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Hierarchically MoS_2 nanospheres assembled from nanosheets for superior CO gas-sensing properties

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ABSTRACT

Hierarchical three dimensional MoS_2nanostructures composed of small sheet-like nanostructures are successfully prepared using a simple two-step hydrothermal process with sodium dodecyl sulfate (SDS), as a surface modifier. The as-preparedMoS_2nanospheres are characterized by XRD, BET, XPS, EDS, SEM and HRTEM. The gas–sensing properties of as–prepared MoS_2nanostructures are tested at 175–230 °C temperatures for 50–500 ppm concentration range, using an efficient ceramic-tube sensor system via an intelligent gas testing system. A high response and selectivity towards carbon monoxide than other gases is observed. Comparative studies of MoS_2nanostructures for different concentration of carbon monoxide gas and definite sensor-stability for different gases are studied, as well. The sensor fabrication and sensing mechanism is discussed as well.

1. Introduction

Due to excellent gas sensing propensities, low cost and long cyclic life, metal oxide semiconductor based gas sensors have been intensively studied. A huge industrial development is causing polluted environment that contains a number of poisonous gases in it such as CO_2, NO_2 and CO etc. Among these gases, CO is found one of the hazardous gases present in the environment, so it is essential to monitor the concentration of the gas by using effective CO gas sensors such as electrochemical sensors, infrared sensors, and surface acoustic wave sensors [1–3]. Among diverse gas sensors, semiconducting metal oxides-based gas sensors are the best performing devices with low cost, easy fabrication, high selectivity and fast detection and have attracted attention of the researchers. Transition metal dichalcogenide (TMCs) nanostructures with high exposed surface area are emerging and potential applicants in industrial applications. Among them, multilayered MoS_2transition metal dichalcogenide analogous to graphene, has 2D layered *n*–type semiconductor with a narrow band gap (~1.82 ev). Naturally it is composed of three atoms layer (S—Mo—S) structure via weak vandar Waals interactions. In short, MoS_2 is more beneficial than graphene due to its abundance, low-cost and friendly environment synthesis, tunable band-gap and versatile morphologies with large exposed surface areas. The multilayered structure and large exposed surface of MoS_2 facilitates high ion-charge carrier mobility and diffusion at active sites of metal-ions for improved sensitivities, during the gas-sensing measurements. Such outstanding properties have proved MoS_2 as a potential candidate for chemical/optical/gas sensors for the detection of hazardous gases and environmental pollutants [4–6]. Among various synthesis routes, hydrothermal method is the cheaper, easy fabrication and environment friendly, give rise to exfoliation for MoS_2 nanosheet and stabilizes the nanostructures to some extent due to surface energy effects. Besides, this solution-based reaction is beneficial for consistent and scaled-up production of atomically thin MoS_2 nanosheets aggregations to nanospheres. The present study explains a simple novel method to prepare high exposed surface area of MoS_2 nanospheres. The high gas sensing response and selectivity of MoS_2 nanospheres was observed towards CO than other gases, at various temperature ranges for different gas concentrations. The sensor-device fabrication and gas sensing mechanism of MoS_2-COion-exchange is discussed in details.

2. Experimental

2.1. Synthesis of hierarchical MoS_2 nanospheres

All chemicals reagents (98% purity, analytic grade) in the in the experiment were of analytical grade (purchased from National Chemical Co., Ltd., China) and used without further purification. For

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nanosheets synthesis: 0.05 g sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$) and 0.03 g thiocarbamide (CH_4N_2S) were dissolved in 40 ml deionized water to form a transparent solution and stirred for 30 min. The solution then was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 100 °C for 18 h. The obtained black precipitates were separated from the solution by centrifugation, washed with distilled water and absolute ethanol for five times, respectively. The obtained black products were dried in air at 80 °C to obtain the MoS_2 powder. Secondly, to synthesis MoS_2 nanospheres, 0.05 g sodium dodecyl sulfate (SDS) was added to the 0.05 g of as-prepared nanosheets powder and dissolved in 20 ml deionized water to form a transparent solution and stirred for 30 min.SDS is used as surface modifier while citric acid ($C_6H_8O_7$) was used to adjust the pH value of the solution. The transparent solution then was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 12 h. The drying process was the same as described before.

2.2. Material characterizations

Surface morphological and structural characterizations were accomplished using X–ray diffraction (XRD) in a Rigaku D/Max–1200X diffractometer with Cu Kα radiation (λ = 1.5406 Å) operated at 30 kV and 100 mA, Hitachi S–4300 field-emission scanning electron microscope (FESEM), transmission electron microscope (TEM, ZEISS, LIBRA200) at an accelerating voltage of 200 kV and multipoint Brunauer–Emmett–Teller (BET) method operated at 77.3 K with a Quanta-chrome NOVA-4200 system. The elemental analysis is carried out through energy dispersive spectroscopy (EDS) and electronic states of elements in the MoS_2 products were detected by X-ray photoelectric spectrum (XPS) with a (Vacuum generators) spectrometer using Al-Kα X-ray (240 W).

2.3. Fabrication of gas-sensor device

To evaluate gas-sensing properties of as-prepared MoS_2 nanospheres for various gases, the measurements were calibrated at CGS–8 (Chemical Gas Sensor–Temperature Pressure) intelligent gas-sensing analyzer system (Beijing Elite Tech Co.,Ltd.). The schematic of the fabricated the gas sensor is given in Fig. 3A(a–d). The as-prepared MoS_2 nanospheres powder was mixed with ethanol via ultra-sonication to make slurry and then a thick film was coated onto an Al_2O_3 ceramic tube to form a sensing film that contains two parallel Au electrodes merged with four Pt wires. The sensor was sintered at 400 °C for 2 h and a Ni–Cr wire was inserted into the tube as a heater then welded on the sensor pedestal for final testing. The gas response was defined as S = Ra/Rg (for reductive) and S = Rg/Ra (for oxidative) circumstances, whereas Rg and Ra are the sensor resistances to the target gas and in air, respectively. The response and recovery time was measured as the time taken by the sensor to reaches about 90% of the maximum or minimum resistance change in the case of adsorption/desorption process [8–10].

3. Results and discussions

Fig. 1(a) shows the XRD diffraction patterns of the as-prepared MoS_2nanostructures. The patterns consist of peaks at (002), (004), (100), (102), (103) and (104), describing hexagonal crystalline structure of MoS_2, is in well-match with the standard JCPDS No.82–2416 of MoS_2. Fig. 2(A, B) show the low and high magnification MoS_2nanosheets and nanospheres, with average width, length and thickness of 27, 375 nm, respectively. Fig. 2(C, D) show the low and high magnification MoS_2 nanospheres, with average width of sheets 20 nm and radius 500 nm, respectively. It can be observed that uniform MoS_2 nanospheres are constructed through thin-sheet nanostructures, forming hierarchical structures which provide hierarchical MoS_2 nanospheres wide specific surface area along-with porous multi-active-site channels. The porous channels might be due to the strong chemical reaction between SDS- thiocarbamide (S-N ion-exchange interactions). Fig. 2(E, F) exhibit TEM, HRTEM and SAED patterns respectively. The narrow strips at the edges of sheet-like nanospheres indicate that MoS_2 is a layered structure. The interplaner distance of adjacent lattice plane for nanosheets and nanospheres is 0.61 and 0.62 nm along (002) planes, respectively. The lattice distance of SAED patterns is in well-consistent with the theoretical values of hexagonal planes of MoS_2 nanostructures. The large lateral-dimension growth in MoS_2, gives a rise onto basal planes with no dangling bonds resulting in large stable planes, which is a significant advantage in gas-sensing applications and is considered as strong contact-panel for sensor species to gas ions. The BET–surface area of as-prepared MoS_2 nanospheres depicted Fig. 1b, is measured approximately 96 $m^2 g^{-1}$, which is higher than the $NiCo_2S_4$ nanostructures [7] and $BiCoO_3$ Microspheres (73.58 $m^2 g^{-1}$) [8]. The high surface area is favorable for the high response of gas sensing due to more active sites present on exposed surfaces, in terms of small pores that can adsorb high number of gas species. The chemical composition of as-prepared MoS_2 nanospheres characterized by energy dispersive spectroscopy (EDS) is shown in Fig. 1(c, d). It can be clearly seen that wt% of Mo (26.20) is in 1:2 ratios to the wt% of S (65.40). The corresponding EDS mapping results are depicted in Fig. 1b, respectively. Fig. 1(e–g) demonstrates electronic states of elements detected by X-ray photoelectric spectrum (XPS). The distinctive peaks of Mo and S are revealed in the survey XPS spectra without any other elements (Fig. 1(g)). In Fig. 1(e), the Mo 3d spectrum of MoS_2 nanospheres shows two peaks at 229.6 and 232.8 eV that are contributed to the doublet Mo 3d5/2 and Mo 3d3/2 of Mo^{4+}. Furthermore, the doublet $S2p_{3/2}$ and $S2p_{1/2}$ is detected at 162.3 and 163.5 eV (Fig. 1(f)). The result confirms theMoS_2 nanospheres are layered structure that can exhibit strong physical absorption which results in enhanced gas sensing properties.

During the formation of MoS_2 nanosheets, thiocarbamide was employed as a source of sulfur ions. Besides, it has a planar molecule containing C═S bonds, which has a unusual property to capitalizes the reaction system to high nuleophilicity and easy hydrolysis of the intermediate sodium molybdate salts. The high nuleophilicity tends the nanosheets formation and crystal growth takes place in [0001] lateral directions.

$$(Na_2)MoO_4 + 2H_2O \rightarrow MoO_3 + 2Na^+ + 4H^+ + 3O^- \quad (1)$$

$$CS(NH_2)_2 + 2H_2O \rightarrow 2NH_3 + H_2S + CO_2 \quad (2)$$

$$4MoO_3 + 2H_2S \rightarrow 4MoO_2 + S + SO_2 + 2H_2O \quad (3)$$

$$MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O \quad (4)$$

During the hydrothermal reaction for the formation of hollow nanospheres, the decomposition of sodium molybdate and the thiocarbamide occurs simultaneously (Eqs. (1) and (2)). Meanwhile, the reduction of Mo^{6+} to Mo^{4+} at high temperature is achieved, that was formed as MoO_3 during initial reaction system. The Mo^{6+} reacts withS^{2-} ions, obtains from the decomposition of $CS(NH_2)_2$, generating MoS_2 nanosheets, as given in Ed. 3 and 4, respectively. The presence of (002) diffraction peaks shows purity and hierarchical structure of MoS_2 nanostructures. It is believed that SDS played an important role in the growth of three dimensional hierarchical MoS_2 nanospheres. The additions of sodium dodecyl sulfate (SDS) integrate the interaction of S^{2-} ions and accelerate the agglomeration process of nanosheets. The mutual interaction of nanosheets, due to large surface area and high surface activity upon the SDS introduction, reinforces the nanosheets to assemble in an irregular pattern, forming the hierarchical MoS_2 nanospheres. SDS being an anionic organic solvent disrupts the non-covalent bonds and tends molecules to lose their shapes, during the nucleation process. Beside supersaturated solution of SDS might provide reverse micelle micro-emulsion that strengthens the electrostatic interactions in the anisotropic growth that binds the sheets-like nanostrips to the MoS_2nanospheres which results in wide surface area-to-volume ratio