Facet-controlled synthesis and facet-dependent photocatalytic properties of SnO\textsubscript{2} micropolyhedrons

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\textbf{ABSTRACT}

The facet-dependent properties of SnO\textsubscript{2} are of fundamental and practical importance. In this study, by adjusting the deposition temperature during chemical vapor deposition, octahedral SnO\textsubscript{2} with the exposed (1 0 1) facet and two other kinds of SnO\textsubscript{2} polyhedrons with (1 0 1) and (1 0 0) facets with different ratios are fabricated controllably based on the vapor–solid growth mechanism. A slight increase in the deposition temperature from 1030 to 1070 °C decreases the surface energy of the reduced (1 0 1) facet with Sn termination, leading to the formation of polyhedrons with different area ratios of (1 0 1) to (1 0 0) facets. By adopting the terephthalic acid fluorescent method, the SnO\textsubscript{2} octahedrons are demonstrated to have the strongest photocatalytic activity due to the formation of surface states induced by 5s electrons of bivalent Sn on the (1 0 1) surface. The results reveal that the photocatalytic properties of SnO\textsubscript{2} microcrystals can be enhanced by facet-controlled synthesis.

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1. Introduction

There has been extensive research on metal oxide nanomaterials due to their favorable properties and versatile applications. Among the various metal oxide materials, SnO\textsubscript{2} has attracted much attention especially in the fields of gas sensors [1], dye-based solar cells [2], lithium-ion batteries [3], supercapacitors [4], transparent conducting electrodes [5], catalyst support [6–8], and photodetector [9]. It has been shown that controlling the exposed facets during synthesis is an effective method to tailor the functionalities of various materials [6–19]. However, the surface-dependent properties of SnO\textsubscript{2} have not been studied as extensively, possibly due to the practical difficulty in obtaining SnO\textsubscript{2} structures with the desirable surface characteristics. In fact, most SnO\textsubscript{2} materials have either an ill-defined morphology or a set of nonsymmetrical \{h k l\} facets, for instance, nanobelts consisting of non-equivalent \{1 0 1\}/\{0 1 0\} or \{1 0 1\}/\{1 0 0\} side surfaces [20]. Since conventional synthetic processes typically employ capping agents or morphology-modifying agents, the effects usually cannot be excluded [21–23]. Therefore, in order to investigate the effects of different facets, it is crucial to develop a simple and surfactant-free technique to synthesize nanostructures with well-defined facets in a controlled fashion. In this respect, chemical vapor deposition (CVD) is an effective method to fabricate nanostructures and microstructures and excludes the influence of surfactants. Some experiments and theoretical calculation indicate that the stoichiometric SnO\textsubscript{2} surface with exposed (1 0 1) and (0 1 0) and reduced termination can be obtained by occupying or vacating the bridging oxygen sites in a certain environment without complex reconstruction(Fig. S1) and hence, these two surfaces can be utilized to investigate the fundamental surface science on SnO\textsubscript{2} [24–26]. On the stoichiometric (1 0 1) and (1 0 0) surfaces, all the Sn ions have a valence of +4. When bridging oxygen atoms are removed, that is, on a reduced surface, the outermost Sn ions become +2 to compensate for the loss of negative charges on the O ions. This significantly changes the facet-dependent optoelectronic properties of the materials. However, although detailed investigation of the surface-dependent properties of SnO\textsubscript{2} microstructures and nanostructures has seldom been performed, it is important to prepare SnO\textsubscript{2} microstructures with (1 0 1) and (1 0 0) facets in a convenient way and to study the facet-dependent photocatalytic activity. In this study, SnO\textsubscript{2} polyhedrons with well-defined facets are fabricated and the facet-dependent photocatalytic activity is studied by the terephthalic acid fluorescent method.
2. Experimental

2.1. Sample preparation

The SnO₂ polyhedrons were prepared on silicon substrates by CVD on an apparatus schematically described in Fig. S2. In a typical process, a mixture consisting of tin powders (3 g) and active carbon (0.5 g) was put on an alumina boat 3 cm long and the alumina boat was inserted into the center of a small quartz tube with a diameter of 1.6 cm and length of 30 cm. The quartz tube confines the reagents in a small volume creating a stable growth environment. The small quartz tube was put at the center of a horizontal quartz tube with a diameter of 5.2 cm in a conventional tubular furnace. A clean Si sample with dimensions of 1 × 1 cm² was mounted on a substrate holder next to the edge of the alumina boat and the vertical distance between the wafer and source was about 0.5 cm. Before heating, the quartz tube was evacuated and Ar was bled into the quartz tube to the ambient pressure. The temperature was ramped up from room temperature to 1030, 1050, or 1070 °C in 30 min and maintained for a period of 3 h. Mixed Ar [50 standard cubic centimeter per minute (sccm)] and O₂ (3.95% O₂) were introduced during the reaction. Afterwards, the furnace cooled naturally to room temperature and white products were produced on the substrate.

2.2. Characterization

A field-emission scanning electron microscope (FE-SEM, Hitachi 4800) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to observe the morphology and size of the products. The crystal structure was investigated by X-ray diffraction (XRD) using monochromatic Cu Kα radiation. The transmission electron microscopy (TEM) images, selected-area electron diffraction (SAED) patterns, and high-resolution transmission electron microscopy (HR-TEM) micrographs were acquired on a JEOL 200CX microscope. X-ray photoelectron spectroscopy (XPS) was performed on the PHI 5000 VersaProbe and fluorescence spectra were acquired on a fluorescence spectrophotometer (Edinburgh FLS-920) with a 50 W xenon lamp as the excitation source. Diffuse reflectance spectra were recorded on a UV–vis-NIR spectrophotometer (VARIAN Cary5000). The Brunauer–Emmett–Teller (BET) surface areas were determined using the nitrogen adsorption–desorption isotherms at 77 K obtained on a Micromeritics ASAP2010 equipment. The samples were degassed at 200 °C before the nitrogen adsorption measurement.

2.3. Photocatalytic activity measurement

The photocatalytic activity was assessed by monitoring the amount of active hydroxyl radicals (·OH) radicals generated by the terephthalic acid fluorescent method.[22,27,28] The process is described briefly as follows. Five milligrams of the as-prepared products was suspended in 80 mL of an aqueous solution containing 0.01 M NaOH and 3 mM terephthalic acid. The suspension was stirred in darkness for 30 min and then irradiated by a 400 W lamp. In the process, 5 mL of the solution were taken out every 20 min and centrifuged for the fluorescent spectral measurement. The 320 nm line of a xenon lamp was used as the excitation source. To evaluate the stability of sample 3, cycling tests were performed. Each run lasted 1 h, and three runs were carried out. The fluorescent spectra were acquired at 20 min intervals. After each run, the suspensions were filtered and the precipitates were collected for the next run.

2.4. Photoelectrochemical measurements

The photocurrents and electrochemical impedance spectra (EIS) were acquired on a three-electrode configuration connected to CHI 660D work station (CH Instrument). The work station used an epoxy-sealed SnO₂ microcrystal sample as the working electrode with an active area of 0.5 cm², a Pt mesh as the counter electrode, Ag/AgCl (3 mol L⁻¹ KCl-filled) as the reference electrode, and 0.5 M Na₂SO₄ aqueous solution as the electrolyte. A 400 W xenon lamp was the light source. On the backside of the Si substrate, an ohmic contact was established using eutectic gallium–indium alloy. The transient photocurrent response was monitored at a constant potential of +0.6 V relative to the working photoanode. The impedance data were collected under an AC perturbation signal of 5 mV over the frequency range between 10,000 and 0.01 Hz.

3. Results and discussion

Fig. 1a and b shows the low- and high-magnification FE-SEM images of the products synthesized at 1030 °C (sample 1), respectively. The particles possess perfect and regular prism morphology with a smooth surface. Fig. 1b reveals that the individual particle is enclosed by four rectangular side facets and eight triangular facets. The adjacent rectangular side facets are perpendicular to each other. The four side facets and eight triangular facets are identified as the {100} and {101} facets, respectively, as schematically shown in Fig. 1c ([the {100} facets shown in light red and {101} facets in light yellow]). The low- and high-magnification FE-SEM images of the products synthesized at 1050 °C (sample 2) in Fig. 1d and e disclose that the individual microcrystal is also enclosed by four rectangular side facets and eight triangular facets, but the length and width of the rectangular side increase and decrease, respectively, compared to sample 1. That is, the particle is compressed along the c-axis (Fig. 1f). The low- and high-magnification FE-SEM images of sample 3 synthesized at 1070 °C are displayed in Fig. 1g and h. Compared to samples 1 and 2, the SnO₂ particles in sample 3 display an octahedral morphology with eight triangular facets only, while the four rectangular side facets are absent. The eight triangular surfaces on the octahedral crystal are {101} facets as shown in Fig. 1i (see analysis below). The average length and width (denoted as “a” and “b” in Fig. S3) of the side facets of samples 1–3 are about (1.2, 0.5), (1.4, 0.2), and (1.8, 0) μm, respectively. The ratio [ {101} ]/[ {100} ] + [ {100} ] of the {101} area is estimated to be about 50, 80, and 100% for the three samples. The calculation is shown in Fig. S3.

The X-ray diffraction patterns are shown in Fig. S4. The diffraction peaks can be indexed to the tetragonal rutile phase of SnO₂ (JCPDS card: 1445) and no impurity peaks are observed. The sharp diffraction peaks imply that the SnO₂ microcrystals have good crystallinity. The intensity ratios of the XRD peaks of the three samples are different from those of the SnO₂ powders indicating preferentially oriented growth. Moreover, the peak intensity of the {100} facet decreases gradually, indicating that the ratio of the {100} area decreases as consistent with the SEM images (Fig. 1). The TEM, SAED, and HR-TEM images of the three samples are depicted in Fig. 2 to provide structural details. The TEM image of sample 1 in Fig. 2a confirms the structure discussed above and the SAED pattern (Fig. 2b) projected along the [010]-axis reveals the single crystalline nature of sample 1. The HR-TEM image in Fig. 2c discloses two groups of clear lattice fringes with an interplanar lattice spacing of 0.264 nm corresponding to the {101} planes. The angle labeled 68° matches well with the theoretical calculation of the angle between the {101} and {101} planes. On the basis of the above analysis and symmetry of SnO₂, the triangular surface of the SnO₂ particle is identified as the {101} facet, whereas the four rectangular lateral surfaces are the {100} facets. The TEM image (Fig. 2d) of sample 2 is taken along the same zone axis [010] and it can be identified in Fig. 2e. The same interplanar lattice spacing shown in Fig. 2f shows that the particle in sample 2 is enclosed by
these facets which are the same as those for sample 1. The TEM image of sample 3 exhibits a well-defined octahedron structure (Fig. 2g). The corresponding SAED pattern in Fig. 2h indicates single-crystal characteristics and the diffraction spots can be indexed to the [001] zone axis of tetragonal SnO2. The HR-TEM image (Fig. 2i) taken from the edge labeled by the white box shows an interplanar lattice spacing of 0.237 nm corresponding to the (1 0 0) plane. These results confirm the conclusion described in Fig. 1. The UV-vis absorption spectra of the three samples are presented in Fig. S5. The absorption spectra of the three samples are almost the same, indicating that their absorption ability is similar.

The growth mechanism of the microcrystals can be explained by vapor–solid (VS) mechanism because no metal catalysts are used and no Sn droplets are present on the microcrystals. In the VS growth process, the surfaces are essentially in thermodynamic (or at least metastable) equilibrium with each other and therefore the process is thermodynamically controlled [29]. Theoretical calculation of the SnO2 surface based on stoichiometric terminations indicates that the sequence of surface energies of rutile SnO2 is (1 1 0) < (0 1 0) < (1 0 1) < (0 0 1) [29,30], in which the (1 1 0) facet has the lowest surface energy and is thermodynamically stable. Therefore, although the (1 1 0) facet is generally believed to appear on the products, it is not observed from our materials. A stable oxide surface can be regarded as a result of the dynamic balance between surface oxygen adsorption and desorption because of oxygen exchange with the atmosphere [31]. The oxygen chemical potential (as a function of oxygen partial pressure and temperature) influences the surface composition. Different degrees of oxidation of the SnO2 surface produce oxidized (stoichiometric), reduced (Sn-terminated), and over-adsorbed (O-terminated) surfaces [32]. Theoretical calculation suggests that the reduced (1 0 1) surface (Sn-terminated) has a lower surface energy than the (1 1 0) surface and can be more stable in a given environment (low oxygen partial pressure or high temperature) [24,25,32]. As the deposition temperature is increased, the surface energy of the reduced (1 0 1) facet diminishes. Hence, when the temperature is increased, the area ratio of the (1 0 1) surface increases as well and in our experiments, when the temperature reaches 1070 °C, only the (1 0 1) surface can be observed as shown in Fig. 1g–i.

To determine the composition and chemical states of the (1 0 1) surface, the XPS spectra are presented in Fig. 3a–c and the valence band spectra of the three samples are shown in Fig. 3d. The XPS data are calibrated to the C 1s peak at 284.6 eV arising from residual carbon on the samples. The fitted data show that the O 1s peak is composed of three components (Table 1). The smallest binding energy peaks (O1) (529.81, 529.80, and 529.78 eV) are assigned to O–Sn4+ bonding, the middle binding energy peak (O2) (530.49, 530.45, and 530.49 eV) to O–Sn4+ bonding, and the largest binding energy peak (O3) centered at 532.65, 532.77, and 531.86 eV to

<table>
<thead>
<tr>
<th>SnO2 samples</th>
<th>O1 (O–Sn4+)</th>
<th>O2 (O–Sn4+)</th>
<th>O3 (O-chem)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>529.81</td>
<td>530.46</td>
<td>532.65</td>
</tr>
<tr>
<td>Binding energy (eV)</td>
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<td>43.8</td>
<td>43.4</td>
</tr>
<tr>
<td>Relative percentage (%)</td>
<td><strong>532.75</strong></td>
<td><strong>37.9</strong></td>
<td>25.0</td>
</tr>
<tr>
<td>Sample 2</td>
<td>529.80</td>
<td>530.49</td>
<td>532.75</td>
</tr>
<tr>
<td>Binding energy (eV)</td>
<td>20.8</td>
<td>41.3</td>
<td>37.9</td>
</tr>
<tr>
<td>Relative percentage (%)</td>
<td><strong>531.53</strong></td>
<td><strong>25.0</strong></td>
<td>25.0</td>
</tr>
<tr>
<td>Sample 3</td>
<td>529.78</td>
<td>530.32</td>
<td>531.53</td>
</tr>
<tr>
<td>Binding energy (eV)</td>
<td>39.1</td>
<td>39.1</td>
<td>25.0</td>
</tr>
</tbody>
</table>
**Fig. 2.** Low-magnification TEM image, SAEA pattern, and corresponding HR-TEM image of the microcrystal particles in the three samples. (a–c) Sample 1; (d–f) Sample 2; (g–i) Sample 3.

**Fig. 3.** O 1s XPS spectra of (a) sample 1, (b) sample 2, and (c) sample 3. (d) Valence band XPS spectra of the three samples.
chemisorbed oxygen species [33]. The percentages of the O1 component in the three samples are about 12.8% (sample 1), 20.8% (sample 2), and 35.9% (sample 3). The trend of the percentages agrees with the variation in the \{101\} area ratios. It is generally considered that Sn\(^{4+}\) with oxygen vacancies can provide active sites to adsorb oxygen species. However, when the percentage of the O1 component is increased, the percentage of the O4 component decreases. On the reduced SnO\(_2\) (101) surface, no under-coordinated oxygen atoms are available and the threefold coordinated surface Sn\(^{4+}\) may also be considered as fully coordinated Sn (II) [25]. The reduced Sn\(^{4+}\) cations have two 5s electrons which can be described as lone pairs without dangling bonds and are generally inactive. Therefore, the reduced SnO\(_2\) (101) surface is quite inert with respect to molecular adsorption [26]. The area ratio of the chemisorbed oxygen species on sample 3 (100% \{101\} surface) is the smallest (Fig. 3c), thus verifying that the (101) surface is tin-terminated with the SnO stoichiometry. It is speculated that the (100) surface is stoichiometrically terminated because the formation temperature of the reduced (100) surface is higher than that of the (101) surface [25]. It has been demonstrated that reduction of the SnO\(_2\) (101) surface results in the formation of Sn 5s lone pair electron surface states that are low in the band gap on top of the bulk valence band maximum [26]. Fig. 3d shows that the valence band edges are at 2.70, 2.61, and 2.36 eV for samples 1–3, respectively. With increasing area ratios of the (101) surface, the separation between the valence band edge and Fermi energy level diminishes gradually, indicating that the surface states on (101) contribute to the shift of the valence band edge toward the Fermi energy level.

The photocatalytic activity is assessed by monitoring the amount of active hydroxyl radicals (\•OH) which are considered as the most important oxidative species in photocatalytic reactions [27]. Terephthalic acid (TA) reacts with \•OH to produce 2-hydroxyl terephthalic acid (TAOH) which emits a unique fluorescence signal at 426 nm. Fig. 4a shows the fluorescence spectra of the three samples in the TA solution associated with TAOH under irradiation of a Xe lamp for 60 min. The fluorescence intensity from sample 3 is the largest, indicating the highest generation ability of \•OH. Fig. 4b depicts irradiation time dependence of the 426 nm emission intensity from different samples. The fluorescence intensity is proportional to irradiation time suggesting good stability of the synthesized SnO\(_2\) microcrystals. With increasing \{101\} area ratios, the photocatalytic activity increases and sample 3 exhibits the strongest photocatalytic activity. The photocatalytic activity also depends on the specific surface area [34] and the larger the specific area, the better is the photocatalytic performance. Hence, the nitrogen absorption–desorption isotherm is acquired to calculate the specific surface areas of the three samples by the BET equation between 0.1 and 0.3 relative pressures (P/P\(_o\)). The results are 0.82, 0.74, and 0.62 m\(^2\) g\(^{-1}\) for samples 1, 2, and 3, respectively. Obviously, the particles in sample 3 have the smallest specific surface area, but they have the strongest photocatalytic activity (Fig. S6), suggesting that the high photocatalytic activity observed from sample 3 is mainly related to the surface structure.

The observed enhancement can be explained by the formation of Sn 5s derived surface states located at the upper edge of the valence band on the reduced SnO\(_2\) (101) surface. The photocatalytic activity enhanced by the surface states can be rationalized by two factors. Firstly, the surface states increase light absorption and secondly, one of the main aspects of photocatalytic activity is to reduce recombination of photogenerated carriers. The surface states may trap holes to enhance separation of electrons and holes. The photogenerated holes in the valence band can be easily transferred to the surface states of the (101) surface resulting in reduced spatial overlapping of the photoexcited electrons and holes and reducing the recombination probability on account of the nature of localization [35]. Based on the above analysis, a schematic diagram of the band gap structures is proposed in Fig. 5. After photoexcitation, the photogenerated electrons in the conduction band (CB) reduce the dissolved oxygen to \•O\(_2^-\) (Eq. (1)) and further reduction of \•O\(_2^-\) generates hydroxyl radicals \•OH (Eqs. (2) and (3)). The holes in valence band (VB) trapped by the surface states react with OH\(^-\) to yield the hydroxyl radicals \•OH (Eq. (4)).

\[
\begin{align*}
\text{O}_2 + e^- & \rightarrow \text{O}_2^- \quad \text{(1)} \\
\text{O}_2^- + 2\text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}_2 \quad \text{(2)} \\
\text{H}_2\text{O}_2 + e^- & \rightarrow \text{•OH} + \text{OH}^- \quad \text{(3)} \\
\text{h}^+ + \text{OH}^- & \rightarrow \text{•OH} \quad \text{(4)}
\end{align*}
\]

The increase in the \{101\} area ratio enables the holes to be transferred to the surface states more easily and this is the reason why sample 3 with 100% \{101\} facet has the strongest photocatalytic capability. Previous theoretical calculation indicates that all crystal facets of SnO\(_2\) dissociate water to different degrees or

Fig. 4. (a) Fluorescence spectra of the three samples in 3 mM terephthalic acid and 0.01 M NaOH solution after irradiation for 60 min. (b) Time dependence of the fluorescence intensity at 426 nm of the three samples in 3 mM terephthalic acid and 0.01 M NaOH solution after 400 W Xe lamp irradiation.

Fig. 5. Schematic illustration of the photocatalytic mechanism under xenon lamp irradiation.
partially adsorb water molecules on the surface [36]. The ability to dissociate water is stronger on the (101) facets than on (100) ones. In the photocatalytic process, the photogenerated holes react with surface OH− groups or adsorbed H2O molecules to generate hydroxyl radicals (•OH) and therefore, adsorption and dissociation of water molecules also help to enhance the photocatalytic activity in the present case.

To evaluate the separation efficiency of photogenerated charge carriers, the transient photocurrent response spectra are acquired from the SnO2 samples and the corresponding results are presented in Fig. S7a. The magnitude of the photocurrent is consistent with the intensity of photoluminescence from the produced TAOH and sample 3 shows the largest photocurrent density. It is well known that the higher the photocurrent, the higher is the separation efficiency of photogenerated carriers. The results confirm that sample 3 has the highest photogenerated charge separation efficiency due to the enhanced hole trapping ability by the surface states. According to the EIS results in Fig. S7b, the diameter of the semicircle in the Nyquist plot, which represents charge-transfer resistance [7,19], decreases from sample 1 to 3, indicating that the increase in the ratio of the exposed (10 1) facets can significantly reduce the recombination rate of the photogenerated electrons and holes.

In order to evaluate the stability of the photocatalytic performance of sample 3, cycling tests are performed to evaluate the amount of generated •OH. Fig. 6 shows the corresponding cycling data. Again, sample 3 exhibits good recycling ability which declines only by about 7% after three cycles providing evidence that the photocatalytic activity of sample 3 is quite stable.

4. Conclusion

Three kinds of SnO2 polyhedrons with tunable (1 0 1) facet ratios are synthesized by varying the deposition temperature in CVD. The temperature-dependent growth of the microcrystals follows the vapor–solid mechanism because no metal catalysts are used and no Sn nanodroplets are present on the microcrystals. The SnO2 polyhedrons with the completely exposed (10 1) facets have the highest photocatalytic activity due to generation of active OH groups. The surface states induced by Sn 5s electrons are believed to be responsible for the superior photocatalytic activity. These findings provide insights into the facet-dependent photocatalytic properties of SnO2 enabling better design and control of the materials characteristics.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2015.05.069.

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Supporting Information for Manuscript

Facet-controlled synthesis and facet-dependent photocatalytic properties of SnO$_2$ micropolyhedrons

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**Fig. S1.** Ball-and-stick models: (a) Reduced and (b) stoichiometric (101) surfaces; (c) Reduced and (d) (100) stoichiometric surfaces of rutile SnO$_2$. 
Fig. S2. Schematic diagram showing the experimental apparatus used in the synthesis of the SnO$_2$ microstructures with different morphologies.
Fig. S3. Model of the rutile SnO$_2$ single crystal.

The percentage of the \{101\} facet is calculated as follows:

$$S_{100} = 4ab$$

$$S_{101} = 8 \times \frac{1}{2} \times \frac{1}{\cos \theta} = \frac{2a^2}{\cos \theta}$$

$$S_{101\%} = \frac{S_{101}}{S_{100} + S_{101}} = \frac{\frac{2a^2}{\cos \theta}}{4ab + \frac{2a^2}{\cos \theta}} = \frac{1}{1 + 2 \cos \theta \times \left(\frac{b}{a}\right)}$$

Here, $\theta$ is $34^\circ$. It is the theoretical value for the angle between the (101) and (001) facets of rutile SnO$_2$. As shown in the model, the parameters $a$ and $b$ denote the length and width of the rectangular side of the SnO$_2$ (100) facet, respectively.
Fig. S4. XRD patterns acquired from the three SnO$_2$ samples.
Fig. S5. UV-vis absorption spectra of the three different SnO$_2$ samples used in this work.
Fig. S6. Normalized fluorescence intensity per unit surface area from three different SnO$_2$ samples in 3 mM terephthalic acid and 0.01 M NaOH solution under a Xenon lamp irradiation. Obviously, the particles in sample 3 have the smallest specific surface area, but they have the strongest photoreactivity.
Fig. S7. (a) Transient photocurrent responses and (b) impedance spectra of the three different SnO₂ samples under a Xenon lamp irradiation.