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Methanol vapor sensor based on poly(styrene-co-butylacrylate)/polypyrrole-EG core–shell nanocomposites

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ABSTRACT

Poly(styrene-co-butylacrylate)/polypyrrole-expanded graphite (EG) core–shell nanocomposites were synthesized by mini-emulsion polymerization. The particles were characterized by FT-IR, SEM, EDX, TEM and *I–V* analysis. TEM and SEM analysis reveals core–shell morphology of composite particles. Composite particles show higher dc-electrical conductivity compared to bare PSBA/PPy core–shell nanocomposites. The responsive capability of the nanocomposites towards methanol vapor was systematically investigated using a simple two probe configuration. The core–shell particles could detect methanol vapor of 100 ppm concentration with good response and recovery time.

1. Introduction

Now-a-days, core–shell particles with conducting polymer within the composite are used to modify the electrical property of the system. Conducting polymers such as polyaniline (PAni), polythiophene, polyacetylene, poly (p-phenylene sulfide), poly (p-phenylene vinylene), polypyrrole (PPy), always have been the center of attraction due to their conducting nature and potential applications such as sensors [1–4], actuators [5,6], light emitting diodes [7], but due to their brittleness it is very difficult to cast a film from these polymers and retain mechanical integrity. Therefore, considerable interest has been given in combining electrically conducting polymers with fillers in order to produce advanced core–shell conducting composites with high mechanical strength. These have several advantages [8]. First, depending on the type of polymer used for the core, these conducting polymer-coated latex particles exhibit very good mechanical strength and easy processing properties. Second, the amount of conducting polymer used can be greatly reduced in the shell phase without significant loss of conductivity. Since the material properties of both the core and the shell can be manipulated with ease, a vast range of particles can be made with controllable properties, useful in applications ranging from fillers and pigments in paints and coatings to highly sophisticated nano-sensors for cellular imaging.

Detection of pollutant gases, especially toxic gases, is significant in order to clean environment contamination. Semiconductor sensors are based on the interaction between the semiconductor and contact gases, which produces a change in electrochemical behavior in the material. There are several reports on the application of PPy and its composites in the detection of chemical substances like CH_3OH, $CHCl_3$, NH_3, vapors of common organic solvents. There has been remarkable deviation of electrical or optical properties whenever PPy interacts with these chemical substances [9,10]. Alcohol vapor is one of the most common gases for this type of sensing materials. Whenever the semiconductors interact with these chemical substances, the possible reactions may be either the conversion of the semiconductor into another compound or the extraction of an electron by oxygen absorbed from the atmosphere, resulting decreasing the electrical conductivity of the semiconductor. If organic vapor is present in the atmosphere, it may result in regain of the conductivity by reacting with the negatively charged oxygen, becoming oxidized and the electrons are returned to the semiconductor solid. The results indicate a higher electrical conductivity

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in the presence of organic vapor than in the pure air. This concept may lead to the development of a novel sensor material and device.

Ding et al. [10] reported a novel strategy to fabricate polystyrene-PAni (PS-PANi) core–shell structures using cationic PS latex particles without any further surface modification. They prepared imidazolium cation functionalized monodispersed PS particles by using precipitation polymerization and emulsion polymerization technique with the aid of ionic liquids containing imidazolium cations. Wang et al. [11] developed a core of a thermoplastic non-conducting polymer surrounded by a corona of a polyelectrolyte PPy was embedded into the corona via oxidative polymerization of the suitable monomer such that an electrical percolating shell is formed. A series of monodispersed poly (styrene-butyl acrylate) (PSBA) copolymer latex particles with different butyl acrylate contents, which was further coated with PPy and studied the effects of the concentration of PPy, the butyl acrylate content in PSBA copolymer and the nature of the counter-anion on the electrical conductivity of compression-molded samples [12]. The methanol sensing behavior of PPy–poly (vinyl alcohol) composite particles was investigated and examined the effect of thickness of the films on their sensing behavior [13]. The alcohol sensing behavior of inkjet-printed PPy thin film also reported and it was found that the value of the fractional resistance change, $\Delta R/R$, of the films increased linearly with increasing concentrations of both ethanol and methanol [14]. PPy-functionalized porous silicon for alcohol sensing had also reported [15]. The dramatic reduction of sensor photoluminescence response to low molecular weight alcohols was attributed to strong interaction with PPy surface layer and suppressed the analyte penetration into porous matrix. In our laboratory, we have synthesized graphene oxide-filled conducting PAni composites and used for methanol-sensing [16]. The dc-electrical conductivity of PAni was found to be 0.075 S cm^{-1} and this value was dramatically change to 0.241 S cm^{-1} by the incorporation of GO into the polymer matrix. A series of nearly monodispersed poly (styrene-co-methyl acrylate) (SMA) copolymer latex particles coated with PPy having different graphite contents were reported [17]. The electrical conductivity of the composites entirely depends upon the concentration of graphite in the PPy shell, the methyl acrylate (MA) content in SMA copolymer and the temperature. The conductivity of SMA/PPy could be further increased by incorporation of Ag nanoparticles in the shell [8]. The dc conductivity of the PPy silver coated SMA core–shell particles increases from 158.73 to 900.0 mS cm^{-1} with increase in silver concentration.

Recently, expanded graphite (EG), a two-dimensional nano sheet of covalently bonded carbon atoms, has received a rapidly growing research interest. This expansion of carbon source material has a strong pressure resistance, flexibility, electrical conductivity and can resist molten metal and permeability of ions. At the same time it is non-toxic, does not contain any carcinogens, it does not negatively impact environment. The thermal stability and electrical properties of polymers could be greatly improved by the incorporation of EG into the polymer matrix. Therefore, the potential of using EG-based materials for various applications such as super capacitor, sensor, has attracted much attention.

In this paper, we report the preparation of PSBA copolymer latex particles with different BA content, which is further coated with PPy and EG. EG with different contents is incorporated along with PPy particles and enhancement in conductivity of PSBA/PPy–EG core–shell composites are studied elaborately. The thermal, electrical and electrochemical properties of the core–shell particles are investigated. The dependence of electrical conductivity on EG content in the shell phase is examined. The responsive behavior of these core–shell particles towards methanol vapor of various concentrations is also investigated using a simple two probe configuration.

Table 1
Preparation for PS-PBA latex core.

Ingredients (in g)	PS-PBA-I	PS-PBA-II (amount in g)	PS-PBA-III	PS-PBA-IV
Styrene	10	10	10	10
Butylacrylate	3	5	7	10
Span-60	0.20	0.20	0.20	0.20
SDBS	0.15	0.15	0.15	0.15
$NaHCO_3$	0.10	0.10	0.10	0.10
Hydroquinone	0.01	0.01	0.01	0.10
BPO	0.15	0.15	0.15	0.15
Water	100	100	100	100

2. Experimental

2.1. Chemicals

The monomers styrene (Sty) and butyl acrylate (BA) were purchased from Aldrich and washed with 5% NaOH and finally washed with distilled water to remove the inhibitors. Pyrrole (Py) and graphite powder (<20 μm) were obtained from Aldrich and used without further purification. Span-60, sodium bicarbonate ($NaHCO_3$), acetonitrile, sodium dodecyl benzene sulfonate (SDBS), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), hydroquinone and ferric chloride ($FeCl_3$) were analytical grade chemicals (Merck) and used as received. EG was prepared by the chemical oxidation method [18]. For all purposes double distilled water was used.

2.2. Synthesis

2.2.1. Preparation of poly(styrene-co-butylacrylate) (PSBA)

The poly(styrene-co-butylacrylate) particles were prepared through emulsion polymerization of styrene (Sty) and butyl acrylate (BA). In a typical synthesis process, Sty (10 g) and BA (3 g) were stirred for 1 h at room temperature. The resulting mixture was kept between 0 and 5 °C for 10 min and then sonicated for 10 min (phase-I). In the meantime, an aqueous solution (phase-II) was prepared by addition of water (70 mL), span-60 (0.20 g), $NaHCO_3$ buffer under simple stirring at room temperature and then kept in the refrigerator for 10 min.

Phase-I and phase-II were mixed together under vigorous stirring for 15 min and then SDBS (0.15 g) was added to the mixture. The resultant mini-emulsion was transferred into a four-necked round bottom glass reactor equipped with a refluxing condenser, a mechanical stirrer, a nitrogen inlet and a thermometer pocket for polymerization. Subsequently, the system was degassed with nitrogen for 30 min at room temperature. When the temperature of the mixture reached 70 °C, benzoyl peroxide (0.15 g) (1% of the monomer, dispersed in 20 mL distilled water) was added to the mixture to initiate the polymerization under continuous mechanical stirring. Polymerization was carried out at 70 °C for 7 h. Polymerization was terminated by adding 1% aqueous solution of hydroquinone. As soon as the temperature of the reactor reaches room temperature, the latex was filtered. A series of PSBA latex was synthesized by varying the amount of BA. Recipe for the preparation of PSBA latex is given in Table 1.

2.2.2. Preparation of poly PSBA/PPy–EG core–shell

The composites particles with core–shell morphology were prepared by taking PSBA as the core component. In a typical synthesis process an emulsion containing 4 g of the PSBA latex was added to a two-necked round bottom flask equipped with a nitrogen inlet and a dropping funnel. The latex was diluted with 30 mL of doubled distilled water and stirred for 10 min. To this, 1.19 g of $FeCl_3$ (in 20 mL doubled distilled water), 1 mL of Py and varying amounts of expanded graphite (EG) (0.5%, 1.0%, 2.0%, 4.0%