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Highly sensitive and selective hydrogen sulfide and toluene sensors using Pd functionalized WO_3 nanofibers for potential diagnosis of halitosis and lung cancer

Nam-Hoon Kim[a], Seon-Jin Choi[a], Dae-Jin Yang[b], Jihyun Bae[b], Jongjin Park[b], Il-Doo Kim[a],*

[a] Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea
[b] Samsung Advanced Institute of Technology, 97, Samsung2-ro, Giheung-Gu, Yongin-Si, Gyeonggi-Do 446-712, Republic of Korea

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ABSTRACT

In this work, we report a remarkably improved toluene response and superior cross-sensitivity against H_2S molecules by combining Pd catalysts and highly porous WO_3 nanofibers (NFs). We functionalized Pd catalysts inside and/or outside of WO_3 NFs synthesized by electrospinning, which is a facile and versatile process for producing webs of metal oxide NFs. Pd-embedded WO_3 NFs were obtained by the electrospinning of a Pd and W composite precursor/poly(methyl methacrylate) (PMMA) solution followed by calcination at 700 °C. Pd nanoparticles (NPs) (6–10 nm) synthesized by a polyol method were decorated on the WO_3 NFs (Pd-NPs/WO_3 NFs) by the attachment of the Pd NPs on as-prepared WO_3 NFs. The gas sensing characteristics of pure WO_3, Pd-embedded WO_3, Pd-NPs/WO_3, and Pd-NPs/Pd-embedded WO_3 NFs were tested using H_2S and toluene gases in a highly humid atmosphere (RH 90%), which is similar to human exhaled breath. The results showed that the Pd-NPs/Pd-embedded WO_3 NFs whose inner and outer layers were decorated by Pd catalysts, exhibited a high toluene response ($R_{air}/R_{gas} = 5.5$ at 1 ppm) and remarkable selectivity against H_2S ($R_{air}/R_{gas} = 1.36$ at 1 ppm) at 350 °C, whereas pristine WO_3 NFs showed superior H_2S response ($R_{air}/R_{gas} = 11.1$ at 1 ppm) along with a negligible response toward toluene ($R_{air}/R_{gas} = 1.27$ at 1 ppm). The highly porous WO_3 NFs decorated with Pd catalysts, exhibited potential feasibility, i.e., a low limit of detection (LOD) of 20 ppb ($R_{air}/R_{gas} = 1.32$) at 350 °C, for application in VOCs sensors, particularly for diagnoses of lung cancer.

1. Introduction

The diagnosis of specific diseases using human exhaled breath has attracted much attention because this method is fast, non-invasive and convenient, leaving no biohazard waste compared to a conventional medical examination. Human exhaled breath contains several hundred volatile organic compounds (VOCs). Particularly, specific VOCs molecules such as acetone (diabetes) [1], pentane (heart disease) [2], ammonia (kidney disorder) [3], nitrogen monoxide (asthma) [3], isoprene (heart disease) [4], and toluene (lung cancer) [5] are known biomarkers that predict specific diseases. Among various diseases, lung cancer is one of the most serious. The five-year survival rate of lung cancer is particularly low compared to other cancers because only 15% of lung cancer cases are diagnosed at an early stage [6]. If lung cancer is diagnosed at an early stage, the rate of death by lung cancer will be significantly reduced. Various gas-sensing techniques including gas chromatography-mass spectroscopy (GC-MS) and optical spectroscopy, are widely used for the detection of exhaled breath biomarkers. However, these measurement techniques have critical limitations. For instance, they are expensive, slow and require bulky equipment, preventing their use as a non-invasive portable device. For this reason, real-time exhaled breath sensors will be very helpful for early stage diagnosis of lung cancer.

A number of studies have been carried out in an effort to develop exhaled breath sensors. Among the various types of exhaled breath sensors, chemoresistive type of exhaled breath sensors based on semiconducting metal oxides (SMOs) are considered to be promising due to their high gas response, rapid response speed, good stability and low cost [7–10].

However, there are several requirements when undertaking a breath analysis using SMOs for a diagnosis of lung cancer. The first, the exhaled toluene level in lung cancer patients is known to be approximately 80–100 ppb (parts per billion), which is two or three-fold higher than the level exhaled by healthy people (20–30 ppb) [5]. Among semiconducting metal oxides, as SnO_2, In_2O_3, Co_3O_4, ZnO, WO_3 and Cr_2O_3, WO_3 shows excellent gas response levels, especially to aromatic hydrocarbons such as

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* Corresponding author. Tel.: +82 42 350 3329; fax: +82 42 350 3310.
E-mail address: idkim@kaist.ac.kr (I.-D. Kim).

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toluene at ppb-level in the dry atmosphere [11–14]. On the other hand, in a humid atmosphere (relative humidity RH 90%, i.e., like human breath), the gas sensing response of typical metal oxide sensors decreases remarkably due to the stable chemisorbed hydroxyl group originating from water molecules on the surface of the SMO sensors ($T < 400\,^{\circ}C$) [15]. Therefore, the development of a highly sensitive SMO sensor which works even in a highly humid atmosphere is necessary. Second, the gas response speed should be fast enough (<15 s) for real-time diagnosis. Third, because there are so many other gases in human breath, interfering gases in human breath represented as H_2S should not lower the accuracy of the breathing sensors, leading to low cross-sensitivity (poor selectivity).

To accomplish these requirements, ever more sensitive, rapidly responding and selective exhaled breath sensors are necessary. Thus far, several nanostructured SMOs have been proposed for exhaled breath sensors. They include WO_3 nanoparticles [11,16], ZnO nanowires [17], Pd-doped TiO_2 nanofibers [18], Pt and Au added WO_3 nanoparticles [19], and IrO_2-loaded WO_3 nanofibers [10], Pt-decorated SnO_2 nanofibers [10]. Among these approaches, as one of the most promising synthetic routes, the electrospinning method has been widely studied [7,20]. In addition, various morphologies which are especially optimized for ultrasensitive gas sensors have been proposed by controlling electrospinning processing parameters [21] such as the flow rate [22] and the degree of phase separation between inorganic precursors and polymers [22,23] as well as their use of a polymeric fiber templating route combined with the PVD deposition of metal oxide layers for the nanotube structure have been proposed [24–26]. These electrospinning-assisted nanostructures have high surface areas, open pores and large voids for enhanced gas responses and are capable of rapid response/recovery operations as they facilitate gas reactions on the surface with good gas accessibility. In addition, the catalytic functionalization of noble metal nanoparticles such as Pt, Pd, IrO_2 and Au on SMOs nanofibers has been introduced to promote gas sensing reactions by reducing the activation energy and thereby increasing the gas response and selectivity while also decreasing the maximum working temperature of the sensors. Also, it is known that the effect of the catalyst on the properties of the sensing layer depend on where the catalyst is applied, i.e. on the surface or on the inner side of the sensing layer. Applying the catalyst to the inside of the sensing layer changes the bulk resistance, whereas a catalyst on the surface can effectively promote a redox-reaction. In this work, we propose a novel VOCs sensing material platform by effectively decorating palladium (Pd) nanocatalysts inside and/or outside of WO_3 NFs. We report remarkably improved toluene response and superior cross-sensitivity levels against H_2S molecules by combining catalytic Pd nanoparticles (NPs) and highly porous WO_3 nanofibers (NFs).

2. Experimental

WO_3 NFs were synthesized by means of the electrospinning of a composite solution which was prepared by dissolving tungsten ethoxide ($W(OC_2H_5)_5$) and poly(methyl methacrylate) (PMMA) in dimethyl formamide (DMF). 0.8 g of tungsten ethoxide ($W(OC_2H_5)_5$) and 0.5 g of PMMA ($Mw = 996{,}000\,g\,mol^{-1}$) were dissolved in 4.0 g of *N,N*-dimethyl formamide (DMF). For the Pd-embedded WO_3 NFs (Pd-embedded WO_3 NFs), 0.0045 g $PdCl_2$ (1 wt% Pd compared to the WO_3 NFs) was added to the precursor solution. After stirring for 6 h at room temperature, the solution was loaded into a plastic syringe connected to a 25-gauge needle. The needle was connected to a high voltage supply and DC voltage of 10 kV was supplied. A constant distance of 15 cm between the needle tip and the collecting steel use stainless (SUS) foil was maintained. SUS foil was wrapped around a grounded rotating cylinder which rotated at a speed of 50 rpm. The collected tungsten/PMMA composite fibers were annealed at 700 °C for 1 h in ambient air and heating rate was $10\,^{\circ}C\,min^{-1}$.

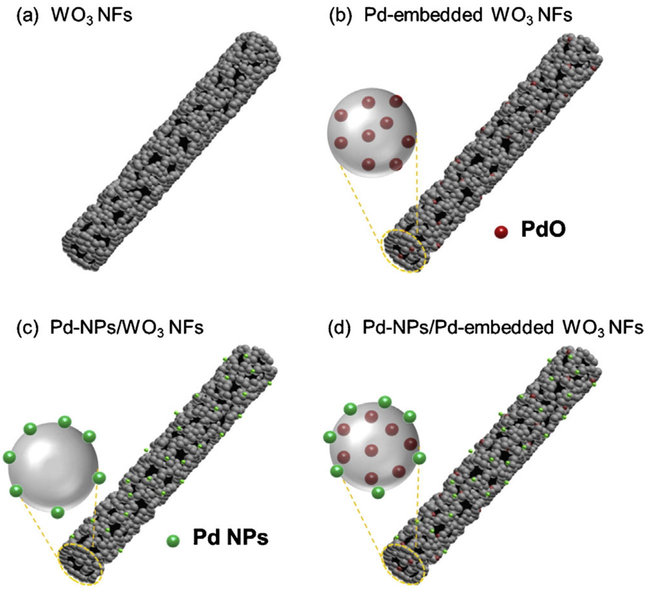

Fig. 1. Schematic illustration of (a) pristine WO_3 NFs (b) Pd-embedded WO_3 NFs (c) Pd-nanoparticles-decorated WO_3 NFs, and (d) Pd-nanoparticles-decorated and embedded WO_3 NFs.

Pd nanoparticles (Pd NPs) were synthesized by a polyol method [27]. 45 ml of ethylene glycol (EG) was heated to 150 °C. 5 ml of EG solution in which 0.5 g of palladium chloride ($PdCl_2$) was dissolved was slowly injected into 45 ml of EG. 0.5 g of polyvinylpyrrolidone (PVP, $Mw = 10{,}000\,g\,mol^{-1}$) was dissolved in 20 ml of EG, and this solution was added to the previously heated EG solution at a rate of $2\,ml\,min^{-1}$. After 1 h, acetone five times the Pd solution in volume was added to the Pd solution. Pd particles were obtained via centrifugation (3000 rpm for 5 min). The obtained powders were dispersed in ethanol for direct use as a Pd catalyst.

For the decoration of Pd NPs onto the outer surface of the WO_3 NFs (hereafter, Pd-NPs/WO_3 NFs), 1 wt% Pd nanoparticles was added to WO_3 NFs which was dispersed in ethanol. After 5 min sonication, ethanol was evaporated at 50 °C. For the Pd-embedded WO_3 NFs decorated with Pd NPs (Pd-NPs/Pd-embedded WO_3 NFs), 0.0036 g $PdCl_2$ and 0.7 wt% Pd NPs were used, in order to make the same Pd/W molar ratio in three different Pd-loaded WO_3 NFs, i.e., Pd-embedded WO_3, Pd-NPs/WO_3 and Pd-NPs/Pd-embedded WO_3 NFs.

Fig. 1 shows schematic illustrations of pristine WO_3 NFs (Fig. 1a), Pd-embedded WO_3 NFs (Fig. 1b), Pd-NPs/WO_3 NFs (Fig. 1c) and Pd-NPs/Pd-embedded WO_3 NFs (Fig. 1d). The loading amounts of the Pd catalysts were carefully controlled and were set to 1 wt% for the Pd functionalized WO_3 sensing materials. For the Pd-NPs/Pd-embedded WO_3 NFs, the content of embedded Pd in the WO_3 NFs was 0.7 wt% and the content of functionalized Pd NPs on the WO_3 NFs was 0.3 wt%, resulting in the total Pd amount of 1 wt%.

Images of the microstructural characteristics of the WO_3 NFs and Pd functionalized WO_3 NFs were taken using a scanning electron microscope (Field Emission SEM, nova230, FEI) and a transmission electron microscope (FE-TEM 300 kV, Tecnai). The morphological distribution of the Pd NPs on the WO_3 NFs was identified using high-resolution transmission electron microscopy (HRTEM). The chemical states of the Pd NPs were investigated by X-ray photoelectron spectroscopy (XPS, Sigma Prove, Thermo VG Scientific). The crystal structures of the prepared sensing materials