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Humidity effect on the monolayer-protected gold nanoparticles coated chemiresistor sensor for VOCs analysis

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Abstract

Two gold-thiolate monolayer-protected nanoparticles were synthesized and used as interfacial layers on chemiresistor sensors for the analysis of violate organic compounds (VOCs). Toluene, ethanol, acetone and ethyl acetate were chosen as the target vapors. Both the resistance and capacitance were measured as the function of analyte concentrations. The effect of humidity on the sensor sensitivity to VOCs was investigated. The sensitivity decreases with humidity increasing, depending on the hydrophobicity of the target compounds. Less effect was observed on the higher hydrophobic compounds. While the relative humidity (RH) increased from 0 to 60%, the sensitivity to acetone decreased by 39 and 37%, respectively on the Au-octanethiol (C_8Au) and Au-2-phenylethanethiol (BC_2Au) coated sensors, while the sensitivity to toluene decreased by 12 and 14%, respectively. These results show that the sensors coated with hydrophobic compounds protected-metal nanoparticles can be employed in high humidity for hydrophobic compounds analysis. The resistance responses to VOCs are rapid, reversible, and linear, while the capacitance response is not sensitive and consequently not applicable for VOCs analysis. The response mechanism was also discussed based on the sensor response to water vapor. The capacitance response is not sensitive to the film swelling in dry environment.

Keywords: Nanoparticle; Chemiresistor; Sensor; Humidity; Vapor analysis

1. Introduction

In recent years, monolayer-protected metal nanoparticles have attracted continuous research interests owing to their unique electronic and electrochemical properties [1–5] as well as potential applications in molecular electronics, catalysis, molecular recognition, gas chromatograph and sensing [6–18]. The monolayer-protected metal nanoparticle consists of a metal core at a few nanometers in diameter and an organic compound shell, which facilitates the dissolving in organic solvent and protects the particles from aggregation. The electronic and electrochemical properties of these materials are determined by the core size and the property of the shell molecules [13,15,16,19–21]. Nanoparticles with different core size can be easily prepared by changing the experimental conditions, such as the synthesis temperature [20] or the molar ratio of metal to shell molecules [4,13,19]. A wide rang of function groups can be incorporated either in the alkyl chain or at the chain terminal, resulting in electrochemical property change [15,16,21,22]. The core-shell reactivity also facilitates the nanoparticles being functionized through place-exchange reactions [3,23,24].

The unique core-shell structure and the obvious advantages make the nanoparticles ideal sensing interfaces for chemiresistor sensors. A thin film of the nanoparticle materials is cast onto patterned microelectrodes and the change in resistance is monitored. Electronic conduction is conducted by electron tunneling or hopping between the metal cores [9,25,26], and can be changed by vapor sorption that causes the insulating monolayer swelling and dielectric property change. The vapor sorption alters the distance between

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cores, resulting in a change in the electron hopping rate. Preliminary studies of gold-thiolate nanoparticles as chemically sensitive interface were conducted in a number of groups [14–17]. Wohltjen and Snow [14] reported a chemiresistor vapor sensor coated with a thin film of octanethiol-encapsulated gold nanoparticles. The test to toluene and trichlorethylene showed that remarkable changes in conductance can be yielded by vapor sorption and desorption. In Cai and Zellers's work [15] lower detection limit than polymer coated SAW sensor was obtained. A dual chemiresistor vapor sensor array using 2-phenylethanethiol and octanethiol-encapsulated gold nanoparticles as sensing interfaces were employed as a GC detector. Compared to the sensor array alone or to single-detector GC systems, the capabilities for vapor recognition were improved by the combination of response patterns and GC retention times. Evans et al. [16] investigated the response of chemiresistor sensors coated with four different Au-arenethiolated nanoparticles with OH, COOH, NH_2, and CH_3 as terminal groups, respectively. The nature of the terminal groups is a key factor to affect the relative strength of the particle–particle and particle–solvent interactions and determines the particles properties. Distinct response patterns to each of eight vapors were obtained. Subsequent work by this group [27] predicted that the sensitivity is related closely to the property of the shell material and the size of the Au core. The responses of OH functionalized nanoparticle films are mainly contributed to the film swelling at high vapor concentrations and to the film permittivity changes at low vapor concentrations. Han et al. [17] investigated two types of networked nanoparticles as sensing film materials on both chemiresistor and quartz crystal microbalance (QCM). One was crosslinked with 1,9-nonanedithiolate and another one was crosslinked through the head-to-head hydrogen bonding at the terminal of the gold-bound 11-mercaptoundecanoic acid. The vapor absorption on QCM sensor was correlated with the film resistance changes measured by the chemiresistor. The group conducted by Murray [25,26] investigated the effect of vapor sorption on the electron-hopping rate using networked nanoparticles, indicating that the vapor sorption results in the electron-hopping rate decreasing. Grate et al. [22] compared the sorption behavior of Au-thiolated nanoparticles film materials with typical sorptive polymers used on vapor sensor, concluding that the nanoparticles materials are less sorptive than the polymers. Synovec's group applied dodecanethiol monolayer-protected gold nanoparticle as stationary phase in open tubular gas chromatography [12,28]. Much faster separation time for nerve agent simulant mixture analysis was achieved by using nanoparticles as stationary phase [28]. The Au-nanoparticle was also used as the sensing interface in ion-selective field-effect transistor for adrenaline analysis based on the potential change resulted from the interaction of the nanoparticles with the target molecules [18].

However, so far little attention was paid on the humidity effect on the sensor response, and neither on the capacitance response. Since the permittivity of water is much higher than that of most organic compounds, capacitance is a useful determinant to elucidate the vapor response mechanism based on the response to water vapor. In addition, the knowledge of humidity effect on the violate organic compounds (VOCs) response is necessary for the sensor applications in field. This paper focus on the humidity effect on the sensor response, and the sensor response to water vapor. Two gold-thiolate monolayer-protected nanoparticles were prepared and were cast on interdigital microelectrodes. Both the resistance and capacitance changes were measured in situ. The response mechanism upon vapor sorption was investigated based upon both the resistance and the capacitance responses.

2. Experimental section

2.1. Chemicals

Octanethiol ($C_8H_{17}SH$), 2-phenylethanethiol, tetraoctylammonium bromide (TOAB), and hydrogen tetrachloroaurate tetrahydrate were obtained from Aldrich Chemical Co. Sodium borohydride was purchased from Fisher Scientific Co. Other chemicals include organic solvents purchased from commercial sources. All chemicals were used as received. Deionized and distilled water was used through the experiment.

2.2. Synthesis

The C_8Au and the BC_2Au nanoparticles were synthesized based on the method first described by Brust et al. [29] and used by others [14–19,27]. Briefly, hydrogen tetrachloroaurate (aq.) was extracted into toluene using five-fold molar excess of the phase transfer reagent TOAB under vigorous stirring. After the aqueous phase was removed, the desired amount of thiols with molar rate of 4:1 of Au to thiol was added, followed by 10-fold molar excess of sodium borohydride. With sodium borohydride addition, the reaction mixture gradually turns dark. Keep stirring for at least 3 h at room temperature, then the organic phase was isolated, washed with water and concentrated to approximate 10 mL at ∼50 °C under reduced pressure. The black product was precipitated by the dropwise addition of the toluene solution into 200 mL of stirred absolute ethanol. After standing overnight at room temperature, the clear solvent was decanted and the collected product was washed with ethanol twice. The product was further re-crystallized by dissolving it in 5 mL of toluene and precipitated in 200 mL of ethanol.

2.3. Instrumentation and measurements

The chemiresistor sensor was fabricated from interdigital microelectrodes consisted of 50 pairs of Au electrodes (Cr adhesion layer) with 15 μm width, 5 mm length, and 15 μm spacing. The sensor was spray-coated with 0.2% gold nanoparticle solution in toluene. The ac resistance changes

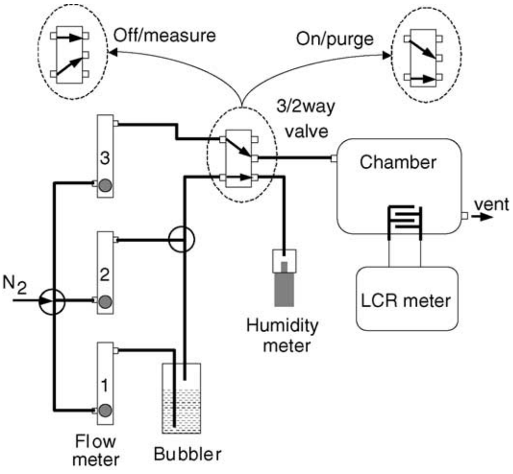

Fig. 1. Schematic illustration of the test system, (a) for the sensor responses to water vapor, (b) For the test of the humidity effect on the sensor response to VOCS.

were monitored in situ using a digital LCR meter (Model TH2816, Tonghui Electronic Co., Ltd., P.R. China) at a signal frequency of 1 kHz. The coating was continued until the desired resistance (∼150 kΩ) achieved. Then the sensor was stabilized at 60 °C overnight. The resistance after heating is lower than the resistance before heating. The heat-treated sensor is much more stable than untreated sensors. The resistance of BC_2Au-coated and C_8Au-coated sensors after heating are around 100 and 120 kΩ, respectively.

The sensor was placed in a chamber equipped with rotor flow meters and a humidity meter (Digital Hygro-Thermometer, model 8708, AZ Inst. Co. Taiwan). Fig. 1 shows the setup for water vapor response test. Both the resistance and capacitance were measured at the same time with the digital LCR meter, which was interfaced to personal computer. The parameter setting and the data collection were carried out with the software provided with the instrument. Nitrogen was used as the blank gas. Dry N_2 was divided into two streams. One stream was bubbled through a liquid water reservoir. The desired humidity was generated by adjusting the flow rate of the dry and wet N_2, and was measured downstream with a commercial humidity meter. While test the water vapor response, dry N_2 was used as blank. The system was first purged with N_2 until stable resistance achieved. Then turn off the 3/2 way valve to conduct the wet N_2 with constant humidity through the system.

While test the humidity effect on the VOC response, wet N_2 at certain humidity was used as the blank. A little modification was made on the setup so that the test air was cycled in a closed system with a volume of 1.12 L including the connect tubes. The system was first purged with wet N_2 until stable resistance achieved. Then turn on the 3/2 way valve to circle the system. Certain volume of the target organic solvent was syringed into the system to get the desired concentration.

The time-dependent resistance and capacitance were recorded in situ. While stable resistance achieved, the 3/2 way valve was switched to continue the next measurement. The measurements were reproduced at least two times on each concentration.

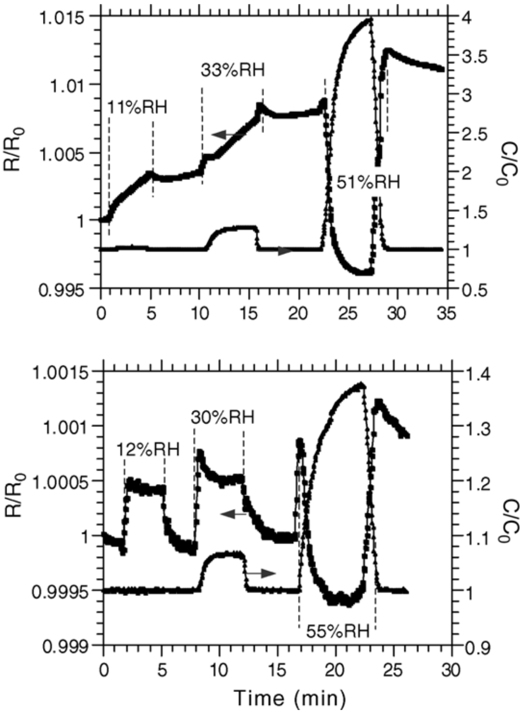

Fig. 2. The sensor response profiles at different humidity. Top: C_8Au coated sensor, bottom: BC_2Au coated sensor, R_o and C_o are the resistance and capacitance in dry N_2, respectively.

3. Results and discussion

3.1. Response characteristics

The response of both C_8Au and BC_2Au coated sensor to water vapor was investigated with dry nitrogen as blank. The tested humidity is from 10 to 60% RH, the highest humidity in field in most cases. The response profiles are shown in Fig. 2 where the responses were normalized relative to the baseline responses, and the water vapor concentration is expressed as relative humidity (RH). Theoretically 1% RH is equivalent to 312 ppm at 25 °C. The sensor response to water vapor at low humidity is different from that at high humidity. At low humidity, there are positive resistance responses (i.e. resistance increases with humidity) but little capacitance response. At high humidity there are negative resistance responses and significant positive capacitance responses. These results suggest that there are two opposite factors affecting the response. The negative factor that results in the resistance decrease becomes significant around 30% RH at which there is a rapid increase in resistance followed by a slow decrease for both the BC_2Au and the C_8Au-coated sensors, indicating that the effect is independent on the film material. With humidity increasing, the negative factor increases and surpasses the positive factor around 40% RH, after which net negative resistance responses were observed as shown in Fig. 3. Also around 30%

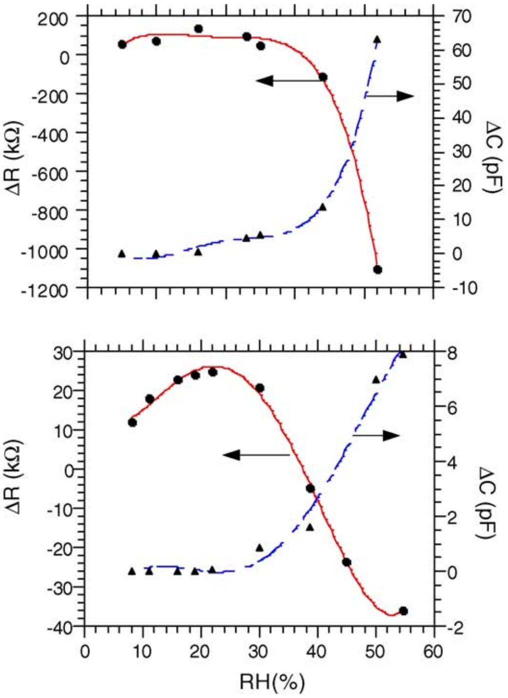

Fig. 3. Humidity-dependent sensor response. Top: C_8Au coated sensor, bottom: BC_2Au coated sensor.

RH the capacitance response becomes significant as shown in Figs. 2 and 3. Around 20% RH a little capacitance response was observed and below 15% RH no capacitance response, although at this humidity significant resistance response was observed. As a comparison, the response profiles to toluene are shown in Fig. 4. There are always positive resistance responses but no capacitance response during the concentration investigated in dry environment. The other three compounds are with the similar response profiles as toluene and the results are not shown. The fact that no capacitance response at low humidity indicates that the capacitance response is not sensitive to the film swelling at low humidity environment because that the positive resistance response can be mainly contributed to the film swelling according to the approach suggested by Neugebauer and Webb [30]:

$$\sigma = \sigma_0\, e^{-\delta_E \beta}\, e^{-E/RT} \tag{1}$$

where β is the electron transfer coupling coefficient typically at the order of 1 Å^{-1}, δ_E the edge to edge core separation, σ_0 the relative conductivity of the dielectric medium separating the metal cores. E is the activation energy required to generate a positive and a negative charged cores from two initially neutral cores. E is inversely proportional to the relative permittivity in the medium separating the cores. This approach was used to explain the response of nanoparticle sensors by Evans' [27] and Murray's group [31].

The first is the tunneling term related to the electron tunneling between two metallic cores, and the second is the hop term related to the electron hopping between two charged cores. The electronic conductivity in monolayer-protected gold nanoparticle materials is determined by the core–core separation (δ_E) and the dielectric properties (σ_0 and E) of the medium separating the metal cores. The vapor absorption on one hand changes the dielectric properties through changing the permittivity of the medium, and on another hand causes the nanoparticle material swelling. Material swelling increases the core separation, resulting in a decrease in the conductivity (σ) based on Eq. (1). Since β is of the order of 1 Å^{-1}, the conductivity is much sensitive to the core separation, giving about three times decrease in conductivity per Å increase in the separation. The direction of resistance response due to the change in the medium dielectric properties is dependent on the permittivity of the vapor absorbed relative to the film medium permittivity. While the vapor permittivity is higher than the medium's, the vapor absorption will increase the medium conductivity. Otherwise the vapor absorption will decrease the medium conductivity. For most organic compounds whose permittivity is close to the medium permittivity, the conductance change caused from the variance in the medium dielectric properties can be neglected compared with that caused from the change in core separation. The film swelling governs the resistance response and positive resistance response was observed as shown in Fig. 4. Actually in most investigations the contribution to the conductance response due to the changes in film dielectric properties was not considered [27,31]. As for water whose relative permittivity is much higher than the medium material permittivity, the partitioning of water into the film can result in a significant change in the medium

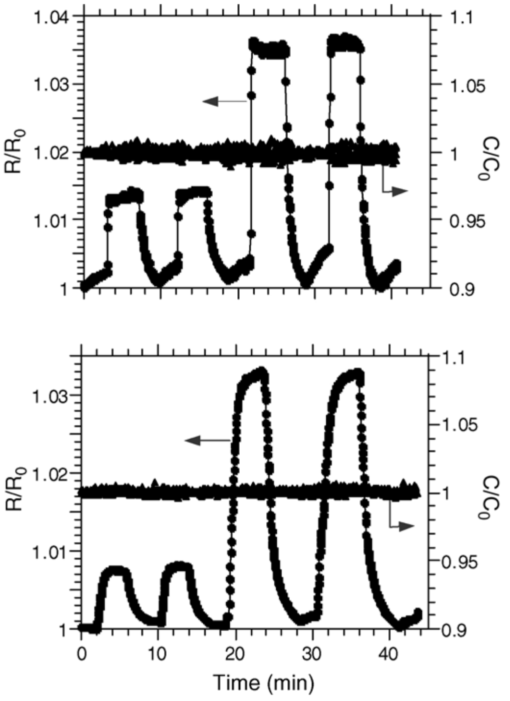

Fig. 4. The sensor response profiles to toluene. Top: C_8Au coated sensor; bottom: BC_2Au coated sensor, R_o and C_o are the resistance and capacitance in N_2, respectively. The other three compounds have similar response profiles. There is no capacitance response.

Table 1
Effect of humidity on the sensitivity

C. R[a] (ppm)			C_8Au			BC_2Au		
			0% RH[b]	20% RH	60% RH	0% RH	20% RH	60% RH
Toluene	100–1000	S[c]	19.6	18.2	17.2	0.52	0.44	0.45
		$\Delta S/S_0$[d] (%)	0.0	−7.1	−12	0.0	−15	−14
Ethyl acetate	120–1200	S	1.99	1.83	1.76	0.17	0.16	0.12
		$\Delta S/S_0$ (%)	0.0	−8.0	−12	0.0	−5.9	−29
Ethanol	200–2000	S	0.71	0.53	0.5	0.035	0.027	0.026
		$\Delta S/S_0$ (%)	0.0	−25	−30	0.0	−23	−26
Acetone	150–1500	S	0.52	0.33	0.32	0.049	0.045	0.031
		$\Delta S/S_0$ (%)	0.0	−36	−39	0.0	−8.2	−37

[a] Concentration range explored in ppm.
[b] Relative humidity.
[c] Sensitivity in Ω/ppm, the sensor noise is 10 Ω (C_8Au-coated sensor) and 2 Ω (BC_2Au-coated sensor), respectively.
[d] Sensitivity change relative to that in dry environment.

dielectric properties, which can partially offset the expected increase in resistance due to the film swelling. The effect of water partitioning on the medium electric properties becomes more significant at higher humidity while water molecules begin to aggregate. The aggregation of water molecules could completely change the film electric properties while ion current exist. The ion current could be caused by the residual TOAB contamination. From the research conducted by Schiffrin's group [32], it is not easy to remove TOAB completely in the nanoparticle compounds prepared according to Brust method [29]. The TOAB contamination influences on the response is still in investigation. Wohltjen and Snow [14] also investigated the response of C_8Au-coated sensor to water vapor, but little resistance response was observed owing to the low sensitivity. They did not investigate the capacitance response.

The little capacitance response in dry environment can be contributed to the low permittivity of the film material. Since the permittivity of the organic compounds is close to the medium permittivity, there is little change in the medium permittivity due to the absorption. At low humidity, the water molecules are scattered and the effect on the medium permittivity is little, a little capacitance response was observed. At high humidity, the water molecules aggregated and caused the film permittivity increase. Abrupt capacitance response was observed as shown in Figs. 2 and 3. The effect of water absorption on the film dielectric property begins significant around 30% RH. With humidity increasing, capacitance response increases exponentially.

Fig. 3 shows that the humidity-dependent resistance responses profiles are different on C_8Au and BC_2Au-coated sensors. This difference may be related to the different residual TOAB contamination. If notice the different scale in Fig. 3, C_8Au-coated sensor is much more sensitive to water than the BC_2Au-coated sensor no matter based on capacitance or resistance response. Same results were obtained on the VOCs' response. Higher sensitivity was always observed on C_8Au-coated sensor. The capacitance increased exponentially with humidity increasing.

3.2. *Effect of humidity on sensor response to VOCs*

Toluene, ethyl acetate, acetone, and ethanol were selected as the target compounds to investigate the humidity effect on the sensor responses. These four compounds represent four classes of functional-group compounds ranging from non-polarity to strong polarity. Responses were linearly with vapor concentration in the investigated concentration, and the correlation coefficients were all over 0.99. Replicate analyses were reproducible, yielding relative standard deviations (R.S.D.s) of <4%. The response profile of toluene in dry environment is shown in Fig. 4. The rest three compounds have the similar response profiles. Absorption of the organic vapors results in the sensor resistance increasing but no change in capacitance in dry environment. In wet environment, the resistance sensitivity decreased with the humidity increasing as expected.

The sensor sensitivities to VOCs at different humidity are summarized in Table 1 . In 60% relative humidity environment, the sensitivity drop ranges from 12% (toluene on C_8Au-coated sensor) to 39% (acetone on C_8Au-coated sensor) compared to the sensitivity in dry environment. Among the four compounds, the humidity effect on toluene is the least and on acetone the biggest. The higher hydrophobicity of the target compounds, the less humidity effect was observed. The results show that sensors coated with hydrophobic compounds protected-metal nanoparticles can be used in high humidity.

As for the capacitance response, the absorption of organic vapors caused little capacitance response at low humidity (RH < 30%), and negative capacitance response at high humidity (RH > 40%) as the result of the replacement of water molecules absorbed with the organic molecules. Such a replacement results in a decrease in the permittivity in the film. Although the concentration of organic vapors is much less than water vapor, the hydrophobic film is more favorable to the hydrophobic target compounds than to water. The capacitance response is slow, low sensitive, and not practicable for sensing application.

4. Conclusions

Two gold-thiolate monolayer-protected nanoparticles were employed as interfacial layers on chemiresistor sensors. Both resistance and capacitance were measured as the function of the vapor concentration. The sensors show positive resistance response to water vapor at low humidity and negative resistance response at high humidity, but little capacitance response at low humidity and significant positive capacitance response at high humidity. The sensor sensitivity to VOCs decreases with the humidity increasing. The capacitance response is not sensitive to the film swelling in dry environment.

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