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Effective organic amine detection by nanoparticle-assembled tin dioxide microspheres: The importance of interparticle porosity on sensing properties

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ABSTRACT

Organic amines are a kind of industrially important starting material for the manufacture of dyes and pharmaceuticals. But monitoring low-concentration amine vapors, especially those with a high molecular weight, is still a challenging task during industrial processes because the low permeability and diffusivity of amines largely limit their interaction with the surface of sensing element. Herein, we report the template-free solvothermal synthesis of uniform nanoparticle-assembled SnO_2 microspheres with an rich interparticle porosity, and the thermal-driven tuning of their porosity structure with the sphere-like morphological preservation. This further allows us to fabricate a sensing film with a tunable interparticle porosity structure and an optimized gas diffusivity in the sensing film. As a result, the optimized SnO_2 sensing film is shown to have the ability to effectively detect low-concentration amine vapors with short response time and high response value in the testing range from 1 to 200 ppm.

1. Introduction

Organic amines, classified as a family of organic compounds containing at least one basic nitrogen atom with unbonded lone pair electrons, are very important intermediates in organic synthesis because of their high reactivity. These compounds are essential in chemical and pharmaceutical engineering to make functional polymers, fertilizers, colorful dyes and drugs [1]. However, most of the organic amines are hazardous to human and can result in severe health problems such as headaches, skin burns, eye irritation, respiratory disease [2]. Furthermore, some amines, like triethylamine, are inflammable and explosive gases. Hence, the concentration of them in the working environment should be controlled properly with the help of some reliable sensors to ensure a safe working environment. In addition, the toxic biogenic amines, such as histamine and tyramine, are generated via the decarboxylation of amino acids during the decay of food due to the relatively higher temperature or enzyme conversion [3–6], especially the protein-rich seafood. Having such unfresh food could cause severe food poisoning. Therefore, researchers have established plenty of methodologies to detect organic amines and the methods are summarized here: the first one is to use chromatography instruments such as high-performance liquid chromatography, gas chromatography [7], to separate and detect organic amines. Another technique is to utilize UV–vis or fluorescence spectroscopy for determination of organic amine by making specific reagents that exhibit some different spectrums, namely peak wavelength and/or intensity, when exposing to amines. These kind of reagents include but not limited to aromatic small molecules [4,8,9], conjugated polymers [10–12], porous metal organic framework [13], ZnO fluorescent film [14], etc. The third approach involves oxide semiconductors to serve as chemiresistors, which show different conductivities upon interacting with the analyte gas. These electrical sensing semiconductor materials include single metal oxide WO_3 [15], MoO_3 microrods [16,17], or mixed metal oxide materials: chromium doped WO_3 [18], SnO_2–ZnO nanocomposite [19], ZnO–Cr_2O_3 heterostructure [20], Cr_2O_3 decorated SnO_2 nanowires [21], thorium incorporated

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SnO_2 [22], ZnO–NiO hetero-nanostructure [2,23]. Except the inorganic semiconductors, organic nanofiber has also been employed as electrical organic amine sensor [24]. Among the aforementioned techniques and materials required for amine detection, oxide semiconductor based chemiresistors have attracted extensive attention due to their tremendous advantages: no expensive and complicated instruments are required; the semiconductors are stable and can be made into a portable device with very low power consumption and small size; the most important point is that they show excellent gas sensing properties.

As we mentioned above, the chemiresistors can give different signals when the amines interact with their surface, so the synthesis of high surface area materials with appropriate pore size is necessary and plays important roles not only in gas sensing fields, but also other applications. This stimulates the exploration of various synthetic approaches to prepare different kinds of such nanomaterials. Herein, we focus on tin dioxide, an important n-type wide-band gap (3.6 eV at 300 K) semiconductor, to constitute porous amine sensing material. SnO_2 has been prepared by many methods which can be summarized as three general ways: the first one is hard template synthesis, during which hexagonal mesoporous silica SBA-15 [25–27], cubic KIT-6 [26], or polymer templates [29,30] were used as sacrificial material to generate porous SnO_2; the second method is soft template synthesis, in which polyvinyl pyrrolidone [31], oleic acid [32], sodium dodecylsulfate and hexadecyl-2-pyridinylmethylamine [33], cetyl trimethylammonium bromide [34], or sodium alginate [35] were employed as pore filling agents to form porous SnO_2 after removal of these templates; the last approach is the template free synthesis of SnO_2 which does not need surfactant or hard template to create the pores [36–40].

In this work, we have successfully synthesized uniform nanoparticle-assembled SnO_2 microspheres with a highly porous structure via a template-free route different from aforementioned methods, and the formation mechanism of such porous materials is discussed. The surface area, pore size, nanoparticle size can be tuned via the thermal treatment of the resulting SnO_2 microspheres. After annealing treatment, the materials show excellent sensing performance toward organic amine and the relationship between the sensing properties and interparticle pore structures are discussed as well.

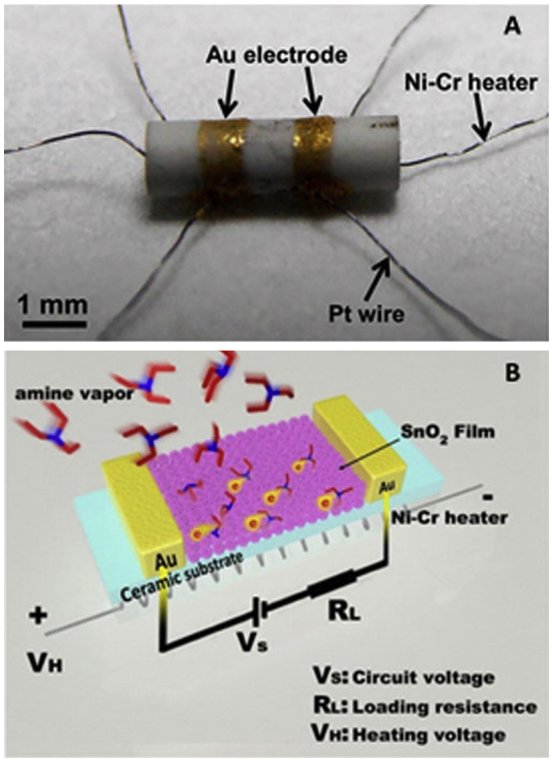
2. Experimental

2.1. Chemicals and reagents

Stannic chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) was purchased from Tianjin Fuchen Chemical Reagent Factory. Glycerol was purchased from Sinopharm Chemical Reagent Co. Ltd. Ethanol and isopropanol were purchased from Beijing Chemical Factory. Triethylamine with a purity of >99% and a water amount of ~0.2% was purchased from Sinopharm Chemical Reagent Co., Ltd. All the above chemicals were used without further purification. Deionized water was used through the experiments.

2.2. Synthesis of porous SnO_2 microspheres

In a typical synthesis, $SnCl_4{\cdot}5H_2O$ (0.35 g, 1 mmol) was dispersed in a mixed solution containing glycerol (8 mL) and isopropanol (30 mL). The resulting mixture was transferred into a 60 mL Teflon-Lined autoclave, followed by thermal treatment at 180 °C for 12 h. After cooling to room temperature, the resulting precipitate was centrifuged and washed thoroughly with ethanol several times, then dried in an oven overnight at 80 °C in air to afford porous SnO_2 microspheres. In order to study the effects of porosity structure on SnO_2 materials' sensing performance, five more samples were prepared by heating the as-synthesized SnO_2 microspheres in air at 450, 550, 650, 750, or 850 °C for 2 h with a ramping rate of 2 °C/min.



Scheme 1. (A) Digital image of the sensor composed of different parts: ceramic tube, two Au electrode, four Pt wires and a Ni-Cr wire. (B) Schematic illustration of the electric circuit for the sensing of amine vapor.

2.3. Material characterizations

The powder X-ray diffraction (XRD) patterns were performed with a Rigaku D/Max 2550 X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) operated at 200 mA and 50 kV. The scanning electron microscopic (SEM) images were carried out on a JEOL JSM 6700F electron microscope. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a Philips-FEI Tecnai G2S-Twin. The infrared (IR) spectra were recorded on a Bruker IFS 66V/S FTIR spectrometer using KBr pellets. The thermal gravimetric analysis curve was recorded on a NETZSCH STA 449C TG thermal analyzer from 25 to 800 °C at a heating rate of 10 °C min^{-1} in air. BET surface area and BJH pore diameter were measured by using a Micromeritics ASAP 2020M system.

2.4. Sensor fabrication and testing

In order to assemble the gas sensor, viscous slurry of the obtained sample was put into a ceramic tube with a diameter of 1 mm and a length of 4 mm. As shown in Scheme 1, the ceramic tube was constructed with a pair of gold electrodes and four platinum wires on two sides of the tube. The operation temperature of the sensor was controlled by the nickel-chromium heating wire located in the center of the tube. To ensure proper comparison between different materials, the same method was used to prepare the sensors, with the only difference being the SnO_2 materials in the tube. A commercial CGS-8 Gas Sensing Measurement System (Beijing Elite Tech Company Limited) was employed to conduct all the gas sensing evaluation.