



# Ammonia sensor based on polypyrrole–graphene nanocomposite decorated with titania nanoparticles

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## Abstract

A composite of polypyrrole (PPy) and graphene nanoplatelets (GNs) decorated with titanium dioxide (TiO<sub>2</sub>) nanoparticles (TiO<sub>2</sub>@PPy–GN) was synthesized by a sol–gel process combined with in situ chemical polymerization. The microstructure, morphology, and crystallinity of the TiO<sub>2</sub>@PPy–GN nanocomposite were characterized by Fourier-transform infrared spectrometry, scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. The results indicate that the TiO<sub>2</sub> nanoparticles with a diameter of 10–30 nm were well dispersed on the PPy–GN composite. The TiO<sub>2</sub>@PPy–GN nanocomposite exhibited good electrical-resistance response to NH<sub>3</sub> at room temperature. Compared to the PPy–GN thin film, the TiO<sub>2</sub>@PPy–GN thin film showed enhanced NH<sub>3</sub>-sensing properties in the form of higher sensitivity and much faster response under the same conditions. The selectivity and stability of the NH<sub>3</sub> sensor based on the TiO<sub>2</sub>@PPy–GN nanocomposite were also investigated.

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## 1. Introduction

Nanostructured materials have been widely explored for the fabrication of gas sensors because of their high surface area, flexibility, and excellent electrical properties [1–3]. Among these materials, conducting polymers have attracted particular interest. Conducting polymers such as polypyrrole (PPy) and polyaniline can be simply prepared in solution and have unique electrical conductivity, redox property, and good stability at room temperature [4–6]. The morphology and surface area of these polymers can also be tuned by changing the dopant species during synthesis [7]. These features are expected to be utilized in gas sensors to lower the detection limit, decrease the response time, and improve the sensitivity

[8–9]. Doping conducting polymers with graphene has been considered an effective way to improve their sensing performance because of the unique properties of graphene and the combined effect of the two materials [10–13].

Graphene, a two-dimensional carbon nanomaterial, has a large surface-to-volume ratio, high specific area, superior electronic conductivity, and excellent chemical stability, which make it desirable for use as a supporting framework for other nanoparticles to carry out sensing processes [14]. Furthermore, its two-dimensional honeycomb structure allows its carbon atoms to be directly exposed to the environment, thus maximizing the sensor's surface area per unit volume and increasing its sensitivity to gas molecules. Moreover, it has intrinsically low electrical noise owing to its crystal lattice, which tends to screen charge fluctuations more effectively than one-dimensional carbon nanomaterials such as carbon nanotubes [15,16]. Therefore, a number of graphene-based gas sensors have been fabricated and excellent sensing performance has been reported [17–19]. To further improve the sensitivity and selectivity of the gas sensors,

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many other materials, such as conducting polymers, metal oxides, and metal nanoparticles, have been added to modify the surface of the graphene sheets [11,17,20].

Titanium dioxide (TiO<sub>2</sub>) is another widely employed material for H<sub>2</sub>, NH<sub>3</sub>, CO, and NO<sub>2</sub> detection because of its inert surface and high sensing abilities. TiO<sub>2</sub> is an n-type semiconductor material with an energy band gap of about 3.33 eV, which cannot be found in other nanomaterials, thus rendering it suitable for providing useful sensing ranges [8]. However, most of the TiO<sub>2</sub>-based gas sensors only work at high temperature, which may restrict its application. Therefore, it is desirable to develop a gas sensor that operates at room temperature while retaining the sensing properties of TiO<sub>2</sub> nanoparticles at the same time [20].

Although the sensing performance of TiO<sub>2</sub> nanoparticles has been studied extensively, to the best of our knowledge, no attempt has been made to examine the performance of a conducting-polymer-graphene composite decorated with TiO<sub>2</sub> nanoparticles. In the present work, a composite of PPy and graphene nanoplatelets (GNs), PPy-GN, was decorated with well-dispersed TiO<sub>2</sub> nanoparticles by the sol-gel method. An ultra-sensitive and highly selective room-temperature NH<sub>3</sub> sensor with fast response was successfully fabricated by drop-coating the nanocomposite on integrated indium-tin oxide (ITO) electrodes. The reproducibility and stability of the sensor were also examined.

## 2. Experimental

### 2.1. Materials

Pyrrole, ammonium persulfate (APS), cetyltrimethylammonium bromide (CTAB), and tetrabutyl titanate (97%), ITO (surface resistivity: 70–100 Ω/sq) were purchased from Sigma-Aldrich, USA. High-purity graphene nanoplatelets (> 99.5%) with a thickness of 4–20 nm and a particle size of 0.5–10 μm, were supplied by Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). All chemicals and reagents were used as received, except for pyrrole, which was distilled before use.

### 2.2. Preparation of TiO<sub>2</sub>@PPy-GN

The PPy-GN composite was prepared according to established procedures [11]. In brief, 0.1 M of pyrrole, 0.1 M of CTAB, 0.1 M of citric acid, and deionized water were mixed with stirring for 3 h. Next, 0.5 M of APS was dissolved in 20 mL of deionized water and slowly added drop by drop from a burette to the prepared solution for 0.5 h. After stirring for 4 h, the solution was filtered and the residue was washed thoroughly with deionized water and methanol, and then dried in an oven at 60 °C. For comparison, PPy was also prepared under the same conditions.

Using the sol-gel method, the PPy-GN composite was then decorated with TiO<sub>2</sub> nanoparticles. Fig. 1 shows a schematic diagram of the preparation of TiO<sub>2</sub>@PPy-GN. First, 0.1 g of the PPy-GN powder was mixed with 2 mL of tetrabutyl titanate and stirred with a magnet for 4 h. Next, 20 mL of ethanol solution was added drop-wise into the mixture with

vigorous stirring. The mixed solution was then dried at 70 °C for 10 h, and the final product was ground into powder.

### 2.3. Sensor fabrication and sensing tests

The NH<sub>3</sub> sensor was fabricated on an ITO substrate. Prior to the fabrication, the ITO electrodes were sonicated in ethanol, washed with deionized water, and then dried in flowing nitrogen. Copper foil tape with conductive adhesive on one side was purchased from Shanghai Mingyu Metal Materials Company Inc., China. The foil was cut into 0.5 cm × 4 cm strips. The electrical contacts were made by attaching two strips of copper foils (with a 5-mm separation) onto the ITO surface. Next, 0.1 g of the TiO<sub>2</sub>@PPy-GN powder was suspended in 5 mL of a *N,N*-dimethylformamide (DMF) solution under sonication for 30 min, after which 0.1 mL of the suspension was drop-coated by a syringe onto the gap between the two copper foils and dried in air.

The sensor testing was carried out in a laboratory-built, airtight chamber by exposing the prepared sensor to various concentrations of NH<sub>3</sub> gas. To measure the gas response, the sensor was placed in the test chamber (volume: 0.5 L) with gas inlet and outlet ports. The gas chamber was purged with N<sub>2</sub> for 30 min before the test. Standard NH<sub>3</sub> (10,000 ppm) and pure N<sub>2</sub> gases were injected into the chamber, and the electrical resistance of the thin film was measured by a multimeter (Keithley 2700, USA) that was connected to a computer for data acquisition. The sensor fabrication and gas testing are illustrated in Fig. 2. The sensor response *S* to NH<sub>3</sub> gas is defined by the following equation:

$$S(\%) = \frac{\Delta R \times 100}{R_{\text{air}}} = \frac{(R_G - R_{\text{air}}) 100}{R_{\text{air}}}$$

where *R<sub>G</sub>* and *R<sub>air</sub>* are the electrical resistances of the sensitive film exposed to NH<sub>3</sub> and dry air, respectively. The response time is defined as the time required for the sensor to reach 90% of the change in total resistance, and the recovery time is the time required for the sensor to return to 10% of the value before exposure to a gas.

For the selectivity experiment, a known gas (CH<sub>3</sub>OH, CO, or H<sub>2</sub>S) with a particular concentration was injected through a syringe. All experiments were carried out at room temperature (25 ± 1 °C) and a relative humidity of 42 ± 3%.



Fig. 1. Schematic diagram for the preparation of the TiO<sub>2</sub>@PPy-GN nanocomposite.

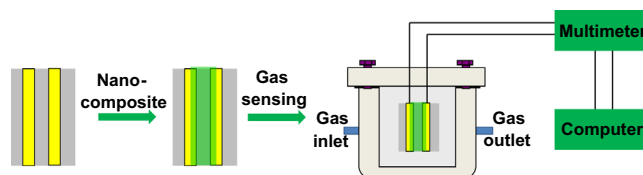


Fig. 2. Schematic diagram of the NH<sub>3</sub> sensor.

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