

Supplementary Information

Regulating Pyrolysis Process of Cation Intercalated MnO₂ Nanomaterials for and Electrocatalytic Urea Oxidation Performance

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Experimental Section

Materials characterizations:

The thermogravimetric analysis (TGA) were performed using a Pyris Diamond TG/DTA under a constant flow of dry nitrogen gas at a heating rate of 5 °C·min⁻¹. The thermogravimetric analysis was performed on a Rigaku Thermo Mass Photo (TG-MS) with a Skimmer type mass spectrometer (MS/EI). The measurements were conducted from 20-800 °C with 5 K/min gradient. Powder X-ray diffraction (PXRD) spectra were recorded on either a D8 Advance (Bruker) or a Rigaku D/max-III A diffractometer (Cu K α , λ = 1.54056 Å) at 293 K. The morphologies were investigated using a JSM-IT500 (Japan) Scanning Electron Microscopy (SEM).

X-ray Absorption Spectroscopy (XAS) test.

The Mn L-edge XANES spectra were measured at the beamline BL12B of National Synchrotron Radiation Laboratory (NSRL, Hefei) using the linearly polarized X-ray beam in the total electron yield (TEY) mode by collecting the sample drain current under a vacuum better than 10⁻⁷ Pa. The beam from the bending magnet was monochromatized utilizing a varied line-spacing plane grating and refocused by a toroidal mirror. The energy range is 100–1000 eV with an energy resolution of ca. 0.2 eV.

Synthesis of bulk 2D MnO₂

In a typical experiment, 3 mmol MnCl₂•4H₂O was added into 10 mL H₂O. After vigorous stirring for 20 min, the MnCl₂•4H₂O was totally dissolved becoming a homogenous solution, called “solution A”. Then, 4.0 g (NH₄)₂S₂O₈ was added into 10 mL H₂O, after vigorous stirring for 20 min, 4.375 g TMAOH (25 % wt) was added into the mixed solution followed by another 20 min stirring and adding amount of water to 20 mL, called “solution B”. Then “the solution B” was added into “solution A” slowly in 10 min under vigorous stirring. The dark brown MnO₂ sample was obtained after vigorously stirring overnight in the ambient atmosphere at room-temperature. After this mild oxidation reaction, the precipitate was washed with methanol and water three times and centrifuged at 6000 rpm for 3 min, then the precipitate was dried in a vacuum oven at 60°C.

Synthesis of colloidal MnO₂

The MnO₂ nanosheets were synthesized in a reported method. Typically, 20 mL of a mixed aqueous solution of 0.6 M TMAOH and 3 wt % H₂O₂ was added to 10 mL of 0.3 M MnCl₂•4H₂O aqueous solution within 15 s. The solution became dark brown immediately as the mixed aqueous solution added,

showing the evidence that Mn^{2+} was oxidized to Mn^{4+} . This whole mixed aqueous solution was vigorously stirred overnight in the ambient atmosphere at room temperature. After this mild oxidation process, the precipitate was washed with water and methanol and centrifuged in a very low speed of $2000 \text{ r}\cdot\text{min}^{-1}$ for 20 mins, after which the precipitate was dried in a vacuum oven at $60 \text{ }^\circ\text{C}$.

Synthesis of 1D- MnO_2

The 1D MnO_2 was synthesized by the hydrothermal method. In a typical synthesis, 2 mmol KMnO_4 and 2 mmol NH_4F were added to 80 ml of distilled water and magnetically stirred at room temperature for 20 min. The sample was then placed into a 100 ml autoclave and heated at $160 \text{ }^\circ\text{C}$ for 24 h. After the sample was washed and dried, a brownish-black powder was obtained.

Synthesis of treated MnO_2 with different pyrolysis condition.

The treated MnO_2 was obtained from pyrolysis the aforementioned three types of MnO_2 by TG-MS with EI source. The measurements were conducted from room temperature to target temperature with $10 \text{ K}\cdot\text{min}^{-1}$ gradient. The samples finally cooled down to room temperature. In our case, the pyrolysis temperatures of partially treated MnO_2 and totally treated MnO_2 are $220 \text{ }^\circ\text{C}$ and $260 \text{ }^\circ\text{C}$, respectively. The pyrolysis temperature of H- MnO_2 are 190 , 220 and $260 \text{ }^\circ\text{C}$, respectively.

Thermogravimetric Analysis Combined with Mass Spectrometry (TG-MS)

The thermogravimetric analysis was performed on a Rigaku Thermo Mass Photo (TG-MS) with a Skimmer type mass spectrometer (MS/EI). The measurements were conducted from 30 - $800 \text{ }^\circ\text{C}$ with $5 \text{ K}\cdot\text{min}^{-1}$ gradient, after which the samples were cooled down to room temperature. The weight of initial samples was about 3.0 mg , and the pyrolysis process was conducted under a helium gas flow of $300 \text{ mL}\cdot\text{min}^{-1}$.

Electrochemical tests.

The UOR performance was tested in a three-electrode system by CV test at scan rates of 5 - $100 \text{ mV}\cdot\text{s}^{-1}$ at an electrochemical station (CHI 760E). An Hg/HgO (saturated KCl solution) electrode was used as reference electrode, while the counter electrode was a graphite rod electrode. The as-obtained MnO_2/NF was directly used as working electrode for electrochemical test in the solution of $1 \text{ M KOH} + 0.33 \text{ M urea}$. The working electrodes underwent active process using CV tests several times until stabilization before data collection. Electrochemical impedance spectroscopy (EIS) measurements of the catalysts were performed at a potential of 1.417 V vs RHE by using an AC voltage with 5 mV amplitude in a frequency range from 10 kHz to 100 mHz .

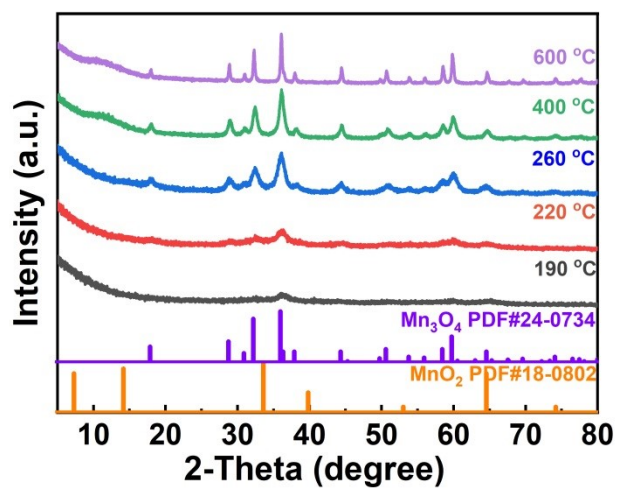


Figure S1 XRD patterns of H-MnO₂ at 190, 220, 260, 400, 600 °C.

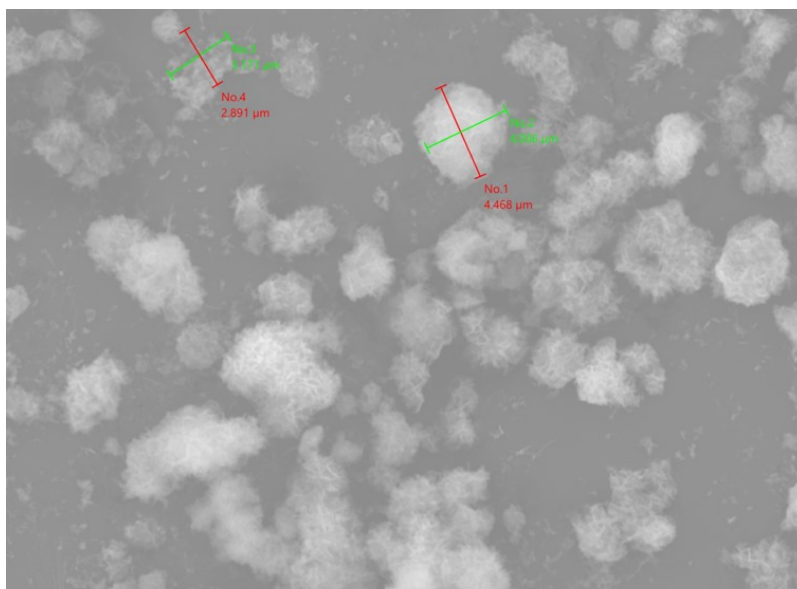


Figure S2 SEM images of 2D-MnO₂ particle size.

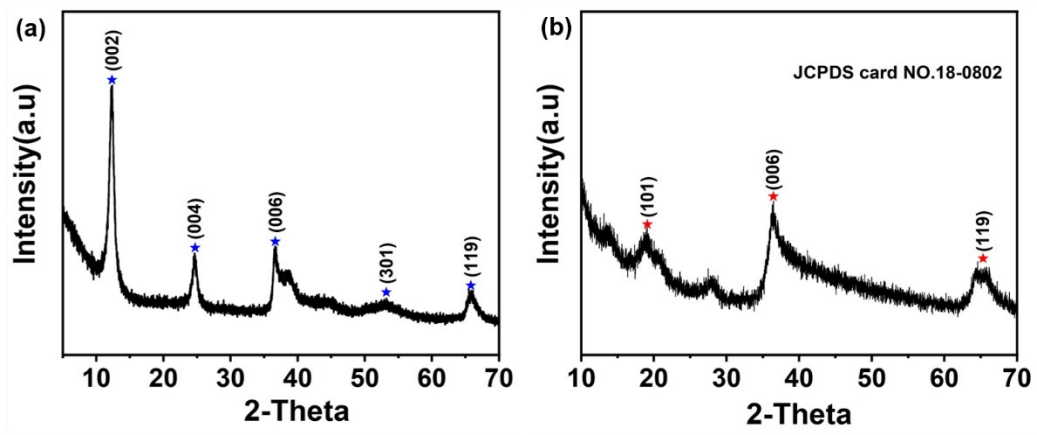


Figure S3 XRD pattern of the bulk 2D MnO₂ (a) and H-MnO₂ (b).

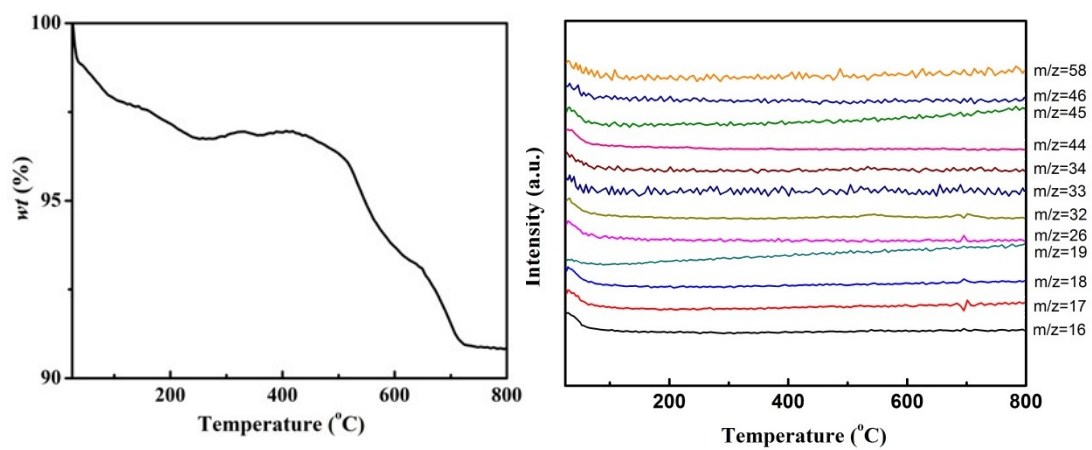


Figure S4 TG-MS analysis of 1D MnO₂ nanomaterials.

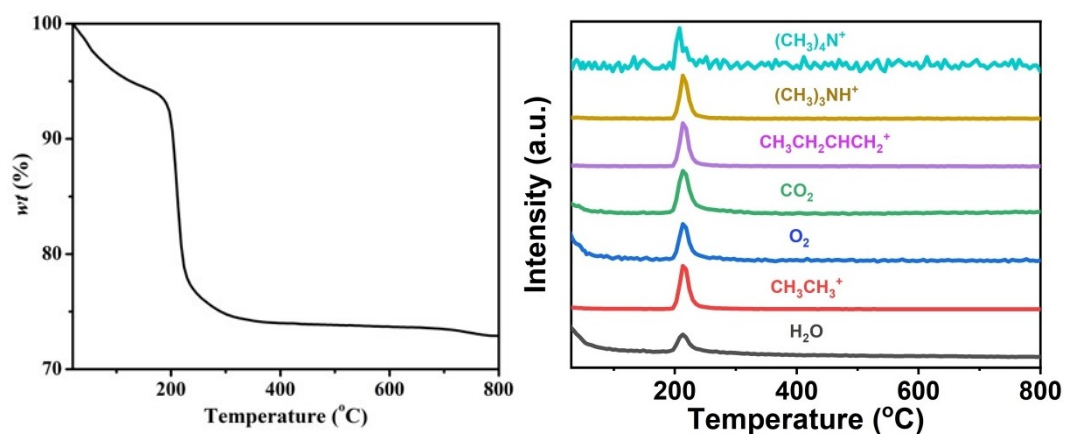


Figure S5 TG-MS analysis of H-MnO₂ nanomaterials.

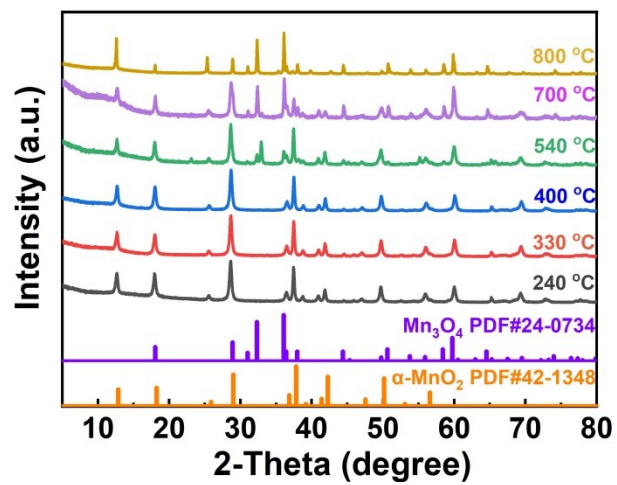


Figure S6 XRD patterns of 1D-MnO₂ at 240, 330, 400, 540, 700, 800 °C.

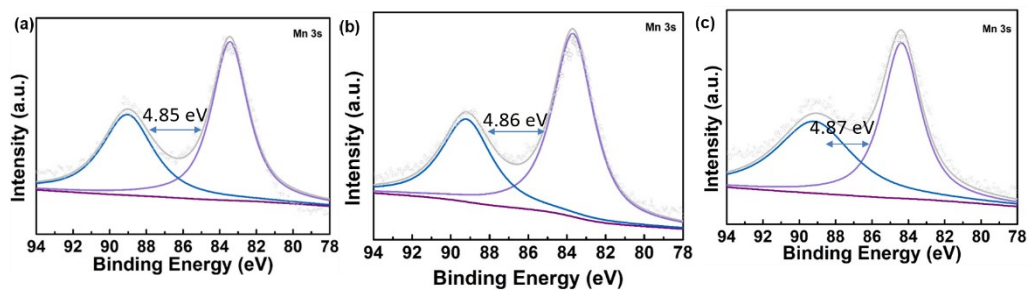


Figure S7 XPS spectra of Mn 3s peak of (a) H-MnO₂-260, (b) 1D-MnO₂-400, (c) 2D-MnO₂-550.

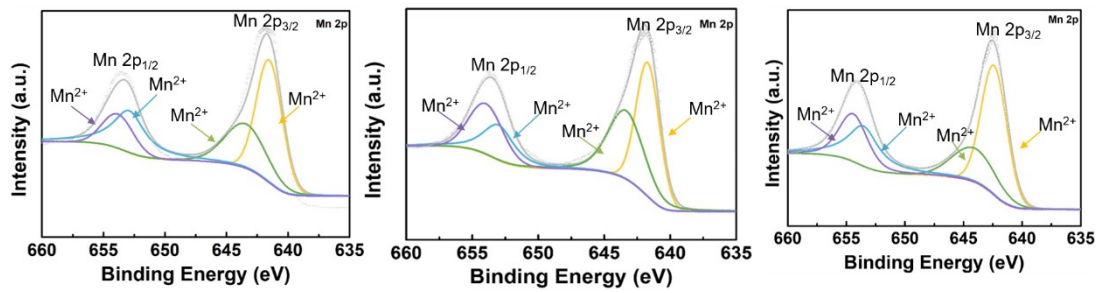


Figure S8 XPS spectra of Mn 3s peak of (a) H-MnO₂-260, (b) 1D-MnO₂-400, (c) 2D-MnO₂-550.

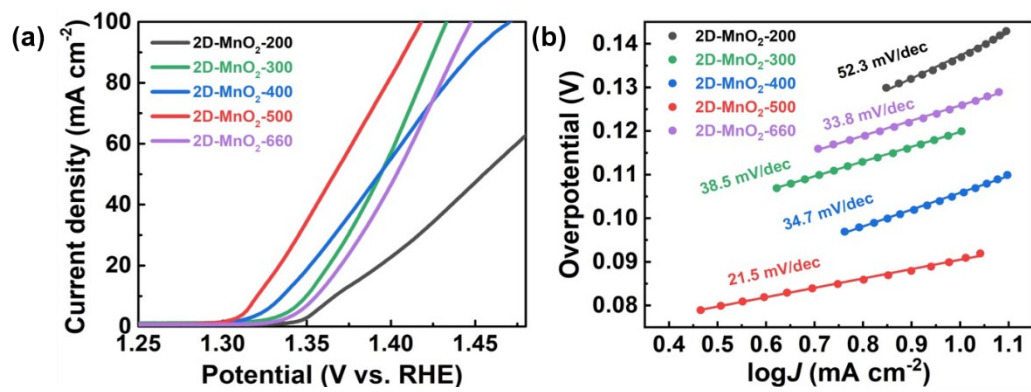


Figure S9 Linear sweep voltammetry (LSV) and Tafel plots of 2D-MnO₂

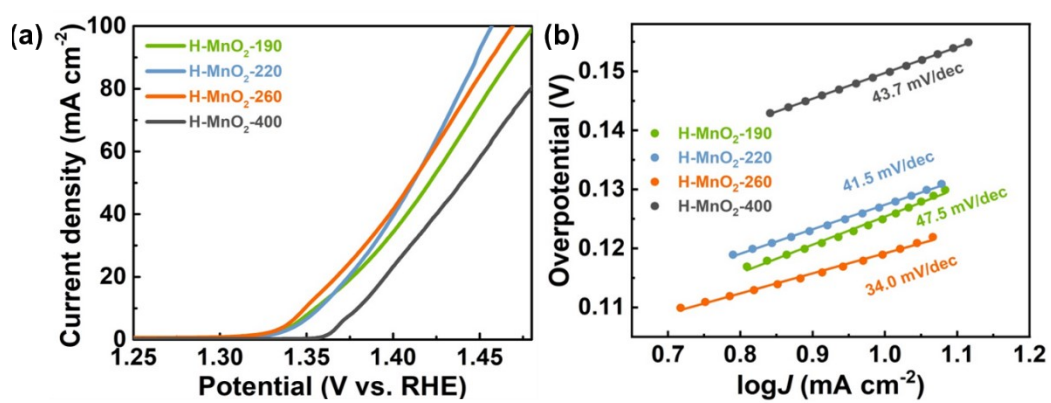


Figure S10 Linear sweep voltammetry (LSV) and Tafel plots of H-MnO₂.

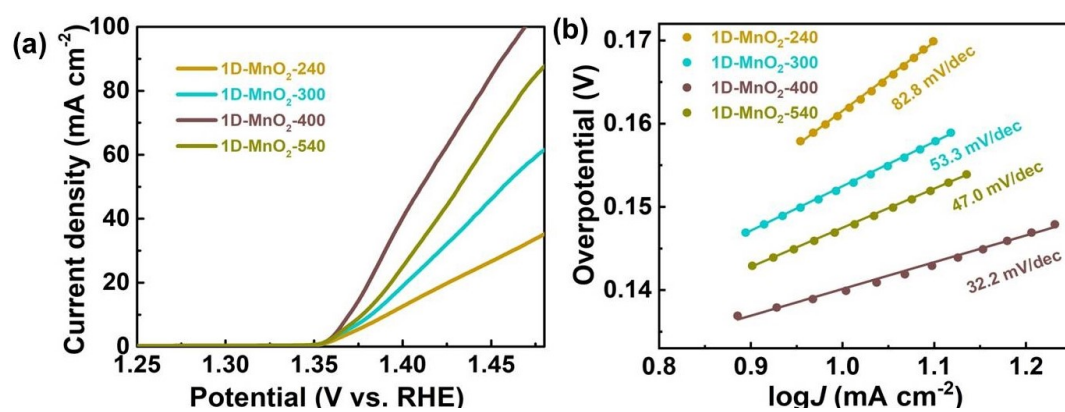


Figure S11 Linear sweep voltammetry (LSV) and Tafel plots of 1D-MnO₂.

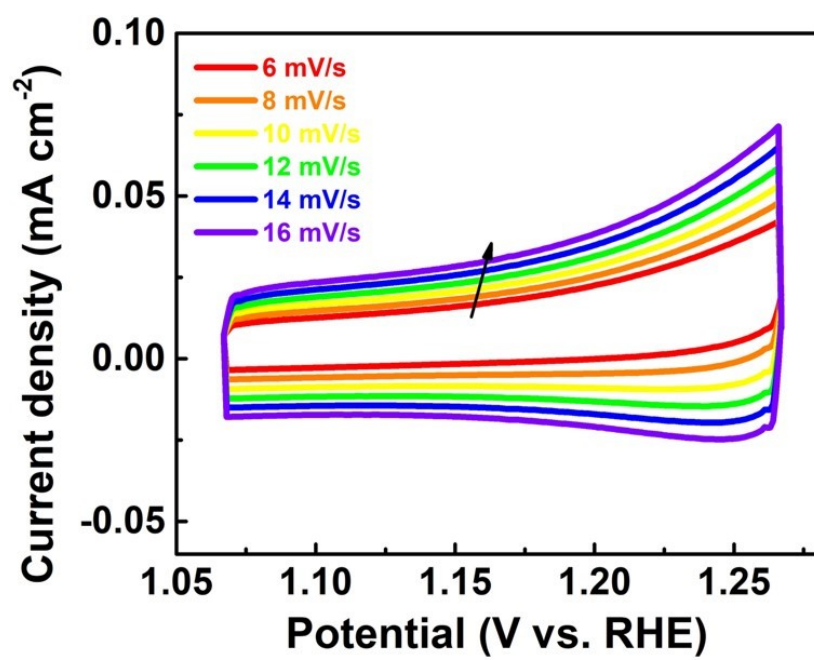


Figure S12 Blank cyclic voltammograms image.