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Au decoration of vertical hematite nanotube arrays for further selective detection of acetone in exhaled breath

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ABSTRACT

Vertically ordered hematite nanotubes decorated with Au nanoparticles are synthesized by a facile electrochemical anodization method and self-agglomeration of Au films. Au decoration significantly enhances the response of hematite nanotubes to acetone at 350 °C and the response to acetone is 2.4 times higher than the response to ethanol, the counterpart target gas. The Au nanoparticles decorated hematite nanotubes exhibit unprecedentedly high and selective responses to acetone at 350 °C with 50% relative humidity condition (calibrated at room temperature, 25 °C). The enhanced gas sensing properties in a humid condition were attributed to the spillover effect by Au nanoparticles and high porosity of hematite nanotubes with a large surface-to-volume ratio. These results indicate that Au nanoparticles decorated hematite nanotubes are promising for use in high quality sensor materials for breath analyzers to diagnose diabetes mellitus.

1. Introduction

The detection of specific volatile organic compounds (VOCs) in the exhaled breath has generated a significant interest in medical diagnostics because it is an inexpensive and non-invasive strategy in detecting diseases [1–4]. The exhaled breath is a complex mixture of the gaseous substances including VOCs at different concentration ranging from parts per billion (ppb) to parts per million (ppm) at humid condition [5]. The exact detection of the specific VOCs in the exhaled breath can offer useful information for the early diagnosis of the diseases. For instance, ammonia (NH_3) is biomarker for the end-stage of renal diseases [6], and hydrogen peroxide (H_2O_2) gives information about lung diseases and respiratory inflammations [7]. Particularly, acetone (CH_3COCH_3) has been attracting attention as a potential biomarker for diabetes, one of the most common diseases for modern human beings, which can eventually lead to severe damages in blood vessels and diseases in arteries [8–10]. The acetone concentrations in the exhaled breath of diabetic patients are higher than 1.8 ppm, whereas the breath of healthy humans contains acetone concentrations less than 0.8 ppm [11]. Therefore, the detection of a low concentration of acetone has the potential to lead to a facile and cost-effective approach for the medical diagnosis of diabetes. Commonly, the detection of specific VOCs in the exhaled breath has been conducted using Gas Chromatography (GC) or Mass Spectrometer (MS) [12]. However, these techniques require expensive and massive equipments where high levels of expertise are necessary. Recently, gas sensors utilizing semiconducting metal oxides have attracted a great attention owing to their advantages such as simplicity in fabrication and operation, portability, painlessness, and cost effectiveness. However, the performance of the conventional gas sensors based on semiconducting metal oxides cannot satisfy the requirements in the breath analysis because the gaseous substances in the exhaled breath are too diverse and low in concentration with humidity interference. In order to overcome these obstacles and improve the gas sensing performance, numerous studies have been focused on the design of the metal oxide nanostructures and surface modification with noble metal nanoparticles for catalytic effects [13,14].

Metal oxide nanostructures with a large surface area are expected to exhibit an excellent gas sensing performance owing to increased active area. Among various nanostructures, one-dimensional (1D)

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nanostructures such as nanorods, nanobelts, nanowires, and nanotubes have been widely investigated for its increased surface activity due to the large surface area and a strong adsorption and desorption ratio of the target gas molecules [15–18]. However, the utilization of 1D nanostructures as gas sensors is still at early stage in the aspect of synthetic methods to achieve a high-yield mass production and low fabrication cost. Alternative to previously studied synthetic methods like hydrothermal or solvothermal reaction, an electrochemical anodization method has been considered as a promising synthetic strategy for the fabrication of metal oxide nanotubes because of its high reproducibility and simplicity in procedures with cost-effectiveness [19–22]. Particularly, an extremely large surface area and high porosity of metal oxide nanotubes facilitate the adsorption and desorption of target gas molecules, which is desirable for high performance gas sensors.

In addition to the design of nanostructures, the utilization of noble metal nanoparticles, such as Pt, Ag, Pd, and Au, which are highly effective catalysts for oxidation can improve the gas sensing performance [23–26]. Xing et al. [27] showed that Au nanoparticles significantly enhance the acetone sensing properties of In_2O_3 nanorods and Kim et al. reported high performance acetone gas sensors using Pd-decorated WO_3 nanorods [28]. However, the effects of Au decoration on metal oxide nanotubes were not extensively studied, and the role of Au nanoparticles in a high level of humid condition remains unclear.

In this paper, we demonstrate a highly selective and sensitive acetone detection achieved by Au-decorated hematite nanotubes and propose the role of Au nanoparticles in gas sensing under humid conditions. Vertically ordered hematite nanotubes with Au nanoparticles were successfully synthesized using a facile electrochemical anodization and electron beam evaporator. This work revealed the following important aspects: (i) the simple and cost-effective synthesis of Au-decorated hematite nanotubes, (ii) the sensors having a large response towards acetone in humid condition, and (iii) the sensors being highly selective to acetone. The results suggest the excellent potential of Au-decorated hematite nanotube sensors for use in breath analyzer to diagnose diabetes noninvasively.

2. Experimental

2.1. Sensor fabrication

Platinum (Pt, 150-nm-thick) interdigitated electrodes (IDEs) with 5 μm spacing were fabricated on SiO_2/Si substrates via photolithography and lift-off method. After then, 500 nm Fe thin films used in this work were prepared by an electron beam evaporator system (Rocky Mountain Vacuum Tech.). Fe films were deposited by an electron beam evaporator using a circular metallic Fe source of 1 inch in diameter with a purity of 99.995%. The base pressure of the chamber was 10^{-6} Torr and the substrate temperature was set to 400 °C. The applied electron beam voltage and current were set at 7.0 kV and 70 mA, respectively, leading to a deposition rate of 2.0 Å/s. The deposited Fe thin films were anodized in an electrolyte consisted of ethylene glycol mixed with 0.3 wt % ammonium fluoride (NH_4F 99.5% purity, Junsei) and 3 vol % H_2O. The anodization was carried out with two electrodes, where the working electrode was the sample and the counter electrode was a Pt mesh. The anodization duration of 3 min at an applied voltage of 200 V resulted in Fe_2O_3 nanotubular structures of ~1.2 μm thickness. After anodization, the sample was washed using deionized water and dried in nitrogen. Next, Au films were deposited on the Fe_2O_3 nanotubes using electron beam evaporator. Au deposited Fe_2O_3 nanotube films were annealed at 550 °C for 5 h in air. During the annealing, the Fe_2O_3 nanotube films were converted to crystalline hematite transition and Au films were agglomerated into Au nanoparticles.

2.2. Material characterization

The morphologies of Au-decorated hematite nanotubes were characterized by environmental scanning electron microscope (XL30 FEG ESEM, FEI) using the acceleration voltage of 15 kV. The crystallinity and phase of the Au-decorated hematite were characterized by glancing angle XRD (D/Max-2500, Rigaku), where Cu Kα radiation (wavelength = 1.5418 Å) was used for the X-ray source and the incident angle was fixed at a small angle (2°). Transmission electron microscopy (TEM) was performed using a JEM- 2100 F field emission transmission electron microscope (JEOL, Peabody, U.S.). Cross-sectional TEM specimens of nanotubes on SiO_2/Si substrates were prepared by mechanical polishing followed by ion milling with Ar ions (FIB, FEI-Helios).

2.3. Sensor measurements

The gas sensing properties of the Au-decorated hematites were measured under external heating by a box furnace. The resistance of the sensor was measured under a DC bias voltage of 1 V using a source measurement unit (Keithley 2400). The relative humidity and the concentrations of test gases were calibrated in a gas mixing chamber at room temperature (25 °C), and then the test gases were injected to a quartz chamber operating at elevated temperatures. The continuous flow rate of 1000 sccm was used for all measurements and the gas flow was controlled by mass flow controllers. The response of the sensors was accurately regulated by the ratio of the fully saturated resistances after exposure to humid air to the base resistance in dry air. The response is defined as R_{air}/R_{gas} for the reducing gases (acetone, ethanol, C_6H_6, CO, C_7H_8, NH_3, and H_2) where R_{gas} and R_{air} denote resistances in the presence and the absence of a test gas, respectively. To evaluate the selectivity of the Au decorated hematite nanotube sensors, we applied Principle Components Analysis (PCA). To perform PCA, we analyzed sensing properties of target gases by MATLAB software-based PCA as an analysis tool. The configuration of the matrix is based on the gas responses and response times from exposure to each VOC gases (acetoen, ethanol, C_6H_6, CO, C_7H_8, NH_3, and H_2).

3. Results and discussion

The schematic illustration for the synthesis procedure of Au-decorated hematite nanotubes by an electrochemical anodization and e-beam evaporator is demonstrated in Fig. 1a. The anodization method which transforms metal oxide thin films into vertically ordered 1D metal oxide nanostructures, such as nanobamboos, or nanotubes was used for this work. A diameter and length of the hematite nanotubes synthesized by anodization are strongly related to the applied voltage and have significant influence on gas sensing performance of themselves. Our previous work observed that ~ 1.2 μm length of hematite nanotubes synthesized by anodization method was the optimal length for the gas sensing [29]. In addition, the crystallinity and grain size of the initial Fe films are crucial for the formation of vertically ordered Fe_2O_3 nanotubes. When the Fe films were deposited at 400 °C, the films were found to be highly textured with columnar grains, which contribute to the uniform anodization of Fe to Fe_2O_3. After anodization, we deposited Au films on Fe_2O_3 nanotubes with varying thicknesses using e-beam evaporator (1, 3, and 5 nm) (Fig S1, Fig. 1b–c), and, the samples were subsequently annealed in ambient air at 550 °C for 5 h. During the annealing, the Fe_2O_3 nanotubes were crystallized to hematite phase (α-Fe_2O_3) and the Au films were agglomerated to Au nanoparticles, resulting in Au-decorated hematite nanotubes. The plain-view SEM images in Fig. 1b and c show the Au (3 nm)-decorated hematite nanotubes synthesized on a Pt-IDE-patterned SiO_2/Si substrate. Through cross-sectional SEM images, we found that the Fe films were fully converted to Fe_2O_3 nanotubes. The synthesized Fe_2O_3 nanotubes were vertically and highly ordered with uniform diameters of ~70 nm as shown in Fig. 1d and e. These results demonstrate that vertically ordered Fe_2O_3 nanotubes were successfully synthesized on Pt-IDE-patterned SiO_2/Si substrate using the anodization method. The