

Synthesis, Structure and Properties of the Manganese-doped Polyoxotitanate Cage $[\text{Ti}_{18}\text{MnO}_{30}(\text{OEt})_{20}(\text{MnPhen})_3]$ (Phen = 1,10-Phenanthroline)

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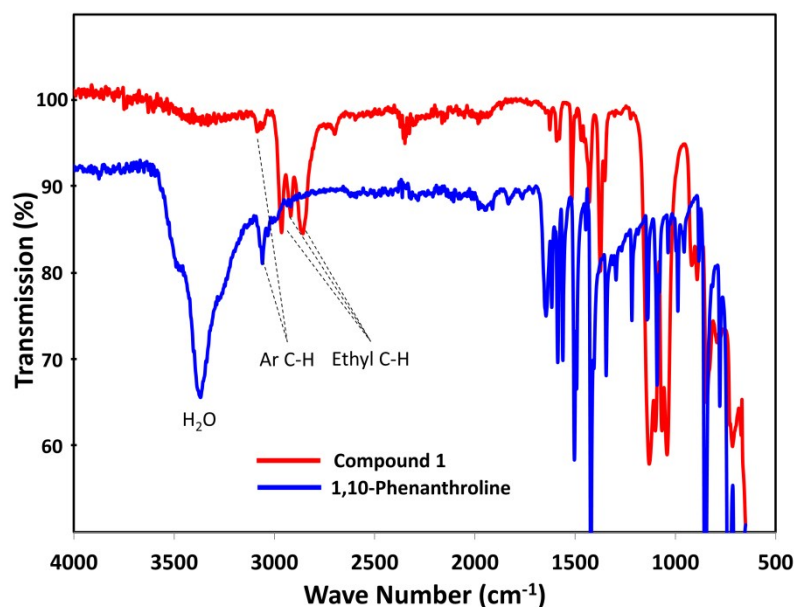


Figure S1. IR spectra of compound **1** (red) and 1,10-phenanthroline powder (blue). Peaks for some functional groups are indicated. The presence of the 1,10-phenanthroline and ethoxide ligands is confirmed by the peaks in the 3100 - 3000 cm^{-1} and 3000 - 2850 cm^{-1} ranges, respectively. The broad peak at 3250 cm^{-1} in the 1,10-phenanthroline spectrum probably corresponds to the water molecules contained in the phen powder sample due to air exposure.

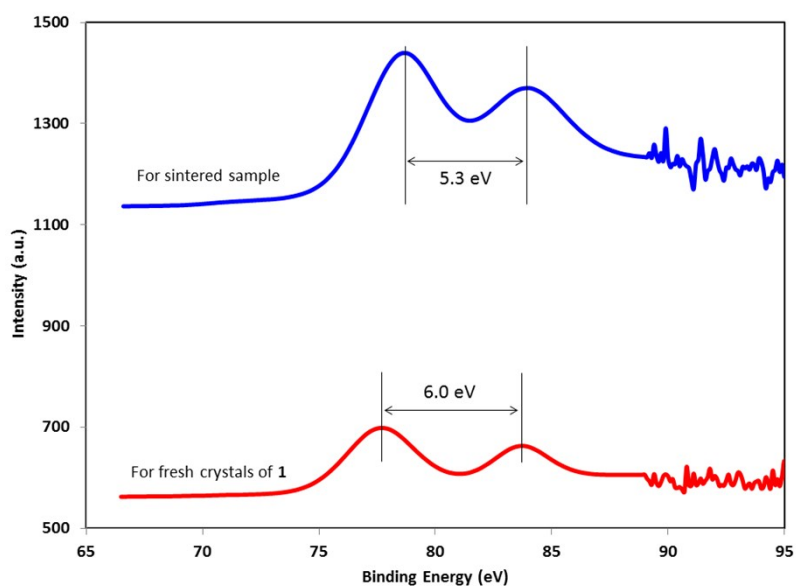


Figure S2. XPS data for Mn 3s of fresh crystal blocks of **1** (red curve) and the 600 °C sintered material (blue curve); the peak-to-peak distance agrees well with the literature value for Mn^{II} and Mn^{III} species, respectively.^{1,2}

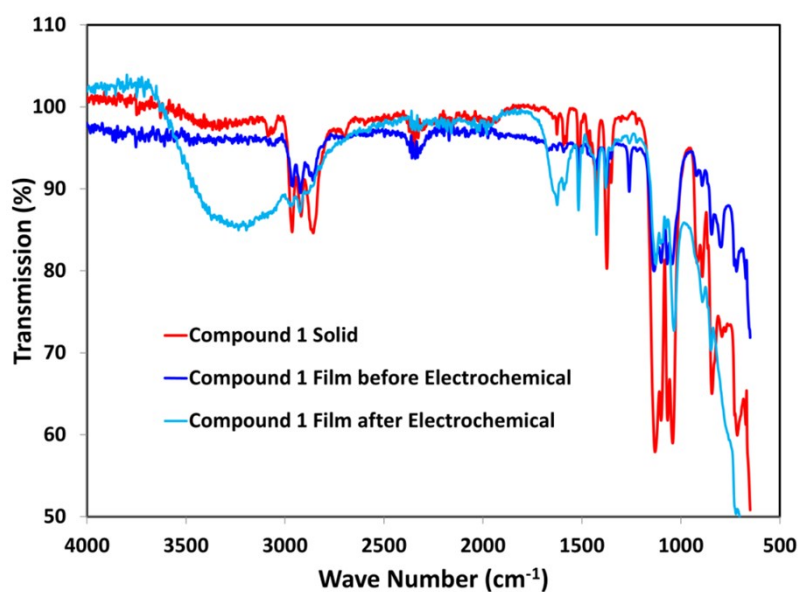


Figure S3. The IR spectra of compound **1** in the form of solid powder (red curve) and drop-cast film before (blue curve) and after (cyan curve) aqueous electrochemical analysis. Most of the peaks are retained after the drop-casting deposition, or even the electrochemical measurement. The extraneous peak at 1260 cm⁻¹ in the blue coloured spectrum corresponds to the methyl group, which might result from ligand exchange with the methanol solvent. The rather broad peak at 3250 cm⁻¹ in the cyan coloured spectrum is due to adsorbed water molecules.

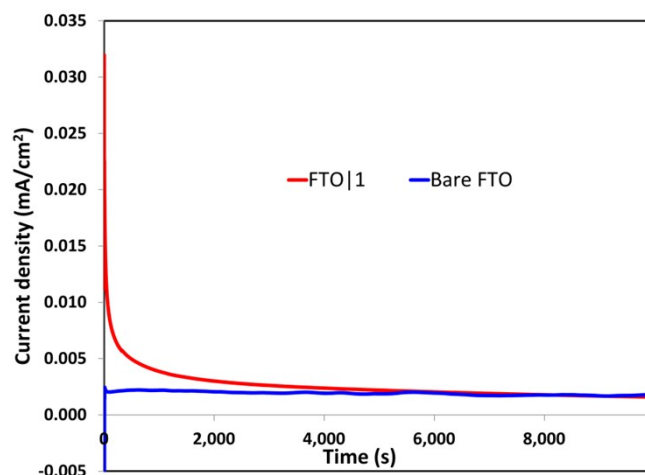


Figure S4. The electrode stability test of FTO|1 in 0.1 M Na₂SO₄ with prolonged reaction period. The current density from bare FTO is also included as a reference. The current density from FTO|1 decays almost exponentially and is identical to that of bare FTO after *ca.* 6000 s. The applied voltage is 2.1 V vs. RHE.

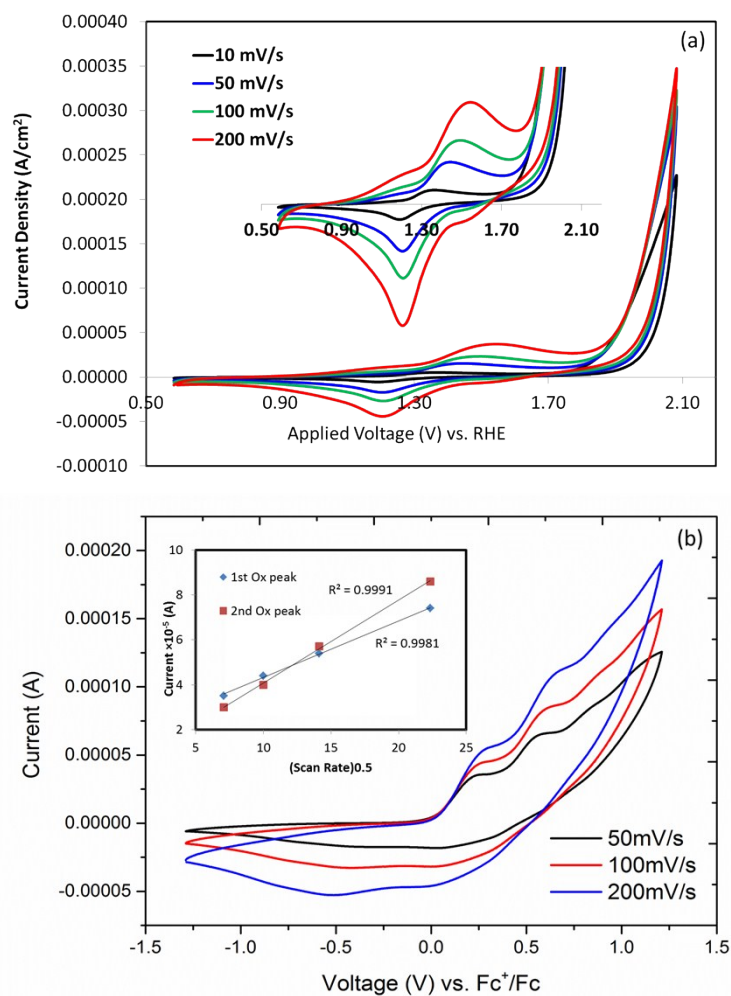


Figure S5. CV of the (a) electrode-based and (b) solution phase electrochemical analysis with different scan rates. Inset of (a) is the magnification of the redox waves. Inset of (b) is to show the linear trend between the oxidation peak heights and the square root of scan rate.

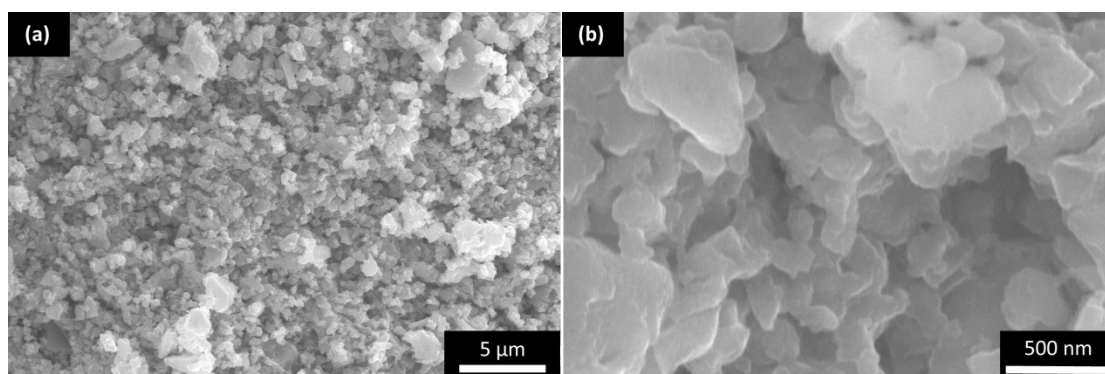


Figure S6 SEM images of the black powdered sample sintered at 600 °C: (a) low and (b) high magnification.

References

- 1 Y. Gorlin and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2010, **132**, 13612.
- 2 C. Bosch-Navarro, E. Coronado, C. Martí-Gastaldo, B. Rodríguez-González and L. M. Liz-Marzán, *Adv. Funct. Mater.*, 2012, **22**, 979.