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Selective H_2S sensor based on CuO nanoparticles embedded in organic membranes

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ABSTRACT

We report on H_2S gas sensors based on CuO nanoparticles that are embedded within polymer membranes of poly-vinyl-alcohol (PVA) and glycerol ionic liquid (IL). The nanoparticles were fabricated by the colloid microwave assisted hydrothermal method that enables a precise control of nanoparticle size. Polymer solutions of PVA and 5% IL were prepared with different concentrations of nanoparticles. Next, the solutions were used to fabricate polymer membranes by the solution casting method. The produced membranes were flexible and they hold semiconducting properties. Each membrane was encapsulated between two electrical electrodes where the top and bottom electrodes were made of stainless steel grid and copper sheet, respectively. A constant voltage was applied across the electrodes, and the electrical current response signal was measured. The measurements revealed that those sensors were sensitive to H_2S gas with concentrations as low as 10 ppm, and they functioned at low temperatures. In addition, their sensing behavior was reversible which enabled repeatable use of those sensors. Those sensors were also selective to H_2S, and they exhibited fast response of 20.4 ± 12.8 s. Moreover, the sensors were easy to manufacture, thus, they have potential to be used for practical field applications.

1. Introduction

H_2S is a highly corrosive and toxic gas that generates harmful effects on the nerve system of human at low concentrations and causes mortalities at higher concentrations [1]. This gas can be produced from hydrodesulfurization of crude oil containing sulfur compounds, and many natural gas fields [2]. In addition, H_2S can be produced from different sources related to petroleum industry such as bacterial reduction of sulfate to H_2S, thermal decomposition of sulfides in kerogen and/or oil, and thermochemical reduction of sulfate to H_2S [3]. Therefore, accurate H_2S sensors should be developed to detect concentrations as low as few tens of ppm to avoid exposure to H_2S gas, especially in fields related to petroleum refining industry.

Various methods have been reported in literatures for detection of H_2S including sensors based on nanoparticles and solid electrolyte sensors [4–6]. Many of those sensors are costly and their operating temperature is high. Therefore, the development of new sensors that include polymer membranes that and nanoparticles is desirable [7]. Such sensors are easy to fabricate, can be operated at low temperature with low electrical power requirement, and flexible [8]. In addition, electronic devices made of organic materials and inorganic nanoparticles are much attractive toward enabling applications such as transparent electronic devices which are power saving, size compactable, and easily portable [9,10].

Ionic liquids represent promising materials that can be used for different applications in chemistry, including gas detection [11]. They exhibit exceptional properties such as: good ionic conductivity attained at room temperature, low values of vapor pressure, volatility and low toxicity, and environmentally friendly [12,13]. Therefore, they can be added to insulating polymers to control their conductivity [10], and to produce membranes that are suitable for electrochemical sensors.

Incorporating nanoparticles within organic polymer to produce gas sensors is an active research field, due to their various practical applications, and it can greatly enhance the sensitivity and selectivity of the sensors [14,15]. Semiconducting metal oxides have been extensively studied recently because of their unique physical and chemical properties that enable their utilization for gas sensing applications [16,17]. In general, metal oxides exhibit poor electrical conductivity since most charge carriers are trapped in surface states. Those carriers are activated to the conduction

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when exposed to a target gas which increase the conductivity of the metal oxide. Herein, copper oxide (CuO) nanoparticles exhibit strong affinity toward H_2S gas, thus, doping a polymer membranes with CuO nanoparticles is expected to enhance the sensitivity of the sensor to H_2S [16,18]. In addition, CuO is an attractive p-type metal oxide semiconductor that has unique electrical, optical, and catalytic properties [19]. Using CuO nanoparticles with a narrow size distribution for these applications would further promote the chemical reactivity of the nanoparticles because as the surface-to-volume ratio of the particle increases, the number of reactive sites increases [20]. CuO is also well known for its low cost and the antifouling properties which is effective for reducing the growth of many microrganisms [21]. Therefore, CuO nanoparticles can be utilized to produce biocompatible implementable devices.

In our previous works, we demonstrated the fabrication of organic polymers that are based on poly-vinyl-alcohol (PVA) and poly-vinyl-alcohol/poly acrylamide co-acrylic acid (PAA) with engineered conductivity [22–25]. The control of the conductivity was achieved by doping the organic polymers with ionic liquids (IL). The ionic liquids serve as both an electrolyte and a diffusion barrier. Our goal in this work is to fabricate H_2S gas sensors that utilize CuO nanoparticles embedded in our newly developed PVA-glycerol organic polymer with controlled conductivity [25]. Herein, a polymer membrane containing an ionic liquid serves as a host for nanoparticles, and then electrically probed with microelectrodes. The suitability of using semiconducting nanoparticles for organic devices was demonstrated in previous reports [10,26]. To the best of our knowledge, H_2S gas sensing behavior of organic gas sensors that utilize CuO nanoparticles was never investigated previously. The sensors presented in this work are easy to manufacture [25], and they are accurate and selective to H_2S, thus, they might be considered for practical production.

2. Experimental

2.1. Materials

Dimethylformamide $(CH_3)_2NC(O)H$ (DMF) with purity of 99.0% was purchased from Sigma-Aldrich. Copper(II) acetate monohydrate $(Cu(CH_3COO)_2{\cdot}H_2O)$ with purity of 99.8% was acquired from Sigma-Aldrich. Commercial PVA-124 was also purchased from Sigma-Aldrich with a molecular weight of 124–186 kg/mol and 99% hydrolyzed. All other laboratory reagents were retrieved from Sigma-Aldrich and used as supplied. Double distilled water was used in the preparation of stock solution of PVA. Glycerol was obtained from Quartek Corp. NC.

2.2. Synthesis of CuO nanoparticles

CuO nanoparticles were synthesized using the colloid microwave assisted hydrothermal process to allow the formation of nanoparticles with precise size control [19]. The synthesis was executed using a microwave reactor (CEM, Discover-SP system, 909156, USA). 60 mg of $Cu(CH_3COO)_2{\cdot}H_2O$ was dissolved in 50 ml of DMF under continuous stirring for 3 h at 25 °C. The produced solution was then kept for 24 h for aging, then it was exposed to microwave radiations at 45 °C with a power of 300 W and radiation frequency of 2455 MHz. The solution was kept under continuous stirring repeatedly to complete the reaction and nucleation process. The working cycle of the microwave reactor was set as 30 s on and 15 s off. The on/off cycle was repeated 10 times. The following reaction describes the formation of CuO nanoparticles [19]:

$$Cu(CH_3COO)_2{\cdot}H_2O + (CH_3)_2NC(O)H \rightarrow CuO + CH_3COO_2 CHN(CH_3)_2 + H_2O \quad (1)$$

It should be noted her that the reaction temperature was kept constant since, in general, nanoparticle size increases with temperature as a result of the decrease in supersaturation at elevated temperature [27]. In addition, the nucleation rate (R_N) increases with temperature according [28]:

$$R_N = \frac{C_0 kT}{\left(3\pi\lambda^3\eta\right)} e^{-\frac{\Delta G^*}{k_B T}}$$

Where C_0 is the initial concentration, k_B is Boltzmann constant,T is temperature,λ is the diameter of the grown species, η is the viscosity of solution, and ΔG^* is the critical free energy.

2.3. Preparation of polymer membranes

The polymer membranes utilized in this work were synthesized by the solution casting method that was described in our previous works [10,22–24,26]. Briefly, 10 g of PVA granules was dissolved in 100 g of double distilled water inside a flask under continuous stirring on a hotplate at 90 °C until it was completely dissolved. This process make up a stock solution of 10% by weight. 50 ml of ethanol was added to the PVA solution after cooling it to room temperature. To dope the membranes with 5% (by weight) of ionic liquid, 0.5 g of glycerol was added to 10 g of PVA stock solution and mixed under continuous stirring condition at 90 °C until the solution becomes completely homogenous and clear. The desired CuO nanoparticle concentration (weight/weight) within PVA-IL was achieved by adding suitable percentage of nanoparticles under continuous stirring at 90 °C.

The resulting transparent polymer solution was then casted on a PTFE plate to form a thin film. The excess water and ethanol were evaporated slowly at 70 °C in a vacuum oven over night. This process produced uniform films that were 100–500 μm thick, as shown in Fig. 1.

2.4. Device fabrication

Polymer membranes were cut into $1 \times 1\,cm^2$ pieces. Thermal evaporation was used to create a gold thin film (50 nm thick) on the backside of each polymer membrane. Each device was fabricated by placing a polymer membrane on a $2 \times 2\,cm^2$ copper sheet that was used as a back contact (in contact with the gold thin film). A stainless steel grid with a grid size of $250 \times 250\,\mu m^2$ was used as a top electrode and pressed on top of the membrane, as shown in Fig. 1.

2.5. Characterization techniques

The size and morphology of nanoparticles were characterized using a transmission electron microscope (TEM). In addition, a Zetasizer (Malvern Instruments, Model ZEN360, England) was used to confirm nanoparticle size. The morphology of the nanoparticles was evaluated using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) apparatus that enabled the evaluation of nanoparticle composition. The crystal structure as well as the composition of nanoparticles were determined using a Shimadzu 6100 X-ray diffractometer (XRD) with Cu-Kα radiation (λ = 1.5406 Å).

Electrical characterization and sensor response measurements of the sensors were performed using a Keithley Instruments source measurement unit (KI 236). The response of the device to different gases was characterized inside a temperature controlled chamber under different concentrations relative to air. The target gases were introduced into a gas mixer, and their flow rates were controlled using Bronkhors mass flow meters. The test chamber was placed