



Three-dimensional hierarchical SnO₂ dodecahedral nanocrystals with enhanced humidity sensing properties



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ABSTRACT

One-step hydrothermal method was adopted to synthesize tin dioxide (SnO₂) nanostructures with different morphologies, i.e., three-dimensional (3D) hierarchical SnO₂ dodecahedral nanocrystals (DNCs), 3D hierarchical SnO₂ nanorods (NRs), and SnO₂ nanoparticles (NPs). The humidity sensors based on the as-synthesized nanostructures were produced to investigate the relationship between morphology and humidity sensing property. The nanosensor based on 3D hierarchical SnO₂ DNCs exhibited superior humidity sensing properties compared to those based on 3D hierarchical SnO₂ NRs and SnO₂ NPs. The enhanced sensing properties for SnO₂ DNCs are attributed to the peculiar 3D open nanostructures and high chemical activity of the exposed {101} facets. The 3D open nanostructures can promote the penetration and diffusion of water molecules, and the exposed {101} facets can improve the adsorption ability of water molecules. Furthermore, density functional theory (DFT) calculations were performed to further confirm that {101} facets can adsorb more water molecules than {110} facets. Our results demonstrate that morphology and surface engineering is an effective strategy to enhance the humidity sensing properties of nanomaterials.

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1. Introduction

Since humidity has a great impact on the industrial production, storage of various goods and environmental monitoring, considerable investigations have been carried out to develop suitable humidity-sensitive materials for the fabrication of high-performance humidity sensors. Many types of functional materials such as metal oxides [1], polymers [2,3] and inorganic/organic hybrids [4] have been utilized as humidity sensing materials. Among the various sensing materials, metal oxides have received intensive interest due to their unique properties such as chemical and physical stability, high mechanical strength and wide operating temperature range [5–7].

Tin dioxide (SnO₂) is a versatile semiconductor material which is commonly used in gas sensor [8,9], lithium-ion battery [10] and solar cell [11]. Recently, SnO₂ has emerged as an important humidity sensing material due to its inherent chemical and physical stability [12] and easy adsorption of water in molecu-

lar or hydroxyl form [13]. However, SnO₂ humidity nanosensors displayed very long response and recovery times and low sensitivity [12,14]. Hence, many scientific and technological efforts have been directed towards improving humidity-sensing performance of SnO₂ humidity nanosensors. For example, many semiconductor hetero-contact systems such as TiO₂-SnO₂ [15], WO₃-SnO₂ [16], and RGO-SnO₂ [17] were reported to possess enhanced sensitivity and fast response and recovery times. However, to our knowledge, little information is available in previous reports about enhancing the humidity-sensing properties of SnO₂ through tuning its morphology and surface architecture.

It has been found that the properties of SnO₂ strongly depend on its morphology and shape. For instance, Wang et al. [18] prepared hierarchical flower-like SnO₂ nanospheres assembled from short nanorods (NRs) for potential applications in gas sensing and lithium-ion battery. Zhao et al. [19] synthesized SnO₂ hierarchical architectures to investigate the relationship between the morphology and photocatalytic activities. However, few investigations focus on the correlation between morphology and humidity-sensing properties.

Herein, we synthesized SnO₂ nanostructures with different morphologies including three-dimensional (3D) hierarchical SnO₂ dodecahedral nanocrystals (DNCs), 3D hierarchical SnO₂ NRs and

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SnO₂ nanoparticles (NPs) through one-step hydrothermal process, and studied the performance of the humidity sensors based on different SnO₂ nanostructures. Interestingly, in our experiments the sensors realized with 3D SnO₂ nanostructures (DNCs and NRs) showed a response time of less than 4 s and a recovery time of less than 13 s, both significantly superior to the SnO₂ NPs. The fast response and recovery times are attributed to the pore channels present in the 3D SnO₂ nanostructures. Moreover, compared with 3D hierarchical SnO₂ NRs, 3D hierarchical SnO₂ DNCs displayed higher sensitivity with an impressive impedance change of 4.2 orders in 11–95% relative humidity (RH) range. The high sensitivity is ascribed to the exposed {101} facets of 3D hierarchical SnO₂ DNCs which can improve the adsorption ability of water molecules and enhance the humidity sensitivity. Furthermore, density functional theory (DFT) calculations are performed to prove that {101} facets can adsorb more water molecules than {110} facets. This work will pave the way to the development of promising practical humidity sensors.

2. Experimental

All chemicals were of analytical grade and used as received. Distilled water was used throughout the whole experiment.

2.1. Synthesis of 3D hierarchical SnO₂ NRs

3D hierarchical SnO₂ NRs were synthesized by a simple hydrothermal method. Typically, under vigorous stirring, 20 mL of 0.75 mol/L NaOH aqueous solution was added to 20 mL of 0.075 mol/L SnCl₄·5H₂O ethanol solution, followed by ultrasonication for 5 min. The above mixture was then transferred into a 100 mL Teflon-sealed autoclave and maintained at 180 °C for 12 h. Subsequently, the resultant precipitates were collected by centrifugation and washed with distilled water and ethanol several times, and then dried at 60 °C for 12 h to obtain SnO₂ product.

2.2. Synthesis of SnO₂ NPs

0.35 g of SnCl₄·5H₂O and 0.6 g of benzimidazole were first dissolved into mixed solution with 20 mL distilled water and 20 mL ethanol, and then transferred into a 100 mL Teflon-sealed autoclave at 180 °C for 18 h. Finally, the obtained sample was rinsed with distilled water and ethanol for several times, and dried in air at 60 °C for 12 h.

2.3. Synthesis of 3D hierarchical SnO₂ DNCs

1 mmol SnCl₄·5H₂O, 10 mmol NaOH and 0.3 g sodium alginate were each dissolved in 20 mL, 20 mL and 30 mL distilled water. After that, NaOH solution was dripped into SnCl₄ solution while stirring to form a homogeneous solution. The mixture was then added into the sodium alginate solution dropwise under stirring and the resulting mixture was put into 100 mL Teflon-sealed autoclave, which was heated at 180 °C for 18 h. After cooling to room temperature, the resultant precipitates were centrifuged and thoroughly washed with distilled water and ethanol several times, and dried in air at 60 °C for 12 h.

2.4. Preparation of TEM samples

TEM samples of SnO₂ nanostructures were prepared by ultrasonication in ethanol for several minutes, and dispersing a drop onto a holey-carbon-film-coated copper grid.

2.5. Characterization

The morphologies of the as-synthesized samples were characterized by scanning electron microscope (SEM, Hitachi S-4800) and the crystal structures of the samples were analyzed by SmartLab XRD with Cu-Kα1 radiation ($\lambda = 1.5406 \text{ \AA}$). Selected-area electron diffraction (SAED) pattern, bright-field (BF) images, and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM2100F TEM with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi instrument with a monochromatic Al Kα radiation ($h\nu = 1486.6 \text{ eV}$) under an ultra-high vacuum (below 10^{-8} Pa). The binding energies were calibrated using C 1s peak (284.8 eV) as a reference.

The nitrogen adsorption-desorption was carried out on an automatic volumetric sorption analyzer (NOVA 1100, Quantachrome, USA) at 77 K. The Brunauer-Emmett-Teller (BET) was used to calculate the specific surface areas of different SnO₂ nanostructures. The pore size distributions were obtained using Barrerr-Joyner-Halenda (BJH) method.

2.6. Measurement of humidity sensing properties

Golden interdigital electrodes (10 mm × 10 mm × 0.5 mm) are employed as the basic test component to fabricate the humidity sensors, purchased from Shenzhen Xingshengjie Electronics Co., Ltd (Shenzhen, China). The schematic diagram of the interdigital electrodes is shown in Fig. S1. As shown in Fig. S1, both the width of a finger and the spacing between the adjacent fingers are about 75 μm. Two leading wires are connected with the gold electrodes by soldering of tin. Prior to use, the interdigital electrodes were ultrasonically cleaned in acetone, then rinsed thoroughly with distilled water and dried in vacuum. The test samples were ground and mixed with distilled water (weight ratio 10:1) to obtain a paste. After that, the paste was uniformly coated onto the sensing area of the interdigital electrodes and then dried in air at 60 °C for 12 h. Fig. S2 presents the cross-sectional SEM images of different SnO₂ nanostructures coated on the electrodes, from which it can be seen the coated films have a thickness of ~10 μm. The different RH levels were generated by various saturated salt solutions in the closed glass chambers at room temperature (25 °C). The eight different standard saturated aqueous salt solutions of LiCl, MgCl₂·6H₂O, K₂CO₃, Mg(NO₃)₂·6H₂O, KI, NaCl, KCl and KNO₃ which yield relative humidities (RHs) of 11%, 33%, 43%, 54%, 69%, 75%, 84% and 95%, respectively, were used to act as humidity sources. The RH levels were monitored by a standard hygrometer. The coated interdigital electrodes were placed successively into the chambers with different RH levels at room temperature and the impedance of the sensors was measured as a function of RH at 25 °C using a precision LCR meter (TH2828, China) and a Metrohm Autolab electrochemical workstation (PGSTAT 302N). To minimize the influence of laboratory climate, the sensors were rapidly switched between the above-mentioned chambers. The applied voltage was alternating current (AC) 1 V, and the frequency varied from 50 Hz to 100 kHz.

2.7. Theoretical calculations

All calculations in the present work were carried out by DMol³ program package in Material Studio [20,21]. Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) was used as exchange-correlation function [22]. The valence orbital of the atoms was described by setting the double-numeric quality with polarization functions (DNP), and DFT semi-core pseudopotentials (DSPPs) were employed to substitute the core electrons

[23,24]. The periodic (3×2) and (2×2) slab models were used to simulate the SnO_2 $\{110\}$ and $\{101\}$ surfaces, respectively.

3. Results and discussion

3.1. Characterization of samples

Fig. 1 displays the XRD patterns of the as-synthesized products. All the diffraction peaks can be indexed to tetragonal structure of SnO_2 (JCPDS no. 41-1445). No notable peak of impurities can be detected, which indicates that no other phase was formed. The diffraction peaks of 3D hierarchical SnO_2 NRs and DNCs are sharp and intense, as shown in Fig. 1(a) and (c). In contrast to the NRs and DNCs, the broader diffraction peaks of SnO_2 NPs are observed from Fig. 1(b). The average crystallite sizes are ~ 45 nm for NRs, ~ 5 nm for NPs and ~ 24 nm for DNCs, respectively, calculated from (110) peaks using Scherrer equation [25].

Fig. 2 presents SEM images of three different SnO_2 nanostructures. It can be seen from Fig. 2(a) that the 3D open nanostructures are assembled from one-dimensional (1D) SnO_2 NRs from their center towards different directions. These NRs are of well-defined quadrangular shape with a diameter of around 50 nm and a length of around 300 nm, as shown in high-magnification SEM image (Fig. 2(b)). Fig. 2(c) is a typical low-magnification SEM image of the as-synthesized SnO_2 NPs, in which a number of NPs are piled together. Fig. 2(d) shows a high-magnification SEM image of SnO_2 NPs, from which it can be seen that the diameter of NPs is 5–10 nm. Fig. 2(e) provides a typical SEM image of 3D hierarchical SnO_2 DNCs, from which it can be seen that 3D nanostructures are assembled from nanocrystals with a diameter of 20–30 nm. Close examinations of Fig. 2(f) show that these nanocrystals are dodecahedral, whose coping is pyramid-shaped as demonstrated in the inset of Fig. 2(f). Compared with NPs, it can be found that plenty of voids and interspaces are present in both 3D hierarchical NRs and DNCs, thus forming loose and porous 3D structures.

The element compositions of as-synthesized products were examined by XPS. Fig. 3(a) shows the XPS profiles of 3D hierarchical SnO_2 DNCs in the range of 0–1200 eV. All the peaks in Fig. 3(a) can be ascribed to Sn, O and C, which demonstrate that Sn, O and C elements exist in the SnO_2 DNCs. To study the detailed element compositions of 3D hierarchical SnO_2 DNCs, high-resolution XPS spectra were also performed. As shown in Fig. 3(b), there are two peaks in the Sn 3d region. The peak located at 485.9 eV corresponds to the Sn 3d_{5/2} and the other located at 494.3 eV is assigned to Sn 3d_{3/2} [26]. The splitting gap between the peaks of Sn 3d_{5/2} and Sn 3d_{3/2} is 8.4 eV, indicating a normal state of Sn^{4+} in the as-prepared SnO_2 DNCs. Fig. 3(c) presents the XPS spectrum of O 1s, from which it can be seen that the O 1s peak is broad and asymmetric, indicating that there could be more than one chemical state according to the binding energy [15]. Using the XPS peak fitting program, the O 1s spectrum can be fitted by three kinds of chemical states including crystal lattice oxygen (Sn–O), surface hydroxyl group (–OH) and adsorbed water (–H₂O). To compare the element compositions of different SnO_2 nanostructures, the SnO_2 NRs and NPs were also analyzed by XPS. Fig. S3 shows the XPS spectra of SnO_2 NRs and NPs, in which the O 1s spectra can be fitted using two kinds of chemical states (lattice oxygen and surface OH group). The different kinds of chemical states inferred from the O 1s spectra indicate that less surface OH groups and water molecules are adsorbed on the surface of the SnO_2 NRs and NPs than on the surface of 3D hierarchical SnO_2 DNCs [15].

The microstructures of different SnO_2 nanostructures were extensively examined by TEM. Fig. 4(a) displays a typical BF TEM image of 3D hierarchical SnO_2 NRs. Consistent with the above XRD pattern and SEM observation, the 3D SnO_2 nanostructures

are assembled from quadrangular-shape NRs with a diameter of 50 nm and a length of around 300 nm. The crystal lattice spacings measured from the HRTEM image are 3.35 Å and 3.15 Å, as indicated in Fig. 4(b), which correspond to $\{110\}$ side facets and $\{001\}$ top facets of nanorod (NR), respectively. The corresponding SAED pattern in Fig. 4(c) reveals that the SnO_2 NRs are single crystals and can be indexed to $[1\bar{1}0]$ zone-axis of tetragonal SnO_2 . Fig. 4(d) displays an atomic model of the ideal SnO_2 cuboid enclosed by $\{110\}$ and $\{001\}$ facets projected along the $[1\bar{1}0]$ direction. It can be seen that the outline of the SnO_2 NRs agrees well with the atomic model. The exposed $\{110\}$ facets is calculated to be $\sim 96\%$ by using $\{110\}/[\{001\} + \{110\}]$. Thus, we conclude that SnO_2 NRs are mainly exposed with $\{110\}$ facets.

Fig. 5(a) presents a typical BF TEM image of SnO_2 NPs. It clearly shows that the size of the NPs is 5–10 nm, which is consistent with the XRD and SEM results. Moreover, the congregation phenomenon of NPs is also found. The SAED pattern (inset in Fig. 5(a)) exhibits homocentric rings, which can be unambiguously attributed to the fact that the NPs are polycrystalline. Fig. 5(b) shows a typical HRTEM image of single nanoparticle (NP), from which the (110) lattice spacing is measured to be 3.35 Å, consistent with that of bulk SnO_2 .

Fig. 6(a) shows a typical BF TEM image, illustrating that 3D SnO_2 nanostructures are composed of DNCs. The inset in Fig. 6(a) is the corresponding SAED pattern, which can be indexed to tetragonal SnO_2 . According to the above SEM and TEM observations, we propose a model of an ideal dodecahedral SnO_2 enclosed by four side facets and eight parallelogram facets, as shown in Fig. 6(b). Fig. 6(c) shows a typical $[010]$ zone-axis HRTEM image of an individual SnO_2 dodecahedral nanocrystal (DNC). This HRTEM image clearly shows that the eight parallelogram facets are identified as $\{101\}$ facets. It can be seen the outline and angle marked in Fig. 6(c) of SnO_2 DNC agree with the model of an ideal dodecahedral SnO_2 enclosed by $\{110\}$ and $\{101\}$ facets projected along $[010]$ direction (Fig. 6(d)). HRTEM image of SnO_2 DNC was taken along $[1\bar{1}0]$ direction to further confirm the exposed facets of the SnO_2 DNC. As shown in Fig. 6(e), the outline of the SnO_2 DNC viewed along $[1\bar{1}0]$ direction is consistent with the dodecahedral SnO_2 model projected along the same direction (Fig. 6(f)). Based on the above TEM observations and structural analyses, we can deduce that the SnO_2 DNCs possess exposed facets of $\{110\}$ and $\{101\}$.

3.2. Humidity sensing properties

The humidity-sensing properties were carried out on the sensor devices obtained from the as-synthesized SnO_2 nanostructures at a frequency of 100 Hz. The response and recovery times are two key factors to evaluate the performance of a humidity sensor [27,28], in which a sensor achieves 90% of the total impedance change in the case of adsorption and desorption, respectively. Fig. 7 shows the response and recovery curves of the sensors based on various SnO_2 nanostructures as the RH switches between 11% and 95% at 25 °C. For the nanosensor based on SnO_2 NPs, it has long response and recovery times ($t > 30$ s), indicating that it will take a long time to reach a stable state. However, the nanosensors based on 3D hierarchical SnO_2 NRs and DNCs possess a response time of less than 4 s and a recovery time of less than 13 s. This reveals that the 3D SnO_2 nanostructures (NRs and DNCs) have faster response and recovery times compared with SnO_2 NPs, which are attributed to the peculiar 3D open nanostructures with more pore channels. That is to say, when the nanosensors based on 3D hierarchical SnO_2 NRs and DNCs are placed in a high RH environment, the 3D open nanostructures can facilitate the diffusion of water molecules through the numerous channels formed by voids and interspaces, and accelerate the formation of steady state of nanosensors [29]. Thus, the 3D hierarchical SnO_2 NRs and DNCs-based nanosensors display fast response

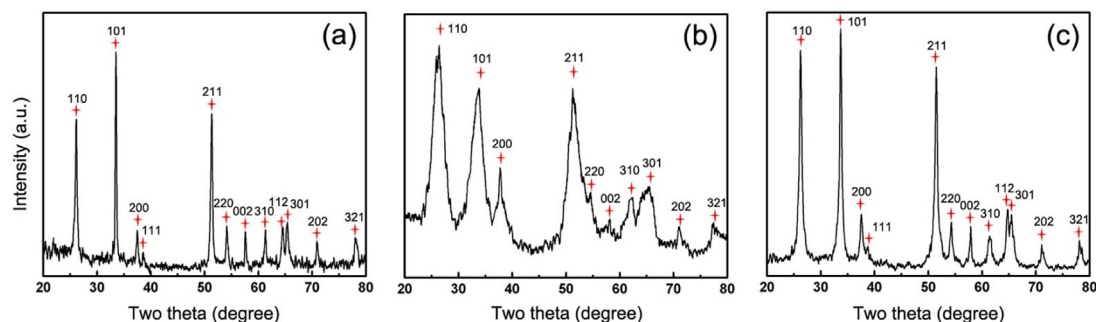


Fig. 1. XRD patterns of as-synthesized 3D hierarchical SnO₂ NRs (a), SnO₂ NPs (b) and 3D hierarchical SnO₂ DNCs (c).

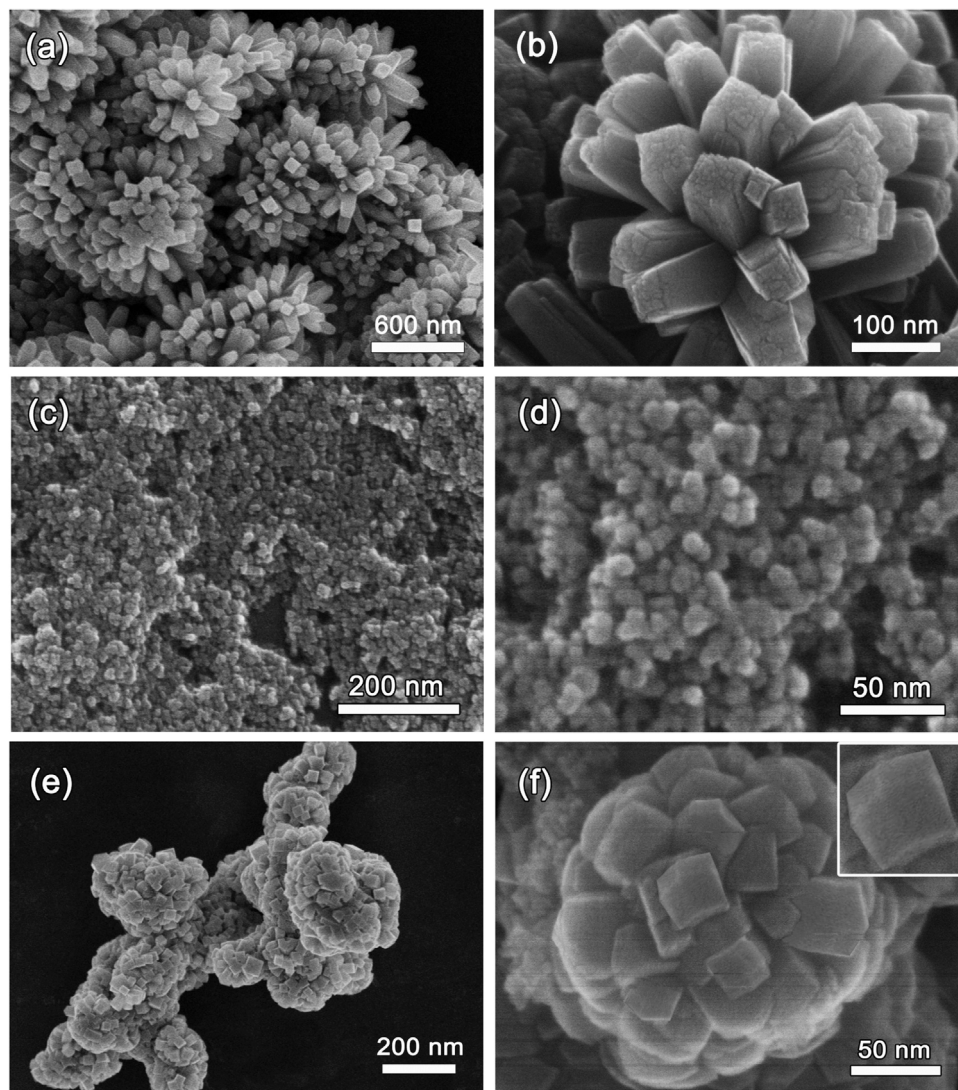


Fig. 2. SEM images of as-synthesized 3D hierarchical SnO₂ NRs (a), SnO₂ NPs (c), and 3D hierarchical SnO₂ DNCs (e); (b), (d) and (f) the corresponding SEM images at high magnification.

times when the RH changes from 11% to 95%. In contrast, when putting those nanosensors in a low RH environment immediately, the adsorbed water molecules on the SnO₂ surface can be desorbed rapidly to cut off the water channels for proton transfers. Therefore, fast recovery times are observed on the nanosensors based on 3D hierarchical SnO₂ NRs and DNCs. However, for the nanosensor based on SnO₂ NPs, the congregation phenomena of the NPs hinders the movement and diffusion of water molecules [29], thus prolong-

ing the response and recovery times. Based on the above analyses, we conclude that the humidity sensors realized with 3D hierarchical SnO₂ NRs and DNCs exhibit faster response and recovery times than that based on SnO₂ NPs.

Fig. 8(a) shows the dependence of impedance on different RHs for the nanosensors based on different SnO₂ nanostructures. When the RH is changed from 11% to 95%, the 3D hierarchical SnO₂ NRs and NPs exhibit poor responses on impedance changes, dropping

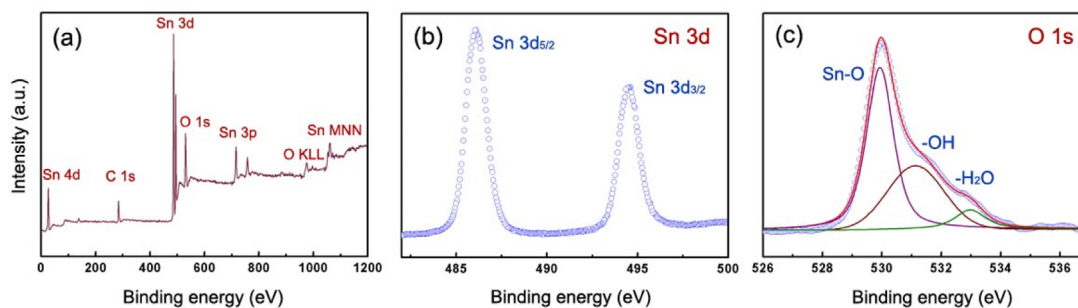


Fig. 3. (a) XPS spectra of 3D hierarchical SnO_2 DNCs scanned from 0 to 1200 eV; Binding energies of Sn 3d (b) and O 1s (c).

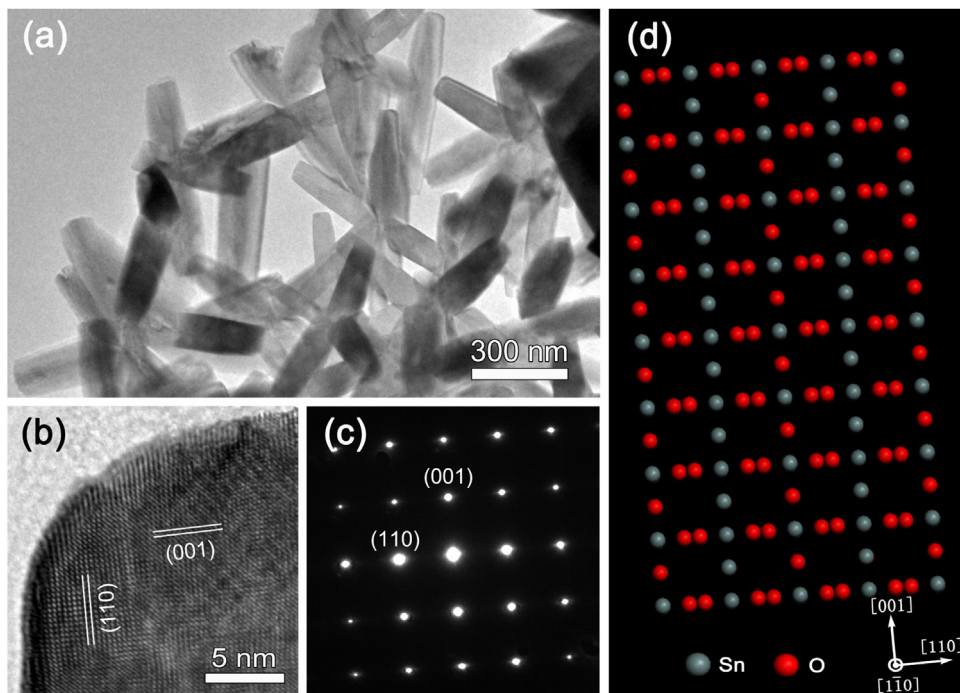


Fig. 4. (a) Typical BF TEM image of 3D hierarchical SnO_2 NRs; (b) HRTEM image of an individual NR viewed along $[1\bar{1}0]$ direction; (c) SAED pattern taken from the NR in (b); (d) Schematic model of an ideal SnO_2 cuboid projected along $[1\bar{1}0]$ direction.

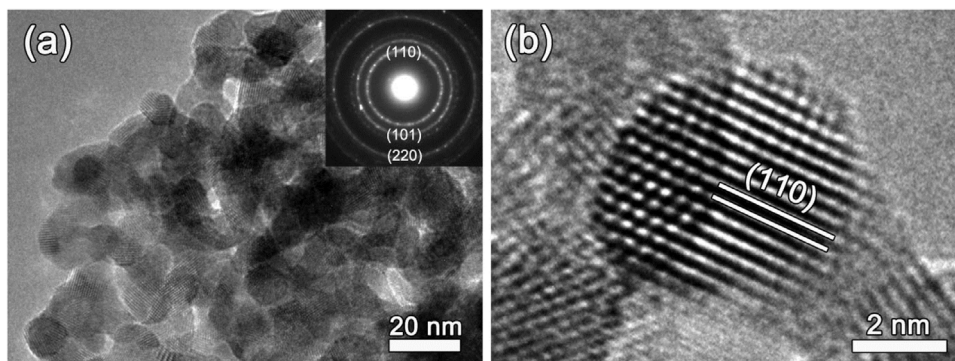


Fig. 5. (a) Typical BF TEM image of SnO_2 NPs, and inset is corresponding SAED pattern; (b) Typical HRTEM image of single SnO_2 NP.

by only one and two orders, respectively. However, the nanosensor based on 3D hierarchical DNCs displays an excellent linearity with the $\log(\text{impedance})$ spanning nearly 4.2 orders of magnitude,

indicating that its humidity sensitivity is much higher than those based on SnO_2 NRs and NPs.

To see the humidity sensing performance of the nanosensors based on SnO_2 DNCs more clearly, we made a comparison of the

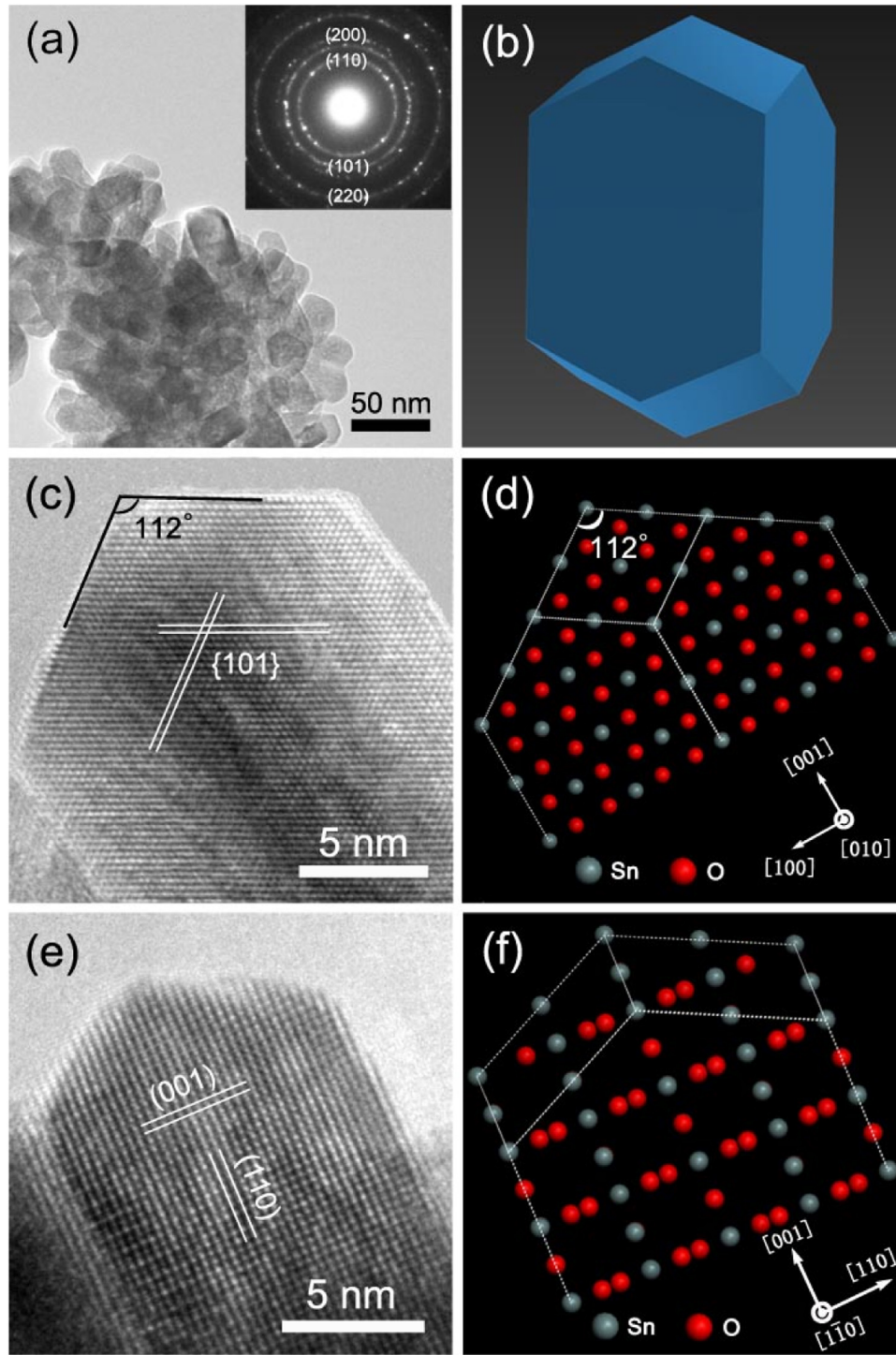


Fig. 6. (a) Typical BF TEM image of SnO_2 DNCs. Inset is SAED pattern; (b) Schematic model of an ideal SnO_2 dodecahedron; (c) Typical HRTEM image for the SnO_2 dodecahedron viewed along the $[010]$ direction; (d) Schematic model of an ideal SnO_2 dodecahedron projected along $[010]$ direction; (e) Typical HRTEM image viewed along the $[110]$ direction; (f) Schematic model of an ideal SnO_2 dodecahedron projected along $[110]$ direction.

nanosensors reported in the literature and in the present study, as summarized in Table 1. It is clearly shown that humidity nanosensor based on SnO_2 DNCs exhibits fast response/recovery times and high sensitivity, which are superior to those based on metal oxides reported in the previous literature.

Hysteresis is another important characteristic of a humidity sensor, which is defined as the maximum difference between the adsorption and desorption processes [13]. Generally speaking, a sensing material experiences a hysteresis effect at increasing and

decreasing RH. The hysteresis was measured by switching the sensor between the closed chambers with RHs of 11%, 33%, 43%, 54%, 69%, 75%, 84% and 95% and then transferred back. The humidity hysteresis deviation (γ_H) was calculated using the equation as follows,

$$\gamma_H = \pm \frac{\Delta R_{\max}}{2F_{Fs}} \quad (1)$$

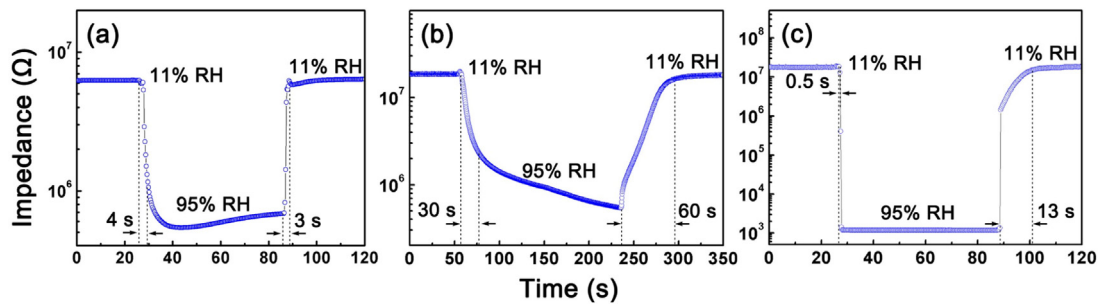


Fig. 7. Humidity response and recovery curves for 3D hierarchical SnO_2 NRs (a), SnO_2 NPs (b) and 3D hierarchical SnO_2 DNCs (c).

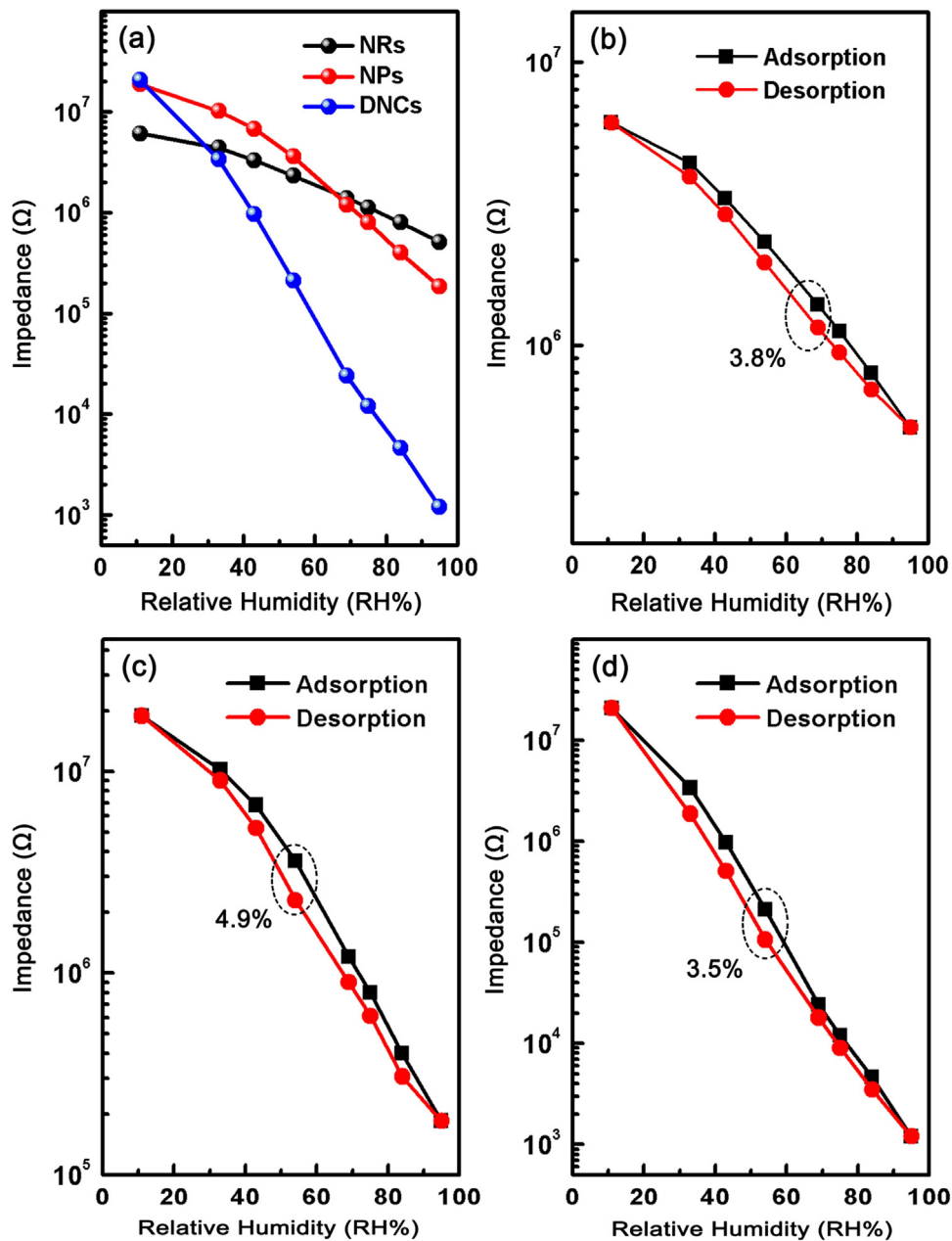


Fig. 8. Impedance measurement of nanosensors fabricated from different SnO_2 nanostructures (a). The humidity hysteresis characteristics of the nanosensors based on 3D hierarchical SnO_2 NRs (b), SnO_2 NPs (c) and 3D hierarchical SnO_2 DNCs (d).

Table 1

Comparison of the sensing properties for various humidity sensors.

Materials	Impedance variation (Ω)	Response time (s)	Recovery time (s)	Reference
Single SnO ₂ nanowires	10^5 – 10^7	120–170	20–60	[12]
SnO ₂ NPs	10^2 – 10^4	32	25	[14]
TiO ₂ -SnO ₂ nanowires	10^4 – 10^7	2.4	30	[15]
WO ₃ -SnO ₂ nanospheres	–	8	29	[16]
RGO-SnO ₂ nanocomposite	–	6	102	[17]
ZrO ₂ -TiO ₂ nanofibers	10^4 – 10^8	5	20	[29]
MoS ₂ -SnO ₂ nanocomposite	–	5	13	[30]
3D hierarchical SnO ₂ DNCs	10^3 – 10^7	0.5	13	this work

where $\Delta R_{\max}$ is the output difference between forward and backward operations and F_{FS} is the full scale output. Fig. 8 shows the impedance measurements of humidity nanosensors realized with different SnO₂ nanostructures. Among the as-fabricated nanosensors, the 3D hierarchical DNCs nanosensor exhibits a narrowest hysteresis loop with a calculated maximum deviation of 3.5% (Fig. 8(d)), indicating that the adsorption and desorption processes are highly reversible.

3.3. Humidity-sensing mechanism

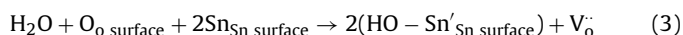
To further understand the sensing mechanism, the complex impedance measurements of the nanosensors based on SnO₂ nanostructures were carried out through shifting the operational frequency from 50 Hz to 100 kHz under different RHs. As shown in Fig. 9(a), the complex impedance curves of 3D hierarchical SnO₂ NRs present one type of shape, in which semicircular curves appear for the RHs from 11% to 95%. The semicircle represents the “non-debye” relation [30], which can be modeled by an equivalent circuit of a resistor (R) and a constant phase element (CPE, Z_{CPE}) in parallel, as shown in Fig. 9(d). These observed semicircles are attributed to the intrinsic impedance [31], indicating only a few water molecules are chemisorbed and a few channels form on the surfaces of SnO₂ nanostructures for the proton transport. However, two types of signals are shown in the complex impedance spectra of the nanosensors based on 3D hierarchical SnO₂ DNCs and SnO₂ NPs. As can be seen from Fig. 9(b) and (c) the complex impedance curves exhibit a semicircle at low RH, and a semicircle together with a straight line at high RH, respectively. The straight line represents Warburg impedance due to the diffusion and transport of protons in the adsorbed water [13]. To model the complex impedance plots of the nanosensors based on NPs and 3D hierarchical SnO₂ DNCs, the equivalent circuits of are depicted in Fig. 9(e) and (f), respectively. Herein, Z_w is introduced to represent the Warburg impedance [31], which implies that many water molecules are adsorbed on the surfaces of SnO₂ DNCs and NPs, leading to formation of several water layers and thus producing numerous water channels distributed in 3D hierarchical SnO₂ DNCs and SnO₂ NPs. The adsorbed water layers exhibit a liquid-like behavior, in which proton hopping occurs in the charge transport by a chain reaction [31] between adjacent water molecules as follows,



The free transfer of proton in the water layer results in an impedance decrease for the nanosensors based on 3D hierarchical SnO₂ DNCs and SnO₂ NPs. From the above complex impedance results, it is concluded that the 3D hierarchical SnO₂ DNCs and SnO₂ NPs can adsorb more water molecules than the 3D hierarchical SnO₂ NRs, which leads to higher sensitivity of nanosensors based on the 3D hierarchical SnO₂ DNCs and SnO₂ NPs. The analyses of XPS spectra obtained from different SnO₂ nanostructures confirm that only a few OH groups and water molecules are adsorbed to form water layers on the surfaces of SnO₂ NRs, in contrary to DNCs and

NPs. That is why NR sensor is characterized with lack of Warburg impedance, as shown in Fig. 9.

It is well known that the surface structure strongly affects the adsorption behavior of materials [8]. According to our TEM results, the 3D hierarchical SnO₂ NRs are mainly exposed with {110} facets, while for the 3D hierarchical SnO₂ DNCs, apart from {110} facets, {101} facets are also exposed. To understand the adsorption mechanism of different surfaces, DFT calculations were performed to investigate adsorption behaviors of OH groups on SnO₂ {110} and {101} surfaces. When SnO₂ nanostructures are exposed to a high amount of moisture, water molecules adsorbed on the SnO₂ surface will react with the lattice oxygen ($\text{O}_{\text{surface}}$) and the surface tin atoms ($\text{Sn}_{\text{surface}}$) according to the following reaction,



HO-Sn'_{surface} forms on the surface of SnO₂ and V_{O} (oxygen vacancy) is generated at the same time [27]. Here Sn'_{surface} is the surface tin atom after the reaction, which is coordinatively unsaturated with one dangling bond.

Fig. 10(a) and (b) shows the optimized adsorption configurations of OH groups on SnO₂ {110} and {101} surfaces, respectively. It can be seen that, the number of OH groups adsorbed on Sn atom of the SnO₂ {101} surface are two times that on {110} surface. For the {110} surface, the OH group is only adsorbed on the bridge site in the middle of two surface Sn atoms. While for {101} surface, besides the bridge sites, OH groups are also adsorbed on Sn atoms owing to the high density of atomic steps on the {101} surface, which is consistent with the XPS results. The OH groups are considered as active sites for the adsorption of water molecules [15], which will greatly improve the humidity sensitivity of nanosensors. Thus, 3D hierarchical SnO₂ DNCs enclosed with {101} facets and {110} facets exhibit higher sensitivity in comparison with 3D hierarchical SnO₂ NRs with exposed {110} facets.

Fig. S4 shows the N₂ adsorption-desorption isotherms of different SnO₂ nanostructures. From the BET measurements in Figs. S4(a)–(c), the specific surface area for the NPs (173.6 m²/g) is more than that for DNCs (23.9 m²/g) and NRs (7.9 m²/g). Figs. S4(d)–(f) present the pore size distribution curves of SnO₂ nanostructures. The pore diameters are calculated to be 34.5 nm, 5.0 nm and 15.8 nm for SnO₂ NRs, NPs and DNCs, respectively. Although the BET specific surface area of SnO₂ NPs is 7 and 22 times that of 3D hierarchical SnO₂ DNCs and NRs, the pore size of NPs is smallest among three different SnO₂ nanostructures. This can be attributed to the pore blockage due to the congregation of NPs which is believed to obstruct the reaction of water molecules with the inner sensing material [32], thus hindering the formation of OH groups and adsorption of water molecules. That is why nanosensor based on 3D hierarchical SnO₂ DNCs is more sensitive than that based on NPs.

Fig. 11 shows the dynamic response of SnO₂ DNCs sensor towards rapid variations in the 11–95% RH range. It is observed from Fig. 11(a) that the impedance of the sensor always reverts to the original value when RH is changed to the former state, indicating that the humidity-sensing process is extremely reversible.

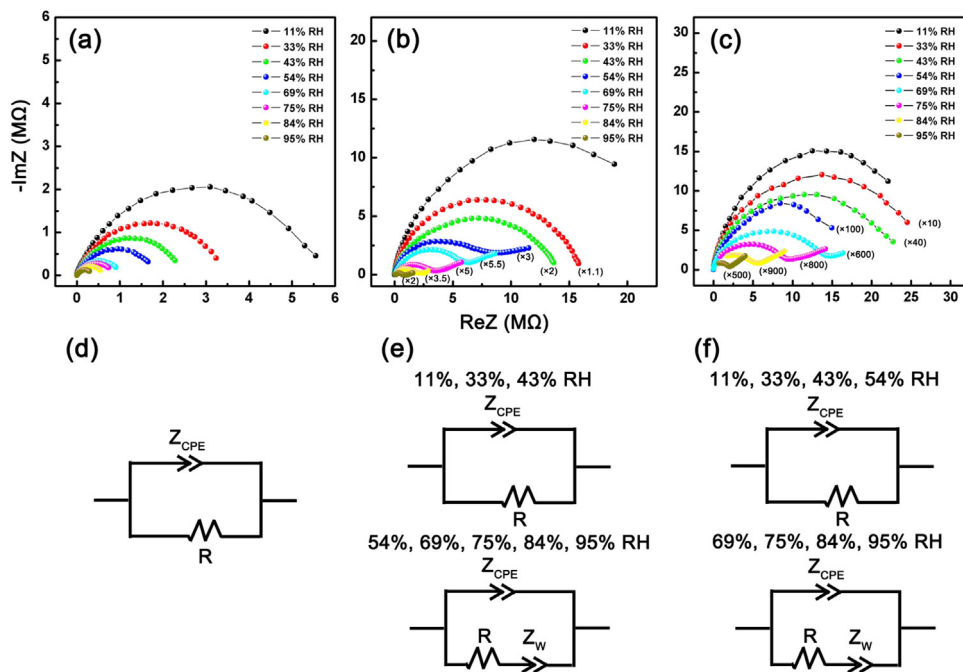


Fig. 9. Complex impedance plots of the as-fabricated nanosensors based on 3D hierarchical SnO_2 NRs (a), SnO_2 NPs (b) and 3D hierarchical SnO_2 DNCs (c). Equivalent circuits of the nanosensors based on 3D hierarchical SnO_2 NRs (d), SnO_2 NPs (e) and 3D hierarchical SnO_2 DNCs (f).

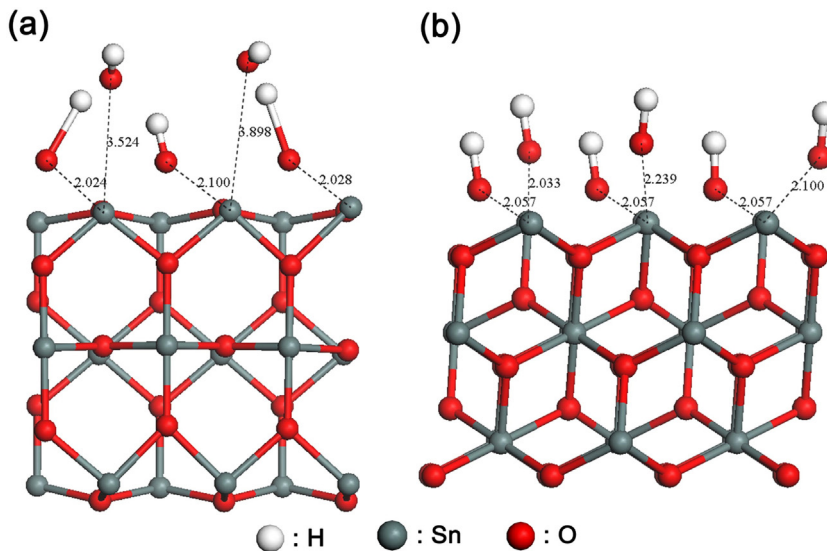


Fig. 10. Adsorption behaviors of OH groups on {110} surface (a) and {101} surface (b).

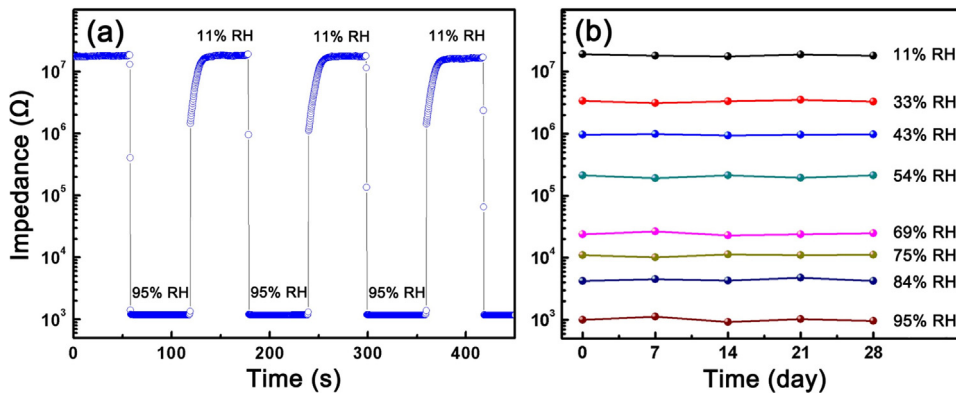


Fig. 11. (a) Repeated response and recovery characteristics of 3D hierarchical SnO_2 DNCs. (b) The responses of 3D hierarchical SnO_2 DNCs monitored at different humidity conditions for 28 days.

Moreover, the response and recovery times do not change during the four repeated loops of measurements, implying a good reproducibility of the humidity response. The sensors were exposed in air for 28 days, and the impedance measurement was performed once a week at different RHs. As can be seen in Fig. 11(b), the impedance of the sensor fluctuates slightly with time. The sensor shows excellent consistency and a minor variation ($\sim 2.1\%$) in impedance is observed at each humidity level.

4. Conclusions

In summary, 3D hierarchical SnO_2 DNCs with exposed {110} and {101} facets were synthesized by a simple hydrothermal route with assistance of sodium alginate. The 3D hierarchical SnO_2 DNCs show excellent humidity-sensing performance including fast response and recovery times, narrow hysteresis loop, high sensitivity, great linearity response and good stability due to the unique 3D open structure and high chemical activity of the exposed {101} facets. Our results demonstrate that it is feasible to improve humidity-sensing properties of SnO_2 sensors by tuning morphology and surface architecture. In addition, the present study motivates us to further explore new synthetic method for the preparation of other metallic oxides with special morphology and high active facets, which could demonstrate promising application prospects in gas sensing, photocatalysis, lithium-ion batteries and optoelectronic devices.

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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.snb.2016.12.043>.

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