



## Facile synthesis of SnO<sub>2</sub>–ZnO core–shell nanowires for enhanced ethanol-sensing performance



Dang Thi Thanh Le<sup>a,\*</sup>, Do Dang Trung<sup>a</sup>, Nguyen Duc Chinh<sup>a</sup>, Bui Thi Thanh Binh<sup>a,b</sup>,  
Hoang Si Hong<sup>c</sup>, Nguyen Van Duy<sup>a</sup>, Nguyen Duc Hoa<sup>a</sup>, Nguyen Van Hieu<sup>a,\*</sup>

<sup>a</sup> International Training Institute for Materials Science (ITIMS), Hanoi University of Science and Technology (HUST), Hanoi, Viet Nam

<sup>b</sup> School of Chemical Engineering, Hanoi University of Science and Technology (HUST), Hanoi, Viet Nam

<sup>c</sup> School of Electrical Engineering (SEE), Hanoi University of Science and Technology (HUST), Hanoi, Viet Nam

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### ABSTRACT

The design of core–shell heteronanostructures is powerful tool to control both the gas selectivity and the sensitivity due to their hybrid properties. In this work, the SnO<sub>2</sub>–ZnO core–shell nanowires (NWs) were fabricated via two-step process comprising the thermal evaporation of the single crystalline SnO<sub>2</sub> NWs core and the spray-coating of the grainy polycrystalline ZnO shell for enhanced ethanol sensing performance. The as-obtained products were investigated by X-ray diffraction, scanning electron microscopy, and photoluminescence. The ethanol gas-sensing properties of pristine SnO<sub>2</sub> and ZnO–SnO<sub>2</sub> core–shell NW sensors were studied and compared. The gas response to 500 ppm ethanol of the core–shell NW sensor increased to 33.84, which was 12.5-fold higher than that of the pristine SnO<sub>2</sub> NW sensor. The selectivity of the core–shell NW sensor also improved. The response to 100 ppm ethanol was about 14.1, whereas the response to 100 ppm liquefied petroleum gas, NH<sub>3</sub>, H<sub>2</sub>, and CO was smaller, and ranged from 2.5 to 5.3. This indicates that the core–shell heterostructures have great potential for use as gas sensing materials.

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## 1. Introduction

One-dimensional (1D) semiconductor metal oxides with nanostructures and/or heterostructures have attracted increasing attention in the fabrication and construction of nanodevices and chemical sensors because they offer size confinement in two coordinates, have better crystallinity, higher integration oxide density, and lower power consumption [1,2]. In chemical and gas sensors, 1D metal oxides demonstrate significantly high sensitivity to surface chemical processes because of their large surface-to-volume ratio and small diameter, which is comparable with the Debye length (a measure of field penetration into the bulk) [1–3].

Mutual nanostructures based on semiconductor metal oxides have recently emerged as a promising pathway for the improvement of their potential applications [5–9]. Heterostructured nanomaterials have received great attention because of their

unique properties, which offer more versatile functions than monolithic nanomaterials when used for nanoscale devices [5–9]. The heterostructures of core–shell nanowires (NWs) appear to be the most attractive for chemical and gas sensors [10–15]. For example, SnO<sub>2</sub>–ZnO, ZnO–CdS, and ZnO–ZnS coaxial nanocables and CuO–SnO<sub>2</sub> p–n junction nanorods have been applied as O<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S gas sensors [11–15]. The sensor device composed of NWs with a single-crystalline core and a polycrystalline shell has advantages over devices made of monolithic NWs or polycrystalline thin films because such core–shell NWs enhance both receptor and transducer functions of the devices [14,15]. Different pathways have been explored for the fabrication of SnO<sub>2</sub>–ZnO and ZnO–SnO<sub>2</sub> core–shell NWs, in which pulsed laser deposition [16] and atomic layer deposition [17] are commonly used in the deposition of a tin oxide shell layer on the nanofibers or nanorods to form core–shell 1D nanostructures [18]. Pulsed laser deposition and atomic layer deposition are excellent methods in the deposition of high-quality thin films with controlled film thickness [37]. However, these methods require expensive equipment and high vacuum for thin film deposition. In addition, the formation of an epitaxial shell layer is not advantageous for sensing applications because of the lack of grain–grain junctions. Recent studies have demonstrated a wet chemical route

\* Corresponding authors. International Training Institute for Materials Science (ITIMS), Hanoi University of Science and Technology (HUST), No. 1, Dai Co Viet Road, Hanoi, Viet Nam. Tel.: +84 4 38680787; fax: +84 4 38692963.

E-mail addresses: [thanhle@itims.edu.vn](mailto:thanhle@itims.edu.vn) (D.T. Thanh Le), [hieu@itims.edu.vn](mailto:hieu@itims.edu.vn) (N. Van Hieu).

for the fabrication of core–shell NWs [38]. The wet chemical route is an inexpensive and facile synthesis method, which enables the fabrication of various metal oxide shells only by changing the precursor solution [39].

In the present study, we demonstrate a facile method to fabricate SnO<sub>2</sub>–ZnO core–shell NWs via thermal evaporation combined with spray-coating technique. The single-crystal SnO<sub>2</sub> NWs function as the core in the heterostructures grown by thermal evaporation, and the grainy polycrystalline shell of ZnO was prepared via a wet chemical route. This synthesis method enables the formation of grainy shell or bead-like shell over the single-crystal SnO<sub>2</sub> NW, which helps increase the grain–grain contact in the materials and enhances the sensing characteristics. The ethanol-sensing performances of these fabricated SnO<sub>2</sub>–ZnO core–shell NWs were investigated in comparison with that of pristine SnO<sub>2</sub> NWs. Our results reveal that the ethanol sensitivity of SnO<sub>2</sub>–ZnO core–shell NWs was 12.5 times higher than that of pristine SnO<sub>2</sub> NWs.

## 2. Experimental

The core SnO<sub>2</sub> NWs were synthesized in a horizontal tube furnace via a vapor–liquid–solid (VLS) growth process. In the first step, the core SnO<sub>2</sub> NWs were synthesized at 800 °C by using a 9 nm gold layer as catalyst for single-crystal SnO<sub>2</sub> NW growth. The growth was carried out on an alumina substrate for 30 min [19–21]. In the second step, the cores SnO<sub>2</sub> NWs were coated with the bead-like ZnO shell layer via spray technique. In this technique, a solution of Zn(CH<sub>2</sub>COO)<sub>2</sub> was sprayed onto the SnO<sub>2</sub> NW wafer, which was kept at 300 °C. Thereafter, the Zn(CH<sub>2</sub>COO)<sub>2</sub>-coated SnO<sub>2</sub> NW was heat-treated at high temperature to convert zinc acetate into ZnO to form the SnO<sub>2</sub>–ZnO core–shell NW structure, as shown in Fig. 1(d). The morphology, crystallinity and composition of the synthesized products were characterized via field-emission scanning electron microscopy (FESEM) operated at 5 kV (JEOL, 6500). Elemental analyses of the synthesized materials were performed via energy dispersive X-ray spectroscopy (EDX).

For the gas sensor fabrication, the as-grown SnO<sub>2</sub> or SnO<sub>2</sub>–ZnO core–shell NWs were dispersed in a mixture of deionized water and isopropyl alcohol (5:5 mL) via ultrasonication. The gas sensors were fabricated by depositing the slurry containing SnO<sub>2</sub> or SnO<sub>2</sub>–ZnO core–shell NWs onto a Pt/Cr interdigitated electrode substrate. After drying, the as-fabricated gas sensors were placed at the sensing chamber and then heat-treated at 600 °C for 2 h to remove any residual organic contaminants. The responses of the fabricated sensors to different gases were evaluated by measuring the resistance/conductance variation upon exposure to various concentrations of different gases. The sensing properties were characterized

at working temperatures ranging from 350 °C to 450 °C. The gas responses to C<sub>2</sub>H<sub>5</sub>OH and to oxidizing gases were defined as  $R_a/R_g$  and  $R_g/R_a$  ( $R_g$ : resistance in gas and  $R_a$ : resistance in air), respectively [40].

## 3. Results and discussion

The morphology of the synthesized materials was characterized via FESEM, as shown in Fig. 2. The typical morphology of SnO<sub>2</sub> NWs, which is the core in the core–shell NW heterostructure, is shown in Fig. 2(A), (B). The as-grown SnO<sub>2</sub> NWs were single crystalline with an average diameter of 150 nm, a length between 5 and 20, and were randomly distributed on the substrate [20]. The NW surface was very smooth because of the VLS growth mechanism for the crystalline SnO<sub>2</sub> NWs with gold as the catalyst in NW growth, as discussed elsewhere [19–21]. However, after ZnO shell layer deposition, the morphology of the NWs significantly changed, as shown in Fig. 2(C), (D). The surface of the SnO<sub>2</sub>–ZnO core–shell NW was not smooth but very rough, which is due to the formation of the polycrystalline ZnO shell layer. A grainy ZnO shell layer that covers the SnO<sub>2</sub> NW core can be observed in the inset of Fig. 2(D). These granules on the NW surface were polycrystalline because the ZnO shell was deposited via wet chemical method without any catalyst. During spray coating, a thin layer of Zn(CH<sub>2</sub>COO)<sub>2</sub> was coated on the SnO<sub>2</sub> NW surface. This layer was converted into ZnO nanocrystals via heat treatment. Thus, the random nucleation of ZnO on SnO<sub>2</sub> NW resulted in the formation of granular structures. The structure with single-crystalline core SnO<sub>2</sub> and polycrystalline shell ZnO possess specific advantages when used as a gas sensor. The grainy and rough outer surface of SnO<sub>2</sub>–ZnO core–shell NWs creates abundant adsorption sites for gas molecules [22], which enhance the sensor receptor function. The homo- and hetero-nanojunctions in the multiple NW network create different potential barriers on the electron percolation paths, which result in significantly enhanced gas sensor performances [13–15].

The crystal structure of the synthesized SnO<sub>2</sub>–ZnO core–shell NW was investigated via X-ray diffraction (XRD), and the results are shown in Fig. 2(E). The main diffraction peaks in the XRD pattern of the as-synthesized SnO<sub>2</sub>–ZnO core–shell NWs can be indexed to a rutile structure of SnO<sub>2</sub>, which is in good agreement with a standard profile of SnO<sub>2</sub> crystals (JCPDS, No. 46-1088). In addition to the SnO<sub>2</sub> diffractions, broad diffraction peaks from the (020) and the (101) lattice planes of ZnO were also identified (JCPDS, No. 36-1451). This result indicates that the ZnO shell was polycrystalline. The diffraction peaks of the SnO<sub>2</sub> phase are stronger and sharper than those of ZnO, which indicate that SnO<sub>2</sub> NWs have a higher crystallinity than ZnO.

The elemental analysis results of SnO<sub>2</sub>–ZnO core–shell NWs via EDX are shown in Fig. 2(F). EDX confirmed the presence of Zn, Sn, and O elements, in which the sharp peaks of Zn, Sn, and O were observed.

Photoluminescence (PL) is a suitable technique used to determine the crystalline quality and the presence of impurities in the materials and exciton fine structures. Fig. 3 shows the PL spectra of the core SnO<sub>2</sub> NWs (black, line 1) and the SnO<sub>2</sub>–ZnO core–shell NWs (red in web version, line 2) measured at room temperature, respectively. The PL spectrum of SnO<sub>2</sub> NWs exhibited a broad emission peak at a visible region of 627 nm (2.0 eV), which was smaller than the band gap of SnO<sub>2</sub> (3.6 eV). The visible emission peaks cannot be ascribed to the direct recombination of a conduction electron in the Sn<sub>4d</sub> band and a hole in the O<sub>2p</sub> valence band [19]. Therefore, the emission peak at 627 nm originates from the luminescence centers formed by tin interstitials or the dangling bonds in SnO<sub>2</sub> NWs [23]. The high density of oxygen vacancies interacts with the interfacial tin, which results in the formation of a

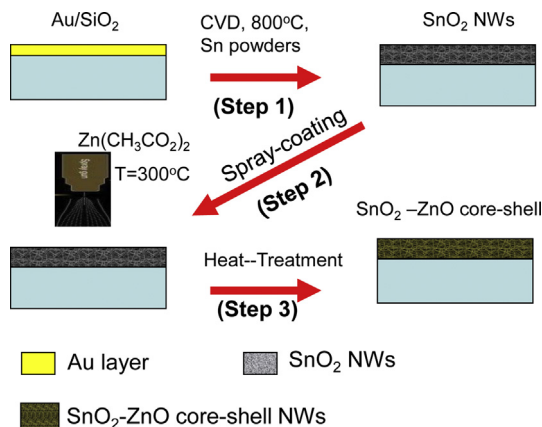


Fig. 1. Schematic of the fabrication of SnO<sub>2</sub>–ZnO core–shell NWs.

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