

## Multivalent manganese oxides with high electrocatalytic activity for oxygen reduction reaction

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### Electronic Supplementary Material

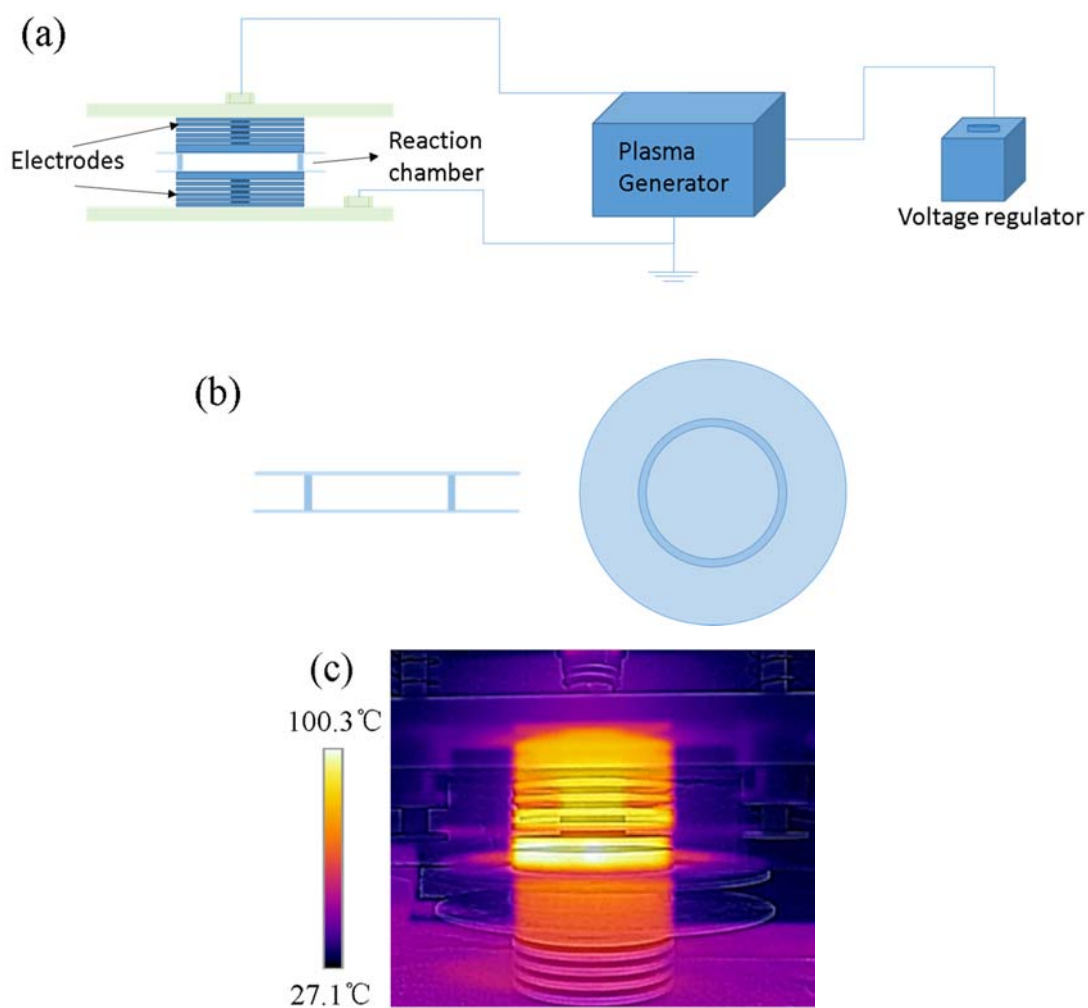
#### Dielectric Barrier Discharge Plasma Treatment

The DBD reactor contains two quartz plate (2 mm in thick and 60 mm in diameter) and one quarter ring (50 mm in diameter) as barrier. The schematic representation of the DBD plasma setup can be found in Fig. S1. In a typical synthesis of MnO<sub>x</sub>@C-D through DBD decomposition, moderate precursor powder was tiled on a reaction chamber after being ground. The sample (about 0.2 g) was loaded on the lower quartz plate that was placed between the two electrodes. The electrodes were clamped on the quartz plates. The DBD plasma was generated by a high voltage generator (CTP-2000K; Corona Laboratory, Nanjing, China), which can supply a voltage from 0 to 30 kV with a sinusoidal waveform at a frequency of about 22 kHz.

The chamber was cooled to room temperature and detached from the electrodes. Then, the powder was stirred to turn over the pristine powder from the lower layer to

the top lever. The performance was repeated 20 times until total DBD decomposition time was 1 h.

The voltage and current were respectively measured using a digital oscilloscope (Tektronix TBS1102B) with a high-voltage probe and a current transformer built into the high voltage generator. The appearance of current pulses implied the generation of a typical DBD.



**Figure S1.** Schematic of (a) DBD plasma system, (b) reaction chamber and (c) IR image of the reaction system taken immediately after DBD treatment.

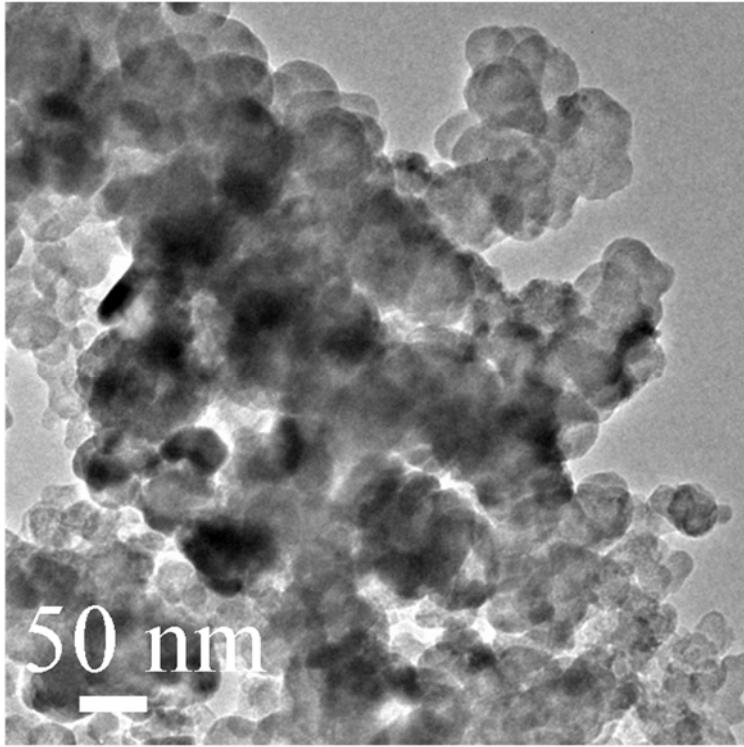
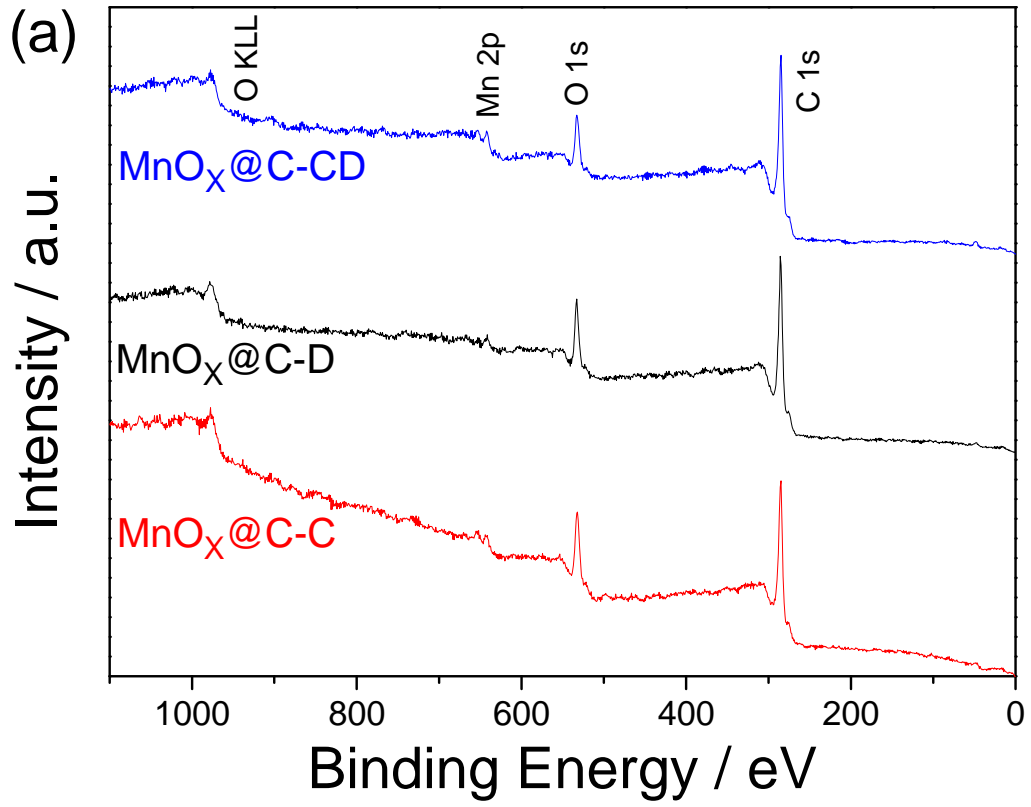
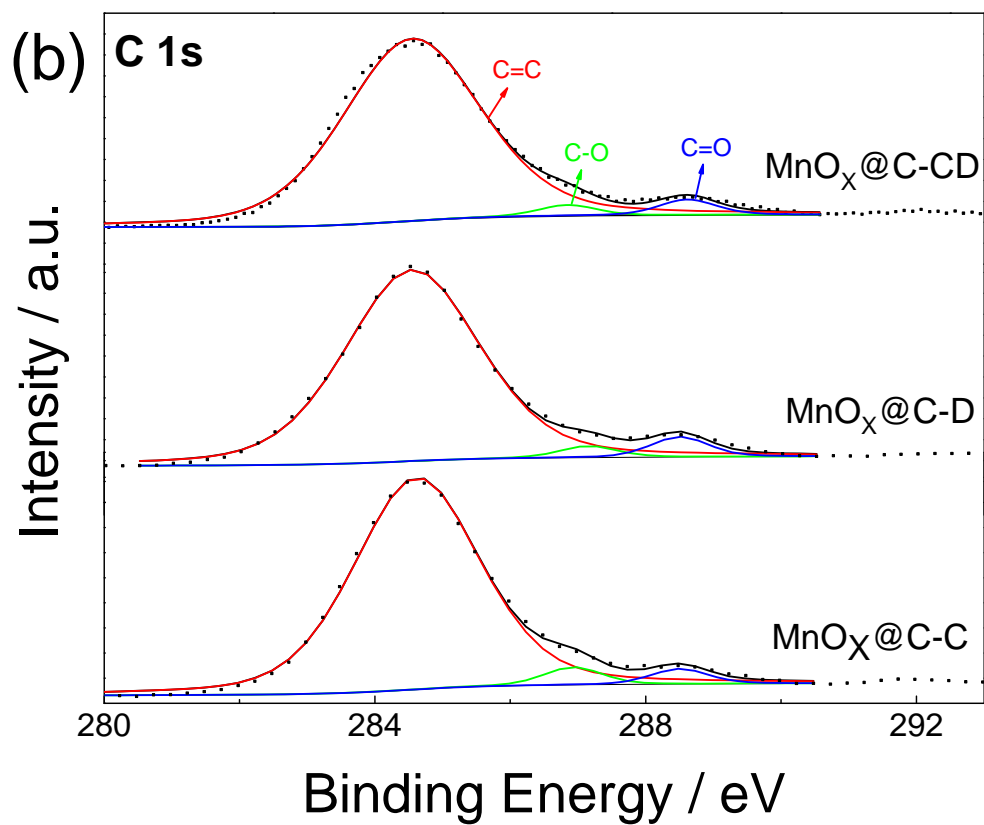
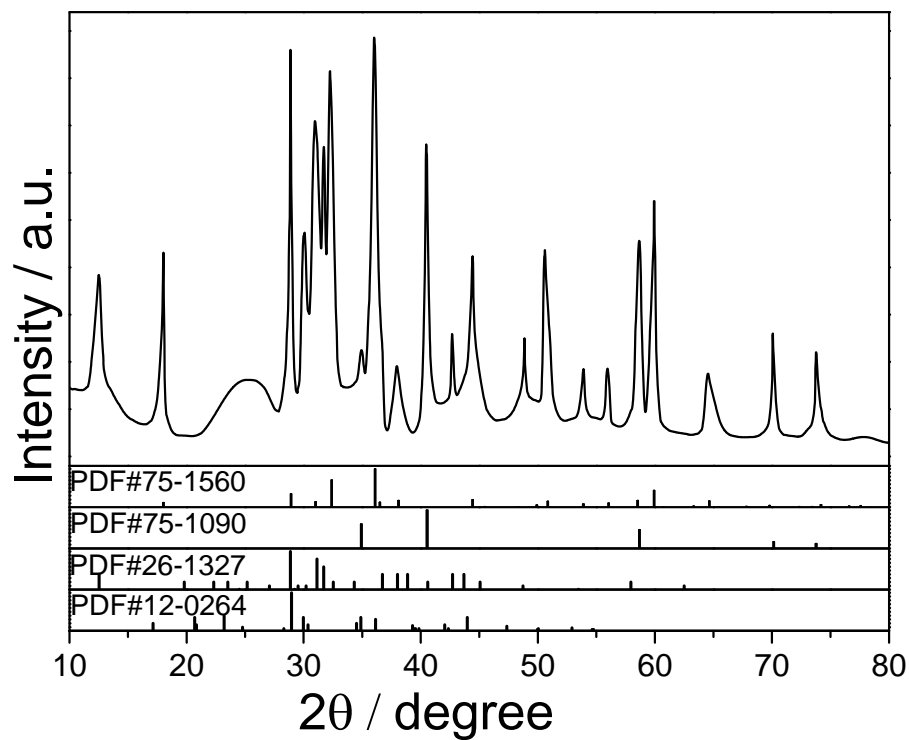


Figure S2. TEM image of MnO<sub>x</sub>@C-CD

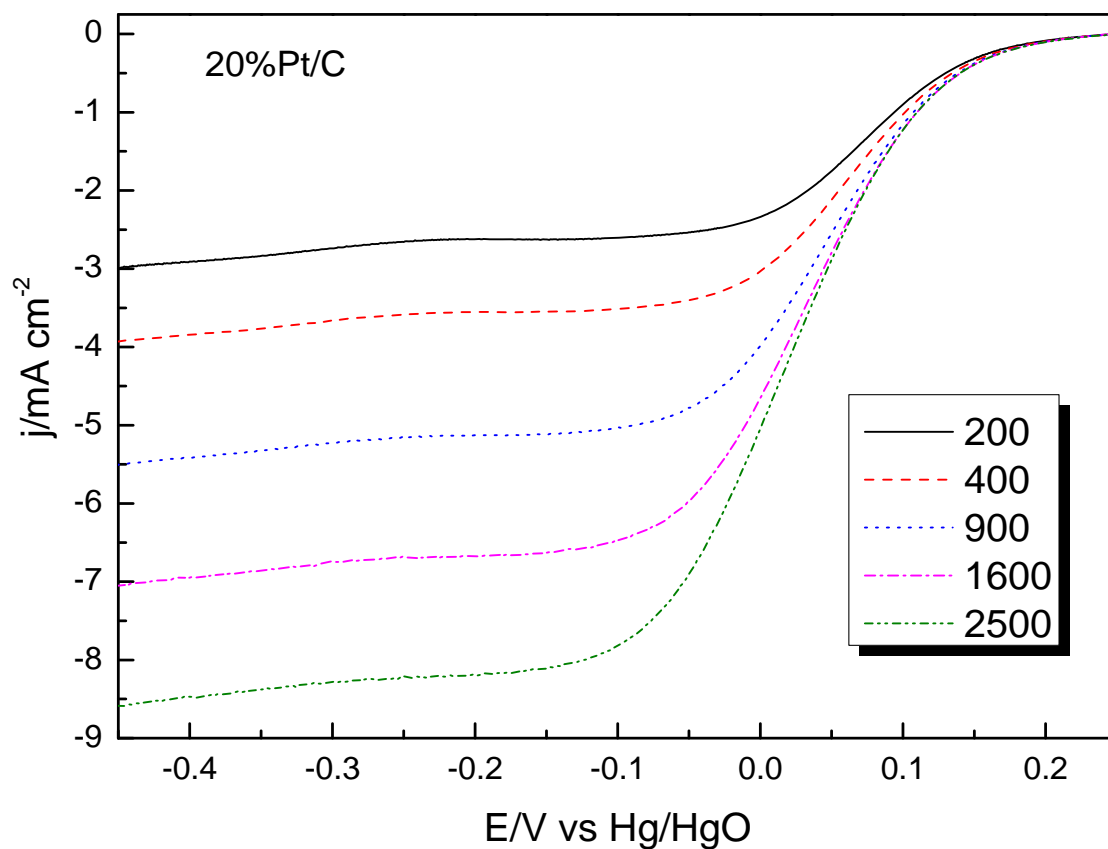




**Figure S3.** XPS spectra of (a) survey scan and (b) C 1s spectrum for MnO<sub>x</sub>@C-CD, MnO<sub>x</sub>@C-D and MnO<sub>x</sub>@C-C.



**Figure S4.** XRD patterns of MnO<sub>x</sub>@C-DBD without wash. PDF#75-1560: Mn<sub>3</sub>O<sub>4</sub>; PDF#75-1090: MnO; PDF#26-1327: K<sub>2</sub>O; PDF#12-0264: K<sub>2</sub>MnO<sub>4</sub>.



**Figure S5.** RDE measurements of commercial 20% Pt/C at different rotating speeds. The potential sweeping rate is  $10 \text{ mV s}^{-1}$ . The electrolyte is 0.1 M KOH solution saturated by  $\text{O}_2$ .