

Tungsten Trioxide Nanoplates Prepared Without Organics at Low Temperature

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Tungsten trioxide (WO_3) nanoplates have been synthesized successfully by a simple reaction of tungsten powder and water without any organics at 300°C . The formation of nanoplates by the reaction of metals with water is suggested to occur due to decomposition of water by the metal giving hydrogen. The nanoplates are having an average thickness of 150nm and an average width of 400nm. A feasible mechanism for the formation of nanoplates has been discussed in view of the experimental results. Compared with other methods, the present method is fast, economical, low temperature, and free of pollution which will make it suitable for large scale production. Moreover, the technique does not require any sophisticated equipments and as such can be extended and expanded to other oxides. To our knowledge, the technique has not been reported in the literature earlier.

1. Introduction

Tungsten trioxide (WO_3) is a good electrochromic, optochromic and gasochromic material [1-2]. It has been used to construct electrochromic windows, infrared switching devices, catalysts, gas sensors for the determination of NO_2 , hydrogen, and ammonia [3-5]. Because their band gap is situated within the solar spectrum range, tungsten trioxides are one of the solar energy transforming materials leading to applications of catalytic activity and photoconductivity [6]. Several synthetic approaches including chemical vapour deposition, electrochemical techniques, sonochemical approach, template mediated synthesis, wet organic and inorganic routes, and thermal methods have been reported to fabricate WO_3 nanostructures. Srivatava et al. have reported sol-gel followed by a dip coating to produce WO_3 nanorods [7]. By altering the composition and concentration of solvents, it was shown that different morphologies and phases of WO_3 can be achieved [8]. Inorganic compounds such as Na_2SO_4 , Rb_2SO_4 and K_2SO_4 have been demonstrated as structure directing agents for the hydrothermal synthesis by Lou et al. [9]. By heating a tungsten foil partly covered with SiO_2 plate in Ar atmosphere at 1600°C , Zhu et al. [10] synthesized micrometer sized tungsten oxide structures with a tree like morphology. Tungsten trioxide nanorods have also been prepared by carbon nanotube template synthesis and through physical vapour deposition [11,12]. By heating WS_2 in oxygen, pine tree like structures were reported [13]. Recently, the single source precursor

route has opened another way for the synthesis of WO_3 nanorods/nanowires by thermal decomposition method [14]. However, a close examination reveals that the above reported techniques are technically complex, requires high temperature, harsh growth conditions, expensive experimental set up, and the use of excessive organics/amines.

Therefore, it provides motivation to synthesize tungsten trioxide nanostructures at low temperatures without additives. To this end, we present a versatile and expedient process to grow tungsten trioxide nanoplates by a simple reaction of tungsten metal with water at 300°C without the use of organics. The nanoplates are having an average thickness of 150nm with an average width of 400nm. The method has several unique advantages. Firstly, different morphologies can be achieved by changing the reaction time and temperature only. Secondly, it is a template free method and does not require any substrate and/or any organics. Third, the pure water is used as solvent as well as the source of oxygen, whereas often boron oxides B_2O_3 at elevated temperatures have been used. Finally, it is a generic method which can be applied to other metal oxides.

2. Experimental

In a typical synthesis, an appropriate amount of tungsten metal powder was taken with 20ml of distilled water in a teflon-lined stainless steel chamber of 50ml capacity and the mixture was well sonicated before placing at desired temperature. The reaction mixture prepared was kept at 300°C in an oven for different times ranging from 12-24h.

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The effect of reaction time was studied in detail while keeping the temperature constant. After the desired time, the system was allowed to cool down naturally and the resulting mixture was centrifuged. The resulting product collected from the reaction vessel was washed with de-ionized water several times and finally dried in air.

The morphology and the size of the products was carried out using high resolution FE-SEM (FEI NOVA NANOSEM-600) coupled with energy dispersive x-ray spectrometer (EDX). X-ray diffraction patterns of the samples were recorded with Siemens D 5005 diffractometer using Cu $K\alpha$ ($\lambda = 0.15141$ nm) radiation.

3. Results and discussion

For the micro-structural analysis, the as-synthesized samples were directly transferred to the FESEM chamber without disturbing the original nature of the products. Fig. 1(a and b) shows the low and high morphology of nanoparticles obtained after the reaction of tungsten powder with water at 300°C and the reaction time was 12h. Fig.1 (c and d) shows low and high magnification of nanoplates prepared at 300°C and the reaction time was extended to 24h. The nanoplates are having average thickness of 150nm with an average width of 400nm. However, the formation of rectangular edges on the nanoplates is not understood. The nanoplates are similar to those reported by Sittisuntorn et al. [15].

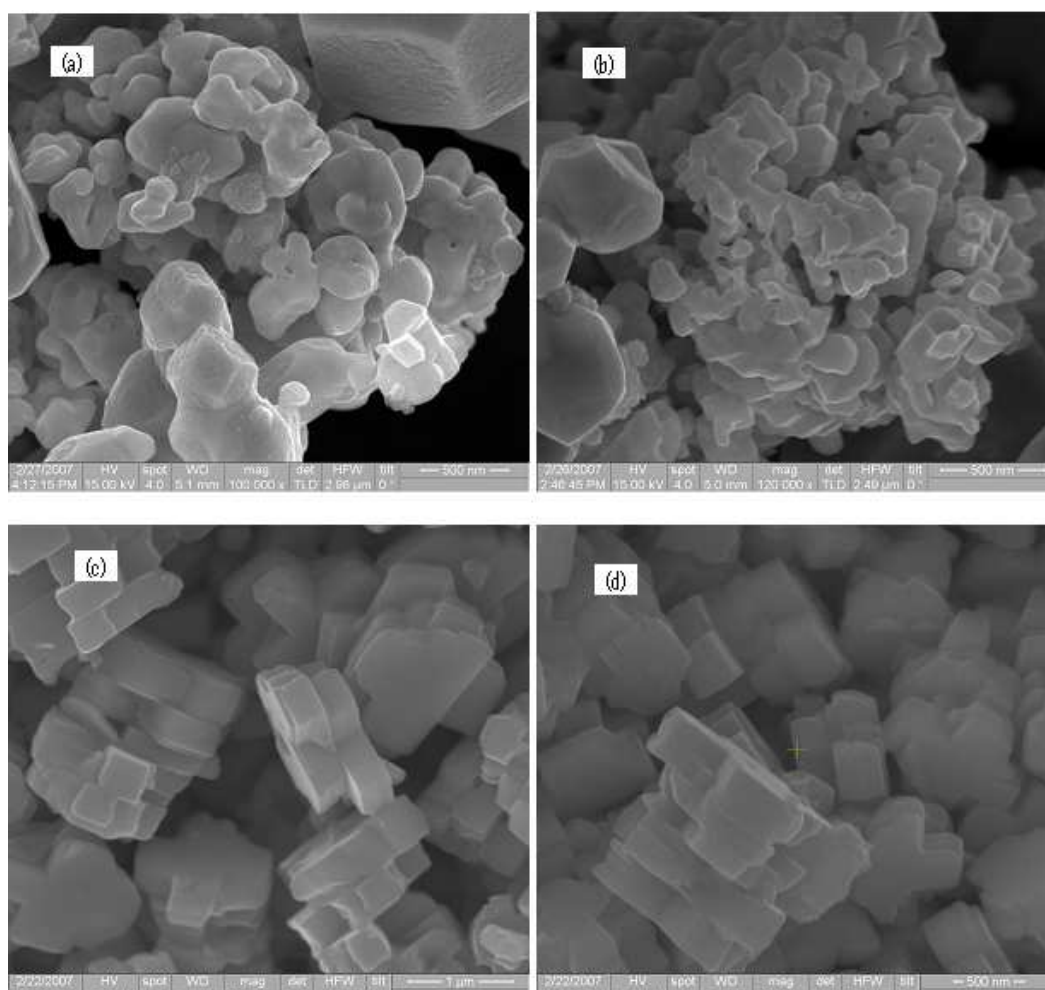


Fig.1: Shows the morphology of various nanoplates. (a and b) shows low and high magnifications of nanoplates synthesized at 300°C for 12 h. (c and d) shows low and high magnifications of nanoplates synthesized at 300°C for 24 h.

The chemical composition of the nanoparticles and nanoplates was detected using energy-dispersive X-ray spectrometry and the result showed that it was composed of W and O elements with an atomic ratio of 1:3 as shown in the representative EDX spectrum (Fig. 2). XRD analysis was carried out to identify the crystalline structure of the tungsten trioxide nanostructures Fig. 3 shows the XRD pattern of nanoparticles prepared at 300°C for 24h. The XRD spectra reveals that the products synthesized are single crystalline and can be marked as cubic-phase WO_3 with no traces of WO_2 (JCPDS card 46-1096). There are no peaks detected for other phases, indicating that single phase of WO_3 with high purity has been prepared.

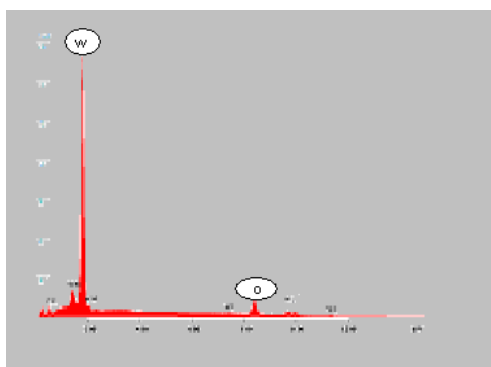


Fig.2: The corresponding EDX analysis confirming the existence of all elements involved in sample prepared at 300°C for 24 h.

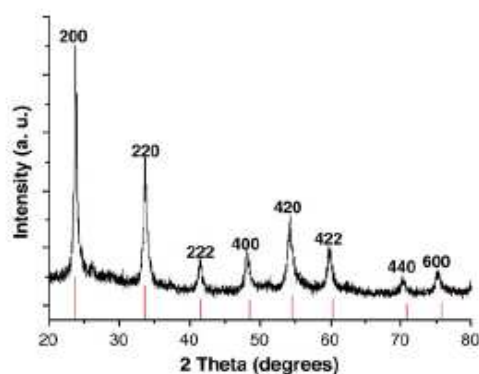
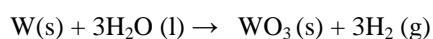


Fig.3: Powder XRD diffraction pattern of nanoplates prepared at 300°C for 24h.

The chemical reaction for synthesizing nanostructures can be expressed as



Here (s), (l) and (g) represent solid, liquid and gas, respectively. Tungsten metal on reaction with water slowly gives out hydrogen (g) and the oxygen liberated reacts with metal to give oxides as shown in above reaction. Most of the studies on tungsten trioxide have used oxides like SiO_2 or B_2O_3 as O source for synthesis of WO_3 which melts around 1600°C and evaporates at high rate when the temperature is higher than 1100°C [16]. In the investigation by Zhu et al. [10], tungsten oxide nanostructures were synthesized by chemical reaction between SiO and metallic tungsten. The SiO plate provided both the source of oxygen and the deposition substrates of nanostructure growth. Therein, a vapour solid (VS) growth mechanism was proposed. In the VS process, chemical species diffuse towards a substrate through an interfacial gas layer and are then adsorbed on the surface of substrate. In a typical VS process, the component of nanowires is evaporated from a solid source in a high temperature zone. As only tungsten filaments acted as the vapour source and as prepared products were tungsten oxide, oxygen must have participated in the growth process of nanostructures. The detailed mechanism responsible for the formation of various tungsten oxide nanostructures is not yet understood. However, water at elevated temperatures plays an essential role in the precursor material transformation because the vapour pressure is much higher and the state of water at elevated temperatures is different from that at room temperature. The solubility and the reactivity of the reactants also change at high pressures and high temperatures and high pressure is favorable for crystallizations.

4. Conclusion

In this report, we described a novel method for the syntheses of tungsten trioxide nanoplates at 300°C from a simple tungsten and water reaction without organics. This synthetic technique has the following advantages:

1. Firstly, it is simple, one step synthesis approach, making it easy to control the growth kinetics.
2. Secondly, the synthesis needs no sophisticated equipments since it is conducted at low temperature under normal atmosphere.
3. Thirdly, the clean surfaces of the as-synthesized nanostructures can be readily functionalized for various applications since

there is neither a capping reagent nor a substrate.

4. Forth, the synthesis is non toxic without producing hazardous waste. Therefore, the technique could be extended and expanded to provide a general simple and convenient strategy for the synthesis of nanostructures of other functional materials with important scientific and technological applications. The relative studies are in process and will be reported in forth coming publications.

Acknowledgments

The author would like to acknowledge World Bank for their financial support for procuring SEM in N. I.T. Srinagar.

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Received: 7 October, 2008

Received Revised Version: 16 June, 2009

Accepted: 29 June, 2009

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