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Novel and Sensitive Ethanol Chemi-Sensor Based on Nanohybrid Materials

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Environmental pollution is one of the global hot issues and need an urgent demand to detect and monitor the pollutants which affect the environment. Ethanol is one of the organic pollutants which cause severe harmful effect on environment due to its toxic nature. For the detection and quantification of organic pollutants, sensors are the promising and reliable technology which has vital role in the environmental and health monitoring. A lot of sensor materials have been exposed but the prospective for industrial development as sensors and environmental supplement are still limited due to its non eco-friendly nature. Therefore, environmental friendly and biodegradable ethanol chemical sensors have been fabricated by efficient utilization of poly propylene carbonate (PPC) and PPC/silica hybrid (H) for the detection and quantification of ethanol in the environment. PPC/silica hybrid membrane has been synthesized by intercalation of silica into PPC matrix using a sol-gel technique. The resulting membrane was characterized by Fourier transform infrared spectroscopy (FTIR), while the morphology of the hybrid was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Both PPC and H performed as best ethanol chemi-sensor in term of sensitivity. Hybrid membrane showed 2.08 times higher sensitivity (0.5698 $\mu A.cm^{-2}.mM^{-1}$) than pure PCC (0.2534 $\mu A.cm^{-2}.mM^{-1}$). Hybrid membrane also displayed 3.1 times lower limit of detection (LOD, 20.70 μM) than pure PCC (64.29 μM). Therefore, hybridization is an efficient route to fabricate proficient aqueous ethanol sensor.

Keywords: Poly propylene carbonate; Tetraethoxysilicate, Hybrid membrane; Structural properties; Ethanol sensing

1. INTRODUCTION

Environmental pollution is one of the severe issues in 21 century. All the environmental pollutions which exist in various forms such as air and water pollutions etc, contribute to health problems. Such environmental pollutions are the main focus of environmentalists and scientists. Various toxic organic pollutants are also directly responsible for these environmental pollutions. Organic pollutants are broadly used in industries and daily life and are the key effluents released by the industries to the environment. These organic effluents effect the environment, aquatic system and human health due to their toxicity, carcinogenicity and hazardous effect [1-13]. Among various organic pollutants, ethanol is the most common organic pollutants which badly effect the environment, due to their toxicity and hazardous nature. Ethanol is one of the organic pollutants which badly distress the environment and human health. The detection and quantification of ethanol is important and urgent for quality control of food, alcoholic beverages and drinking water [1-6].

Metal oxide nanostructures have widely been used as chemical sensors for the detection of organic pollutants but all these materials are synthesized by hydrothermal methods at high temperature [1-13]. Also these materials are neither environmental friendly nor bio-degradable. Here we are introducing environmental friendly and bio-degradable polymer which has gained increasing interest due to their environmental safety. Throughout the world today, the development of biodegradable materials has been a focus of enormous research challenge to the community of scientists. These materials tend to substitute synthetic materials in all the applications which cause huge amount of waste, for example, packaging. PPC is a polymer which can synthesize by copolymerization of propylene oxide and carbon dioxide. It is a key ingredient of greenhouse gases that cause global warming. It is a biodegradable aliphatic polycarbonate which could allow degradation under the natural environment and have gained considerable interests due to the imperative demand of green materials [14]. Due to biodegradability property, PPC is important in the field of biomedical and packing materials [15]. PPC is a smart green environmental material for many applications [16]. Therefore it is needed to evaluate its chemical sensing properties. However PPC alone has limited properties and does not fulfill the desired requirement. For this purpose silica is selected as inorganic nanofiller to improve various properties of PPC because hybridization of a polymer with inorganic nanofiller is a route to enhance its properties.

Polymer-inorganic hybrids particularly silica based composite is talented group of materials having high properties and wide range of practical applications [17-20]. Various methods have been used for the development of these materials. Among these synthetic procedures, sol-gel is the main route for the developments of advanced materials with high performance [17]. Sol-gel method involves hydrolysis and condensation of starting materials at mild conditions. Sol-gel procedure is well known method for the synthesis of well design, pure and controlled nano size multifunctional composite materials based on organic, inorganic and even biological components. These multifunctional materials have numerous applications in various fields including chemical and biological sensors, optical devices, catalysis, functional smart coating, fuel and solar cells, and as membranes in separation sciences especially in pervaporation and food packaging [21-25]. The main reason for wide range applications and high performance of silica-hybrid materials are due to their high thermal, mechanical and other properties which generally imported by incorporation of silica into the polymer matrix.

Therefore, in the present investigation we have made an attempt to develop hybrids by incorporation of silica precursors into PPC matrix so as to improve the PPC performance as chemical sensor. The chemical structure of the PPC and nanohybrid was confirmed on the basis of FT-IR spectrum while the morphologies were corroborated via X-ray diffraction (XRD) and scanning electron microscopy (SEM). The resulting hybrid demonstrated excellent sensing properties in terms of higher sensitivity and lower limit of detection.

2. EXPERIMENTAL

2.1. Materials and methods

Polypropylene carbonate (PPC) and tetraethylorthosilicate (TEOS) were purchased from Sigma-Aldrich. All the chemicals were of reagent grade and used without further purification. Distilled water was used throughout the study. For the synthesis of hybrid membrane, PPC (2.85 g) was dissolved in 17.0 ml of acetone with a constant stirring for about 30 min at room temperature. TEOS (0.15 g) was added to PPC solution and followed by addition of water (0.106 g) along with HCl (10 wt% of H_2O). The resulting mixture was stirred for 5.0 hours at room temperature and after terminating the reaction, the hybrid solution was cast onto a glass plate. After casting on glasss plate, the hybrid was subsequently dried for one hour at 50 ^{0}C and then membrane was peeled-off.

For the detection of ethanol, I-V technique was used in which a cell is constructed consisting film of PPC (contact surface area, 0.1 cm^2) and hybrid membrane (contact surface area, 0.1 cm^2) as a working electrode (directly) and Pd wire is used a counter electrode. Ethanol solution is diluted at different concentrations in DI water and used as a target chemical. Amount of 0.1 M phosphate buffer solution was kept constant as 20.0 mL throughout the investigation. Solution is prepared with various concentrations of ethanol from 0.17 mM to 8.5 M for both PPC and hybrid membrane. The sensitivity is calculated from the ratio of voltage and current of the calibration plot. 0.1 M phosphate buffer solution is used at pH 7.0 which has been prepared by mixing 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 solution in 100.0 mL de-ionize water.

The characterizations of PPC and hybrid membrane were carried out by using various techniques. The chemical structure of PPC and composition of the synthesized hybrid membrane were analyzed by Fourier transform infrared spectrometer (FT-IR) (Excalibur Series FT-IR). The structural characterizations were performed by X-ray diffraction (XRD) pattern by using Rigaku diffractometer using the Ni-filtered Cu-K_α1 radiation (λ = 1.5405 Å). The surface morphology of PPC and hybrid membrane was studied by using a JEOL Scanning Electron Microscope (JSM-840A, Japan). Before scanning, all specimens were coated with a conductive layer (400 Å) of sputtered gold. Chemical sensing performances of PPC and hybrid membrane were analyzed by electrometer (Kethley, USA) using I-V technique in two electrode system.

3. RESULTS AND DISCUSSION

3.1. Structural and morphological characterization of the PPC and hybrid

Fig. 1A shows the FT-IR spectra for PPC.

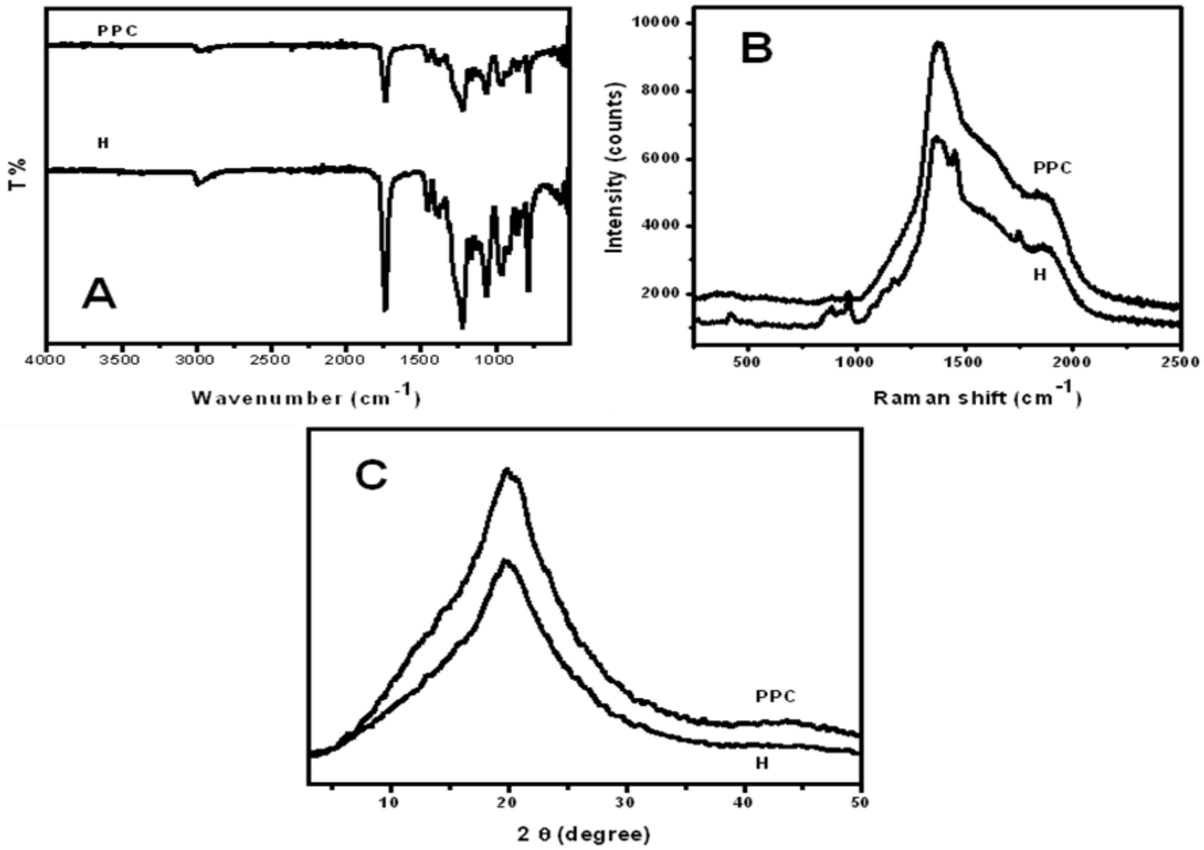


Figure 1. Typical (A) FT-IR spectrum, (B) Raman spectrum, (C) XRD patterns of PPC and H synthesized via sol-gel process.

PPC and hybrid were structurally illustrated by FTIR spectroscopy. PPC displayed FTIR peaks at 2800-2900 cm^{-1}, 1750 cm^{-1}, 1360, 1220 and 775 cm^{-1}, and 1100 cm^{-1} which confirms the presence of C-H, C=O, C-O, and C-O-C functional groups. FTIR spectrum of hybrid membrane also displayed stretching vibration band at 2800-2900 cm^{-1}, 1750 cm^{-1}, 1360, 1220 and 775 cm^{-1}, and 1100 cm^{-1} which are responsible for C-H, C=O, C-O, C-O-C functional groups, respectively. All the FTIR peaks of PCC were also found in the spectrum of hybrid membrane, indicating the synthesis of hybrid membrane. The intensity of peak related to C-O-C stretching was amplified for hybrid membrane which anticipated due to the creation of Si-O-Si bonds by adding TEOS. These results confirm the synthesis of hybrid membrane by electrostatic interaction of SiO_2 and PPC. The data is in good agreement with our previous report [26].

The chemical structures of PPC and hybrid membrane were also supported by Raman spectroscopy [Fig. 1B]. Raman spectrum of PPC shows peaks at 415 cm^{-1} (C-O-C deformation), 880 cm^{-1} (C-COO stretching), 962 cm^{-1} (C-C stretching and CH_3 rocking), 1071 cm^{-1} (C-O stretching), 1131 cm^{-1} (CH_3 asymmetric rocking), 1169 cm^{-1} (COC asymmetric stretching), 1366 cm^{-1} (CH deformation and CH_3 symmetric deformation), 1452 cm^{-1} (CH_3 asymmetric deformation), and 1751 cm^{-1} (C=O stretching). All these characteristics peaks of PCC were detected in the spectrum of hybrid membrane but less crystalline as compared to PPC, suggesting the formation of hybrid membrane [27].

The morphological structures of PPC and hybrid membrane films were studied by powder X-ray crystallography as shown in Fig. 1C. Both PPC and hybrid membrane displayed broad halo at 4.4 Å indicate that both PPC and synthesized hybrid membrane are amorphous without crystalline or crystalline-amorphous phase. PPC and hybrid membrane did not show any peak related to crystalline or crystalline-amorphous phase. The XRD peak of PPC exhibited higher intensity as compared to hybrid membrane which specifies that incorporation of silica reduces the crystillinity of the PPC. The XRD data is in good agreement with the data reported by Seo et al [28].

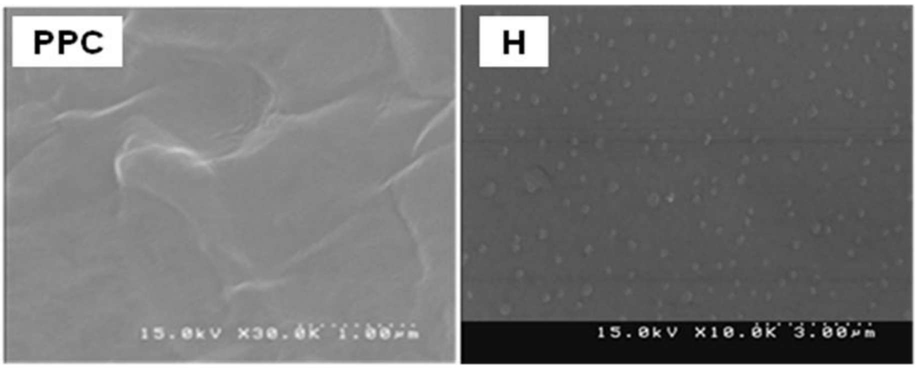
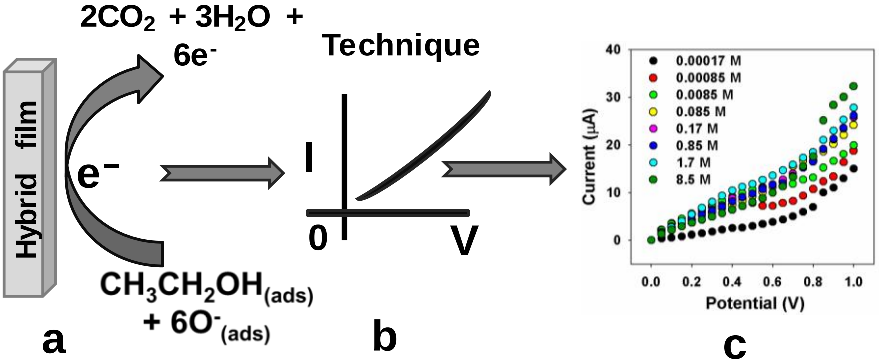


Figure 2. Typical SEM images of PPC and H synthesized via sol-gel process.



Scheme 1. Schematic views of (a) Hybrid membrane film, (b) I-V detection technique, and (c) outcome of I-V experimental result in presence of hybrid membrane film.

Fig. 2 shows the SEM images of the surfaces of PPC and hybrid membrane. SEM image of the hybrid membrane clearly shows that there is no aggregation and agglomeration of particles which suggests that silica particles were well dispersed in the PPC matrix. It is confirmed that the silica atoms were well and consistently dispersed in the PPC matrix. The data is consistent with the data reported by Zhou et al [29].

PPC and hybrid membrane were employed for the detection of ethanol by using their thin-films as a working electrode, where the electrical responses have been executed by I-V method [1-5], which is presented in the scheme 1. The electrical responses of hybrid membrane without ethanol (gray-dotted line) and with 100.0 μL ethanol (dark-dotted line) in 0.01 M phosphate buffer solution (pH = 7.0) are shown in Fig. 3A. It is observed by injecting the target chemical from the Fig. 3A that hybrid membrane shows a significant increased in the electrical current which reflects the sensitivity of hybrid membrane towards ethanol. Thus by injection of target chemical, increase in electrical response suggest that hybrid membrane has rapid and sensitive response to the ethanol. The fast electron exchange and good electro-catalytic oxidation properties are responsible for the high electrical response of hybrid membrane sensor towards ethanol [6-8].

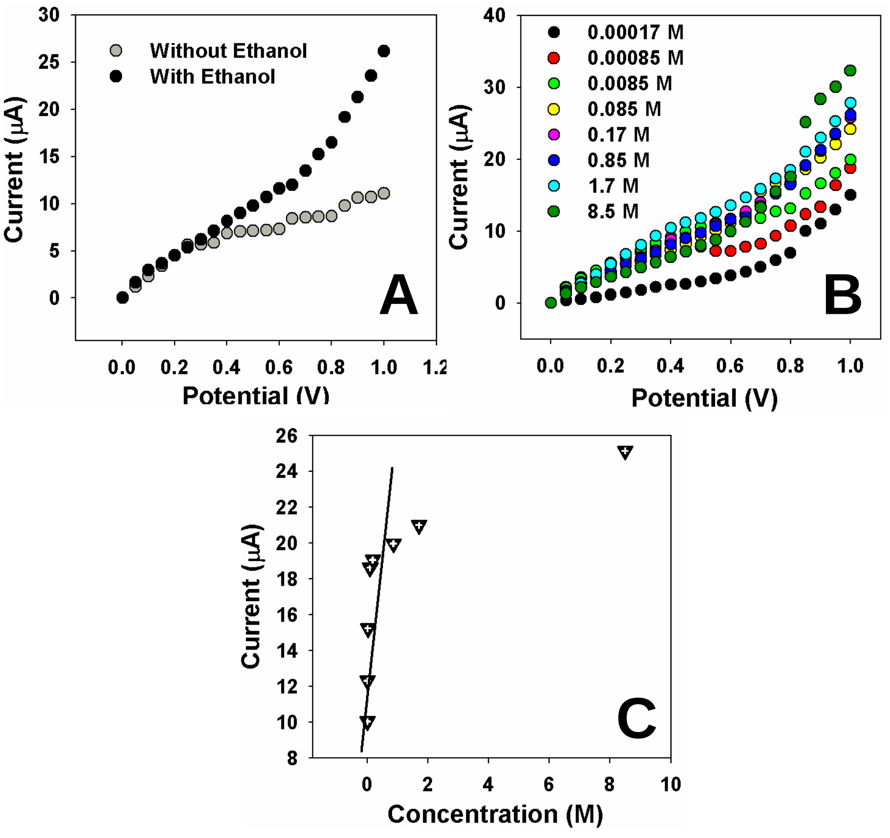


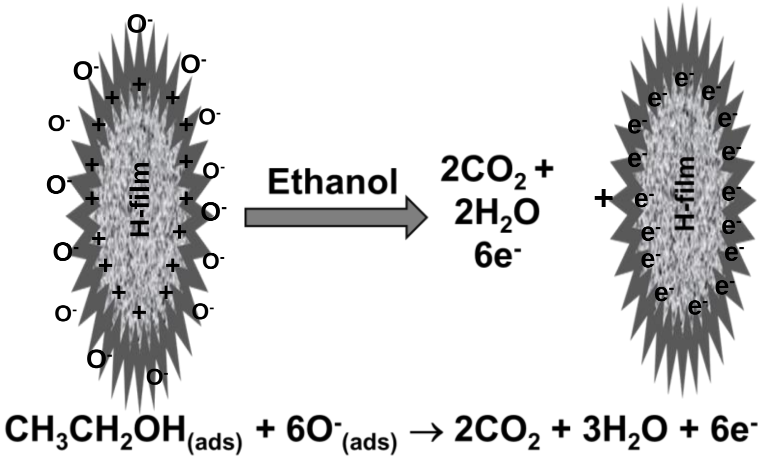
Figure 3. I-V curves of H (A) with and without ethanol, (B) with concentration variation of ethanol and (C) calibration curve.

Ethanol undergoes two-step process by applying to I-V technique and increases the conductivity. The first step involve either dehydrogenation or dehydration which produces CH_3CHO (eq. 1) or C_2H_4 (eq. 2) as intermediates, respectively.

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad (1)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (2)$$

In second step CH_3CHO or C_2H_4 undergoes oxidation by the surrounding oxygen molecules which are physisorbed on the surface sites and produces CO_2, CO, and H_2O [scheme 2].



Scheme 2. Mechanism of ethanol in the presence of hybrid membrane film.

The concentration of ethanol was varied from 0.17 mM to 8.5 M by adding de-ionized water to ethanol in different proportions and investigated the effect of ethanol concentration on the electrical response of hybrid membrane thin film. Ethanol was successively added in the range of 0.17 mM to 8.5 M into continuously stirred 0.01 M PBS solution (pH = 7.0) and the graph for hybrid membrane is depicted in Fig. 3B. Each I-V response to varying concentration of ethanol (delay of time, 1sec) shows current of hybrid membrane as a function of ethanol concentration at room conditions. It is observed that by increasing the concentration of target ethanol, the current steadily increased. Increasing electrical current with increasing ethanol concentration indicates that the hybrid membrane film conductivity increased which is ascribed to the increase in ions providing excess electron to the conduction band of the material [9-11].

The calibration curve of hybrid membrane sensor is plotted from the variation of target ethanol concentration and displayed in Fig. 3C. In calibration curve, initially the current increases with increase in ethanol concentration and after certain concentration, electrical response become constant which clearly shows that the hybrid membrane is sensitive to ethanol at lower concentration while at high concentration, saturation of the sensor takes place. Thus calibration curve [Fig. 3C] depicts two sensitivity regions; region at lower concentrations is linear with correlation coefficient (R) of 0.6464. The sensitivity is calculated from the slope of the lower concentration region of calibration curve, which is 0.5698 $\mu A.cm^{-2}.mM^{-1}$. The linear dynamic range of this sensor exhibits from 0.17 mM to 0.85 M and the detection limit was estimated based on signal to noise ratio (S/N), to be 20.70 μM. Above

2.0 mM concentration the sensor become saturated. This sensor shows higher sensitivity at low concentration region and would be useful at lower ethanol concentration at room temperature. Sensor showed high sensitivity at lower concentration while at higher concentration the electrical responses become contact. This higher sensitivity of sensor at lower concentration is due to availability of the free surface for physic-sorption process which plays a major role in sensitivity of the sensor. At higher concentration, chemisorption process takes place which cause saturation of the sensor. Thus chemisorption process effect the sensor performance due to the unavailability of free hybrid membrane sites for ethanol adsorption [11-13].

PPC based ethanol chemical sensor was studied in order to check the effect of silica on the performance of PCC for the detection of ethanol. PPC based ethanol sensor showed sensitivity of 0.2534 $\mu A.cm^{-2}.mM^{-1}$ with a response time less than 10 sec. The sensing results demonstrate that addition of silica is responsible for higher sensitivity and lower detection limit (20.7 μM). Thus the formation of hybrid membrane by addition of silica significantly increased the sensitivity which is 2.08 times higher than that of pure PPC. This increase in sensitivity of PPC by addition of silica may be due to the increase in meso-porous behavior of PPC. The hybrid membrane provides more surface area for the adsorption of ethanol which results in high electrical response and thus high porosity is responsible for high sensitivity.

4. CONCLUSIONS

Using the sol-gel technique, PPC based hybrid membrane was successfully synthesized using TEOS as silica precursor. The structure of PPC and hybrid membrane were evaluated by FT-IR and Raman spectroscopy, while the morphology has been confirmed by XRD and SEM. PPC/silica hybrid film showed the superior sensing properties and lower detection limit as compared to PPC toward the detection of ethanol. Thus silica plays an important role in improving the sensing property of PPC and consequently expands its application as chemical sensor.

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