Nanostructured Tungsten Trioxide (WO$_3$): synthesis, structural and morphological investigations

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Abstract. Tungsten trioxide (WO$_3$) has attracted considerable attention due to its promising and remarkable properties. In this study, we have prepared WO$_3$ nanostructures via a simple chemical method using tungsten carbide (WC) as a precursor. This novel approach has many advantages such as high yields, simple methodology and easy work up. The X-ray diffraction (XRD) pattern initially revealed the formation of the intermediate phase of tungsten trioxide hydrate (WO$_3$.H$_2$O), then the complete transformation to pure WO$_3$ after annealing at 600°C for 5h in air atmosphere. The prepared WO$_3$ nanostructures crystallized into a monoclinic phase. The Scanning electron microscopy (SEM) image indicates the exceptional porous morphology, which consisted of hollow sphere-like shape with a uniform distribution. Fourier transform infrared (FTIR) spectroscopy confirmed the structural composition and the purity of the formed WO$_3$. The experimental results proved that our simple approach offers a promising route to prepare WO$_3$ nanostructures as high performance material for advanced applications.

Keywords: Nanostructures, tungsten trioxide, hollow sphere

1. Introduction

Tungsten oxide (WO$_3$) is well known as an n-type semiconductor with a band gap of 2.8 eV, and exists in various crystallographic phases including monoclinic, hexagonal, cubic and orthorhombic [1]. This material is widely considered for various applications such as: gas sensors, field-emission devices, energy storage devices and especially in photocatalysis due to its activity in visible light, thermal stability and resilience to photo-corrosion [2].

For more than a decade, synthesis of nanomaterials with desired morphology and composition has been the most challenging task in the field of nanoscience and nanotechnology. Recently, many methods have been reported for the synthesis of WO$_3$ nanostructures, providing the advantages of controlled shape, size and crystallinity [3,4]. By altering the reaction conditions in the synthesis process, such as the amount of the precursors, the concentration of the solvent, the temperature and the reaction time, it was shown that the morphology of these nanostructures can be tuned, resulting in different and unique properties [5,6].

In the present paper, we report a large scale synthesis of nanostructured WO$_3$ using a simple chemical method and a subsequent thermal treatment without any special equipment. We demonstrate the successful transformation from WC to WO$_3$. Moreover, the experimental investigations reveal the porous morphology with hollow sphere-like shape, the pure phase, the high quality and the good crystallinity of nanostructured WO$_3$. 
2. Experimental section

2.1. Preparation of $\text{WO}_3$

Nanostructured $\text{WO}_3$ is obtained by simple chemical oxidation followed by a calcination process [7], as presented in Figure 1. Briefly, $\text{WO}_3$ nanostructures were prepared by oxidative reaction using strong acids, which were added drop wise to WC and stirred for 3 days. The as-obtained precipitate of tungsten oxide hydrate $\text{WO}_3\cdot\text{H}_2\text{O}$ were centrifuged (5000 rpm), dried at 60°C. Then, the thermal treatment took place in a furnace oven at 600°C for 5 h.

![Synthesis method of nanostructured WO3](image)

**Figure 1**: Synthesis method of nanostructured WO3

2.2. Characterizations

Morphology and particle size of the samples was evaluated using a field emission scanning electron microscope (FE-SEM) (Quanta 250 FEG, FEI). The crystalline structure was characterized using an X-ray diffractometer (XRD) (Phillips X’pert MPD, Cu-K) and the data were collected between scattering angle (2θ) from 10° to 60° at scanning rate 2° min$^{-1}$. The phase composition was investigated by Fourier Transform Infrared spectroscopy using Vertex 70 spectrophotometer, with a resolution of 4 cm$^{-1}$ over a wavenumber range of 400-4000 cm$^{-1}$.

3. Results and Discussion

The crystalline nature of the prepared samples was identified by analysing its X-ray diffraction (XRD) spectra, which are shown in Figure 2. After oxidation of WC, all the characteristic peaks presented in Fig 2a could be assigned to the orthorhombic phase of tungsten oxide hydrate $\text{WO}_3\cdot\text{H}_2\text{O}$ (JPDS: 43-0679 with lattice constants of $a = 0.5238$ nm, $b = 0.1070$ nm, and $c = 0.5120$ nm). The high intensity and narrow peaks reflect the good crystallinity of the obtained $\text{WO}_3\cdot\text{H}_2\text{O}$. 
After annealing at 600°C for 5 hours (Fig 2b), strong and sharp diffraction peaks are observed at $2\theta = 19.1^\circ, 22.9^\circ, 23.4^\circ, 24.1^\circ, 26.4^\circ, 28.1^\circ, 29.8^\circ, 33.1^\circ, 33.9^\circ, 41.6^\circ, 49.82^\circ, 50.43^\circ$ are associated to the (011), (002), (200), (120), (112), (022), (202), (220), (222), (232) and (114) crystalline planes of the monoclinic phase of WO$_3$ with good crystallization, which is associated with JCPDS card N° 83-0950. The intense diffraction peak located at $24.1^\circ$ corresponding to the (002) plane indicates that WO$_3$ crystals were preferentially grown in the (200) direction. It has been observed by Deepa et al that the increase in annealing temperature led to a considerable improvement in the crystallinity [8].

Moreover, the crystallites size is one of the critical parameters that influences the metal oxide nanostructures properties, which is calculated by using Scherrer’s equation:

$$D = \frac{k\lambda}{\beta\cos \theta}$$  

where D is the crystallite size, k is a shape factor, $\lambda$ is the X-ray wavelength (0.15406 nm), $\beta$ is the full width at half maximum intensity in radians and $\theta$ is the Bragg angle. After annealing at 600°C, the average crystallite sizes calculated along the main principal peak (002), (020) and (200), have values of about 29, 26 and 21 nm, respectively. Furthermore, no outsider peaks were observed for any impurities, which mean that WO$_3$.H$_2$O is converted to WO$_3$ completely with high quality and good crystallinity.

The morphology study is performed to investigate the surface and the shape of the nanostructured WO$_3$. As seen from the SEM image (Fig 3), porous morphology is obtained. Close view demonstrates that the surface is homogeneous and consisted of interconnected hollow spherical particles. On our previous work, the morphology of the same sample heated at 500°C is dominated by the rod-like shape and their size estimated to be 56 nm, which demonstrated that the temperature is a principal parameter in the formation of nanostructured WO$_3$ [7]. Moreover, Marques et al have reported in their work that the morphology and the crystallographic structures of WO$_3$ nanostructures could be affected by the precursor type as well as the pH values [3].
In order to determine the exact composition of the sample, and to gain more information on its crystal structure, FTIR measurement was implemented. The infrared spectrum of monoclinic WO₃ (Figure 4) shows a large band with characteristic frequency vibrations in the range 400-1000 cm⁻¹ [9, 10]. The band at 982 cm⁻¹ is observed in the range of (Metal=Oxygen) vibrations, which is characteristic for stretching vibrations of W=O bond. The band at 620 cm⁻¹ is attributed to W–O stretching vibrations, while the band at 714 cm⁻¹ is assigned to the W-O-W bridging modes of the WO₆ (octahedral) corner-sharing species. Note also the presence of the two bands at 832 and 756 cm⁻¹ which are attributed to the inter-bridge stretching O-W-O and the corner-sharing mode W-O-W, respectively. In addition, from this spectrum it can be proved that WO₃ did not retain any amount of adsorbed water after annealing, which reflect by the absence of the broad band around 3380 cm⁻¹ characteristic of H₂O stretching vibration. The FT-IR analysis is in accordance with the crystallographic structure attributed by XRD.

Figure 3: morphology of WO₃ annealed at 600°C

Figure 4: Infrared spectrum of WO₃ annealed at 600°C
4. Conclusion
In summary, considerable research has been devoted to the synthesis of nanostructured WO$_3$. Among all methods, our approach provides a facile, fast, scalable and economic method for the production of desirable quality WO$_3$ nanostructures without any special equipment. Moreover, the synthesized sample was reported for the first time using WC as precursor in a chemical route. XRD analyses confirmed the formation of monoclinic phase with (200) as preferred orientation direction. SEM observations showed the interesting porous morphology, which consisted of hollow sphere-like shape. Furthermore, FTIR bands present more evidence of the best quality and the high purity of nanostructured WO$_3$

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5. References
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