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Modification of SnO_2 Nanowires with TeO_2 Branches and Their Enhanced Gas Sensing †

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Abstract: We prepared a highly sensitive and selective NO_2 sensor, based on the TeO_2 branched SnO_2 nanowires (NWs), in terms of vapor-liquid-solid method, with subsequent growing of branches on the stems of SnO_2 NWs. Fabricated sensors showed a high response higher than 10 to 10 ppm of NO_2 gas at 100 °C. We investigated the associated sensing mechanisms, with respect to the enhancement of sensing behaviors by the addition of TeO_2 branches. Based on the results obtained in this work, we believe that the present sensor with an efficient fabrication technique, and high sensitivity and selectivity can be used for detection of NO_2 gas in real applications.

Keywords: SnO_2 nanowires; TeO_2 branches; gas sensing

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1. Introduction

Nanostructures are attractive and important structure in gas sensor criteria, because they can be manipulated easily and gas sensing properties are different depending on their morphologies [1]. Among that one-dimensional nanowires have been experimented as attractive materials to chemical gas sensors. Especially, the branched nanowires are tested for several reasons [2]. First, they have strength of 1-D nanowires. They have a linear path of charge transportation, which reduces carrier diffusion lengths and improves electron transportation. Second, branched nanowires have large surface area than 1-D nanowires, which enables many reactants to react on the surface of sensing materials. Accordingly, it enhances gas sensing properties such as sensitivity and selectivity.

2. Experimental

The fabrication procedures of TeO_2 branched SnO_2 nanowires are as follows. First, SnO_2 nanowires were fabricated by thermal evaporation of Sn powder. Sn powder (purity: 99.9%, Sigma-Aldrich) was used as the source material. The substrate was set to 900 °C for 1hr to heat 3 nm-Au coated Si substrates. A mixture of O_2 and Ar gases (O_2: 3%; Ar: 97%) was set at a fixed 2 Torr pressure. Then, TeO_2 branches were grown onto the surface of SnO_2 nanowires with the same VLS procedure only with the different temperature of 370 °C. For the sensing experiments, Ti/Au electrodes were sputtered on specimens with a turbo sputter coater (Emitech K575X, Emitech Ltd., Ashford, Kent, UK) and as-fabricated sensors were placed in a horizontal quartz tube furnace for gas sensing test. Through mass flow controllers, concentrations of target gases were manipulated by changing the mixing ratio of the target gas and dry air, with a total flow rate of 500 sccm. The resistances of sensors in the presence of air (R_a) and target gas (R_g) were measured and the sensor response for oxidative gas (NO_2) was calculated as $R = R_g/R_a$, and for reducing gases was calculated as $R = R_a/R_g$.

3. Results and Discussion

Figure 1a is SEM images of SnO_2 nanowires and Figure 1b–d is SEM images of TeO_2 branched SnO_2 nanowires with annealing temperature at 320, 370 and 420 °C. Branches were grown randomly onto the surface of SnO_2 nanowires. Figure 2a shows an XRD pattern of pristine SnO_2 nanowires, exhibiting reflection peaks that can be indexed to the tetragonal rutile SnO_2 phase (JCPDS card: No. 41-1445). Figure 2b–d show XRD pattern of SnO_2 nanowires with orthorhombic TeO_2 (JCPDS card: No. 52-1005) branches with different temperature. Figure 3a shows low magnification TEM images of TeO_2 branched SnO_2 nanowires. Figure 3b,c shows SAED pattern and Lattice-resolved TEM image of TeO_2 branched SnO_2 nanowires.

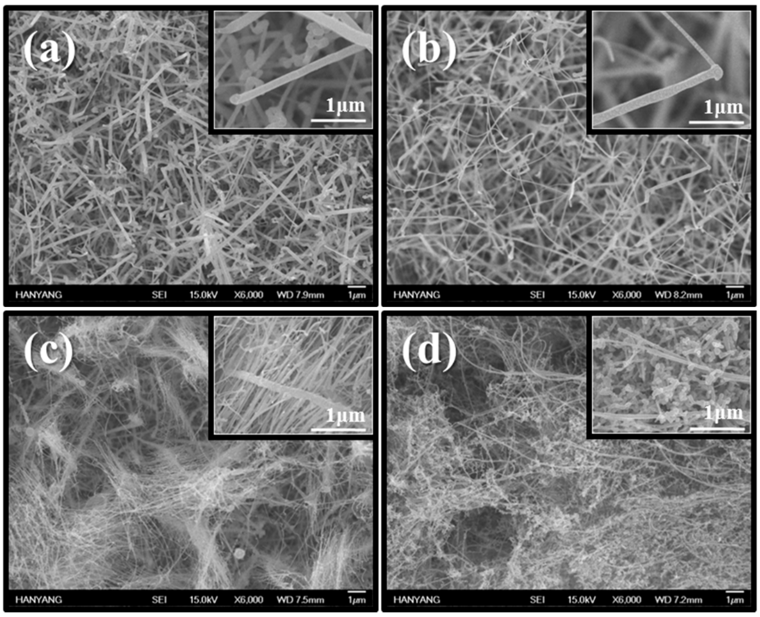

Figure 1. SEM images of (**a**) SnO_2 nanowires, TeO_2 branched SnO_2 nanowires with annealed at (**b**) 320 °C, (**c**) 370 °C, and (**d**) 420 °C.

Figure 4 shows the sensing performances of pristine SnO_2 nanowires and TeO_2 branched SnO_2 nanowires. Figure 4a shows the sensor responses, revealing that the responses of branched SnO_2 nanowires are higher than those of pristine SnO_2 nanowires at temperatures in the range of 25–150 °C. Figure 4b shows the response times, indicating that the response time tends to decrease with increasing the temperature and that the response time of TeO_2 branched SnO_2 nanowires is shorter than that of pristine SnO_2 nanowires. Figure 4c shows the recovery times, exhibiting that the response time also tends to decrease with increasing the temperature and that the response time of branched SnO_2 nanowires is shorter than that of pristine SnO_2 nanowires.

We investigated the associated sensing mechanisms, in regard to the enhancement of sensing performances by the incorporation TeO_2 branches. It is revealed that not only the TeO_2 branches themselves but also the heterojunctions of SnO_2/TeO_2 play a crucial role in enhancing the sensing behaviors.

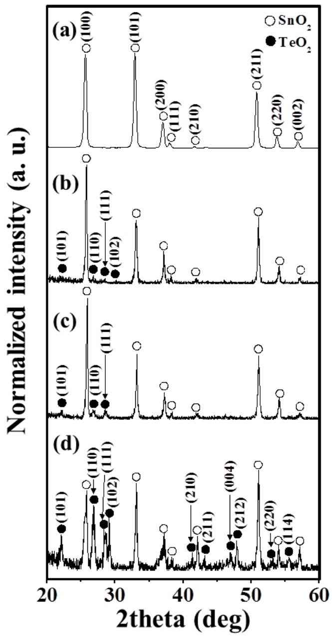

Figure 2. XRD images of (**a**) SnO_2 nanowires, TeO_2 branched SnO_2 nanowires with annealed at (**b**) 320 °C, (**c**) 370 °C, and (**d**) 420 °C.

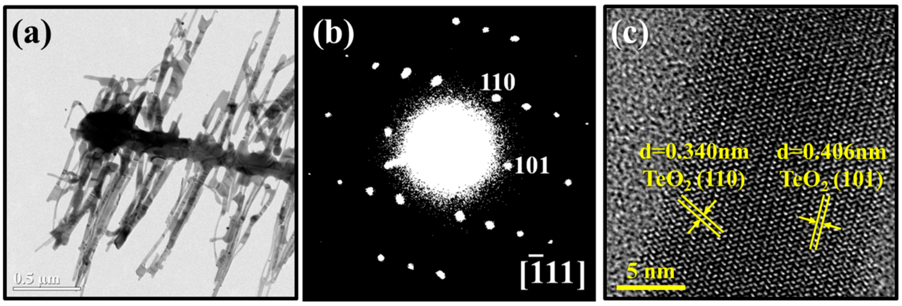

Figure 3. TEM analysis of a TeO_2 branched SnO_2 nanowires with annealing temperature of 370 °C. (**a**) Low-magnification TEM image, (**b**) SAED pattern, and (**c**) Lattice-resolved TEM image.

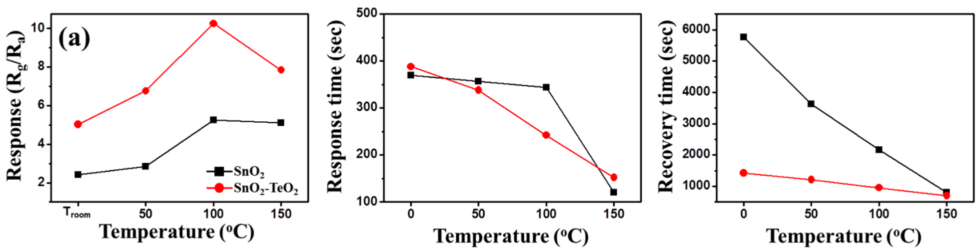

Figure 4. (**a**) Response curve of SnO_2 nanowires (Black) and TeO_2 branched SnO_2 nanowires (Red), (**b**) Response times and (**c**) Recovery times of SnO_2 nanowires and TeO_2 branched SnO_2 nanowires

4. Conclusions

In this work, a highly sensitive and selective NO_2 sensor, based on the TeO_2 branched SnO_2 nanowires (NWs) were synthesized by an efficient route. Fabricated sensor showed a high response to 10 ppm of NO_2 gas at optimal temperature of 100 °C, demonstrating an excellent selectivity of sensor towards NO_2 gas. The superior sensing properties of branched NWs sensor relative to the pristine sensor were mainly attributed to the branch-induced high surface area of sensor and formation of homo-and heterojunctions between SnO_2 and TeO_2.

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Conflicts of Interest: The authors declare no conflicts of interest

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