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Research Paper

Enhanced NH_3 gas-sensing performance of silica modified CeO_2 nanostructure based sensors

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ABSTRACT

The silica modified CeO_2 gas sensing nanomaterials are synthesized using a sol-hydrothermal route. The 8%silica-CeO_2 has larger specific surface areas of 83.75 m^2/g and smaller crystalline size of 11.5 nm than pure CeO_2, respectively. Compared to pure CeO_2, the 8%silica-CeO_2 based gas sensor exhibits significant enhancement NH_3 gas-sensing performance. At room temperature, it shows much better gas response of 3244% to 80 ppm of NH_3 gas and lower detection limit (0.5 ppm) towards NH_3 gas. It is also found that the gas response of the NH_3 gas sensors increases linearly with the increase of NH_3 gas concentration. Moreover, the NH_3 gas sensor have good reversibility, stability and selectivity. The reason of enhanced NH_3 gas-sensing performance is not only because of the increased specific surface areas, but also due to the electrolytic conductivity of NH_4^+ and OH^- on the surface.

1. Introduction

Being one of the major air pollution resources, ammonia gas (NH_3) is commonly released from organic nitrogenous animal and vegetable matters, organic decomposition, industrial effluents and motor vehicles [1]. It is also one of the important industrial chemicals, which have been used to make pharmaceuticals, plastics, fertilizers, cleaning products, dyes, explosives and synthetic fibers. However, ammonia is hazardous substance and may cause burns and swelling in the airways, or lung damage, and skin and eye damage. Therefore, an ammonia sensor with high response, good selectivity, long-term stability and low detection limit is critical and urgently needed. So far, various materials have been explored to detect NH_3 gas, such as SnO_2 [2–5], V_2O_5 [6], WO_3 [7,8], Co_3O_4 [9,10], ZnO [11–13], TiO_2 [14], carbon nanotubes [15,16], graphene [17,18], etc. However, the gas response using these materials is not high enough, and the detection limit of ammonia is above ppm level. Most of these sensors need to be operated at an elevated working temperature. Therefore, it is still a challenge to design and fabricate new types of gas sensors with a high response to detect sub-ppm level of NH_3 at room temperature.

As one of the potential sensing materials for environmental gas monitoring, cerium oxide (CeO_2) has advantages of good resistance to chemical corrosion, non-toxicity, safety and reliability. therefore, it has attracted significant attention as gas sensors for CO [19,20], H_2S [21], C_2H_5OH [22], and carbon disulfide [23], acetone [24]. Improved gas sensing performance can be further achieved by modifying of structures CeO_2. For example, the gas response of sensors could be significantly increase by incorporation of Pt nanoparticles onto CeO_2 nanowire [19]. Gas sensor based on mixtures of CeO_2-Fe_2O_3 enhanced adsorption and subsequent oxidation of methanol [25]. Core-shell structures of CeO_2/TiO_2 nanorods exhibited enhanced response and selectivity to ethanol vapor [26]. Gas sensor based on CeO_2-ZnO showed improved gas response and selectivity to ethanol than pure CeO_2 sensor [27]. It is well documented that the addition of silica in metal oxides can stabilize the nanocrystal and enhance their catalytic activity [28,29]. Moreover, according to the paper reported by George et al. [30], the silica surface is terminated by lots of hydroxyl groups at the atmospheric pressure and temperatures below 150 °C, and the hydroxyl groups have extraordinary ability of water absorption [31]. Therefore, at room temperature, ammonia molecules will be adsorbed and react with water molecules on the surface of silica modified CeO_2 to produce NH_4^+ and OH^- ions. The NH_4^+ and OH^- ions will result in a

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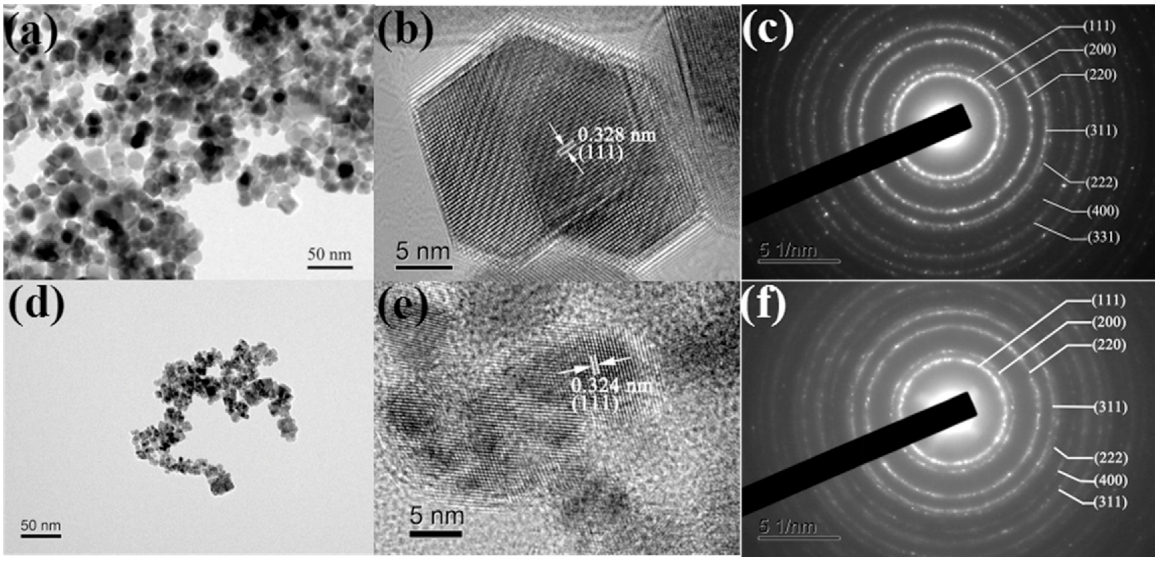

Fig. 1. (a) TEM image, (b) HRTEM image and (c) the selected area electron diffraction pattern (SAED) of pure CeO_2; (d) TEM image, (e) HRTEM image and (f) SAED of 8%silica-CeO_2.

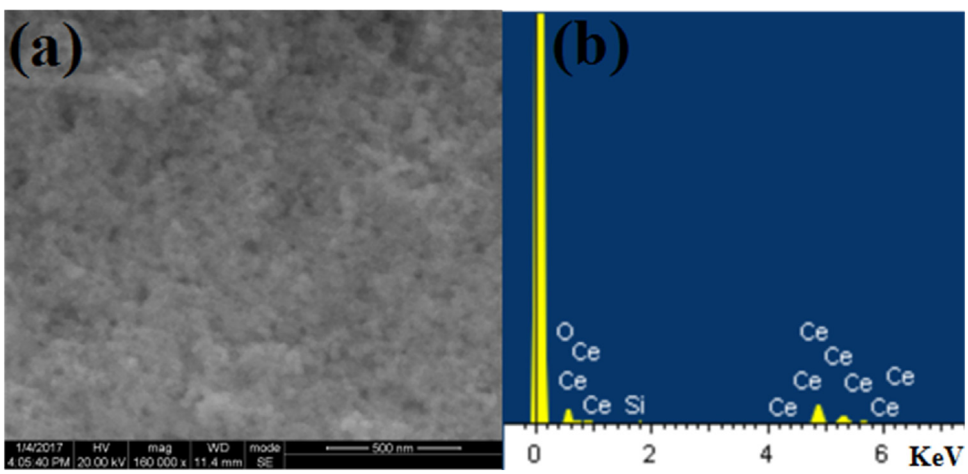

Fig. 2. (a) SEM image and (b) EDS pattern of 8%silica-CeO_2 film.

decrease of electric resistance, which will increase the gas response of the sensor. However, the NH_3 gas-sensing property of gas sensor based on silica modified CeO_2 nanomaterials have not reported.

In this work, we report a NH_3 gas sensor based on the silica modified CeO_2 nanostructures with a high gas response and detection limit of sub-ppm level, operated at room temperature. In addition, gas-sensing mechanisms of the gas sensors are also discussed.

2. Experimental

The pure CeO_2 and silica modified CeO_2 nanomaterials were synthesized using a sol-hydrothermal process. Firstly, at 50 °C, a certain amount of tetraethoxysilane (TEOS) was added into 60 mL 0.01 mol/L nitric acid (HNO_3) solution. Then, 10 mmol $Ce(NO_3)_3{\cdot}6H_2O$ was added under a constant magnetic stirring. Subsequently, 15 mL $NH_3{\cdot}H_2O$ was dropwise added into the above solution under continuous stirring to form a sol. After stirred at room temperature for 30 min, the sol was transferred into an autoclave for hydrothermal reaction at 150 °C for 10 h. The precipitates from autoclave was washed centrifugally with distilled water for three times and then dried at 70 °C for 12 h. Finally, the precipitates were treated at 400 °C for 1 h in air to obtain the final 8%silica-CeO_2 samples. The SiO_2 content was defined as $SiO_2\% = M_{SiO2}/(M_{SiO2} + M_{CeO2})$, where M_{SiO2} and M_{CeO2} were molar quantities of SiO_2 and CeO_2, respectively. Pure CeO_2 was prepared using the same synthesis process without TEOS.

X-ray diffraction (XRD, D/MAX-2500) with Cu Kα radiation was used to characterize the crystalline structures of the samples. Morphologies and sizes of synthesized samples were studied using a high resolution transmission electron microscope (HRTEM, JEM-2100F). The morphologies of film samples were observed using a scanning electron microscope (SEM, Inspect F50, USA) attached with Energy Dispersive Spectrometer (EDS). The chemical compositions of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific,) with Al Kα radiation. The specific surface area was measured by the N_2 physisorption apparatus (JW-BK122W, JWGB SCI. TECH.). UV–vis diffuse reflectance spectra (DRS) was recorded using UV-2550 spectrophotometer (Shimadzu Corporation, Japan). Fourier transform infrared (FT-IR) spectra are recorded on a FT-IR Transmittance spectrometer (FT-IR, Nicolet 6700, USA) in the range of 400–4000 cm^{-1} at room temperature. The element analysis was conducted by Inductive Coupled Plasma Emission Spectrometer (ICP, AtomScan 16, TJA, USA).