of photocatalysis and photoelectrocatalysis (especially in the field of water splitting). However, it is necessary to pay attention to the instability and short carrier diffusion

length of the material itself. Furthermore, because of the differences in crystal structure and band structure between the two crystal phases (α phase and β phase), their properties and synthesis methods are different. For instance, the photo-generated electrons (holes) of the β phase have more significant reduction (oxidation) activity than that of the α phase, so the β phase is suitable for photocatalytic degradation. The α phase has a wider light absorption range and higher carrier separation efficiency, so it has potential for use in photoelectrocatalysis.

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