Electronic Supplementary Information

Dual-site Electrocatalytic Nitrate Reduction to Ammonia on Oxygen Vacancy-Enriched and Pd-Decorated MnO$_2$ Nanosheets

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S1. Characterizations

X-ray diffraction patterns were recorded on an X-ray diffractometer (XRD, Model D/max RA, Rigaku Co., Japan) with the Cu $K\alpha$ radiation. The morphology, size, elemental mapping and the crystal lattice fringe of the catalyst were investigated by the transmission electron microscopy (TEM, JEM-2010, JEOL, Japan) and scanning electron microscopy (SEM, Hitachi S-570, Hitachi, Japan) that equipped with an energy dispersive X-ray spectroscopy (EDS). The X-ray photoelectron spectroscopy (XPS) patterns were obtained on the ESCALAB 250 spectrometer (Thermo Fisher Scientific, UK). The NRR tests were controlled using the PARSTAT 3000 electrochemical workstation (Princeton CO., USA). The Pd mass loading on electrode was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICP2060t, Tianrui, China). The presence of oxygen vacancy in electrode was determined with the combined analyses of XPS and electron paramagnetic resonance (EPR, Bruker ESP 500, Germany). The concentrations of NO_3^--N, NO_2^--N and NH_3-N were analyzed by the gas-phase molecular absorption spectrometer (GMA 3370, Beiyu CO., China).
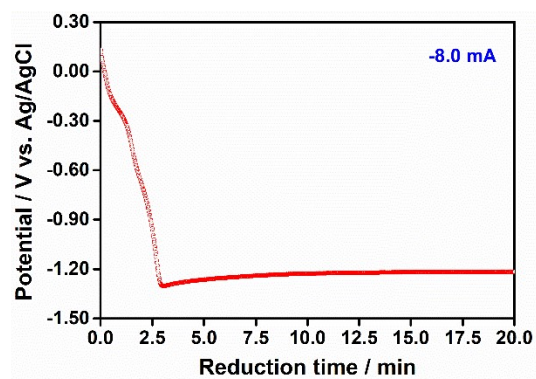
Fig. S1. Plotting of the working potential versus the reaction time during the generation of O_v on the MnO_2/Pd foam under a current of -8.0 mA.
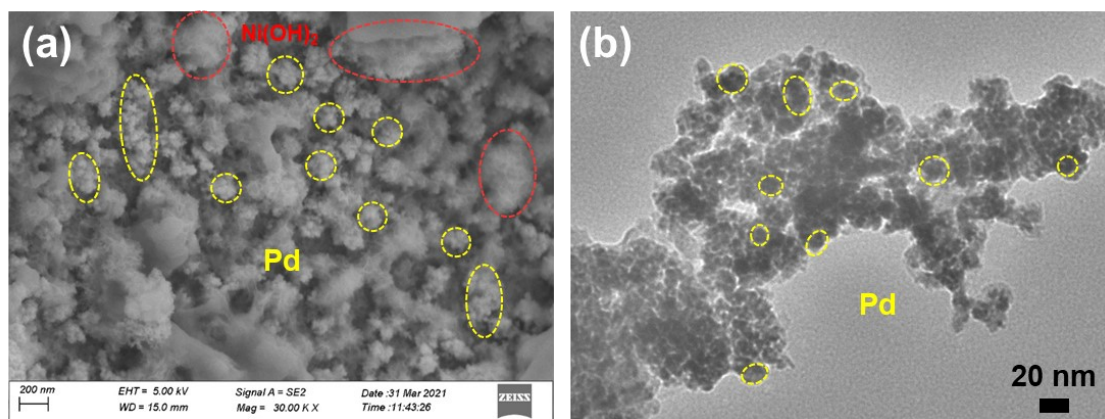
Fig. S2. Representative (a) SEM image of the Pd/foam and (b) TEM image of the particle that is scraped from the Pd/Ni foam.
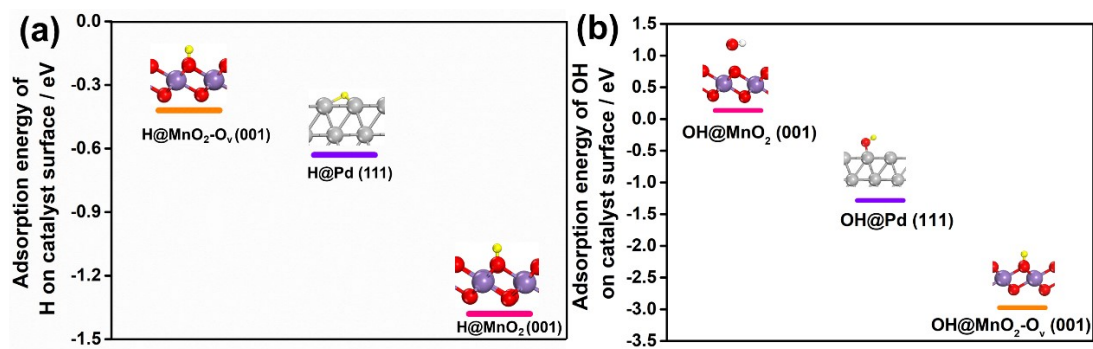
Fig. S3. The calculated adsorption energies of H and OH on MnO_2 (001), Pd (111) and MnO_2-O_v (001).

Table S1. The redox potential for the conversion

Number	Reaction	Redox potential / V vs. NHE
1	$MnO_2 + 4H^+ + e^- = Mn^{3+} + 2H_2O$	+0.95
2	$MnO_2 + 4H^+ + e^- = Mn^{2+} + 2H_2O$	+1.23
3	$Mn^{2+} + 2e^- = Mn^0$	-1.185