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Sonochemical synthesis of SnO_2 nanobelt/CdS nanoparticle core/shell heterostructures

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Received (in Cambridge, UK) 20th July 2004, Accepted 19th August 2004
First published as an Advance Article on the web 27th September 2004

SnO_2 nanobelt/CdS nanoparticle core/shell heterostructures are successfully achieved *via* a simple sonochemical approach; their ethanol-sensing properties are discussed.

One-dimensional (1D) nanocrystals in the forms of tubes, wires, and belts represent a broad class of nanoscale building blocks that can be used to assemble a range of electronic and photonic devices.[1–6] A major area of application for these 1D nanocrystals has been reported to be the sensing of important molecules, either for medical or environmental health purposes, as the recent work has shown with carbon nanotubes,[2] Si nanowires,[3] Pt nanowires,[4] In_2O_3 nanowires,[5] and SnO_2 nanobelts.[6,7] Among them, semiconducting metal oxide systems, particularly those synthesized from inexpensive In_2O_3, SnO_2, and ZnO, are of great interest owing to their high chemical stability and good flexibility in fabrication. It has been reported that the SnO_2 nanobelt sensors have several advantages over conventional thin film devices such as low operating temperatures and no ill-defined coarse-grain boundaries.[6,7] However, some questions still remain for the development of highly sensitive sensors based on the 1D nanocrystals. For example, how to improve the gas sensitivity and selectivity of these 1D nanocrystals has been unclear up to now. In this communication, we report a simple and efficient sonochemical route to coat SnO_2 nanobelts with a beplastered layer of CdS nanoparticles. In comparison with the uncoated SnO_2 nanobelts, enhanced sensing properties of the SnO_2 nanobelt/CdS nanoparticle (SnO_2@CdS) core/shell heterostructures have been observed.

Our synthetic approach follows the sonochemical synthesis of CdS nanoparticles in a neutral aqueous solution, in which the SnO_2 nanobelt carriers are presented. The SnO_2 nanobelts used in this work were prepared by thermal evaporation of metallic Sn powders at 800 °C.[8] The obtained SnO_2 nanobelts were singly crystalline with rutile structures, and usually 30–200 nm in width, 10–50 nm in thickness, and several hundreds of microns in length. In a typical case, SnO_2 nanobelts (10 mg), cadmium chloride (500 mg), and thiourea (250 mg) were added to 100 ml distilled water in a sonication cell that was attached to a sonicator horn. The reaction mixture was irradiated with a high-intensity ultrasonication (100 W, 40 kHz) for different periods ranging from 1 to 3 h.[9] Argon gas was bubbled through the reaction mixture for 30 min prior to the sonication to expel dissolved oxygen. After irradiation the excess CdS nanoparticles were separated from the reaction mixture by centrifugation. Then the resulting powders were washed thoroughly (three times) with doubly distilled water and ethanol, centrifuged at 10 000 rpm, and allowed to dry in air before characterization.

Fig. 1a and Fig. 1b show the typical transmission electron microscopy (TEM) images of the uncoated SnO_2 nanobelt cores and the sonochemically generated SnO_2@CdS core/shell heterostructures, respectively. It can be seen that the SnO_2 nanobelt cores have typically smooth surfaces throughout the entire length of the belt. Moreover, the SnO_2 nanobelt cores are singly crystalline with a rutile structure as determined by the selected-area electron diffraction (SAED) pattern (inset of Fig. 1a).[8] As shown in Fig. 1b, a large amount of CdS nanoparticles are well dispersed on the surfaces of the SnO_2 nanobelt cores, demonstrating that sonochemical synthesis of the SnO_2@CdS core/shell heterostructures is successfully achieved. The CdS nanoparticles are nearly spherical in shape and have typical sizes in the range of 10–20 nm. The SAED pattern of the SnO_2@CdS core/shell heterostructures shown in the inset of Fig. 1b reveals the additional diffraction rings of hexagonal structured CdS, apart from the diffraction spots of rutile SnO_2 nanobelts. Detailed microstructure information of the CdS nanoparticle shells is further characterized by high-resolution TEM, as shown in Fig. 1c. The measured spacing of the crystallographic planes is 0.315 nm, which corresponds to the {101} lattice plane of the hexagonal structured CdS crystal. It states that the sonochemical growth of CdS nanoparticles is along the $<101>$ direction.

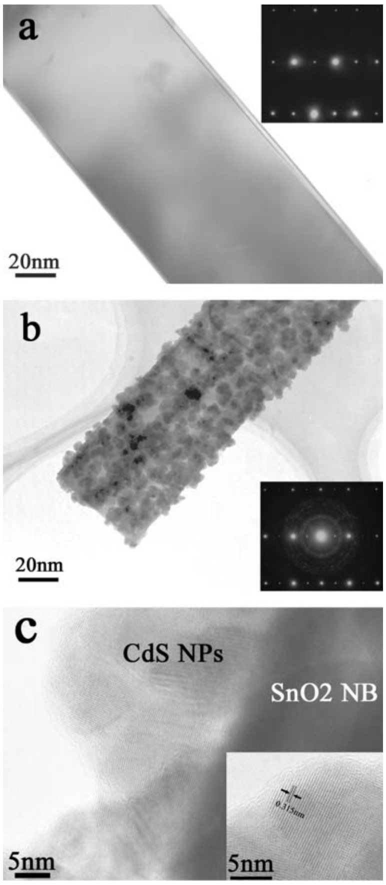

Fig. 1 (a) TEM image of the uncoated SnO_2 nanobelts. Inset shows the corresponding SAED patterns; (b) general morphology of the SnO_2 nanobelt/CdS nanoparticle core/shell heterostructures produced by 3-h sonication. Inset shows the corresponding SAED patterns; (c) HRTEM image of the CdS nanoparticles coated on the surfaces of the SnO_2 nanobelts. Inset shows an individual CdS particle. The terms “NPs” and “NB” represent nanoparticles and nanobelt, respectively.

It is known that power ultrasound effects chemical changes due to cavitation phenomena involving the formation, growth, and implosive collapse of bubbles in liquid, which generates localized hot spots having temperatures of roughly 5000 °C, pressures of about 500 atmospheres, and lifetimes of a few microseconds.[10]

DOI: 10.1039/b411018h

These extreme conditions can drive chemical reactions such as oxidation, reduction, dissolution and decomposition, which has been exploited to prepare a variety of metal nanoparticles,[11] oxide nanorods,[12] and metal sulfide nanoparticles.[13] Sonication of the precursor in the presence of a support material provides an alternative means of trapping the produced nanoparticles,[11a,13a] which has been used in this work to produce the SnO_2@CdS core/shell heterostructures. On the basis of a comparison with the previous sonochemical studies on metal sulfide nanoparticles,[13a,13c] the reaction occurring during sonication which leads to the formation of the SnO_2@CdS core/shell heterostructures would be:

$$H_2O \text{)))))} \; H^{\bullet} + OH^{\bullet} \tag{1}$$

$$2H^{\bullet} + RS \rightarrow H_2S + R^{\bullet} \; (RS = H_2NCSNH_2) \tag{2}$$

$$S^{2-} + Cd^{2+} \rightarrow CdS \tag{3}$$

$$n(CdS) + SnO_2 \rightarrow SnO_2@CdS \tag{4}$$

Reaction (1) represents the formation of primary radicals ($H^{\bullet}$ and $OH^{\bullet}$) from the ultrasound-initiated dissociation of water.[11] Reactions (2) and (3) represent the main reactions leading to the formation of CdS nanoclusters in solution.[14] The generated CdS nanoclusters can interact with the SnO_2 nanobelt carriers in the solution and form a CdS–capped SnO_2 nanobelt composite, which is termed as a SnO_2@CdS core/shell heterostructure in this work.

The SnO_2@CdS core/shell heterostructures are expected to find applications for highly efficient photoelectrochemical cells, as the recent work has shown with a carbon nanotube@CdS core/shell composite.[15] Such applications can be attributed to the efficient charge separations in SnO_2@CdS core/shell heterostructures. It is known that SnO_2 is an *n*-type direct wide bandgap semiconductor ($E_g = 3.6$ eV) while CdS is a short bandgap one ($E_g = 2.4$ eV). The conduction band of CdS (−0.8 V *vs.* NHE) is more negative than that of SnO_2 (0.0 V *vs.* NHE). Consequently, in a thermal equilibrium of a SnO_2–CdS heterojunction, electrons from the external CdS shell layer will flow into the inner SnO_2 nanobelt cores, forming an accumulation layer of electrons in the potential well adjacent to the interface of SnO_2/CdS. Using two semiconductors in contact having different redox energy levels of their corresponding conduction and valence bands has actually been considered as one of the most promising methods for the development of photoelectrochemical cells.[16]

It is also found that the SnO_2@CdS core/shell heterostructures have appealing gas-sensing properties, which has, to the best of our knowledge, not been reported previously. For example, enhanced ethanol-sensing properties of the SnO_2@CdS core/shell heterostructures are observed and will be discussed in this work. Fig. 2 shows the typical response curves of the SnO_2 nanobelt sensors and the SnO_2@CdS core/shell heterostructured sensors to 100 ppm ethanol vapors in air at an operating temperature of 400 °C.[17] The sensitivity of the sensors is defined as $S = G_{ethanol}/G_{air}$, in which the G_{air} represents the conductance in air while the $G_{ethanol}$ is that in the 100 ppm ethanol vapor. The jump of the conductance can be attributed to the variation of carrier density in the SnO_2 nanobelts that relates to the absorption–desorption of oxygen.[6,7] From Fig. 2, an improved ethanol-sensing performance of the SnO_2@CdS core/shell heterostructures is clearly observed.[18] Considering the efficient charge separations in SnO_2@CdS core/shell heterostructures, we suggest that the CdS nanoparticles would be served as additional electron sources that can greatly improve the electron conduction in SnO_2 nanobelts. It may provide a new means of improving gas-sensing properties of SnO_2 materials beside the noble metal addition[19] and UV light irradiation.[6a] We are currently investigating the details of the sensing mechanisms of the SnO_2@CdS core/shell heterostructures, which will be reported elsewhere.

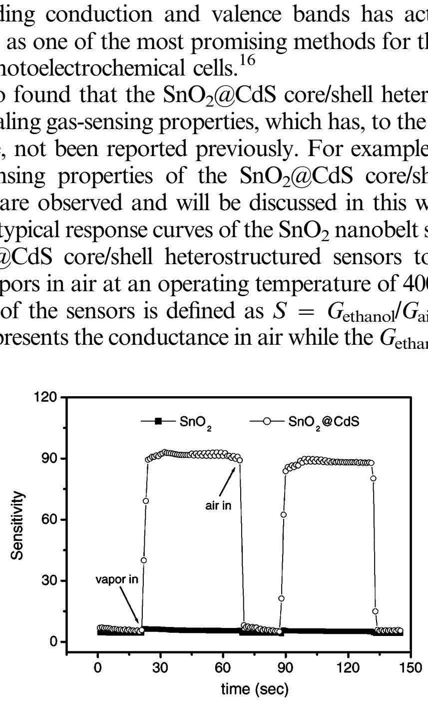

Fig. 2 Response curves of the SnO_2 nanobelt sensors and the SnO_2@CdS core/shell heterostructure sensors to 100 ppm ethanol vapors in air at a working temperature of 400 °C.

In conclusion, *via* a simple and efficient sonochemical approach, SnO_2 nanobelt/CdS nanoparticle core/shell heterostructures are successfully prepared and tested for the detection of ethanol vapor in air. It is possible that, by further optimizing the growth parameters such as source materials, the method used herein could be extended for other core/shell semiconductor systems.

This work is supported by the Special Funds for Major State Basic Research Project (No.G2001CB3095) and the National Natural Science Foundation of China (No. 69925410 and 60236010). T. Gao thanks the financial support from the China Postdoctoral Science Foundation.

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