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# Controlled synthesis of Sn-based oxides via a hydrothermal method and their visible light photocatalytic performances†

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Controlled synthesis of Sn-based oxides with a different valence state is still a challenge. Here, we developed a facile hydrothermal method for selective preparation of SnO<sub>2</sub>, Sn<sup>2+</sup> doped SnO<sub>2</sub> (Sn<sup>2+</sup>–SnO<sub>2</sub>), and SnO/SnO<sub>2</sub> composites, and SnO with SnCl<sub>2</sub> as a precursor. The valence state of Sn was regulated successively from Sn<sup>4+</sup> to Sn<sup>2+</sup> through controlling the hydrothermal solution from an O<sub>2</sub>-rich to an O<sub>2</sub>-deficient atmosphere, which was achieved by adding H<sub>2</sub>O<sub>2</sub> or urea into the solution. The structure, absorption, morphology, and the visible light photocatalytic performance of the products were investigated systematically. SnO<sub>2</sub>, Sn<sup>2+</sup>–SnO<sub>2</sub>, SnO/SnO<sub>2</sub>, and SnO could be prepared in a H<sub>2</sub>O<sub>2</sub>-contained, H<sub>2</sub>O, urea-contained, and N<sub>2</sub> purged urea-contained solution, respectively. For Sn<sup>2+</sup>–SnO<sub>2</sub>, the doping amount of Sn<sup>2+</sup> could be further tuned by varying the hydrothermal temperature, while for SnO/SnO<sub>2</sub>, the coupling amount of SnO could be controlled by the dosage of urea. Visible-light-induced photocatalytic degradation of methyl orange was achieved successfully on Sn<sup>2+</sup>–SnO<sub>2</sub> and SnO/SnO<sub>2</sub>. However, further work is still required to improve the stability of the samples due to vulnerability of Sn<sup>2+</sup>.

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## 1. Introduction

As a variable valence metal, Sn-based oxides can be in the form of univalent (SnO and SnO<sub>2</sub>) or heterovalent oxides (Sn<sub>2</sub>O<sub>3</sub> and Sn<sub>3</sub>O<sub>4</sub>, formed by regulating Sn<sup>2+</sup>/Sn<sup>4+</sup> ratio<sup>1</sup>). The univalent SnO and SnO<sub>2</sub> have attracted considerable attention during the past years because of their excellent optical, electrical, and electrochemical properties.<sup>2–8</sup> For SnO, it can be used as anode materials in Li-batteries,<sup>7</sup> coating materials,<sup>9</sup> and catalysts for cyclization of maleamic acid.<sup>9</sup> Furthermore, as Sn<sup>2+</sup> can be easily oxidized to Sn<sup>4+</sup> through a heat treatment in air, it can be used as a sacrificial template to prepare SnO<sub>2</sub>, another versatile Sn oxide. Due to its high optical transparency in the visible range, the remarkable receptivity to variation of gas, the low resistivity, and the excellent chemical stability, SnO<sub>2</sub> has been extensively used in transparent conductive electrodes,<sup>4</sup> gas sensors,<sup>10,11</sup> Li-batteries,<sup>5</sup> sensitized solar cells,<sup>12</sup> and photocatalysts.<sup>13–15</sup> To optimize the SnO and SnO<sub>2</sub> performances,

various preparation methods including sol-gel, precipitation, hydrothermal, solvothermal, thermal evaporation, electrospinning, and laser ablation have been developed to manipulate their sizes, structures, and morphologies.<sup>8</sup> Taking SnO<sub>2</sub> as an example, the particle size can be reduced through a surfactant-assisted solvothermal<sup>16</sup> or hydrothermal<sup>17,18</sup> route, while as for the morphologies, 0 to 3 dimensional SnO<sub>2</sub> nanostructures, such as nanoparticles, nanorods, nanowires, nanotube, nanosheets, and the 3D hierarchical architectures self-assembled from these low-dimensional nanostructures, have been subtly fabricated.<sup>8</sup> Although the structure and the morphology of the Sn oxides can be readily controlled by using different preparation routes, there still is a lack of a versatile fabrication route to control the component of the product, which is a key prerequisite for the applications. Most of the preparation methods are only suitable for the preparation of one of the Sn oxides.

Semiconductor-based photocatalytic technology possesses a great potential in the environmental remediation for its “green”, high efficiency, and broad applicability.<sup>19,20</sup> Photocatalytic degradation of pollutants on Sn oxides, especially SnO<sub>2</sub>, has been extensively investigated. Unfortunately, as a well-known n-type semiconductor, SnO<sub>2</sub> can only be activated under UV irradiation due to the wide-band gap energy (3.5–3.8 eV).<sup>21–23</sup> Furthermore, the activity is significantly restricted by the quick recombination of photo-induced charge carriers (e<sup>−</sup> and h<sup>+</sup>). Although the separation of e<sup>−</sup> and h<sup>+</sup> can be improved by compositing SnO<sub>2</sub> with TiO<sub>2</sub>,<sup>24,25</sup> ZnO<sup>26,27</sup> and Zn<sub>2</sub>SnO<sub>4</sub>,<sup>28,29</sup> extending SnO<sub>2</sub> absorption to visible light range which accounts

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for 43% of the solar spectrum is still required to maximize the utilization of sunlight. Doping (non)-metallic elements is an effective strategy to narrow the band gap. However, the sample thermal stability and the separation of  $e^-$  and  $h^+$  are generally hampered by the doping with heterogeneous elements. These disadvantages can be avoided by a self-doping approach,<sup>30–33</sup> which introduces no impurity elements into the sample. The validity of the self-doping has been confirmed on the  $Ti^{3+}$  doped  $TiO_2$  and some  $Sn^{2+}$  doped Sn ternary oxides ( $Sn^{2+}$ - $SnM_2O_6$ ,  $M = Ta$  or  $Nb$ ).<sup>34–36</sup>

Meanwhile, some other reports noted that SnO incorporated samples have a significant visible light activity in the degradation of organic pollutants.<sup>1,37–40</sup> These works arouse our interest that the visible light photocatalytic performance of  $SnO_2$  may also can be promoted by doping with  $Sn^{2+}$  or incorporating with some  $Sn^{2+}$ -contained species like SnO,  $Sn_2O_3$  or  $Sn_3O_4$ . The visible light photocatalytic performances of some  $Sn^{2+}$ -contained samples, such as  $SnO_{2-x}$ ,<sup>41</sup>  $Sn_3O_4$ ,<sup>42</sup>  $SnO$ - $TiO_2$ ,<sup>43</sup>  $SnO/Sn_3O_4$ ,<sup>1</sup> and  $Sn_3O_4/TiO_2$ ,<sup>44</sup> demonstrate the feasibility of the strategy.

However, it remains difficult to incorporate  $Sn^{2+}$  species into  $SnO_2$  as  $Sn^{2+}$  is easily oxidized to  $Sn^{4+}$ . Controlling the Sn oxidation state is still a critical challenge. Recently, Fan's work<sup>41</sup> indicates that  $Sn^{2+}$  self-doped  $SnO_2$  can be skillfully prepared by a synproportionation reaction by adding Sn powder to the reaction solution:  $Sn + Sn^{4+} \rightarrow Sn^{2+}$ , while another work indicated that SnO and  $SnO_2$  can be selectively prepared by controlling the solution pH.<sup>45</sup> These methods are limited to the preparation of one or two kinds of the Sn oxides. As far as we know, a facile method to synthesize a series of Sn oxides in a controlled way is still highly desired.

Herein, we developed a simple hydrothermal method to selective prepare a series of Sn oxides. Including  $SnO_2$ ,  $Sn^{2+}$  doped  $SnO_2$  ( $Sn^{2+}$ - $SnO_2$ ),  $SnO/SnO_2$  composite, and SnO were successfully synthesized through controlling the solution composition. The visible light photocatalytic performance of the samples was then evaluated by the degradation of methyl orange (MO) solution.

## 2. Experiments

### 2.1 Chemicals and preparation of Sn oxides

Analytical grade  $SnCl_2 \cdot 2H_2O$ , urea ( $CO(NH_2)_2$ ),  $H_2O_2$ , and MO were purchased from Aladdin Reagent Co. Ltd, Shanghai, China and used as received.

**Preparation of  $Sn^{2+}$ - $SnO_2$ .** 1 g  $SnCl_2 \cdot 2H_2O$  was dissolved in 80 mL deionized water. After stirring for 30 min, the solution was then transferred into a Teflon-lined stainless autoclave and maintained at an elevated temperature for 24 h. The yellow products were centrifuged and rinsed alternatively in water and ethanol, and finally dried at 60 °C in a vacuum oven.

**Preparation of  $SnO/SnO_2$ .**  $SnO/SnO_2$  was prepared *via* a similar hydrothermal process in urea-contained solution at 160 °C for 24 h.

**Preparation of SnO and  $SnO_2$ .** Pristine  $SnO_2$  and SnO were synthesized in  $H_2O$  with 3 g urea added. For the preparation of  $SnO_2$ , 1 mL  $H_2O_2$  (30%) was further added to promote the

conversion of  $Sn^{2+}$  to  $Sn^{4+}$  before the hydrothermal treatment at 160 °C, while for SnO, the solution was purged with  $N_2$  before the treatment.

### 2.2 Characterization

X-ray diffraction patterns of the samples were recorded on a Bruker D8 Advance diffractometer. UV-visible diffuse reflection spectra (UV-vis DRS) were recorded on a Vis-NIR spectrophotometer (TU-1950, Persee) with  $BaSO_4$  as a reference. Simultaneous thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of the  $Sn^{2+}$ - $SnO_2$  prepared at different temperatures were performed on a Shimadzu DTG-60H TG/DTA thermal analyser.  $N_2$  adsorption-desorption isotherms were obtained at 77 K by using a Micromeritics ASAP 2020 surface area analyzer. The morphologies were examined by a scanning electron microscopy (SEM, JSM-6610LV, Hitachi) and a transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN). X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) using Al K $\alpha$  X-ray beam (1486.6 eV).

### 2.3 Photocatalytic decolorization of MO

Photocatalytic degradation of MO solution was carried out in a tubular reactor which was surrounded by a water cooling jacket. A 300 W Xe lamp (CEL-HXF300) was used as a light source with a UV cut off filter ( $\lambda > 400$  nm). The picture of the reaction system can be found in Fig. S1 (see ESI<sup>†</sup>). In a typical experiment, 100 mg sample was dispersed in 100 mL 10 ppm MO. The suspension was then stirred for 30 min in the dark to reach an adsorption-desorption equilibrium. During irradiation, the solution temperature was controlled at 20 °C by a Julabo F12 cooling bath (Julabo Labortechnik, Germany). 3.8 mL suspension was withdrawn through a pipette every 10 min. The residual MO in the supernatant was monitored by a spectrophotometer (TU-1950, Persee).

### 2.4 Measurements of the photocurrent and the formation of hydroxyl radicals ( $\cdot OH$ )

The photocurrent test was conducted on a CHI 660E electrochemical workstation (Chenhua, Shanghai) in a conventional three-electrode cell with Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and the samples as the working electrode. The working electrode was fabricated by drop casting the sample powder dispersed water onto a FTO glass substrate ( $0.6 \times 0.6$  cm) followed by drying the electrode at room temperature. 0.2 M  $Na_2SO_4$  aqueous solution was used as the electrolyte.

The formations of  $\cdot OH$  in the photocatalytic process were determined by photoluminescence (PL) technique with terephthalic acid (TA) as a probe molecule. The procedure was similar to the degradation of MO except that the solution was replaced by 100 mL  $5 \times 10^{-4}$  M TA and  $2 \times 10^{-3}$  M NaOH mixed solution. The fluorescence signal of TAOH adduct was measured by a fluorescence spectrophotometer (JASCO FP-6500).



### 3. Results and discussion

#### 3.1 Characterization of $\text{Sn}^{2+}$ - $\text{SnO}_2$ and $\text{SnO}_2$

Fig. 1a shows the XRD patterns of  $\text{Sn}^{2+}$ - $\text{SnO}_2$  prepared at different hydrothermal temperature. The diffraction peaks can be assigned to tetragonal  $\text{SnO}_2$  (JCPDS No. 77-447). The broad peaks at  $2\theta$  ca. 27, 34, and  $52^\circ$  can be ascribed to the reflections of the (110), (101), and (211) planes of  $\text{SnO}_2$ .<sup>46</sup> The intensity of these peaks improves gradually with the hydrothermal temperature, indicating that the crystallization of  $\text{SnO}_2$  is favoured by an elevated temperature. The top of Fig. 1a shows the XRD pattern of the prepared  $\text{SnO}_2$ . The diffraction peak can be assigned to tetragonal  $\text{SnO}_2$  and are more pronounced and sharpened than the sample prepared in pure  $\text{H}_2\text{O}$ . This result suggests that, besides the conversion of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ , the crystallization of  $\text{SnO}_2$  was also promoted by the addition of  $\text{H}_2\text{O}_2$ . Similar function of  $\text{H}_2\text{O}_2$  has been reported.<sup>47,48</sup>

Fig. 1b shows the UV-vis DRS spectra of the  $\text{Sn}^{2+}$ - $\text{SnO}_2$ . An absorption threshold at ca. 500 nm can be observed and the absorption edge shows a blue-shift with the hydrothermal temperature. A change of the samples color from pale yellow to slight brown then can be observed (see the inset of Fig. 1b).

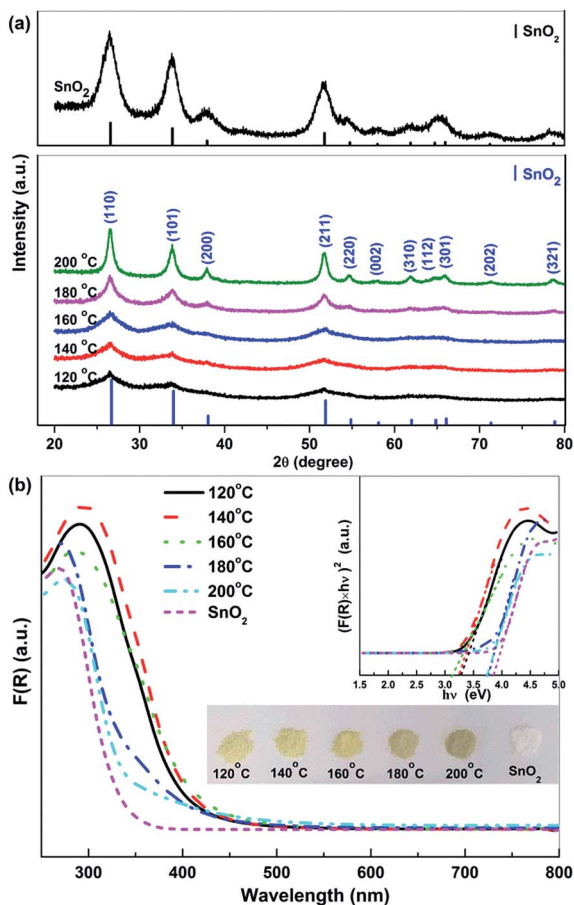


Fig. 1 (a) X-ray diffraction patterns and (b) UV-vis DRS spectra of the  $\text{Sn}^{2+}$ - $\text{SnO}_2$  prepared at different temperatures and  $\text{SnO}_2$ . The inset of (b) shows the corresponding Tauc plots and the appearance of the samples.

Although the samples show the same tetragonal structure as that of pristine  $\text{SnO}_2$ , their colour is quite darker than  $\text{SnO}_2$ , indicating the doping of  $\text{Sn}^{2+}$ .<sup>11</sup> As shown in the inset of Fig. 1b, Tauc plot approach<sup>49</sup> was used to determine  $\text{Sn}^{2+}$ - $\text{SnO}_2$  band gap energy ( $E_g$ ). The results (summarized in Table 1) indicate that, for the samples prepared below  $160^\circ\text{C}$ , the  $E_g$  is only ca. 3.10 eV. Further enhancing the hydrothermal temperature to  $200^\circ\text{C}$ , the samples  $E_g$  are close to 3.60 eV. The  $E_g$  of the prepared  $\text{SnO}_2$  is 3.73 eV and it is consistent well with the reported value.<sup>41,50–53</sup> This result clearly indicates that the absorption of  $\text{SnO}_2$  could be extended to the visible light region by doping with  $\text{Sn}^{2+}$ .<sup>11,41</sup> As  $\text{Sn}^{2+}$  tends to be oxidized to  $\text{Sn}^{4+}$  at an elevated temperature, the increase of  $E_g$  with hydrothermal temperature should be caused by the reduction of  $\text{Sn}^{2+}$  doping content.

$\text{SnO}_2 \cdot \text{H}_2\text{O}$  shows a similar diffraction pattern to the tetragonal  $\text{SnO}_2$ .<sup>50</sup> TGA and DTA analyses of the prepared  $\text{Sn}^{2+}$ - $\text{SnO}_2$  were carried out to further corroborate the identification. As shown in Fig. 2a, an initial mass loss of 1.0% can be observed below  $120^\circ\text{C}$ . It can be attributed to the dehydration of the adsorbed water, which leads to the endothermic peak in Fig. 2b. A second mass loss ca. 1.0% is occurred around  $400^\circ\text{C}$  due to the volatilization of the contaminated  $\text{Cl}^-$ . After that, the TGA curves have no change. The result rules out the possibility that the products are  $\text{SnO}_2 \cdot \text{H}_2\text{O}$  as its theoretical weight loss is larger than 10%. It also rules out the presence of  $\text{SnO}$  component in the samples, which shows a weight increases around  $570^\circ\text{C}$ <sup>54</sup> due to the oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ . Thus, based on the results shown in Fig. 1 and 2, it can be deduced that the samples prepared at different temperatures in  $\text{H}_2\text{O}$  are  $\text{Sn}^{2+}$ - $\text{SnO}_2$ .

Fig. 3 shows the SEM images of the prepared  $\text{Sn}^{2+}$ - $\text{SnO}_2$ . The samples prepared below  $200^\circ\text{C}$  (Fig. 3a–d) are mainly composed of rods with a length of about  $15\ \mu\text{m}$  and a diameter of about  $3\ \mu\text{m}$ . With enhancing the preparation temperature, the surface of the rods becomes coarse and some small particles are present, suggesting the decomposition of the rods. When the temperature reaches  $200^\circ\text{C}$ , no any rods can be observed (Fig. 3e). Pristine  $\text{SnO}_2$  prepared in the  $\text{H}_2\text{O}_2$ -contained solution (Fig. 3f) shows a similar morphology feature as the sample prepared at  $200^\circ\text{C}$ .

#### 3.2 Characterization of $\text{SnO}/\text{SnO}_2$ and $\text{SnO}$

Fig. 4a shows the XRD patterns of the  $\text{SnO}/\text{SnO}_2$  prepared in different urea-contained solutions. When no urea was added, the resulted sample was  $\text{Sn}^{2+}$ - $\text{SnO}_2$  as shown by Fig. 1. For the samples prepared in urea-contained solution, two sets of diffraction peaks originated from tetragonal  $\text{SnO}_2$  (JCPDS No. 77-447) and  $\text{SnO}$  (JCPDS No. 78-1913) can be observed, confirming the formation of  $\text{SnO}/\text{SnO}_2$  composite. As shown in the top of Fig. 4a, the diffraction pattern of the sample prepared in  $\text{N}_2$  purged solution can be assigned to  $\text{SnO}$ , along with two very small diffraction peaks of  $\text{SnO}_2$  (110) and (211).

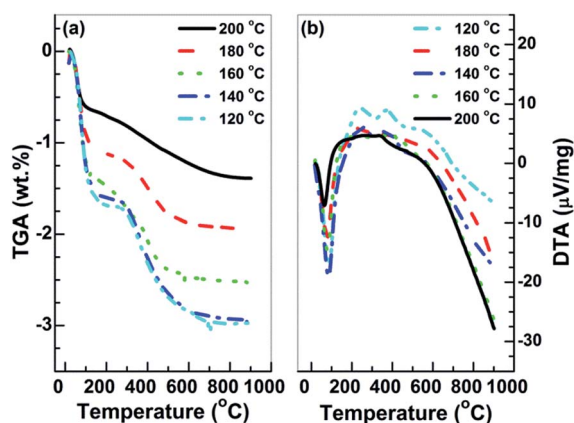
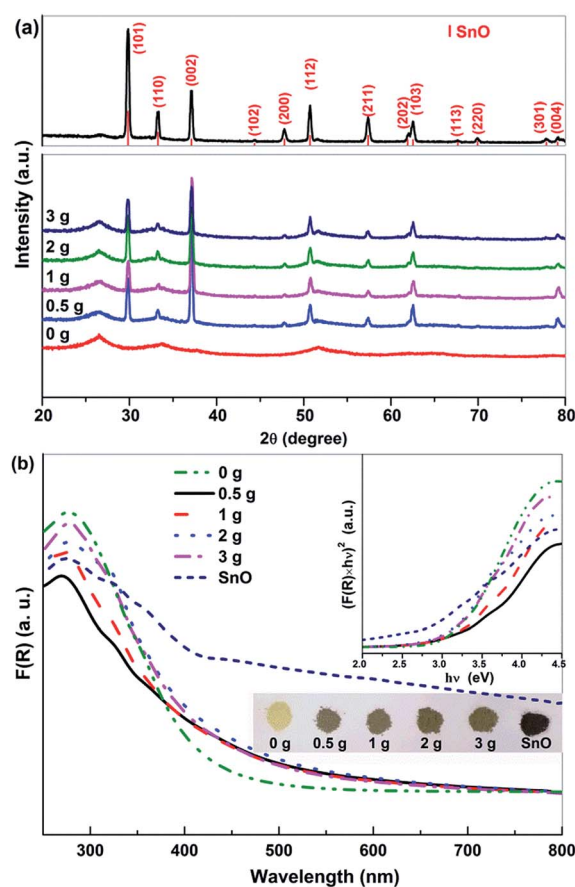
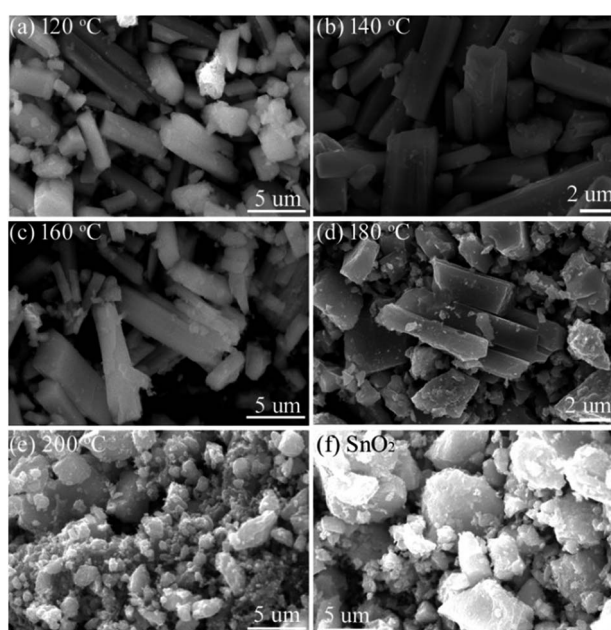
Fig. 4b shows the UV-vis DRS of the prepared  $\text{SnO}-\text{SnO}_2$  and  $\text{SnO}$ . The composite show an apparent visible light absorption and the thresholds extend to ca. 700 nm. With an increase of urea dosage, the absorption coefficient of the resulted  $\text{SnO}-$





**Table 1** Summary of the hydrothermal conditions and the characterization results of the  $E_g$  and the BET surface area of the prepared Sn oxides

Reaction condition	Product	$E_g$ (eV)	BET area ( $\text{m}^2 \text{g}^{-1}$ )
Temp. ( $^{\circ}\text{C}$ ) (without urea)	120	$\text{Sn}^{2+}\text{-SnO}_2$	100.1
	140		—
	160		116.4
	180		—
	200		99.9
Urea (g) (temp. $160^{\circ}\text{C}$ )	0	$\text{Sn}^{2+}\text{-SnO}_2$	116.4
	0.5	$\text{SnO/SnO}_2$	—
	1.0		79.2
	2.0		—
	3.0		77.1
3 g urea + 1 mL $\text{H}_2\text{O}_2$ , $160^{\circ}\text{C}$	$\text{SnO}_2$	3.73	173.3
3 g urea + $\text{N}_2$ purged, $160^{\circ}\text{C}$	$\text{SnO}$	2.71	5.2

**Fig. 2** (a) TGA and (b) DTA curves of the  $\text{SnO}_2$  prepared at different temperatures.**Fig. 4** (a) X-ray diffraction patterns and (b) UV-vis DRS spectra of the  $\text{SnO/SnO}_2$  composites prepared in different urea-containing solutions and the prepared  $\text{SnO}$ . The inset shows the corresponding Tauc plots and the appearance of the samples.**Fig. 3** SEM images of the samples prepared at different temperatures (a) 120, (b) 140, (c) 160, (d) 180, (e) 200  $^{\circ}\text{C}$ , and (f)  $\text{SnO}_2$  prepared at  $160^{\circ}\text{C}$  in  $\text{H}_2\text{O}_2$ -contained solution.

$\text{SnO}_2$  is improved and the sample colour changes from slight brown to dark brown as shown in the inset of Fig. 4b. The absorption of  $\text{SnO/SnO}_2$  is gradually extended to the visible range with an increase of urea dosage.  $\text{SnO}$  shows the highest visible light absorption coefficient due to its black colour and the  $E_g$  is 2.71 eV, agreeing well with the reported result.<sup>1</sup> The  $E_g$



of SnO/SnO<sub>2</sub> samples were estimated by Tauc plots (the inset of Fig. 4b) and the results are summarized in Table 1.

Fig. 5 shows the SEM images of the prepared SnO/SnO<sub>2</sub>. Resembling the sample prepared in water (without urea, Fig. 5a), rod-like samples (Fig. 5b–e) with a length of about 15 μm and a diameter of about 3 μm were also obtained in the urea-contained solution. However, a decomposition of the rods can be observed with an increase of urea dosage and the surface becomes rough (Fig. 5b–e). Some small particles then appear and distribute on the rods surface. As shown in Fig. 5f, the morphology of the prepared SnO is quite different to SnO/SnO<sub>2</sub> composites. The sample is composed of many tightly aggregated strips.

The morphology feature of the SnO/SnO<sub>2</sub> was further characterized by TEM using the sample prepared in 3 g urea-contained solution as a representative. As shown in Fig. 6a and b, some nanosheets and small rods with a diameter of *ca.* 10 nm and a length of *ca.* 300 nm (indicated by the arrows in Fig. 6b) can be observed. The small rods are covered by the nanosheets. The SAED pattern in Fig. 6c indicates the polycrystalline nature of the nanosheets. The diffraction rings from the inner to outward can be indexed to the (110), (101), (200), and (211) planes of SnO<sub>2</sub>, respectively. Two sets of lattice space with *d* values of 0.26 and 0.33 nm can be found in the HRTEM images (Fig. 6d and e), which corresponds to the (101) and (110) planes of tetragonal SnO<sub>2</sub>. The results suggest that the sheet-like particles are SnO<sub>2</sub>. As for the small rods, the HRTEM image (Fig. 6f) demonstrates that the *d* value of the lattice space is 0.29 nm, which corresponds to the (101) plane of SnO.<sup>43</sup> Thus, the small rods are SnO. Similar structure of SnO has been reported in SnO/SnO<sub>2</sub> composite.<sup>40</sup>

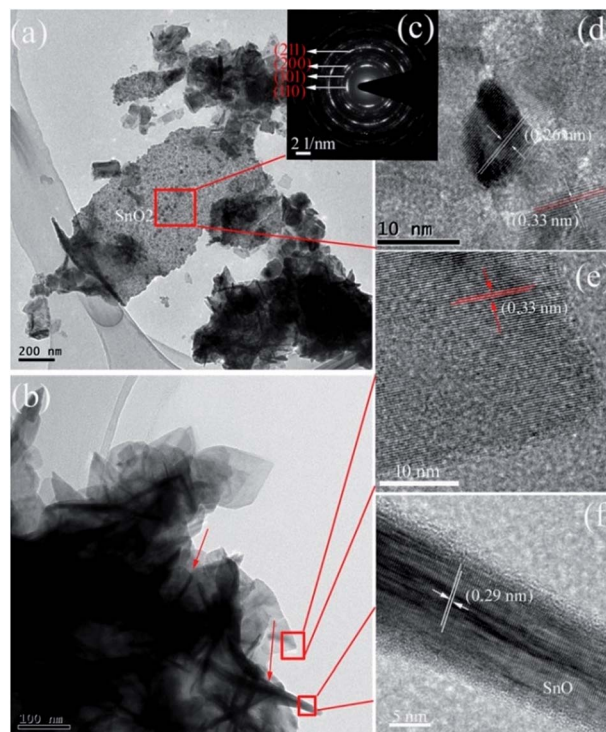


Fig. 6 (a and b) TEM, (c) SAED, and (d–f) HRTEM images of the prepared SnO–SnO<sub>2</sub> in 3 g urea-contained solution.

Some of the prepared samples including SnO<sub>2</sub>, Sn<sup>2+</sup>–SnO<sub>2</sub>, SnO/SnO<sub>2</sub> and SnO were analyzed by XPS to study the chemical states of Sn and O. The survey spectra (Fig. S2–a†) clearly indicate that, besides the adventitious C, the samples are composed of Sn and O. The double peaks located at the binding energy of 486.7 and 495.2 eV with a spin–orbit splitting energy of 8.5 eV can be ascribed to the Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub>, respectively. As shown in Fig. 7, except for SnO<sub>2</sub>, the Sn 3d<sub>5/2</sub> peak can be

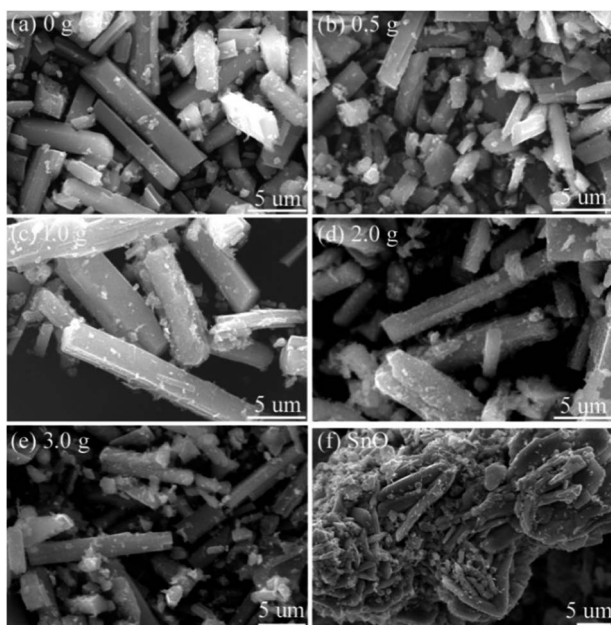


Fig. 5 SEM images of the samples prepared in different urea-contained solutions (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 3.0 g, and (f) the prepared SnO.

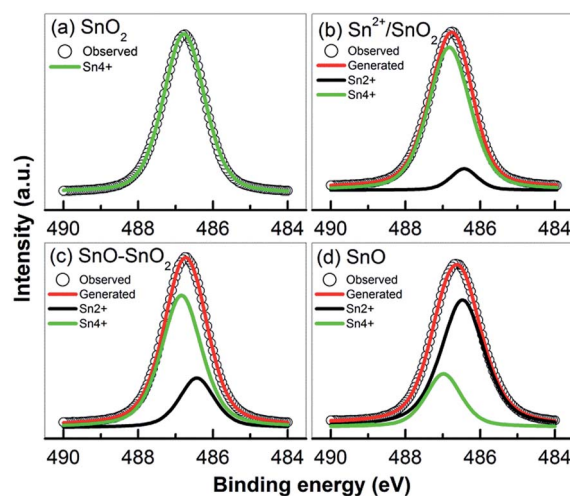


Fig. 7 High resolution XPS of Sn 3d<sub>5/2</sub> peak taken from (a) SnO<sub>2</sub>, (b) Sn<sup>2+</sup>–SnO<sub>2</sub> (prepared at 160 °C), (c) SnO/SnO<sub>2</sub> (prepared in 3 g urea added solution), and (d) SnO.



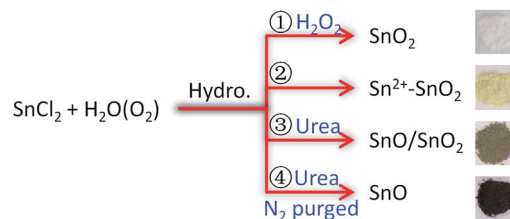


deconvoluted into two peaks centered at 486.4 and 486.8 eV, which can be assigned to  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$ , respectively.<sup>55</sup> The lack of a prominent binding energy shift of Sn 3d for different oxidation states can be attributed to the Madelung effects.<sup>56</sup> No  $\text{Sn}^{2+}$  signal can be detected in  $\text{SnO}_2$  (Fig. 7a) suggesting that the oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  can be effectively achieved by adding  $\text{H}_2\text{O}_2$  into the solution. However, as shown in Fig. 7b, if no  $\text{H}_2\text{O}_2$  was added, although most of  $\text{Sn}^{2+}$  was oxidized to  $\text{Sn}^{4+}$  by the dissolved  $\text{O}_2$ , about 9.3%  $\text{Sn}^{2+}$  (based on the ratio of the  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  peak areas) was reserved due to the depletion of dissolved  $\text{O}_2$ . This  $\text{Sn}^{2+}$  can be incorporated into  $\text{SnO}_2$  lattice as a self-doping element. When urea was added, the  $\text{Sn}^{2+}$  content was substantially improved to *ca.* 25.1%. The decomposition of urea at 160 °C provides an anaerobic environment to preserve more  $\text{Sn}^{2+}$  component, which is survived in a form of  $\text{SnO}$  as indicated by the XRD results (Fig. 4a). The signal of  $\text{Sn}^{4+}$  still can be found on the prepared  $\text{SnO}$  in Fig. 7d and its percentage is determined to be *ca.* 24.8%. Considering that XPS is a surface characterization technique and only trace amount of  $\text{SnO}_2$  was observed in the XRD pattern (Fig. 4a), this  $\text{SnO}_2$  should be on  $\text{SnO}$  surface and is formed by the oxidation of  $\text{Sn}^{2+}$  in an ambient environment.<sup>55,57</sup> The bulk of the sample should still be  $\text{SnO}$ . Fig. S2-b† shows the high resolution of O 1s spectrum. All the samples exhibit a broad and asymmetric O 1s peak which can be resolved into two peaks, one centered at 530.0 eV and the other at 531.7 eV. The peaks can be assigned to the crystal lattice oxygen in  $\text{SnO}$  or  $\text{SnO}_2$  (ref. 47) and the adsorbed  $\text{O}_2$  or surface -OH group.<sup>38</sup>

The above results indicate that the composition of the product is determined by the atmosphere of the hydrothermal solution, which is achieved by controlling the solution composition.  $\text{Sn}^{2+}$  can be oxidized to  $\text{Sn}^{4+}$  along with its hydrolysis in  $\text{H}_2\text{O}$ . The dissolved  $\text{O}_2$  serves as the oxidant.<sup>14,41</sup> Due to the limitation of  $\text{O}_2$  content, some  $\text{Sn}^{2+}$  can survive as a self-doping monomer in the product, leading to the formation of  $\text{Sn}^{2+}$ - $\text{SnO}_2$ . This  $\text{Sn}^{2+}$  residue can be eliminated by adding  $\text{H}_2\text{O}_2$  into the solution. Then pristine  $\text{SnO}_2$  can be produced. But when urea was added, the decomposition of urea at 160 °C (ref. 58) could lead to a mixture atmosphere of  $\text{O}_2$  and  $\text{CO}_2$ . Some part of  $\text{Sn}^{2+}$  precursor then was oxidized to  $\text{SnO}_2$ , while the other was converted to  $\text{SnO}$  under the protection of  $\text{CO}_2$ , resulting in a  $\text{SnO}/\text{SnO}_2$  composite. In this urea-contained solution, if the dissolved  $\text{O}_2$  was removed by purging with  $\text{N}_2$  before the hydrothermal treatment,  $\text{SnO}$  then can be produced. The traces of  $\text{SnO}_2$  in  $\text{SnO}$  as shown in Fig. 4 may be caused by the oxidation of  $\text{SnO}$ , which occurs during the collection or storage of  $\text{SnO}$ . The selective preparation of these Sn oxides is briefly described in Scheme 1.

### 3.3 Photocatalytic activity

The visible light photocatalytic performances of the prepared samples were examined by the degradation of MO. Fig. S3 and S4† show the time-dependent decolorization of MO over the prepared samples. As shown in Fig. S5,† the azo bond (N=N) and the two benzene rings (B1) and the small one at 270 nm



- ①  $\text{Sn}^{2+} + \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{Sn}(\text{OH})_4 \rightarrow \text{SnO}_2$
- ②  $\text{Sn}^{2+} + \text{OH}^- + \text{O}_2 \rightarrow \text{Sn}(\text{OH})_x \text{ (} 2 < x < 4 \text{)} \rightarrow \text{Sn}^{2+}\text{-SnO}_2$
- ③  $\text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{CO}_2 + \text{OH}^-$   
 $\text{Sn}^{2+} + \text{OH}^- + \text{O}_2 + \text{CO}_2 \rightarrow \text{Sn}(\text{OH})_2 + \text{Sn}(\text{OH})_4 \rightarrow \text{SnO}/\text{SnO}_2$
- ④  $\text{Sn}^{2+} + \text{OH}^- + \text{N}_2 \rightarrow \text{Sn}(\text{OH})_2 \rightarrow \text{SnO}$

**Scheme 1** Briefly diagram the conversion of  $\text{SnCl}_2$  to the desired Sn oxides by controlling the hydrothermal solution composition.

(B2), respectively.<sup>59</sup> In the presence of  $\text{Sn}^{2+}$ - $\text{SnO}_2$  and  $\text{SnO}/\text{SnO}_2$ , a decrease of B1 with irradiation time can be observed in Fig. S3 and S4,† suggesting the destruction of the conjugated structure of MO. After irradiation for *ca.* 60 min, a complete decolorization of MO can be realized over these samples except for  $\text{Sn}^{2+}$ - $\text{SnO}_2$  prepared at 200 °C (Fig. S3-e†) and the solutions become colourless (as shown in the inset of Fig. S4-d†). However, the absorption of B2 still can be observed and is even improved with irradiation time. The increase of B2 suggests that these samples have low activity to cleave the highly stable aromatic rings. The accumulation of the fragments formed from the destruction of the chromophore bond accounts for the increase of B2. MO cannot be decolorized by the prepared  $\text{SnO}_2$  (Fig. S3-f†) as it cannot be activated by visible light. This result eliminates the possibility that the decolorization of MO is caused by a photosensitized oxidative process.<sup>60</sup> Blank tests indicate that MO cannot be decomposed without the photocatalyst or the irradiation (Fig. S3-g and h†). Although  $\text{SnO}$  shows the highest visible light absorption coefficient, only 10% MO was decolorized after irradiation for 50 min. This may be caused by the fact that the 'OH which accounts for the decolorization of MO cannot be effectively produced on  $\text{SnO}$  (see below) and the BET surface area is as low as  $5.2 \text{ m}^2 \text{ g}^{-1}$  (Table 1).

The temporal change of MO concentration was measured by the absorbance of B1 to compare the photocatalytic performance of the prepared samples. As shown in Fig. 8, the activity of  $\text{Sn}^{2+}$ - $\text{SnO}_2$  is slightly improved by enhancing the preparation temperature from 120 to 160 °C, then drops sharply with further increasing the temperature to 200 °C. Only 43% MO was decolorized after irradiation for 70 min on the sample prepared at 200 °C. The sample prepared at 160 °C shows the highest activity and the complete decolorization of MO can be achieved within 30 min. As the BET surface area of  $\text{Sn}^{2+}$ - $\text{SnO}_2$  samples is around  $100 \text{ m}^2 \text{ g}^{-1}$  (Table 1), the activity reduction of the samples prepared at high temperature should be caused by the decrease of  $\text{Sn}^{2+}$  doping amount. As for the prepared  $\text{SnO}/\text{SnO}_2$ , the activity seems less impacted by the urea amount, as well as the BET surface area (*ca.*  $78 \text{ m}^2 \text{ g}^{-1}$ , Table 1). Their activities are comparable to each other.



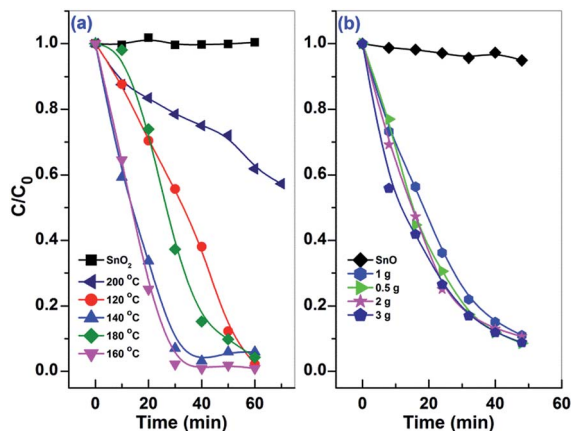


Fig. 8 The temporal changes of MO concentration with irradiation time over the (a)  $\text{Sn}^{2+}$ - $\text{SnO}_2$  prepared at different temperatures and  $\text{SnO}_2$ , and (b)  $\text{SnO}/\text{SnO}_2$  prepared in different urea-contained solutions and  $\text{SnO}$ .

The photocatalytic stability of  $\text{Sn}^{2+}$ - $\text{SnO}_2$  and  $\text{SnO}/\text{SnO}_2$  was investigated by reusing the photocatalysts. Unfortunately, as shown in Fig. 9, a deactivation of the samples can be observed. The activity can sustain for 3 runs on  $\text{Sn}^{2+}$ - $\text{SnO}_2$ , while on  $\text{SnO}/\text{SnO}_2$ , it can only sustain for 1 run. Considering that the visible light photocatalytic activity is originated from  $\text{Sn}^{2+}$  species and the oxidation potential of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  is only 0.15 V (vs. SHE),<sup>11,41</sup> the deactivation of the samples is caused by the oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  during the reaction.

### 3.4 Proposed reaction mechanism

The photocurrents of the prepared  $\text{Sn}^{2+}$ - $\text{SnO}_2$ ,  $\text{SnO}/\text{SnO}_2$ ,  $\text{SnO}$ , and  $\text{SnO}_2$  were measured under visible light irradiation to

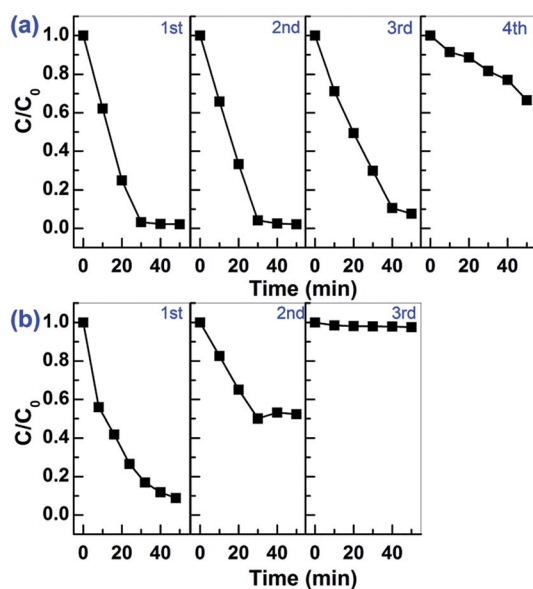


Fig. 9 Cycling tests for the photocatalytic decolorization of MO on (a)  $\text{Sn}^{2+}$ - $\text{SnO}_2$  prepared at 160 °C and (b)  $\text{SnO}/\text{SnO}_2$  prepared in 3 g urea added solution.

investigate the generation and the separation of the photo-induced charge carriers. As shown in Fig. 10, only  $\text{Sn}^{2+}$ - $\text{SnO}_2$  and  $\text{SnO}/\text{SnO}_2$  show apparent reversible photocurrent responses with light on and off. The result confirms that a visible light response can be involved by doping  $\text{SnO}_2$  with  $\text{Sn}^{2+}$  or coupling it with  $\text{SnO}$ . Surprisingly, although  $\text{SnO}/\text{SnO}_2$  shows a comparable photocatalytic activity to  $\text{Sn}^{2+}$ - $\text{SnO}_2$ , the photocurrent density of  $\text{SnO}/\text{SnO}_2$  is substantially lower than the latter. A decay of the photocurrent with irradiation time can be observed on both of the samples, further suggesting their instability. Although  $\text{SnO}$  shows a visible light absorption, the photocurrent is negligible. It seems that the photo-induced charge carriers are consumed by  $\text{SnO}$  itself, rather than migrating to the surface to form a current. This may be the reason why  $\text{SnO}$  shows quite low performance for the decolorization of MO (Fig. 8b) and the activity of  $\text{SnO}/\text{SnO}_2$  can only sustain for one run (Fig. 9b). The photocurrent of  $\text{SnO}_2$  is negligible as it cannot be activated under visible light.

The photocurrent results suggest that the charge carriers can be generated on  $\text{Sn}^{2+}$ - $\text{SnO}_2$  and  $\text{SnO}/\text{SnO}_2$  under visible light irradiation. These charge carriers can further react with the adsorbed  $-\text{OH}$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$  to form the active radicals.  $\cdot\text{OH}$  is one of the key active species for the degradation of pollutants. According to the band structures of  $\text{SnO}/\text{SnO}_2$  and  $\text{Sn}^{2+}$ - $\text{SnO}_2$  (Fig. S6†),  $\cdot\text{OH}$  can be induced by the photogenerated  $h^+$  in these samples as the standard reduction potential of  $\cdot\text{OH}/-\text{OH}$  is 1.99 V.  $\cdot\text{OH}$  formed on these samples was trapped by TA. As shown in Fig. S7,† the characterized fluorescence peak of TAOH at 425 nm can be observed on the prepared  $\text{Sn}^{2+}$ - $\text{SnO}_2$  (Fig. S7a-e†) and  $\text{SnO}/\text{SnO}_2$  (Fig. S7g-k†) and the signal increases gradually with irradiation time. It suggests that the prepared  $\text{Sn}^{2+}$  incorporated  $\text{SnO}_2$  samples have the capability to form  $\cdot\text{OH}$  under the visible light irradiation. For  $\text{SnO}$ , the formation of TAOH is far slower than the  $\text{Sn}^{2+}$  incorporated  $\text{SnO}_2$  samples and ceased after irradiation for ca. 25 min. Other control tests indicated that the formation of  $\cdot\text{OH}$  on  $\text{SnO}_2$  is negligible and cannot be perceived for the tests without a photocatalyst or illumination (Fig. S7m-o†). The formation efficiency of  $\cdot\text{OH}$  on

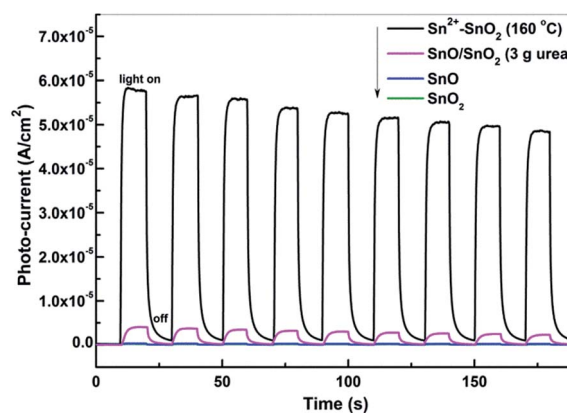


Fig. 10 Photocurrent responses of  $\text{Sn}^{2+}$ - $\text{SnO}_2$  prepared at 160 °C,  $\text{SnO}/\text{SnO}_2$  prepared in 3 g urea added solution,  $\text{SnO}$ , and  $\text{SnO}_2$  under visible light irradiation ( $\lambda > 400$  nm).



the prepared Sn<sup>2+</sup>-SnO<sub>2</sub> and SnO/SnO<sub>2</sub> samples is generally in agreement with their photocatalytic performances shown in Fig. 8. This relevance suggests that at least ·OH accounts for the degradation of MO. The visible-light-induced e<sup>-</sup> and h<sup>+</sup> are aroused by the doping of Sn<sup>2+</sup> (ref. 41) or the coupling of SnO component<sup>38,40,61</sup> (the electronic contributions from 5s orbitals of Sn<sup>2+</sup>). These charge carriers can be trapped by O<sub>2</sub>, H<sub>2</sub>O, or adsorbed -OH to generate ·OH or other oxidative species, which eventually lead to the decomposition of MO. Besides, Sn<sup>2+</sup> also can be oxidized to Sn<sup>4+</sup> by these oxidative species, leading to the deactivation of Sn<sup>2+</sup>-SnO<sub>2</sub> and SnO/SnO<sub>2</sub> (Fig. 9).

## 4. Conclusions

We have developed a simple and effective hydrothermal method to selective preparation of SnO<sub>2</sub>, Sn<sup>2+</sup>-SnO<sub>2</sub>, SnO/SnO<sub>2</sub>, and SnO with SnCl<sub>2</sub> as precursor. Through adding H<sub>2</sub>O<sub>2</sub> or urea, the solution can be tuned from an O<sub>2</sub>-rich to O<sub>2</sub> deficient atmosphere, which facilitates the transformation of Sn<sup>2+</sup> to SnO<sub>2</sub> and the preservation of Sn<sup>2+</sup> (in a form of doping Sn<sup>2+</sup> or SnO component), respectively. The absorption of SnO<sub>2</sub> can be successfully extended to the visible light region after self-doping with Sn<sup>2+</sup> or coupling with SnO, which endows a visible light photocatalytic activity for MO degradation. Unfortunately, due to the oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup>, the activities of the samples are quite unstable. Further work is still required to improve their photo-stability. Nonetheless, we believe that this work provides a simple method to selective preparation of different Sn-based oxides, which is essential for their applications, such as the detection of NO and NO<sub>2</sub> based on SnO or SnO<sub>2</sub>.<sup>61</sup> The work also provides a useful concept that is, through controlling the atmosphere of the solution, the oxidation state of metal oxides can be readily tuned by a hydrothermal method.

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