

## Supporting information

### **An X-ray Absorption Spectroscopic Study of a Highly Thermally Stable Manganese Oxide Octahedral Molecular Sieves (OMS-2) with High Oxygen Reduction Reaction Activity**

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### ***In situ* X-ray Absorption Near Edge Structure (*In-situ* XANES)**

*In situ* studies of the K-edge changes to the Mn atoms during transformation from AMO to the OMS-2 phase were conducted in the transmission mode at the X18A beamline of the National Synchrotron Light Source (NSLS). A Silicon (111) channel-cut double crystal monochromator was used to monochromatize the synchrotron radiation. The incident and transmitted beam intensities were monitored using ionization chambers filled with N<sub>2</sub>. The samples were diluted by h-BN with a ratio of (1:8) then pressed into pellets and heated in the oven *in situ* as shown in Scheme S2. The sample was mounted in the center of the heating cell and fixed by clips. The temperature was ramped at 10°C/min to 450°C in an air atmosphere with a heating cartridge (K-type). Before the measurements were taken, a thin Mn foil reference was

used for energy calibration. The *ex-situ* study was done by calcination of as-prepared materials at 450°C at different times. The XANES data were analyzed using Athena software where background and post and pre-edge corrections were made.

### **X-ray Diffraction**

The powder X-ray diffraction was done using a Rigaku Ultima IV diffractometer equipped with a Cu K $\alpha$  ( $\lambda=0.15406$  nm) radiation source. The beam was operated at currents and voltages of 44 mA and 40 kV, respectively. The XRD measurements of prepared samples were carried out at room temperature and  $2\theta$  was varied continuously from 5.0 to 80° at a scan rate of 2.0°/min. The Debye-Scherrer equation was used to determine the particle sizes of the OMS-2 material. The instrumental line broadening correction was done by using a LaB<sub>6</sub> standard for integral width correction. The (110), (310), and (110) peaks were used to calculate the average value of crystallite size.

### **Fourier Transform Infrared (FTIR).**

A Thermo-Scientific Nicolet FT-IR Model 8700 equipped with a deuterated triglycine sulfate (DTGS) detector was used to obtain the FTIR spectra of the samples. Prior to the acquisition of spectra, the samples were diluted with KBr in a 1:100 ratio and then pressed into visually transparent pellets. The spectra were recorded within the 4000–400 cm<sup>-1</sup> range.

### **Electron Microscopy (EM)**

The morphology of the fully prepared HT-OMS-2 materials and materials calcined at lower temperatures were examined by using a field emission Zeiss DMS 982 Gemini scanning electron microscope (FE-SEM). The Schottky beam emitter operated at a voltage and current of 2.0 kV and 1.0 mA respectively. FE-SEM samples were prepared by sonicating the prepared HT-OMS-2 materials in absolute ethanol for 5 min to form a suspension. A few drops of the suspension were

drop casted on a silicon chip, which was mounted on an aluminum stub with double-sided carbon tape. Further structural studies were performed using a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV. HT-OMS-2 samples for TEM were prepared by placing a drop of suspension containing HT-OMS-2 powder in 2-propanol on a holey carbon-coated copper grid.

#### **Thermogravimetric analysis (TGA).**

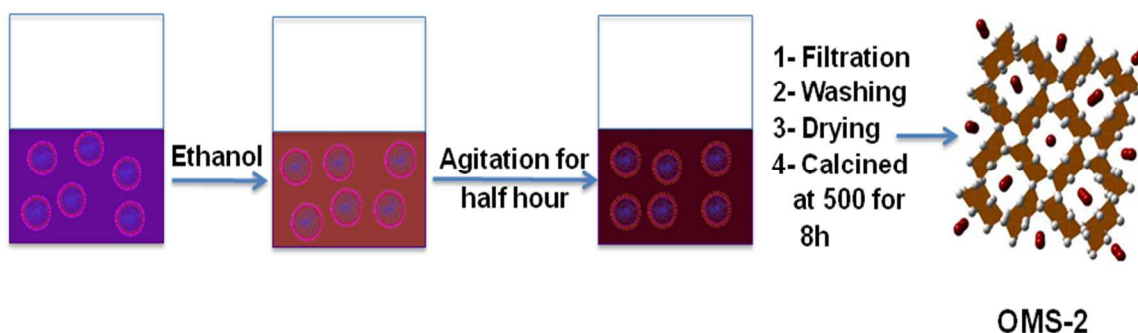
Thermogravimetric analysis was done to monitor the thermal weight profile of HT-OMS-2 and the AMO precursor using a Hi-Res TGA instrument model 2950. The samples were heated under nitrogen or air from room temperature to 1000°C with a heating rate of 10°C/min.

#### **Temperature Programed Desorption – Mass Spectroscopy (TPD-MS).**

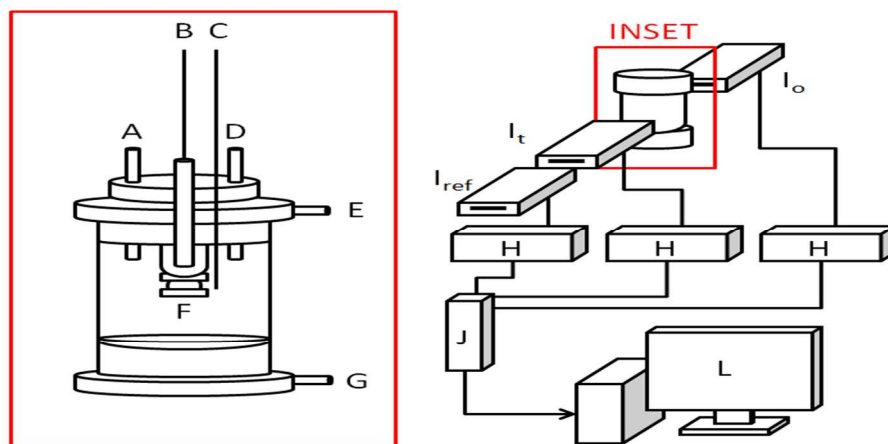
The gas evolution and uptake of the AMO and HT-OMS-2 materials were examined by using (TPD-MS). The mass spectrometer used was an MKS eVision quadrupole residual gas analyzer with 70 eV electron impact ionization. The sample (20 mg) was packed into a 9 mm O.D. quartz tube. The tube was loaded into a tubular temperature controlled furnace. Swagelok Ultra-Torr fittings (3/8") were connected to both ends of the quartz tube and appropriate adapters were used to deliver the gases to and from the fittings. The exit gases were vented to air. A "T" in the exit gas line was connected to a 5' heated 1/16" O.D. stainless steel tube through which the exit gases were sampled into a bypass low pressure sampling manifold. The gases were introduced into the high vacuum mass spectrometer chamber from the low pressure manifold through an orifice. The sample was cleaned under helium for 2 h at room temperature followed by heating and monitoring of gas evolution and uptake to 900°C at 10°C/min in air. The gas flow rate was controlled by an MKS mass-flow controller.

### Brunauer–Emmett–Teller (BET).

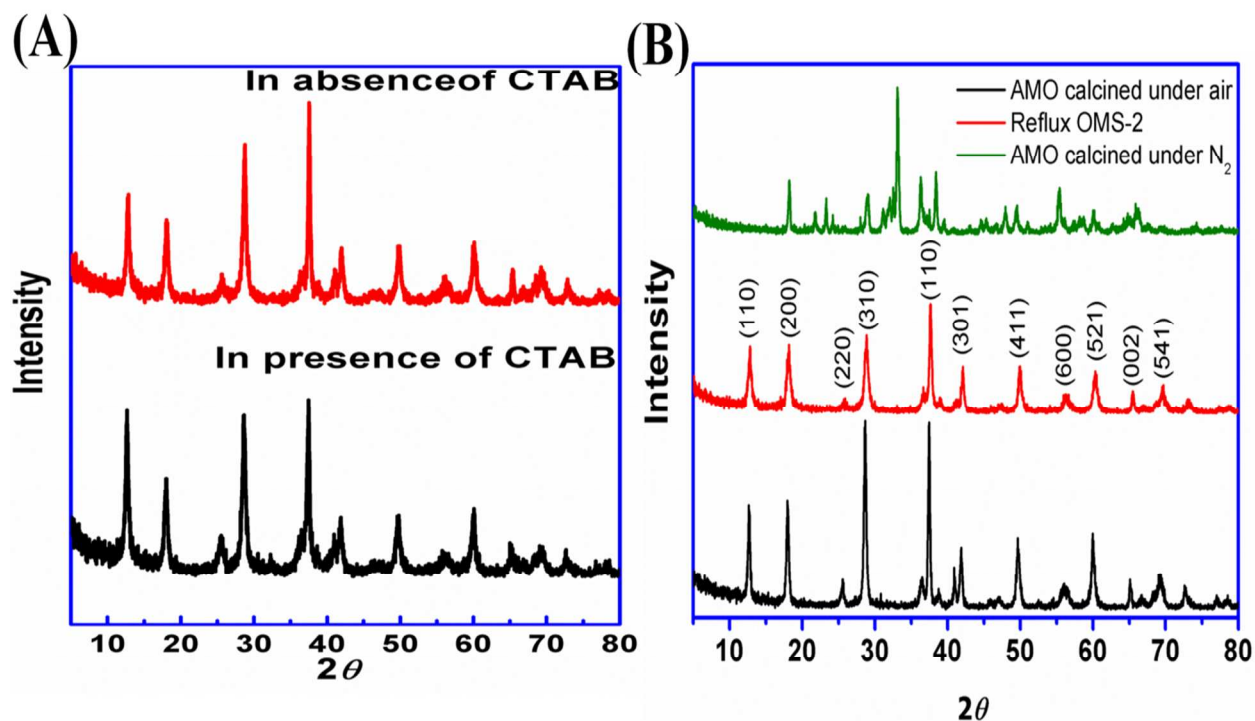
Brunauer–Emmett–Teller (BET) methods were used to determine the specific surface area of samples using a Micromeritics ASAP 2010 instrument. The measurements were done using a multipoint method and N<sub>2</sub> gas as the adsorbate at 77K. Each sample was degassed at 200°C for 12 h before the measurement.



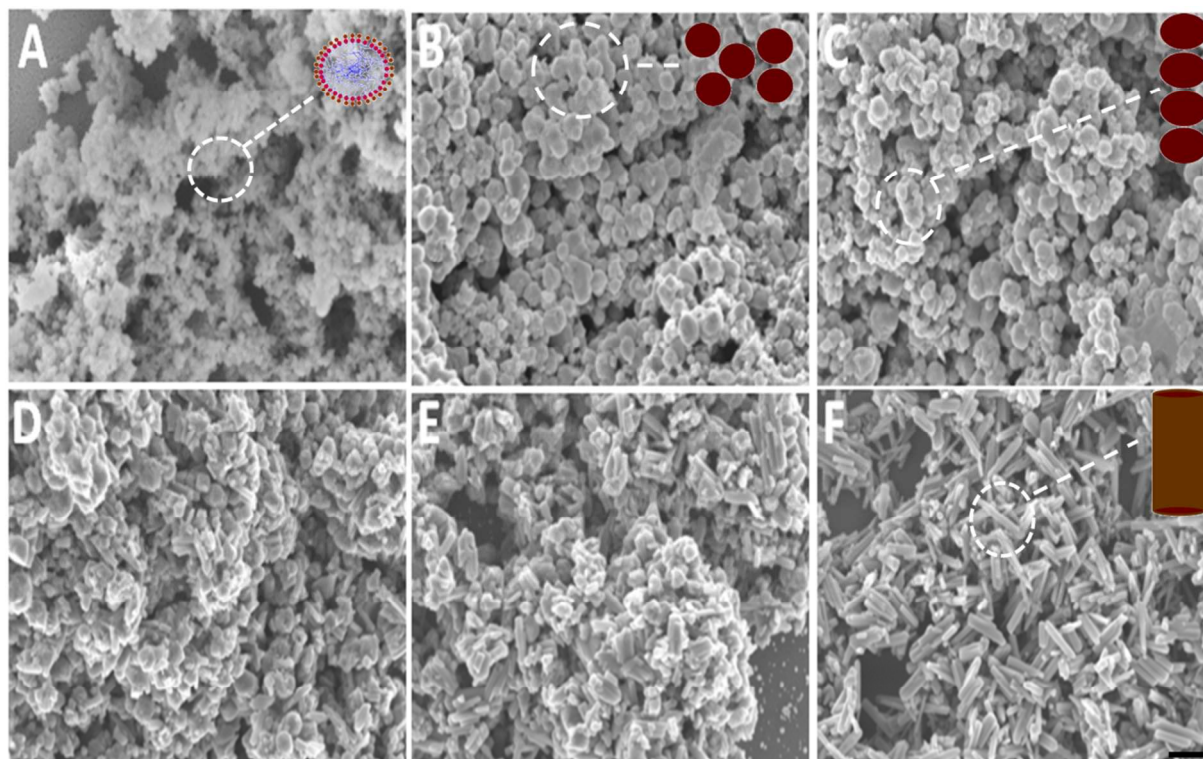
**Scheme S1.** Synthesis and Formation of Highly Thermally Stable OMS-2.



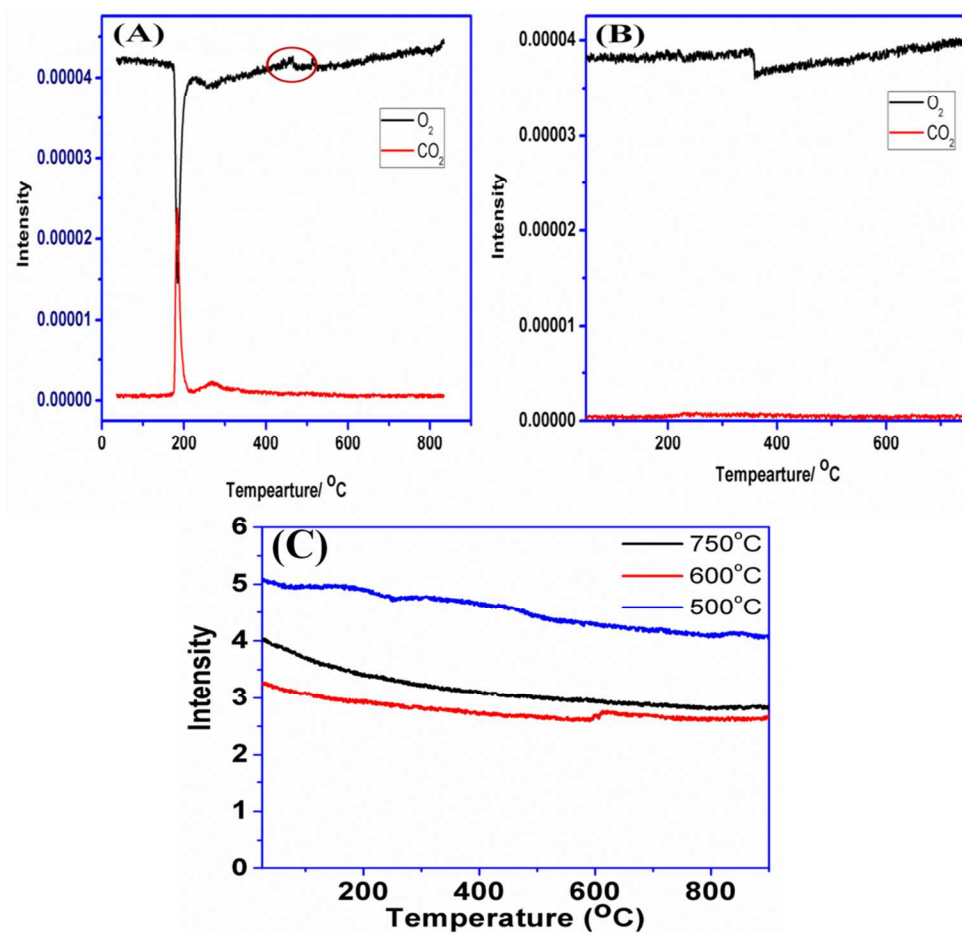
**Scheme S2.** Design for the In-situ X-ray Absorption Cell and data acquisition setup. Inset is hot cell design. A) Gas Inlet B) Cartridge heater (Omega Engineering) C) Type K thermocouple D) Gas outlet E) Water cooling inlet F) Sample diluted in h-BN for analysis G) Water cooling outlet. H) Keithley Ammeters I<sub>o</sub>, I<sub>t</sub>, I<sub>ref</sub> Ionization chambers J) Data Acquisition Board L) PC terminal.



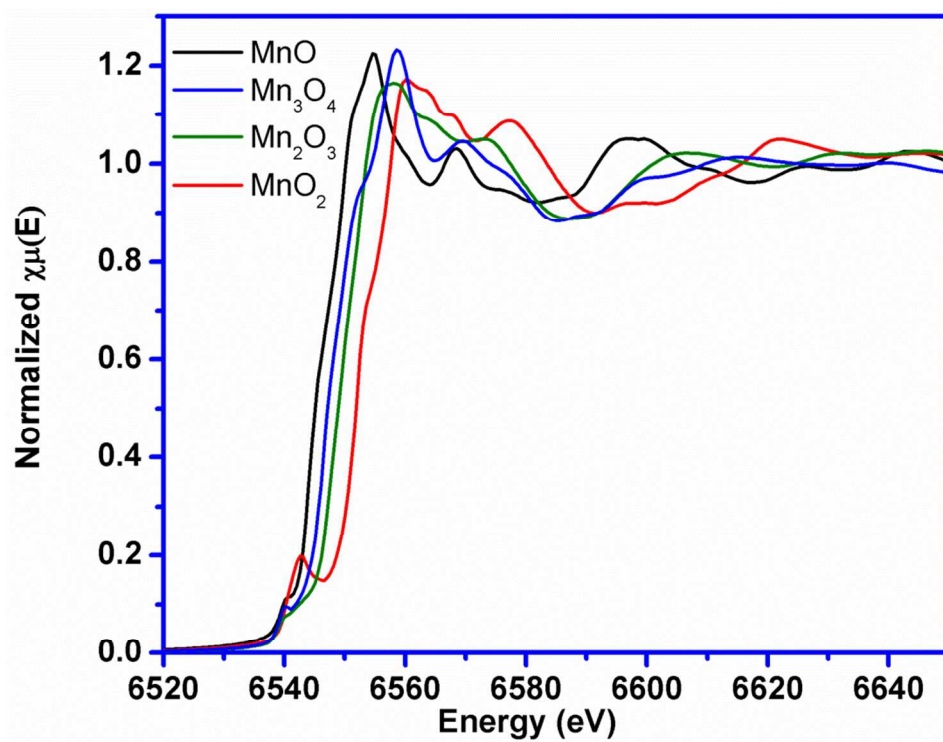
**Figure S1.** (a) XRD of OMS-2 materials synthesized in presence and absence of CTAB. (b) The XRD of as-made materials calcined under air and  $N_2$  atmospheres compared with reflux OMS-2.



**Figure S2.** FE-SEM images showing time dependent morphology study of the OMS-2 short nanorods formation at 500°C in presence of CTAB. (a) as-made manganese oxide materials. (b-f) calcined for 0.5, 1, 4, 6, and 12 h, respectively. (the scale bar is the same 250 nm).

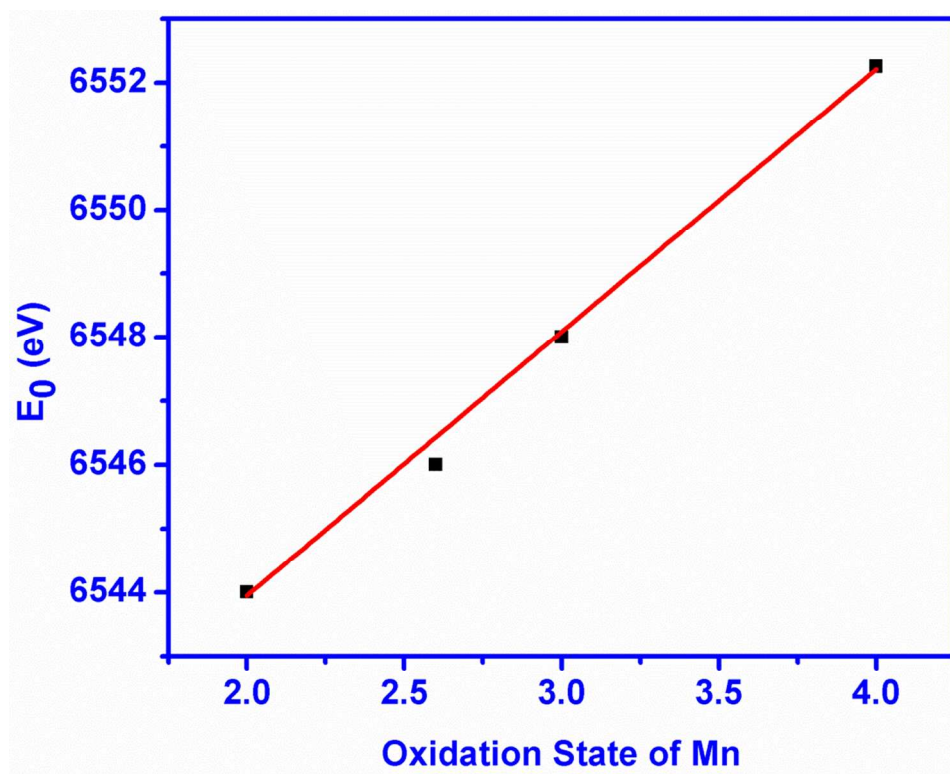


**Figure S3.** TPD for as-made material (A) in presence and (B) in absence of CTAB (C) TPD of OMS-2 at different temperatures (500, 600, and 750°C)

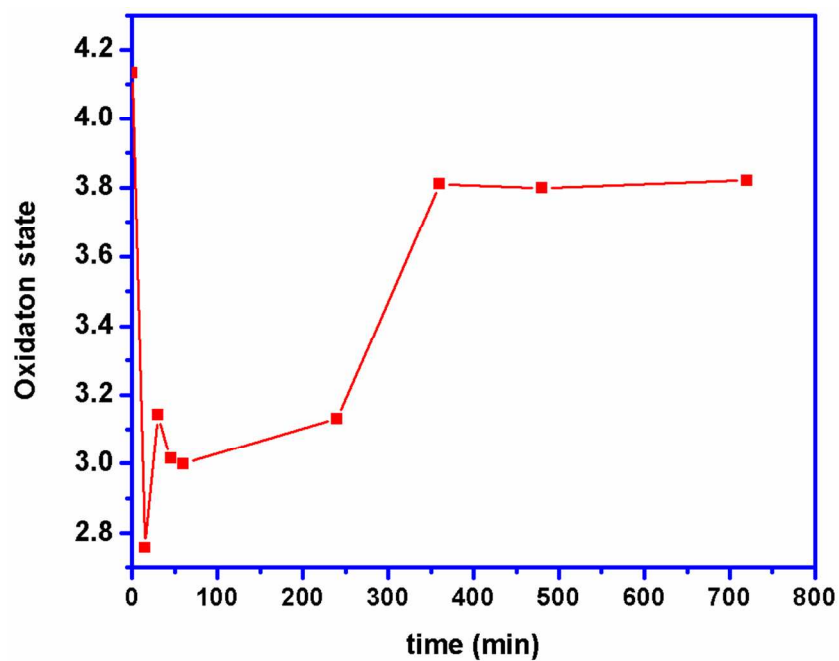


**Figure S4.** XAS spectra for K-edge of Mn in different manganese oxides (MnO, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>).

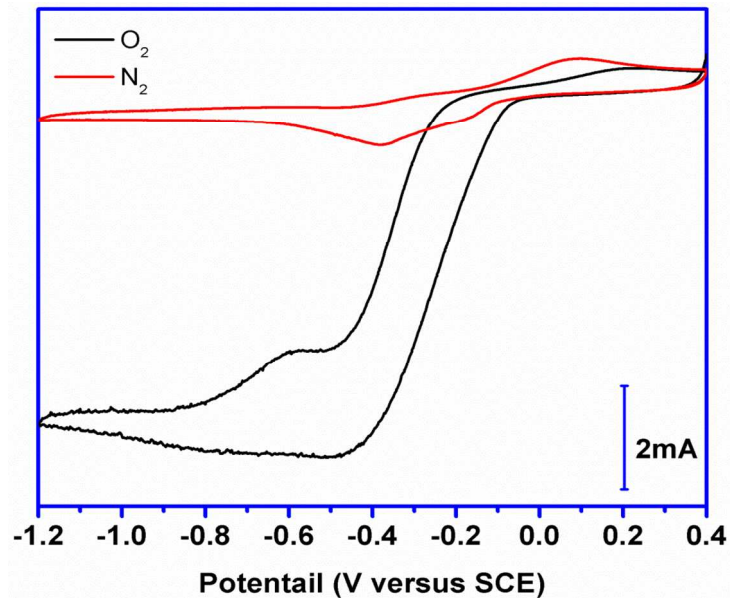




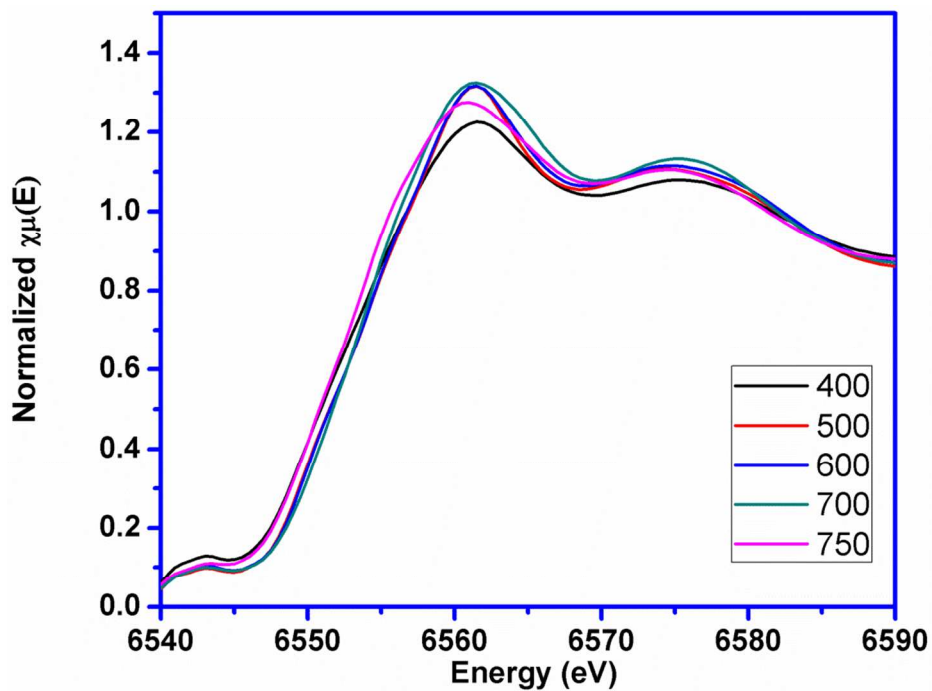
**Figure S5.** Oxidation state standard calibration curve for manganese oxides K-edge.



**Figure S6.** Change in the oxidation state of Mn-K edge with the time of thermal transformation of AMO.



**Figure S7.** Cyclic voltammograms for OMS-2 calcined at 500°C in  $O_2$  and Ar saturated atmospheres at a scan rate of  $5 \text{ mVs}^{-1}$  and 0.1 M KOH solution at room temperature.



**Figure S8.** XANES for OMS-2 calcined at different temperatures.