Short Communication

Porous Tin Oxide Nanoplatelets as Excellent-Efficiency Photoelectrodes and Gas Sensors

Yi-Zhou Zhang\textsuperscript{1,2}, Huan Pang\textsuperscript{2,*}, Yanqiu Sun\textsuperscript{3}, Wen-Yong Lai\textsuperscript{*}\textsuperscript{1}, Ang Wei\textsuperscript{1}, Wei Huang\textsuperscript{*}\textsuperscript{1}

\textsuperscript{1} Key Laboratory for Organic Electronics & Information Displays (KLOEID), Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications (NUPT), Nanjing 210046, China
\textsuperscript{2} College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang, 455000, Henan, P. R. China.
\textsuperscript{3} College of nano science & technology, Soochow University, Suzhou, 215006, Jiangsu, P. R. China.
\textsuperscript{*}E-mail: iamwylai@njupt.edu.cn; iamwhuang@njupt.edu.cn; huanpangchem@hotmail.com

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Porous SnO\textsubscript{2} nanoplatelets are successfully synthesized by calcinations of SnS\textsubscript{2} nanoplatelets. Interestingly, the measurement of dye-sensitized solar cells shows that porous SnO\textsubscript{2} nanoplatelets is a good candidate of photoelectrode materials in dye-sensitized solar cells with large improvement in photoconversion efficiency. More importantly, the as-prepared porous SnO\textsubscript{2} nanoplatelets also exhibit good gas-sensing properties to ethanol.

Keywords: Porous SnO\textsubscript{2} nanoplatelets; Dye-sensitized solar cells; Gas-sensing

1. INTRODUCTION

Recently, many efforts have been devoting to synthesize various micro-nanostructures, such as nanodots, nanorods, nanowires, nanoplates, nanospheres and three-dimensional ordered superstructures, due to their interesting properties of such micro-nanostructures and their potential applications in lots of fields [1-6], including catalysis [7], optoelectronics [8], lithium-ion batteries [9], drug delivery system [10], sensors [11, 12] and antibacterial agent [13, 14]. However, methods to manipulation of these ordered structural materials have often need surfactants [15-17], copolymers [18, 19], and porous alumina as templates. Patterned-metal-catalyzed routes have also been used [20-22]. However, the main drawback of these methods is the need for complete template removal, otherwise impurities will exist in the final products [23-27]. Controlled solution-growth synthesis routes for the
growth of inorganic materials are attractive because of the simplicity of the synthesis process. Therefore, there is significant interest in developing spontaneous generation of novel patterns with tailored structures and shapes by facile, hard template-free, solution-based, morphology controlled approaches to building novel self-generated micro-nanostructures.

Tin oxide (SnO$_2$), an $n$-type semiconductor with a wide band gap ($E_g = 3.6$ eV, 300 K), is a promising candidate for the future generation of cost-effective photovoltaic solar cells in the field of dye-sensitized solar cells (DSSCs). [28–32] SnO$_2$ possesses remarkable receptivity variation in gaseous environment and excellent chemical stability, and is widely used in chemical sensors, dye-sensitized solar cells and transparent conductors. [33, 34] Because SnO$_2$ has a lower isoelectric point (iep, at pH 4–5) than anatase TiO$_2$ (iep at pH 6–7), which leads to less adsorption of the dye with acidic carboxyl groups (for example, (Bu$_4$N)$_2$[Ru(Hdcbpy)$_2$(NCS)$_2$] (N719)), [35] SnO$_2$-based DSSCs were developed with less success, and the conversion efficiencies of SnO$_2$ photoelectrodes reported so far are much lower than those of TiO$_2$ in the past decade. [36, 37]

Recently, besides SnO$_2$-based film sensors, many SnO$_2$ nanostructured materials are used as gas sensors by researchers. [38–41] The large surface area of SnO$_2$ nanomaterials is crucial for light harvesting and gas absorbing, thus porous SnO$_2$ nanomaterials hold great promise as photoelectrodes and gas sensors. However, to date, there are few reports about synthesis of porous SnO$_2$ nanomaterials and successful application in photoelectrodes or gas sensors.

In this article, we report an easy route to synthesize porous SnO$_2$ nanoplatelets. The measurement of DSSCs shows that porous SnO$_2$ nanoplatelets is a good candidate of photoelectrode materials in DSSCs with large improvement in photoconversion efficiency. The as-prepared porous SnO$_2$ nanoplatelets exhibited good gas-sensing properties to ethanol.

2. EXPERIMENT

2.1. Synthesis of SnS$_2$ nanoplatelets and porous SnO$_2$ nanoplatelets.

![Scheme 1](image)

Scheme 1. A simple route of synthesis porous SnO$_2$ nanoplatelets.

All chemicals were analytical grade and used as received without further purification. Deionized water was used throughout. Scheme 1 shows the simple route of our work. Firstly, 0.2 g
sodium diethyldithio carbarnate, 0.16 g SnCl$_4$, were mixed in 10 mL deionized water and 10 mL ethanol, then the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 200 °C for 12 h. After the reaction was completed, the resulting products were filtered off, washed with absolute ethanol and distilled water several times, and then dried in the air; porous SnO$_2$ nanoplatelets can be obtained by calcining 0.05 g thus prepared SnS$_2$ nanoplatelets at 450 °C for 1 h in the air.

2.2. Characterization.

The morphology of the as-prepared samples was observed by a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) at an acceleration voltage of 10.0 kV. The phase analyses of the samples were performed by X-ray diffraction (XRD) on a SHIMADZU, XRD-6000 with Cu K$_\alpha$ radiation (\(\lambda = 1.5418 \text{ Å}\)). Transmission electron microscopy (TEM) images, HRTEM image and the corresponding selected area electron diffraction (SAED) pattern were captured on the JEM-2100 instrument microscopy at an acceleration voltage of 200 kV.

2.3 Solar Cell Electrolyte.

The electrolyte solutions were freshly prepared immediately before each set of experiments as previously reported. [42] The electrolyte, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (made in house), 0.1 M LiI (Lancaster), 0.05 M I$_2$ (Lancaster), and 0.5 M 4-tert-butylpyridine (Aldrich) in acetonitrile, was introduced into the cell via a vacuum filling method.

2.4 Photoelectrochemistry.

The photoanode consisted of colloidal SnO$_2$ deposited upon an FTO substrate sensitized with either Ru(deeb)(bpy)$_2$(PF$_6$)$_2$, Ru(deeb)$_2$(dpp)(PF$_6$)$_2$, or Ru(deeb)$_2$-(bpz)(PF$_6$)$_2$. The counter electrode consisted of an FTO substrate with a thin Pt coating. Measurements were performed in a two electrode cell at room temperature using the I$_3^-/I^-$ redox mediator, and at 0 °C for the (SeCN)$_2$/SeCN$^- \text{ and }$ (SCN)$_2$/SCN redox mediators, with preparation methods discussed elsewhere. [42] A 150 W Xe lamp coupled to a f/2 0.2 m McPherson monochromator was used for incident photon-to-current efficiency (IPCE) measurements. The 488 nm laser line of an Innova argon ion laser was used as the excitation source for photocurrent density vs photovoltage and for irradiance-dependent measurements. Plasma lines were removed using a 488 nm notch filter, and the flux was attenuated using a beam collimator. Incident irradiances were measured using an S370 UDT optometer. Photocurrents and photovoltages were obtained using a Keithley 617 electrometer and a Keithley 199 System DMM/Scanner, respectively.
2.5. Structure and Preparation of the Sensor Device

The structures of the sensor device and the measurement system are the same as in the report. [43] The as-prepared porous SnO$_2$ nanoplatelets were directly coated on the outer surface of the ceramic tube and dried in air, then calcined at 350 °C for 3 h. The sensor response was defined as $S = \frac{R_{\text{air}}}{R_{\text{gas}}}$, where, $R_{\text{air}}$ is the resistance in dry air and $R_{\text{gas}}$ is that in the dry air mixed with detected gases.

3. RESULTS AND DISCUSSION

3.1. Structures and Morphologies of as-prepared SnS$_2$ nanoplatelets and porous SnO$_2$ nanoplatelets

XRD patterns in Figure 1a show the diffraction peaks of the as-prepared SnS$_2$ nanoplatelets (JCPDS-831705). The diffraction peaks are sharp enough, from which we can conclude that as-prepared SnS$_2$ nanoplatelets crystallize well.

![XRD patterns and SEM images](image)

**Figure 1.** a) XRD patterns of SnS$_2$ nanoplatelets and SnO$_2$ porous nanoplatelets; b) SEM image of SnS$_2$; c) SEM of SnO$_2$ porous nanoplatelets, and d) Corresponding TEM images, (in inset of d SAED and HRTEM).

The diffraction peaks of SnO$_2$ (JCPDS 77-0450) turned wider after the removal the S atom by being calcined at 450 °C for 3 h in the air, which can be attributed to the small crystallite size of SnO$_2$
nanoparticles (JCPDS 77-0450). The morphologies of the samples are measured by FSEM, TEM (HRTEM). Figure 1b is the SEM image of the SnS$_2$ nanoplatelets, they are hexagon and have smooth surfaces. The width of each SnS$_2$ nanoplatelets is about 400-500 nm.

**Figure 2.** a) $I$-$V$ characteristics of the DS made from porous SnO$_2$ nanoplatelets at an illumination intensity of 1000 Wm$^{-2}$ 1.5 AM; b) Schematic diagram illustrating the energy levels of SnO$_2$ and excited energy levels of the Ru-dye.

After being calcined in the air, the SnS$_2$ nanoplatelets transform into porous SnO$_2$ nanoplatelets completely, which can be proved by the XRD pattern (Figure 1a). The porous SnO$_2$ nanoplatelets maintain the morphologies of the SnS$_2$ nanoplatelets well and have the same width as the SnS$_2$ nanoplatelets (Figure 1c). Unlike the SnS$_2$ nanoplatelets, the porous SnO$_2$ nanoplatelets have coarse surfaces. From Figure 1d, we can see that the porous SnO$_2$ nanoplatelets are composed of many SnO$_2$ nanocrystals. These nanocrystals do not felsite and form many mesopores observed in the porous SnO$_2$ nanoplatelets. In the inset of Figure 1d are the corresponding SAED and HRTEM of the porous SnO$_2$ nanoplatelets (the Figure 1d), which show the polycrystalline nature of porous SnO$_2$ nanoplatelets and good crystallinity of each SnO$_2$ nanoparticle, in good consistency with XRD pattern (Figure 1a).

### 3.2 Dye-sensitized Solar Cells Measurement of the Porous SnO$_2$ Nanoplatelets

The CB and VB potentials of SnO$_2$ and excited levels of the Ru-dye are shown in Figure 3a. With the absorption of light, the electron in the dye excited level can be transferred to the CB of SnO$_2$. Once the electrons are transferred to the CB of SnO$_2$ from the excited dye, the electrons traverse effectively. The overall photoconversion efficiency ($\eta$) of the porous SnO$_2$ nanoplatelets DSSC is 3.5 %, remarkably about two times higher than those of SnO$_2$ multilayered hollow microspheres ($\eta=1.4$%), and more than two times higher than those of nano-SnO$_2$ ($\eta=1.0$%) DSSCs. [44] The improvement in $\eta$ value of the porous SnO$_2$ nanoplatelets might be caused by the higher high surface area, leading to better adsorption of dye and increased light absorption by the porous SnO$_2$ nanoplatelets structure.
3.3. Gas-Sensing Properties of the Porous SnO$_2$ Nanoplatelets

Figure 3 shows the ethanol sensing performance of the porous SnO$_2$ nanoplatelets. Ethanol gas sensing was measured in a closed chamber, and the sensing test was performed at 300 °C. Figure 3a shows the response and recovery characteristics of the porous SnO$_2$ nanoplatelets before and after being exposed to ethanol. $R_{\text{gas}}$ and $R_{\text{air}}$ are the resistance values of the sensors in mixed ethanol–air vapor and in air, respectively. The sensing properties are reproducible; the sensors show almost exactly the same response whether they are exposed to ethanol gas or not (Figure 3a). Figure 3b shows the sensing properties of our sample and SnO$_2$ nanoparticles commonly used in gas sensing, we can find that porous SnO$_2$ nanoplatelets have higher sensitivity; the value of $R_{\text{air}}/R_{\text{gas}}$ of our sample obtained at 20 ppm ethanol gas is almost the same as the $R_{\text{air}}/R_{\text{gas}}$ value obtained at 30 ppm ethanol gas for the commonly used SnO$_2$ nanoparticles. Beside, the response of the porous SnO$_2$ nanoplatelets is steady, which can be explained by the large absorption volume of SnO$_2$ nanoplatelets.

4. CONCLUSIONS

Porous and polycrystalline SnO$_2$ nanoplatelets were prepared by using SnS$_2$ nanoplatelets as a template. The porous SnO$_2$ nanoplatelets exhibit excellent photoconversion efficiency and high sensitivity and good reversibility toward ethanol gas. The good photoconversion efficiency and gas-sensing properties were attributed to the small size of SnO$_2$ nanoparticles and the porous microstructure of the SnO$_2$. This simple synthetic route to porous nanomaterials sheds light on the synthesis of many other metal oxides with similar structure.

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