

Electronic Supplementary Information

**Tuning Porous Nanostructures of MnCo_2O_4 for Application in
Supercapacitors and Catalysis**

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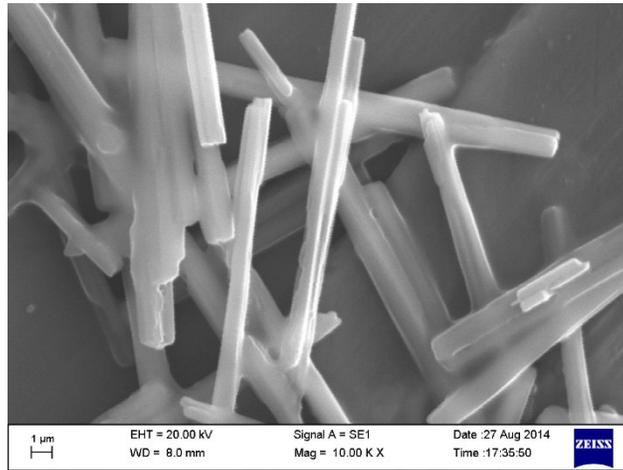


Fig. S1. SEM images of as-prepared MnCo₂O₄.

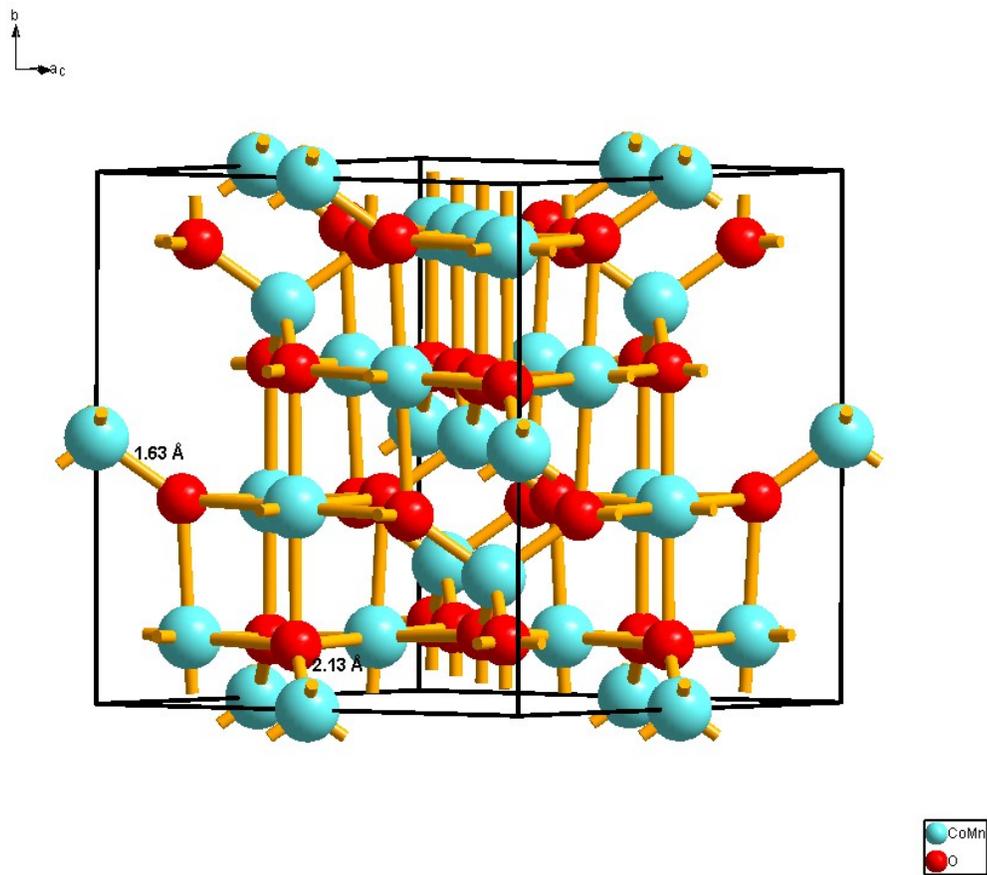


Fig. S2. Schematic of unit cell structural design of MnCo_2O_4 spinel from refinement data.

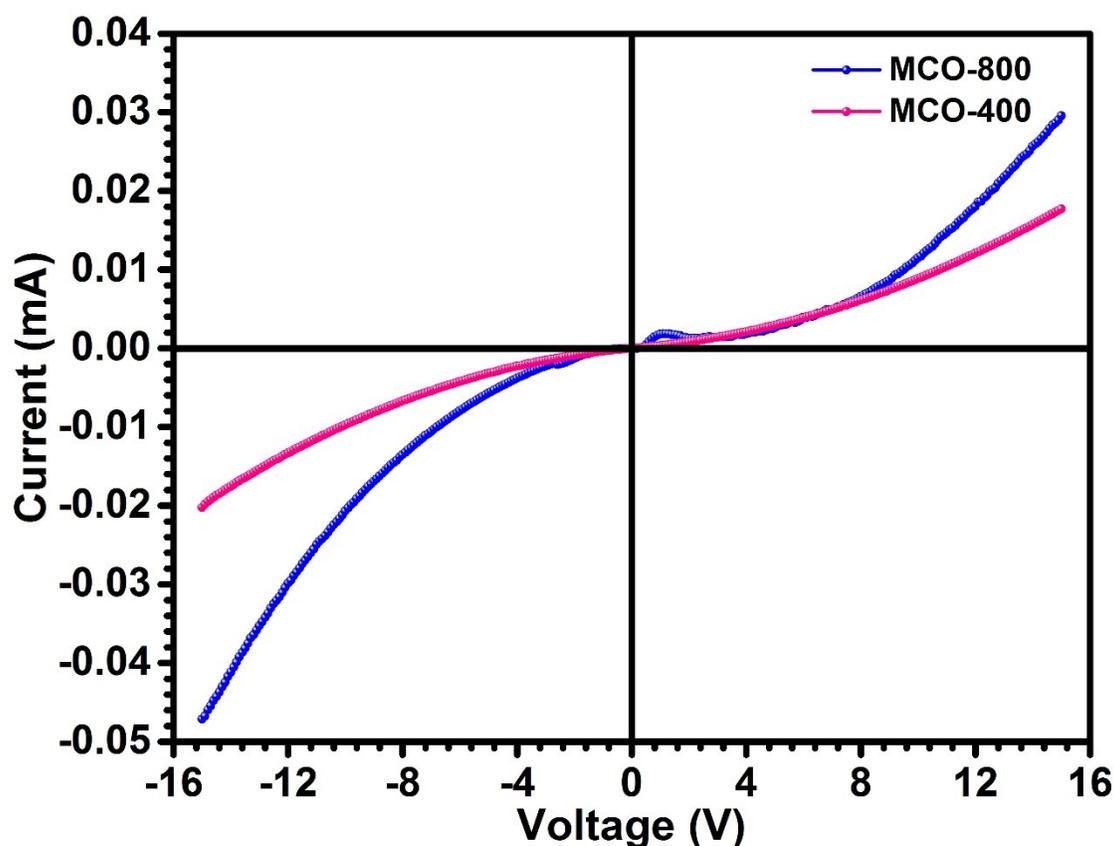


Fig. S3. I-V characteristic curves for the electrode materials MCO-400 and MCO-800.

The graph in Fig. S3. depicts two room temperature I-V characteristic curves for the spinel oxides MCO-400 and MCO-800. These two I-V plots are symmetrical, non-rectifying and linear in the small voltage range, suggesting that the materials in the form circular pellets have good ohmic-contact characteristics. Preferably, when a small voltage is provided, the current flowing through the ohmic interfacial junction should be a linear function of the voltage applied. The ohmic resistance is determined to be the inverse of dI/dV at 0 V [S1]. The ohmic behavior is very important to the electrochemical measurements, because the specific capacitance is affected by ohmic contact resistance of interface of material and current collector.

For further analysis of the composition of the spinels calcined at 400°C and 800°C, the energy dispersive x-ray (EDX) analysis and elemental mapping of the micro-sized rectangular bars are depicted in Fig. S4 (a) and (b), respectively. The results prove the existence of Mn, Co and O on the spinel structure. The elemental mapping images confirmed that these elements were uniformly distributed on the surface.

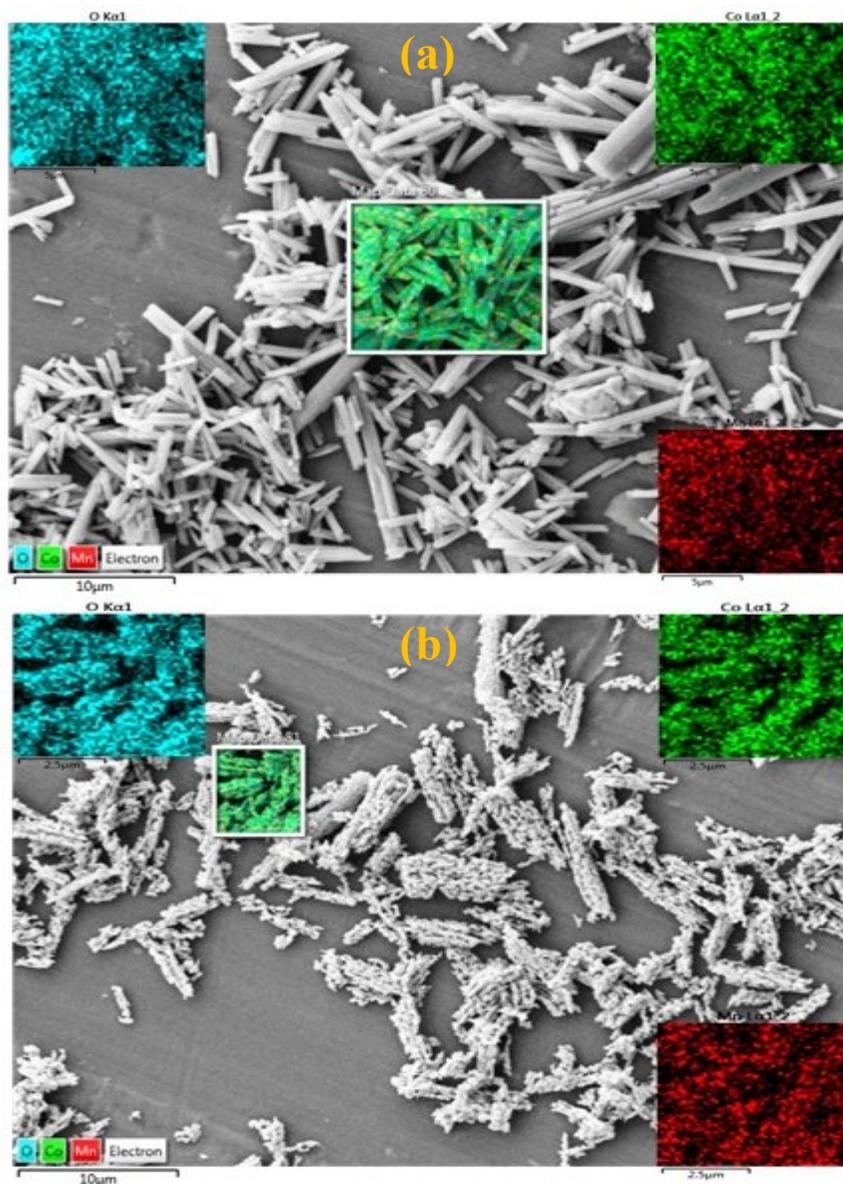
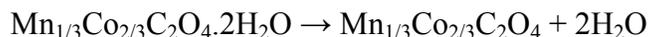


Fig. S4. Elemental mapping of micro-sized rectangular bars of manganese cobaltite spinel calcined at (a) 400°C and (b) 800°C containing Mn, Co and O.

The thermal decomposition of $\text{Mn}_{1/3}\text{Co}_{2/3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ shown in Fig. S5 involves two steps. The endothermic reaction at 200°C is the release of water of crystallization according to reaction



The one step water release confirms the formation of an oxalate solid solution. If the synthesis product was a mixture of two oxalates, this process would have involved two steps. The thermal decomposition of the anhydrous oxalate starts around 290°C and goes upto 625°C. Beyond this, the smooth rectangular bar changes to corn-like rough structure. According to TG data, the corresponding weight loss Δm is ~53% at the decomposition of oxalate complex.

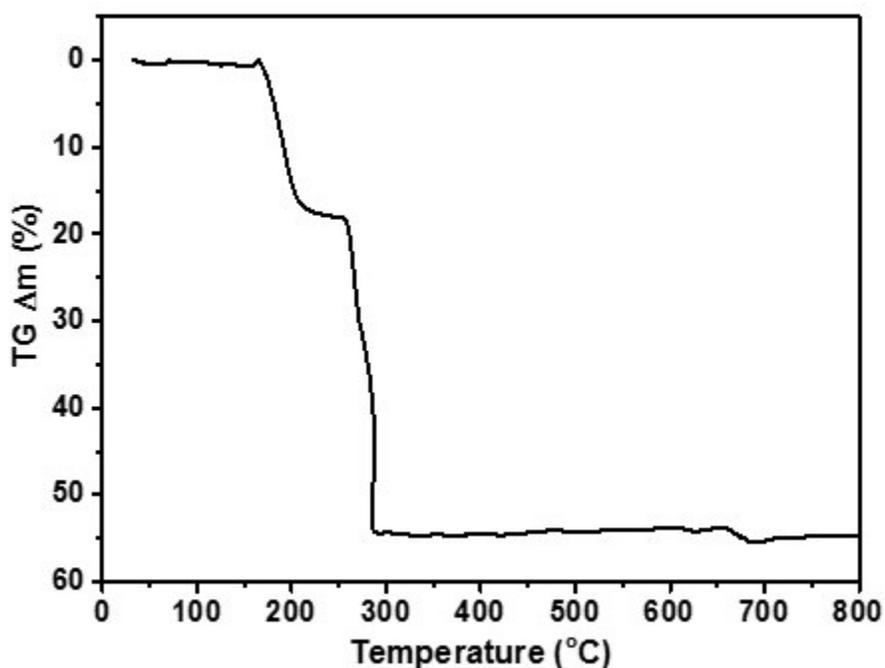


Fig. S5. TGA curve of as-prepared powder of MnCo_2O_4 for co-precipitation method.

Fig. S6 displays FTIR spectrum of MnCo_2O_4 calcined at both 400°C and 800°C . The spectra of both the samples show that the governing phase is a spinel oxide. At low frequencies, the spectrum shows two very strong (VS) absorptions at ~ 657 and ~ 561 cm^{-1} for MCO-400 and ~ 647 and ~ 551 cm^{-1} for MCO-800. According to Zhan et al. [26], the IR spectrum of the cubic spinel Co_3O_4 contains two bands, at 667 and 577 cm^{-1} inherited to metal-oxygen (Co-O) vibrations. In addition, the spectra of the MCO-400 and MCO-800 samples show a weak band at ~ 1629 cm^{-1} and ~ 1627 cm^{-1} , respectively, from which it can be inferred that the sample contains very minor quantity of the mixed oxalate and/or an intermediate carbonate phase.

Moreover, the weak, broad band centered at ~ 3403 cm^{-1} and 3424 cm^{-1} , respectively for MCO-400 and MCO-800 in the spectra can be assumed as the presence of adsorbed water since, with reference to SEM results, these samples consist of long rectangular bars and, accordingly, has a large specific surface. The presence of adsorbed water in the sample is also evident from TG data, which demonstrate that the adsorbed water is fully removed by 200°C .

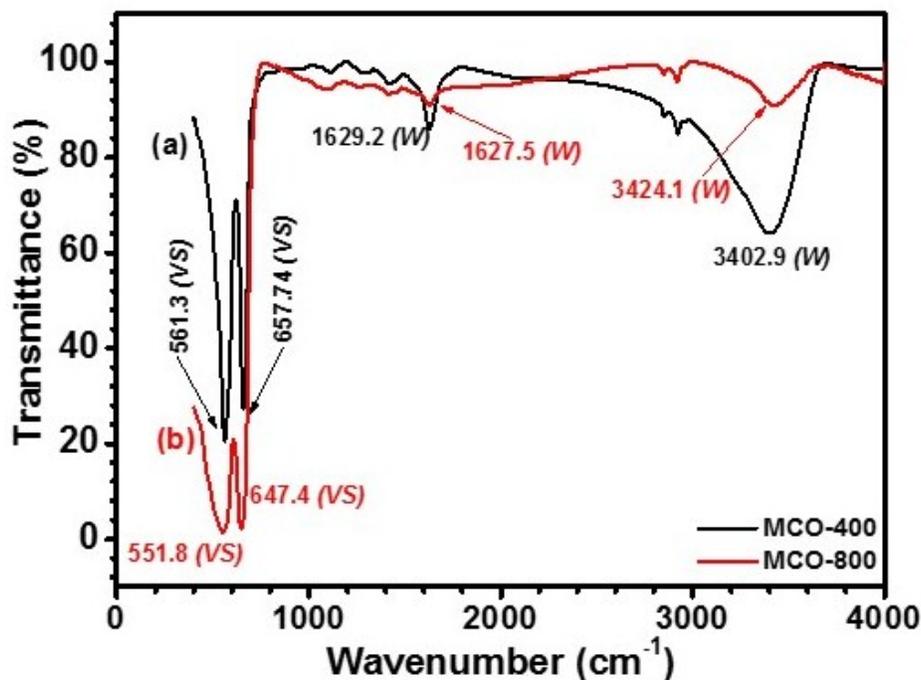


Fig. S6. FTIR spectrum of MnCo_2O_4 calcined at (a) 400°C and (b) 800°C for co-precipitation method.

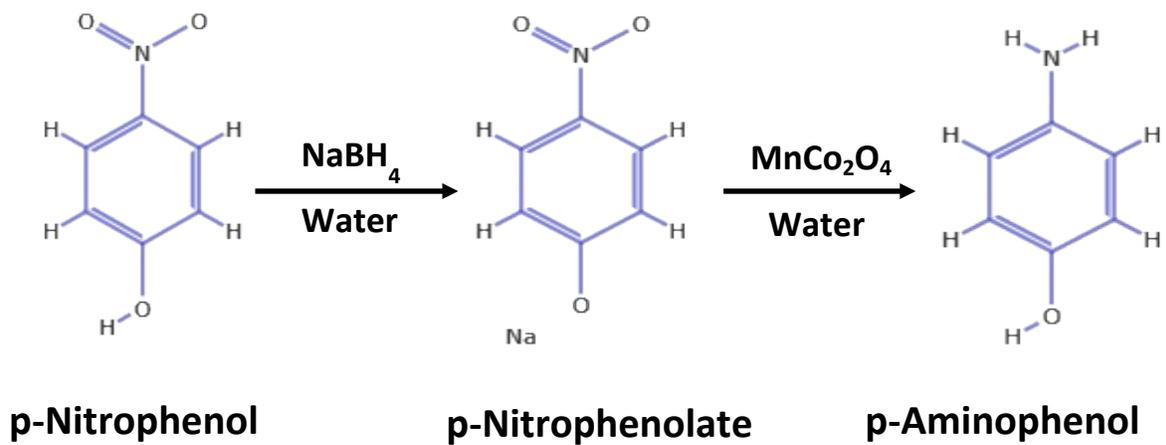


Fig. S7. Reduction reaction scheme of p-nitrophenol to p-aminophenol.

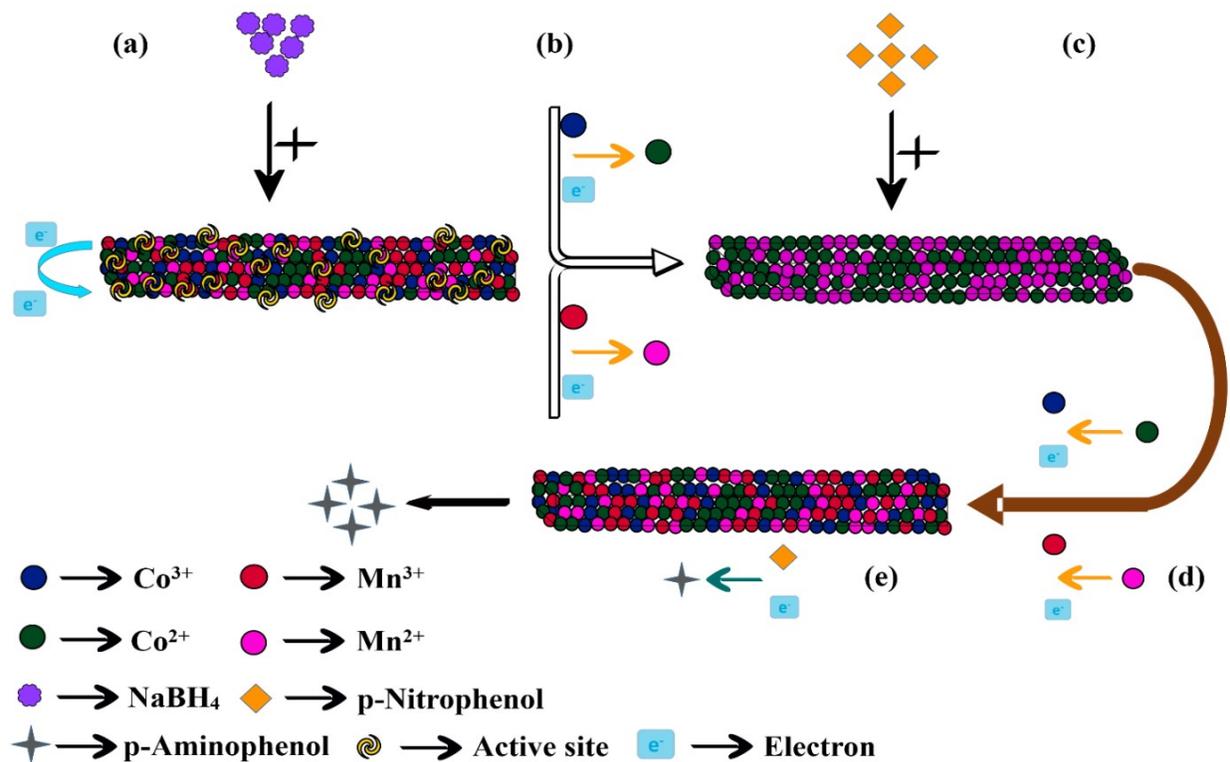


Fig. S8. Suggested mechanism of the reduction catalysis of $p\text{-NP}$: (a) Adsorption of BH_4^- anions on the catalyst surface, provides electrons to the catalyst. (b) Each Mn^{3+} and Co^{3+} get reduced using these electrons to form Mn^{2+} and Co^{2+} . (c) Adsorption of $p\text{-NP}$ on the catalyst surface. (d) Each Mn^{2+} and Co^{2+} get oxidized into Mn^{3+} and Co^{3+} and contribute their electrons to $p\text{-NP}$. (e) $p\text{-NP}$ molecules receive electrons to form $p\text{-AP}$ and finally $p\text{-AP}$ molecules get desorbed from the catalyst.

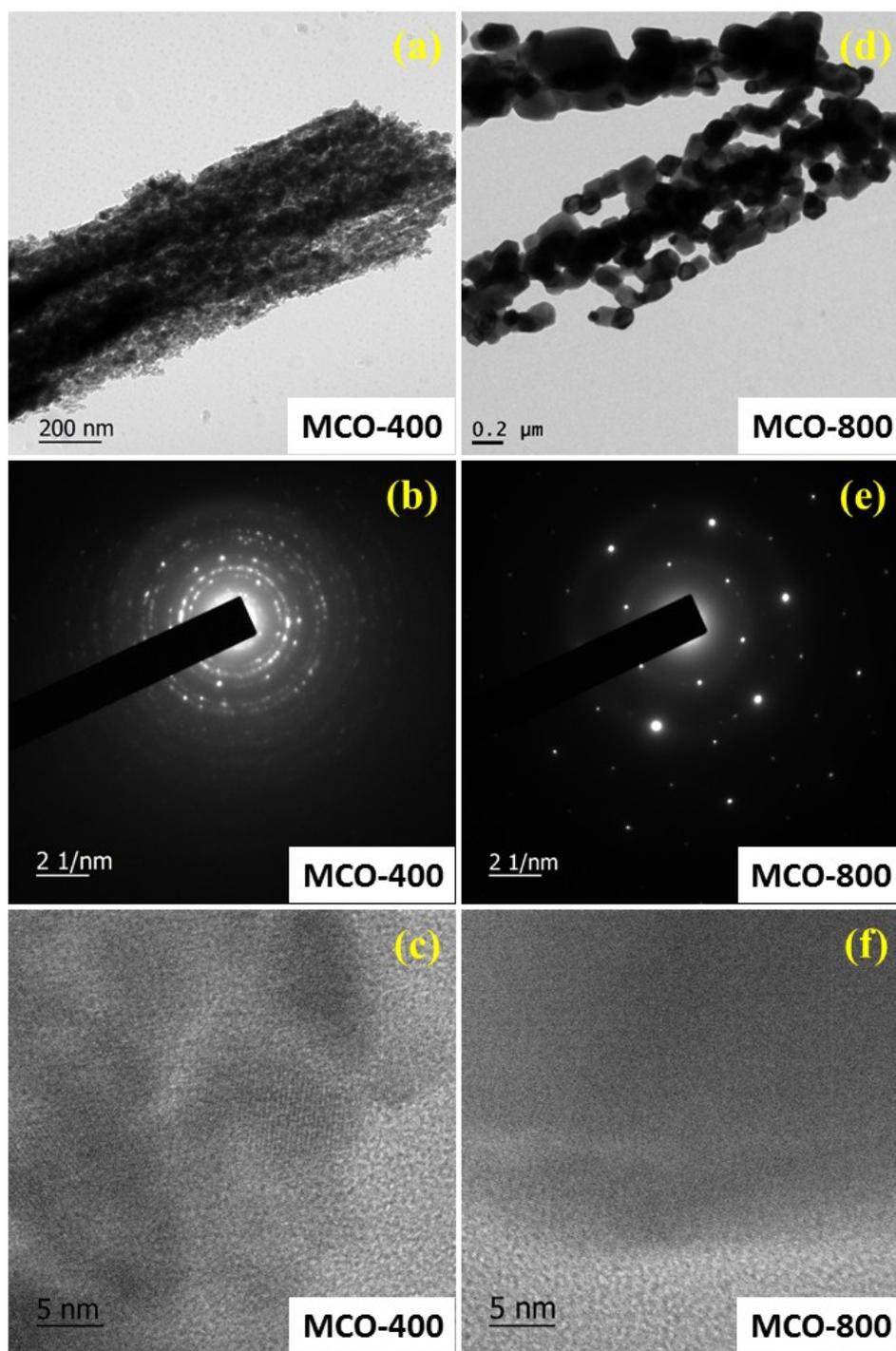


Fig. S9. HRTEM micrographs for samples MCO-400 from (a) to (c) and for MCO-800 from (d) to (f) showing images, SAED and fringe patterns.

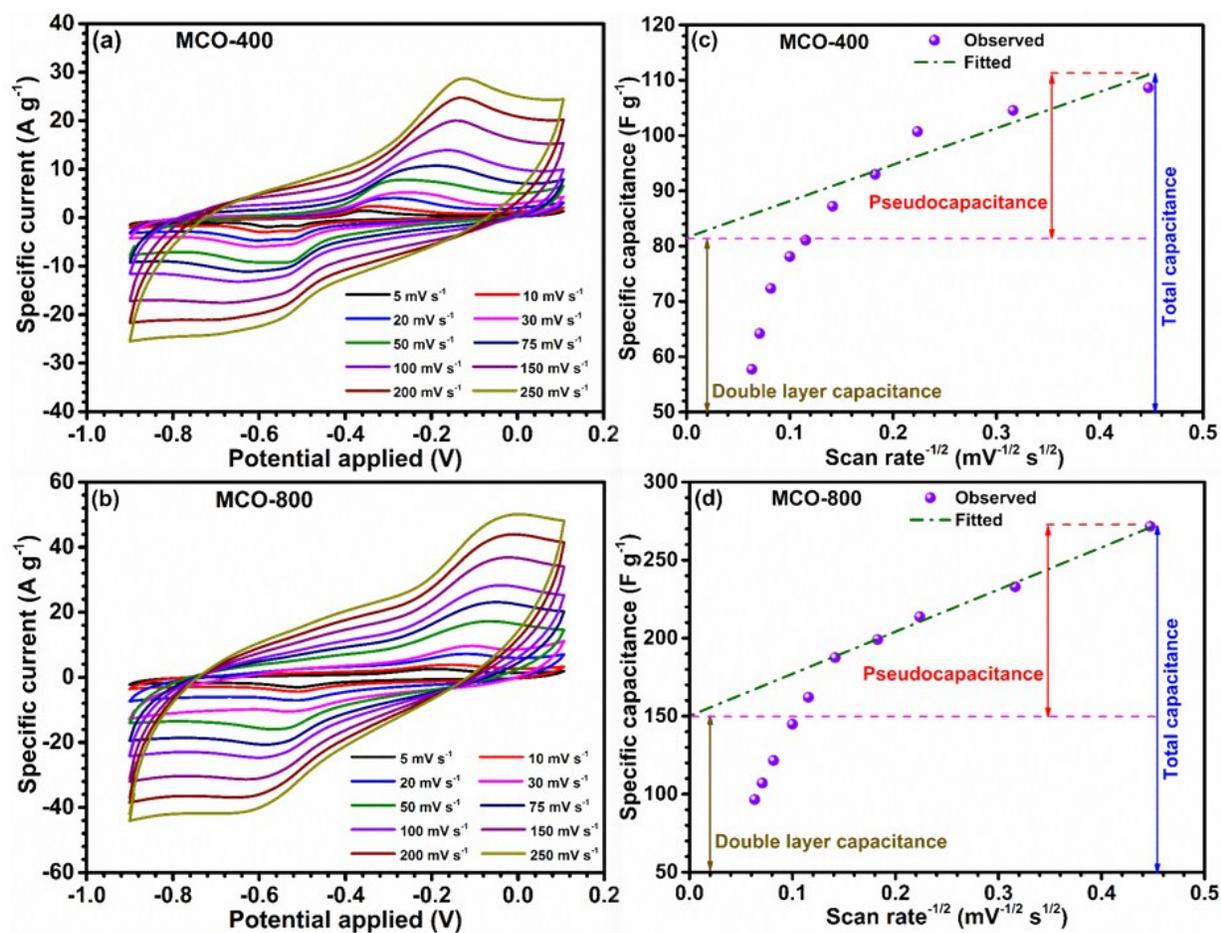


Fig. S10. CV curves of (a) MCO-400 and (b) MCO-800 at different scan rates; Quantification of double-layer and pseudocapacitance for (c) MCO-400 and (d) MCO-800.

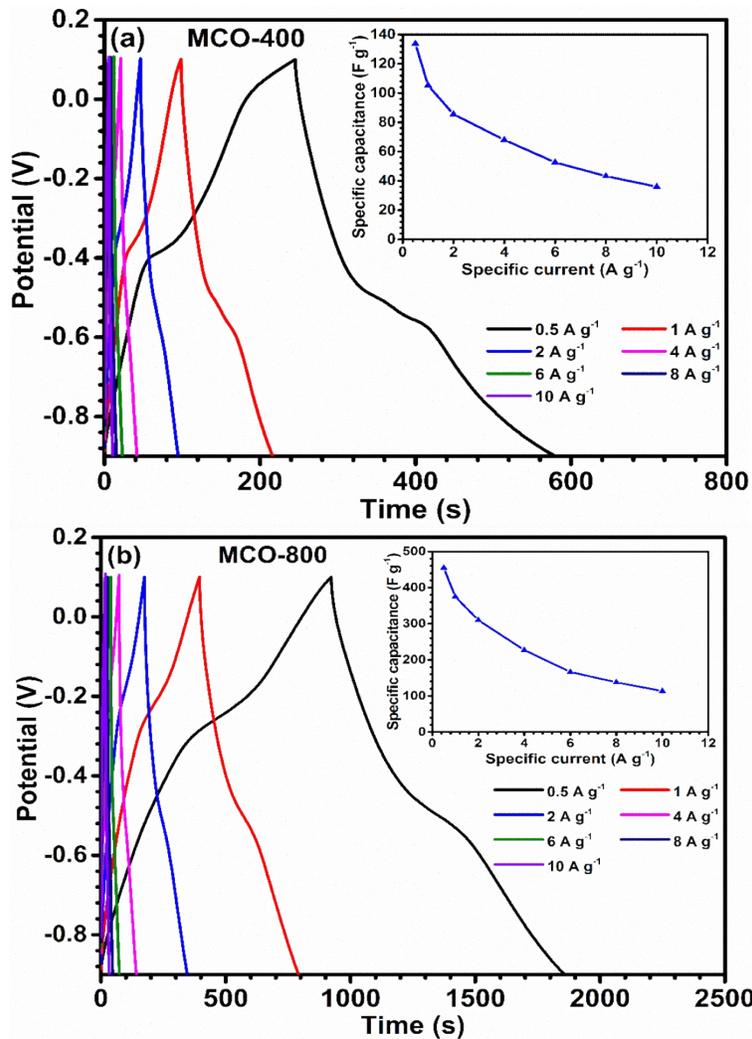


Fig. S11. Galvanostatic charging-discharging profile of (a) MCO-400 and (b) MCO-800 at different specific currents and (insets) specific current dependence of the specific capacitance for (a) MCO-400 and (b) MCO-800.

References

- [S1] Y.-J. Ma, Z. Zhang, F. Zhou, L. Lu, A. Jin and C. Gu, *Nanotechnol.*, 2005, 16, 746-749.
 [S2] Y. Zhan, C. Yin, W. Wenzhong and G. Wang, *Mater. Lett.*, 2003, 57, 3402-3405