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Synthesis, characterization, and CH_4-sensing properties of conducting and magnetic biopolymer nano-composites

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ABSTRACT

In this study, the magnetic biopolymer nanocomposites were prepared by the reaction of Fe_3O_4 nanoparticles containing carboxymethyl cellulose with polyvinyl alcohol. The conductivity of the magnetic nanocomposites was increased by adding conducting materials such as multiwall carbon tubes (MWCNTs) and polyaniline (PANI). The prepared nanocomposites were analyzed by Fourier transform infrared spectroscopy, differential scanning calorimetry/thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. The results revealed that Fe_3O_4 nanoparticles were spherically shaped with spinel structure having average diameters varying from 10 to 15 nm. The analyses of the gas sensing data indicated that the nanocomposites with MWCNTs showed significant CH_4 sensing properties at a slightly high operating temperature. In the case of nanocomposites with PANI, no response was observed either at the room temperature or higher temperature up to 60 °C.

1. Introduction

Since the past few decades, researchers have directed their interest toward the detection of harmful species in the atmosphere that may have evolved due to hazardous environmental pollution. Hazardous environments, such as in coal mines, lead to several accidents and huge loss of properties due to a sudden rise in toxicant levels, including that of carbon monoxide (CO) and flammable gases such as methane (CH_4), and low concentration of oxygen to breathe [1]. Therefore, for the sustainable growth of these industries and safety of the workers, it is necessary to regularly monitor the levels of oxygen, CH_4, carbon dioxide, CO, etc. within the factories or mines. Moreover, it is important to detect the gases evolved from several fields such as household, vehicles, and industrial emissions because these emissions directly affect human beings [2–4]. Previously, detection methods based on semiconductor gas sensors, catalytic gas sensors, optical gas sensors, and electrochemical gas sensors were used to detect a gas leakage via sound alarm. However, these methods had several drawbacks in terms of stability, cost, and performance ratios [5]. Nowadays, metal oxide-based semiconductors gas sensors such as SnO_2, ZnO, CuO, TiO_2, and WO_3 have been studied largely due to their greater impact [6–10]. However, the use of metal oxide detectors is often limited at high temperatures because of which we have modified the composition and starting materials in the present study. Recently, Fe_3O_4 nanoparticles (NPs) have received significant interest for their potential use as gas sensors because of their excellent surface reactivity and temperature-dependent morphology [11–13]. In addition, Fe_3O_4 is a promising oxidizing agent due to the mobility of rich oxygen ion at the material surface and support for gas sensing properties [14–16]. The multi-walled carbon nanotubes (MWCNTs) are conducting materials used to enhance the mechanical and conduction properties of polymeric matrix [17–20]. Therefore, MWCNTs are used as reinforcing materials for natural polymers used in the development of several biosensors and bioelectronic materials [21–23]. Few hybrid materials containing inorganic or organic moieties have been used as gas sensors and have shown superior performance than the individual inorganic and organic materials [24–26]. However, both possess specific drawbacks. The inorganic semiconductor sensing materials have limited capability at high temperatures while the organic semiconductors, such as polyaniline (PANI), polypyrrole, and polythiophene, show sensitivity toward the gases even at normal temperature. In addition, they have long response time due to their highly ordered structure [27,28]. Few studies have focused on the preparation of organic-inorganic hybrids materials in a polymer matrix and its use as sensing materials for the detection of

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toxic gases. Commercially available conducting polymer sensors require high power consumption since they provide adequate sensitivity only at high temperatures. Intense research is underway to develop new sensing materials and devices for a wide range of applications, especially, at room temperature. It has been shown that the graphene and carbon nanotube based detectors can operate at room temperature

In the present study, we have prepared hybrid nanocomposites based on MWCNTs and PANI and have used them as a sensor for sensing methane. The magnetic bio-polymer nanocomposites were prepared by the reaction of Fe_3O_4 NPs containing carboxymethyl cellulose with polyvinyl alcohol. The conductivity of the magnetic nanocomposites was increased by adding conducting materials such as MWCNTs and PANI.

2. Experimental methods

2.1. Materials

Aniline, polyvinyl alcohol (PVA), ammonium persulphate ($(NH_4)_2S_2O_8$), hydrochloric acid (HCl), carboxymethyl cellulose (CMC), acetonitrile, ethanol, and MWCNTs were purchased from Sigma-Aldrich (Germany) and were used as received. Ferric chloride hexahydrate, ferrous chloride tetrahydrate, and other chemicals were purchased from Merck (Germany).

2.2. Synthesis

2.2.1. Synthesis of Fe_3O_4 NPs

The co-precipitation method was employed to prepare Fe_3O_4 NPs using ferric chloride and ferrous chloride as iron (III) and (II) sources, respectively. The ferric chloride (3.24 g, 2 mmol) and ferrous chloride (1.98 g, 1 mmol) were dissolved in deionized water. Then an excess amount of aqueous NH_4OH solution was added with vigorous stirring for 30 min at 60 °C to achieve the Fe_3O_4 precipitate [29].

2.2.2. Synthesis of Fe_3O_4/Hydrogel/MWCNTs nanocomposites

The carboxymethyl cellulose (1 g) was dissolved in 2% (v/v) NH_4OH aqueous solution and mixed with PVA (1 g). The semi-IPN hydrogels were prepared by raising the pH of the mixture up to neutral by adding 1% (v/v) acetic acid solution. In this mixture, 0.5 g Fe_3O_4 was added and sonicated in an ice bath for 10 min. The resulting Fe_3O_4 containing hydrogel was centrifuged followed by the removal of the supernatant and was further washed. In another beaker, the pristine MWCNTs (0.5 g) were dispersed in 40 ml of distilled water by a probe sonicator. The aqueous solution of MWCNTs was mixed with Fe_3O_4 containing hydrogel. Subsequently, the heterogeneous solution was ultrasonicated for 30 min for homogenization and dried in a vacuum oven to obtain the Fe_3O_4/Hydrogel/MWCNTs composites.

2.2.3. Synthesis of Fe_3O_4/Hydrogel/PANI nanocomposites

Aniline (1 ml) was dissolved in 15 ml of 0.5 M HCl in a 100 ml beaker. In another beaker, ammonium persulphate (0.575 g) was dissolved in 10 ml of 0.5 M HCl. Then, the two solutions were mixed properly. The homogenized mixture was used for polymerization. The process of polymerization was completed within 30 min, and the resulting product was washed several times with water to remove the unreacted materials. Polyaniline (0.50 g) was mixed with Fe_3O_4 containing hydrogel and homogenized using water bath ultrasonication for 10 min, and subsequently dried under vacuum at 60 °C for 24 h to obtain Fe_3O_4/Hydrogel/PANI composites. The details of the measurements, gas sensing, and conductivity assay are given in the supplementary data.

3. Results and discussions

3.1. FTIR analysis

The FTIR spectra of the hybrid nanocomposites are given in Fig. 1. The broad band at 3311 cm^{-1} is attributed to –OH group of the polyvinyl alcohol [30]. The methylene groups present in the nanocomposites were confirmed by the appearance of strong bands at 2918–2852 cm^{-1} due to νCH_2 *sym* and *asym* stretching [31]. The FTIR spectrum of the hybrid nanocomposites showed an intense band at 1732 cm^{-1}, which corresponded to the vibration of the carbonyl bond (C=O). The spectrum of Fe_3O_4/Hydrogel/PANI composites showed certain characteristic bands of PANI that were assigned as follows: the bands at 1589 and 1490 cm^{-1} showed the characteristic C=N and C=C stretching of the quinoid and benzenoid rings, respectively. The peaks at 1261 and 800 cm^{-1} were assigned to the C—N stretching (aromatic amine) and C—H (aromatic ring) out-of-plane bending vibration, respectively [32].

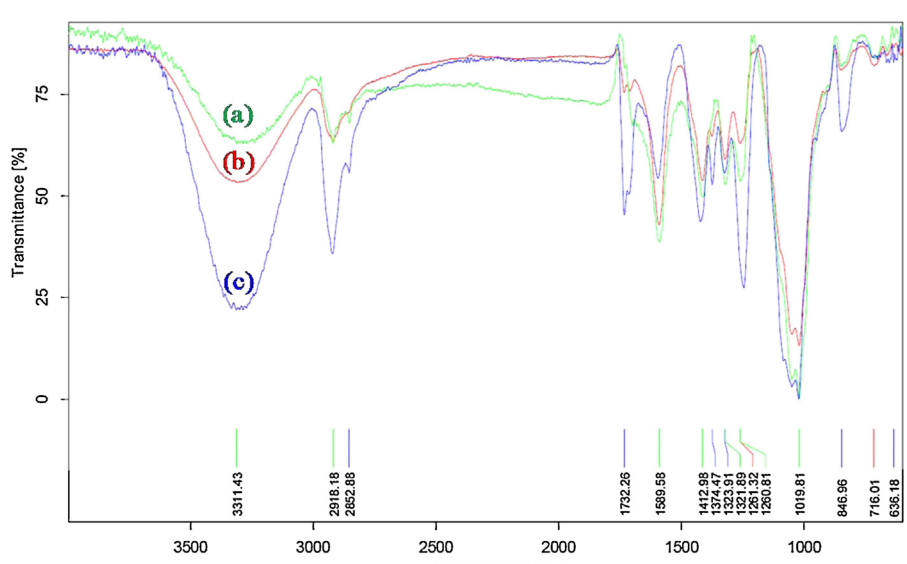

Fig. 1. FTIR spectra of (a) Fe_3O_4/Hydrogel (b) Fe_3O_4/Hydrogel/PANI, and (c) Fe_3O_4/Hydrogel/MWCNTs nanocomposites.