

Sol-gel Template Synthesis and Liquid CO₂ Developed TiO₂/CdS Composite Nanowire Arrays

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ABSTRACT

TiO₂/CdS composite nanowire (~ 200 nm diameter and ~ 50 μm length) arrays were successfully prepared by the sol-gel template method. An anticipated good nanowire arrays was obtained by using liquid or supercritical CO₂ to develop the target materials in purification process. The morphology, crystallinity, and composition of the product was characterized by SEM, XRD, and EDX.

INTRODUCTION

Since the successful growth of carbon nanotubes, one-dimensional materials have received increasing attention, both because of their fundamental importance and their wide-ranging potential applications in nano devices [1-4]. Fabrication of nanoscale heterogeneous composites offers additional possibilities in developing novel functional materials. The study of interparticle electron transfer between dissimilar semiconductor particles has attracted much interest [5,6]. Combining two semiconductor particles together offers an opportunity to sensitize a semiconductor material having a large band gap and energetically low-lying conduction band by using a second semiconductor having a small band gap and an energetically high-lying conduction band [7,8]. Oxide semiconductors with a sufficiently negative conduction band, such as TiO₂ ($E_g = 3.2\text{eV}$), generally have too large band gap energies to utilize the main mass of the solar energy spectrum [9]. Semiconductors with a somewhat smaller band gap, such as CdS ($E_g = 2.6\text{eV}$), have been investigated embedded in TiO₂ to study photosensitization. Charge transfer from one semiconductor into another can lead to efficient and longer charge separation, which is anticipated to have potential applications in photocatalysis and solar energy conversion [10].

Several different strategies for fabrication of semiconductor nanoparticle composite films have been reported, including Langmuir-Blodgett (LB) techniques, self-assembly, and mechanical mixing method [10-12]. To our knowledge, there are no reports of large- and small-band gap composite semiconductor nanowires. Although there are some reports that use sol gel method for preparation of individual component semiconductors, the results are not ideal. Lei et al [13] reported fabrication of TiO₂ nanowire arrays, but they could not get very good arrays: all of the nanowires are bundled. Cao et al [14] used the sol gel technique to prepare CdS nanowires arrays, but from their experimental procedures, it is impossible to get a stable sol, and furthermore, many impurities would be introduced into the final product. This is the first report using sol-gel template method and liquid CO₂ development to successfully fabricate high purity TiO₂/CdS composite nanowires in anticipated arrays.

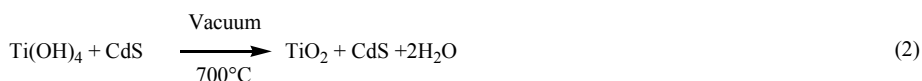
EXPERIMENTAL DETAILS

Titanium (IV) isopropoxide, cadmium acetate hydrate were purchased from Aldrich. They were not further purified before use. Titanium (IV) isopropoxide (5ml) was added to 25 ml absolute ethanol, and the resulting solution was stirred in an ice bath. To another 25 ml portion of ethanol were added cadmium acetate (0.5g) and one drop of 0.5M HCl. Cadmium acetate solution was mixed with titanium (IV) isopropoxide in ice bath, the solution at this time is still colorless and transparent. Then, a saturated H₂S water solution was slowly added until a yellow white, semi-transparent sol obtained. Adjusting this sol to a appropriate viscosity in order to get a high filling of purposed materials in the nanochannel after a porous alumina membrane (pore diameter, 200nm) immersed in the sol. After the desired immersion time, the membrane was taken out from the sol, and dried in air for 1 hour at room temperature. The membrane was then placed in a quartz cell in a high vacuum tube furnace (10⁻⁷ Torr) and annealed at 700°C for 6 hours. After annealing, the membrane was anchored to a substrate with super glue, and polished with a 13 micron sand paper, then the membrane was immersed into 6 M aqueous NaOH for 20 minutes to remove the alumina template. The surplus of NaOH was washed away with water or ethanol. The resulting one side polished composite membrane was attached to a SEM sample stub with conductive tape, and a very thin layer of Au was sputtered onto its surface. The SEM images were obtained using a JEOL JEM-6300 scanning electron microscope. Prior to EDX, and XRD measurements, both sides of composite membrane were polished and immersed in 6M NaOH for 20 min to completely remove the alumina. The residue, comprised of isolated nanowires, was collected, washed with distilled water or ethanol, dried in vacuum at room temperature. The powder XRD analysis was performed using Enraf Nonius FR 590 X-ray diffractometer with Cu-K_α radiation (λ = 0.154178nm).

For liquid CO₂ development of our samples, ethanol was used to wash away the surplus of NaOH. After the NaOH was completely removed, the free-templated nanowires with its substrate was always kept immersed in ethanol, and then transferred to a 2.5 mL high pressure stainless cell together with ethanol. Liquid CO₂ was injected in this cell from one inlet, released from one outlet. During this process, the nanowires on the substrate are always kept wet in ethanol and liquid CO₂. Repeating the exchange process many times, the ethanol was completely replaced, and the nanowires in pure liquid CO₂ were taken out from the cell after the liquid CO₂ was slowly released.

RESULTS AND DISCUSSION

The formation of this kind of sol–gel can be described simply as follows:



CdS nanoparticles and TiO₂ sol are simultaneously formed, and the CdS nanoparticles are ultimately embedded in a three-dimensional infinite network (-Ti-O-bonds), the gel. Figure 1 shows scanning electron microscope (SEM) images of TiO₂/CdS nanowires obtained after removal of the alumina membrane by dissolution in 6 M NaOH. The surplus of NaOH was washed away by water or ethanol, dried in air. Figure 1 (a) shows that all of the nanowires are collapsed, and Figure 1 (b)

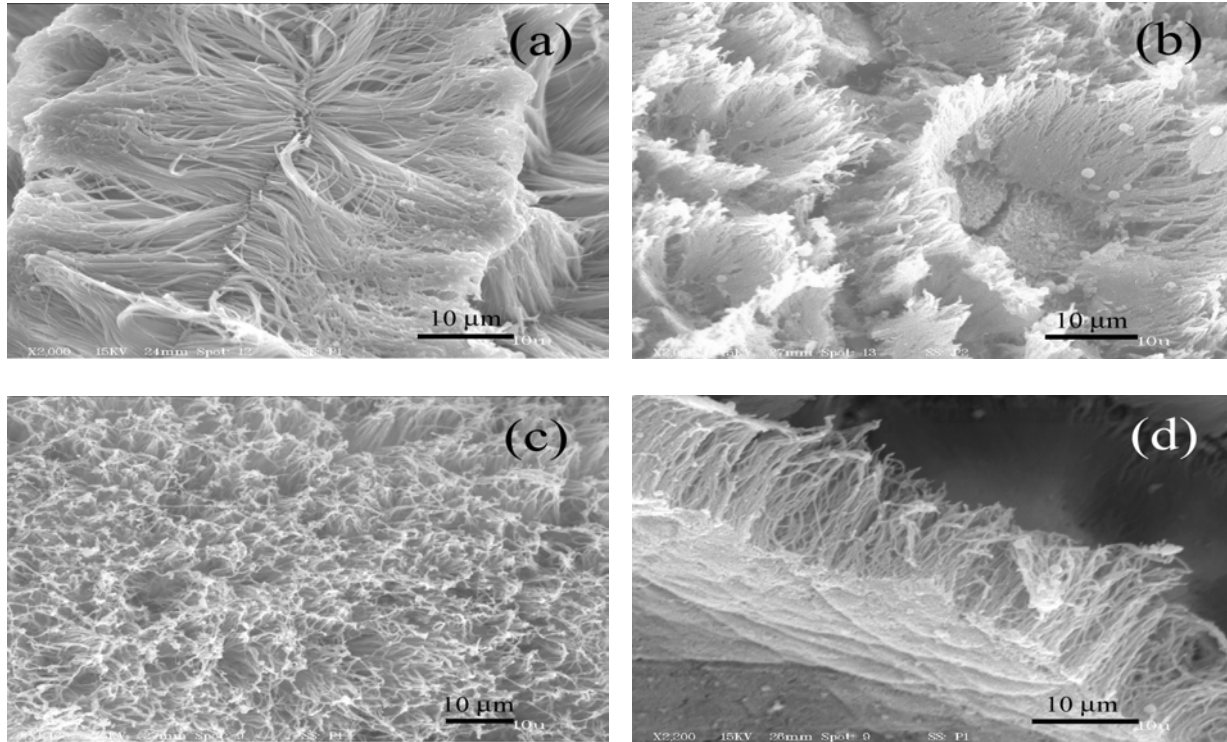


Figure 1. SEM images of TiO_2/CdS composite semiconductor nanowires prepared by sol-gel template method and developed in water or ethanol; (a) collapsed nanowires; (b) bundled nanowires; (c) top surface view of SEM image of this composite nanowires developed in liquid CO_2 ; (d) a cross-sectional view of SEM image of the nanowires developed in liquid CO_2 ; neither views [(c) and (d)] show collapsed nor bundled morphologies (scale bar 10 μm).

image reveals bundled nanowires around areas where the nanowires have been stripped from the substrate. These two morphologies were caused by solvent-induced interfacial force during the drying process from water or ethanol. In order to solve this problem and to try to get a good array of nanowires, a low surface tension solvent must be applied to develop this material. After comparison of surface tension of different solvents, H_2O , ethanol, and liquid CO_2 , the surface tension of liquid CO_2 (0.005 N/m) is much less than that of H_2O (0.072 N/m) and ethanol (0.024 N/m). Also, ethanol is miscible with liquid CO_2 enabling the exchange with CO_2 . After using liquid CO_2 as a solvent, the morphology of prepared nanowires was greatly improved: no collapsed or bundled nanowires. Figure 1 (c) shows the SEM image of the top surface of the nanowire array washed with liquid CO_2 . Figure 1 (d) shows the SEM image of a cross section of nanowire array.

Figure 2 shows the X-ray diffraction (XRD) pattern of TiO_2/CdS composite semiconductor nanowires. There are three different phases in the composite nanowires: 2θ values of 24.5° , 26.5° , 28.3° , 52.2° and 53° correspond to the crystal planes of (100), (002), (101), (112), and (201) of Greenockite CdS, in good agreement with the JCPDS file No. 6-314. 2θ values of 25.3° , 36.9° , 37.8° and 48.1° correspond to the crystal planes of (101), (103), (004) and (200) of anatase phase of TiO_2 , in good agreement with the JCPDS file No. 21-1272. 2θ values of 27.4° , 36.16° , 39.2° , 41.3° , 44° ,

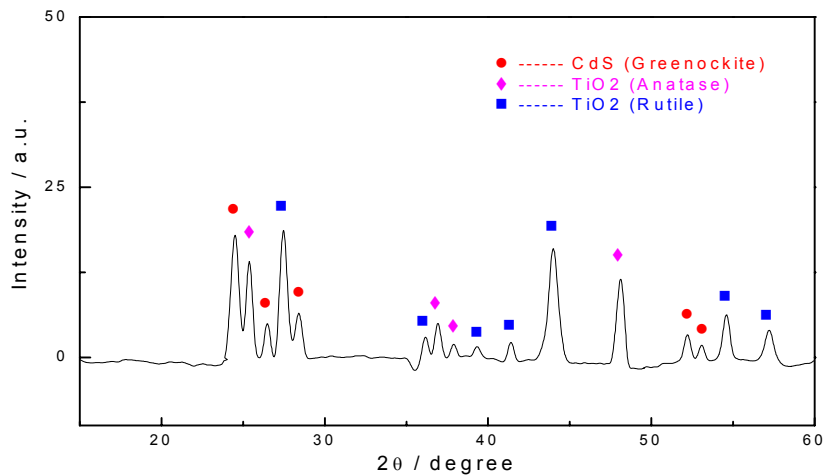


Figure 2. X-ray diffraction pattern (XRD) of TiO₂/CdS composite semiconductor nanowires; ● : CdS; ◆ : TiO₂ (Anatase); ■ : TiO₂ (Rutile).

54.6° and 57° correspond to the crystal planes of (110), (101), (200), (111), (210), (211) and (220) of rutile phase of TiO₂, also in good agreement with the JCPDS file No. 21-1276.

Figure 3 shows Energy Dispersive X-ray Analysis (EDX) spectrum of TiO₂/CdS composite nanowires. In this EDX spectrum, peaks of Ti, O, Cd and S are found. Quantitative analysis results indicate an atomic composition of 60.31% O, 4.65% S, 31.01% Ti and 4.03% Cd, which is very close to the corresponding stoichiometry.

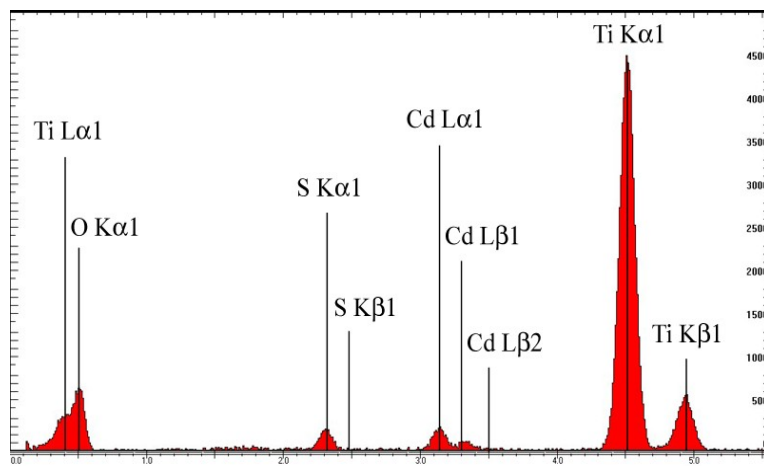


Figure 3. Energy Dispersive X-ray analysis (EDX) of TiO₂/CdS composite semiconductor nanowires using saturated H₂S water solution as S²⁻ source.

CONCLUSIONS

TiO₂/CdS composite nanowire arrays were successfully prepared by the sol-gel template method. The morphology, crystallinity, and composition of the product was characterized by SEM, XRD, and EDX. Solvent-induced phenomena sometimes have undesirable influences on the morphology of carefully designed nanomaterials. The solvent-induced forces appear to be the origin of the collapsed or bundled morphology exhibited by sol-gel-templated processing of TiO₂/CdS nanowire arrays. Liquid and supercritical CO₂ drying of nanostructures can eliminate the effect of capillary (or interfacial tension) forces on the final morphology and enable the unique properties and potential applications of these important materials to be realized.

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