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Chemically functionalized 3D reticular graphene oxide frameworks decorated with MOF-derived Co_3O_4: Towards highly sensitive and selective detection to acetone

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ABSTRACT

Here, we have newly developed chemically functionalized three-dimension (3D) graphene oxide hydrogels (FGH) decorated with metal-organic frameworks (MOFs)-derived Co_3O_4 nanostructures, in which the Co_3O_4 nanostructures are uniformly distributed in 3D FGH frameworks. It is found that the Co_3O_4/FGH composites exhibits excellent acetone sensing properties, for instance, it shows an ultra-high response ($R_{gas}/R_0 = 81.2$) to 50 ppm acetone, which was ~20 times higher than that of pristine Co_3O_4 film, a short response time (~20 s), and a distinct cross-selectivity against other interfering gases. Notably, upon exposure to 1 ppm acetone in air, the composites still can express an apparent response ($R_{gas}/R_0 = 4.06$). The excellent acetone sensing properties of Co_3O_4/FGH can be mainly attributed to the unique porous structures of 3D FGH frameworks and the modulation of electrical transport properties of the Co_3O_4/FGH junctions in the composites. The Co_3O_4 nanostructures uniformly distributed in 3D FGH frameworks can easily adsorb a great amount of acetone gas molecules through the unique porous frameworks and produce a great deal of electrons, which can be transferred to the p-type FGH frameworks through Co_3O_4/FGH junctions so that the resistance of Co_3O_4/FGH composites is greatly increased. Therefore, the acetone response of the composites is dramatically enhanced because of the Co_3O_4/FGH junctions. This study presents a new idea of building MOF-derived oxides/FGH junctions to enhance gas response of oxide-based gas sensors, and has great potential in fabrication of new generation gas sensors.

1. Introduction

Recently, metal-organic frameworks (MOFs) are applied to be ideal versatile precursors or sacrificial templates for fabricating numerous nanostructured materials [1,2]. For example, Zeolitic Imidazolate Framework 67 (ZIF-67)-derived Co_3O_4, one of the most important p-type semiconductor with a normal spinel structure [3,4], has been widely applied as energy storage [5], heterogeneous catalysts [6], Lithium-ion battery [7,8] and gas sensors [9]. Specially in gas detection area, fabricating different nanostructures of Co_3O_4 such as nanospheres [4], nanorods [10], nanocages [11] and nanosheets [12], is an important strategy to enhance the gas sensing properties. Compared with the traditional fabrication methods which are decomposition of the cobalt salts precursors [13], MOF-derived Co_3O_4 nanostructures have the advantages of large surface area, facile forming process and low energy consumption. Noticeably, the large surface area can increase more interaction sites between gas and sensing materials. For instance, Qin et al. synthesized Co_3O_4 hollow concave nanocubes with extremely high specific surface ($120.9\ m^2\ g^{-1}$) using MOFs as template, and the Co_3O_4 hollow nanacubes presented high response to ethanol with a fast response speed (~10 s) and a low detection limit (at least 10 ppm) [9]. Thus, MOF-derived nanomaterials as an essential kind of hybrid crystals have attracted intensive interests in the preparation of multifunctional materials for its simple and low-energy consumption synthetic process [14,15]. However, as gas sensing materials, semiconductor metal oxides (SMOs) often display weak electronic transmission capacity and cross response to interfering analytes, leading to requiring more complicated operating conditions (e.g. high operating temperature and non-interfering environment). Therefore, it is essential to select efficient electronic

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transfer materials modified with metal oxides for selective real-time detection of certain analytic gases.

Since Novoselov et al. reported that graphene was able to detect individual gas molecules [16], graphene and its functionalized derivatives have attracted considerable interests in gas sensor area. In particular, 3D porous graphene-based frameworks are abundant in porous channel, can significantly provide a great amount of gas free access and facilitate the gas sensing performance. Nevertheless, 3D foam-like graphene with the fast transport channel of charge carriers is usually prepared by template-directed chemical vapour deposition (CVD) method [17], which requires more complicated synthesis conditions (e.g. high vacuum and high temperature [18]). Instead of using templates or CVD method, a facile hydrothermal self-assembly process has been utilized to synthesize chemical functionalized 3D porous graphene oxide hydrogels (FGH) [19,20]. In this method, hydroquinones are acted as reducing regent and functionalizing molecules as well. The 3D FGH gels possess large surface area and numerous reaction sites, which is easy to be modified with functional groups on its surface. Thus, chemically functionalized 3D FGH-based composites may have the advantages for real-time detection of certain analytic gases.

Acetone (CH_3COCH_3), a critical member of volatile organic compounds (VOCs) family, is not only the most commonly used chemical reagents in industry and laboratory but also generally known as a breath biomarker of diabetes patients. The acetone concentration is more than 18 ppm in diabetic patients compared with its concentration from 3 to 9 ppm in healthy human body [21]. Therefore, the detection of acetone is increasingly essential for environmental monitoring and individual safety protection [22–25]. In view of the unique 3D structure and superior electron transmission ability of FGH, we have newly developed a facile and scalable method to synthesize Co_3O_4/FGH composites through pyrolysis of ZIF-67/FGH composites for highly sensitive and selective detection of acetone. In detail, ZIF-67/FGH composites were annealed in air atmosphere with a fast ramping rate of 5 °C/min to obtain approximately granular Co_3O_4/FGH composites. Furthermore, the functionalization of MOF-derived Co_3O_4 onto 3D FGH is a facile and versatile way for fabricating novel electronic transmission frameworks with uniformly distributed SMOs, which is required for high performance gas sensors [26]. On top of that, the acetone sensing properties and sensitization effect of the Co_3O_4 with FGH was further investigated.

2. Experimental

2.1. Materials

Hydroquinone ($C_6H_6O_2$, ≥99.5%), cobalt nitrate hexahydrate [($Co(NO_3)_2{\cdot}6H_2O$), AR, 99%] were purchased from Aladdin chemicals Co. Ltd. (China). 2-methylimidazole (Hmin, 99.0%) was purchased from Sigma-Aldrich. Graphite (300 Mesh) was purchased from Nanjing XFNANO Materials Tech Co. Ltd. Other regents were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). All chemicals were used as received without further purification.

2.2. Synthesis of functionalized three-dimensional (3D) graphene oxide hydrogels (FGH)

GO was prepared by oxidation and exfoliation of natural graphite powder with modified Hummer's method [27,28]. For synthesis of FGH, a facile hydrothermal reaction method was applied [19,20]. 50 mg hydroquinone ($C_6H_6O_2$) was dispersed into 5 mL 2 mg/ml GO aqueous solution with a continuous magnetic stirring. The transparent gelatinous mixture was transferred into a Teflon-lined autoclave and kept at 100 °C for 12 h. Then, the autoclave was naturally cooled down to room temperature. The as-prepared solid FGH was taken out by a tweezer. The solid FGH was mechanically crushed to pieces, then centrifuged and washed with deionized water and ethanol for several times. Finally, the 3D FGH powders were obtained by freeze drying.

2.3. Synthesis of ZIF-67, granular Co_3O_4 crystals

ZIF-67 was synthesized by mixing cobalt precursors and Hmin in deionized water with a continuous stirring at room temperature [9,29]. 0.45 g $Co(NO_3)_2{\cdot}6H_2O$ and 5.5 g Hmin were dissolved in deionized water, separately. Then, $Co(NO_3)_2{\cdot}6H_2O$ aqueous solution was rapidly added into a solution of Hmin under continuous stirring for 6 h at room temperature. The bright purple dispersion mixture were dried at 60 °C for 24 h in air, and purified by centrifugation and washed with deionized water and methanol. The granular Co_3O_4 crystals were prepared by annealing ZIF-67 at 300 °C in air for 3 h with a heating rate of 5 °C/min. After the calcination treatment, purple MOFs precursor was finally transformed into black powders.

2.4. Synthesis of ZIF-67/FGH, Co_3O_4/FGH composites

For synthesis of ZIF-67/FGH composites, we adopted the following operation steps. The as-prepared FGH was dispersed in deionized water, then mixed the FGH dispersion with $Co(NO_3)_2{\cdot}6H_2O$ aqueous solution under magnetic stirring for 2 h 5.5 g Hmin was added into the mixture in sequence under stirring for 6 h at room temperature. The as-prepared samples were dried at 60 °C for 24 h in air, and purified by centrifugation and washed with deionized water and methanol. The granular Co_3O_4/FGH composites were obtained by pyrolysis of ZIF-67/FGH composites with the same annealing process as Co_3O_4.

2.5. Materials characterizations

The microstructures and morphologies of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, FEI) and high-resolution transmission electron microscopy (HRTEM, JEM-2100 UHR, FEI). The X-ray diffraction (XRD) analysis with a Philips X'Pert diffractometer in reflection mode using Cu-Kα1 radiation (λ = 1.5406 Å) from 2θ = 10 to 90° were carried out to analyze the crystal structures. The chemical compositions and states were investigated by using X-ray photoelectron spectroscopy (XPS, ULVAC-PHI5000). Thermal stability was measured by thermal gravimetric analysis (TG-DTA, NETZSCH STA 449C). Ultraviolet photoelectron spectroscopy (UPS) was carried out to investigate the work function of the samples.

2.6. Evaluation of sensing performance

The gas sensing characteristics were measured by home-made testing equipment described elsewhere [30], which included gas flow-controlled system, resistive-type heater system and electrical signal testing system. The response of sensors was investigated by resistance changes (R_{gas}/R_0) of sensing layer (Co_3O_4 and Co_3O_4/FGH) that printed on alumina substrate with Pt-interdigitated electrodes printed by photolithography and thermal evaporation. Before carrying out the tests, the synthetic air was firstly introduced into the testing chamber to exclude the residual gases. Then the sensor resistances were stabilized for several minutes, the different concentrations of acetone gas (diluting standard acetone gas with dry compressed N_2) were injected by using computer-driven digital mass flow controllers at a total constant