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Controlling synthesis and gas-sensing properties of ordered mesoporous In_2O_3-reduced graphene oxide (rGO) nanocomposite

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Abstract Herein, we describe a strategy for fabricating ordered mesoporous In_2O_3-reduced graphene oxide (rGO) nanocomposite through ultrasonic mixing, where ordered mesoporous In_2O_3 nanoparticles are synthesized via the nanocasting route by using mesoporous silica as a hard template, which possess ordered mesostructure with a large surface area of 81 m^2 g^{-1}, and rGO nanosheets are synthesized from graphite via graphene oxide (GO) as intermediate. After coupled with rGO, mesoporous In_2O_3 could maintain its ordered mesostructure. We subsequently investigate the gas-sensing properties of all the In_2O_3 specimens with or without rGO for different gases. The results exhibit the ordered mesoporous In_2O_3-rGO nanocomposite possesses significantly enhanced response to ethanol even at low concentration levels, superior over pure mesoporous In_2O_3 nanoparticles. Similar strategy could be extended to other ordered mesoporous metal oxide–rGO nanocomposite for improving the gas-sensing property.

Keywords Mesoporous material · Indium oxide · Graphene · Nanocomposite · Nanocasting · Gas sensor

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1 Introduction

There is an increasing concern on semiconducting metal oxide gas sensors in past decades regarding the awareness of environmental protection and human health. Various nanostructured metal oxides with high surface area have widely investigated as sensing materials [1–5]. Among them, ordered mesoporous metal oxides have attracted considerable attention since their accessible pores benefit not only the diffusion of gas molecules for increasing response rate, but also the reduction in aggregation and sintering for enhancing their thermal stability under high temperature during the fabrication and work process of gas sensor [6–13]. For example, Tiemann and co-workers [13] reported the improved sensitivity of mesoporous In_2O_3 to CH_4. Mao et al. [14] also reported the enhanced sensitivity of hierarchically mesoporous hematite microsphere toward formaldehyde (HCHO). Lai et al. [15] presented a low-cost synthesis of mesoporous In_2O_3 with tunable pore wall thickness by directly using solvent-extracted mesoporous silica with different pore sizes as a template. The gas testing results showed that the sensitivity of mesoporous In_2O_3 to HCHO sharply increases with reducing the pore wall thickness. The gas-sensing properties of those mesoporous metal oxide sensors could be further improved by doping noble metals. Tu et al. [16] reported that Pt-doped mesoporous In_2O_3 possess a significantly higher response than those without doping Pt. Lai et al. [17] reported the enhanced gas-sensing properties of Ag-doped mesoporous In_2O_3 toward HCHO. Nevertheless, the rising cost resulted from noble metals may limit their practical application.

Graphene is a kind of interesting material with some extraordinary properties including ultra-large specific surface area, unusual mechanical strength and high electrical conductivity, which has attracted enormous attention

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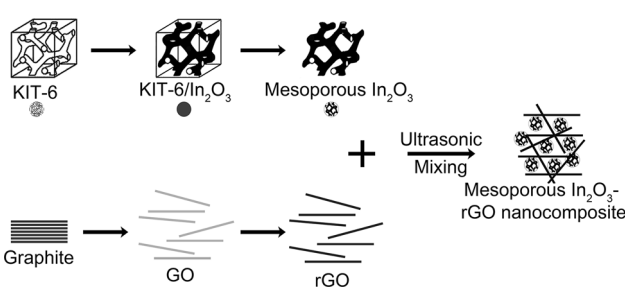
[18, 19]. Recently, several groups have reported that the gas-sensing properties of metal oxide sensors could be significantly improved after coupled with graphene. For example, Deng et al. [20] have synthesized an reduced graphene oxide (rGO)-conjugated Cu_2O nanowire mesocrystal via a one-pot hydrothermal treatment of copper (II) acetate in the presence of *o*-anisidine and graphene oxide (GO), which exhibit a higher response to NO_2 than individual Cu_2O nanowire or rGO. Choi et al. [21] have also reported the enhanced response of SnO_2 nanofibers functionalized with rGO to acetone and hydrogen sulfide. To the best of our knowledge, however, there is no report on ordered mesoporous metal oxide–rGO nanocomposite for gas sensors.

In this work, we have successfully synthesized ordered mesoporous In_2O_3 nanoparticles via the nanocasting route directly using mesoporous silica as a hard template and then mixed them with rGO to form an ordered mesoporous In_2O_3-rGO nanocomposite under the assistant of ultrasonication (Scheme 1). The gas-sensing testing results exhibit that ordered mesoporous In_2O_3-rGO nanocomposite possesses significantly enhanced response and relatively high selective toward ethanol, which suggests the potential application of the ordered mesoporous In_2O_3-rGO nanocomposite for detecting ethanol.

2 Experimental

2.1 Synthesis of ordered mesoporous In_2O_3 nanoparticles

Ordered mesoporous silica KIT-6 was synthesized at hydrothermal temperature of 130 °C according to the established procedures [22]; 0.6 g of KIT-6 was dispersed in 10 mL of ethanol, followed by addition of 1.2 g of hydrated indium nitrate under stirring in a Teflon beaker. After all the solvent had evaporated, the resulting powder was heated in a ceramic crucible in an oven at 250 °C for 3 h, in order to decompose indium nitrate. Finally, the silica template was removed at room temperature using 2 mol L^{-1} NaOH aqueous solution. The solid product was recovered by centrifugation, followed by washing with water several times and then drying at 70 °C overnight. Other mesoporous metal oxides could be also synthesized by similar procedure.



Scheme 1 Schematic illustration of the fabrication process of ordered mesoporous In_2O_3-rGO nanocomposite

2.2 Synthesis of GO and its reduction

First, GO was synthesized by the modified Hummers' method [23, 24]. A 2 g of natural graphite powder and 1.5 g of $NaNO_3$ were placed in a flask. Then 46 mL of concentrated H_2SO_4 was added slowly with stirred in an ice-water bath. A 7 g of $KMnO_4$ powder was added gradually under stirring, and the mixture was stirred for 2 h and then heated at 35 °C for 2 h, followed by adding gradually 100 mL of deionized water. The mixture was heated at 90 °C for 30 min and then added gradually 200 mL of deionized water. After the temperature reduced to 60 °C, 30 mL of H_2O_2 (5 wt%) was added. The mixture was centrifuged and washed with 100 mL of HCl solution (5 wt%) and 900 mL of deionized water. A 1 g of graphite oxide was dispersed in 1,000 mL of deionized water under ultrasonication for 30 min. The mixture was centrifuged at a speed of 1,000 r min^{-1} for 10 min, followed by discarding the solid and repeating ultrasonic step for three times. GO was collected from the mixture by centrifugation at a speed of 15,000 r min^{-1} for 30 min and dried at room temperature for 72 h; 0.2 g of GO was dispersed in 200 mL of deionized water, followed by adding 0.25 g of hydrazine solution (80 wt%). The pH of suspension was adjusted to 10 by adding 2.4 mL of concentrated ammonia solution. The mixture was heated under stirring at 90 °C for 3 h and cooled to room temperature. rGO was collected from the mixture by centrifugation at a speed of 15,000 r min^{-1} for 30 min and dried at room temperature for 72 h.

2.3 Synthesis of ordered mesoporous In_2O_3 nanoparticle-rGO nanocomposite

A 0.2 g of ordered mesoporous In_2O_3 nanoparticle was dispersed in 5 mL of deionized water, followed by adding 0.05 wt% of rGO water suspension relative to the amount of ordered mesoporous In_2O_3 nanoparticles dispersed in the solution. The mixed solution was ultrasonicated for 15 min, and the solid composite was collected by filter and dried at 70 °C overnight.

2.4 Characterization

The powder X-ray diffraction (XRD) patterns were recorded with a Bruker AXS D8 advanced diffractometer (Bruker,