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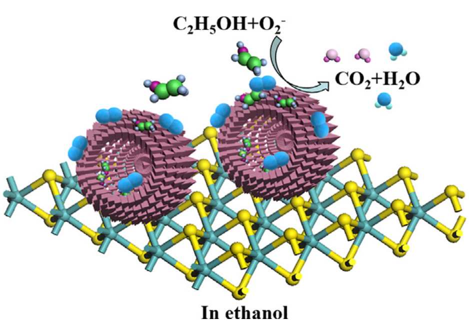
# Hierarchical assembly of urchin-like alpha-iron oxide hollow microspheres and molybdenum disulphide nanosheets for ethanol gas sensing

Dongzhi Zhang [a,*], Xin Fan [a], Aijun Yang [b,*], Xiaoqi Zong [a]

[a] College of Information and Control Engineering, China University of Petroleum (East China), Qingdao 266580, China
[b] State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, China

## GRAPHICAL ABSTRACT

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## ABSTRACT

In this paper, we fabricated a high-performance ethanol sensor using layer-by-layer self-assembled urchin-like alpha-iron oxide (α-$Fe_2O_3$) hollow microspheres/molybdenum disulphide ($MoS_2$) nanosheets heterostructure as sensitive materials. The nanostructural, morphological, and compositional properties of the as-prepared α-$Fe_2O_3$/$MoS_2$ heterostructure were characterized by X-ray diffraction (XRD), energy dispersive spectrometer (EDS), scanning electron microscopy (SEM), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS), which confirmed its successful preparation and rationality. The α-$Fe_2O_3$/$MoS_2$ nanocomposite sensor shows good selectivity, excellent reproducibility, fast response/recovery time and low detection limit towards ethanol gas at room temperature, which is superior to the single component of α-$Fe_2O_3$ hollow microspheres and $MoS_2$ nanosheets. Furthermore, the response of the α-$Fe_2O_3$/$MoS_2$ nanocomposite sensor as a function of ethanol gas concentration was also demonstrated. The enhanced ethanol sensing properties of the α-$Fe_2O_3$/$MoS_2$ nanocomposite sensor were ascribed to the synergistic effect and heterojunction between the urchin-Like α-$Fe_2O_3$ hollow microspheres and $MoS_2$ nanosheets. This work verifies that the hierarchical α-$Fe_2O_3$/$MoS_2$ nanoheterostructure is a potential candidate for fabricating room-temperature ethanol gas sensor.



## 1. Introduction

Ethanol is one of the most commonly and widely encountered alcohols. Besides, ethanol has many applications in many fields

* Corresponding authors.
*E-mail addresses:* dzzhang@upc.edu.cn (D. Zhang), yangaijun@mail.xjtu.edu.cn (A. Yang).

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in the world, such as food, biomedical, chemical industries and transport driving [1,2]. Exposure to ethanol vapor for a long time results in health problems such as drowsiness, headache, liver damage and difficulty in breathing. In addition, due to the extensive use of ethanol as a beverage, ethanol drinking is one of the main causes of car accidents in the world [3]. For example, alcohol-impaired driving fatalities accounted for 31% of the total motor vehicle traffic fatalities in the United States. And for drivers, the maximum allowable limit in Italy is 130 ppm in breath (0.05% in blood) and it is 208 ppm in breath (0.08% in blood) in USA [4]. Therefore, it is important to detect ethanol vapor at ppm level.

In recent years, metal oxide semiconductors such as $SnO_2$, $TiO_2$, $Co_3O_4$ and $Fe_2O_3$, have attracted considerable attention due to their potential application in various fields [5–9]. As an n-type semiconductor, $\alpha$-$Fe_2O_3$ is a good candidate for constructing gas sensors due to its unique advantages, such as nano-size, good electrochemical properties, and simplicity of integration [10]. Chu et al. reported the synthesis of $\alpha$-$Fe_2O_3$ hollow balls by a facile hydrothermal method for gas-sensing application, and found that the $\alpha$-$Fe_2O_3$ hollow balls were sufficient towards ethanol sensing [11,12]. Wang et al. prepared porous $\alpha$-$Fe_2O_3$ hollow microspheres with much higher response than that of $\alpha$-$Fe_2O_3$ nanoparticles to ethanol vapor [13]. Tan et al. reported the synthesis of hollowed-out hierarchical $\alpha$-$Fe_2O_3$ nanorods via the interfacial-reaction of $FeC_2O_4{\cdot}2H_2O$ with NaOH, and the gas sensing measurement revealed that the hollowed-out hierarchical $\alpha$-$Fe_2O_3$ nanorods exhibit high response and ultra-fast response/recovery characteristics to acetone and ethanol [14]. The above investigation indicated that the $\alpha$-$Fe_2O_3$ with hollowed-out nanostructure exhibits excellent gas sensing performance due to its large surface area to volume ratio to facilitate the diffusion of gases.

Novel properties of graphene have been well documented, whereas the importance of graphene-like two-dimensional (2D) molybdenum disulphide ($MoS_2$) nanosheets is attracted considerable interest over recent years [15]. $MoS_2$ has strong potential as a building block for constructing gas sensors due to its tunable bandgap and unique electrical properties [16]. Nagarajan et al. investigated the electronic and adsorption behavior of alcohol vapor molecules on $MoS_2$ nanosheets by density functional theory (DFT) method, and the adsorption of alcohol molecules on $MoS_2$ nanosheets are verified with the variation on energy band gap, adsorption energy and Mulliken charge transfer [17]. Although the exact sensing mechanism of $MoS_2$ is still unclear, the excellent gas sensing properties of $MoS_2$ are worthy of further investigation. The first-principles calculation shows that the charge transfer between the gas molecules and $MoS_2$ nanosheets is responsible for the observed changes in its resistance [18]. As a kind of n-type semiconductor, intrinsic $MoS_2$ has a natural direct band gap (1.2–1.9 eV), and large surface-to-volume ratio, outstanding field-effect transistor (FET) behavior. Layered $MoS_2$ is one of the typical graphene analogues. Compared to graphene which is a semimetal with a zero band gap, the tunable bandgap of $MoS_2$ endows it a better candidate nanomaterial for highly sensitive gas sensors [19].

As an alternative cost-effective approach, layer-by-layer (LbL) self-assembly technique is based on sequential electrostatically adsorptions of ionized polyelectrolytes and oppositely charged materials in aqueous solutions. It is a solution-based bottom-up approach to fabricate hierarchical nanocomposite thin film as promising sensitive materials [20–22]. The LbL self-assembly approach has many advantages over other alternative methods, such as simplicity, substrate-independence, low-cost, low temperature deposition, controllable thickness from nanometers to micrometers, and no complex or costly equipment required [23]. Zhang et al. presented a high-performance ammonia sensor based on layer-by-layer self-assembled $Co_3O_4/MoS_2$ film, which high sensitivity, good repeatability, stability, and selectivity and fast response/recovery properties toward ammonia sensing [19]. Su et al. fabricated a novel flexible $NO_2$ gas sensor by the layer-by-layer covalent anchoring of graphene oxide film, which exhibited a strong sensitivity and acceptable linearity between 1 and 20 ppm, high reproducibility and long term stability [24].

In this work, we demonstrated a high-performance ethanol sensor based on urchin-Like $\alpha$-$Fe_2O_3$ hollow microspheres/$MoS_2$ nanosheets nanocomposite prepared by LbL self-assembly method. The sensor was fabricated on the substrate of printed circuit board (PCB) with interdigital electrodes (IDE). The self-assembled hierarchical $\alpha$-$Fe_2O_3/MoS_2$ heterostructure was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy dispersive spectrometry (EDS). The $\alpha$-$Fe_2O_3/MoS_2$ nanocomposite sensor shows good selectivity, excellent repeatability, fast response/recovery time and low detection limit towards ethanol gas at room temperature, which is superior to the single component of $\alpha$-$Fe_2O_3$ hollow microspheres and $MoS_2$ nanosheets. The enhanced ethanol sensing properties of the $\alpha$-$Fe_2O_3/MoS_2$ nanocomposite sensor were ascribed to the unique nanostructure, synergistic effect and heterojunction.

## 2. Experiment

### *2.1. Sensor fabrication*

$Na_2MoO_4{\cdot}2H_2O$, thioacetamide, oxalic acid, and $Fe(NO_3)_3{\cdot}9H_2O$ used in this work were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Polyelectrolytes including 1.5 wt% poly(diallyldimethylammonium chloride) (PDDA) and 0.3 wt % poly(sodium 4-styrenesulfonate) (PSS) were obtained from Sigma-Aldrich Inc. 0.5 M NaCl was added in both PDDA and PSS solutions for ionic strength All the reagents were used without any further purification.

The urchin-like $\alpha$-$Fe_2O_3$ hollow microspheres and $MoS_2$ nanosheets were prepared by a facile hydrothermal route. In the synthesis process of $\alpha$-$Fe_2O_3$, 2 mmol $Fe(NO_3)_3{\cdot}9H_2O$, 2 mmol thioacetamide and 4 mmol oxalic acid were dissolved into 40 mL deionized (DI) water with stirring for 30 min. And then, the as-prepared solution was transferred into a 50 mL stainless-steel autoclave and heated at 140 °C for 12 h. Afterward, when the autoclave cooled down to room temperature, the final product of FeOOH suspension was washed with DI water and anhydrous ethanol for several times to remove excess ions. At last, the $\alpha$-$Fe_2O_3$ sample was further anneal-treated at 300 °C in air [13,25]. In the synthesis process of $MoS_2$, $Na_2MoO_4{\cdot}2H_2O$ (1.0 g) and thioacetamide (1.2 g) were dissolved into 80 mL of DI water and subsequently stirred for 0.5 h. Then, 0.6 g of oxalic acid was added with stirring for another 0.5 h. The resulting suspension was hydrothermally treated at 200 °C for 24 h. At last, the $MoS_2$ sample was further anneal-treated at 700 °C in argon for 2 h [26].

The $\alpha$-$Fe_2O_3/MoS_2$ nanocomposite was deposited as sensing material on the substrate of printed circuit board (PCB) with interdigital electrodes (IDE) via LbL self-assembly technique. The IDEs pattern has a profile size of 1 × 1 cm, the electrode thickness is 50 μm, the electrode width and gap both is 200 μm. The LbL fabrication process of $\alpha$-$Fe_2O_3/MoS_2$ nanocomposite sensor was shown in Fig. 1. Two layers of PDDA/PSS were self-assembled as precursor layers for substrate charge enhancement, and then five layers of $\alpha$-$Fe_2O_3/MoS_2$ were deposited via sequential immersion of $\alpha$-$Fe_2O_3$ and $MoS_2$ solutions. The immersing time was 10 min for PDDA and PSS, and 15 min for $\alpha$-$Fe_2O_3$ and $MoS_2$. Intermediate rinsing with DI water and drying with nitrogen stream were required after each monolayer assembly to reinforce the interconnection between layers. Afterward, the $\alpha$-$Fe_2O_3/MoS_2$ nanocomposite sen-