

# Electrochromic Tungsten Molybdenum Oxide: Synthesis with Phase and Morphology Control

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Presence of a myriad of  $\text{WO}_3$  phases demands a stringent control over the microstructure and phase to attain the desired tailoring of the properties. Among several applications, such as electrochromicity, photocatalysis and gas sensing, the electrochromic behaviour of this material has gained significant attention. Here, we thoroughly investigate the growth mechanism of the different  $\text{WO}_3$  phases under solvothermal reaction conditions, along with their electrochromic behaviour. Under the same synthetic conditions, we explore the effect of Mo-doping into the  $\text{WO}_3$  lattice, leading to the formation of new mixed oxide phases. Experiments involving the growth mechanism of different phases for  $\text{WO}_3$  and  $\text{W}_x\text{Mo}_{1-x}\text{O}_3$  show that  $\text{WO}_3$  can form two different phases, i.e. hexagonal and orthorhombic, directed by the presence of oxalic acid in the reaction medium. Interestingly, when oxalic acid is used as a capping reagent, a plate-like 2-D morphology of the orthorhombic  $\text{WO}_3$  phase is obtained, whereas absence of capping agent yields to a 1-D rod-like morphology corresponding to a hexagonal phase of  $\text{WO}_3$ . DFT-based calculation of oxalate binding strength on different  $\text{WO}_3$  surfaces clearly shows that binding energy of the oxalate is higher on the orthorhombic {002} surface than on hexagonal {11-20} surface. Moreover, our experiments show that when a Mo precursor is introduced in the same reaction medium, formation of a 2-D plate-like morphology was observed, but the structure is closely related to the hexagonal  $\text{WO}_3$  phase. STEM-EDS profiling of the elemental composition shows that the flakes have a  $\text{W}_{0.5}\text{Mo}_{0.5}\text{O}_3$  composition. In terms of electronic properties, the orthorhombic  $\text{WO}_3$  shows significant presence of reduced  $\text{W}^{5+}$  species, indicating a difference in the reducibility. All these factors, viz. phase, morphology and electronic property affect the electrochromic efficiency of the material. In this spirit, we explored the intercalation kinetics of  $\text{H}^+$  in the two phases of  $\text{WO}_3$ . Our electrochromicity experiments show that the hexagonal phase has a faster kinetics of  $\text{H}^+$  diffusion. This trend is also supported by ab initio calculations, which shows a higher intercalation energy in the orthorhombic phase compared to that in hexagonal one, indicating towards a slower proton intercalation. Electrochemically measured diffusion coefficient values also reinforce this observation. We have further investigated the electrochromic property of the mixed oxide phase, illustrating the effect of Mo incorporation into the  $\text{WO}_3$  lattice.

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[2] Salje, E. et. al., (1978), *J. Solid State Chem.*, 24, 239-250.

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