

Development of High-Performance Supercapacitor Electrodes Using Novel Ordered Mesoporous Tungsten Oxide Materials with High Electrical Conductivity

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Synthesis of m-WO_{3-x}, m-WO₃ and b-WO₃: Mesoporous silica KIT-6 was used as a hard template and synthesized following the reported procedure.¹ KIT-6 was impregnated with phosphotungstic acid in two steps. In first impregnation stage, 1.2 g of phosphotungstic acid was incorporated into the pores of 0.45 g KIT-6 by impregnation method and calcined at 350 °C under air. In the second impregnation step, 0.6 g of phosphotungstic acid was incorporated into the pores of prepared composite, and calcined at 550 °C under air to obtain WO₃/KIT-6. HF etching of WO₃/KIT-6 generated m-WO₃. To obtain m-WO_{3-x}, WO₃/KIT-6 composite was heat-treated at 600 °C under Ar/H₂ (4 wt%) atmosphere for 4 hours and further stirred with 5 wt% HF solution for the removal of silica.² b-WO_{3-x} (bulk WO_{3-x}) was prepared following the same procedure for m-WO_{3-x} except KIT-6 was not used.

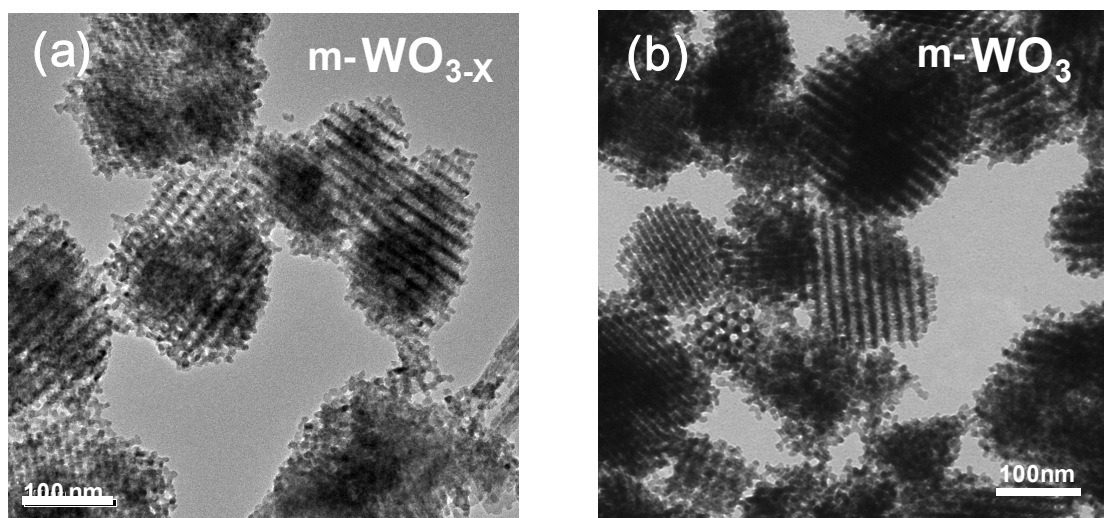


Figure S1. TEM images of (a) $m\text{-WO}_{3-x}$ and (b) $m\text{-WO}_3$. Both materials were synthesized using KIT-6 hard template and have the same ordered pore structure.

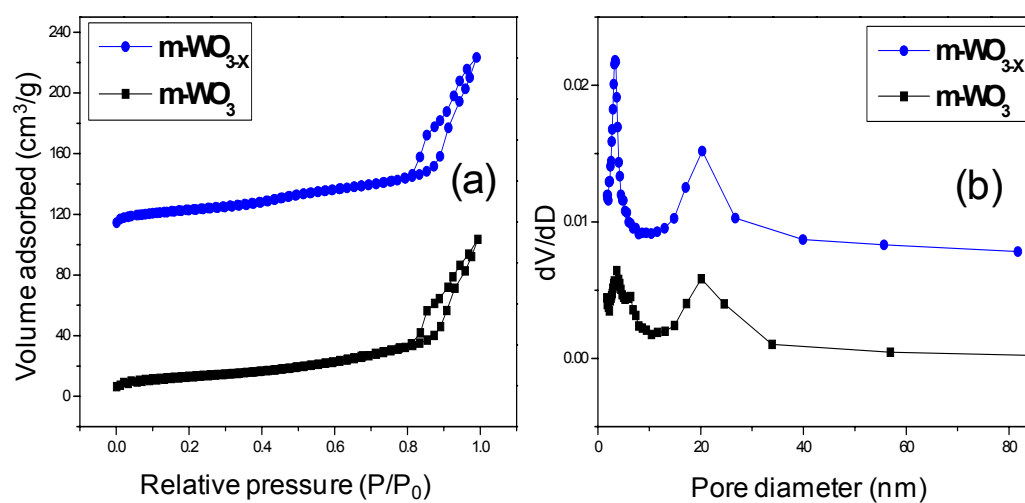


Figure S2. (a) Nitrogen adsorption-desorption isotherms of $m\text{-WO}_{3-x}$ and $m\text{-WO}_3$ (b) Pore size distributions of $m\text{-WO}_{3-x}$ and $m\text{-WO}_3$ estimated from adsorption branch using BJH (Barett-Joyner-Halenda). The pore structure of $m\text{-WO}_3$ judged by N_2 isotherm and pore size distributions is nearly identical to that of $m\text{-WO}_{3-x}$. An N_2 adsorption shows

two distinct jumps at $\sim 0.5 P/P_0$ and $\sim 0.9 P/P_0$, corresponding to uniform 3.5 nm pores and ~ 20 nm pores observed in pore size distributions, respectively. ~ 20 nm sized pores might be produced by filling phosphotungstic acid in either one of two chiral channels and removal of KIT-6 template.²

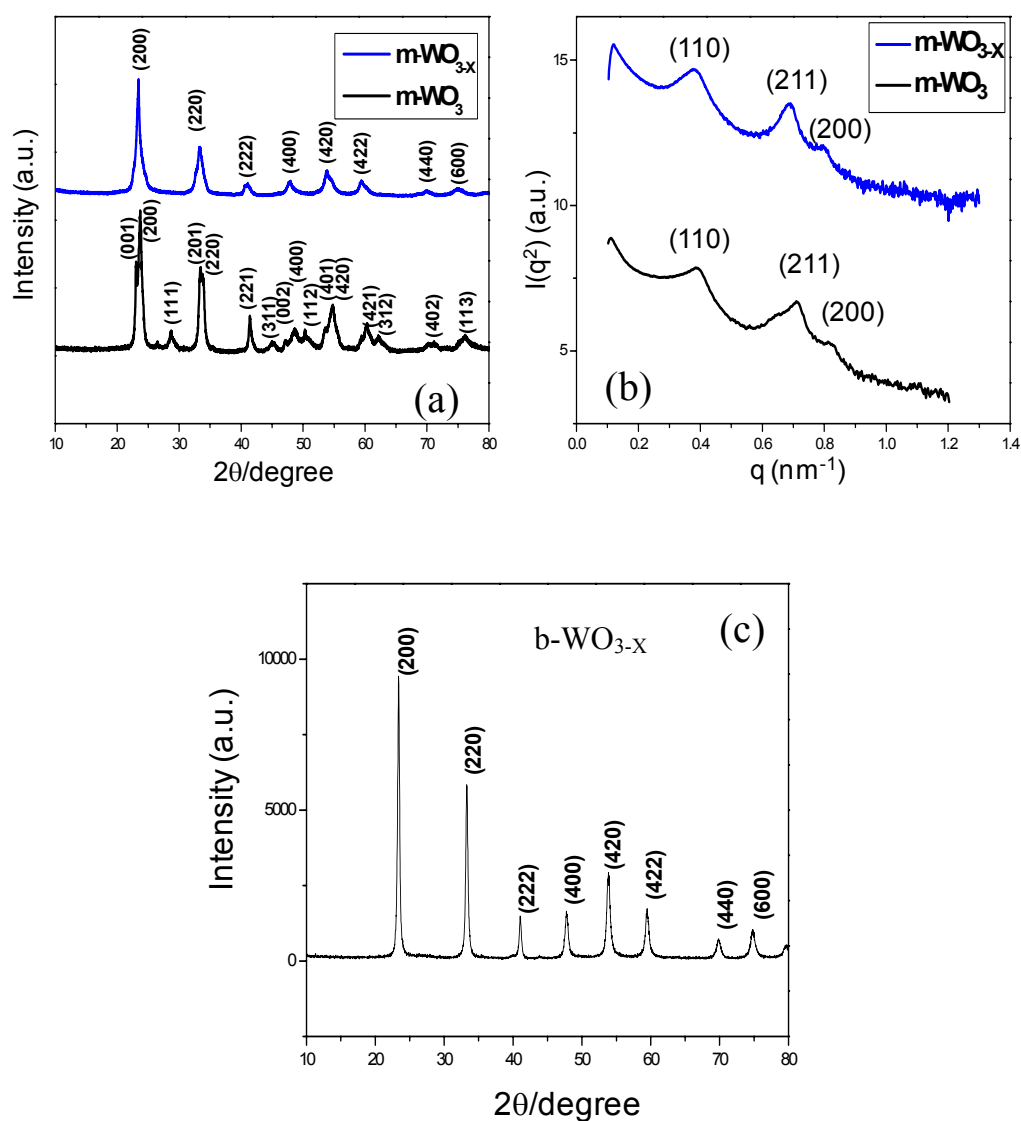


Figure S3. (a) XRD patterns of $m\text{-WO}_{3-x}$ and $m\text{-WO}_3$. Diffraction peaks in $m\text{-WO}_{3-x}$

can be indexed to the cubic WO_{3-x} phase (JCDPS:46-1096). The XRD pattern of m-
 WO_3 is well-matched with tetragonal phase (JCDPS:89-1287) (b) Small angle X-ray
scattering (SAXS) patterns of m- WO_{3-x} and m- WO_3 . (c) XRD pattern of b- WO_{3-x} .
Diffraction peaks in b- WO_{3-x} can be indexed to the cubic WO_{3-x} phase (JCDPS:46-
1096)

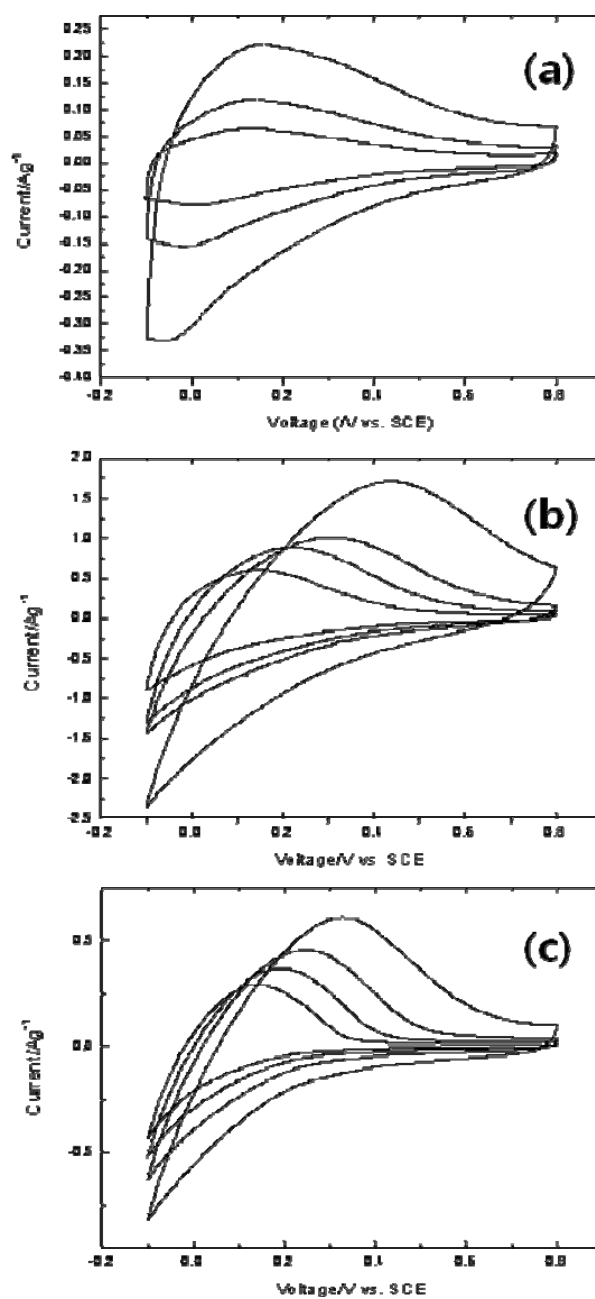


Figure S4. Cyclic voltammograms with change of scan rate from 5 to 50 mV/s for b-WO_{3-x} (a), m-WO_{3-x} (b) and m-WO₃ (c)

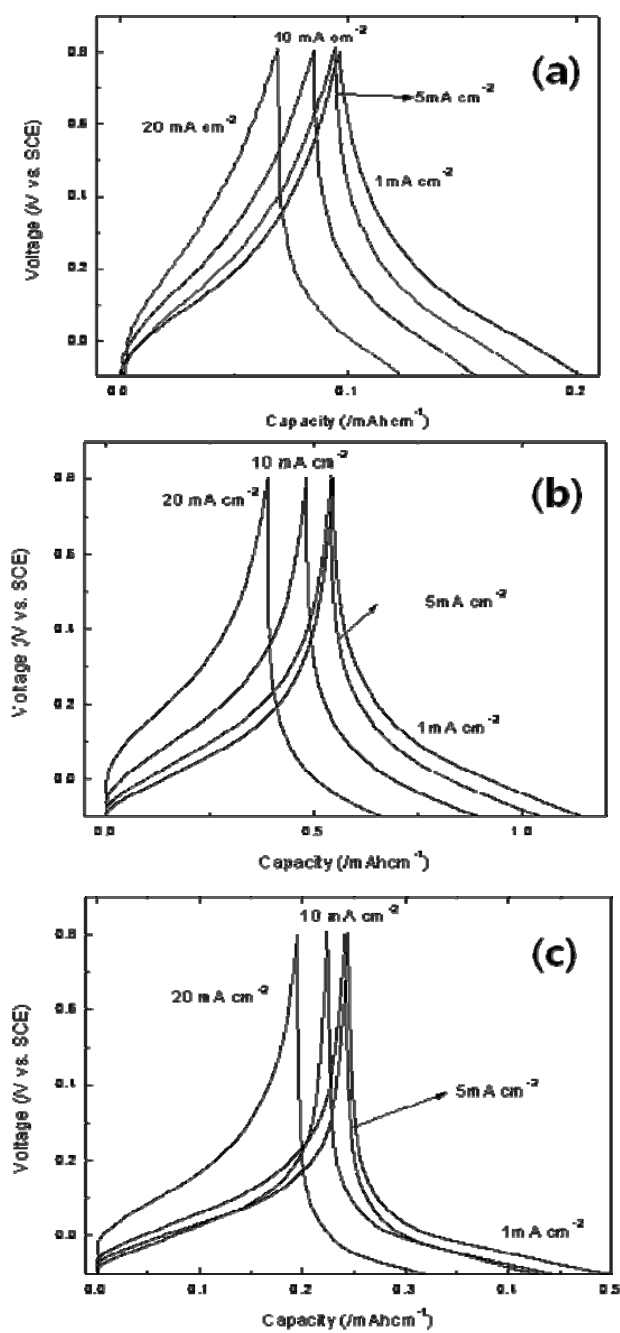


Figure S5. Galvanostatic charge-discharge patterns with change of applied current from 1 to 20 mA/cm² for b-WO_{3-x} (a), m-WO_{3-x} (b) and m-WO₃ (c)

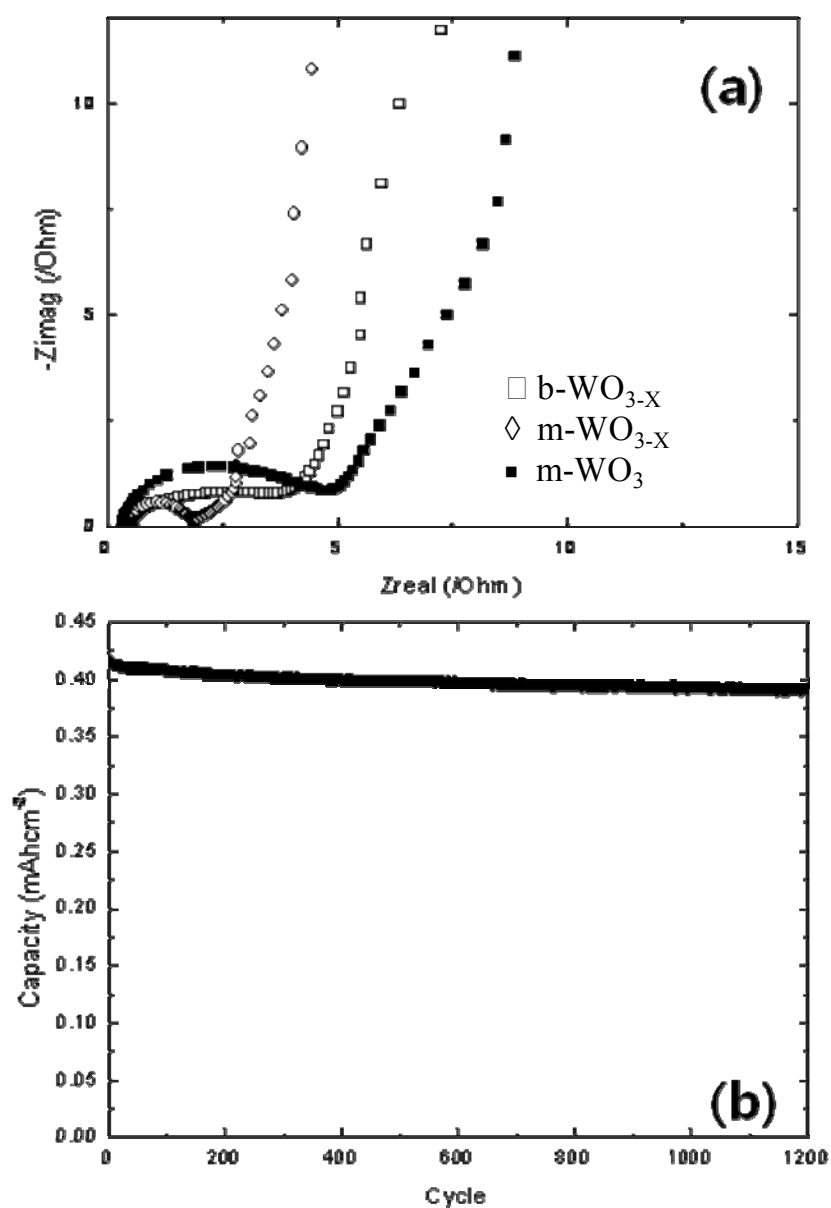


Figure S6. (a) Electrochemical impedance spectra for three tungsten oxide electrodes when 5 mV voltage magnitude from 5 mHz to 10⁵ Hz at open circuit voltage (OCV). (b) Change of capacity with cycles of m-WO_{3-X} electrodes.

References

1. F. Kleitz, S. H. Choi, R. Ryoo, *Chem. Commun.* 2003, 2136.
2. (a) Shi, Y.; Guo, B.; Corr, S. A.; Shi, Q.; Hu, Y. -S.; Heier, K. R.; Chen, L.; Seshadri, R.; Stucky, G. D. *Nano Lett.* 2009, **9**, 4215. (b) Kang, E.; An, S.; Yoon, S.; Kim, J. K.; Lee, J. *J. Mater. Chem.* 2010, **20**, 7416.