

## Large-Scale Synthesis of Tungsten Oxide (WO<sub>3</sub>) Nanoleaves, Nanoparticles and Nanoflakes

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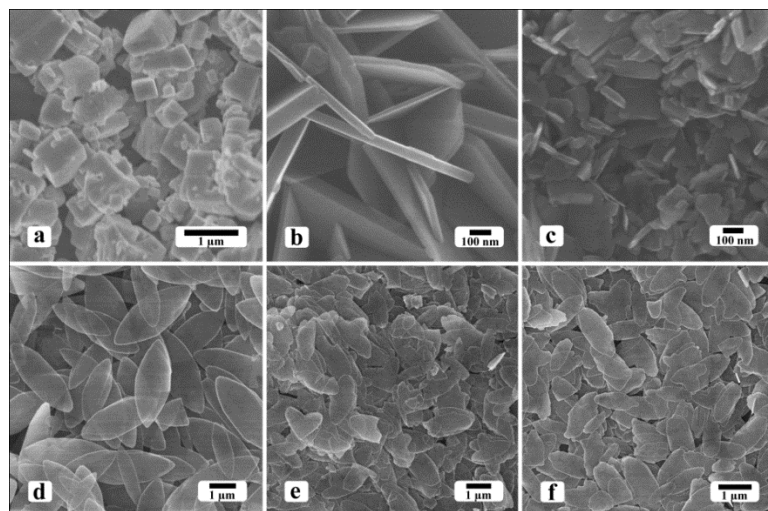
Among several metal oxides, tungsten oxide (WO<sub>3</sub>) has an interesting set of properties that make it a suitable candidate for a wide range of applications (e.g., electrochromic or photochromic devices, batteries, gas sensors and photocatalysts). WO<sub>3</sub> is an n-type semiconductor with a widely tunable band gap, ranging from  $E_g \sim 2.5\text{--}2.8$  eV at room temperature to  $\sim 1.7$  eV at 800°C. It can capture approximately 12% of the solar spectrum and can absorb light in the visible spectrum up to 500 nm at ambient temperature. In 2010, a quantum yield of 19% was reported in photocatalytic water splitting using a cesium-enhanced WO<sub>3</sub> photocatalyst [2, 3].

In this study, WO<sub>3</sub> nanoparticles (NPs), nanoflakes (NFs) and leaf-shape nanoplatelets (LNPs) were synthesized using the acid precipitation method in the presence of either urea, thiourea or oxalic acid. The hydrothermal (HT) technique at 100°C was also used for the synthesis of some samples. A 15mM sodium tungstate solution (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O) was used as W precursor. 6N hydrochloric acid was added drop wise to the solution at T=10°C to produce WO<sub>3</sub>·H<sub>2</sub>O white precipitates. The HT process was carried out using oxalic acid as chelating agent. The WO<sub>3</sub>·H<sub>2</sub>O precipitates were centrifuged, washed and added to the aqueous solutions containing either urea, thiourea or pure water at room temperature (RT). Finally, the solutions were centrifuged, washed several times and dried at 60°C. The obtained materials were sintered for 3 hours at 700°C to reach the desired WO<sub>3</sub> structure and remove the oxygen vacancies. The materials were characterized using powder x-ray diffraction (XRD), scanning electron microscopy (SEM, JEOL JSM-7500F) and transmission electron microscopy (TEM, Carl Zeiss LEO 922 EFTEM) and high resolution TEM (HRTEM, JEOL JEM-2200FS). The elemental compositions of the samples were determined using x-ray energy dispersive spectrometry (XEDS).

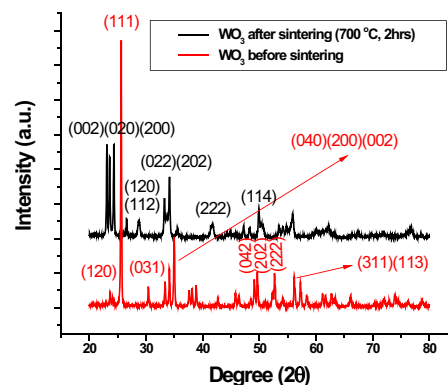
SEM images recorded from six samples are shown in the montage of Fig. 1. Fig. 1(a, b & c) illustrate that by adding CsNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>, the microscopic morphology of the WO<sub>3</sub> material can be changed from NPs (cubic shape) to NFs using the HT process. Recrystallization in pure water, urea or thiourea at RT produces transparent WO<sub>3</sub> LNPs, as illustrated in Fig. 1(d, e & f). XEDS (in the SEM and TEM) confirmed that only the O and W elements are present before and after sintering. XRD recorded prior to and after sintering of the materials are shown in Fig. 2. The chelating agent does have an influence on the structure of the products. Figs. 3 and 4 display HRTEM images recorded before and after sintering. XRD and HRTEM data show that the structure of the WO<sub>3</sub> products changes from orthorhombic to monoclinic and that a better crystallinity is achieved.

### References

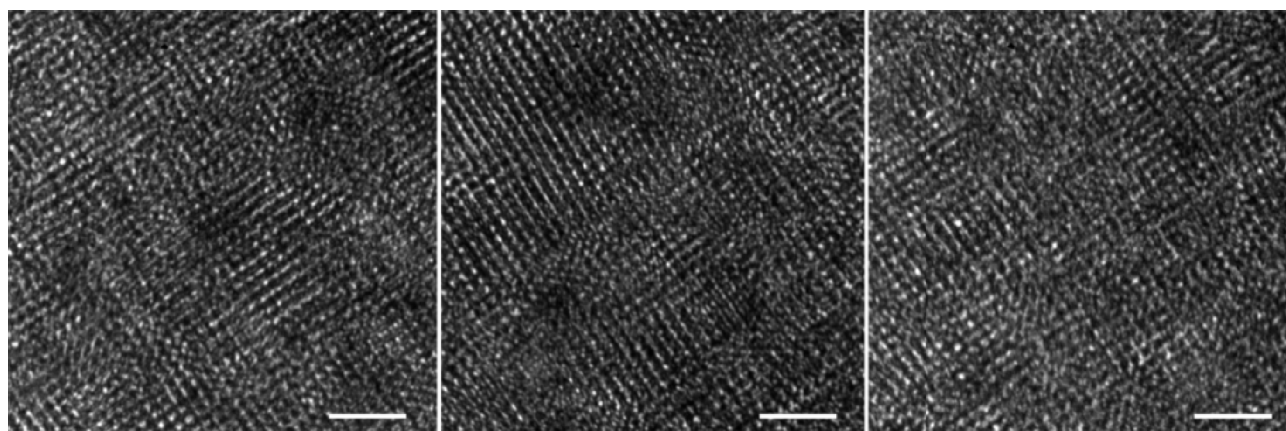
- [1] A. Mukherji, R. Marschall, A. Tanksale, Ch. Sun, S. C. Smith, G. Q. Lu, L. Wang, *Adv. Funct. Mater.* 2011, 21, 125.
- [2] Zhi-Gang Zhao and Masahiro Miyauchi, *Angew. Chem. Int. Ed.* 2008, 47, 7051.
- [3] Y. Miseki, H. Kusama, H. Sugihara and K. Sayama, *J. Phys. Chem. Lett.* 2010, 1, 1196.



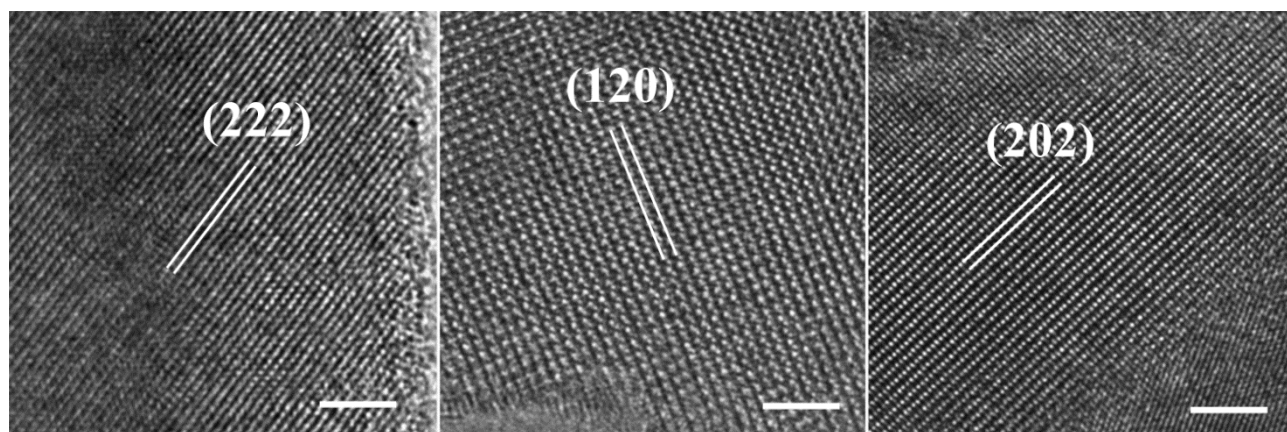
**Fig. 1.** SEM images recorded from  $\text{WO}_3$  products synthesized using (a) HT with 0.3M oxalic acid, (b) HT with 0.3M oxalic acid and 0.003M  $\text{CsNO}_3$ , (c) HT process with 0.45M oxalic acid and 0.003M  $\text{CsNO}_3$  and 0.003M  $\text{SO}_4^{2-}$ , (d) pure water at RT, (e) urea at RT and pH=7 and (f) thiourea at RT and pH=7.



**Fig. 2.** XRD recorded from  $\text{WO}_3$  products before and after sintering. They are in good agreement with  $\text{WO}_3 \cdot \text{H}_2\text{O}$  (JCPDS No.43-0679) and with  $\text{WO}_3$  (JCPDS No.43-1035) for as synthesized and sintered materials, respectively.



**Fig. 3.** HRTEM images recorded from as synthesized  $\text{WO}_3$  products. Barscale: 2 nm.



**Fig. 4.** HRTEM images recorded from  $\text{WO}_3$  products after sintering. Barscale: 2 nm.