

# 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 volatile 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.

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## 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 differ-

ent 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 range 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<sub>2</sub>, and CH<sub>3</sub> 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-mercaptopundecanoic 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 volatile 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<sub>8</sub>H<sub>17</sub>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<sub>8</sub>Au and the BC<sub>2</sub>Au 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

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