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Growth of Highly Crystalline Bundles of WO_3 Nanorod under Facile Hydrothermal Condition

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Abstract

Large scale, highly crystalline WO_3 nanorods bundles have been synthesized using sodium tungstate ($Na_2WO_4.2H_2O$) as precursor and sodium chloride (NaCl) as growth directing agent under single step hydrothermal route at 180 °C for 12 hrs. The morphology and structural characterizations were carried out using Scanning electron microscopy, Transmission electron microscopy, X-ray diffraction and Raman spectroscopy techniques. The nanorods were identified as hexagonal phase having diameter ~10 nm and length upto ~10 μm. Further these WO_3 nanorods can be applied as novel gas sensors and can be potentially used as precursor for the growth of two dimensional WS_2.

Keywords: WO_3, Nanorod, Hydrothermal Synthesis, SEM, XRD, Raman, HRTEM.

Introduction

Tungsten oxide has attracted considerable attention due to its distinctive optical [[1, 2]], electrical [[3, 4]] and structural [[5]] properties. It is an indirect band gap semiconductor, suitable for harvesting visible range of solar spectrum [[6, 7]]. It is one of the promising materials for various optoelectronic devices, such as electrochromic devices [[8]], highly sensitive gas sensors[[9, 10]], information display, rewritable devices[[11]] etc. Various nanostructures, such as nanoparticles [[12]], nanorods [[1]], nanotubes[[13]], and nanosheets [[14]], have drawn attention for use in number of fields due to their high surface to volume ratio and size-dependent properties. Among the several nanostructures one dimensional (1D) nanostructure is more promising due to its dimensionality and size which is regarded as significant factor for the excellent and novel properties.

Several synthesis methods have been developed for the growth of nanostructured WO_3 powders such as chemical vapor deposition [[15]], sol-gel [[14]] approach, laser ablation [[16]] etc. Depending on the synthesis conditions: temperature, pressure, it can be crystallize into monoclinic or hexagonal phase.

Govender et al. reported synthesis of WO_3 by laser pyrolysis technique and observed change in morphology by changing precursor concentrations [[17]]. Shankar et al. reported synthesis of WO_3 nanorods using carbon nanotube as templet under hot filament chemical vapor deposition method [[18]]. However, hydrothermal synthesis has a lot of benefits, being a simple, low cost and efficient way to prepare large-area devices, and thus many researchers have carried out the synthesis of WO_3 nanostructures via hydrothermal approach. Further, for realization of potential applications of WO_3 nanorods in various fields at industrial scale, its large scale production, in cost effective and ecofriendly way is required

Keeping all the above points in view, in the present work, we report growth of parallel aligned WO_3 nanorods bundle via a facile wet-chemical hydrothermal synthesis route. Hydrothermal approach is easy and cost effective in comparison to other expansive vacuum approach or laser ablation approach etc. X-ray diffraction and Raman characterization reveals the presence of hexagonal phase of WO_3 nanorods. Further, this one dimensional WO_3 nanorods having diameter ~10 nm is promising candidates for electrochromic or photochromic applications and due to high surface to volume ratio this is suitable material as precursor for growth of two dimensional TMDs (WS_2, WSe_2 etc.).

Methods

Precursors, $Na_2WO_4.2H_2O$, NaCl and HCl were purchased from Himedia, India. All the chemicals used in the present work were of analytical grade and used without any further purification.

Schematic of hydrothermal synthesis has been shown in figure 1. Here, $Na_2WO_4.2H_2O$, NaCl and HCl were used as precursors for the growth of WO_3 nanorods. In a typical synthesis process, 3.3 g of $Na_2WO_4.2H_2O$ and 1.16 g of NaCl were dissolved in 76 mL of DI water. Further, 3 molar HCl was slowly added drop by drop into the solution with continuous magnetic stirring until the pH value of the solution was reached ~3.0. Then transparent solution was transferred into a Teflon-lined autoclave of 100 mL capacity. Further, this autoclave was put into an oven for hydrothermal reaction at

180 °C for 12 hrs. When the reaction was over autoclave was cooled down to room temperature, a white product on the Teflon wall was obtained, which was scratched and washed several times using ethanol and DI water respectively. After washing, the solution was filtered and dried at 60 °C in oven.

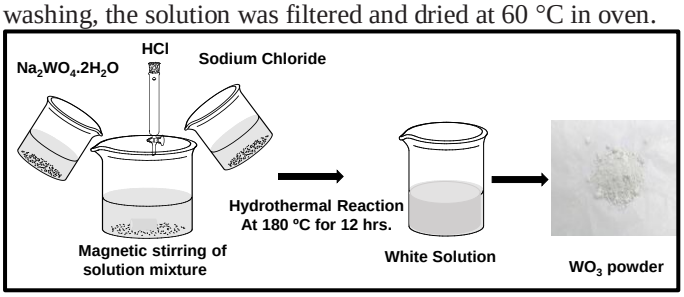

Figure 1: Schematic for the hydrothermal synthesis of WO_3 nanorods

Growth of WO_3 nanorods can be explained according to the following reactions [[19]]:

$$Na_2WO_4 + 2HCl \rightarrow H_2WO_4 + 2NaCl \quad (1)$$

$$H_2WO_4 \rightarrow WO_3\ (crystal\ nucleus) + H_2O \quad (2)$$

$$WO_3\ (crystal\ nucleus) \rightarrow WO_3\ (nanorods) \quad (3)$$

Results

The structural morphology of the as synthesized WO3 powder was characteized using Scanning electron microscope (SEM FEI, USA) using beam current of 10 µA and an accelerating voltage of 25 kV. The phase of the product was identified through X-ray diffraction (XRD, Pan analytical, USA) at room temperature, using Cu Kα (λ~1.54 Å) radiation at 35 kV and 40 mA in a 2θ range from 10° to 80°. High resolution transmission electron microscope (HRTEM) images, of the WO3 nanorods were obtained from FEI Technai, G2 electron microscope, at an accelerating voltage of 200 kV. Raman spectra of the as synthesized WO3 nanorods were recorded at room temperature with Raman spectrometer (Renishaw, Germany). The spectra were recorded with, 532 nm laser excitation and laser power was 5 mW.

Discussion

Figure 2(a) shows the SEM image of as synthesized WO_3 powder and inset showing the SEM image of WO_3 powder dispersed over silicon substrate after 25 minutes sonication in DI water. From this figure we can clearly see a bundle like structure, which is composed of a number of parallel aligned nanorods. Inset of figure 2(a) reveals the detailed morphology of this bundle like structures. Each bundle contains number of WO_3 nanorods that are ~10nm in diameter, and these nanorods are aligned in parallel fashion to form bundle like structures.

Further, microstructure of nanorods was characterized using HRTEM. Figure 2(b) shows the HRTEM image of the WO_3 nanorods. Lattice fringes can be clearly seen in HRTEM image, indicating highly crystalline growth of the as-synthesized hexagonal WO3 nanorods. The lattice spacing between two adjacent lattice planes perpendicular to the growth direction was measured and spacing of 0.381 nm was found. It corresponds to the *d*-spacing of (0002) planes, which indicates that nanorod was grown along the [0002] direction [20].

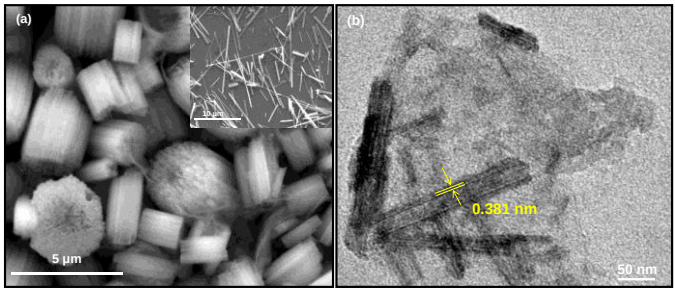

Figure 2: (a) SEM micrograph of WO_3 nanorod bundles, inset showing dispersed WO_3 nanorods over silicon wafer and (b) HRTEM image of WO_3 nanorods.

Figure 3 shows the XRD pattern of the as synthesized WO_3 powder. All of the peaks were indexed and it perfectly matches to the hexagonal phase of WO3 structure (JCPDS 85-2460). In this XRD pattern no peaks were found corresponding to the nonstoichiometric tungsten oxides and tungsten oxide hydrates, indicating the formation of pure hexagonal phase WO3. Sharp diffraction peaks confirm highly crystalline growth of WO_3 nanorods. Thus, it can be inferred from XRD pattern that the as-synthesized product consists of highly crystalline hexagonal phase WO_3 nanorods.

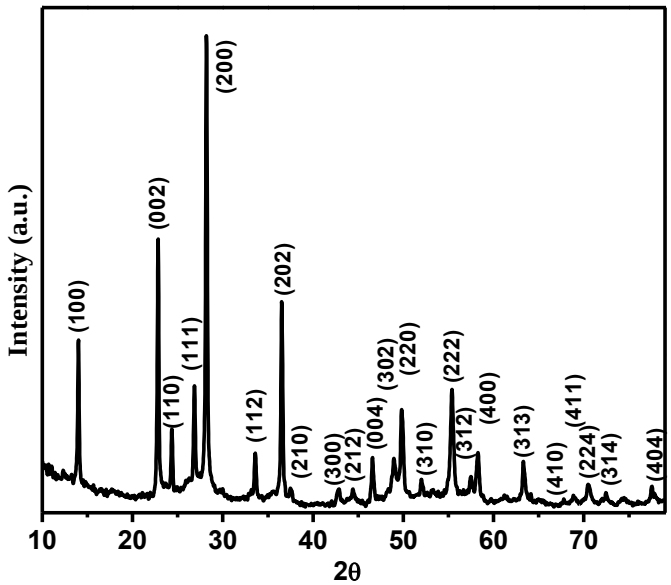

Figure 3: XRD of the as synthesized WO_3 nanorod bundles.

Raman spectroscopy was also performed to investigate the presence of WO_3 nanorods. Figure 4 shows the Raman spectra of the as synthesized WO_3 nanorods. From analyzing the spectra, different peaks can be assigned as follows: The major vibrational modes of the WO_3 nanorods, located at ~813 cm^{-1} and a weak shoulder at 757 cm^{-1} are corresponding to the stretching of O−W−O in nanorods and also the ~813 cm^{-1} peak confirms the presence of hexagonal phase of WO_3 nanorods [[21]]. Raman shift at 668 cm^{-1} is due to the out-of-plane wagging ν(O−W−O). Two peaks, at 242 and325 cm^{-1} can be assigned to ν(O−W−O) and δ(O−W−O), vibration modes, respectively. Nanorods also exhibit a stretching of O−W−O in place of the bending, resulting in a 240 cm^{-1} peak [[22, 23]]. Hence, Raman study also depicts the presence of hexagonal WO3 nanorods.

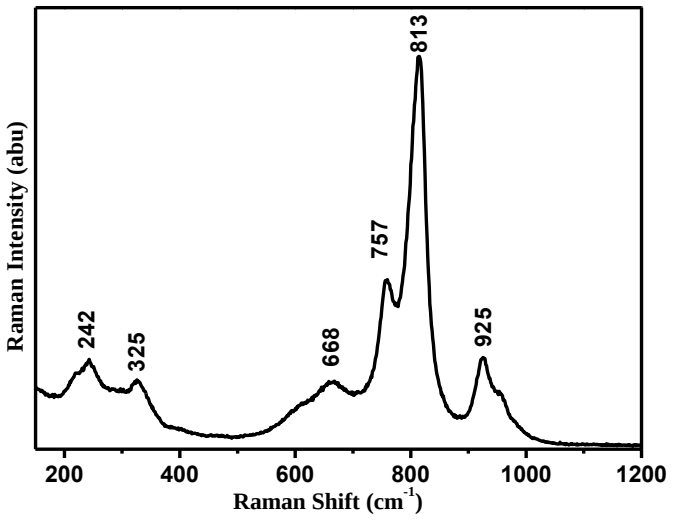

Figure 4: Raman spectra of as synthesized WO_3 powder.

Conclusion

In conclusion, bundles of WO_3 rod shaped nanostructures of single crystalline hexagonal phase are synthesized emplyoing hydrothermal synthesis method where $Na_2WO_4.2H_2O$ was used as precursor and NaCl as structure directing agent. Good quality growth of WO_3 nanorods was found under optimized concentrations of NaCl and pH value ~3.0. Further, uniform and highly crystalline hexagonal phase WO_3 nanorods synthesized in present work, have potential to improve the performance of electrochromic devices and an important material for growth of 2D WS_2, WSe_2 etc.

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