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One novel humidity-resistance formaldehyde molecular probe based hydrophobic diphenyl sulfone urea dry-gel: Synthesis, sensing performance and mechanism

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ABSTRACT

The work designs a novel hydrophobic organic dry-gel named diamino diphenyl sulfone (DDS) urea for selectively detecting formaldehyde in air. It is synthesized by using octadecylisothiocyanate and diamino diphenyl sulfone as reactants in tetrahydrofuran solution at 70 °C. The dry-gel is obtained by freezing drying. Sulfanilamide urea dry-gel acts as the contrastive material which is synthesized in a similar condition. The dry-gel coated Quartz Crystal Microbalance (QCM) sensor exhibits a rapid and reversible selective response towards formaldehyde gas. Repeated measurement results show high sensitivity and low detection limit (1 ppm) for formaldehyde detection. The gas sensing and contact angle tests indicate its stability under different humidity conditions. Based on the adsorption isotherm experiments, it reveals that adsorption enthalpy change between DDS urea dry-gel and HCHO molecules locates the range of chemical adsorption, endowing the sensor satisfactory selectivity and reversibility. Sensing mechanism of formaldehyde sensor has been proved by a simulation calculation based on a quantum chemistry software Gaussian though comparing the interaction between amine group or carbamido and formaldehyde. The calculation results reveal that Schiff base interaction between the amine group and aldehyde group is more responsible for formaldehyde sensing instead of hydrogen bond interaction between carbamido and aldehyde group.

1. Introduction

Formaldehyde (HCHO), one of volatile organic compounds (VOCs), has attracted much attention to the environmental security owing to its serious harm to our life [1]. It is well known that long term exposure to formaldehyde even a few part per million (ppm) may cause cancer or other allergens [2,3]. Nowadays, many people are focusing on formaldehyde because it is the scariest gas in our room from interior decoration [4,5]. But it is still an urgent problem on how to real-time monitor and give an alarm while we are suffering from a daily indoor poisoning as a result of formaldehyde exposure. Therefore, scientists have developed many methods to detect gaseous formaldehyde, such as colorimetric [6], GC–MS [7], and fluorescence [8], etc. However, these detecting methods are either costly or time-consuming, and difficult to detect in real time. Thus there is a pressing need to develop a rapid, facile, and on-site formaldehyde detecting method. It is known that the chemical sensor with high-performance characteristics may be a promising analytical tool [9–11], because chemical sensors are usually fabricated by coating an active sensing material onto the surface of a specific transducer device [12–14]. Chemical sensors can detect a variety of gases such as CO_2, moisture, and liquefied petroleum gas, etc [15–20]. Thus, to design advantageous sensing materials becomes a key to the successful implementation of a chemical sensor. As for the gas sensor, the Quartz Crystal Microbalance (QCM) is widely used as a reliable transducer for the rapid and real-time detection [21–26]. Different kind of coating material with various characteristics, sensitivity, selectivity and stability has been considered to detect different gases [27–29]. Among them, QCM formaldehyde sensor has developed quickly over these years [30]. Researchers usually employ amine-functional group as a probe to recognize formaldehyde, and then design new sensing material including amino-functional groups to improve sensing properties

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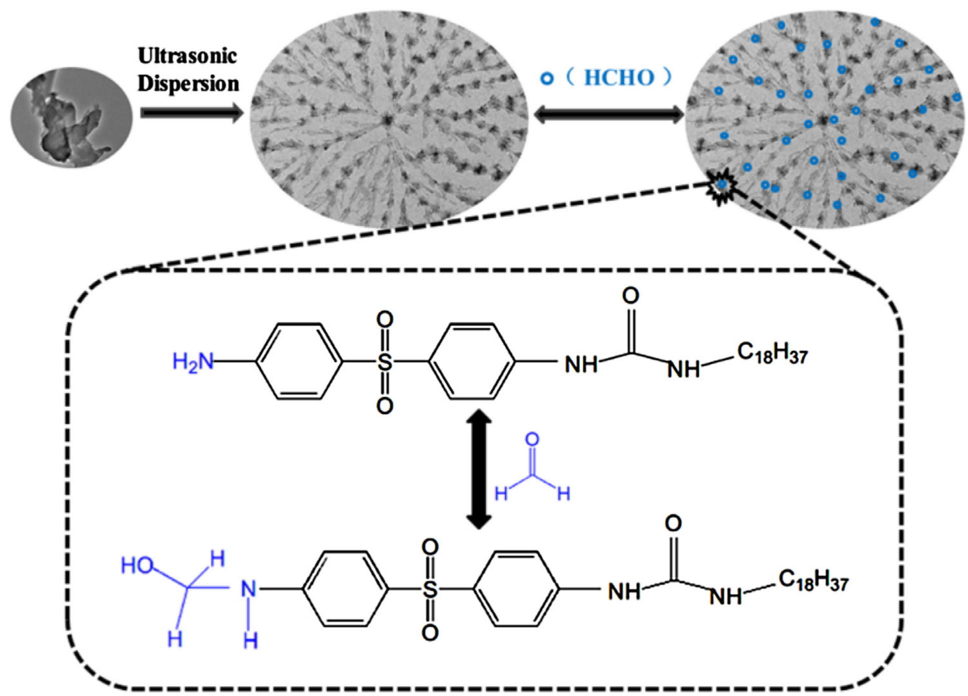

Scheme 1. Scheme of the dispersion process of DDS urea dry-gel and adsorption mechanism of formaldehyde molecules.

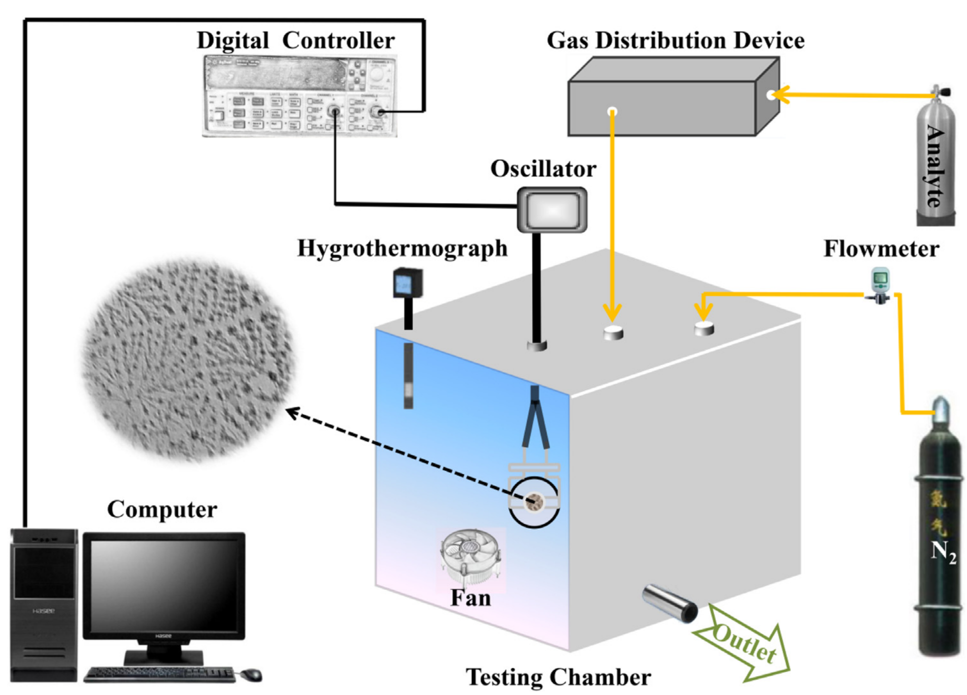

Fig. 1. Schematic of a gas testing system.

of formaldehyde sensor [31]. But these amine-functionalized material does not have a good resistance to humidity.

As important chemical raw materials, diphenyl sulfone and its derivatives have strong electron withdrawing groups, special conjugated structure, oxidation resistance, and high chemical stability [32]. Besides, their hydrophobicity and heat-resistant stability make them have potentiality as a substrate of sensing materials. Furthermore, different locations of two benzene rings in diphenyl sulfone can be grafted with various functional groups to achieve ideal selectivity toward specific gas. Therefore, these derivatives of diphenyl sulfone are suitable candidates to be employed as sensing materials for QCM. But now diphenyl sulfone is always used as curing agent, leprosy drug production, and engineering plastics synthesis material [33,34]. The report about diphenyl sulfone and its derivatives based molecular probes for designing gas sensor is very limited.

In order to improve the selectivity and humidity resistance of amino-functionalized formaldehyde sensing materials based on QCM, we design a new formaldehyde molecular probe including an amino-functional group for selective recognition and hydrophobic