Materials Research Express

PAPER

SnO$_x$@β–SnO heterostructures and their enhanced photocurrent in photoelectrochemical cell

Qian Zheng $^{1,}$ Xianghua Zeng $^2$ @, Weiwei Xia $^1$, Qihong Lu $^1$, Jiawei Sun $^1$ and Min Luo $^1$

$^1$ College of Physics Science and Technology & Institute of Optoelectronic Technology, Yangzhou University, Yangzhou 225002, People’s Republic of China

$^2$ College of Electrical, Energy and Power Engineering, Yangzhou University, Yangzhou 225127, People’s Republic of China

E-mail: xhzeng@yzu.edu.cn

Keywords: SnO$_x$@β–SnO, Sn$^{2+}$ doped, photoelectrochemical cell, photocurrent, heterostructure

Abstract

To improve the effective separation of the photogenerated electrons and holes, SnO$_x$@β–SnO composites on titanium meshes were prepared by using a standard one-step hydrothermal procedure. As photoanodes in photoelectrochemical cell, the SnO$_x$@β–SnO composites exhibited a photocurrent density of 150 μA cm$^{-2}$ at 0.0 V versus Ag/AgCl under visible light illumination. The improved photocurrent can be explained as, the Sn$^{2+}$ 5s impurity states in SnO$_2$ have a band gap energy of 2.24 eV, SnO$_x$@β–SnO composites construct a type-II heterojunction. And titanium meshes have a good conductivity, which is beneficial to transferring electron from the conduction band of SnO$_2$ to external circuit. Furthermore, the SnO$_x$@β–SnO heterostructures have a larger electrochemical specific surface area, and stronger light absorption from 350–800 nm.

Introduction

Photoelectrochemical cell has attracted many attentions due to its potential applications in the renewable energy. But the improvement of the energy conversion, and charge separation efficiency, as well as the catalyst stability is still a challenge, where people have made many efforts to deal with. Semiconductor heterostructures were regarded as the suitable photocatalysts, as these structures can efficiently enhance the charge transfer and separation.

Tin oxides, with three ordinal types, SnO$_2$ and SnO, and Sn$_3$O$_4$ can be applied in water splitting, supercapacitor [1] and phototransistor [2]. SnO$_2$ with a wide band gap has an excellent photocatalytic activity restricted only to UV light region. Because of the existence of defect in SnO$_2$ nanomaterials, we can prepare SnO and Sn$_3$O$_4$, which will be beneficial to the visible light absorption. Therefore SnO$_x$/SnO$_2$ heterostructures were prepared to study the photocatalytic activity or gas sensitivity. For example, Sn$_3$O$_4$/SnO$_2$ heterostructures were used as gas sensor [3], SnO$_x$/Sn$_3$O$_4$ heterostructures were used as photocatalyst [4]. And SnO$_x$ compounds were used as active oxygen reduction reaction (ORR) catalysts to promote reaction kinetics [5]. And SnO$_x$/SnO$_2$ heterojunctions assembled from ultrathin nanosheets showed improved properties of gas sensors [6–8].

As the structure phases of the catalysts are tightly related to the energy conversion, and charge separation efficiency, it is important to study theirs effects on photocurrent. The phase changes of SnO$_2$ to Sn$_3$O$_4$/SnO$_2$ to SnO/SnO$_2$ were reported via changing precursor initial pH [9], but there is no discussion on the photocurrent, nor on SnO/SnO$_2$ related water splitting. Recently, Zaraska et al prepared porous anodic SnO$_2$/SnO$_x$ films under different sets of annealing conditions and obtained a maximal photocurrent density of 30 μA cm$^{-2}$ with a UV illumination light [10]. And Tian et al [11] prepared SnO and Sn$^{4+}$–SnO nanosheets with a solvothermal method. The Sn$^{4+}$–SnO nanosheets have a photocurrent density of 4 μA cm$^{-2}$, higher than pristine SnO nanosheets, because of the lower electron transfer resistance after doping Sn$^{4+}$ compared to pristine SnO. Usually we intend to believe that nanosheets have much more specific areas, which will be helpful for the semiconductor contacting to electrolytes. There are rarely studies of photocurrent on the microspheres composed with nanoparticles for SnO$_x$. 

© 2020 The Author(s). Published by IOP Publishing Ltd

3 June 2020

PUBLISHED

26 May 2020

ACCEPTED FOR PUBLICATION

19 May 2020

RECEIVED

2 March 2020

OPEN ACCESS

© 2020 The Author

Attribution to the work must maintain the terms of the Creative Commons Attribution 4.0 International licence.

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
In the paper, by using a standard one-step hydrothermal procedure with different ratios of Tin (II) chloride dehydrate \(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}\) to sodium citrate dehydrate \(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}\), we obtained two kinds of tin oxides microspheres (Sn-1, Sn-2) on titanium mesh. XRD patterns and Raman spectra show that sample Sn-1 is composed mainly with SnO and a fraction of \(\beta\)-SnO, and sample Sn-2 was composed with SnO and \(\beta\)-SnO nanoparticles. Then the two samples were used as photoanodes in PEC. The results show that Sn-2 has a photocurrent density of 150 \(\mu\text{A cm}^{-2}\) under on/off of 20 s at 0.0 V versus Ag/AgCl with illumination of 564 \(\pm\) 60 nm 300 mW cm\(^{-2}\) incident intensity, which is four times higher than that of Sn-1. The improved photocurrent density can be ascribed to the type-II energy band alignment between SnO\(_2@\beta\)-SnO composites, larger electrochemical specific surface area and stronger light absorption from 500–800 nm.

**Experimental section**

**Sample preparation**

SnO nanomaterials were prepared by the standard one-step hydrothermal procedure. Tin (II) chloride dehydrate \(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}\) and sodium citrate dihydrate \(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}\) were used as raw materials provided by Sinopharm Chemical Reagent Company. Before deposition, the cleared titanium mesh with a size of \(1 \times 1\) cm\(^2\) was handled with the hydrophilicity treatment. Then, 0.0048 M of \(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}\) and 0.005 M of \(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}\) were dissolved in a mixture of 20 mL deionized water and 20 mL alcohol under constant magnetic stirring for approximately 1 h. When all compounds were dissolved, 20 mL precursor solution was transferred to a Teflon-lined autoclave of 50 mL reaction bomb, sealed and kept at 180 °C for 12 h. Then, the titanium meshes covered with SnO\(_2\) composites were cleaned by the deionized water and dried in an oven under 60°C. Finally we obtained the sample Sn-1. Following same procedure, modulating the concentration of the \(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}\) to 0.015M, we obtained the sample Sn-2.

**Structural characterization**

The morphologies and crystal phases were checked by a Hitachi S4800 filed-emission scanning electron microscopy (SEM) and a powder x-ray diffractometer (XRD, MiniFlex 600, Rigaku) with mono–chromatized Cu Kα radiation, respectively. High-resolution transmission electron microscopy (HRTEM, Tecnai G2 F30 S–TWIN) and selected area electron diffraction (SAED) images were obtained at the accelerating voltage of 300 kV. Raman measurements were conducted at room temperature on a Renishaw inVia Reflex Raman spectrometer with 532 nm lines. A 532 nm laser caused an incident power at the prepared nanomaterials of 3 mW, which used output power of 20 mW and objective lens magnified 50 times. Light absorption measurements were carried out using a UV–vis–NIR spectrophotometer (UV–vis, Cary-5000, Varian) with an integrating sphere. In addition, the chemical states of Sn and O elements were analyzed by x-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250Xi) which was equipped with a standard monochromatic Al-kα source (\(h\nu = 1486.6\) eV).

**PEC measurements**

The electrochemical characteristics of as-prepared Sn-1, Sn-2 photoanodes were evaluated by photocurrent curves, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Mott–Schottky plots on the Zanner CIMPS electrochemical workstation (Germany) using a three-electrode cell, where SnO\(_2\) photoanodes, a Pt wire and an Ag/AgCl were applied as working, counter and reference electrodes, respectively. A 300 W Xe lamp (CEL-HXF 300, Beijing Au-light, China) was employed as incident light source in 0.1 M Na\(_2\)SO\(_4\) electrolyte solution.

**Results and discussion**

The morphologies were investigated with SEM images, as shown in figures 1(a), (b). Figures 1(a), (b) is the SEM images of Sn-1 and Sn-2 microspheres on Ti mesh. The SEM images show that there are sparsely distributed microspheres with a size of 1 \(\mu\)m for Sn-1, as shown in figure 1(a). With increasing the precursor of \(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}\), the microspheres with a diameter of 1 ~ 2 \(\mu\)m are densely covered on the surface of Ti mesh, as figure in 1(b). TEM and HRTEM characterization were carried out to investigate the crystal structures and microstructure feature. TEM image of a selected Sn-2 microsphere is displayed in figure 1(c). Those microspheres connect together, which will be beneficial to the carriers' transportation. Figure 1(d) is the HRTEM image of Sn-2, and well resolved lattice fringes with spacing of 3.34 and 2.64 Å can be assigned to the reflections of the (110) and (101) of SnO\(_2\) (JCPDS No. 41–1445), respectively. And spacing of 2.65 and 1.78 Å (inset of figure 1(d)) is also consistent with (113) and (222) planes at 33.79° and 51.15° of SnO (JCPDS No. 07-0195), as shown in figure 1(e). The selected-area electron diffraction (SAED) patterns (inset) are harmony with
the planes observed in the HRTEM image [12]. Figure 1(e) is the XRD patterns of Sn-1 and Sn-2. For sample Sn-1, the crystalline structure can be indexed to Sn₃O₄ (JCPDS No. 16-0737) as the typical peaks at $2\theta = 27.19^\circ$ and $32.43^\circ$ match well with the (111) and (1-12) planes; while the peaks at $27.67^\circ$, $32.94^\circ$ and $50.48^\circ$ match well with the (−102), (021) and (−114) planes of SnO (JCPDS No. 07-0195).

Raman spectrum was carried out to explain the compositions, as shown in figure 2(a). It can be seen that there are two obvious peaks at 170 and 585 cm⁻¹ for Sn-1. As the peak at around 170 cm⁻¹ is the typical peak of the intrinsic phonon modes of Sn₃O₄ [13, 14], indicating that the dominant components of sample Sn-1 are Sn₃O₄ nanoparticles. Same as for Sn-2, an obvious peak at ~619 cm⁻¹ corresponds to the A₁g phonon modes of SnO₂, a peak at ~577 cm⁻¹ is assigned to surface defects of the SnO₂ nanocrystals [15].

UV–vis–NIR absorption spectra were recorded to investigate the effect of the Sn vacancies on the optical/electronic of the prepared samples, as shown in figure 2(b), where two samples exhibited a strong visible light absorption, but sample Sn-2 has a stronger absorption from 350 to 800 nm than sample Sn-1. There are two obvious absorbance edges between 400 and 800 nm. Samples Sn-1 and Sn-2 have a strong absorption edge at 501.5 (2.47 eV) and 541.07 nm (2.24 eV), respectively, with the same weak absorption edge at 739.4 nm.
suggesting that it is not a homogeneous distribution of the defects in the prepared samples. For Sn-1, 2.47 eV corresponds to the energy of Sn2\(^{2+}\) 5s in Sn3O4, and 2.24 eV is to the energy of Sn2\(^{2+}\) 5s in SnO2. Similar observation was reported, such as the values of 2.53 eV for defected SnO2 [16], SnO (2.53 eV) [17] and SiO\(_2\)/SnO\(_2\)/Sn\(_2\)O\(_3\) nanomaterials [18]. As reported, self-doping of SnO\(_2\) -x nanocrystals with Sn2\(^{2+}\) red-shift their absorption to the visible region and simultaneously produces oxygen vacancies, which can effectively scavenge photogenerated holes and thus enable the color switching of redox dyes using visible light [19]. Here the reduction of band gaps for Sn3O4 and SnO2 can be ascribed to the oxygen vacancies. The second band gap at 1.68 eV is in agreement with the range of 1.7 ∼ 2.2 eV for the Sn2\(^{2+}\)-doped SnO2 [20], and the calculation of 1.7 eV for \(\beta\)-SnO [21].

Figure 3(a) shows a survey XPS spectrum from the NPs, it indicates the presence of the following elements: Sn, O and adventitious C. No contaminants from the nanoparticle synthesis were detected on the sample surface. XPS spectrum of the Sn 3d core level regions is shown in figure 3(b). The double spectral lines of Sn 3d at the binding energy ∼487.1 and ∼495.5 eV for Sn-1; 486.9 and 495.3 eV for Sn-2, with a spin–orbit splitting of 8.4 eV were regarded as Sn 3d 5/2 and Sn 3d 3/2 [22]. Two Sn 3d 5/2 peaks can be well fitted with one single peak at 487.0 eV for Sn-1 and 486.88 for Sn-2 with a respective FWHM of 1.61 and 1.31 eV. These binding energies of Sn 3d 5/2 are higher than that reported for Sn2\(^{2+}\) (486.4–486.5 eV) and slightly lower than that reported for Sn4\(^{4+}\) (487.2–487.5 eV) [23]. It can thus be hypothesized that both samples might contain tin in both II and IV oxidation states, and the lower Sn 3d 5/2 binding energy of Sn-2 implies larger amount of Sn2\(^{2+}\) in SnO2-x sample [24, 25]. The asymmetric peak was observed in the O-1s region (in figure 3(c)), which can be deconvoluted into two components at binding energies of 530.45 and 532.18 eV for sample Sn-1, and 530.88, 531.74 and 533.67 eV for sample Sn-2, as displayed in figure 2(d) and table 1. The peak at ∼530 eV was associated to Sn2\(^{2+}\) and that ∼531.8 to SnO2 (Sn4\(^{4+}\)) [26]. The peak at 533.67 eV can be indexed to - OH groups, which was thought to stem from the hydrated water [27]. From the table 1, we find that the ratio of P1 to P2 intensity increases from 1.3 to 1.96, implying that sample Sn-2 has relative higher Sn2\(^{2+}\) than that of sample Sn-1, in agreement with the result of the bandgap redshift.

The measurement of the self-powered PEC-type detector was carried out using a continuous visible-light pulse with an on-off interval of 10 s (or 20 s) at different intensities under a Xe lamp with a wavelength of 564 ± 60 nm, as shown in figure 4(a). The maximal photocurrent density of Sn-2 is over 200 \(\mu\)A cm\(^{-2}\), about four times larger than that of sample Sn-1. This value is much larger than ever reported self-powered photodetectors (SPPDs) [28], 75 \(\mu\)A cm\(^{-2}\) in SnO\(_2\) [29] and 60 \(\mu\)A cm\(^{-2}\) in Sn2\(^{2+}\)–SnO\(_2\) composites [30].
To investigate the changes of the electrochemical specific surface area, the difference in current density variation plotted against scan rate is shown in figure 4(b). The linear slope, equivalent to twice of the double-layer capacitance ($C_{dl}$), was used to represent the ECSA. We found that the slope of Sn-2 is about seven times larger than that of samples Sn-1, meaning that Sn-2 has quite larger electrochemical specific surface area, which will be beneficial to the improvement of photocurrent of Sn-2.

Electrochemical impedance spectroscopy (EIS) was also performed to measure the charge transfer resistance ($R_{ct}$) occurring at the interface of photoelectrode/electrolyte, as shown in figure 4(c). For each EIS spectrum, two distinct parts composing a semicircle in the high-frequency region and a straight slope in the low-frequency region are considered to be related to the charge transfer process and diffusion-limited process, respectively. The intercept at the real axis represents the resistance at interface between photoelectrode material and Ti mesh substrate ($R_s$) and the diameter of semicircle equals to the charge transfer resistances ($R_c$), respectively. It is obvious that the Sn-2 electrode possesses a lower $R_s$ and $R_c$, consistent with the higher photocurrent of Sn-2, in figure 4(a). Mott–Schottky plots of Sn-1 and Sn-2 electrodes were used to estimate the electron density, as shown in figure 4(d). Figure 4(d) is Mott–Schottky plots at fixed frequencies of 1 kHz on SnO$_x$ photoelectrode registered in 0.1 M Na$_2$SO$_4$ electrolyte (pH 7), (inset) Linear fitting of MS.

| Sample | Peak | BE (eV) | Ratio |
|--------|------|---------|-------|
| #1     | P1   | 530.45  | 56.54%|
|        | P2   | 531.84  | 43.46%|
| #2     | P1   | 530.88  | 49.59%|
|        | P2   | 531.74  | 25.30%|
|        | P3   | 532.67  | 25.11%|

Figure 4. (a) Photocurrent responses under on/off of 20 s at 0.0 V versus Ag/AgCl with illumination of 564 ± 60 nm 300 mW cm$^{-2}$ incident intensity; (b) Charging current density differences plotted against scan rate. The linear slope, equivalent to twice of the double-layer capacitance ($C_{dl}$); (c) EIS recorded at −0.5 V with the frequency range from 0.1 Hz to 0.5 MHz; (d) Mott–Schottky plots at fixed frequencies of 1 kHz on SnO$_x$ photoelectrode registered in 0.1 M Na$_2$SO$_4$ electrolyte (pH 7), (inset) Linear fitting of MS.

Table 1. O1s Binding energy (eV).
where $E_{fb}$ is the flat band potential and $E$, $q$, $A$, $\varepsilon$, $\varepsilon_0$ and $N_d$ are the external applied potential, the elementary charge, the area of the metal contacts, the dielectric constant, the vacuum permittivity, and the carrier concentration, respectively. The optical static dielectric constant $\varepsilon$ is equal to 7.1 [31] or 10 [32]. The flat potential $E_{fb}$ is obtained as $-0.37$, $-0.16$ V versus Ag/AgCl for Sn-1 and Sn-2, respectively. From equation (1), the charge carrier density $N_d$ can be calculated from the following

$$\frac{1}{C^2} = \frac{2(E - E_{fb})}{A^2q\varepsilon_0N_d},$$

where $E_{fb}$ is the flat band potential and $E$, $q$, $A$, $\varepsilon$, $\varepsilon_0$ and $N_d$ are the external applied potential, the elementary charge, the area of the metal contacts, the dielectric constant, the vacuum permittivity, and the carrier concentration, respectively. The optical static dielectric constant $\varepsilon$ is equal to 7.1 [31] or 10 [32]. The flat potential $E_{fb}$ is obtained as $-0.37, -0.16$ V versus Ag/AgCl for Sn-1 and Sn-2, respectively. From equation (1), the charge carrier density $N_d$ can be calculated from the following

$$N_d = \left(\frac{2}{q\varepsilon_0A^2}\right)[d(1/C^2)/dV]^{-1}.$$

In figure 4(d), linear regions with positive slopes can be observed between $-0.5$ and $0.1$ V, indicating an n-type semiconductor. From the inset of figure 4(d), it shows that the carrier density $N_d$ of Sn-2 is 1.36 times of Sn-1.

Figure 5(a) shows the current density versus applied potential under dark and visible light irradiation, Sn-2 presented the better PEC property under illumination than Sn-1. The higher photocurrent density at different bias potentials for Sn-2 suggests more efficient charge carrier collection in SnO$_x$ nanoparticles under visible light illumination [33]. Figure 5(b) presented cyclic voltammograms recorded over a wide potential range, i.e., from $-0.6$ to $0.4$ V versus AgCl. One anodic current peak at $-0.5$ V was observed for Sn-2, which can be attributed to Sn$^{2+} \rightarrow$ Sn$^{4+}$ stepwise oxidation processes forming different Sn$^{2+}$/Sn$^{4+}$ oxide/hydroxide species, consistent with the reported results [34]. Sn-2 has a larger dark current from $-0.6$ to $-0.2$ versus AgCl, meaning higher donor (electron) density as the charge transfer in the dark is dominated by the major carrier (electron). Comparing figures 5(c) and (d), one can find that sample Sn-2 has nearly seven times larger double-layer capacitance ($C_{dl}$) in comparison to Sn-1, indicating the fast transfer of carriers at the electrode/electrolyte interface and the efficient separation of electrons and holes for Sn-2 happen.

Using the previous band gap [34] of Sn$_3$O$_4$, we present the energy band structure of Sn-1 in figure 6(a), where the energy band structure of SnO is taken from [21], by Wang $et$ $al$. The energy band alignment of Sn-2 is displayed in figure 6(b). For Sn-2, the Sn$^{2+}$-dopant in SnO$_2$ introduces more oxygen vacancies leading to the reduction of bandgap. And the electrons can excite from Sn$^{2+}$ 5s impurity state to the conduction band consisting of Sn$^{4+}$ 5s orbitals with an energy of 2.24 eVdue to the introduction of Sn$^{2+}$ 5s impurity state in SnO$_2$. Furthermore, under visible light illumination, electrons can be excited from the valence band to the conduction band of SnO, as the conduction band of SnO$_2$ is more positive to than that of SnO versus NHE, the photogenerated electrons can transfer from the conduction band of SnO to that of SnO$_2$, and holes transfer from
Sn$^{2+}$ 5s impurity state to the valence of SnO, thus, the photogenerated electrons and holes (e-p) are effectively separated.

The photocurrent density decay for Sn-2 can be explained as the photocorrosion. Figure 6 shows that the conduction band energy of β-SnO is 0.6 V above NHE, in addition to the electrons transfer from the conduction band energy of β-SnO to SnO$_2$, Sn(II) → Sn(IV) oxidation processes will occur$^{27}$, leading to the gradually decreased photocurrent density. As reported, photocorrosion existed in many semiconductor materials$^{[35]}$, which can be ameliorated with wide-band gap semiconductors capping them as protective layers$^{[36–38]}$.

**Discussions and conclusions**

From the discussions of HRTEM images, XRD patterns, Raman spectra and energy band gaps, we can conclude that the dominant content of sample Sn-1 is Sn$_3$O$_4$ nanoparticles with a small fraction of SnO, while the main content of Sn-2 is SnO$_2$ nanoparticles with a fraction of SnO.

Because of the good conductivity of Ti net, more generated electrons can be collected by electrode and transfer to the working electrode (Pt/FTO) by the external circuit. The generated holes are driven from the valence band of SnO into the interface of SnO$_x$ nanoparticles /electrolyte and captured by the reduced form of the redox molecule (h$^+$ + OH$^-$ → OH$^-$). While for sample Sn-1, it is hard to realize the e-p separation. Furthermore, Sn-2 has a stronger visible absorption from 350 to 800 nm, the stronger light absorption can be ascribed to densely distributed microspheres covering on the surface of Ti mesh; Sn-2 has a larger electrochemical specific surface area, which is helpful to the ions’ transfer between photoelectrode and electrolyte. Therefore, sample Sn-2 exhibits a maximal photocurrent density more than 200 μA cm$^{-2}$ under on/off of 20 s at 0.0 V versus Ag/AgCl with illumination of 564 ± 60 nm 300 mW cm$^{-2}$ incident intensity. This value is higher than previous reports of Sn-based nanostructures with a one-step procedure without any annealing treatments.

Defects in a semiconductor will induce impurity states, which generally lie within the semiconductor band gap. Those defect-induced localized states can selectively capture the approaching charge carriers, leading to spatial charge separation and thus an improved photocatalytic activity. Therefore it is an important subject to modulate defect behavior in semiconductors. Using a standard one-step hydrothermal procedure we obtained Sn$_3$O$_4$ microspheres (Sn-1) and Sn$^{2+}$ self-doped SnO$_2$ microspheres (Sn-2) without any annealing treatments, and obtained a maximal photocurrent density more than 200 μA cm$^{-2}$. From the results, the photostability needs to be further improved. In the future work we will consider it through heterostructural growth.

**Acknowledgments**

This work was supported by the National Key Research and Development Program of China (Grant No. 2017YFB0403101), the National Natural Science Foundation of China (Grant 61604127, 61474096).

**Notes**

The authors declare no competing financial interest.
ORCID iDs

Xianglehua Zeng  https://orcid.org/0000-0003-4775-6764

References

[1] Wang Y K, Liu Y H and Zhang J M 2013 Colloidal electrostatic self-assembly synthesis of SnO2/Graphene nanocomposite for supercapacitors J. Nanopart. Res. 17 1120

[2] Guan X W, Wang Z W, Hota M K, Alsahreef H N and Wu T 2019 P-type SnO thin film phototransistor with perovskite-mediated photogating Adv. Electron. Mater. 5 1800338

[3] Zeng W W, Liu Y Z, Mei J, Tang C Y, Luo K, Li S M, Zhan H R and He Z K 2019 Hierarchical SnO2–SnO3 heterostructural gas sensor with high sensitivity and selectivity to NO2 Sensors & Actuators: B. Chemical 301 12701

[4] Xia W W, Wang H B, Zeng X H, Han J, Zhu J, Zhou M and Wu S D 2014 High efficiency photocatalytic activity of type-II SnO/ SnO3 heterostructures via interface charge transfer Cryst. Eng. Comm. 16 6841–7

[5] Shen X C et al 2019 Dual-site cascade oxygen reduction mechanism on SnO/Pt–Cu–Ni for promoting reaction kinetics J. Am. Chem. Soc. 141 9463–7

[6] Shankamugasundaram A, Basak P, Satyaranayana L and Manorama S V 2013 Hierarchical SnO/SnO2 nanostructures: formation of in situ P–N junctions and enhanced H2 Sensing Sensors and Actuators B 185 263–73

[7] Li N, Fan Y, Shi Y, Xiang Q, Wang X H and Xu J Q 2019 A low temperature formaldehyde gas sensor based on hierarchical SnO/SnO2 nano-flowers assembled from ultrathin nanosheets: synthesis, sensing performance and mechanism Sensors & Actuators: B. Chemical 294 106–15

[8] Yin G L et al 2019 Enhanced gas selectivity induced by surface active oxygen in SnO/SnO2 heterojunction structures at different temperatures RSC Adv. 9 1903–8

[9] Huda A, Ichwani R, Handoko C T, Yudono B, Bustan M D and Gulo F 2019 Enhancing the Visible-Light Photoresponse of SnO and SnO2 Through The Heterostructure Formation Using One-Step Hydrothermal Route Mater. Lett. 238 264–6

[10] Zaraska L, Gawlik K, Wiercigroch E, Malek K, Koziol M, Andrzejczuk M, Marecz M M, Jarosz M, Brzozka A and Sulkia G D 2019 The effect of anodizing potential and annealing conditions on the morphology, composition and photoelectrochemical activity of porous anodic tin oxide films Electrochem. Acta 319 18–30

[11] Tian B, Gao W, Ning X F, Wu Y Q and Lu G X 2019 Enhancing water splitting activity by protecting hydrogen evolution activity site from poisoning of oxygen species Appl. Catalysis B 249 138–46

[12] Lu H D, Lin B C, Chen S Y and Shen P Y 2011 Pulsed laser ablation induced fragmentation, transformation, internal stress, Sn2+ /Sn+ + Cosignature, and optical property change of SnO2 powders in water J. Phys. Chem. C 115 24577–24585

[13] Sangaleli L, Depero I E, Allieri B, Pioselli F, Comini E, Sberveglieri G and Zocchi M 1998 J. Mater. Res. 13 2457–60

[14] Wang H B, Zeng X H, Xia W W, Zhou X, Zhou M and Shen X S 2015 Nanosheet-built tin-oxides hollow microsphere and their phase transition with an annealing treatment Mater. Res. Bull. 70 697–703

[15] Kar A, Kundu S and Patra A 2011 Surface defect-related luminescence properties of SnO2 nanorods and nanoparticles J. Phys. Chem. C 115 118–24

[16] Yang Y, Wang Y and Yin S 2017 Oxygen vacancies confined in SnO2 nanoparticles for desirable electronic structure and enhanced visible light photocatalytic activity Appl. Surf. Sci. 420 399–406

[17] Wang J X, Lu C, Liu X C, Wang Y Q, Zhu Z X and Meng D W 2017 Synthesis of Tin Oxide (SnO and SnO2) Micro/Nanostructures With Novel Distribution Characteristic and Superior Photocatalytic Performance Mater. Des. 115 103–11

[18] Sun M, Su Y, Du C, Zhao Q and Liu Z 2014 Self-doping for visible light photocatalytic purposes: construction of SnO/SnO2/ SnO2: Sn2+ nanostructures with tunable optical and photocatalytic performance RSC Adv. 4 30820–7

[19] Han D, Jiang B, Feng J, Yin Y and Wang W 2017 Photocatalytic self-doped SnO2-x nanocrystals drive visible-light-responsive color switching Angew. Chem. Int. Ed. 56 7792–6

[20] Long J, Xue W, Xie X, Gu Q, Zhou Y, Chi Y, Chen W, Ding Z and Wang X 2011 Sn++ dopant induced visible-light-activity of SnO2 nanoparticles for H2 production Catal. Commun. 16 215–9

[21] Wang J, Umezawa N and Hosono H 2016 Mixed valence tin oxides as novel van der Waals materials: theoretical predictions and potential applications Adv. Energy Mater. 6 1501190

[22] Zhang L, Ge S H, Zuo Y L, Zhang B M and Xi L 2010 Influence of oxygen flow rate on the morphology and magnetism of SnO2 nanostructures J. Phys. Chem. C 114 7541–7

[23] Themlin J M, Chitaib M, Hennard L, Lambin P, Darville J and Gilles J M 1992 Characterization of Tin oxides by x-ray–photoemission spectroscopy Phys. Rev. B 46 2460

[24] Jiqbal M Z, Wang F P, Feng T, Zhao H L, Rafique M Y, Din R, Farooq M H, Javed Q and Faraz Khan D 2012 Facile Synthesis of Self-Assembled SnO Nano–Square Sheets and Hydrogen Absorption Characteristics Mater. Res. Bull. 47 3902–7

[25] Liang Y, Liu Z M, Cao H Y and Pan X Q 2010 Microstructural, optical, and electrical properties of SnO thin films prepared on quartz via a Two-Step Method ACS Appl. Mater. Interfaces 2 1060–5

[26] Anuchai S, Phanichphant S, Tantrawisat D, Plueengphon P, Boovornratanares T and Inceesungvorn B 2018 Low Temperature Preparation of Oxygen-Deficient Tin Dioxide Nanocrystals and A Role of Oxygen Vacancy in Photocatalytic Activity Improvement J. Colloid Interface Sci. 512 105–14

[27] Katić J, Hušković M M, Šarić I and Petrucci M 2016 Semiconductor properties of the oxide films formed on tin: capacitive and XPS studies J. Electrochem. Soc. 163 C221–7

[28] Qian W W Y, Zeng X H, Dong J, Wang J and Xu Q 2017 Visible-light Self-powered Photodetector and Recoverable Photocatalyst Fabricated from Vertically Aligned SnO3 NanoFlakes on Carbon paper J. Phys. Chem. C 121 19036–43

[29] Fan C M, Peng Y, Zhu Q, Lin L, Wang X W and Xu A W 2013 Synproportionation reaction for the fabrication of Sn2+ – self-doped SnO2-x Nanocrystals with Tunable Band Structure and Highly Efficient Visible Light Photocatalytic Activity J. Phys. Chem. C 117 24157–66

[30] Wang J, Li H, Meng S, Ye X, Fu X and Chen S 2017 Controlled Synthesis of Sn-Based Oxides Via a Hydrothermal Method and Their Visible Light Photocatalytic Performances RSC Adv. 7 27024–32

[31] Ali Yldirim M, Yldirim ST, Sakar E F and Ates A 2014 Synthesis, characterization and dielectric properties of SnO2 thin films Spectrochimica Acta Part A 133 60–5
[32] Metikôs-Hukovic M, Omanovic S and Jukić A 1999 Impedance spectroscopy of semi-conducting films on tin electrodes Electrochim. Acta 45 977
[33] Hoang S, Guo S, Hahn N T, Bard A J and Mullins C B 2012 Visible light driven photoelectrochemical water oxidation on nitrogen-modified TiO₂ nanowires Nano Lett. 12 26–32
[34] Xia W W, Qian H Y, Zeng X H, Sun J W, Wang P D, Luo M and Dong J 2019 TiO₂@Sn₃O₄ nanorods vertically aligned on carbon fiber papers for enhanced photoelectrochemical performance RSC Adv. 9 23334–42
[35] Mor G K, Varghese O K, Wilke R H T, Sharma S, Shankar K, Latempa T J, Shin Choi K and Grimes C A , 2008 p-Type Cu-Ti-O Nanotube Arrays and Their Use in Self-Biased Heterojunction Photoelectrochemical Diodes for Hydrogen Generation Nano Lett. 8 1906–11
[36] Azevedo J, Tilley S D, Schreier M, Stefk M, Sousa C, Araújo J P, Mendes A, Grätzel M and Mayer M T 2016 Tin oxide as stable protective layer for composite cuprous oxide water-splitting photocathodes Nano Energy 24 10–6
[37] Chen C L, Wei Y L, Yuan G Z, Liu Q L, Lu R R, Huang X, Cao Y and Zhu P H 2017 Synergistic effect of Si doping and heat treatments enhances the photoelectrochemical water oxidation performance of TiO₂ nanorod arrays Adv. Funct. Mater. 27 1701573
[38] Krýsa J, Imrich T, Paušová Š, Krýsová H and Neumann-Spallart M 2019 Hematite films by aerosol pyrolysis: influence of substrate and photocorrosion suppression by TiO₂ capping Catal. Today 335 418–22