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Study on Preparation and Gas Sensing Property of PANI

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Abstract

In the paper,We can prepare the PANI in different conditions of acid (HCl, HNO_3, H_2SO_4 and $C_7H_6O_6S \cdot 2H_2O$) by using aniline monomercc chemical oxidative polymerization.With the test of scanning electron microscopy (SEM) ,it shows that the powder of preparation is nanoscale particles, and the size of particle is in the order of tens to hundreds of nanometers. It has good dispersion, but the particle size is nonuniform; With differential thermogravimetric analyzer (DTA) test ,we can obtain the properties of powder in temperature of thermal decomposition and stability. At the room temperature, we test the sensitivity of gas for the ammonia concentration range of 1-7ppm. The result shows that, in different conditions of acids (HCl, HNO_3, H_2SO_4 and $C_7H_6O_6S \cdot 2H_2O$) ,the relationship of sensitivity of gas sensor is linear in response to ammonia gas.With the analysis of the sensitive mechanism for ammonia gas of PANI material,ultimately, we can concluded that, in different conditions of acid, doped PANI materials are suitable to be detected for ammonia in a wide concentration range, the recovery time of response to ammonia gas is shorter and more stabile for the larger organo functional proton acid ($C_7H_6O_6S \cdot 2H_2O$).

Keywords:*PANI; gas sensitivity; ammonia*

1. Introduction

Gas sensitive material is refer to a class of materials that the resistance of materials varies with changes of the surrounding gas environment. At present, the gas sensing materials can be divided into two categories: organic and inorganic materials. Inorganic gas sensitive material is with the representative of SnO_2, ZnO, Fe_2O_3 and TiO_2.Its preparation method is simple and cost of raw materials is low, and some inorganic gas sensitive material has become commercialized. Such sensor made by sensitive material has fast response speed , stable electromotive force, wide measuring range of oxygen partial pressure and high temperature resistance. It has been used extensively in automotive exhaust and oxygen testing of steelmaking process . But the biggest drawback of the sensor is that it has higher operating temperatures (300-450 ℃),and poor selectivity [1-2]. Compared with inorganic sensitive material such as polypyrrole, polyaniline (polypyrrole) [3-4] (polyaniline) [5], metal phthalocyanine (phthalocyanine) [6] and other organic sensitive material, it has good stabilities. With the increase of temperature , the resistance value rises gradually, and it has good thermal stability at different temperatures. Among many organic sensitive materials, polyaniline (PANI) has cheap raw material, simple synthesis, high temperature resistance , excellent antioxidant performance, high conductivity and potential solutions, melt processing possibilities. In addition, polyaniline can build film easily and the film is soft and strong and it has good electricity denaturation. It has a broad application prospects in terms of household goods and high-tech[7].

Polyaniline is a intrinsic conductive polymeric material that has a special conjugated electronic structure. Eigenstate polyaniline is hardly conductive, but it can become conductive after doping of protonic acid . And conductivity can be enhanced in several

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orders of magnitude for the condition that polyaniline is made by different doping acid .In this paper, with ammonium persulfate as oxidant, under different conditions of acid (HCl, HNO_3, H_2SO_4 and $C_7H_6O_6S \cdot 2H_2O$) ,we synthesis the polyaniline gas sensing material, and made the ammonia sensitive elements. We also compare the effects of different dopants on the polyaniline gas sensing properties, and analyze its sensitive mechanism.

2. The Experiment

2.1 Reagents and Instruments

Reagent: ammonium persulfate ($(NH_4)\ 2S_2O_8$, the analytically pure, Beijing Jing Biological technology Co., LTD.) aniline (Pan, the analytically pure, Tianjin Kermel Chemical Reagent Co., Ltd.), hydrochloric acid (HCl, the analytically pure, Tianjin Wenda precious Chemical Reagent Factory), nitrate (HNO_3, the analytically pure Tianjin Wenda precious Chemical Reagent Factory), sulfuric acid (H_2SO_4, the analytically pure, Tianjin Wenda precious Chemical Reagent Factory), sulfosalicylic acid ($C_7H_6O_6S \cdot 2H_2O$, Tianjin Guangfu Fine Chemical Industry Research Institute), N- methyl pyridine complex pyrrolidone (C_6H_9NO, the analytically pure, Tianjin light complex Fine Chemical Industry Research Institute).

Instruments: ZCT-B differential thermal weightlessness instrument (Beijing precision instrument Gaoke Instrument Co. Ltd.), Agilent-34972A data acquisition system (Agilent Technologies), Quanta-200 scanning electron microscope (FEI).

2.2 Preparation of PANI

Aniline (Pan) was purified by air distillation before using for spare. Other reagents were analytically pure, without further purification. We dissolved the 2.5ml aniline into 68ml1mol/L hydrochloric acid, and added 0.16g/ml ammonium persulfate about 25ml slowly in the mechanical stirring condition, (the molar ratio of aniline and ammonium persulfate is 1:1). It last about 30 min, and the reaction under 5 ℃ last abour 6 hours. When the reaction stops we can filter, respectively ,washing the filter cake with 0.01mol/L hydrochloric acid, deionized water and anhydrous ethanol ,vacuum drying at 65 ℃ for 24 hours to obtain polyaniline.The process, is shown in figure 1. By replacing hydrochloric acid with nitric acid, sulfuric acid ,sulfosalicylic acid, the same methods was used for synthesis of PANI.

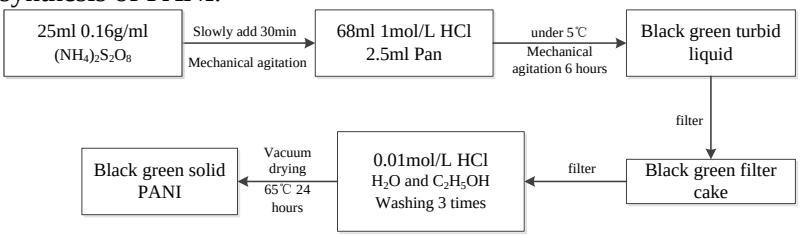


Figure 1. Preparation of PANI

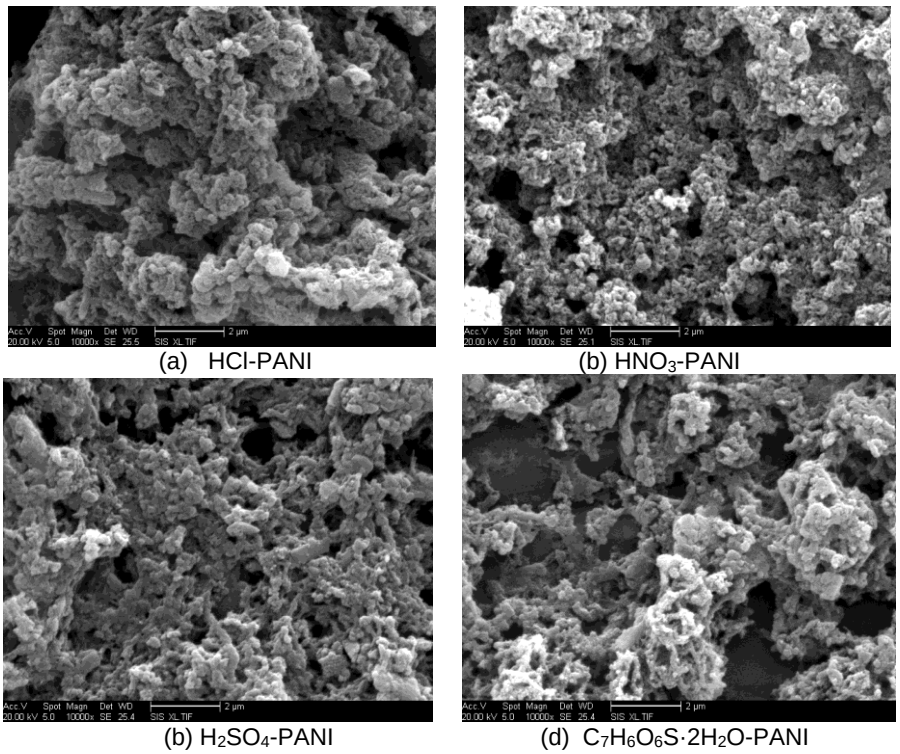
2.3 Making and Measurement of Components

This experiment adopts the production process of traditional heating type gas sensor, using polyaniline material as the gas sensing material, and N- methyl pyrazole collaterals alkane ketone as solvents.After fully grinding, using fine brush coating to the surface of ceramic tube, respectively ,making HCl-PANI, HNO_3-PANI, H_2SO_4-PANI and $C_7H_6O_6S \cdot 2H_2O$-PANI gas sensors at room temperature. We test properties of gas sensitive components by static gas testing system.

3. Results and Discussion

3.1 Characterization of Materials

Figure 2 is the 10000 times scanning electron microscopy (SEM) diagram for different proton acid doped polyaniline.



(a) HCl-PANI (b) HNO_3-PANI

(b) H_2SO_4-PANI (d) $C_7H_6O_6S{\cdot}2H_2O$-PANI

Figure 2. SEM Photographs of PANI

As you can see from Figure 2, polyaniline material either doped by hydrochloric acid, nitric acid, sulfuric acid, or sulfosalicylic acid are the macromolecular chain formed by the large molecules together. Its shape is sheet structure of flower , and the size of flower is about tens to hundreds of nanometers, uneven and different. And in Figure 2 (a), (b), (c) ,we can seen that doped polyaniline's extent of polymerization in inorganic small molecular protonic acid (HCl, HNO_3, H_2SO_4) is high, and molecule's gap is small, about 20-40nm.From Fig. 2 (d) we also can seen that the organic functional protonic acid ($C_7H_6O_6S$ 2H2O) doped polyaniline's extent of polymerization is relatively low, and relatively the gap is large ,about 100-150nm.

The thermal decomposition temperature has a large impact on the performance of polyaniline. If the temperature is too high, it will cause degradation of the macromolecular polyaniline chains. Therefore, to determine the thermal decomposition temperature of polyaniline, we do the experiments of differential thermal gravimetric analysis for polyaniline. Figure 3 is the thermal gravimetric curve diagram of polyaniline that the heating rate is 10 ℃/ min (TG-DTA).

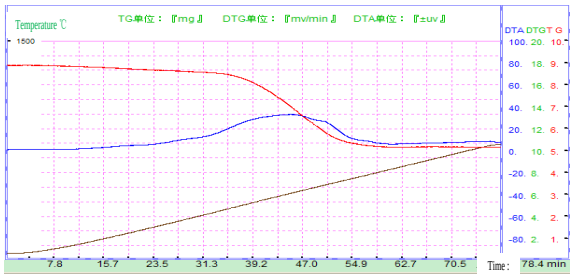


Figure 3. TGA Curves

According to the analysis, the thermal decomposition of polyaniline can be divided into 3 stages:: 1、weight loss in the first step happened under 100 ℃is caused by detachment of water molecules from the polyaniline matrix; 2、weight loss between 100~250 ℃is a process of decomposition weightlessness that temperature of dopant hydrochloric acid removing from the material is low without removal agent; 3、the weight loss between 250~320 ℃is caused by the decomposition of part of polymer chain and the material containing small oligomers. The weight loss above 320 ℃is caused by the degradation of macromolecular chain, DEG C polymer decompose completely when the temperature reach 590℃.Then with the increase of the temperature , curve of TG and DTG is not change. Therefore, polyaniline can be decomposed completely above 250 ℃.

3.2 Gas Sensing Properties

The response time of the experiment is required that the initial stable resistance reach 90% time of stable value; the recovery time is required that when the element remove from the measured gas, resistance recover to 110% value of initial stable resistance. At room temperature, we have a test of the ammonia gas sensing properties respectively on components made by polyaniline material doped by hydrochloric acid, nitric acid, sulfuric acid and sulfosalicylic acid. Figure 4 is the dynamic response curve of the polyaniline gas sensitive element doped by hydrochloric acid with the range of 1-7ppm for ammonia concentration .

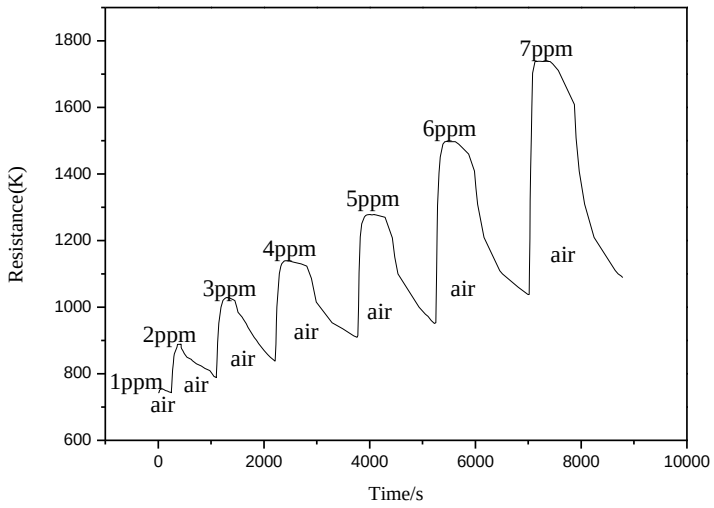


Figure 4. Response Curve of H2Cldoped Polyaniline with Ammonia at Different Concentrations

As can be seen, the resistance of polyaniline gas sensor doped by hydrochloric acid increases with increasing ammonia concentration. Response time is about 40s, and the

recovery time is about 960s. Figures 5, 6, 7, is the response curve that,respectively, component made by polyaniline material doped by ,nitric acid, sulfuric acid and sulfosalicylic acid changes with different concentration of ammonia . As can be seen, the resistance of element increases with increasing ammonia gas concentration, made by polyaniline material doped regardless of inorganic small molecule protonic acid (hydrochloric acid, nitric acid, sulfuric acid), or large size of the organic function protonic acid (sulfosalicylic acid) .

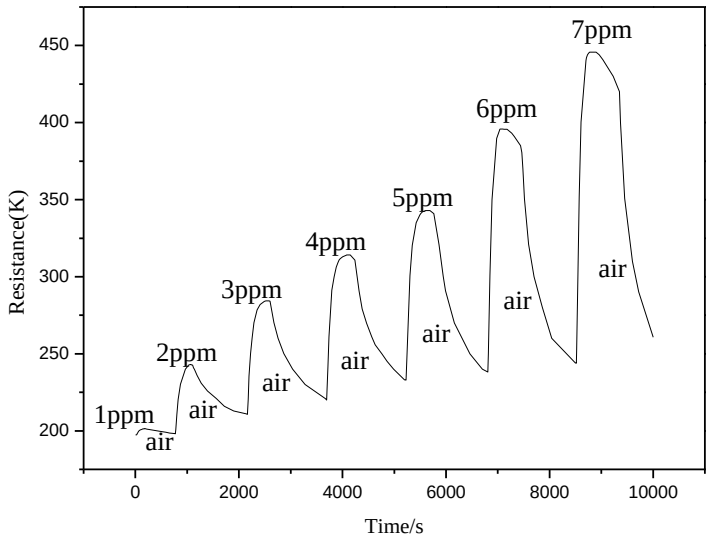


Figure 5. Response Curve of HNO3doped Polyaniline with Ammonia at different Concentrations

Compared with other doping elements, response time and the recovery time for the elements of polyaniline material doped by sulfuric acid ,is longer . We also found that the response time and recovery time is shortest for the element made by sulfosalicylic acid doped polyaniline material. The response time is about 41s,and the recovery time is about 480s. Relatively ,Respond-recovery time of other elements is long.

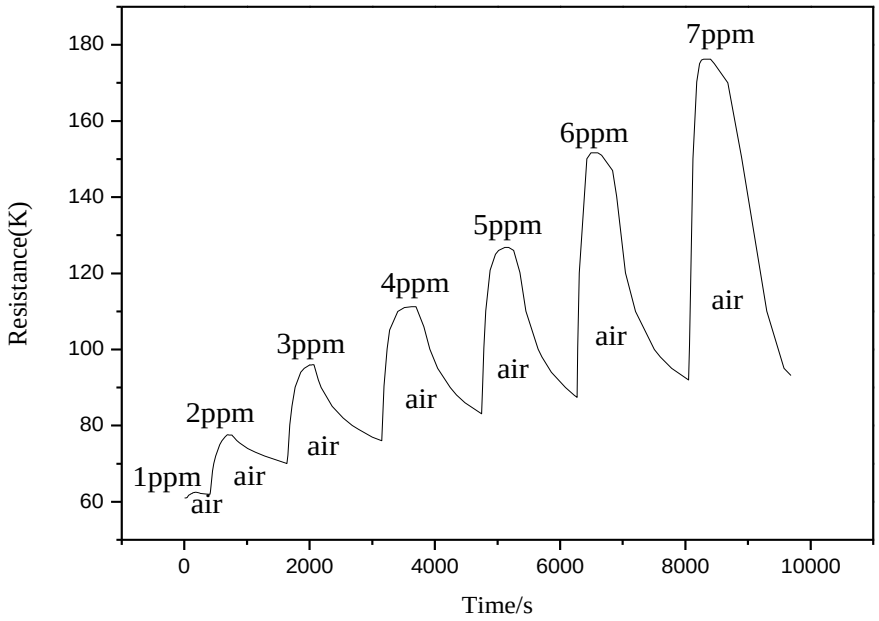


Figure 6. Response Curve of H2SO4 doped Polyaniline with Ammonia at Different Concentrations

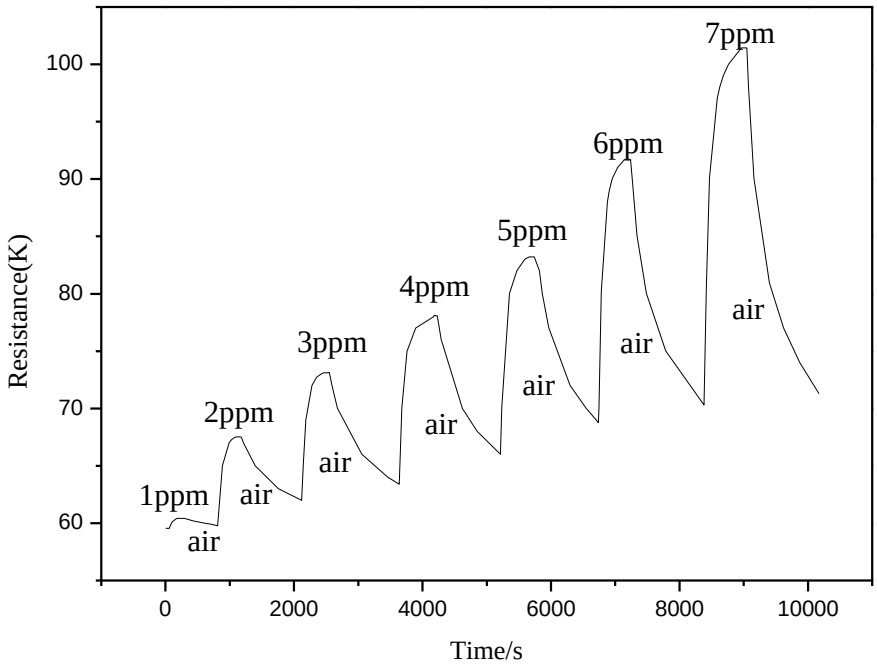


Figure 7. Response Curve of C7H6O6S • 2H2O Doped Polyaniline with Ammonia at Different Concentrations

Figure 8 is the sensitivity curves of different acid doped polyaniline gas sensors changing with ammonia concentration. The sensitivity is represented by resistance ratio for Rg of sensors at detected gas with different concentrations and R0 in the clean air, namely Rg/R0.

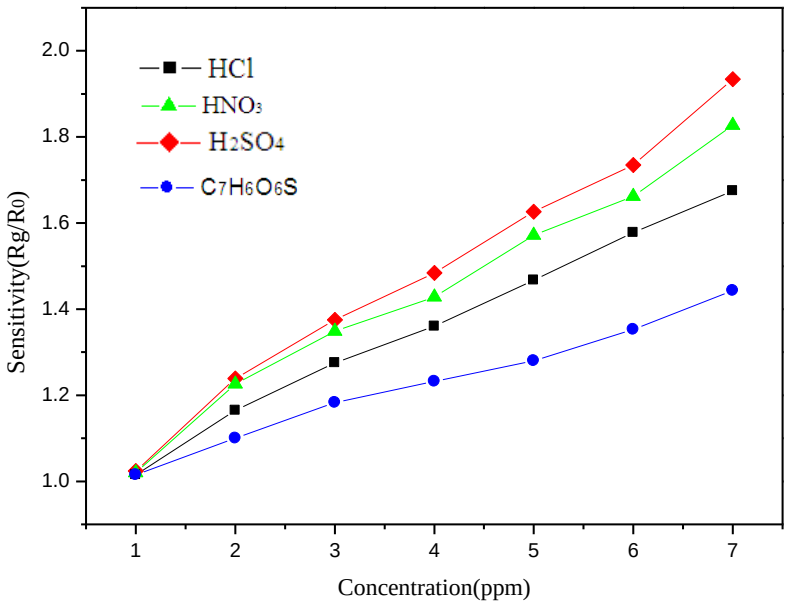


Figure 8. Sensitivity Varies with the Ammonia Concentration Curve

As can be seen from figure 8, the sensitivity of polyaniline element doped by inorganic small molecular protonic acid (HCl, HNO_3, $H2SO_4$) and polyaniline gas sensors doped by the large organic functional proton acid ($C_7H_6O_6S \cdot 2H_2O$), increases with the decrease of the ammonia concentration, and it shows a good linear relationship. Under normal circumstances, if the relationship between sensitivity of gas sensor and concentration of

measured gas is linear or near, the sensor can be tested and used in a wide range of concentration. Therefore, it's suitable for the polyaniline materials doped by HCl, HNO_3, H_2SO_4 and $C_7H_6O_6S \cdot 2H_2O$ to be detected in a wide concentration range of Ammonia. The changing in sensitivity curve of polyaniline material doped by $C7H_6O_6S \cdot 2H_2O$ is relatively more stable, so we can conclude that the stability of polyaniline material on the environment of doped by C7H6O6S · 2H2O is more stable than doped by HCl, HNO_3, $H2SO_4$.

3.3 Sensitive Mechanism

The sensing mechanism of Polyaniline on ammonia gas and inorganic semiconductor oxides is different. Typical characteristics of polyaniline is that doped by proton acid (i.e.: H + H+) ,it has high conductivity. The experiment study the the gas sensitive mechanism of polyaniline doped by HCl, HNO_3, H_2SO_4 and $C_7H_6O_6S \cdot 2H_2O$ on ammonia. When prepared polyaniline encounter ammonia in the acidic environment, compared with the amine of polyaniline, affinity of ammonia molecules and acid is more stronger, so it's more easier to capture original doped acid combined by amino of polyaniline and ammonia when it contact with polyaniline. Polyaniline lost part of doping points, and doped level decreases. The conductance decreases, and the resistance increased.When meet the air, ammonia molecules will be removed from the molecular chain, so that the material conductivity abilities will be restored, and the resistance decreases.

At the same time, with the experiment data and scanning electron microscope photos ,we can conclude that: because the doped organic functional proton acid ($C_7H_6O_6S \cdot 2H_2O$) changes the degree of polymerization and molecular gap size of polyaniline, the adsorption and desorption for sensitive element on ammonia detection is faster, and thus it improves the recovery time,and the stability.

4. Conclusion

In this experiment, we synthesize different doped polyaniline material with polymerization acids (HCl, HNO_3, H_2SO_4 and $C_7H_6O_6S \cdot 2H2O$) by chemical oxidative, and it was characterized with SEM, DTA method, and we also study the low temperature gas sensing properties. The experiment is at room temperature (20 ℃).Through gas sensitivity testing for different polyaniline material doped by acid (HCl, HNO_3, H_2SO_4 and $C_7H_6O_6S \cdot 2H_2O$)on ammonia, in results we can find that, compared with the polyaniline material doped inorganic small molecular protonic acid, the larger size polyaniline material doped by organic functional protonic acid on ammonia has a short response time and recovery time. The response time is about 41s, and the recovery time is about 480s; and the PANI materials sensitivity varies linearly with the ammonia concentration increasing. Thus, we can conclude that, response and recovery time of the polyaniline material on ammonia is short, and it has low operating temperature, good reversibility, and a wide concentration range for ammonia to be detected . The larger size organic functional proton acid doping polyaniline material not only improve the response time and recovery time on ammonia, but also improve the stability.

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