



Controllable preparation of WO₃ nanorod arrays by hydrothermal method

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ABSTRACT

WO₃ nanorod arrays (WNRs) were synthesized on indium tin oxide conducting substrates by hydrothermal method. The effects of preparing conditions such as the precursor solutions concentration (H⁺ and Na₂WO₄), the additive NaCl, growth temperature and reaction time on the morphologies of WNRs have been systematically investigated by scanning electron microscopy, X-ray diffraction, Raman spectrum and ultraviolet visible absorption spectrum. It is shown that the pH value of the precursor solutions plays an important role in determining the morphology of as-prepared WNRs, which leads to different band gap energies. The orientation, density, and crystallinity of WNRs can be controlled by changing the amount of additive NaCl, Na₂WO₄ concentration and reaction temperature, respectively. Moreover, the growth mechanism of the WNRs was also discussed.

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1. Introduction

Ordered semiconductor nanoscale materials on substrates (nanowire, nanorod, nanotube arrays) have aroused great research interest because of their well-organized alignment and morphology [1–3]. It has been realized that the crystalline structure, the orientation and the density of this type of materials on substrates have significant impacts on their related properties [4,5] compared to that with random direction. As a result, the controllability of preparing conditions plays an important role in synthesizing well oriented nanorod/tube arrays on substrates. Recently, great progress has been made on controllable preparation of metal oxide semiconductor nanowire/rod/tube arrays, such as ZnO [6,7], TiO₂ [8,9], SnO₂ [10], Fe₂O₃ [11], etc. In our previous works [12–14], controllable preparation of ZnO, TiO₂ and SnO₂ nanorod arrays has been realized on different substrates by hydrothermal approach. It is demonstrated that the preparing conditions including the pre-treatment of substrates, the precursor solution, growth temperature and time have great influences on the morphological features and the alignment ordering of these nanorod arrays, which lead to unique properties.

Among the numerous transition metal oxides, WO₃ is an indirect band gap semiconductor and has been found useful in electrochromic devices [15], semiconductor gas sensors [16,17], photocatalysts [18,19], etc. Generally, WO₃ nanorod arrays (WNRs) have been synthesized by a number of techniques, including chemical vapor deposition (CVD) [20,21], thermal evaporation [22,23], electrochemical anode oxidation [24], sol–gel processing [25], and hydrothermal approach [26–29]. Deb et al. [30] deposited mat-like WO₃ nanowire arrays and nanoparticle thin film on quartz substrates by CVD method. The morphology and crystalline structure of the obtained WO₃ are controlled by the chamber

pressure and the oxygen content. Yong et al. [31] prepared monoclinic WO₃ nanowire arrays on a tungsten substrate by thermal evaporation of WO₃ powder at elevated temperature in a tube furnace. It has been found that the presence of WO₃ powder is crucial in producing WO₃ nanowires at high temperature. Compared to CVD or thermal evaporation process that requires sophisticated equipments and rigorous conditions such as relatively high temperature and single-crystalline substrates, the hydrothermal routes are more convenient, controllable and economic for large-scale preparation of WO₃ nanowire/rod arrays. Shibuya et al. [26] reported the preparation of well-ordered WO₃ nanotrees which are composed of WO₃ nanotrunks and WO₃ nanobranched on tungsten plate substrate. Similarly, Zhang et al. [27] synthesized hexagonal structured WO₃ films with tree-like morphology on tungsten foils. The film thickness and the crystal structure of the film can be controlled by changing the duration and annealing temperature, respectively. However, the opacity of the tungsten plate substrate limits its photoelectrochemical properties. Recently, Su et al. [28] synthesized hexagonal WO₃ nanowire arrays on fluorine doped tin oxide (FTO) substrates by hydrothermal method. They demonstrated that nanowire or nanoflake arrays are selectively deposited by adjusting the composition of precursor solutions. Zhang et al. [29] obtained hexagonal WO₃ nanowire arrays and microbricks on FTO-coated glass with the addition of ammonium sulfate. To date, controlling the orientation, morphology, growth density and diameter distribution of well-aligned WO₃ nanorod/nanowire arrays by hydrothermal approach is still the most challenging issues. However, detailed studies are inadequate up to now. So, it is necessary to explore systematically the effects of preparing conditions on the growth of well-aligned WNRs on transparent substrates.

In this paper, we described the hydrothermal growth of WNRs under various conditions. We demonstrated that the preparing conditions such as H⁺ concentration, Na₂WO₄ concentration, the amount of additive NaCl and reaction temperature and time have great influences

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on the morphological features, the alignment ordering and band gap energy of WNRs on indium tin oxide (ITO) substrates. Furthermore, the growth mechanism of the WNRs was also discussed.

2. Experimental section

2.1. Materials

All chemicals (Beijing Chemicals Reagent Company) were of analytical reagent grade and used without further purification. All the aqueous solutions were prepared using double distilled and ion-exchanged water. ITO glass plates ($10 \Omega/\text{cm}^2$, $3.5 \times 1.0 \text{ cm}^2$) were used as substrates and were cleaned by standard procedures prior to use.

2.2. Hydrothermal synthesis

The precursor solution was prepared as follows: sodium tungstate dihydrate powder ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 8.25 g, 0.025 mol) was dissolved

in distilled water (25 ml). Then the pH values of the solutions were adjusted by the following two steps. Firstly, the pH value of the solution was acidified to 2.0 with HCl (2 M) by magnetic stirring, and white precipitate was generated. Secondly, the solution was diluted to 250 ml and oxalic acid was added to the mixture to adjust the final pH values. After that a homogeneous precursor solution was formed.

After stirring for 30 min, 20 ml of the precursor solutions was transferred into a 50 ml Teflon-lined autoclave and sodium chloride (NaCl) was added to it. Then the hydrothermal growth was carried out at fixed temperature for some time in a sealed Teflon-lined autoclave by immersing the ITO substrates in the precursor solutions. After the reaction was finished, the autoclave was cooled to room temperature naturally. Subsequently, the as-deposited substrates were rinsed repeatedly with deionized water and dried in air for further characterization.

In order to investigate the effects of experimental parameters on the preparation of WNRs, the pH values varied from 2.0 to 2.7 with an interval of 0.1, the additive amount of NaCl from 0.0 to 1.0×10^{-2} mol with an interval of 2.5×10^{-3} mol, the concentration of Na_2WO_4 are 0.025, 0.050,

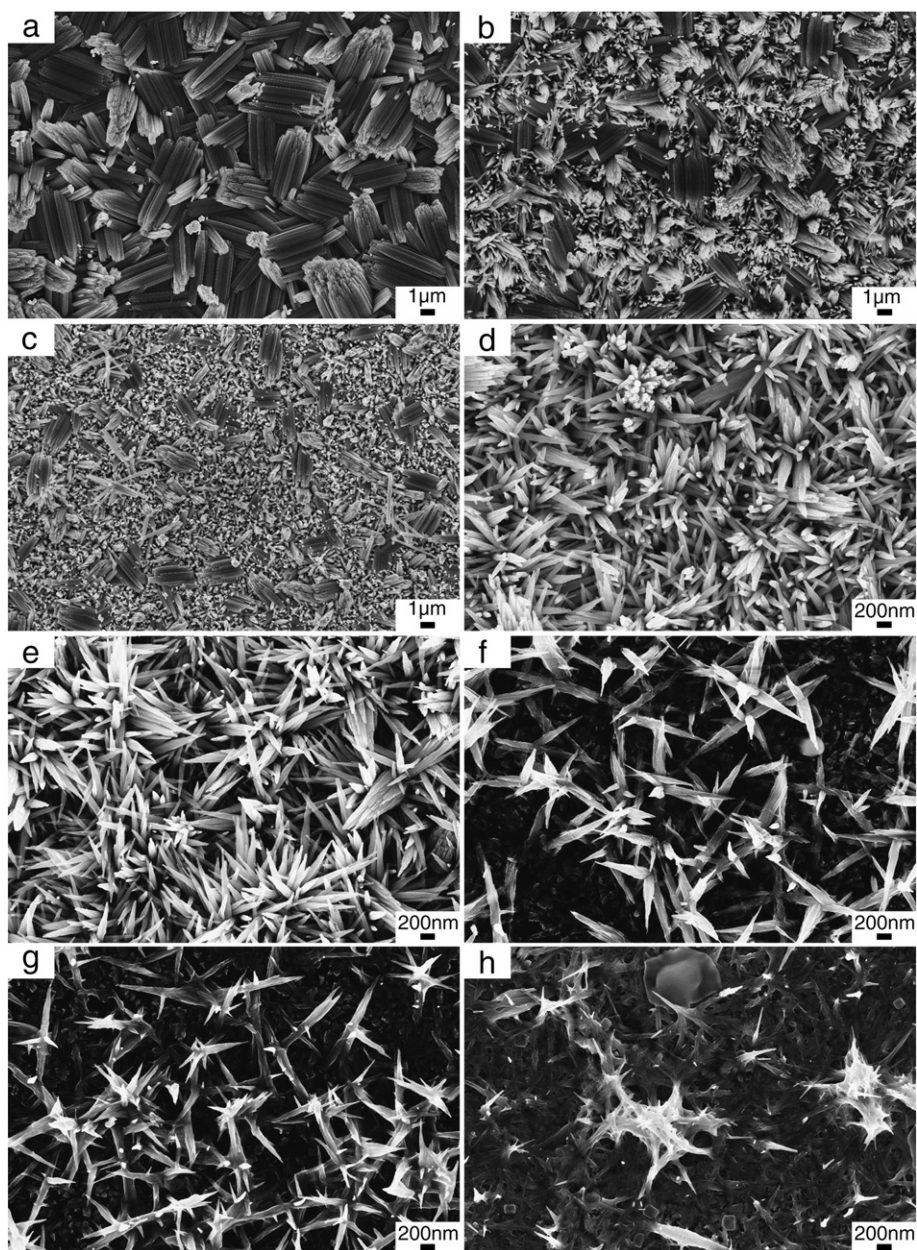


Fig. 1. FESEM images of the samples synthesized at different pH values: (a) 2.0, (b) 2.1, (c) 2.2, (d) 2.3, (e) 2.4, (f) 2.5, (g) 2.6, and (h) 2.7 (concentration of Na_2WO_4 : 0.10 M, additive NaCl amount: 5.0×10^{-3} mol, reaction temperature: 170 °C, reaction time: 4.0 h).

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