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Unique polyhedron CeO_2 nanostructures for superior formaldehyde gas-sensing performances

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ABSTRACT

Highly exposed surface area CeO_2 polyhedral nanostructures were successfully prepared via a two-step hydrothermal route for gas-sensing applications. The surface chemistry and formation of polyhedral nanostructures was attributed to the interaction between polyvinylpyrrolidone and ammonium bicarbonate surfactants with parent ceria. The synthesized polyhedron CeO_2 structures were characterized using XRD, XPS, BET, SEM, EDS and TEM, respectively. The polyhedrons exhibited a high specific surface area 98.76 m^2/g. For gas-sensing applications, the CeO_2 polyhedrons were exposed to different gases at various temperatures, from a low to high concentration range (1–150 ppm). At an optimal temperature 220 °C, superior gas-sensing response towards formaldehyde was observed than other target gases. The enhanced sensor response was attributed to multi-faceted polyhedral nanostructures. The polyhedral structure based sensors have great potential in industrial sensing applications.

1. Introduction

At present, the rapid developments in commercial and industrial sectors have drawn adverse effects on human health caused by environmental pollution. To overcome human health risk and protect environmental accidents, it is necessary to figure out the toxic factors effecting at very low concentrations in the air. Therefore, it is vital to detect and control the harmful gases in the air for personal life safety. Consequently, the demand of a high sensitive gas sensor that efficiently can sense toxic gases at very low concentrations is essential to decrease the environmental hazards for human health [1–4].

Among various environmental hazardous gases, formaldehyde (HCHO) a colorless and intense-odor gas, is one of the most volatile/toxic reducing gas and commercial organic compound that arises from the building decorative material and is causing many serious diseases [5,6]. Besides, its intense odor may cause human lungs-cancer as edema, nausea or asthma by the interaction of gas molecules with proteins. Even at very concentrations of formaldehyde (0.5–3 ppm) can produce irritations in the eyes and nose and life demise at higher concentrations (+15 ppm). Hence, nominal detection approach for significant detection of formaldehyde gas is of great importance to protect human health and environmental risk from its hazardous effects [7–10]. To detect and sense different or a specific target gas, the selection of material plays a vital role in the industrial applications. At recent, gas-sensors research is based on metal oxides with co-doped metallic and non-metallic materials, metal oxides and sulfides among which ZnO, SnO_2, SnO_2, WO_3, NiO, Co_3O_4, In_2O_3 and CuO/Cu_2O [11–15].

Among rare earth metal oxides, the pure cerium oxide (CeO_2) as sensing material has unique properties such as strong capability to absorb/release oxygen by mutual electronic transition between Ce^{3+} and Ce^{4+}, abundant oxygen vacancies, easy oxidization and high ionic mobility. Owing these rich properties along with its abundance on earth makes it a lost cost and alternative source of metal materials using in versatile applications such as photocatalysis, energy storage devices, solar cell and gas sensors [4–6]. Besides, multifaceted nanostructures being-building blocks assembled by using low-dimension nanomaterials such as nanosheets, nanowires, nanoparticles, and nanorods are of abundant benefits in high performance for photocatalytic activities, electrochemical supercapacitors, water splitting, solar cells, and particularly for its significant tendency towards enhanced gas sensing properties in detecting hazardous and toxic gases [16–18].

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The present study gives insights on the simple and novel synthesis and characterization of high exposed surface area of CeO_2 polyhedral nanostructures. The role of addition of PVP as a capping agent and surfactant is explained. Gas-sensors were fabricated based on the as-prepared polyhedral nanostructures. The outstanding gas-sensor stability, sensing response and high selectivity of polyhedral CeO_2 architectures for various gas concentrations and at different temperatures, along with sensing mechanism is described as well.

2. Experimental

2.1. Preparation of CeO_2 polyhedrons

The chemicals used were analytically grade and high purity (98%) by Keshi Co. Ltd., China. To synthesis CeO_2, 0.5 g cerium nitrate hexahydrate $Ce(NO_3)_3$ and 20 mL ammonium bicarbonate (NH_5CO_3) aqueous solution were dissolved with vigorous stirring in 40 mL of distilled water. Another solution containing 0.15 g of polyvinylpyrrolidone (PVP) and 0.0.8 g NaOH in 20 mL of distilled water and 10 mL ethanol was synthesized, at the same time. The second solution was poured into the above solution drop wise and dynamically stirred for 30 min. After the two solutions became homogenous, then transferred into a 100 mL Teflon-lined stainless steel autoclave and put into an oven heated at 160 °C for 12 and 24 h, respectively. Final products were carefully washed and filtered four times with ethanol and distilled before they were dried at 70 °C to obtain the CeO_2 powder.

2.2. Characterizations of polyhedrons

The CeO_2 nanostructures were characterized using Cu-Kα radiation (λ = 1.5406 Å) D/Max-1200 × –ray diffraction (XRD), Al-Kα X-ray (250 W) X-ray photoelectric spectrum (XPS) Vacuum generator spectrometer used for structural analysis, morphologies were investigated using a Jeol-1200 (FESEM) field emission scanning electron microscope and ZEISS, LIBRA200 (TEM) transmission electron microscope operated at 200 kV. The gas sensing measurements were taken at a Chemical Gas Sensor–1Temperature Pressure (CGS–1TP) intelligent gas sensing system Beijing Elite Tech Co., Ltd., China.

3. Results and discussions

3.1. Morphology formation mechanism

The XRD patterns of as-synthesized CeO_2 polyhedrons shown in Fig. 1(A), comprises of sharp crystalline peaks at the (111), (200), (220), (311), (222), (400), (311) and (420) planes corresponding standard CeO_2 Space group (Fm3¯m, JCPDS card no. 43–1002), indicating the high phase purity and good crystallinity of obtained CeO_2. Chemical composition of the CeO_2 polyhedrons was measured using XPS analysis, shown in Fig. 1 (C, D). Fig. 1(C) shows Ce 3d spectra and corresponding peaks fitting of CeO_2 polyhedral nanostructures. It is observed that Ce basically exits in mixed valance states as, Ce^{3+} and Ce^{4+}, respectively. It confirms the non-stoichiometric nature of ceria, which comprises multiple d-splitting systems such as $3d_{3/2}$ and $3d_{5/2}$. There are six Ce 3d binding energy peaks of $3d_{3/2}$ and $3d_{5/2}$ for Ce^{4+} oxidation and two peaks for Ce^{3+} oxidation. The peaks at 882.4, 898.6 and 917.3 eV corresponds to Ce^{4+} states, while peaks at 888.4 and 902 eV correlates to Ce^{3+}, respectively. The Ce^{4+} states directly represent the existence of O-vacancies in CeO_2 crystals, while Ce^{3+} indirectly indicates that oxygen vacancies hosted into the crystal lattice due to the Ce^{3+} and Ce^{4+} state transformations [7,8]. The presence of oxygen vacancies in turns strong adsorption of gas species on the sensor surface and confirms CeO_2 a potential candidate for gas sensor applications. The O 1s states (Fig. 1(D)) at 283.2, 284.1 and 286.0 ev, corresponds to adsorbed oxygen species of the lattice oxygen O^{2-} in Ce^{4+} states. Fig. 2G confirms the atomic wt% and elemental ratio of as-synthesized CeO_2 polyhedrons [31,32]. Fig. 2 (A, B) shows low and high magnification SEM images of CeO_2 polyhedron. The polyhedrons are made up of diamond and rectangular faced shapes with an average length and width of 1 µm and 780 nm, respectively while average particle size is 890 nm. Fig. 2 (C, D) displays TEM, HRTEM images and SAED patterns taken at the lateral edges. The HRTEM results indicates that the crystal structure basically are grown along [111], with corresponding lattice distance of 0.32 nm. The low and high magnification SEM images of CeO_2 nanostructures prepared at 12 h, pre-based nuclei of polyhedral nanostructures are shown in Fig. 2S (Supplementary Information). The N_2 adsorption/desorption isotherm for BET–surface area of CeO_2 polyhedrons shown in Fig. 1 F and measured surface was approximately 98.76 $m^2\ g^{-1}$. The wide exposed surface area of multi-facets polyhedral nanostructures implies that polyhedral nanostructures are highly favorable for strong gas sensing ion-species interactions and providing more active sites resulting in superior gas sensing response. The surface area of pre-matured polyhedral nanostructures prepared as 12 h was 65.76 $m^2\ g^{-1}$, which is less than that of 24 h post-matured state, So low gas sensing performance are exhibited by pre-matured nanostructures. A plausible formations mechanism for polyhedrons is depicted in Fig. 2 (E). During the reaction system Ce^{3+} has strong affinity with OH^- forming $Ce(OH)^{2+}$ polyatomic group at the initial stages, while supersaturation occurs at high temperatures forming CeO (HCO_3) by the interaction of CO_3^{2-} with positive charged group and develops fast nucleation for initial crystal nuclei. At 12 h reaction time, the shape of polyhedron is not completely modulated due to insufficient surface-active agents in PVP along-with OH^- ions. With increasing the reaction time to 24 h while keeping constant temperature, the reactions system undergoes mild-structural formations, leading to polyhedron nanostructures. Meanwhile, PVP intertwine to form the lateral nanostructures while adsorbing on the rectangular faces of the polyhedrons and encapsulation of PVP limits the agglomeration of $[10\bar{1}0]$ and $[010\bar{1}]$ faces [9,10].

$$NH_4OH \leftrightarrow NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$

$$2HCO_3 \leftrightarrow CO_2 + CO_3^{2-} + H^+ - OH^- \quad (2)$$

$$Ce^{3+} + OH^- + CO_3^{2-} \Rightarrow CeO(HCO_3) \quad (3)$$

$$4CeO(HCO_3) + O_2 \rightarrow 2H_2O + 4CO_2 + 4CeO_2 \quad (4)$$

The addition of PVP surfactant facilitates effective control of size and shape of metal ions through nucleation i.e. impaired metal ions reduction through strong coordinative bonding of PVP-Ce^+ ions and endures growth of large facets in nanocrystals. PVP in the formation of CeO_2 polyhedrons might be undergoing the following stages: Firstly, PVP donates a loan-pair of O_2 and N_2 atoms to Ce^{3+}-Ce^{4+} ions by imparting sufficient electronic density in electrostatic interactions thus forming a coordination complex during the structure formations in chemical reaction system. Secondly, with elongating the reaction time to 24 h, PVP strongly stimulates nucleation process for metal ions due to PVP- Ce^{3+}/Ce^{4+} complex. Thirdly, the steric effects (large C–N, C=O chains) of polymer PVP hinder aggregation of interior structural formations in polyhedrons and serve as antiagglomeration agents at the same time and allow adequate quantity of PVP to reside on the surface of polyhedron to stabilize the nanostructures [19,20]. The large expose surface of multi-faced polyhedral nanostructures are extremely advantageous for using in gas sensors because wide surface decreases gas diffusion length, fast carriers mobility and large expose surface area for multi-adsorption as compared to 1D or 2D gas sensor nanomaterials.

3.2. Gas–sensing measurements

Recent developments in the gas sensor fabrication with excellent sensing outputs, ease in measurement, low cost device fabrication and high accuracy in sensing electrical resistances by gas molecule-material