



Fabrication of polyaniline/zeolite composites and their response towards nitrogen dioxide



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ABSTRACT

A composite of Polyaniline with zeolite erionite was synthesized by chemical oxidative polymerization method. The effect of cation type, cyclic interval, NO₂ concentration over time, zeolite content on the response of polyaniline and polyaniline/zeolite erionite composites towards NO₂ was studied. Na-form shows largest response towards NO₂ because of small electronegativity. The effect of cyclic interval on the response of the composite was studied and it was found that with increasing no. of cyclic intervals the response decreases. The response of the nanocomposite on exposing to NO₂ first increases and then attains a constant value after some time.

With increase in zeolite content; the response goes on increasing and attains a steady state beyond 50% zeolite content. The composites were characterized by FTIR, SEM and XRD techniques.

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1. Introduction

Nitrogen dioxide belongs to a family of highly reactive gases called nitrogen oxides (NO_x). These gases are formed when fuel is burned at high temperatures, also from motor vehicle exhaust and stationary sources such as electric utilities and industrial boilers. A suffocating, brownish gas, nitrogen dioxide is a strong oxidizing agent that reacts in air to form corrosive nitric acid, as well as toxic organic nitrates. It also plays a major role in the atmospheric reactions that produce ground-level ozone (or smog). Nitrogen dioxide can irritate lungs and lower resistance to respiratory infections such as influenza. The effects of short-term exposure are still unclear, but continued or frequent exposure to concentrations that are typically much higher than those normally found in the ambient air may cause increased incidence of acute respiratory illness in children. Nitrogen oxides in the air can significantly contribute to a number of environmental effects such as acid rain and eutrophication in coastal waters. Several gas sensing materials have been developed for NO₂ detection [1]. Many efforts have been

paid for the development of the sensors for monitoring the presence of NO₂ gas in the atmosphere. A variety of materials including semiconducting metal oxides, carbon nanomaterials and organic materials were explored for the detection of NO₂ gas at low concentrations using chemiresistors and field effective transistors. The semiconducting metal oxide based sensors offer sensitive detection of NO₂ gas, but the major limitations of these sensors are high operating temperatures and hence high power requirement and also cross sensitivity to alcohols and other interferences. Thus, many efforts are currently in the progress for the development of sensitive NO₂ gas sensors operating at room temperature.

Conductive polymer based sensors have many advantages over metal sensors; they are less expensive, lighter, and can be operated at lower temperature. Polyaniline (PANI) is one of the most favorable conducting polymer because of simple synthesis, low priced monomer, environmental stability etc [2]. Various studies have been carried out utilizing polyaniline for the detection of gases like methanol vapor [3,4], H₂ [5], SO₂ [6], NH₃ [7], CO₂, NO₂ [1]. However, there still remain certain issues in using polyaniline as a gas or vapor sensor material: the sensitivity, the selectivity to a particular species amongst others, and its temporal response towards a target gas.

Since, zeolites are aluminosilicates made of SiO₄ and AlO₄ tetrahedra building blocks which result in a ring structure. They are

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three-dimensional (3D) frameworks connecting channel systems and well-defined micropores and mesopores. They have an open porosity that gives rise to an exceptionally high surface area. Aluminum ions replace silicon ions and introduce a negative charge into the framework. This charge needs to be compensated by an exchangeable cation, such as an alkaline or alkaline-earth cation and thus, the ion exchange property is provided. These cations are bound to the host framework but are mobile along the channels [8]. In addition to the adsorptive property, the high surface area and porosity, the presence of mobile ions, the variable chemical composition and the controllable acidic–basic properties and catalytic activity, zeolites are attractive candidates for numerous applications as chemical sensing materials [9,10] and can be operated at room temperatures. Keeping in view the above background we became interested to study the response of polyaniline/zeolite erionite composites towards nitrogen dioxide and also the effect of various cations on the response of the composite.

2. Experimental

2.1. Materials

Aniline monomer (Merck) was used for the synthesis of polyaniline. Ammonium Persulphate (Merck) was used as an initiator for the polymerization of aniline monomer. Sodium aluminate (Merck) and silica sol (Merck) were used for the synthesis of zeolite erionite. Tetramethyl Ammonium Chloride (Aldrich) was used as template for the synthesis of zeolite. N-methyl pyrrolidone (Merck) was used for dissolving polyaniline and composites to form thin films.

2.2. Synthesis of zeolite erionite

For batch preparation of erionite (Si/Al = 9), 25 ml water, 6 g sodium hydroxide and 15 g potassium hydroxide were mixed; to this solution 10 g sodium aluminate was added and stirred at boiling point until clear solution was formed. Solution was cooled to room temperature and then 11 g tetramethyl ammonium chloride was added drop wise with vigorous stirring. In a separate beaker 90 g silica sol was dissolved in 115 ml distilled water and stirred for 4 h. This solution was then transferred to the previous one resulting in the formation of thick gel. The obtained gel was then kept at room temp. for 2 h in polypropylene bottle and then placed in teflon lined autoclave and kept in a preheated oven at 175 °C for 72 h. After immersing the autoclave in cold water, the resulting material was washed and centrifuged until pH \leq 9 and subsequently dried at 110 °C. The obtained sample was grinded into powder and calcined by heating at 540 °C for 7 h in order to remove water [11].

2.3. Ion exchange of zeolite erionite

Na-form of zeolite erionite (Si/Al = 9) was converted into ion exchanged forms by exchanging Na ion present in the parent zeolite with other metal ions viz: Fe, Cu etc. by stirring zeolite material in alkali metal salt solutions. A mixture containing 5 g of zeolite erionite and 144 ml of 0.0125 M metal nitrate [Fe(NO₃)₃ and Cu(NO₃)₂] was stirred at 353 K for 24 h. The sample was dried for 12 h at 393 K and calcined at 723 K for 4 h to remove nitrate ions from the surface [12].

2.4. Conversion of zeolite in to H-form

Na-form of zeolite erionite (Si/Al = 9) was converted into H-form by mixing 9.0 g of synthesized zeolite, 7.230 g of NH₄Cl and

13.80 ml of deionized water with 0.1 M hydrochloric acid solution, in order to reach pH 4.0. The mixture was stirred at 80 °C for 30 min. Then the material was filtered under suction and washed with deionized water. After removal of chlorides, the resulting material, NH₄-zeolite, was placed in an oven at 60 °C for 24 h. The ammonium form of zeolite was converted into H-form by calcinations over 60 min at 500 °C.

3. Synthesis of polyaniline/zeolite erionite composites

The aniline monomer was inserted into erionite (Si/Al = 9) structure by polymerization using ammonium persulfate as initiator. 1, 2, 3, 4, 5 g of erionite were added in 200 ml of HCl aqueous solution (1 M) containing a particular volume of aniline monomer. The mixture was then magnetically stirred for 48 h at room temperature. Then 8.09 g of ammonium persulphate dissolved in 200 ml of distilled water were added drop wise for a period of 6 h and the solution was magnetically stirred at a temperature of –2––5 °C. The composite was filtered and washed with 20/80 methanol/water solution till it becomes colorless [13].

3.1. Formation of films

0.50 g of polyaniline or composite was dissolved in 20 ml of N-methyl pyrrolidone and stirred magnetically at normal temperature. The solution was filtered to remove any undissolved particles. Then the films of polyaniline and composites were prepared by casting 50 μ l of the solution on a glass surface (1 \times 1.5 cm) and dried for 48 h at 50 °C [13].

3.2. Instrumentation

A two point probe was utilized for measuring resistance of polyaniline and the composite thin films. A Scanning Electron Microscope (SEM LEO440i-England) was utilized for analysing the surface of polyaniline and composites. A Fourier Transform Infra-Red spectroscopy (Bruker Tensor, 27-Germany) was employed for analysing the interactions between organic and inorganic phases. An X-Ray diffractometer was used for determining the crystallinity of the synthesized materials (see Fig. 1).

3.3. Chemical vapor response detection

Fig. 2 illustrates the schematic diagram of gas sensing assembly, comprised of gas suppliers (calibration test gas cylinders equilibrated with N₂ gas cylinder for dilution), digital thermal mass flow controllers (Sierra SmartTrak 2), a glass sensing chamber, LCR to apply a constant voltage and to measure the resistance. The test sensor was installed in the glass chamber with a diameter of 2.0 inches and a length of about 10.0 inches, and connected to the LCR via copper wires. In this study, nitrogen dioxide was used as the detecting gas. For gas sensing measurements, small amounts of test gas were carried by N₂ into the glass chamber through a mixing chamber, as shown in Fig. 2.

The experiment was carried at 28 \pm 2 °C and 20% humidity. The humidity was measured by using dew point sensor (Owlstone, Model no. OHG-4, UK). The gas was diluted from 100 ppm to 2.5 ppm. Initially both the chambers contain nitrogen till the sample shows a constant resistance. Then nitrogen was evacuated from the chamber and 2.5 ppm of NO₂/N₂ was injected into the mixing chamber. The concentration of NO₂ was checked by NO₂ detector. Then gas was allowed to enter into the working chamber. After the saturation in resistance was obtained the gas was evacuated from the working chamber and N₂ was injected into working chamber. The response of the sensor (R%) is calculated as – R

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