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Polyhedral α-Fe_2O_3 crystals@RGO nanocomposites: Synthesis, characterization, and application in gas sensing

Haojie Song [a, b], Linxuan Xia [a], Xiaohua Jia [b, *], Wenming Yang [a, **]

[a] School of Material Science and Engineering, Jiangsu University, Zhenjiang, 212013, PR China
[b] School of Materials Science & Engineering, Shaanxi University of Science & Technology, Xi'an, 710021, PR China

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ABSTRACT

Polyhedral α-Fe_2O_3 crystals@reduced graphene oxides (RGO) nanocomposites were prepared through the dehydration and recrystallization of a hydrothermally synthesized β-FeOOH precursor. The structures and morphologies of the nanocomposites were investigated by various characterization techniques, including X-ray diffraction (XRD), field-emission electron scanning microscopy (FE-SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The characterization results showed that the polyhedral α-Fe_2O_3 crystals@RGO nanocomposites were formed by growing the α-Fe_2O_3 polyhedron particles with diameters of 120–190 nm on the RGO nanosheets. The gas sensing performances of the as-prepared nanocomposites were examined and compared with bare α-Fe_2O_3 polyhedron based sensors. The polyhedral α-Fe_2O_3 crystals@RGO nanocomposites sensors delivered substantial response towards 50 ppm acetone reaching up 14.7. This value was 1.6 fold higher than that obtained with α-Fe_2O_3 polyhedron at 260 °C. Furthermore, the sensors recovered their initial states in a short time after exposure to fresh air. These remarkably enhanced acetone-sensing performances could be attributed to the improved conductivity, catalytic activity towards oxygen reduction reaction, and the increased gas adsorption ability of the polyhedral α-Fe_2O_3 crystals@RGO nanocomposites.

1. Introduction

The demand for accurate sensors to monitor and control environmental pollution during manufacturing processes has gained increasing interest in recent years [1–3]. Gas sensors are devices composed of active sensing materials connected to signal transducers. Therefore, the selection and development of potential sensing materials play an important role in designing high-performance gas sensors [4,5]. Graphene is a unique two-dimensional (2D) carbon nanomaterial comprising of carbon atoms connected by covalent sp2 bonds to form honeycomb-like sheets [6]. This particular architecture gives to graphene many interesting properties, such as high surface-area-to-volume ratio, relevant adsorptivity, outbound chemical/thermostability, and excellent electrical properties [6,7] and is applied to miniature device (such as conductive switching and bioimaging) [8,9], catalysis [10,11], energy storage [12–15]. In addition, graphene has been fiery studied during the past few years as gas sensing materials [16–20]. However, low response and poor selectivity of intrinsic graphene limit its use in gas sensing [21].

The modification of graphene is considered as an effective way to improve the sensing performances of graphene-based sensors [17–19]. Many metal oxides/RGO composites have been reported with combined outstanding properties of both the semiconductor metal oxides and graphene materials to result in enhanced sensing properties thanks to the synergetic effects [4,17,22,23]. For instance, Deng et al. [4] prepared RGO-conjugated Cu_2O nanowire mesocrystals to manufacture a highly sensitive sensor toward NO_2 at room temperature, surpassing the performance of standalone systems based on Cu_2O nanowires networks and RGO sheets. Wang et al. [23] synthesized *P*-doped ZnO nanosheets@GO nanocomposites with high sensitivities towards acetone, attributed to the unique 2D-2D structure of rigid ZnO and flexible GO. Zhang et al. [19] prepared RGO/SnO_2 p-n heterojunction aerogels as efficient 3D sensing frameworks for phenol detection. The aforementioned studies provided strong evidence that defective graphene exhibits distinctive behavior when compared to pristine graphene.

Among the metal oxides in gas sensing properties (ZnO, SnO_2,

* Corresponding author.
** Corresponding author.
E-mail addresses: jiaxiaohua@sust.edu.cn (X. Jia), ywm@ujs.edu.cn (W. Yang).

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Fe_2O_3, among others), hematite (α-Fe_2O_3) is an n-type semiconducting material with a direct band gap (E_g) of 2.1 eV. α-Fe_2O_3 has widely been applied as gas sensing material due to its friendly environmental character, low-cost, high stability, and elevated resistance to corrosion [19,23–26]. However, in spite of these virtues, α-Fe_2O_3 is still suffering from some limitations in gas sensing, including high operating temperatures (typically > 300 °C), poor selectivity, and low response [27].

As research advances and to overcome the issues related to pure α-Fe_2O_3, α-Fe_2O_3 gas sensing materials are gradually improving by combining pure α-Fe_2O_3 with other metal oxides to form heterojunction, composting with metals to promote the catalytic effects, as well as through hybridizing with carbon nanomaterials to improve conductivity [28–35]. In this respect, Liang et al. [33] investigated the gas sensing properties of α-Fe_2O_3@graphene nanocomposites with different graphene contents and found that the content plays a significant role in enhancing the specific surface area, hence the gas response. Liang et al. [34] improved the gas sensing performances of Fe_2O_3 gas sensors using graphene as sacrificial templates and by setting more open framework structures as gas transmission galleries. Guo et al. [35] used a facile electrospinning method to produce RGO/α-Fe_2O_3 composite nanofibers with lower resistances due to the unique π-π conjunction structure of RGO that facilitated the electron transfer to α-Fe_2O_3. The resulting gas sensors based on Fe_2O_3 and graphene composites showed improvements in terms of response towards the analyte. However, ideal characteristics of a gas sensor should not only be limited to good response but also broader response range from low to high concentration, low optimal operating temperature, quick response and recovery, high stability, and moderate influence on the environment.

In this study, polyhedral α-Fe_2O_3 crystals@RGO nanocomposites were successfully prepared through dehydration and recrystallization of a hydrothermally synthesized β-FeOOH precursor. The crystal structures and morphologies of the as-prepared nanocomposites were examined by various analytical methods. The polyhedral α-Fe_2O_3 crystals@RGO nanocomposites were used to fabricate gas sensing devices and tested for detection of various gases, the as-assembled sensors showed high performances towards the detection of acetone, and the relation between the gas sensing properties and structure of the α-Fe_2O_3@RGO nanocomposites was discussed.

2. Experimental

2.1. Material and methods

2.1.1. Material

The graphene oxide (GO) (JCGO-95-1-2.6) was purchased from Nanjing Jicang Nano Technology Co., Ltd. (China). Ferric chloride ($FeCl_3 \cdot H_2O$, 99.0%), ammonium fluoride (NH_4F, 99%) and ethanol (CH_3CH_2OH, ≥99.7%) were from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The distilled water was obtained by our laboratory filtration system. All the reagents were used as received without further purification.

2.1.2. Methods

The GO (5 mg) was first dispersed in 50 mL absolute ethyl alcohols by ultrasonic treatment for about 2 h. Meanwhile, $FeCl_3 \cdot H_2O$ (1.3514 g, 5 mmol) was dissolved in 50 mL distilled water to form a homogeneous solution through magnetic stirring. NH_4F (0.1850 g, 5 mmol) was subsequently added to the above-mentioned $FeCl_3$ solution and stirred for 30 min. Next, the mixture was added drop by drop into the dispersed GO/ethanol agent under magnetic stirring and maintained for 30 min. Subsequently, the mixtures were transferred into a 250 mL round-bottom flask at room temperature then refluxed at 90 °C in an oil bath for 8 h. The obtained product was washed several times with ethanol and distilled water and used as a precursor, which then was ultrasonically dispersed in 80 mL ethanol for 30 min.

A flow of ash water mixtures was then introduced into a 100 mL PTFE stainless steel reactor, and heated at 150 °C for 10 h. The sediment was centrifuged and subsequently washed twice with ethanol and distilled water. The finally obtained powder was dried in a vacuum freeze dryer. For comparison, pure α-Fe_2O_3 was prepared using the above process but without the addition of GO. A possible synthetic mechanism of α-Fe_2O_3 crystals@RGO nanocomposites was proposed in Fig. 1.

2.2. Characterization

The crystal phases of the samples were examined by X-ray diffraction (XRD, Holland Philips X′ pert X-ray diffractometer with Cu-Kα radiation, $\lambda = 1.5406$ Å) over the 2θ range of 10–70°. Fourier transform infrared spectroscopy (FTIR) spectra were obtained with a NEXUS 670 spectrometer. Raman spectra were recorded on a Dilor Labram-1B multichannel confocal microspectrometer with 532 nm laser excitation. Scanning electron microscopy (SEM) images were obtained using a JOEL JSM-7001F field-emission scanning electron microscope (FESEM). TEM images, selected area electron diffraction (SAED) image and HRTEM image were recorded by a JEM-2100 transmission electron microscope. The chemical composition and bonding states were investigated by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Escalab 250Xi) using a monochromatized Al Kα X-ray source ($h\nu = 1486.6$ eV). The specific surface area and pore distribution were examined by the Brunauer-Emmett-Teller (BET) model and Barrett-Joyner-Halenda (BJH) theory, respectively. A Micromeritics TriStar II 3020 static volumetric analyzer was employed for that purpose. The gas sensing properties of the sensors were tested by a WS-30A gas sensing measurement system.

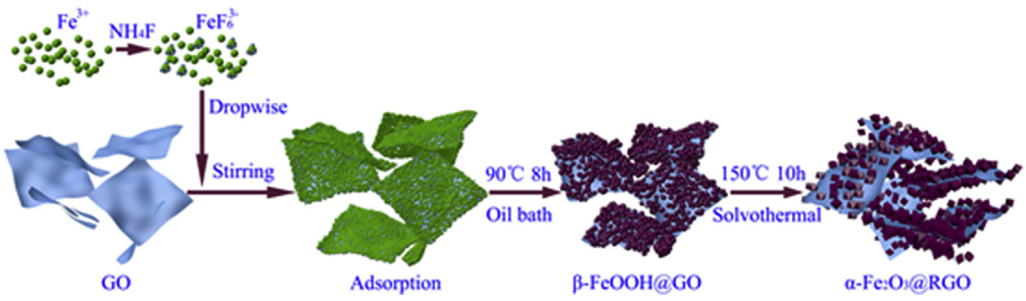

Fig. 1. A schematic diagram of the α-Fe_2O_3@RGO nanocomposites preparation process.