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Pd loaded spider-web TiO_2 nanowires: Fabrication, characterization and gas sensing properties

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ABSTRACT

Pd loaded spider-web TiO_2 nanowires were fabricated using Ti foil to sense volatile organic compound (VOC). The spider-web TiO_2 nanowires on Ti foil were synthesized in an aqueous 1 M sodium hydroxide (NaOH) solution at 220 °C by hydrothermal method. In order to load palladium the spider-web TiO_2 nanowires and palladium (II) acetate [$Pd(OAc)_2$] powder were placed at a certain distance in a quartz boat inside a furnace for a thermal process. The samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) techniques. VOC gas sensing properties of the spider-web nanowires have been investigated in the concentration range of 500–5000 ppm at 200 °C. The results show that the sensor response for Pd loaded spider-web TiO_2 nanowires increase depending on the increments of the VOC concentration. The maximum sensor response was obtained for isopropyl alcohol.

1. Introduction

Nanomaterials offer many conveniences to investigate the development of material properties according to particle size. The synthesis, characterization, and application of nano materials are commonly utilized due to many advantages to use. There are many kinds of nanomaterials such as nanotubes [1,2], nanowires [3,4], and nanorods [5,6] produced for various applications. Metal oxide nanostructures such as zinc oxides, nickel oxides, titanium oxides, molybdenum oxides, vanadium oxides and tin oxides are the most used ones. Titanium oxide nanostructures are one of the most practical structures because of advantages of wide band gap, environmental friendliness and low cost materials providing applications such as photovoltaic, photocatalytic and sensing applications [7]. Moreover, titanium dioxide (TiO_2) nanowires have a wide variety of synthesis methods and application area. E. S. Aydil et al. have produced TiO_2 nanowires of almost 105 nm diameter on Ti bulk by hydrothermal method at 220 °C [8]. They reported tens of micrometers long oriented single crystalline TiO_2 nanowires fabricated on Ti foil. Yong Liu et al. have synthesized TiO_2 nanowires on fluorine doped tin oxide (FTO) glass at 150 °C for 1–48 h by hydrothermal method [9], fabricating oriented nanowires of about 7–8 nm diameter and of 9.6 mm length. Wu-Qiang Wu et al. fabricated TiO_2 nanowires on Ti foil by hydrothermal method at 220 °C for 24 h [10]. A novel double-layered photoanode based on oriented hierarchical anatase TiO_2 nanowire arrays (13 mm) and nanoparticles (6–24 mm) on a Ti-foil substrate was designed. Zhenxing Yue et al. fabricated TiO_2 nanowires of 200 nm diameter by anodic aluminum oxide (AAO) [11]. The synthesized TiO_2 NWs and NTs have an outer diameter of almost 200 nm and length of almost 60 μm, respectively, corresponding to the nominal pore size and thickness of the AAO membrane. Jaeyoung Lee et al. synthesized TiO_2 nanowires in diameter of 200 nm by the automatic dipping technique using a porous alumina template [12]. Seok Lee et al. synthesized TiO_2 nanowires by catalyst-assisted vapor–liquid–solid (VLS) and vapor–solid (VS) techniques [13]. They reported TiO_2 nanowires ranging from 25 to 50 nm diameters and up to tens of micrometers length. Myung Hwa Kim et al. produced TiO_2 nanowires in diameter of 25–150 nm by atmospheric pressure chemical vapor deposition (APCVD) [14].

Metal oxide materials can be loaded, making them more useful for any application, especially gas sensor. To improve gas sensing properties of metal oxide materials, they can be loaded with Pd [15–18], Pt [19,20], Au [21], Co, Cu [22], and Ag [23].

In this study, TiO_2 nanowires on Ti foil by hydrothermal method, obtained spider-web like structures were obtained, and these TiO_2 nanowires were loaded with Pd. TiO_2 nanowires have grown

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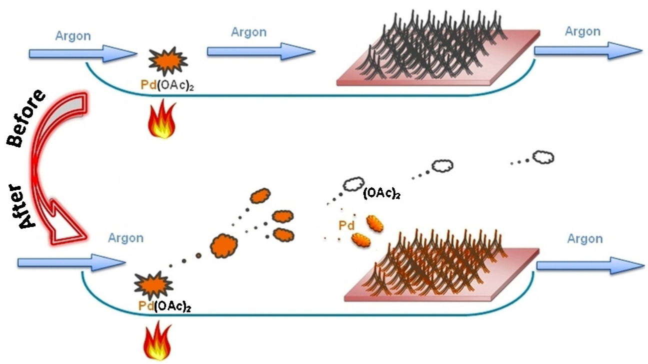

Fig. 1. A schematic illustration for fabrication steps of **Pd-S_W TiO_2 NWs** after hydrothermal process.

randomly, and then groups of wires combined during process. We called these structures "spider-web" shaped nanowires. Gas sensing properties of these structures were measured against VOC in the concentration range of 500–5000 ppm at the temperature of 200 °C. It is found that spider-web TiO_2 nanowires are insensitive to VOCs at 200 °C. In contrast, the sensor response of Pd loaded spider-web TiO_2 nanowires is noticeable for VOCs, especially for isopropanol.

2. Materials and methods

2.1. Fabrication of spider-web TiO_2 and Pd loaded spider-web TiO_2 nanowires

Titanium (Ti) foil (1.25 cm × 2.25 cm) was rubbed with silicon carbide paper (Struers) and then polished with 3 μm and 1 μm DP suspension (Struers). After mechanical polishing, the Ti foil was ultrasonically cleaned in acetone, isopropyl alcohol and methanol for 10 min for each process. The cleaned Ti foil was placed into the bottom of a 260 ml teflon beaker containing 40 ml of 1 M aqueous NaOH solution and treated in stainless steel autoclaves at 220 °C for 4 h. After hydrothermal process, the sample was rinsed with deionized water and dried under dry nitrogen flow. The sample was kept for an hour in 0.6 M HCl solution to exchange Na^+ ions with H^+ ions. TiO_2 nanowires were annealed in a quartz furnace at 650 °C for 2 h. TiO_2 nanowires were synthesized after four steps as described above. TiO_2 nanowires and Palladium (II) acetate [$Pd(OAc)_2$, 47% Pd for synthesis, Merck] powder were subjected to heat treatment inside a furnace under argon gas flow to load palladium on TiO_2 nanowires. Fig. 1 shows a schematic illustration about the fabrication of Pd loaded TiO_2 nanowires. TiO_2 nanowires and the Pd source were placed at a certain distance inside a quartz boat under the argon ambient at 450 °C for an hour. The 450 °C temperature was reached in 45 min, and then kept for an hour and then cooled to room temperature. Pd source was placed into the highest temperature area of the furnace. Since light or heat reduces palladium acetate to palladium [24], the acetate was put out carrying with argon gas. Hence, the evaporated material carrying with Ar penetrated TiO_2 nanowires due to the temperature difference. The samples were also annealed during this process. After a heat treatment for an hour, Pd loaded TiO_2 nanowires were finally obtained.

Morphology of the nanowires were investigated at various stages of the synthesis using the scanning electron microscopy, energy dispersive X-ray (SEM and EDX, Philips XL 30S), X-ray diffraction (XRD, Rigaku Smartlab X-ray diffractometer with Cu-Kα radiation, λ = 0.15418 nm), and X-ray photoelectron spectroscopy (XPS, Phobus 150 Specs electron analyzer with conventional X-Ray source (Al Kα)) employed with an accelerating voltage of 15 kV.

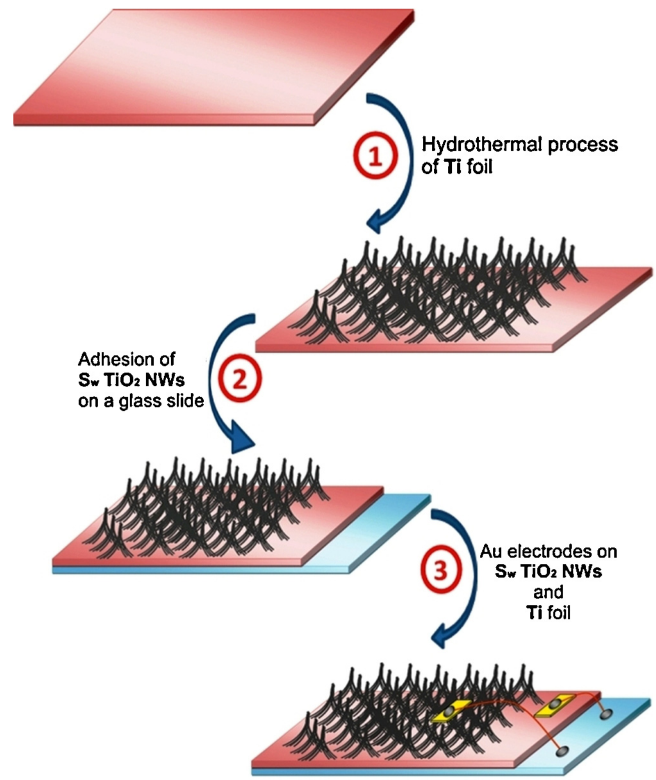

Fig. 2. A schematic illustration for fabrication steps of **S_W TiO_2 NWs** sensor device.

2.2. Temperature dependent electrical properties of spider-web TiO_2 and Pd loaded spider-web TiO_2 nanowires

Current–voltage (*IV*) measurements were performed to investigate the electrical properties of pristine and Pd loaded TiO_2 nanowires. 2-point probe connected to a source meter (Keithley 6517A) was used for electrical measurements. The data of IV characteristic was plotted with gold (Au) as the metal contact. From the IV curve, the information of resistivity can be obtained from the equation below:

$$\rho = \frac{V}{I}\frac{A}{L}(\Omega\,\text{cm}) \quad (1)$$

where ρ is resistivity, resistance (V/I) calculated from the *IV* curve, *A* is Au electrode area and *L* is distance between metal contacts. The resistance is calculated by linear fitting slope values in *I–V* graphs for both pristine and Pd loaded TiO_2 NWs, related to the temperature.

2.3. Gas sensing

Pristine and Pd loaded TiO_2 nanowires devices were investigated for VOC sensing measurements. Pristine TiO_2 nanowires were synthesized using hydrothermal method. TiO_2 nanowires were loaded by subjecting TiO_2 nanowires to the heat treatment with a Pd source to obtain crystallized Pd–TiO_2. Then, Au electrodes with average thickness of 200 nm were evaporated on Ti foil and the nanowires with a Leybold Univex 450 coater system. Fig. 2 shows a schematic illustration about the sensor device of TiO_2 nanowires. There are three steps to obtain sensor devices. Firstly, TiO_2 nanowires were fabricated hydrothermally on Ti foil (1.25 cm × 2 cm) and then adhered to a glass slide using a silver paste. Finally, the thin wires were used for carrying the contacts on TiO_2 nanowires to the glass slide in order to avoid the pressure. The size of the gold electrodes pad on TiO_2 NWs and Ti foil