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Synergistic improvement of gas sensing performance by micro-gravimetrically extracted kinetic/thermodynamic parameters

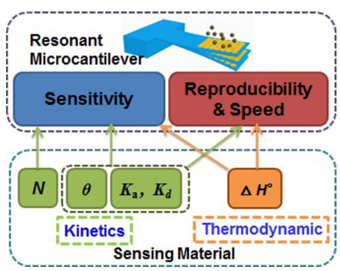
Shuanbao Guo, Pengcheng Xu, Haitao Yu, Zhenxing Cheng, Xinxin Li *

State Key Lab of Transducer Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, 865 Changning Road, Shanghai 200050, China

HIGHLIGHTS

- Sensing material can be comprehensively optimized by using gravimetric cantilever.
- Kinetic-thermodynamic model parameters are quantitatively extracted by experiment
- Sensing-material performance is synergistically optimized by extracted parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method is explored for comprehensive design/optimization of organophosphorus sensing material, which is loaded on mass-type microcantilever sensor. Conventionally, by directly observing the gas sensing response, it is difficult to build quantitative relationship with the intrinsic structure of the material. To break through this difficulty, resonant cantilever is employed as gravimetric tool to implement molecule adsorption experiment. Based on the sensing data, key kinetic/thermodynamic parameters of the material to the molecule, including adsorption heat $-\Delta H^{\circ}$, adsorption/desorption rate constants K_a and K_d, active-site number per unit mass N' and surface coverage θ, can be quantitatively extracted according to physical–chemistry theories. With gaseous DMMP (simulant of organophosphorus agents) as sensing target, the optimization route for three sensing materials is successfully demonstrated. Firstly, a hyper-branched polymer is evaluated. Though suffering low sensitivity due to insufficient N', the bis(4-hydroxyphenyl)-hexafluoropropane (BHPF) sensing-group exhibits satisfactory reproducibility due to appropriate $-\Delta H^{\circ}$. To achieve more sensing-sites, KIT-5 mesoporous-silica with higher surface-area is assessed, resulting in good sensitivity but too high $-\Delta H^{\circ}$ that brings poor repeatability. After comprehensive consideration, the confirmed BHPF sensing-group is grafted on the KIT-5 carrier to form an optimized DMMP sensing nanomaterial. Experimental results indicate that, featuring appropriate kinetic/thermodynamic parameters of $-\Delta H^{\circ}$, K_a, K_d, N' and θ, the BHPF-functionalized KIT-5 mesoporous silica exhibits synergistic improvement among reproducibility, sensitivity and response/recovery speed. The optimized material shows complete signal recovery, 55% sensitivity improvement than the hyper-branched polymer and 2∼3 folds faster response/recovery speed than the KIT-5 mesoporous silica.

1. Introduction

On-site detection of trace-level bio/chemical molecules has become an important concern to meet the highly required

* Corresponding author. Tel.: +86 21 62131794; fax: +86 21 62131744.
E-mail address: xxli@mail.sim.ac.cn (X. Li).

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applications like environmental monitoring, chemical production and food-safety security [1–7]. Known as a kind of toxic chemicals, organophosphorus (OP) compounds are widely used as pesticides and other functional agents [8]. To achieve trace-level OP detection, chemical sensors have been intensively developed that show promise in high-sensitivity, low cost and on-site detection comparing with the conventional bulky instruments like GC–MS (gas chromatography–mass spectrometry) [9,10]. Among the developed sensing devices, micro-gravimetric chemical sensors, such as resonant microcantilevers and quartz-crystal microbalance (QCM) sensors, are composed of two key parts: adsorption-type sensing material and mass-to-frequency signal transducer [11–21]. As for the studies on adsorption/sensing materials, some are focused on improving sensitivity or limit of detection (LOD). Meanwhile, some other efforts are made to enhance sensing reproducibility and response/recovery speed. However, how to impartially evaluate and comprehensively improve all these important performances of a micro-gravimetric chemical sensor is still a challenging task.

The molecular adsorption type sensing material can be viewed into its physical–chemistry insight, as is described in the previous studies by the authors [22–24]. Appropriate gas adsorption/sensing materials can be designed based on analysis of the molecule interaction mechanism. According to physical–chemistry theory, molecule-adsorption relevant thermodynamic parameters include adsorption heat (i.e., enthalpy value of $-\Delta H^{\circ}$) and fractional surface coverage θ. For an adsorbing-type gas sensor, the preferred value of $-\Delta H^{\circ}$ is between 40 kJ mol^{-1} and 80 kJ mol^{-1}. Lower $-\Delta H^{\circ}$ than 40 kJ mol^{-1} indicates physisorption of weak adsorbing capability and low sensitivity, while higher $-\Delta H^{\circ}$ than 80 kJ mol^{-1} indicates chemisorption that features high sensitivity but irreversible chemical reaction and poor reproducibility [25]. On the other hand, some key kinetic parameters, such as adsorption/desorption rate constant (K_a, K_d) and number of active sites (N), are required to feature as high value as possible. The reason lies in that such high values bring quick adsorption/desorption speed and large sensing response (i.e. high sensitivity). Similarly, moderate θ value (normally $<<1$) is normally required for fast desorption after sensing and wide concentration range of the detected gas.

During last decade, hyper-branched polymer (HBP) modified with 2,2-Bis(4-hydroxyphenyl)-hexafluoropropane (BHPF) sensing groups has been developed and utilized as sensing material for OP vapors like DMMP (dimethyl methylphosphonate, lab simulant of toxic organophosphorus agents) [21,26]. However, along with the required detection concentration becoming lower and lower, such conventional sensing material shows insufficient sensing performance. Considering that the hyper-branched polymer is a kind of flexible material, the inner sensing groups of the hyper-branched polymer are hard to be rapidly accessed by the detected OP molecules. Aiming at improving detection performance to trace-level OP vapor with micro-cantilever sensor, we herein describe our optimization method for DMMP adsorption/sensing nanomaterial. Based on quantitative extraction of kinetic and thermodynamic parameters of the OP adsorption materials, the comprehensively evaluating and optimizing method is explored to overall and synergistic improvement among sensitivity, repeatability and response/recovery speed.

2. Experimental

2.1. Chemicals

2,2-Bis(4-hydroxyphenyl)-hexafluoropropane (BHPF), tetrahydrofuran (THF), poly(ethylene oxide)-block-poly(propylene oxide)-block-poly (ethylene oxide) tri-block copolymer Pluronic F127 (Mw = 12600, $PEO_{106}PPO_{70}PEO_{106}$) were purchased from Sigma–

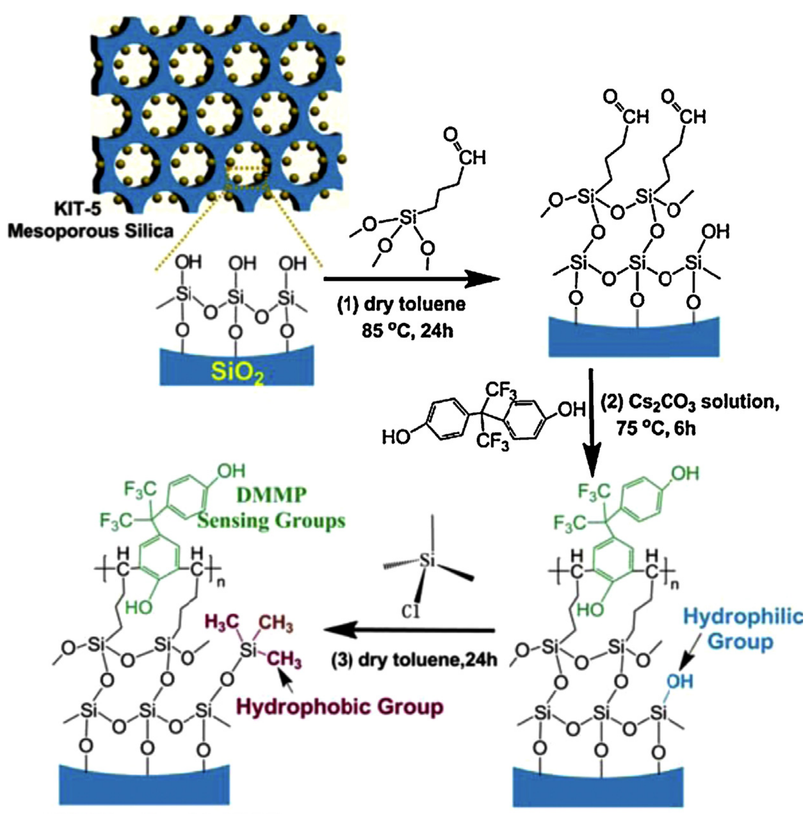

Fig. 1. Schematic of the functionalized KIT-5 material preparation.