



# Photo-crosslinked thiol-ene based hybrid polymeric sensor for humidity detection



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## ABSTRACT

This study describes the preparation and characterization of new surface modified carbon nanotube particles (CNT) containing thiol-ene based hybrid polymers by photo-polymerization of pentaerythritol tetrakis, glyoxal bis(diallyl acetal), trimethylol propane triacrylate monomers and their usage for humidity sensing. CNT surface was photografted with polyethylene glycol acrylate (PEGA) to produce hydroxyl groups. Hydroxyl functionalized CNT/PEGAs were acrylated using isocyanatoethyl methacrylate (IEM) in order to improve the dispersion and interfacial interaction in composites. Furthermore, different amounts of gold nanoparticles containing compositions were also prepared. The humidity sensing properties of two samples were investigated by impedance measurements. The effects of CNT/Au modification, the applied potential bias and alternating current frequency on the electrical properties and the humidity sensitivity were determined. FCNT0 and FCNT5Au0.5 exhibit extremely high selectivity against humidity compare to various solvents; ethanol, acetone, methyl acetate and chloroform. FCNT0 has a reasonable good sensor performance for humidity measurements. It has high sensitivity, selectivity, stability, response/recovery and linear response properties in a full range of humidity measurements.

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## 1. Introduction

Humidity sensors are widely applied in various applications for many aspects, such as industrial, medical, ecological and environmental monitoring. Relative humidity sensors can be mainly classified into ceramic, semiconductor and polymer humidity sensors [1–4]. Among the sensitive materials various polymers such as polyimides [5–8], polysulfones [9], polyesters [10–12], conducting polymers [13–16], polyelectrolytes [17–19], and composites with a variety of organic and inorganic materials [20–26] have been widely used in humidity sensors to date. Most of the polymer based humidity sensors are based on the measurement of the changes in resistance and capacitance, as a result of the interaction between water molecules and sensitive polymeric layer. Traditionally, capacitive humidity sensors, which response to water by varying their dielectric constants, consist of hydrophobic materials having somewhat hygroscopic sites in order to respond to

moisture. In spite of their excellent fast and linear humidity response over a wide range of humidity, it was reported that the capacitive type of humidity sensors exhibit undesirable high hysteresis, comes from large voids in the polymeric structure, existed as a consequence of humidity adsorption [27,28]. The formation of voids may deform the polymers and shorten the lifetimes of the sensors. The cross-linking, graft polymerization and modification of the sensitive dielectric layers were suggested to reduce or eliminate the hysteresis as well lifetimes of the sensors [29–32]. In this study, the new impedimetric type of humidity sensors based on photo-crosslinked thiol-ene polymeric materials are reported for the first time. It was proposed that the synthesized polymers have some highly hydrophilic polar sites and they can be used as non-deformable humidity sensitive materials. The humidity sensing properties of the sensors, including sensitivity, selectivity, response/recovery time, stability, hysteresis and the effect of applied potential bias, frequency and CNT/Au were investigated.

## 2. Materials and methods

### 2.1. Materials

Polyethylene glycol acrylate, carbon nanotube, gold nanoparticle, isocyanatoethyl methacrylate, pentaerythritol tetrakis, glyoxal

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bis(diallyl acetal), trimethylol propane triacrylate, 1-hydroxycyclohexyl phenyl ketone, camphorquinone and all solvents were obtained from the Sigma Aldrich.

## 2.2. Carbon nanotube (CNT) modification by photografting

CNT functionalization was performed similar to the previous work which was conducted on polyaniline [33]. CNT powder dispersed in a solution consisting of %25 polyethylene glycol acrylate and %75 t-butyl alcohol-distilled water (3:1) by an ultrasonicator and exposed to UV light at 350 nm for 15 min. After completion of the UV exposure, the photografted CNT was immediately immersed in 1,4-dioxane for about 1 h to dissolve all soluble unbounded polymers at its surface, then washed with methanol, and dried at 80 °C for 4 h. A schematic illustration of the reaction between CNT and PEGA is shown in Fig. 1.

## 2.3. Preparation of surface modified CNT

Photografted CNT (1 g) powder was dispersed in a dichloromethane (20 mL) and 3 g of isocyanatoethyl methacrylate (IEM) was added. This mixture was stirred for 3 h at 250 rpm at 40 °C. Dichloromethane was then evaporated under vacuum. The resulting resin was dried in a vacuum oven at 40 °C for 48 h. A schematic illustration of the reaction between CNT/PEGA and IEM is shown in Fig. 2.

## 2.4. Preparation of UV curable hybrid polymers

UV-curable formulation was prepared by mixing different amounts surface modified CNT (0, 1, 2 and 5 wt%), Pentaerythritol tetrakis(3-mercaptopropionate), glyoxal bis(diallyl acetal), trimethylol propane triacrylate (TMPTA), and the photoinitiators (1-hydroxycyclohexyl phenyl ketone (IRGACURE 184) and camphorquinone). A schematic illustration of the preparation of surface modified CNT and different amounts of gold nanoparticles containing UV curable hybrid polymers are shown in Fig. 3. The prepared formulation was then transferred in a round shaped Teflon® mold ( $R = 4$  mm). After 180 s irradiation under UV-lamp, 1 mm thick polymeric support was obtained. Formulation of hybrid polymers are given Table 1.

## 2.5. Characterization techniques

FTIR spectrum was recorded on Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer. Thermogravimetric analyses (TGA) of hybrid polymers were performed using a Perkin-Elmer Thermogravimetric

analyzer Pyris 1 TGA model. Samples were run from 30 to 750 °C with heating rate of 10 °C/min under nitrogen and air atmospheres, respectively.

SEM imaging of the hybrid polymers were performed on Philips XL30 ESEM-FEG/EDAX. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a platinum coating.

The wettability characteristics of hybrid polymers were performed on a Kruss (Easy Drop DSA-2) tensiometer. The contact angles ( $\theta$ ) were measured by means of sessile drop test method in which drops were created by using a syringe. Measurements were made using 3–5  $\mu$ l drops of distilled water. For each sample, at least five measurements were made, and the average was taken.

## 2.6. Instruments and measurements of sensor

The sensing properties of the hybrid polymers were studied by using the interdigitated gold electrodes (IDE) (glass substrate:  $L 22.8 \times W 7.6 \times H 0.7$  mm, 150–200 nm Au thickness,  $125 \times 2$  digits, 10  $\mu$ m electrode bands/gaps) (Dropsens, Spain). The hybrid polymers formulation of FCNT0 and FCNT5Au0.5 were coated on the IDE electrodes by screen printing method. The formulations were casted on the glass electrodes by using a piece of rubber, then the coating was subjected to UV irradiation [34].

The measurements of I-V characteristic and impedance were achieved with an LCR meter (HIOKI 3522-50) in a 250 mL of four necked glass test chamber under the conditions of the measurement frequency and applied voltage at ambient temperature of  $20 \pm 0.5$  °C. An Aalborg SDPROC flow controller and two AFM 26 mass flow meters were used to obtain different vapor compositions in flow rate of 200 mL/min. An ambient air supplied from an air pump was also used to see the effect of the contaminants in the laboratory atmosphere. A Carl Roth P330 capacitive type of commercial humidity sensor (measuring range: 0–99% RH, accuracy: of  $\pm 3\%$  RH) was used to measure actual humidity and temperature.

## 3. Results and discussion

In this study, a series of surface modified CNT containing UV curable hybrid polymers were prepared and characterized. All surface modified CNT and gold nanoparticles were successfully dispersed in UV-curable hybrid polymers matrix. Furthermore the humidity sensing properties of FCNT0 and FCNT5Au0.5 coded formulations were studied.

### 3.1. Structural characterization

ATR-FTIR spectra of CNT and the surface modified CNT are shown in Fig. 4 and also hybrid polymers are shown in Fig. 5.

As seen from Fig. 4, surface modified CNT exhibited characteristic absorption peaks at about  $3300$   $\text{cm}^{-1}$ ,  $2920$   $\text{cm}^{-1}$ ,  $1720$   $\text{cm}^{-1}$  and  $1637$   $\text{cm}^{-1}/810$   $\text{cm}^{-1}$  for N–H, C–H, C=O and C=C double bond stretching vibrations, respectively. From these results it is clearly that CNT was modified successfully.

Fig. 5 shows the FT-IR spectra of FCNT0, FCNT5 and FCNT5Au0.5 polymers.

The absence of the reactive thiol band at  $2570$   $\text{cm}^{-1}$  and C=C double band at  $1638$   $\text{cm}^{-1}$  and  $810$   $\text{cm}^{-1}$  in the spectra indicate that the desired reaction is successfully completed [35]. In ATR-FTIR spectra of the nanocomposites we could not be able to detect any absorption bands for the modified CNT and gold nanoparticles, because of their low amounts in the composites.

### 3.2. Morphology of the photocured hybrid polymers

SEM images of the fractured surface of UV-curable hybrid polymers are given in Fig. 6a–e. It is clearly observed that the surface modified CNT and surface modified CNT-Au are uniformly dispersed in and

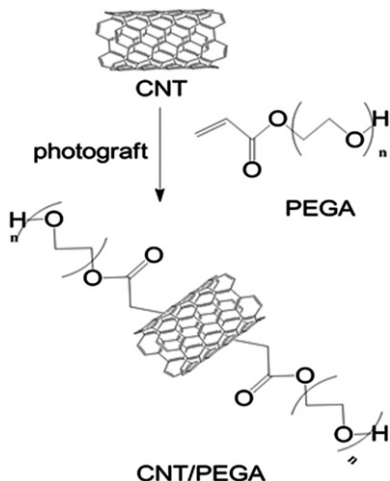


Fig. 1. CNT modification by photografting.

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