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# Highly sensitive NH<sub>3</sub> gas sensor based on the porous Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets with ppb level detection limit

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## Abstract

Porous Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets sensing material was synthesized using a facile sol-hydrothermal process. The average thickness of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets was about 8 nm, and the nano-sheets were found to have a mesoporous structure with an average pore size around 2.1 nm. The mesoporous structure of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets resulted in larger specific surface areas of 185.4 m<sup>2</sup>/g and more pore volumes of 0.51 cm<sup>3</sup>/g than those of CeO<sub>2</sub>, which was beneficial to the absorption of target gas. Due to the special mesoporous structures in the nano-sheets and the plenty of hydroxyl groups on the surface, the NH<sub>3</sub> sensors made of the porous Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets showed a higher sensitivity (87 to 100 ppm NH<sub>3</sub>) and a lower detection limit (100 ppb) at room temperature than the sensors made of pure CeO<sub>2</sub> nano-sheets prepared using the similar process. And they exhibited good selectivity, reproducibility and long-term stability to NH<sub>3</sub> detection at room temperature.

**Keywords:** CeO<sub>2</sub>, Nano-sheets; Porous; Sol-hydrothermal; Gas sensor

## **1. Introduction**

CeO<sub>2</sub> based nanomaterials have attracted considerable attention in recent years due to their optical and magnetic properties, superior catalytic performance, oxygen storage capacity and excellent gas sensing performance. They have found a wide range of applications in catalysis [1, 2], storage oxygen materials [3], fuels cells [4], supercapacitors [5], ferromagnetic oxides [6], gas sensors [7-10] and luminescence materials [11, 12]. Various CeO<sub>2</sub> based nanostructures have been synthesized using sol-gel method [13], electro-spinning [14, 15], hydrothermal method [16-20], and precipitation method [21, 22]. These nanostructural morphologies generally include nanoparticles [13, 22], nanowires [18], nanorods [17, 19], nanosheets [16, 17], nanofiber [14, 15] and nanoflowers[20], which can be successfully used as gas sensing materials. For example, Liao *et al.* [23] made a gas sensor using CeO<sub>2</sub> nanowires decorated with Pt nanocrystals prepared using a hydrothermal method, and the sensor showed a good selectivity for detection of CO. Barreca *et al.* [24] synthesized CeO<sub>2</sub> columnar nanostructures using a chemical vapour deposition method and demonstrated their high sensitivity for detection of gaseous ethanol and nitrogen dioxide. Lei *et al.* [9] prepared CeO<sub>2</sub> nanofibers using a two-step electrospinning and calcination method for real-time CO sensing. Michela *et al.* [25] prepared hollow CeO<sub>2</sub> microspheres with 3D architectures using a microwave-assisted coprecipitation method for detection of CO. Yang *et al.* [26] synthesized CeO<sub>2</sub>/graphene-like nano-sheet composites using a solvothermal method

for sensing NO<sub>x</sub> gas.

Among these CeO<sub>2</sub> nanostructures, porous nano-sheets would be one of the best nanostructures for gas sensing due to their extremely high surface-to-volume ratio and thus effective adsorption of gas molecules. Doping various elements into CeO<sub>2</sub> is commonly regarded as a good method to further improve its sensing properties and these elements include Ti [27], B [28], Zn [29] and In [15]. Zr-doped CeO<sub>2</sub> was previously applied to enhance catalytic property [30, 31]. The improved catalytic performance would be beneficial for its gas sensing performance. The addition of Zr can significantly and effectively prevent the rapid growth of CeO<sub>2</sub> crystallite size, thus maintaining a small crystal sizes in the nanostructures. This can provide a larger specific surface area and higher pore volumes than those of CeO<sub>2</sub> nanostructures, thus would be beneficial for improvement in gas sensing performance. However, up to now, preparation of porous nano-sheets structures of Zr-doped CeO<sub>2</sub> and characterization of their gas sensing mechanisms have never been explored.

In the study, we prepared Zr doped CeO<sub>2</sub> porous nano-sheet structures using a facile surfactant-free sol-hydrothermal process. These Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets showed excellent NH<sub>3</sub> sensing performance at room temperature than pure CeO<sub>2</sub> nano-sheets, which was prepared using the similar process. The Zr doped CeO<sub>2</sub> nanoporous structures have been characterized thoroughly in this paper, and their NH<sub>3</sub> sensing performance and mechanisms have been investigated.

## **2. Experimental procedures**

### **2.1 Synthesis of samples**

Zr doped CeO<sub>2</sub> samples were prepared using a sol-hydrothermal process. All chemicals used in the synthesis processes were of analytical grade purity. In order to prepare Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets, 10 milli-mol (mmol) Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 1 mmol ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, and 5 mmol NaNO<sub>3</sub> were dissolved into 80 ml deionized water under a constant stirring to form a transparent solution. Ammonia (NH<sub>3</sub>·H<sub>2</sub>O, 27%) of 20 ml was added into the solution drop-by-drop within 10 min under a continuous stirring to form a yellow semi-transparent sol. Subsequently, 2 mL hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was dropped into the sol. The sol was continually stirred for about 30 min until the color of the sol was turned into reddish-brown. Then the obtained reddish-brown sol was hydrothermally reacted at 100 °C Teflon-lined stainless steel autoclave of 120 mL for 20 hours. Finally, the hydrothermal precipitates were filtered by distilled water and dried at 60 °C for 10 hours to obtain light-yellow Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> powder samples. Using the same process, the pure CeO<sub>2</sub> sample was prepared without addition of ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O in the reaction.

## **2.2 Characterization**

X-ray diffraction (XRD, CuK $\alpha$ , 40kV, 60mA, Rigaku D/max-2400) was conducted to characterize the crystalline structure and average crystalline sizes of samples. Morphologies and micro/nanostructures of samples were studied using Inspect F50 scanning electron microscope (SEM) and JEOL 2010 F field emission gun electron microscope (TEM). Energy-dispersive X-ray spectroscopy (EDX) analysis was carried out to obtain the dot-mapping of various elements in nano-sheets. Thickness of nano-sheet was measured using an atomic force microscope (AFM, CSPM4000). A

nitrogen physisorption apparatus of JW-BK122W was used to measure the nitrogen adsorption-desorption isotherms of samples at 77 K. Prior to N<sub>2</sub> physisorption, all the samples were dehydrated at 200 °C for 2 hours under a vacuum. The pore diameter distribution and specific surface area were obtained using density functional theory (DFT) and Brunauer–Emmett–Teller (BET) method, respectively. The total pore volumes ( $V_{\text{total}}$ ) were calculated using the adsorption amount at P/P<sub>0</sub> of 0.99. X-ray photoelectron spectroscopy (XPS, Kratos Axis-Ultra DLD apparatus with Al K $\alpha$  radiation) was conducted to analyze the chemical states of different elements of samples. The element analysis of Zr was conducted by Inductive Coupled Plasma Emission Spectrometer (ICP, AtomScan 16, TJA, USA).

### 3. Results and discussion

#### 3.1 Morphologies and structure of samples

XRD spectra of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> and pure CeO<sub>2</sub> samples are shown in **Fig. 1**. All the diffraction peaks of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> and CeO<sub>2</sub> are in a good agreement with JCPDS card for cubic fluorite CeO<sub>2</sub> (JCPDS NO. 34-0394). This indicates that for both CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub>, the fluorite cubic phase structure was synthesized by hydrothermal reaction without calcination. No peaks of any other phases could be detected, indicating that the Ce<sup>3+</sup> was completely transformed into CeO<sub>2</sub> during the synthesis process. The crystallite sizes  $L$  of samples were estimated according to the Scherrer formula:  $L = K\lambda/(\beta\cos\theta)$  ( $\lambda=0.15406$  nm,  $K=0.89$ ,  $\beta$  is the peak width at half height, and  $\theta$  is the diffracting angle). The obtained crystallite sizes of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> are 3.2 and 2.8 nm, respectively. The crystallite sizes of the

$\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  are smaller than that of  $\text{CeO}_2$ , because the addition of  $\text{Zr}^{4+}$  could prevent the rapid growth of  $\text{CeO}_2$  crystallite size. In addition, no characteristic peaks of the zirconium oxide in **Fig. 1** are observed in  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$ . Due to similar ionic radii and Pauling electronegativity values of  $\text{Zr}^{4+}$  (0.072 nm) and  $\text{Ce}^{4+}$  (0.087 nm) ion, the Zr ions could substitute  $\text{Ce}^{4+}$  ones to form a stable substitutional solid solution. Moreover, the high-resolution of (111) peaks of XRD spectra of  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  samples were further compared (as shown in the Fig.S2). A small shift of the (111) peak to high angle is observed, which should result from the doping of  $\text{Zr}^{4+}$  in  $\text{CeO}_2$ . It is also found that the characteristic peaks of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  have a weaker intensity and a larger half peak width than that of  $\text{CeO}_2$ , indicating the decreasing of crystallinity and diameter of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  due to the  $\text{Zr}^{4+}$  doping in  $\text{CeO}_2$ . Based on the above results, it can be confirmed that  $\text{Zr}^{4+}$  was successfully doped into the  $\text{CeO}_2$ .

**Fig. 2** shows the morphologies of pure  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  obtained from SEM and TEM analysis. Both  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  samples are consisted of a large number of nano-sheets from SEM images (**Figs. 2a** and **2d**) and TEM images (**Figs. 2b** and **2e**). Some wrinkle-like patterns could be observed in TEM image shown in **Figs. 2b** and **2e**, which is a common feature for the ultrathin nano-films [32]. AFM analysis (shown in **Fig. 3** and **Fig. S1**) reveal that thickness of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets is about 8 nm. Based on HRTEM images of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets shown in **Figs. 2c** and **2f**, both the  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets are composed of numerous nanoparticles. The diameters of  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-particles



are in the range from 2 nm to 4 nm, which is in agreement with the results obtained from XRD analysis. The lattice spacing of 0.329 nm of pure CeO<sub>2</sub> (shown in **Fig. 2c**) agrees well with that of the (111) planes of the cubic CeO<sub>2</sub>. The Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-crystal has a lattice spacing of 0.325 nm (see **Fig. 2f**), and the lattice spacing of the (111) planes is smaller than that of pure CeO<sub>2</sub> (0.329 nm) because of substitution of Ce<sup>4+</sup> (0.087 nm) with Zr<sup>4+</sup> (0.072 nm). The SAED patterns (see the inset images shown in **Figs. 2c** and **2f**) proves the good crystallization of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub>, and they are correspondent to the fluorite phase structure of CeO<sub>2</sub>.

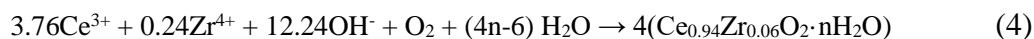
**Figs. 4b** and **4c** show the typical EDX elemental mapping of the Ce and Zr elements in Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> sample (**Fig. 4a**). Clearly, Ce and Zr elements are homogenously distributed in the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets as shown in **Figs. 4b** and **4c**, indicating the formation of a uniformly substitutional solid solution. This is consistent with the conclusion from the XRD analysis. Furthermore, the content of Zr in the CeO<sub>2</sub> is 6.0 % from the EDX analysis (see **Fig. S3** of the EDX pattern of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets). Moreover, the ICP analysis also found that the molar percentage of Zr in Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> sample is 6.01%. Therefore, we define this nanomaterial as Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub>.

In the synthesis process, ammonia (NH<sub>3</sub>·H<sub>2</sub>O) and H<sub>2</sub>O<sub>2</sub> decompose and form OH<sup>-</sup> and O<sub>2</sub> in aqueous solutions as listed in reaction formula (2) and (3):

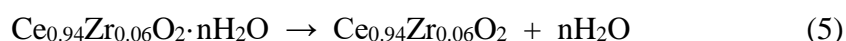


In the presence of O<sub>2</sub> in the alkaline solution, the Ce<sup>3+</sup> ions are unstable and the

hydrated  $\text{Ce}^{4+}$  oxide can be easily formed. At the same time, the  $\text{Zr}^{4+}$  ions could enter into the lattice sites of  $\text{CeO}_2$  by substituting  $\text{Ce}^{4+}$  ions to form  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2 \cdot n\text{H}_2\text{O}$  according to the following reaction:



In the hydrothermal process,  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nanocrystals could be formed through crystallization of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2 \cdot n\text{H}_2\text{O}$  under elevated temperatures and pressure.



The porosity of the  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets were characterized and the  $\text{N}_2$  adsorption-desorption isotherms and pore size distributions are shown in **Fig. 5**. Both the adsorption-desorption isotherms of  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets exhibit typical type-IV isotherms with a hysteresis loop that corresponds to a mesoporous structure. The pore size distribution of  $\text{CeO}_2$  and  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets are concentrated at around 2.5 nm and 2.1 nm, respectively, indicating the formation of mesoporous structures in the nano-sheets. The pores could be accumulated among the nanoparticles during their growth and coalescence. The mesoporous structures of nano-sheets result in large specific surface areas and pore volumes, which are beneficial to the absorption of target gas molecules during gas sensing. The specific surface area and pore volume of  $\text{CeO}_2$  are  $135.0 \text{ m}^2/\text{g}$  and  $0.40 \text{ cm}^3/\text{g}$ , respectively. Compared with the  $\text{CeO}_2$  nano-sheets, the  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets have a larger specific surface area and pore volume of  $185.4 \text{ m}^2/\text{g}$  and  $0.51 \text{ cm}^3/\text{g}$ . Because of their smaller crystallite sizes, larger specific surface areas and pore volumes, the  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets should have a better sensing

performance than pure CeO<sub>2</sub>.

**Fig. 6** shows the XPS results of the CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets. In **Fig. 6a**, both Ce 3d XPS spectra of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets show six peaks at the binding energy of 881.9 eV, 887.9 eV, 897.9 eV, 900.4 eV, 906.9 eV and 916.1 eV, which are attributed to the characteristic of Ce (IV) 3d states with three pairs of spin-orbit splits [33]. The peaks located at 881.9 eV, 887.9 eV and 897.9 eV are corresponding to the Ce 3d<sub>5/2</sub>, and the peaks at 900.4 eV, 906.9 eV and 916.1 eV are corresponding to the Ce 3d<sub>3/2</sub>. The three pairs of binding energy (916.1 and 897.9 eV, 906.9 and 887.9 eV, 900.4 and 881.9 eV) are corresponding to the final state of Ce (IV) 3d<sup>9</sup>4f<sup>0</sup> O2p<sup>6</sup>, Ce (IV) 3d<sup>9</sup>4f<sup>1</sup> O2p<sup>5</sup> and Ce (IV) 3d<sup>9</sup>4f<sup>2</sup> O2p<sup>4</sup>, respectively [34]. This is in a good agreement with the characteristic chemical valence of Ce<sup>4+</sup> ions. The results are consistent with the conclusions drawn from XRD analysis.

As illustrated in **Fig. 6b**, the O 1s XPS spectra of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets show two obviously peaks at binding energies of 528.7 eV and 530.7 eV, respectively. The main peak centered at 528.7 eV is attributed to the lattice oxygen in the CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> crystals [34, 35]. The peak at a higher binding energy of 530.7 eV is indexed to hydroxyl group on the surface of nanoparticles [36]. It is obvious that there are much more hydroxyl groups on the surface of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nanoparticles due to the large peak areas at 530.7 eV.

The XPS spectrum of the Zr 3d of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets is shown in **Fig. 6c**. There are double peaks at binding energies of 182.0 and 184.4 eV, which are attributed to the Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> characteristic signals of chemical valence of

Zr<sup>4+</sup> ions in the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets. The atomic ratio on the surface of sample could be estimated by the XPS peaks areas. The obtained Zr:Ce atomic ratios was 6.9:93.1 in the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets. The content of Zr on the surface of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets is close to the results of EDX.

### **3.2 Gas sensing properties of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based gas sensors**

To investigate the gas sensing property, the CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets were used as the sensing materials to make a gas sensor, and its response-recovery process to target gas of NH<sub>3</sub> was monitored. The schematic illustration of the gas-sensing testing system is shown in **Fig. 7**. An appropriate bias voltage of 5 V was applied during gas sensing testing. Both the CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based gas sensors showed good ohmic contacts from I-V curves in **Fig. S4**. The response and recovery behaviors of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based gas sensors were investigated at room temperature. The gas response(R) of sensors is defined as the resistance ratio:  $R = R_a/R_g$  [37], ( $R_g$ : resistance of sensors in the target gas;  $R_a$ : resistance of sensors in air).

The dynamic response-recovery curves and response of gas sensor to NH<sub>3</sub> with various concentrations are shown in **Fig. 8**. From the **Figs. 8a** and **8c**, both the CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensors exhibit excellent gas sensing performance to NH<sub>3</sub> even at sub-ppm level. When the NH<sub>3</sub> was injected into the testing chamber, the resistance of sensor was dramatically decreased and reached a steady state immediately. After the NH<sub>3</sub> was extracted from the chamber, the

resistance of the gas sensors was recovered quickly to the initial value, indicating a good reversibility of the sensor. From **Figs. 8b** and **8d**, when the NH<sub>3</sub> concentration is higher than 5 ppm, the relationship between the response and concentrations shows a good linear characteristic.

Compared the sensing performance of two sensors made of the with different nano-sheets materials shown in **Figs. 8b** and **8d**, the gas sensor based on the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets shows better response and lower detection limit than those based on the CeO<sub>2</sub> ones. For example, the response of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor is 150 to 500 ppm NH<sub>3</sub>, which is 1.2 times higher than that of CeO<sub>2</sub> (with a response of 122). The detection limit of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor to NH<sub>3</sub> is 100 ppb, which is obviously much lower than the detection limit of CeO<sub>2</sub> of 500 ppb (as shown in **Figs. 8a** and **8b**). Therefore, the addition of Zr ions in the CeO<sub>2</sub> remarkably improves the NH<sub>3</sub> gas sensing performance.

Fig. 9 shows the dynamic response-recovery curves of sensors based on the different Zr doping ratios. The response values towards 500 ppm NH<sub>3</sub> of those sensors are 122, 134, 150 and 29 to pure CeO<sub>2</sub>, Ce<sub>0.98</sub>Zr<sub>0.02</sub>O<sub>2</sub>, Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> and Ce<sub>0.90</sub>Zr<sub>0.10</sub>O<sub>2</sub> respectively. Therefore, the sensor based on Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> has optimal sensing performance to NH<sub>3</sub>.

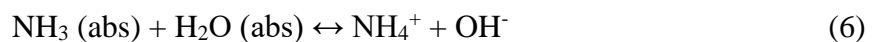
**Table 1** Comparison of NH<sub>3</sub> sensing properties of different metal oxide based gas sensors.

Sensing materials	Response to 100 ppm	Detection limit (ppm)	Response at detection limit	Operating temperature (°C)	Refer.
Co <sub>3</sub> O <sub>4</sub> nanorods	9.3	0.2	1.2	25	[38]
SnO <sub>2</sub> nanowire	9	300	9	200	[39]
SiO <sub>2</sub> @graphene	7.9%	5	2.8	25	[40]

Flower-like Pd-ZnO <sub>2</sub>	81.8	5	7.1	210	[41]
NiO/SnO <sub>2</sub> nanospheres	55	5	12	300	[42]
PbS/TiO <sub>2</sub> nanotubes	17.5	2	4	25	[43]
ZnO nanorods	22.6	20	1.02	25	[44]
Hierarchical In <sub>2</sub> O <sub>3</sub>	~	5	1.9	300	[45]
CeO <sub>2</sub> nano-sheets	50	0.5	1.1	25	This work
Ce <sub>0.94</sub> Zr <sub>0.06</sub> O <sub>2</sub> nano-sheets	87	0.1	1.2	25	This work

Many NH<sub>3</sub> gas sensors based on metal oxides have been reported in literature, including the metal oxides of Co<sub>3</sub>O<sub>4</sub> [46], SnO<sub>2</sub> [39], In<sub>2</sub>O<sub>3</sub> [45] and ZnO [47]. **Table 1** selects examples of different types of NH<sub>3</sub> gas sensors in literature. Compared with other types of NH<sub>3</sub> sensors listed in **Table 1**, the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based gas sensor shows the best sensing performance, including a lower detection concentration to 0.1 ppm, higher response and at a much lower working temperature, i.e., room temperature.

The sensing mechanism to NH<sub>3</sub> for the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor could be explained by the electrolytic conductivity of NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup>. **Fig. 10** shows a schematic diagram of the NH<sub>3</sub> reaction mechanism on the surface of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets. Because there are lots of hydroxyl groups on the surface of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets sensing materials, which was verified from XPS analysis, the H<sub>2</sub>O molecules can be easily absorbed on the surface of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets at ambient environment and room temperature. Due to the large specific surface area, the amount of absorbed moisture/water molecules would be quite large. When the gas sensor is exposed to NH<sub>3</sub>, the NH<sub>3</sub> molecules can be quickly absorbed on the surfaces of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets and then react with H<sub>2</sub>O molecules based on the following chemical reaction:

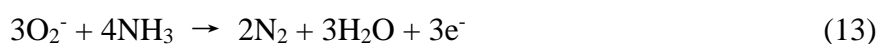


Therefore, the electrolyte of  $\text{NH}_4^+$  and  $\text{OH}^-$  could be produced. Because of the electrolyte conductivity of  $\text{NH}_4^+$  and  $\text{OH}^-$ , the resistance of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  is decreased accordingly. The chemical reaction (6) is reversible. Thus, when the sensor is exposed to ambient environment (i.e. air), the reversed chemical reaction of Eq. (6) results in formation of  $\text{NH}_3$  molecules and  $\text{NH}_3$  gas is then desorbed from the surface of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets. The resistance of sensor is then increased to the initial value. Because desorption of  $\text{NH}_3$  is slower than adsorption, the recovery time is longer than the response time (as shown in the **Fig. 8a**).

To verify the sensing mechanism of  $\text{NH}_3$  reaction with  $\text{H}_2\text{O}$  molecules on the sensor, we did the  $\text{NH}_3$  sensing by increasing the working temperature above 100 °C. At such an elevated temperature, the absorption of  $\text{H}_2\text{O}$  molecules is minimized, and thus the response is almost non-detectable. This clearly indicates that the absorption of water molecules on the surface of the  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets is critical for the good sensing performance at room temperature, but not at high temperature, at which the water molecules would be removed from the surface. Because the  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets have larger specific surface areas and higher pore volumes than those of  $\text{CeO}_2$ , which has been proven by the nitrogen adsorption-desorption isotherms measurement shown in **Fig. 5**, the  $\text{NH}_3$  gas molecules are more easily diffused and absorbed on the surfaces of  $\text{Ce}_{0.94}\text{Zr}_{0.06}\text{O}_2$  nano-sheets, thus resulting a better gas sensing performance than that of the pure  $\text{CeO}_2$ .

It have been reported that the doped  $\text{Zr}^{4+}$  in  $\text{CeO}_2$  can introduce much oxygen vacancies on the surface of  $\text{CeO}_2$  [48]. At room temperature, the oxygen molecules in

air will be absorbed on the surface of CeO<sub>2</sub> and form surface superoxide complex defects of  $Ce^{4+} - O_2^{\bullet-}$  with these oxygen vacancies [49, 50]. The  $Ce^{4+} - O_2^{\bullet-}$  was very active [50], which is beneficial to the reaction of  $O_2^-$  with NH<sub>3</sub> as the following chemical reaction:



The released electrons from the above reaction will lead to the decrease of the resistance sensor, which result in the increased response of the sensor to NH<sub>3</sub>. Therefore, the oxygen vacancies resulted from doping of Zr<sup>4+</sup> in CeO<sub>2</sub> also enhanced the response of the NH<sub>3</sub> sensor based on Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets.

Good selectivity is critical for the NH<sub>3</sub> gas sensor [51]. Therefore, the selectivity of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor was investigated by comparing the response to C<sub>2</sub>H<sub>5</sub>OH, CO, H<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub> and ethyl acetate operated at room temperature. The tests were conducted with the same gas concentration of 100 ppm at room temperature. The measurement results are shown in **Fig. 11a**. Clearly, the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based gas sensor exhibited a good response only towards the NH<sub>3</sub> gas. For other detected gases, the response was insignificant. The sensing mechanism of other gases is based on the redox reaction on the surface of metal oxide. However, the surface of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets is occupied by many hydroxyl groups, which could delay the redox reactions on the surface, thus the response is not high.

Reproducibility and long-term stability of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor were further investigated. **Fig. 11b** shows the reproducibility of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub>



nano-sheet based sensor when exposed to 10 ppm and 40 ppm NH<sub>3</sub> gas for four times at room temperature. All the curves of response and recovery processes are reproducible without apparent changes during injection and extraction of ammonia at same NH<sub>3</sub> gas concentration, indicating its good reproducibility. In order to investigate the stability of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor, the response to NH<sub>3</sub> gas were tested by repeatedly exposing the sensor to fixed NH<sub>3</sub> concentration (i.e., 10 ppm and 40 ppm, respectively) within a month at room temperature. The obtained response results are shown in **Fig. 11c**. Clearly, a nearly constant response to 10 ppm and 40 ppm NH<sub>3</sub> gas can be obtained by repeating the tests within the month, indicating that the sensor has a good long-time stability.

#### **4. Conclusions**

In this study, we used a facile surfactant-free sol-hydrothermal process to prepared porous Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets. In the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets, Zr<sup>4+</sup> ions were identified to occupy lattice sites of CeO<sub>2</sub> matrix to form a substitutional solid solution. The developed mesoporous structure with pore size around 2.1 nm was formed in the nano-sheets in the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets and it have large specific surface area and pore volume. It was proved that the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based NH<sub>3</sub> sensor showed a good response to NH<sub>3</sub>, even at 100 ppb level, and good reproducibility, selectivity and long-term stability. The excellent sensing property is not only due to the special mesoporous structures in the nano-sheets, but also due to the plenty of hydroxyl groups on the surface. So, the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor has a good application prospect in NH<sub>3</sub> gas detecting.

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**Fig. 1.** XRD spectra of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> samples.

**Fig. 2.** (a) SEM, (b) TEM and (c) HRTEM images of CeO<sub>2</sub>; (d) SEM, (e) TEM and (f) HRTEM images of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub>. (Inset images in Figs. 2c and 2f were selected area electron diffraction (SAED) pattern).

**Fig. 3.** 3D AFM image of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets.

**Fig. 4.** TEM image (a) and the corresponding elemental mapping analysis of Ce mapping image (b) and Zr mapping image (c).

**Fig. 5.** N<sub>2</sub> adsorption isotherms of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets. (inset: pore size distributions).

**Fig. 6.** (a) Ce 3d and (b) O 1s XPS spectra of CeO<sub>2</sub> and Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets; (c) Zr 3d XPS spectra of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets.

**Fig. 7.** The schematic illustration of the gas-sensing testing system.

**Fig. 8.** Fig. 8. Dynamic response-recovery curve and response data of gas sensors to NH<sub>3</sub> gas with various concentrations at room temperature. ((a, b) CeO<sub>2</sub> based gas sensor (c,d) Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based gas sensor).

**Fig. 9.** The dynamic response-recovery curves of sensor based on the different Zr doping ratios to 500 ppm NH<sub>3</sub> gas at room temperature.

**Fig. 10.** Schematic diagram of the NH<sub>3</sub> reaction mechanism on the surface of Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets.

**Fig. 11.** (a) Selectivity, (b) Reproducibility and (c) Long-term stability of the Ce<sub>0.94</sub>Zr<sub>0.06</sub>O<sub>2</sub> nano-sheets based sensor at the room temperature.