

Wet-chemical Synthesis of Electrochromic WO_3 and $\text{W}_x\text{Mo}_{1-x}\text{O}_3$ Nanomaterials with Phase and Morphology Control

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Nanoscale WO_3 has emerged as a multifunctional material as it has found various applications in electrochromic devices [1], gas sensing [2] and photocatalysis [3]. A wealth of literature is available on synthesis of different phases of WO_3 with distinct morphologies. However, a thorough understanding of the growth mechanism of the material is still lacking. Furthermore, owing to the comparable ionic radii of W and Mo, WO_3 phases can be alloyed with MoO_3 under same synthetic conditions, leading to new mixed oxide phases. The electrochromic efficiency depends on the ability to control the phases and the morphology in these systems.

In this work, we investigate the growth mechanism of different phases for WO_3 and $\text{W}_x\text{Mo}_{1-x}\text{O}_3$ through experiments in conjunction with *ab initio* simulations. Our experiments show that WO_3 can form two different phases, *i.e.* hexagonal and orthorhombic, depending on the presence of oxalic acid in the reaction medium. Interestingly, while the orthorhombic WO_3 phase forms a plate-like 2D morphology, the hexagonal WO_3 phase shows a 1-D rod morphology (**Figure 1**). Density Functional Theory (DFT) calculations for binding of the oxalate species on the different surfaces show a higher binding strength on the orthorhombic {002} surface compared to that of hexagonal {1 $\bar{1}$ 20} surface. On the other hand, when Mo is introduced in the reaction medium, the hexagonal phase with a 2-D plate-like morphology is the preferred phase that is formed (**Figure 2**). Quantification of the flakes through scanning transmission electron microscopy (STEM) coupled with energy dispersive spectroscopy (EDS) reveals the $\text{W}_{0.5}\text{Mo}_{0.5}\text{O}_3$ composition (**Figure 3**).

The synthesized phases not only vary in terms of morphology, but also show quite different electronic properties. For instance, the orthorhombic WO_3 shows significant presence of reduced W^{5+} species, indicating a difference in the reducibility. This indeed affects the concerned property, namely the electrochromicity of the material. Thus, different phase and morphology of WO_3 influence the intercalation kinetics of the H^+ in the two phases. Our electrochromicity experiments clearly show that hexagonal phase has a faster kinetics of H^+ diffusion, compared to that of the orthorhombic phase. Complementary DFT calculations show that the intercalation energy is higher in case of the orthorhombic WO_3 , indicating a slower kinetics. Electrochemically measured diffusion co-efficients further confirm this notion. This results in a time lag of colour switching *viz.* 4.4s during coloration and 5.6s during decoloration for the orthorhombic WO_3 . We have further investigated the electrochromic property of the mixed oxide phase, illustrating the effect of Mo incorporation in the lattice [4].

References:

- [1] Cong, S. *et al.*, *Adv. Mater.*, **26**, (2014), 4260-4267.
- [2] Van, P.T.H. *et al.*, *ACS Appl. Mater. Interfaces.*, **6**, (2014), 12022-12030.
- [3] Liu, J. *et al.*, *Adv. Funct. Mater.*, **24**, (2014), 6029-6037.

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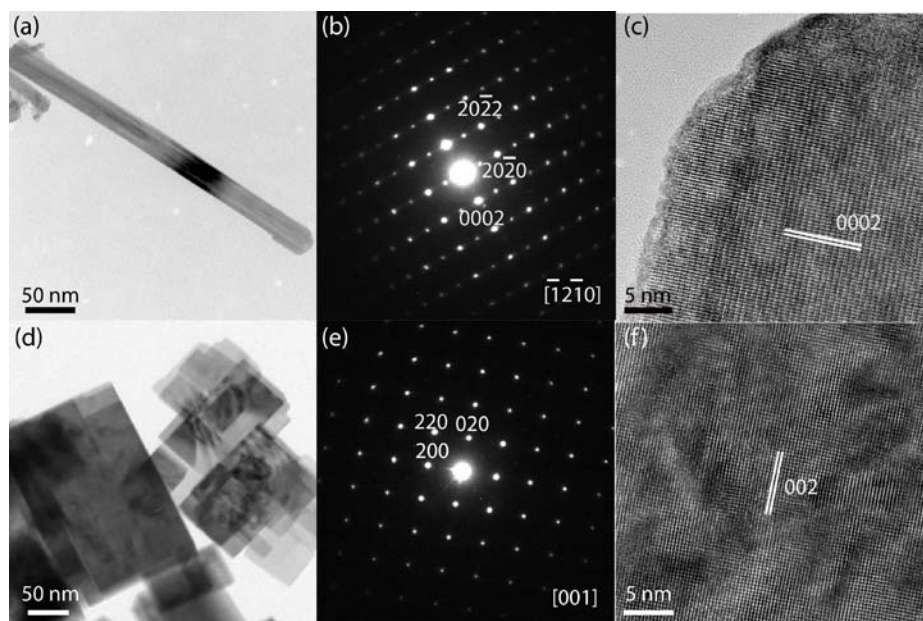


Figure 1. Bright field (BF) image of the WO_3 nanorod synthesized without any capping agent; (b) SAED pattern; (c) HRTEM micrograph along $[\bar{1}2\bar{1}0]$ zone from a nanorod; (d) LM; (e) SAED and (f) HRTEM images of the synthesized WO_3 flakes (with oxalic acid as a capping agent).

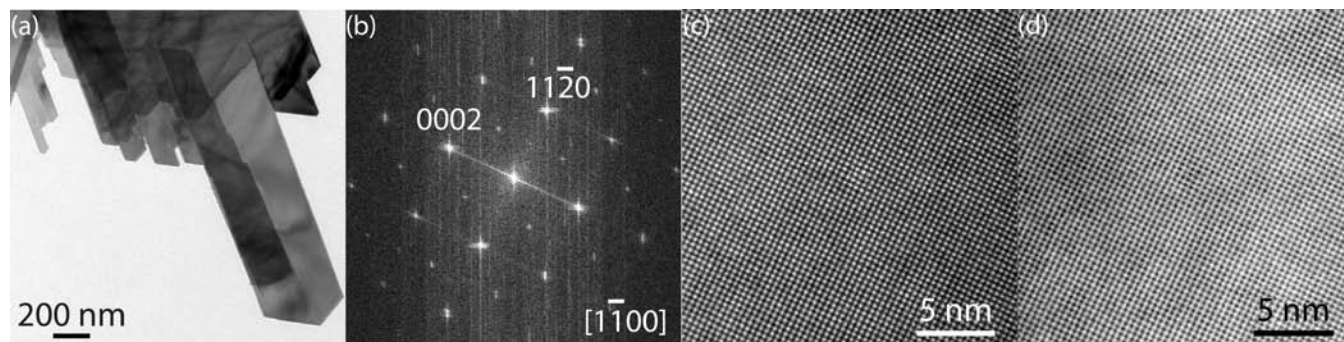


Figure 2. BF image of $\text{W}_x\text{Mo}_{1-x}\text{O}_3$ flakes; (b) FFT from the (c) HAADF HR-STEM and its corresponding (d) BF HR-STEM of flakes oriented along the $[\bar{1}\bar{1}00]$ zone axis.

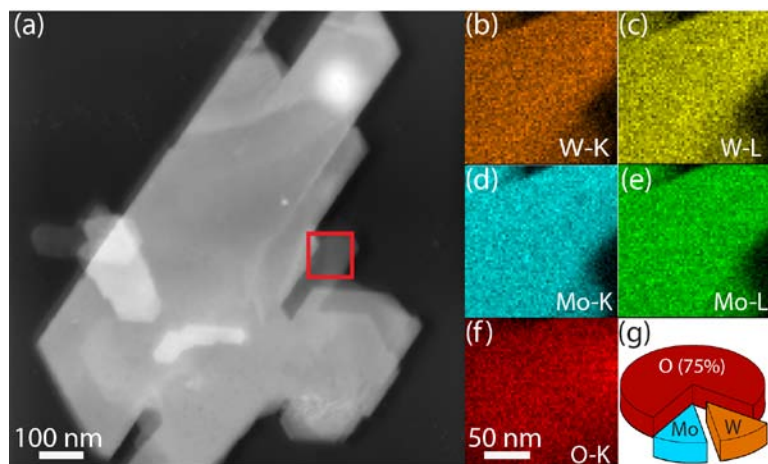


Figure 3. (a) LM-HAADF image of the $\text{W}_x\text{Mo}_{1-x}\text{O}_3$ flakes; (b-f) elemental mapping showing presence of W, Mo and O in the flakes; (g) elemental quantification showing $\text{W}_{0.5}\text{Mo}_{0.5}\text{O}_3$ stoichiometry.