Supporting Information (SI)

Electrocatalytic Oxidation of 5-Hydroxymethylfurfural by MnO_2 with Tunable Surface Oxidation States

Yongle Zhang,[#] Yingyi Tu,[#] Yunying Huo,Guang Pan, Qiao Zhang,* Zhiting Liu, Guangxing Yang , Feng Peng*

School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, China

[#] *These authors contributed equally to this work.*

*Corresponding author, Emails: zhangqiao@gzhu.edu.cn (Q. Zhang)

fpeng@gzhu.edu.cn (F. Peng)

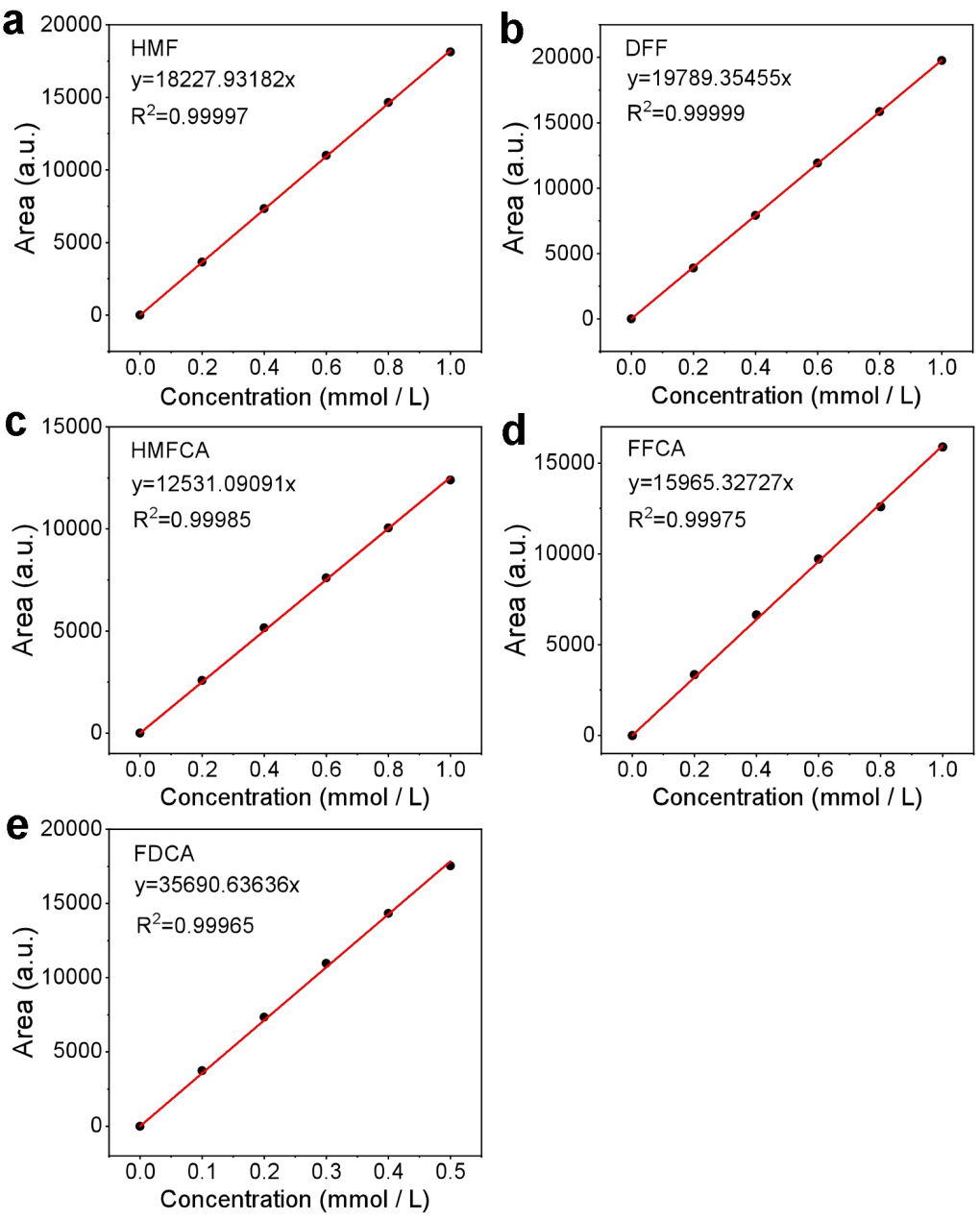

Fig. S1 High performance liquid chromatography (HPLC) calibration curves after electrolysis.5-hydroxymethylfurfural (HMF) calibration curve (a), 2,5-diformylfuran (DFF) calibration curve (b), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) calibration curve (c), 5-formyl-2-furan carboxylic acid (FFCA) calibration curve (d), 2,5-furandicarboxylic acid (FDCA) calibration curve (e)

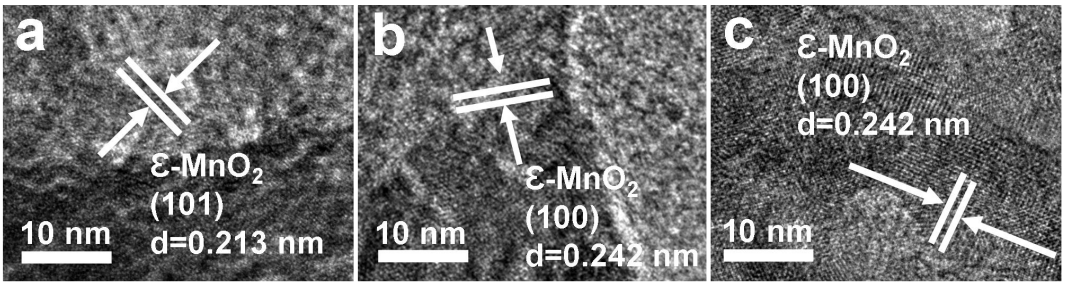

Fig. S2 HRTEM images of ε-MnO_2, ε-MnO_2/b and ε-MnO_2/bp catalysts.

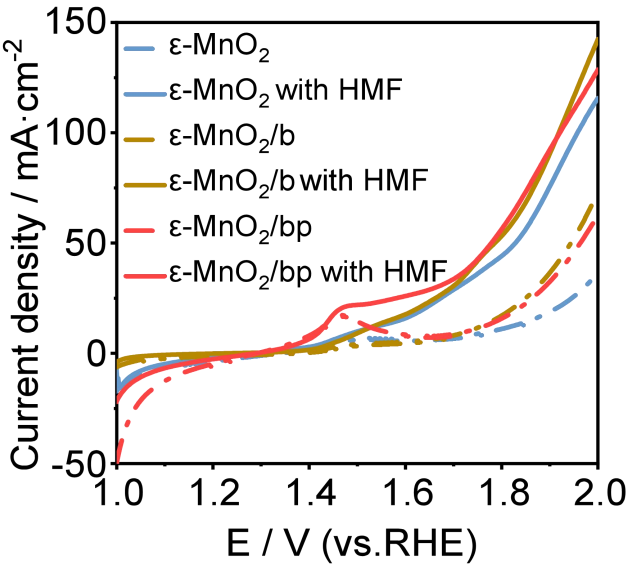

Fig. S3 Linear sweep voltammetry (LSV) curves of ε-MnO_2, ε-MnO_2/b and ε-MnO_2/bp catalysts in 1M KOH with and without HMF (50 mM).

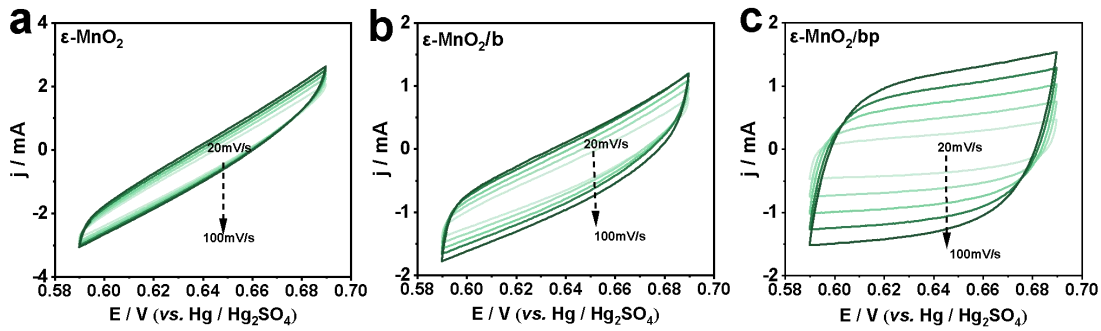

Fig. S4 Cyclic Voltammetry (CV) curves of ε-MnO_2, ε-MnO_2/b and ε-MnO_2/bp catalysts.

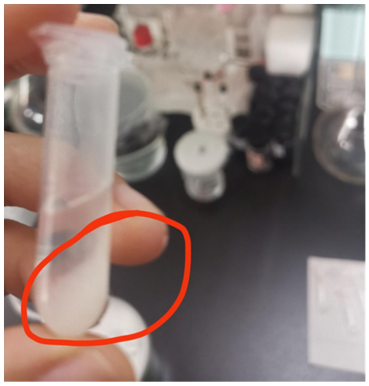

Fig. S5 The products precipitated from 60 ℃ to room temperature under acidic conditions.

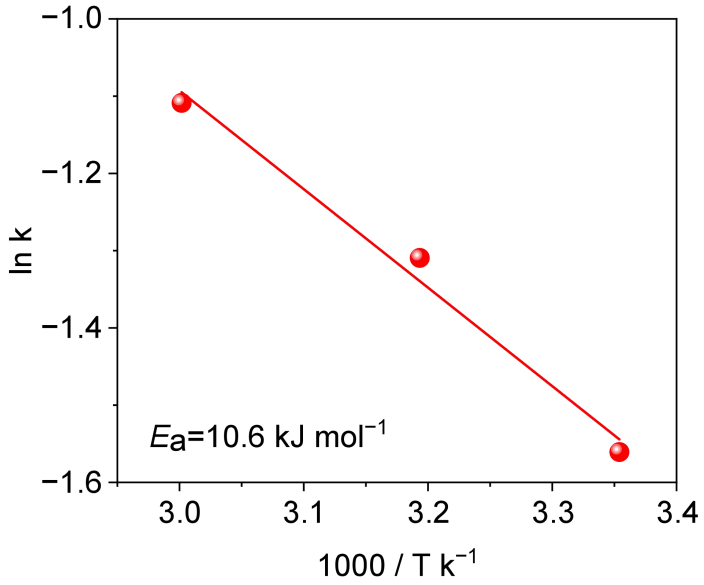

Fig. S6 The Arrhenius curves of HMF electrochemical oxidation corresponding the reaction rate constants at different temperatures at different temperature.

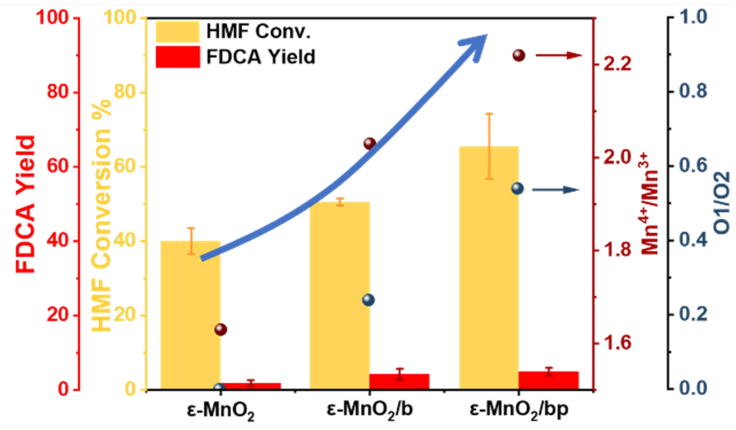

Fig. S7 Comparison diagram of ionic effects and activities of ε-MnO_2, ε-MnO_2/b and ε-MnO_2/bp catalysts.

Table S1. Mn 2p, O 1s binding energy and relative strength of ε-MnO_2, ε-MnO_2/b and ε-MnO_2/bp catalysts.

Catalysts	Binding energy (eV) Mn $2p_{1/2}$		Binding energy(eV) Mn $2p_{3/2}$		Mn^{4+}/ Mn^{3+}	Binding energy (eV)		O1/O2	AOS
	Mn^{4+}	Mn^{3+}	Mn^{4+}	Mn^{3+}		Lattice oxygen (O1)	Adsorbed oxygen (O2)		
ε-MnO_2	655.06	653.75	643.38	642.2	1.63	0	532.4	0	1.97
ε-MnO_2/b	654.47	653.41	643.02	641.89	2.03	529.88	532.11	0.24	2.65
ε-MnO_2/bp	654.55	653.66	643.1	642.25	2.23	530.29	532.12	0.54	3.66

Table S2. Mn 2p, O 1s binding energy and relative intensity of ε-MnO_2/bp catalyst before and after reaction.

Catalysts	Binding energy(eV) Mn $2p_{1/2}$		Binding energy(eV) Mn $2p_{3/2}$		Mn^{4+}/ Mn^{3+}	Binding energy(eV)		O1/O2	AOS
	Mn^{4+}	Mn^{3+}	Mn^{4+}	Mn^{3+}		Lattice oxygen (O1)	Adsorbed oxygen (O2)		
ε-MnO_2/bp	654.55	653.66	643.1	642.25	2.23	530.29	532.12	0.54	3.66
ε-MnO_2/bp after	654.84	653.77	643.15	642.3	1.78	530.35	532.11	0.49	3.55