Solar Hydrogen Production from Cost Effective Stannic Oxide Under Visible Light Irradiation

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Abstract

Visible-light-driven stannic oxide was synthesized by facile one-pot solvothermal method from SnCl₂·2H₂O and methanol. The as-prepared powder was identified by XRD as the low crystalline phase of SnO₂, and its absorption edge reached about 530 nm, presenting good potential to respond to visible light. Under visible light irradiation (λ > 420 nm), the as-prepared tin oxide showed good anodic photocurrent effects on FTO photoelectrode, and showed hydrogen and oxygen evolution activities under electron donor (methanol) and acceptor (AgNO₃), respectively, even without any co-catalyst loading. The visible-light-driven mechanism for this SnO₂-x maybe ascribed to Sn²⁺ self-doped into Sn⁴⁺ and formed an energy gap between the band gap of SnO₂.

Keywords: Photocatalyst, Water splitting, Stannic oxide, Photoelectrochemical

Introduction

Acquisition of clean hydrogen energy by splitting of water using plentiful solar energy is considered as an ideal way to resolve the global renewable energy demand and environment problems [1–4]. In particular, photocatalytic or photoelectrochemical splitting water is one of the most ideal ways considering resource sustainability, environmental, and cost issues [5, 6]. The urgent work for water splitting by photocatalysis is to design and develop semiconductor photocatalysts with appropriate band gap to make best use of solar energy and band edges to meet oxidation and reduction water requirement as well as high quantum yield and high stability [7]. Up to now, the development of photocatalysts experienced from binary oxides (TiO₂, ZnO, Fe₂O₃) [8], ternary oxides (SrTiO₃, K₂Nb₆O₁₇, NaTaO₃) [9], to multi elements compounds (K₂Ce₂MₓO₃₀ (M = Ta, Nb)) [10], especially solid solution compounds (Ga₃N₅O, ZnGeN₂-ZnO) [11], and series of (oxy) nitrates (Ta₃N₈, TaON, LaTiO₂N) [12, 13], (oxy) sulfides (Sm₃Ti₂SₓO₉, Cu₂ZnSnS₄) [14] based on band engineering methods, as well as from p block photovoltaic cell semiconductors candidates such as GaInP/GaAs, GaPN, GaAsPN, p-InGaN, etc. [15]. Additionally, the morphologies of film or powder with nanowire, nanorod/nanotube, and nanobel etc. are extensively controlled [16]. Unfortunately, most of them failed to satisfy the mentioned above requirements simultaneously.

SnO₂ is a well-known semiconductor with band gap about 3.6–3.8 eV. However, wide band gap and low conduction band edge (more positive than that of H⁺/H₂) of SnO₂ restrict its utilization as a photocatalyst for water splitting [17]. In the most cases, SnO₂ was used as a part of composite or coupled photocatalysts, such as in SnO₂-TiO₂ [18], SnO₂-ZnO [19] for its lower conduction band edges to facilitate the transferring photo-generated electrons from the host photocatalyst.

In this communication, visible-light-driven SnO₂-x was synthesized by facile one-pot solvothermal method from the precursors of SnCl₂·2H₂O. The as-prepared powder was identified through X-ray diffraction (XRD) as pure SnO₂ phase, and ultraviolet–visible spectroscopy (UV-vis) spectrum indicated its absorption edge about 570 nm, corresponding to band gap of 2.17 eV, presenting good potential to respond to visible light. The photoelectrochemical and photocatalytic water splitting activities under visible light were presented.
Methods
Reagents
All chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, and used as received without further purification. The super pure water (18.25 MΩ cm) was used as solvent for photoelectrode preparation and photocatalytic measurement.

Preparation of Powder SnO_{2-x}
SnO_{2-x} was prepared by conventional solvothermal method with 0.02 mol SnCl\_2·2H\_2O (SnCl\_4·5H\_2O) dissolved into 100 mL methanol solvent and stirring for 30 min. Then, adjusting the pH value from initial 1.0 to 3.0 by dipping 0.02 mol/L NH\_3·H\_2O slowly with stirring, getting white floccule. After reacting for 2 h, the mixture was transferred into a 200 mL Teflon-lined autoclave and heated at 423 K for 20 h. The yellow slurry was obtained from washing with deionized water and ethanol several times, and dried at 343 K for 12 h, got the targeted sample.

Preparation of SnO\_2-x Electrode
Porous thin film electrodes were prepared by electrochemical deposition method on conductive fluorine-doped tin oxide glass (FTO, Ahahi Glass Co.). The electrochemical deposition was carried out in an acetone solution (40 mL) containing as-prepared powder (40 mg) and iodine (15 mg), which was dispersed by sonication treatment. As an example, this sample prepared by SnCl\_2·2H\_2O with methanol as solvent and adjusted pH value to 3.0 by NH\_3·H\_2O, XRD pattern identified its pure SnO\_2 phase with poor crystalline (Fig. 1a), and UV-vis spectrum (Fig. 1c) revealed its absorption edge is about 570 nm, corresponding to band gap of 2.17 eV, showing great potential to response to visible light. While for these SnO\_2 from precursors of SnCl\_2·5H\_2O and SnCl\_4·5H\_2O with SnCl\_2·2H\_2O (molar ration 1:1) under the same procedures above, their absorption edges are almost the same at about 370 nm. Moreover, with the precursor SnCl\_4·5H\_2O, we cannot get visible-light-driven SnO\_2 by co-precipitation method in air and by hydrothermal method in water. Furthermore, for precursor SnCl\_2·2H\_2O in methanol solvent, with the increase of pH value, the obtained powder became the mixture of SnO\_2 and SnO (Fig. 1b). The XPS of the as-prepared powder was measured by X-ray powder diffraction on Geiger-flex RAD-B, Rigaku; Cu K\_α). Scanning electron microscopy (SEM) images were obtained on field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi). UV-vis diffuse reflectance spectrum was recorded by spectrophotometer (JASCO, V-670). The Brunauer-Emmett-Teller (BET) surface area was measured using a BELSORP-mini instrument (BEL Japan) at 77 K. The elements and valence states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Fisher K-Alpha, America). Transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) images of samples were performed on Tecnai G2 F20 transmission electron microscopy at 200 kV accelerating voltage.

Results and Discussion
The as-prepared powder was identified by XRD patterns. The compositions, absorption properties, and crystallite of as-prepared samples closely depended on the preparation conditions, such as tin precursors (SnCl\_2·2H\_2O, SnCl\_4·5H\_2O), pH values, and consequently further heat treatment. As an example, this sample prepared by SnCl\_2·2H\_2O with methanol as solvent and adjusted pH value to 3.0 by NH\_3·H\_2O, XRD pattern identified its pure SnO\_2 phase with poor crystalline (Fig. 1a), and UV-vis spectrum (Fig. 1c) revealed its absorption edge is about 570 nm, corresponding to band gap of 2.17 eV, showing great potential to response to visible light. While for these SnO\_2 from precursors of SnCl\_2·5H\_2O and SnCl\_4·5H\_2O with SnCl\_2·2H\_2O (molar ration 1:1) under the same procedures above, their absorption edges are almost the same at about 370 nm. Moreover, with the precursor SnCl\_4·5H\_2O, we cannot get visible-light-driven SnO\_2 by co-precipitation method in air and by hydrothermal method in water. Furthermore, for precursor SnCl\_2·2H\_2O in methanol solvent, with the increase of pH value, the obtained powder became the mixture of SnO\_2 and SnO (Fig. 1b). The XPS of the as-prepared powder was measured to characterize the elemental compositions and chemical states, as shown in Fig. 2. The survey scan spectra (Fig. 2a) of the SnO\_2 and SnO\_2-x (SnCl\_2·5H\_2O as precursor) sample clearly indicate the obvious peaks of Sn, C, and O. Figure 2b showed that the binding energy of Sn 3d in SnO\_2-x decreased by 0.2 eV as compared to pure SnO\_2 (from 486.9 to 486.7 eV for Sn 3d\_5/2) and from 495.4 to 495.2 eV for Sn 3d\_3/2. As shown in Fig. 2c, the Sn 3d\_5/2 signal of SnO\_2-x sample centered at 486.7 eV can be deconvoluted by the
multi-Gaussian function into two parts centered at 486.8 and 485.8 eV assigned to Sn $^{4+}$ and Sn $^{2+}$, which confirmed the presence of Sn$^{2+}$ dopants in the prepared SnO$_2$-$x$ because of the formation of oxygen vacancies which (cut down) the binding energy of Sn 3d to preserve charge neutrality [20]. Figure 2d showed that O 1s transition peak shifted 0.2 eV (from 530.6 to 530.4 eV) upon self-doping of Sn$^{2+}$, and the formation of oxygen vacancies was also considered to enhance the absorption.

Fig. 1 XRD patterns of prepared SnO$_2$ a with different precursors, b different pH values of SnCl$_2$·2H$_2$O as precursor (JCPDS#72-1147 and 85-0712 of SnO$_2$ and SnO), and c UV-vis DRS spectra with different precursors

Fig. 2 Survey XPS spectra (a), the Sn 3d XPS spectra (b), the O 1s XPS spectra (d) of SnO$_2$ and prepared SnO$_2$-$x$, and c the Sn 3d$_{5/2}$ XPS spectra of prepared SnO$_2$-$x$. 
in the visible-light region \([21, 22]\). The optical absorption properties of prepared \(\text{SnO}_2\) as different precursors were studied by UV-vis DRS spectroscopy (Fig. 1c). The visible light response ability of prepared \(\text{SnO}_2\) by \(\text{SnCl}_2\cdot2\text{H}_2\text{O}\) as precursor was attributed to the incorporation of \(\text{Sn}^{2+}\) into the lattice of \(\text{SnO}_2\) \([20]\). These obvious differences in control preparation conditions indicated that the visible-light-driven mechanism for as-prepared \(\text{SnO}_2\) had great relation with \(\text{Sn}^{2+}\) species in oxygen inefficient situation.

The microstructure of prepared \(\text{SnO}_2\) was obtained by SEM, TEM, and HRTEM. The SEM images illustrated regular spherical particle in diameter of about \(1–2\ \mu\text{m}\) (Fig. 3a, b), while their BET surface areas are about \(100 \text{ m}^2/\text{g}\), and the crystal size is about \(2.5\ \text{nm}\) from BET measurement, which is consistent with that from calculation by Scherrer equation. As shown in Fig. 3c, we can see that prepared \(\text{SnO}_2\) showed regular spherical particle consisted with SEM image. The HRTEM image (Fig. 3d) indicated that the lattice fringes measured with a spacing of \(0.33\ \text{nm}\) were clearly visible, corresponding to the \((110)\) atomic plane of \(\text{SnO}_2\) with a tetragonal cassiterite phase.

The photocurrent effect on as-prepared \(\text{SnO}_2\) electrode under visible light \((\lambda > 420\ \text{nm})\) was shown in Fig. 4a. For this photoelectrode without any treatment, although there showed obvious photoanodic current, a N-type semiconductor responsive characters, the photocurrent properties are not so normal in slow increase and decrease responsive to light on and off, which may be ascribed to the surface capacity effect. For this with further heat treatment at \(150\ \text{°C}\) in air, there showed not only the increase of current density, but also the improvement of its photocurrent properties. From Fig. 4a, the as-prepared \(\text{SnO}_2\) posed with onset potential less than \(0\ \text{V}\) Vs reversible hydrogen electrode (RHE), that is to say, the as-prepared \(\text{SnO}_2\) with conduction band located negative than that of \(\text{H}^+/{\text{H}_2}\), indicating that the as-prepared \(\text{SnO}_2\) can split water without bias potential. To make certain the potential of the band edges for as-prepared \(\text{SnO}_2\), the photocatalytic water decomposition in powder for half reaction under visible light was carried out in a gas circular system. As shown in Fig. 4b, c, the as-prepared \(\text{SnO}_2\) demonstrated obvious \(\text{H}_2\) and \(\text{O}_2\) evolution activities under visible light irradiation\((\lambda > 420\ \text{nm})\) with the presence of
electron donor (methanol) and acceptor (AgNO₃) respectively even without any co-catalyst loading and modification. And with the loading of Pt (1 wt.%) by in-situ photo-deposition method from H₂PtCl₆, the activities were prompted greatly. The hydrogen and oxygen evolution activities under visible light further confirmed that the as-prepared SnO₂₋ₓ poses appropriate band edges to meet the requirement for water redox reaction. The wavelength dependence on photocurrent (Fig. 4d) showed good agreement with absorption edge, indicating the band transition properties. The photocurrent density of prepared SnO₂₋ₓ time dependance was measured under visible-light irradiation at a bias potential of 0.6 V Vs RHE (Fig. 4e). After 10,000 s of irradiation, the photocurrent density is slowly reduced to zero. It can be found that the stability of prepared SnO₂₋ₓ is poor which is due to the oxidation of Sn²⁺.

SnO₂, a known wide band-gap semiconductor, phases with different oxygen composition. Non-stoichiometry of SnO₂, in particular oxygen deficiency or impurity dopants, can donate electrons into the conduction band, and the conduction band is a single band of s-type character that is strongly dispersed with a minimum at the T-point of the Brillouin zone, which make it a good electron conduction [23]. Additionally, for these visible-light-driven Sn²⁺ including compounds Sn₂Nb₂O₇ (SnNb₂O₆), and Sn²⁺ ion-exchange Sn²⁺/K₄Nb₆O₁₇, Sn²⁺/KTiNbO₅, it was ascribed that the Sn 5s² contributes to the top of the valence band, and locates in about 0.7~1.4 eV negative than that of O 2p [24]. So here, for as-prepared SnO₂₋ₓ...
the visible-light-driven mechanism maybe ascribed to the energy levels that are formed between Sn$^{2+}$ 5s orbital and O 2p orbital. On the other hand, the valence state of Sn$^{2+}$ is more negative than that of Sn$^{4+}$ (illustrated in Scheme 1) resulting in doping in the lattice that will cause charge imbalance to form oxygen vacancies, which has an effect on the surface properties and charge transfer of the catalyst.

### Conclusion

Cost-effective stannic oxide photocatalyst has been successfully synthesized by facile one-pot solvothermal method from SnCl$_2$-2H$_2$O and methanol. It is significant to show visible light responsive ability and photoelectrolysis water decomposition activities. The visible-light-driven mechanism for this SnO$_2$-$x$ maybe ascribed to self-doping by Sn$^{2+}$ generating oxygen vacancies to preserve charge neutrality which can enhance the performance of photocatalyst. Further work focusing on the improvement of activities and stability are under investigations.

### Abbreviations

BET: The Brunauer-Emmett-Teller; CB: The conduction band; E$_{\text{red/ox}}$: E (Ag/ AgCl) + 0.0591 pH + 0.197; FTO: Fluorine-doped tin oxide glass; HRTEM: High-resolution transmission electron microscopy; RHE: Reversible hydrogen electrode; SEM: Scanning electron microscopy; TCD: Thermal conductivity detector; TEM: Transmission electron microscope; UV-vis: Ultraviolet–visible spectroscopy; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction

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### Authors’ Contributions

These authors contributed equally. All authors read and approved the final manuscript.

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### Availability of Data and Materials

All data generated or analyzed during this study are included in this published article.

### Competing Interests

The authors declare that they have no competing interests.

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