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High-performance humidity sensors utilizing dopamine biomolecule-coated gold nanoparticles☆

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ABSTRACT

This study presents a simple process for producing resistance-based humidity sensors utilizing dopamine (DA)-coated gold nanoparticles (AuNPs) as the sensing material. Highly hydrophilic dopamine biomolecules are physically bonded to 4–6 nm AuNPs to enhance humidity sensing performance. Results show that the DA-coated AuNPs have good humidity sensing performance in the range of 20–90% R.H. The measured resistance response is more than 1900 times greater than sensors using the same AuNPs without a DA coating. The developed humidity sensor shows rapid response time for water adsorption (5 s) and desorption (10 s). Moreover, a 3-day long-term measurement at low medium and high humidity ranges also showed that the developed sensor has good stability. The method developed in this study provides a simple and inexpensive method to produce high-performance humidity sensors by using DA-coated AuNPs.

1. Introduction

Moisture distributed in nature is normally measured as a physical quantity called humidity, which is usually divided into absolute and relative humidity. The ability to accurately measure changes in relative humidity is necessary in industrial and daily life applications [1]. Furthermore, being able to precisely control humidity by using high-performance humidity sensors is important for many applications in such agriculture, industry, healthcare, and the storage of many items [2,3]. Although many commercial humidity sensors have been developed, they suffer from a number of drawbacks including slow response rate, low sensitivity, complex fabrication processes and a low degree of stability. Since the first miniaturized humidity sensor was fabricated in 1994 [4], many miniaturized humidity sensors have been reported via a variety of working mechanisms and different sensing materials. Humidity sensors with higher sensitivity and faster time response are the competing factors for developing these sensors. In general, sensing materials with large specific surface areas were usually used to enhance the sensing performance of the humidity sensors.

In general, typical sensing materials for commercial available humidity sensors can be divided into metal oxides [5,6], ceramics [7,8], and polymers [9,10]. However, most miniaturized commercial humidity sensors may suffer from the disadvantages of lower sensing performance or slower response time. Since using these humidity sensors for the industrial applications, it is not durable for operating with a high temperature environment or achieving the lower power consumption. In addition, the conventional solid state humidity sensors is usually require a waiting period of more than 30 s to allow the sensor to reach a stable water adsorption state [11]. Alternatively, polymer-based humidity sensing materials, such as polyethyleneimine (PEI), usually require a longer response time of 4–6 min [12]. The humidity sensor with a nano-porous film composed of polycarbonate and cellulose also required a long period of time (4–8 min) for water adsorption [13]. Since the polymer-based sensing materials exhibit a long response time, they may not meet the requirement for immediate and rapid humidity measurements. Therefore, it is important to develop humidity sensors with rapid sensing response. Moreover, to enhance the ability of analyzing the measured response by humidity variation is also one of the important factors for developing high performance humidity sensors. Nohria et al. [14] presented a resistive-type humidity sensor, which was measured by the poly-aniline film that has been self-assembled on an interdigital electrode. The resistance responses only showed the resistance change of 700 Ω in the humidity range of 50–90% R.H. Yao et al. [15] also reported a novel material for humidity sensing, which used the core-shell structure of polyvinyl alcohol (PVA) coated gold nanoparticles as the sensing material. However, the sensing performance for this new material only showed the capacitance change of 0.66 nF in the humidity range of 11.3–93%

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R.H. Therefore, it is difficult to achieve the accurate measurement for the small humidity change with these humidity sensors.

A number of recent reports indicated that the nano-materials have shown great potential for developing high performance humidity sensors due to the large specific surface area for water adsorption. Kuang et al. [16] developed a humidity sensor made by a SnO_2 nanowire as the humidity sensing material. The water molecules substituted the pre-adsorbed of oxygen molecules on the SnO_2 surface and changed the electrical property of the sensing film. Thus, the increased conductivity was easily used as the indicator to measure the humidity variation in the range of 30–85% R.H. Alternatively, polyimide doped with the deliquesce salt of magnesium chloride was reported for developing high performance humidity sensors. Great capacitance response was obtained in the humidity range of 15–95% R.H. [16–19]. Therefore, sensing materials based on nanostructures can significantly improve the conductivity of the typical humidity sensors. Moreover, gold nanoparticles (AuNPs) have been well known for having large surface-to-volume ratio and widely used for chemical and biochemical sensor applications. Many studies have also reported that the interdigital electrodes coating with the nano-particles can provide a large electric conductivity change for vapor sensing [20–22]. Besides, AuNPs have been used as the sensing materials for humidity sensor, such the ligand capped of AuNPs was also reported for high performance measurement of the humidity variation [23,24]. Since the surface property of the AuNP is considered to be hydrophobic, the surface requires a modification toward the hydrophilic property for using a humidity sensing material. Dopamine (DA) is known as a neuron transmission molecule that transfers transmitting neuron signals in the synapse. This biomolecule is considered to be highly hydrophilic due to the exposed of amino and hydroxyl groups. Xi et al. [25] developed DA for surface modification of hydrophobic co-polymer membranes to significantly improve surface hydrophilicity. Furthermore, DA-AuNPs have even been reported to have an ability for surface modification of the PDMS micro-channel, which solved the difficulties in controlling electro-osmotic flow and residue [26]. Therefore, the DA-AuNPs can absorb water molecules on the big surface area and shows the potential for high performance humidity measurement.

This study provides a novel highly hydrophilic molecule of dopamine (DA) for surface modification of AuNPs to be used for a humidity sensing material. The proposed sensor exhibits a high-sensitive and high-performance of humidity measurements, due to the large specific surface area of the AuNPs can provided the better humidity sensing performance. In addition, the hydrophilic nature of the modified DA molecules on the AuNP surface provides better moisture adsorption. The mechanism for enhancing the sensing performance of developed sensor is clearly discussed and the sensing performance is also systematically investigated. The surface morphology, effects of temperature, the influence of the number of DA-AuNP coating layers, time response, and long term stability of the proposed humidity sensor are presented in this study. Hence, the proposed humidity sensor presents a material for sensitive humidity variation measurements with rapid response times.

2. Working principle of the humidity sensor

This work presents a novel humidity sensing material for developing a resistance-based humidity sensor. The measurement of humidity variation in this work was performed using 25 pairs of planar interdigital electrodes with a total surface area of 8 mm × 8 mm. The proposed humidity sensor exhibits a fast response time, low noise to signal ratio and repeatability. Since the measured change in resistance is significantly correlated to the humidity variation, this work provides a novel material to enhance the moisture adsorption ability in resistive-type humidity sensors. The working principle of the proposed humidity sensor is based on the hydrophilic amine groups of the exposed DA molecules on the AuNP surface, which have the affinity to adsorb water molecules as shown in Fig. 1(A). Because the water molecules dissociate into H^+ and OH^- at room temperature, Eq. (1) provides evidence of the link between H^+ and $R\text{-}NH_2^-$. When the chip is placed in a high humidity environment, the increase of existing OH^- leads to increased conductivity in the chip. This dynamic behavior of localized charges on DA-modified AuNP has been reported [27]. Hence, the more water molecules that have been adsorbed on the DA-AuNP, the lower resistance that can be measured from the proposed sensor chip.

$$R\text{-}NH_2^- + H_2O \rightarrow R\text{-}NH_3 + OH^- \qquad (1)$$

Furthermore, surface modification of DA molecules on the AuNP surface can greatly enhance sensor sensitivity due to the higher concentration of the exposed DA on the AuNP surface, increasing water adsorption. Before humidity measurements using the proposed humidity sensor are made, it is essential to know the water adsorption ability of the sensing material. Fig. 1(B) presents the contact angle of the sensor surfaces of AuNPs with and without the DA coating. The obvious variation between each surface treatment shows that the contact angle without coated DA was 45°, while the coated surface achieved the low contact angle of 15°. Results indicated the surface energy significantly increased by coating with DA. Thus, the hydrophilic property of the sensor surface was greatly enhanced, and the sensitivity for the humidity sensing was improved. Therefore, the exposed DA molecules on the AuNP surface play an important role in water adsorption ability.

3. Materials and methods

3.1. Reagent

Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$) (99.99%), tetra-*n*-octylammonium bromide (98%), and 4-(dimethylamino)pyridine (DMAP) were purchased from Alfa Aesar® and sodium borohydride ($NaBH_4$) were supplied by Acros®. Dopamine hydrochloride (DA) was purchased from Sigma–Aldrich®. In this study, deionized and distilled water was used throughout for the preparation of DA-coated AuNP colloids.

3.2. Preparation of the gold nanoparticles for sensing materials

First, a volume of 20.0 μL aqueous gold-salt solution (1 M) was added to 30.0 mL toluene dissolved with 15 mM tetraoctylammonium bromide (TOAB) and stirred for 3 min [28]. Then, 10 mL $NaBH_4$ reduction agent (0.4 M) was added into the toluene bath of gold-salt solution and stirred for 10 min. At this time, AuNPs with diameters around 13 nm immediately occurred and a ruby red color was present in top layer of toluene. Second, 1.0 mL of the toluene-based synthesized AuNPs was extracted and added into a 1.0 mL 4-(dimethyl-amino)pyridine (DMAP) solution (0.2 M) for the AuNP phase transfer, which causes the DMAP molecule to be adsorbed onto the nanoparticle surface for crossing over the water/toluene phase boundary [29]. Finally, 0.5 mL DA solution was added into the DMAP-AuNP colloids and stirred for 10 min. The DA molecules replaced the DMAP molecules on the AuNP surface and produced the developed humidity sensing material of DA-AuNPs. Fig. 2(A) presents the TEM image of the prepared AuNPs in 1 M DA solution, where the diameter of the particles was 4–6 nm. Fig. 2(B) presents the FESEM (JEOL, JSM-6700F) image showing the DA-AuNPs on the sensor substrate. Note that the measured size for the DA-AuNPs