



Hematite nanostructures: Morphology-mediated liquefied petroleum gas sensors



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ARTICLE INFO

Article history:

Received 2 March 2013

Received in revised form 11 July 2013

Accepted 22 July 2013

Available online 30 July 2013

Keywords:

α -Fe₂O₃

Structures

Morphology

LPG sensors

ABSTRACT

Liquefied petroleum gas (LPG) sensors of hematite nanostructures viz. nanoparticles, nanoparticle-chains and nanorods, chemically synthesized from iron nitrate, sulfate and chloride precursors, respectively, in presence of urea as pH regulating agent are explored. These nanostructures were examined for their structures and morphologies. The Hematite morphology has an impact on crystal structure, Raman shift and charge transfer resistance value. On the basis of results presented herein, we proposed an importance of hematite nanostructures as a sensing material for the LPG sensors. Superior LPG sensor sensitivity of nanoparticles-chains (77.89%) over nanoparticles (68%) and nanorods (58.80%) at 1000 ppm LPG gas levels are imply that the hematite nanostructure (surface area) plays an important role in mediating charge transfer reaction.

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1. Introduction

The increasing concern for air-pollution and industrial safety establishes a need to monitor combustible and toxic gases for healthy and comfortable life. Tremendous efforts have been made to develop gas sensors at low temperatures [1,2]. Recently, researchers proved an importance of one-dimensional (1D) nanostructure semiconducting oxides over traditional thin and thick film sensors such as high surface-to-volume ratio, dimensions comparable to the extension of surface charge region, etc. [3–6]. The working mechanism of a gas sensor includes in the convection of electrical conductivity due to surface reactions such as oxidation or reduction caused by different gas exposures [7] which in fact, depends on the active centers and the defects existing on the surface layer of materials. Compared with conventional materials such as bulk or thin films applied to gas sensors, 1D nanostructures such as nanowires, nanorods (NRs), nanoribbons, and nanotubes, etc. have a relatively higher gas sensor response due to their ultrahigh surface-to-volume ratio. Reactions at grain boundaries

could strongly modify the transport quality [8,9]. Because of low power consumption, low-cost, easy operation and high compatibility with microelectronic processing, etc., number of gas sensors of nanostructures of metal oxide semiconductors have widely been exploited to date [10].

Hematite, i.e., iron oxide (α -Fe₂O₃), generally an n-type semiconductor with energy gap of 2.1 eV, is the most thermodynamically stable phase among all available iron oxide phases under ambient conditions [9]. Owing to its environmental friendliness, high chemical and thermal stabilities, it has been previously envisaged in a variety of fields including gas sensors [10], lithium batteries [11], catalysts [12], pigments [13], magnetic devices [14], etc. Moreover, research on the intrinsic relationship between the morphology/size and the sensor property has engendered an urgent need for adjustable synthetic strategies, where the size and morphology of the hematite can be controlled with required functionalities. Accordingly, various physical and chemical methods so far have been adopted to synthesize hematite in diverse morphologies, such as nanoparticles (NPs) [15], NRs [16], nanotubes [17], hollow-spheres [18], nanobelts [19], nanoplates [20] and complex hierarchical structures [21,22], etc. Hydrothermal chemical method with structure-directing agent has proven its effectiveness in growing hematite nanostructures of various kinds [23,24]. For many decades, the hematite has been proved to be one of the good gas sensing candidates for the detection of gases including hydrogen [25], liquefied petroleum gas (LPG) [26], carbon monoxide [27], nitrogen dioxide [28], hydrogen sulfide [29], oxygen [30]

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and ethanol [31], etc. Of these, LPG is a combustible gas and it is widely used as fuel for domestic heating and industrial use. It is one of the extensively used gases in day-to-day activities. There is a need to detect the leakage in its early stages before explosion and perform active suppression [32]. In order to accomplish this, more attention has already been paid to the development of the gas sensors for the detection of LPG using several doped and undoped metal oxides [33].

In continuation with our hematite-based research [34], in this work the relationship between the hematite morphology and the LPG gas sensor performance is demonstrated. Different nanostructures of hematite viz. nanoparticle-chains (NPCs), NPs, and NRs are chemically synthesized onto glass substrates and further used for their structure, morphology and electric properties. The experimental results clearly demonstrate the potential of hematite nanostructures as sensing material in the fabrication of LPG sensors. Charge transfer resistance, gas sensitivity, response time and recovery time are found to be dependent on the hematite morphology type.

2. Experimental details

All reagents used in this experiment were of analytical grade, obtained from Sigma–Aldrich and were used without further purification. Distilled water was used throughout the experiment. Glass-substrates used for deposition were cleaned for 10 min in detergent water, acetone and isopropyl alcohol separately from an ultrasonic bath, dried in a stream of argon and stored for further use. In a typical synthesis of hematite nanostructures viz., NPC, NPs and NRs method, 25 ml stock solutions of 0.2 M $\text{Fe}_2(\text{SO}_4)_3$, 0.2 M $\text{Fe}(\text{NO}_3)_3$ and 0.2 M FeCl_3 , respectively, were mixed with 0.4 M urea (25 ml) separate solution and sealed in three falcon tubes with each of 50 ml capacity and maintained at 90 °C for 12 h. Glass substrates were placed vertically in these tubes by maintaining inclined positions. After completion of the reactions, reddish iron oxide-hydroxide films obtained onto glass substrates were taken off, thoroughly washed with water, dried under a stream of argon and air-annealed at 500 °C for 30 min before further measurements and LPG sensors.

The crystallographic orientations of the deposited hematite films of said nanostructures were examined using X-ray diffraction (XRD) from 20° to 80° in 2 theta range with a step of 1° per min. The X-ray source was $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$). The morphologies were recorded using a field-emission scanning electron microscopy (FE-SEM, Hitachi S-4200) images. For electrochemical impedance spectroscopy (EIS) measurements, impedance analyzer (COMPACTSTATe: IVIUM Switzerland) was used. The sensor response was determined using $S = (R_a - R_g/R_a) \times 100\%$ relation, where R_a and R_g represent the resistances of the film in air and upon exposure to LPG, respectively.

3. Results and discussion

3.1. Structural elucidation and morphological evolution studies

Fig. 1A–F presents the FE-SEM images of hematite NPC, NPs and NRs nanostructures at two different magnifications wherein, the growth of all nanostructures was uniform and crack-free. The NPC were nearly two micrometers in lengths and about 40 nanometers in widths. Physically, several NPC were connected to form corn-type architecture. These corns were wide at centers and narrow at their ends (Fig. 1A and B). The $\alpha\text{-Fe}_2\text{O}_3$ NPs of irregular dimensions (close to 40 nm) were agglomerated and close to one another. Surfaces were smooth and polished (Fig. 1C and D). Growth of NRs was in the bundle form (Fig. 1E and F). Few NRs, with 100–200 nm

in lengths and 40–60 nm in diameters, were compiled together to form stick-type elongated architecture. Under close inspection it was found that these individual nanorods were bifurcated at some places along their lengths (Fig. 1E and F) which may be effective in LPG sensors application on account of their excessive surface areas.

The XRD spectra of three different hematite nanostructures, i.e., NPC, NPs and NRs, deposited on glass substrates, are shown in Fig. 2A. The peaks appearing in the XRD are indexed using the JCPDS data (JCPDS 88-2346) with hexagonal unit cell. No impurity phases and peak shift were observed, suggesting a hematite ($\alpha\text{-Fe}_2\text{O}_3$) structures was same for all three forms. The (0 1 2), (1 1 0), (1 1 3), (0 2 4) and (0 1 8) reflection planes showed relatively higher intensified for NPC as compared to NRs and NPs. Though all morphologies exhibit same structure, their degree of crystallinity was lower for NRs and NPs and higher for NPC. Effect of XRD peak intensity on electrical resistivity is recently investigated for ZnO thin films [35]. Due to fewer oxygen ions, and a lower ionic diffusion resistance, i.e., a higher charge transfer resistance, relatively smaller (0 0 2) peak intensity for ZnO NPs compared with other planes is reported [36]. In short, different crystallinities exist in hematite nanostructure contributed respective peak intensity in X-ray pattern and demonstrated different electrochemical properties (discussed below). Fig. 2B shows the Raman spectra of hematite nanostructures during irreducible vibrational modes wherein the acoustic A_{1u} and the A_{2u} modes are optically silent. The symmetrical modes are Raman active and the anti-symmetrical modes are infrared active [37]. Infra-red active modes were absent as hexagonal structure of hematite has an inversion center. These spectra revealed that all peaks correspond to $\alpha\text{-Fe}_2\text{O}_3$, consistent to XRD results, and were free from any peak resembling with other phases of iron oxide. Peak positions at 229 cm^{-1} and 500 cm^{-1} were assigned to the A_{1g} modes whereas, remaining five peak positions at 249, 295, 302, 414 and 615 cm^{-1} are due to the E_g modes [38].

3.2. Charge transfer resistance kinetics

The charge transfer kinetics in hematite nanostructured electrodes was studied in dark by applying an AC open circuit potential of -0.697 V amplitude in the frequency range of 1 mHz to 1 MHz using EIS spectra (see Ref. [34, Fig. 5] for more details). The impedance spectra for all nanostructures show one semicircle which can be attributed to charge transfer resistance at the fluorine-tin-oxide/ Fe_2O_3 /electrolyte interfaces in non-uniform-type photo-electrochemical cells. At high frequency region the crossover point of the highest frequency with the real part of the impedance is a combinational resistance of the electrolyte resistance, intrinsic resistance of substrate and contact resistance between the active material and the current collector. Nyquist plots were different for different hematite nanostructures suggesting that in spite of same structure, the charge transfer resistance and the series resistances were different. The lowest charge transfer resistance value was assigned to NRs (1512 Ω) compared to NPs (1730 Ω) and NPC (1870 Ω) forms. Series resistance of NRs electrode is higher than NPs and NPC electrodes which could have accounted for difference in their surface areas as surface area of NRs (13.66 $\text{m}^2 \text{ g}^{-1}$) was smaller than NPs (15.99 $\text{m}^2 \text{ g}^{-1}$) and NPC (65.62 $\text{m}^2 \text{ g}^{-1}$), respectively. This confirmed that the electrode surface area and morphology had a direct impact on series resistance and charge transfer resistance [34]. To corroborate this observation DC two-point electrical conductivity measurement was operated for all nanostructures between $\pm 10 \text{ V}$ voltage span using Keithley 2400 source meter at room temperature (Fig. 3A) [39]. Electrical conductivities for hematite NPC, NRs and NPs structures were 40.00×10^{-9} , 23.09×10^{-9} and $7.47 \times 10^{-9} \text{ S/cm}$, respectively, and supporting that the electrical resistivity of hematite is morphology

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