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Cellulose nanocrystal/graphene oxide composite film as humidity sensor

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ABSTRACT

Cellulose nanocrystal/graphene oxide composite was reported as a humidity sensor in this study. The composite film was fabricated using simple blending the materials followed by oven drying. The composite film offers a unique advantages of cellulose combined with functionality of GO. It was capitalized to design renewable, flexible and cheap humidity sensor. Performance of the composite film as a humidity sensor was evaluated on the basis of relative capacitance change at different humidity level. Synthesized composite film was characterized using scanning electron microscope, Fourier transform infrared spectroscope, and X-ray diffraction. Environmental effect such as temperature was taken into account on the sensor performance. The sensing mechanism is explained on the basis of presence of hydrophilic functional groups in the composite. The linear and fast response of the developed sensor is advantageous.

1. Introduction

Monitoring and controlling humidity play a very important role in many industries. Controlling living environment, intelligent control for laundry, smart control for cooking in microwave ovens are some examples of humidity sensors. Humidity sensors are being used in automobile industries for window defogger and motor assembly line; in medical field respiratory equipment, incubators, medicine processing; in agricultural sectors to control greenhouse air, monitoring soil condition. Researchers are working hard to improve the performance of humidity sensor such as fast response, good sensitivity and small hysteresis. There are several transduction techniques for designing humidity sensors: for example, resistive, capacitive, optical, mechanical and acoustic techniques [1–10].

Generally, there are two types of humidity sensors: resistive type [11,12], and capacitive type [11,13]. A number of materials such as porous ceramic, electrolytes, polymers are being used for humidity sensors [14–16]. Humidity sensing ceramics include TiO_2, Al_2O_3 as sensing materials to develop the sensors [17,18]. Ceramics show high mechanical strength as well as high resistance to temperature. On the other hand polymers are more compatible with IC production process. Some examples of humidity responsive polymer are cellulose acetate, poly methyl methacrylate, etc. [19,20]. Also, porous silicon has been reported as humidity sensing material [21].

Cellulose, the most abundant source of raw material on earth, is renewable material that can maintain our resources from the environment so as to overcome degradation of natural environmental services and diminished productivity. It is a kind of solid polymer which colorless, odorless and nontoxic. Some promising properties are also possessed, such as high mechanical strength, hydrophilicity, relative thermo-stabilization, biocompatibility, piezoelectricity, light weight, low material price and eco-friendly [22]. Composites based on cellulose are being used for coatings, pharmaceuticals, laminates, textile, optical films, etc. Recently, cellulose has been reported as a smart material [23]. Nowadays, cellulose became a very promising material for the development of flexible devices because of its light weight, low cost, environment friendly, good optical properties [24,25]. Recently, nanocrystalline form of cellulose is reported as high dielectric material which makes it a very good choice for development of many devices. To improve its properties, functional groups should be incorporated with it.

Graphene, tightly packed carbon atoms in two dimensional honey comb structure, is a nanomaterial of the day. It provides many opportunities for sensor development [26]. Graphene has a high surface area, good mechanical strength, high carrier mobility

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at room temperature, quantum hall effect, increased electrical and thermal conductivity, optical transparency and excellent thermal conductivity [27]. Graphene Oxide (GO), a functional derivative of graphene, contains hydroxyl, ether, carboxyl and carbonyl functional groups. Presence of these functional groups make it easy to blend GO in other polymer matrix. Inclusion of GO in cellulose matrix can improve its mechanical, electrical as well as dielectric properties [28]. Many GO based sensors like solvent sensors, temperature sensors have already been reported [29,30].

Present work reports a simple fabrication process of cellulose nanocrystal (CNC) – GO composite film and its humidity sensor application. The CNC-GO composite film can offer a unique advantages of cellulose combined with functionality of GO. These synergistic advantages of CNC-GO composite film can be capitalized to design renewable, flexible and cheap humidity sensor. The morphology and structure of the composite film are studied using a scanning electron microscope (SEM), Fourier transform infrared spectroscope (FTIR) and X-ray diffraction (XRD). The humidity sensing capacity of the composite film is tested by measuring the capacitance change with different relative humidity and environmental effect on the sensor performance was also studied by considering the temperature change.

2. Experimental details

2.1. Materials

Natural flake graphite, Avicel (cellulose microcrystalline from cotton linter with a size ~50 μm), potassium permanganate ($KMnO_4$), phosphoric acid (H_3PO_4), hydrochloric acid (HCl) and 30% hydrogen peroxide (H_2O_2) solution were procured from Sigma-Aldrich. Sulfuric acid (H_2SO_4), ethanol was purchased from Daejung, South Korea.

2.2. Material preparation

The CNC base matrix in this study was prepared by H_2SO_4 (175 mL of 30% (v/v) aqueous) hydrolysis of Avicel powder (20.0 g) under mechanical stirring (200 rpm, 6 h) at 60 °C [31]. Alkaline treatment of Avicel powder was done before acid hydrolysis to remove the non-cellulosic components. The resulted suspension of CNC was washed with deionized (DI) water several times to ensure a neutral pH suspension. Then the suspension was homogenized using a homogenizer and dialyzed overnight. Besides, GO was synthesized by the improved graphene oxide synthesis method [32] and dispersed in DI water. Then GO suspension was mixed with CNC suspension at a desired ratio (5 wt% and 10 wt%) followed by homogenization.

To make a CNC-GO composite film, the suspension was poured in a plastic petri dish and dried in an oven at 60 °C to evaporate the water and turn into a solid film. After 8 h of drying, GO blended CNC composite film (CGO) was obtained. The number after abbreviation, CGO, represents the weight percentage of GO present in the composite film. Finally, the film was collected and stored in a dried box. To compare the results, a pure CNC composite film was also fabricated following the same method.

2.3. Humidity sensor fabrication

To fabricate the humidity sensor, an interdigital transducer (IDT) patterned electrode was deposited on a PET substrate using traditional lift off process. After that CNC/GO solution was poured drop wise on the pattered electrode and dried in the oven at 60 °C. Then two end of the IDT patterned electrode was wired and connected to an LCR meter (HP 4284A). Fig. 1 shows the schematic of the fabricated sample. The comb distance of IDT electrode was 27 μm.

3. Characterization

The morphology of CNC was investigated using atomic force microscope (Veeco AFM). JEOLJSM −6400 F microscope was used to capture SEM images of the samples to investigate the morphology. The SEM samples were prepared by coating a platinum layer using ion sputter (EMITECH, K575X). The FTIR spectra was taken using a FTIR spectroscope (Bruker Optics, Billerica, MA) in the range of 500–4000 cm^{-1} by averaging 16 scans (resolution was 4 cm^{-1}) at 1 min intervals to demonstrate the grafting of GOs to CNC. XRD patterns of the samples were checked with an X-ray diffractometer (DMAX-2500) using CuKα target radiation at 50 mA and 45 kV, at scanning rate of 0.0151 min^{-1}. The diffraction angle was varied from 10° to 40°.

The variation in dielectric constant of the CNC matrix and its composites was measured within the frequency range of 20 Hz to 10 kHz using the LCR meter. The measurement was performed at 25 °C and 25% relative humidity (RH) at 1 V.

To evaluate the humidity sensor performance of the composite film, relative capacitance change was measured with the change of relative humidity using the LCR meter at 1 kHz and 1 V. Humidity was changed using an environmental chamber (Kwang-Myung Science, South Korea) that can control its inside temperature and humidity. To check the response of the sensor, relative humidity was increased step by step with 5% increment. To justify the

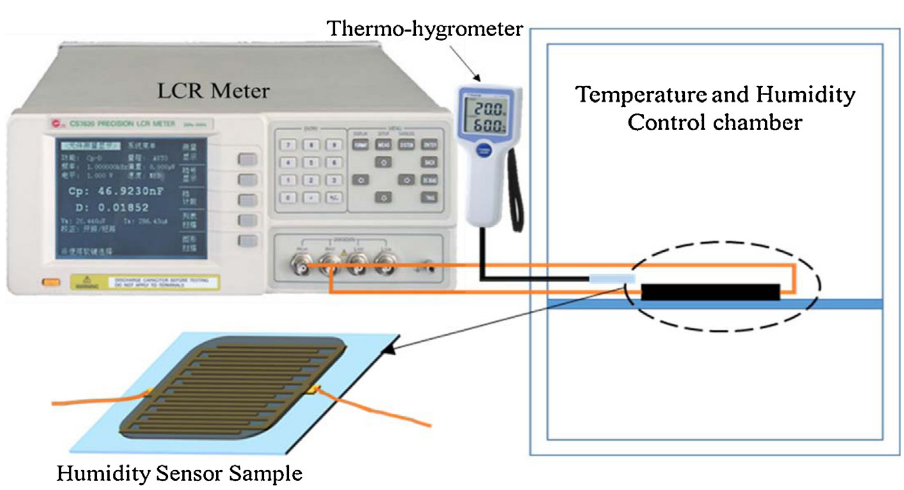

Fig. 1. Schematic diagram of the fabricated sensor and its performance measurement.