

Electronic Supplementary Information (ESI)

## Oxygen reduction activity of Pd-Mn<sub>3</sub>O<sub>4</sub> nanoparticles and performance enhancement by voltammetrically accelerated degradation

*Chang Hyuck Choi, Sung Hyeon Park, and Seong Ihl Woo\**

*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, 305-701, Republic of Korea*

\*E-mail: siwoo@kaist.ac.kr

### **Supporting information table of contents:**

**Fig. S1** Atomic ratio between Pd and Mn at the surface of the prepared nanoparticles calculated from XPS analysis.

**Fig. S2** XPS-Pd<sub>3d</sub> (left) and -Mn<sub>2p</sub> (right) results of the prepared nanoparticles; (a) Pd, (b) Pd-Mn<sub>3</sub>O<sub>4</sub>-140 and (c) Pd-Mn<sub>3</sub>O<sub>4</sub>-180. The peaks in Pd<sub>3d</sub> are assigned to Pd<sup>0</sup>, PdO and PdO<sub>2</sub>.

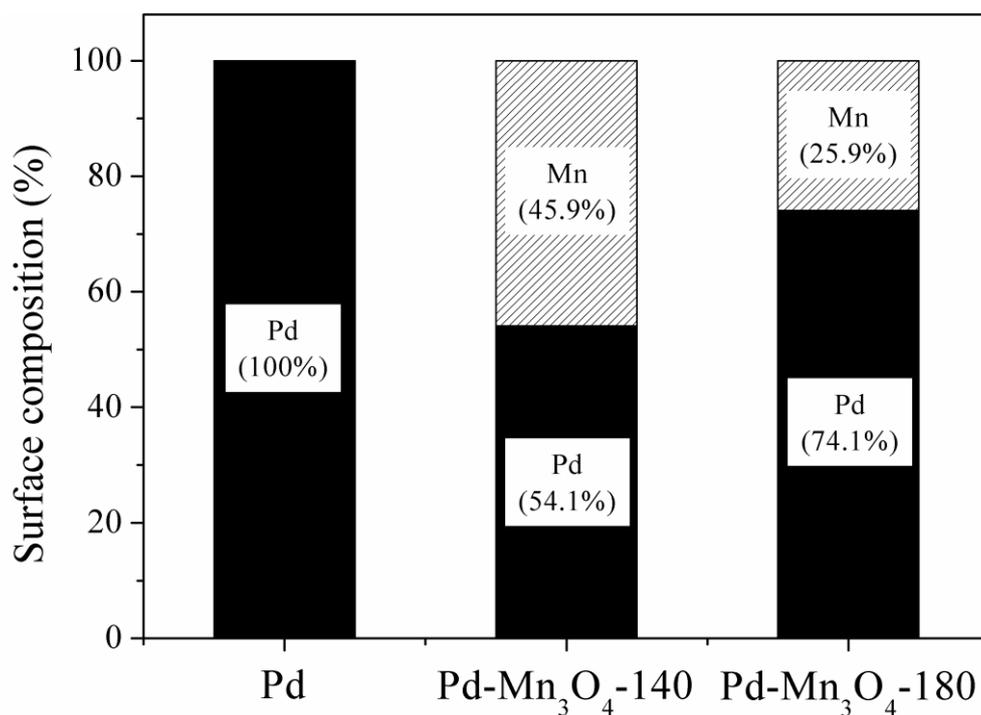
**Fig. S3** Oxygen reduction reactivities of prepared catalysts in the (i) absence and (ii) presence of methanol in oxygen saturated 1M HClO<sub>4</sub> for (a) Pd/C, (b) Pd-Mn<sub>3</sub>O<sub>4</sub>-140/C, (c) Pd-Mn<sub>3</sub>O<sub>4</sub>-180/C and (d) Pt/C.

**Fig. S4** Comparison of ADT results at (a) the 1<sup>st</sup> cycle and (b) the 100<sup>th</sup> cycles for the prepared catalysts; (I) Pd/C, (II) Pd-Mn<sub>3</sub>O<sub>4</sub>-140/C and (III) Pd-Mn<sub>3</sub>O<sub>4</sub>-180/C. The graph inserted in the right-hand corner in each Fig. shows the magnified results from 0.35 to 0.65 V (vs Ag/AgCl).

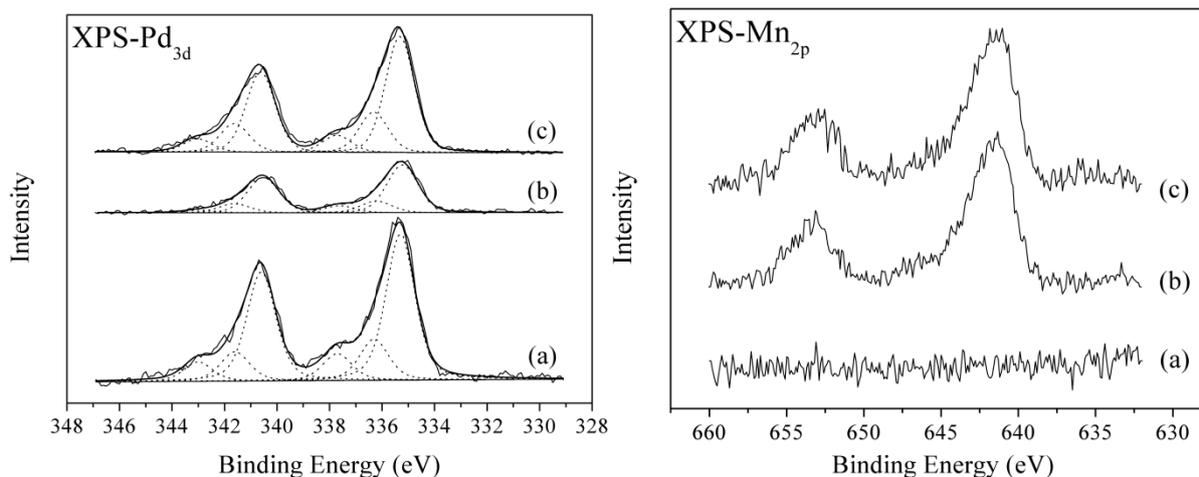
**Fig. S5** ADT results at the 1<sup>st</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycles of (a) Pd/C, (b) Pd-Mn<sub>3</sub>O<sub>4</sub>-140/C and (c) Pd-Mn<sub>3</sub>O<sub>4</sub>-180/C. The graph inserted in the right-hand corner in each Fig. shows the magnified results from 0.35 to 0.65 V (vs Ag/AgCl).

**Fig. S6** Schematic ADT-modification process on the surface of Pd-Mn<sub>3</sub>O<sub>4</sub>-140 nanoparticles. Red and yellow spheres indicate the Mn<sub>3</sub>O<sub>4</sub> and Pd, respectively, which construct Pd-Mn<sub>3</sub>O<sub>4</sub>-140 nanoparticles.

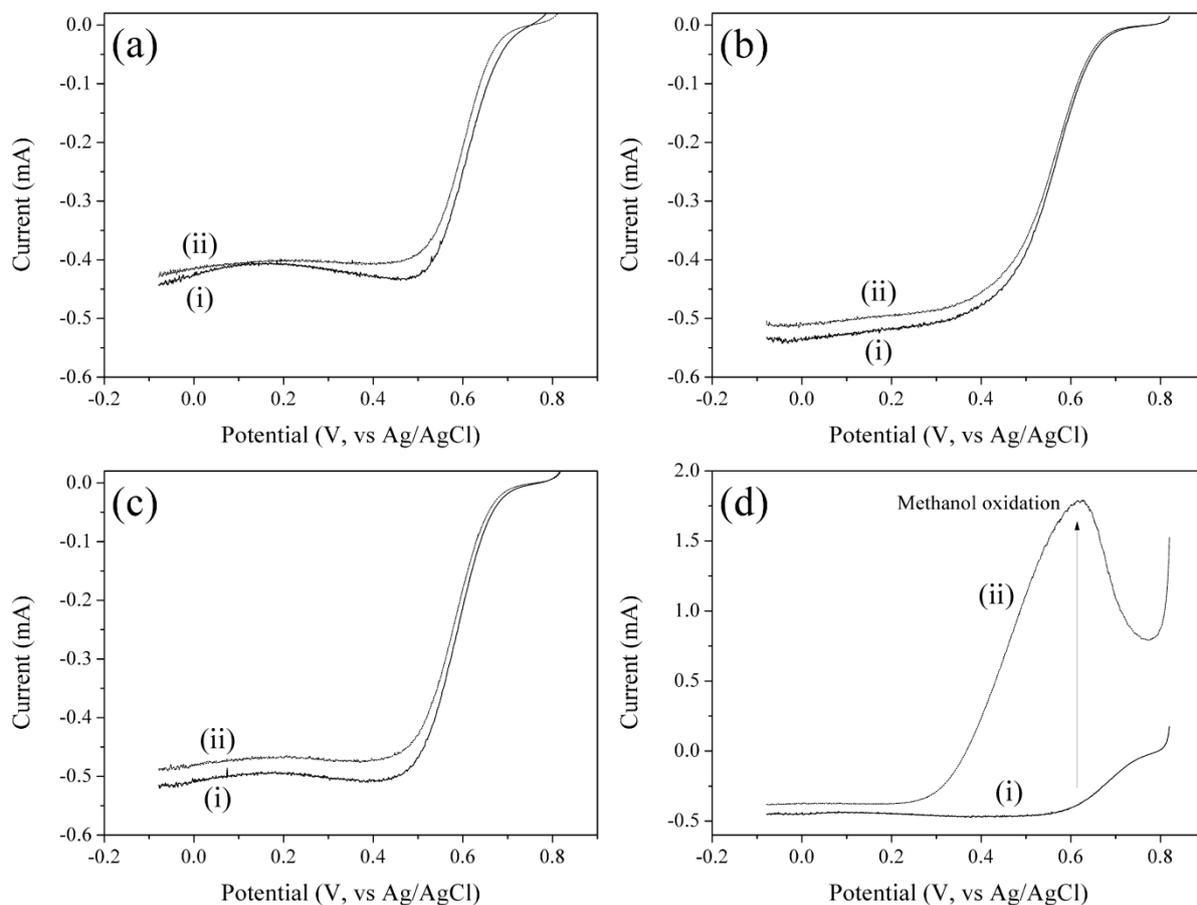
**Fig. S1** Atomic ratio between Pd and Mn at the surface of the prepared nanoparticles calculated from XPS analysis.



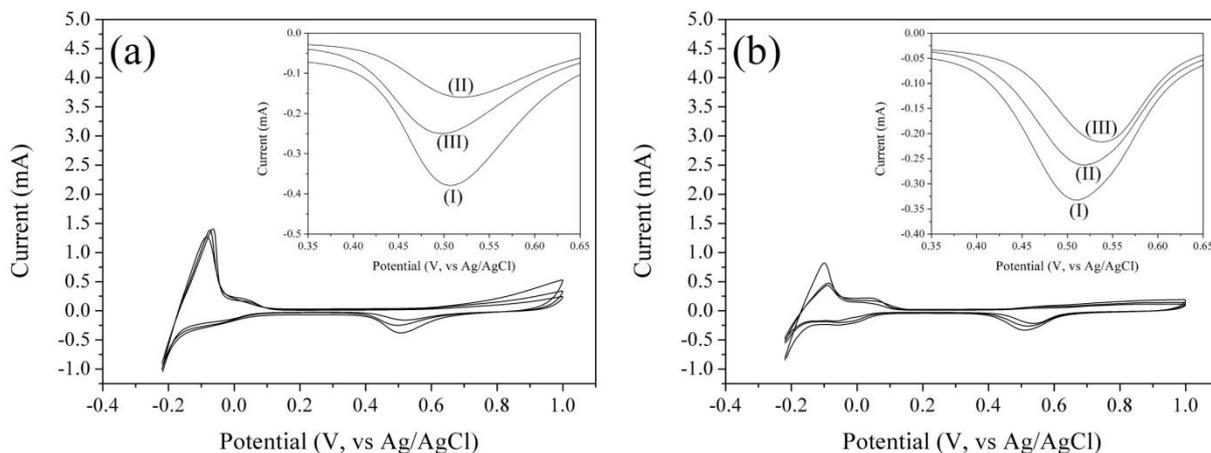
**Fig. S2** XPS-Pd<sub>3d</sub> (left) and -Mn<sub>2p</sub> (right) results of the prepared nanoparticles; (a) Pd, (b) Pd-Mn<sub>3</sub>O<sub>4</sub>-140 and (c) Pd-Mn<sub>3</sub>O<sub>4</sub>-180. The peaks in Pd<sub>3d</sub> are assigned to Pd<sup>0</sup>, PdO and PdO<sub>2</sub>.



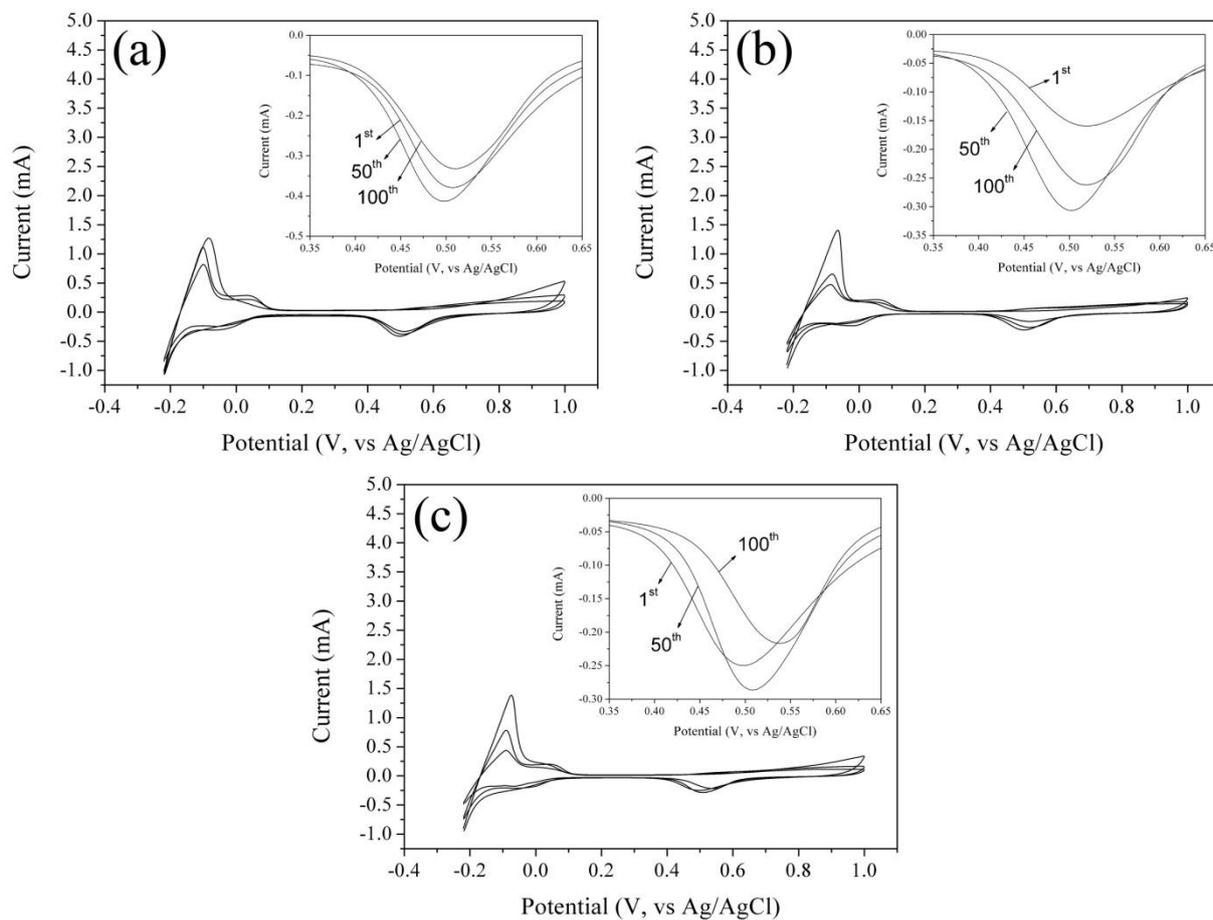
**Fig. S3** Oxygen reduction reactivities of prepared catalysts in the (i) absence and (ii) presence of methanol in oxygen saturated 1M HClO<sub>4</sub> for (a) Pd/C, (b) Pd-Mn<sub>3</sub>O<sub>4</sub>-140/C, (c) Pd-Mn<sub>3</sub>O<sub>4</sub>-180/C and (d) Pt/C.



**Fig. S4** Comparison of ADT results at (a) the 1<sup>st</sup> cycle and (b) the 100<sup>th</sup> cycles for the prepared catalysts; (I) Pd/C, (II) Pd-Mn<sub>3</sub>O<sub>4</sub>-140/C and (III) Pd-Mn<sub>3</sub>O<sub>4</sub>-180/C. The graph inserted in the right-hand corner in each Fig. shows the magnified results from 0.35 to 0.65 V (vs Ag/AgCl).



**Fig. S5** ADT results at the 1<sup>st</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycles of (a) Pd/C, (b) Pd-Mn<sub>3</sub>O<sub>4</sub>-140/C and (c) Pd-Mn<sub>3</sub>O<sub>4</sub>-180/C. The graph inserted in the right-hand corner in each Fig. shows the magnified results from 0.35 to 0.65 V (vs Ag/AgCl).



**Fig. S6** Schematic ADT-modification process on the surface of Pd-Mn<sub>3</sub>O<sub>4</sub>-140 nanoparticles. Red and yellow spheres indicate Mn<sub>3</sub>O<sub>4</sub> and Pd atoms, respectively, which construct Pd-Mn<sub>3</sub>O<sub>4</sub>-140 nanoparticles.

