Facile synthesis of the composites of polyaniline and TiO2 nanoparticles using self-assembly method and their application in gas sensing

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Abstract: The composites of polyaniline (PANI) and TiO2 nanoparticles with different contents were prepared in the aqueous solution of phosphoric acid, in which the phosphoric acid was selected as protonic acid and improved the conductivity of PANI. In these composites, the granular TiO2 nanoparticles with size of about 60 nm were coated by a layer of PANI film with a thickness of about 5 nm on their outer surface. After TiO2 nanoparticles doped, the gas sensing properties of gas sensors constructed by a liquid-gas interfacial self-assembly method obviously improved, which their sensitivity increased several times to NH3 from 10 ppm to 50 ppm than pure PANI. Especially when the mass ratio of titanium dioxide to aniline monomer was 2:1, it exhibited the best sensitivity (about 11.2 to 50 ppm), repeatability and good selectivity to NH3 at room temperature. The formation of p–n junction in the composites of PANI and TiO2 nanoparticles was the important factors of excellent gas sensing properties. Meanwhile when the mass ratio of m(TiO2)/m(Ani) was 2:1, it had the best proportion and showed the best gas sensing properties. It will provide a method to improve the gas sensing properties of PANI and optimum proportion of TiO2 nanoparticles, which is favorable for industrial application.

Keywords: titanium dioxide; polyaniline; self-assembly; gas sensing; p–n junction

1. Introduction

With the improvement of science and technology and the development of society, our material life is more convenient and abundant. The accompanying industrial safety, environmental protection and public safety such as chemical plant explosion, toxic gas leakage and PM 2.5 has been paid more attention day by day [1]. Gas sensor, as a sensing component, can monitor the composition and content of various toxic and harmful gases qualitatively or quantitatively in real time [2–6]. In many kinds of gas sensors, for example catalytic combustion gas sensor, electrochemical gas sensor, thermal conductivity gas sensor, infrared gas sensor and solid electrolyte gas sensor and so on, semiconductor gas sensor senses gases information by the change of semiconductor characteristics (such as resistance) caused by the adsorption of target gases on the surface of sensitive film, which is usually made by inorganic semiconductor metallic oxide materials for instance ZnO, SnO2, In2O3, Co3O4, WO3 and TiO2 and so on [7]. Generally speaking, it has the advantages of small size, light weight, easy integration and intelligence and been widely used in industrial hazardous gas leakage, toxic and harmful gas detection, flammable and explosive gas early warning and other fields [8–9]. However, for its applications such as flammable and explosive gas detection, semiconductor gas sensor still has
some shortcomings such as long response time, low sensitivity and especially high working
temperature which will bring higher energy consumption, shorten the sensors work time and may
become a source of the explosion. Therefore, it is necessary to develop a gas sensor operating at the
lower temperature (even room temperature) and maintain excellent gas sensing performance such as
high sensitivity, stability and selectivity etc.

Compared with the above inorganic semiconductor metallic oxide gas sensing materials,
polyaniline (PANI), a p-type conductive polymer, has been widely used in metal anti-corrosion, drug
delivery, electromagnetic shielding, secondary batteries, supercapacitors and other fields for its own
unique advantages such as good environmental stability, cheap, low density, and easy to obtain and
excellent flexibility and so on [10]. Especially for the room temperature sensitivity and tunability of
conductivity under the action of electrochemical redox and protonic acid, PANI is an ideal room
temperature sensitive material and has been paying more and more attention in the field of gas
sensing in recent years [11-13]. However, pure PANI sensors have some problems such as low
sensitivity, low detection limit, slow response and long recovery time [14]. Titanium dioxide (TiO2),
a typical n-type semiconductor metallic oxide with the wide energy gap (3.2 eV), exhibits excellent
photocatalytic activity, stability, non-toxicity, low cost and unique physical and chemical properties
and has also application in the areas of photocatalysis, solar cells and gas sensors [15-16]. The doping
of TiO2 nanoparticles into PANI material will improve the sensing features of gas sensors. In order
to give full play to the advantages of organic and inorganic materials, the composites of conductive
polymer and inorganic semiconductor metallic oxide have become one of the research hotspots in
materials science, which not only improve the sensitivity properties of gas sensors, but also can work
at room temperature. The presence of p-n junction owing to the composition of PANI (p-type) and
TiO2 nanoparticles (n-type) could be the important factor with excellent gas sensitivity [17-20]. So the
presence of TiO2 nanoparticles into PANI will obtain excellent performances of gas sensors.

Herein, using ammonium persulfate as oxidant the composites of PANI and TiO2 nanoparticles
(namely TiO2@PANI) with different contents are prepared in the aqueous solution of phosphoric
acid, and the gas sensing properties of products are studied. The phosphoric acid is used as a kind of
protonic acid, which can change the conjugate state of the polymer chain and improve the
conductivity of PANI. The gas sensing test results show the gas sensing properties of the composites
are better than those of pure PANI, and when the mass ratio of titanium dioxide to aniline monomer
is 2:1, the gas sensors have the best gas sensing properties. Meanwhile the ammonia (NH3) is selected
as the target gas, which is a colorless and pungent gas and generated by animals and plants rotting,
livestock farms, industrial nitrogen fixation and domestic refuse dump. NH3 gas is harmful to
people’s health. When a small amount of it is inhaled by people, it will cause rhinitis, pharyngitis, sore
throat and hoarseness. In severe cases, hemoptysis, pulmonary edema, white or bloody sputum,
dyspnea even death can be happened. So achieving real-time monitoring and prediction to NH3 gas
is of great realistic significance and broad application prospects.

2. Experimental

2.1. Materials

Aniline (C6H7N, Ani), Ammonium persulfate ((NH4)2S2O8, APS), Phosphoric acid (H3PO4,
PA), Sodium laurylsulfonate (C12H25SO3Na, SDS), methanol and ethanol were analytical reagent
and purchased from Sinopharm Chemical Reagent limited corporation, Shanghai, China. Nano
titanium dioxide powder (TiO2) with an average particle size of 60 nm was purchased from Alfa
Aesar Chemical Reagent limited corporation, Shanghai, China. All of the chemical reagents were
used directly without any further purification. Deionized water was obtained from a pure water
device (Milli-Q, Millipore, MA, Molsheim, France).

2.2. Synthesis of TiO2@PANI

Firstly, 0.18 g Ani and 3.3 g SDS was dissolved in 10 ml deionized water and stirred for 15 min
in an ice bath. Then a certain amount of nano TiO2 powder was added in the above solution and kept
for 15 min, in which the mass ratio of TiO₂ and Ani was 0, 0.5, 1, 2 and 5, respectively. Next, 10 ml PA solution (0.1 mol/L) was added to the reaction solution and stirred for 30 min. Then 0.4568 g APS was dissolved in 10 ml deionized water and added drop by drop into the mixed solution after cooling to 0 °C. The mixed solution was stirred for 24 hours without stop in the ice bath. After reaction, the resulting precipitate was collected and washed several times with deionized water, ethanol and methanol, respectively. Finally, the obtained TiO₂@PANI products were dried in a vacuum oven at 45 °C for 24 hours.

2.3. Construction of sensors by a liquid-gas interfacial self-assembly method

Here the gas sensors were constructed by a liquid-gas interfacial self-assembly method and the details were as follows. Firstly, 10 mg as-dried TiO₂@PANI products was dispersed in deionized water and ethanol mixture with the volume ratio of 50% and treated with sonication for 60 min. Then the above 200 μL mixed solution was slowly dropped on the deionized water surface from one side of a 500 ml beaker which was full of deionized water, and the emerald green dispersions spread out on the surface of the water and formed a thin film. Last, a piece of flat electrode was slowly scooped the emerald green thin film from the underside of liquid surface and dried in air at room temperature, and the gas sensors were fabricated.

2.4. Characterization methods and the gas sensing measurements

The field-emission scanning electron microscopy (Hitachi, SU8020, Tokyo, Japan) and the high-resolution transmission electron microscopy (JOEL, JEM-2010, Tokyo, Japan) was used to observe the morphologies of products. A NICOLET MX-1E Fourier transformed spectrometer with KBr tablet (Thermo Fisher Scientific, Waltham, MA, USA) was used to measure the FTIR spectra of the products. The X-ray diffraction (XRD) was performed on a Philips X’Pert X-ray diffractometer (Almelo, The Netherlands) which the Cu-K line is 0.15419 nm. All the gas sensing performances were measured in a static system with a volume of 20 L. A 10 V regulated power supply was obtained by a DC power supply (Agilent U8002A, San Jose, CA, USA), and the voltage changes of sensing devices under different conditions were collected by a multimeter (Agilent mod, U3606A, San Jose, CA, USA). A certain amount of target gas was injected into in the measurement system by syringe with different capacity, which was calculated based on the injected amount. All the measurements were operated at room temperature (25 °C) in an air ambient.

3. Results and discussion

3.1. Morphology

In order to improve the gas sensitivity of the PANI, the n-type semiconductor TiO₂ nanoparticles (NPs) are used to synthesize TiO₂@PANI gas sensing thin film, the morphology of products is observed by field-emission scanning electron microscopy. From Figure 1a, it is obvious that the phosphoric acid (PA) doped PANI prepared by the method of liquid phase oxidation without TiO₂ nanoparticles is fiber network structure with a diameter of about 100 nm. The length of PANI is also very short, and it is adhesive between each other. From Figure 1b, it can be seen that the TiO₂ purchased from Alfa Aesar Chemical Reagent limited company are NPs, and the diameter of them is about 60 nm. Some TiO₂ NPs are united together with each other to form large particles, so full ultrasonic treatment is needed before using. After adding TiO₂ NPs in the reaction system, there are no nanofibers generated as shown in Figure 1a. The surface of TiO₂ NPs is coated by a layer of PANI film in Figure 1c. This indicates that a good encapsulation effect on TiO₂ NPs can be achieved by the above method. From the scanning electron microscope photograph of cross section in Figure 1d, it can be seen that the gas sensing thin film is relatively uniform and the thickness of the film is about 2 um. In addition, the film is formed by the accumulation of granular complex, so it is relatively loose and there are a lot of pore structures, which is favorable to improve the properties of the gas sensors.
Figure 1. SEM images of (a) the PA doped PANI; (b) pure TiO2 NPs; (c) TiO2@PANI products at m(TiO2)/m(Ani)=2:1 and (d) cross section of gas sensing thin film prepared by the liquid-gas interfacial self-assembly method at m(TiO2)/m(Ani)=2:1.

The transmission electron microscope (TEM) photograph of TiO2@PANI products at m(TiO2)/m(Ani)=2:1 is shown in Figure 2a. It can be clearly seen that the black granular TiO2 NPs are about 60 nm in size and coated by a layer of PANI film on their outer surface. It can be better observed that the spacing of the lattice stripe of TiO2@PANI is about 0.352 nm, which is correspond to the TiO2 crystal plane space of (101) face with anatase structure from Figure 2b [21]. Figure 2c is the selected area electron diffraction pattern of the TiO2@PANI, and it is well matched with the TiO2 crystal type [22]. On the surface of TiO2 NPs, polyaniline film also can be seen in the TEM photograph and the thickness of the coating is about 5 nm, but there is no lattice stripe or diffraction pattern found for the poor crystalline substance. However, in Figure 2d from the energy spectrum of the TiO2@PANI it is visible that the product contains the elements of the coated polyaniline. It means the TiO2 NPs coated by polyaniline have been successfully prepared by the above method.
Figure 2. (a) TEM image of the TiO2@PANI product at m(TiO2)/m(Ani)=2:1 and the scale is 50 nm in the lower-left corner; (b) HRTEM image of the product and the scale is 5 nm; (c) the selected area electron diffraction and (d) the energy spectrum of the TiO2@PANI sample.

3.2. Structure characterization

In order to demonstrate the structure of products, the FTIR spectrum of pure TiO2 NPs, the PA doped PANI and the TiO2@PANI samples at m(TiO2)/m(Ani)=2:1 is measured, and the results are shown in Figure 3. From the FTIR spectra of pure TiO2 NPs (Figure 3a), only three main absorption peaks are be found. The wide peak at the 660 cm$^{-1}$ is caused by the telescopic vibration of the Ti-O bond in the NPs [23]. The sharp absorption peak near the 1636 cm$^{-1}$ is due to the characteristic absorption peak of hydrophilic property of TiO2 NPs, which absorbs the moisture in the air [24]. The broad peak of 3450 cm$^{-1}$ is caused by the stretching vibration of hydroxyl groups on the surface of TiO2 NPs [25]. In Figure 4b and 4c, several characteristic absorption peaks are appeared, and the peak at 1143 cm$^{-1}$ corresponds to N=C stretching mode of the quinoid units [26]. The absorption peak near 1304 cm$^{-1}$ is C-H telescopic vibration on the benzene ring [27], and at the 800 cm$^{-1}$ it is the C-H outer bending vibration on the symmetric substitution of benzene ring [28], and at 1480 and 1384 cm$^{-1}$ they are the C=C stretching vibration on the benzene ring [29]. The appearance of these peaks indicates that the products have the molecular structure of PANI. Compared to the infrared absorption spectra of TiO2@PANI products and pure TiO2 NPs, it is found that the absorption peak near 660 cm$^{-1}$ is weaker for the TiO2@PANI, while the other peaks are largely unchanged. That is because PANI film is coated on the surface of TiO2 NPs. At the same time, the characteristic absorption intensity of PANI is also weakened. The reason is that the amount of TiO2 NPs is more than the PANI and the signal of PANI is reduced [30].
Figure 3. FTIR spectrum of (a) pure TiO2 NPs; (b) the PA doped PANI and (c) TiO2@PANI products at m(TiO2)/m(Ani)=2:1.

Figure 4 is a XRD diffraction pattern of the above three samples. The pure TiO2 NPs shows a good match between the peak position and the diffraction peak of TiO2 in Figure 4a [31]. The major peaks in the XRD pattern are in agreement with standard JCPDS card (No. 21-1272). The strong and sharp peak types and the smooth baseline indicate a good crystallinity. However, for the XRD diffraction pattern of PANI films prepared by phosphoric acid in Figure 4b, the crystalline properties are not good and only a broad reflection peak appears at about 23°, indicating an amorphous pattern. Figure 4c is the XRD diffraction pattern of the TiO2@PANI sample produced at m(TiO2)/m(Ani)=2:1. It is obvious that almost the same sharp diffraction peaks appear at the corresponding position of pure TiO2 NPs, thus it can be seen that the encapsulation of PANI does not affect the crystal structure of TiO2 NPs. However, the intensity of the diffraction peak becomes weaker, which may be the result of the existence of PANI coating [32]. In addition, according to the Scherrer formula:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

Where D is grain size, K is a constant (K=0.89), \( \lambda \) is X ray wavelength, and \( \beta \) is half peak high width of peak integral. From this we can calculate that the average particle size of TiO2 NPs is about 60 nm, which is consistent with the results of SEM and HRTEM.

Figure 4. XRD pattern of (a) pure TiO2 NPs; (b) the PANI films prepared by phosphoric acid and (c) TiO2@PANI sample produced at m(TiO2)/m(Ani)=2:1.
3.3. Gas sensing properties:

The gas sensor devices are fabricated with different \( \text{m(TiO}_2/\text{m(Ani)}} \) ratios from 0 to 5 on flat electrodes, and the sensing performances of these sensors to NH3 gas are measured in ambient air at room temperature. Gas sensitive response curves of the sensors to NH3 gas ranging from 10 to 50 ppm at room temperature are shown in Figure 5. The gas sensitive response is defined as \( R_g/R_0 \), where \( R_g \) and \( R_0 \) is the resistances of the sensor devices after and before exposure to NH3 gas. It can be seen that after addition of TiO2 nanoparticles to the reaction system the gas sensitive response of PANI is obviously improved. As the content of TiO2 nanoparticles increases, the gas sensitive responses of TiO2@PANI samples also increase. When the ratio of \( \text{m(TiO}_2/\text{m(Ani)}} \) reaches to 2, the gas sensor device has the best gas sensitivity and the gas sensing response of sensor is as high as about 11.6 to 50 ppm NH3 gas. However, with the continued increasing of TiO2 nanoparticles to 5 the gas sensing response of sensor obviously decreases. So with the \( \text{m(TiO}_2/\text{m(Ani)}} = 2:1 \), the sensing performances of sensors is superior to different NH3 concentrations ranging from 10 to 50 ppm when comparing to other sensors fabricated with different TiO2 contents. Meanwhile, with the increase of NH3 concentration, the response behaves linear rise, which is favor with the practical application of the sensors. In addition, it is obvious that when the gas sensor devices are exposed to different contents of NH3 gas, the response of the TiO2@PANI samples is very rapid, which means that the resistances of the gas sensor is rapidly increasing and will be stable after a certain time. When they are exposed to air, the recovery of gas sensors is faster and gradually approaching the baseline. The response time (defined as the time for reaching 90% of the full response change of the sensor after it is exposed to testing gas) of gas sensor devices is about dozens of seconds. It is found that the addition of TiO2 nanoparticles almost has no effect on the response time of the sensors, but the gas sensitive response is obviously improved.

![Figure 5](image.png)

**Figure 5.** Gas sensing response of the sensors deposited with TiO2@PANI samples at different \( \text{m(TiO}_2/\text{m(Ani)}} \) to NH3 gas ranging from 10 to 50 ppm at room temperature.

From the above discussion, it can be seen that the TiO2@PANI sample with \( \text{m(TiO}_2/\text{m(Ani)}} = 2:1 \) has the best gas sensitivity. Besides the reproducibility response is also a very important index for gas sensors. So the repeatability response curves of TiO2@PANI samples with \( \text{m(TiO}_2/\text{m(Ani)}} = 2:1 \) are measured to 50 ppm ammonia, and the result is shown in Figure 6. The gas sensitive responses of gas sensors with 5 repeats are 10.7, 11.0, 10.8, 11.2 and 12.0 at room temperature, respectively. There are little noticeable changes, which mean that the gas sensors have a good stability for NH3 gas and it is favorable for the industrial applications.
Figure 6. The reproducibility response curves of TiO2@PANI samples with m(TiO2)/m(Ani) = 2:1 to 50 ppm NH3 gas at room temperature.

Including the sensitivity and repeatability response, the selectivity of gas sensors is also an important index. Here, six different kinds of gases such as nitrogen dioxide (NO2), ethanol (C2H6O), acetone (C3H6O), hydrogen sulfide (H2S), methane (CH4) and sulfur dioxide (SO2) with different concentrations are selected as the interference gases, and the sensitivity contrast histogram is shown in Figure 7. It can be seen that the sensitivity of the gas sensors with m(TiO2)/m(Ani) = 2:1 to 50 ppm ammonia, 50 ppm nitrogen dioxide, 100 ppm ethanol, 100 ppm acetone, 100 ppm hydrogen sulfide, 100 ppm methane and 100 ppm sulfur dioxide is 1.3, 3.0, 1.2, 1.6, 0.9, 1.0 and 1.3 at room temperature, respectively. By comparison, these selected gases have little interference to the gas sensors. The difference sensitivity between the interference gases and target gas (NH3) is greater, the selectivity of gas sensors is better. So it can be concluded that the gas sensors with m(TiO2)/m(Ani) = 2:1 shows a good selectivity to NH3.

Figure 7. The sensing responses of TiO2@PANI samples with m(TiO2)/m(Ani) = 2:1 to NH3 (50 ppm), NO2 (50 ppm), C2H6O (100 ppm), C3H6O (100 ppm), H2S (100 ppm), CH4 (100 ppm) and SO2 (100 ppm) at room temperature.

From the above results, it can be seen that the gas sensors fabricated with different m(TiO2)/m(Ani) ratios have better gas sensing properties. When the ratio of m(TiO2)/m(Ani) is 2, the gas sensor device has the best gas sensitivity, repeatability and selectivity. The TiO2 nanoparticles are typical n-type semiconductor materials, and they realize their gas-sensing properties by the adsorption of oxygen on the surface [33]. It usually needs higher temperature, and at room
temperature it no gas sensitive response to ammonia. However, when a certain amount of TiO2 nanoparticles is added to PANI materials forming composites, the sensitivity of the composites to ammonia gas will be greatly improved and the gas sensing mechanism also changes greatly [34]. In these composites comprised by the n-type TiO2 nanoparticles and p-type PANI materials, the electron transfer is affected by the composite mode and ratio of the both materials in the detection of target gas. The concentration of holes in p-type PANI materials is higher, and the electrons are abundant in n-type TiO2 nanoparticles. It forms a p-n junction, and the two kinds of carriers diffuse mainly on the p-n junction. With the diffusion of carriers, there will be formed a layer of negatively charged particles region on the p-type region of p-n junction and a layer of positively charged particles region on the n-type region, which is a strong local electric field and points from the n-type region to the p-type region. This is favorable for the transmission of electrons and enhances the sensitivity of gas sensors. Furthermore in the composites system of PANI and TiO2 nanoparticles, the different proportion of TiO2 nanoparticles in the composites determines the channels of electronic transmission. When the proportion of TiO2 nanoparticles is low, the current preferentially passes through the PANI channel for the high conductivity. When the content of TiO2 nanoparticles increases, the p-n junction interface formed by PANI and TiO2 nanoparticles increases obviously. The current can pass preferentially from these p-n junction interfaces with forward bias, and the sensitivity of gas sensor also improves. However, if the proportion of TiO2 nanoparticles is too high, PANI will not be a continuous phase in the composites and the sensitivity of the gas sensors will decrease [35-36]. From the above experiments it can be seen that when the mass ratio of m(TiO2)/m(Ani) = 2:1 it has the best proportion under the experimental condition.

4. Conclusions

In summary, the composites of PANI and TiO2 nanoparticles were successfully prepared in the aqueous solution of phosphoric acid, in which phosphoric acid was used as dopant too. From the experiment results it could be clearly seen that the granular TiO2 nanoparticles were about 60 nm in size and coated by a layer of PANI film on their outer surface. Then the gas sensors with different contents of TiO2 nanoparticles were constructed by a liquid-gas interfacial self-assembly method and exhibited better gas sensing properties than pure PANI to NH3 from 10 ppm to 50 ppm. The composites prepared at the mass ratio of titanium dioxide to aniline monomer of 2:1 exhibited the best gas sensitivity (about 11.2 to 50 ppm), stability and selectivity to NH3 at room temperature. The formation of p-n junction in the composites was the important factors of excellent gas sensing properties, and it achieved the optimum proportion with m(TiO2)/m(Ani) = 2:1. It provided a preparation method of gas sensor for detecting nitrogen concentration at room temperature with good gas sensing properties.

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