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# **Highly Active Methanol Oxidation Electrocatalyst based on 2D NiO Porous Nanosheets: A Combined Computational and Experimental Study**

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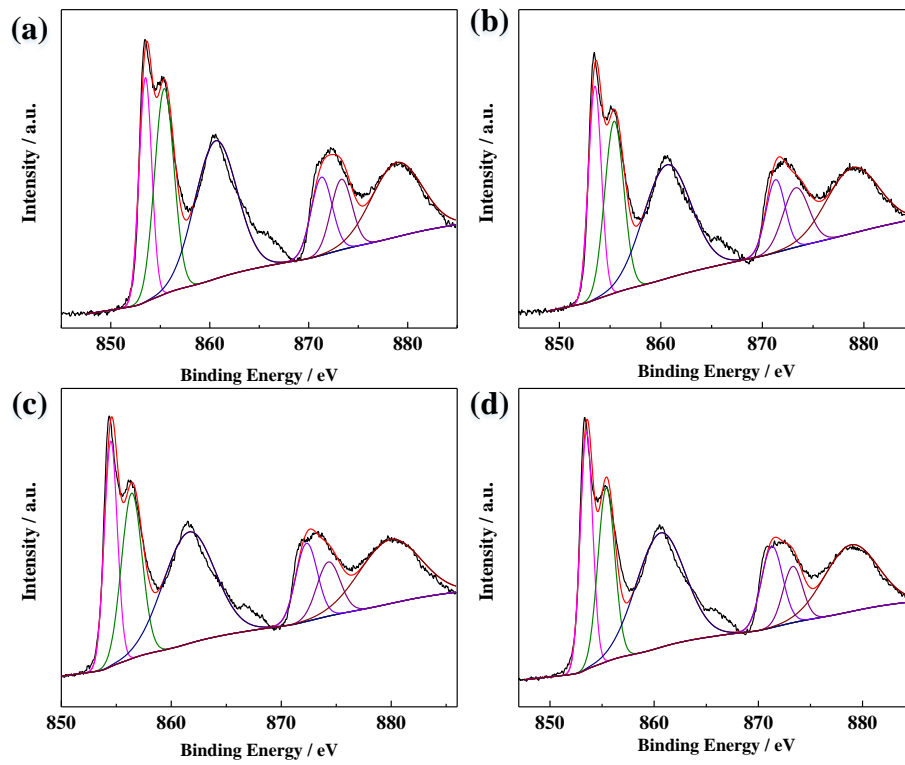


Fig.S1: Ni 2p XPS spectra of the 350-NiO (a), 450-NiO (b), 550-NiO (c) and 650-NiO.

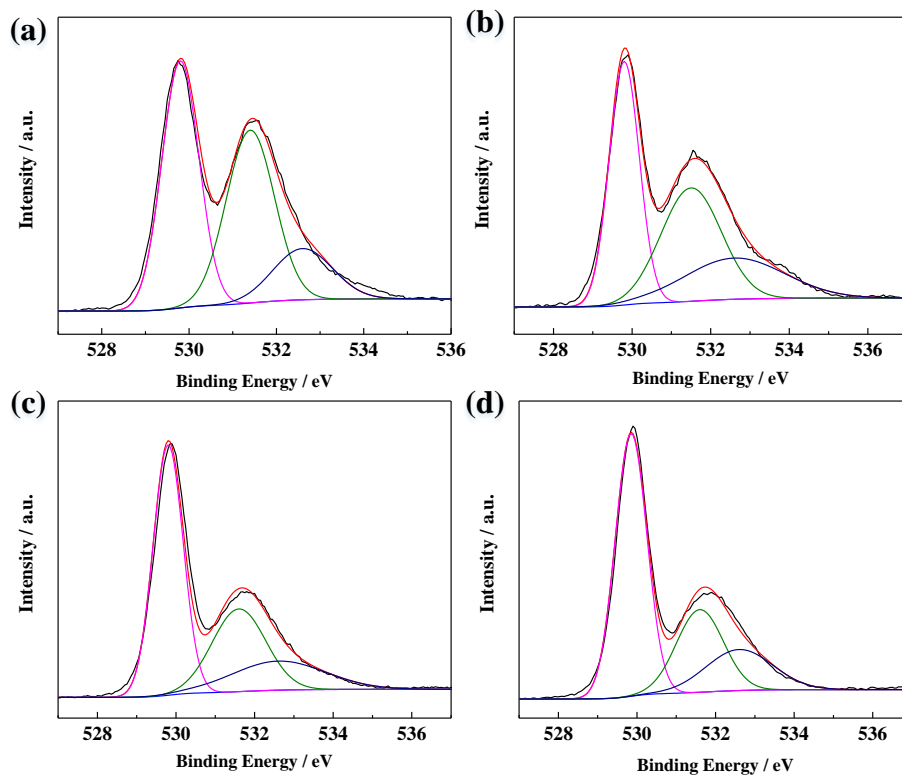


Fig.S2:O 1sXPS spectra of 350-NiO (a), 450-NiO (b), 550-NiO (c) and 650-NiO.

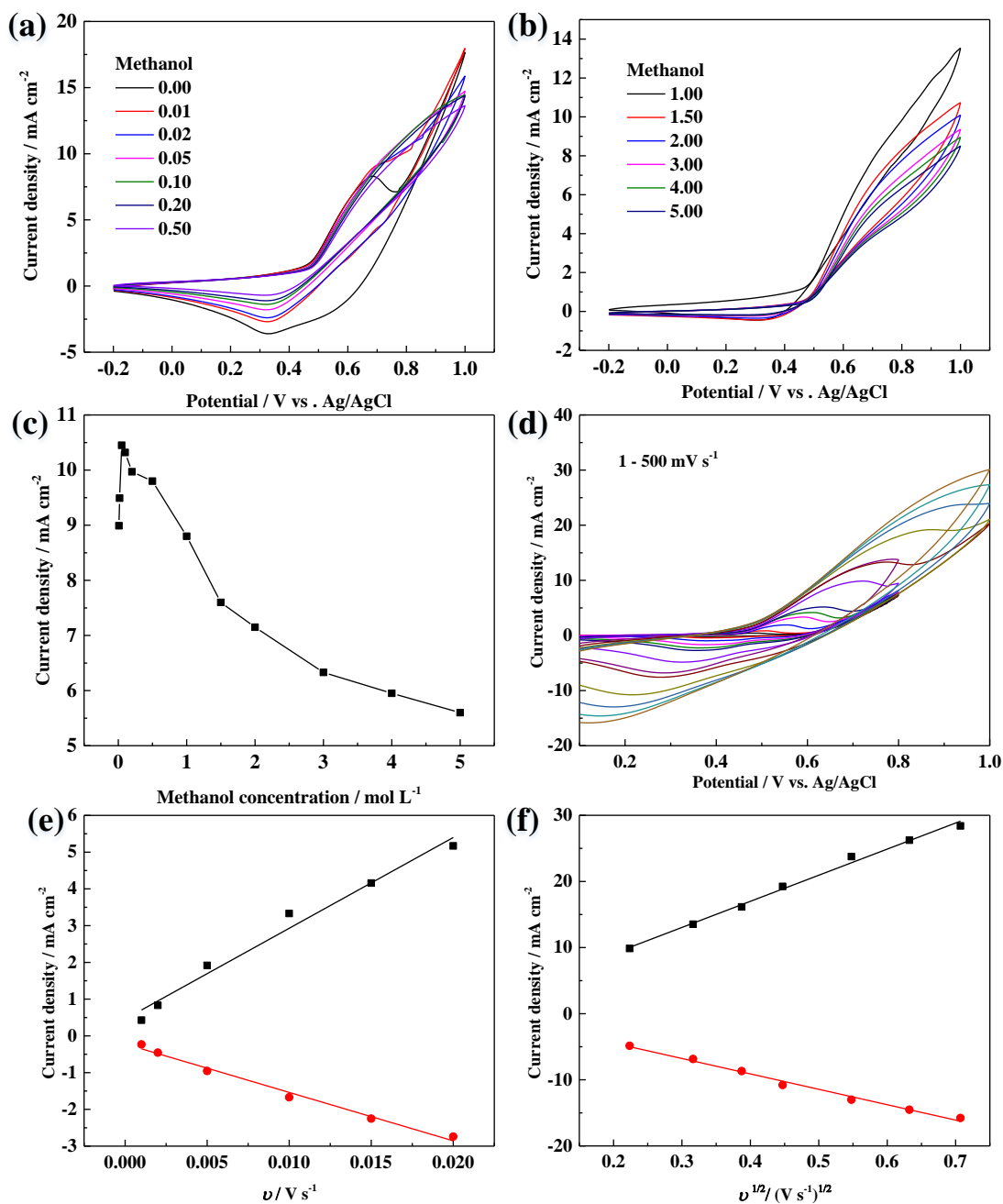


Fig.S3:350-NiO. (a) and (b) CV curves under different methanol concentration at 50 mV s<sup>-1</sup>, (c) comparison of oxidation peaks of methanol at different concentrations; (d) CV curves at different scan rates (1, 2, 5, 10, 15, 20, 50, 100, 150, 200, 300, 400, 500), (e) relationship of current densities of oxidation and reduction peaks at low sweep speed (1, 2, 5, 10, 15 and 20 mV s<sup>-1</sup>), (f) relationship of current densities of oxidation and reduction peaks at higher sweep speed (50, 100, 150, 200, 300, 400 and 500 mV s<sup>-1</sup>); under the 0.1 M KOH solution in the N<sub>2</sub>-saturated.

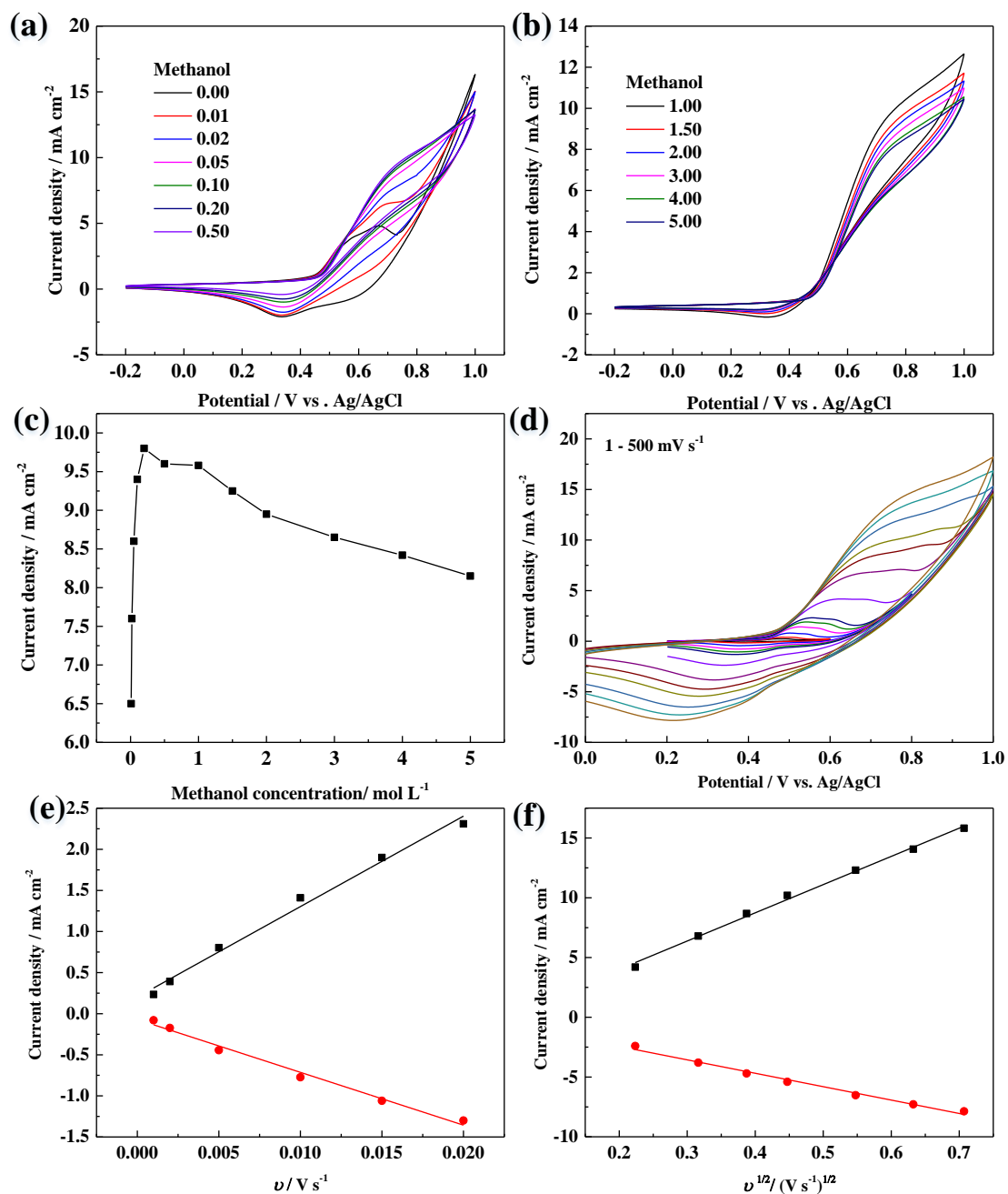


Fig.S4:450-NiO. (a) and (b) CV curves under different methanol concentration at  $50 \text{ mV s}^{-1}$ , (c) comparison of oxidation peaks of methanol at different concentrations; (d) CV curves at different scan rates (1, 2, 5, 10, 15, 20, 50, 100, 150, 200, 300, 400, 500), (e) relationship of current densities of oxidation and reduction peaks at low sweep speed (1, 2, 5, 10, 15 and 20  $\text{mV s}^{-1}$ ), (f) relationship of current densities of oxidation and reduction peaks at higher sweep speed (50, 100, 150, 200, 300, 400 and 500  $\text{mV s}^{-1}$ ); under the 0.1 M KOH solution in the  $\text{N}_2$ -saturated.

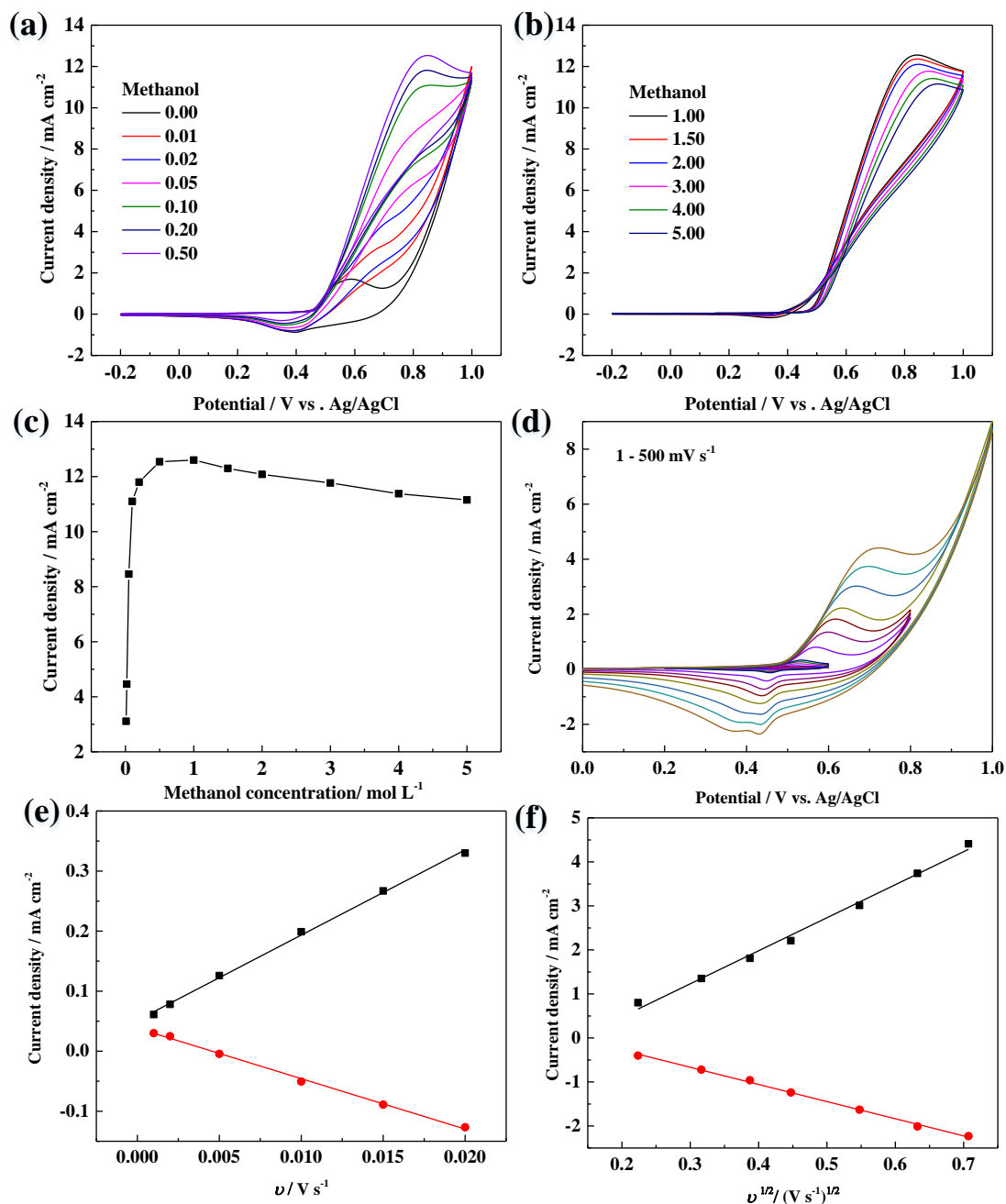


Fig.S5:550-NiO. (a) and (b) CV curves under different methanol concentration at 50 mV s<sup>-1</sup>, (c) comparison of oxidation peaks of methanol at different concentrations; (d) CV curves at different scan rates (1, 2, 5, 10, 15, 20, 50, 100, 150, 200, 300, 400, 500), (e) relationship of current densities of oxidation and reduction peaks at low sweep speed (1, 2, 5, 10, 15 and 20 mV s<sup>-1</sup>), (f) relationship of current densities of oxidation and reduction peaks at higher sweep speed (50, 100, 150, 200, 300, 400 and 500 mV s<sup>-1</sup>); under the 0.1 M KOH solution in the N<sub>2</sub>-saturated.

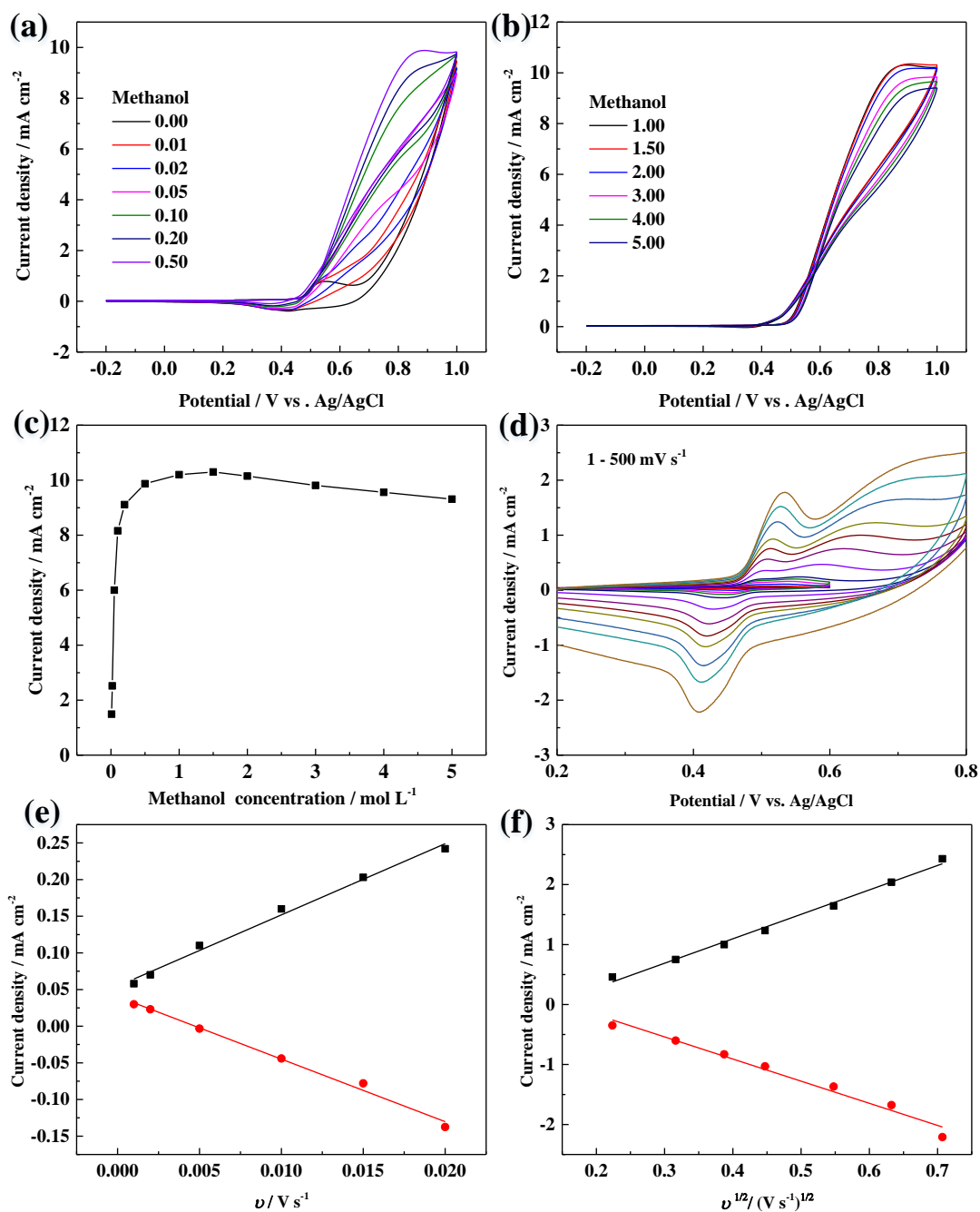


Fig.S6:650-NiO. (a) and (b) CV curves under different methanol concentration at  $50 \text{ mV s}^{-1}$ , (c) comparison of oxidation peaks of methanol at different concentrations; (d) CV curves at different scan rates (1, 2, 5, 10, 15, 20, 50, 100, 150, 200, 300, 400, 500), (e) relationship of current densities of oxidation and reduction peaks at low sweep speed (1, 2, 5, 10, 15 and 20  $\text{mV s}^{-1}$ ), (f) relationship of current densities of oxidation and reduction peaks at higher sweep speed (50, 100, 150, 200, 300, 400 and 500  $\text{mV s}^{-1}$ ); under the 0.1 M KOH solution in the  $\text{N}_2$ -saturated.



Table S1: Adsorption sites, configurations, energies, and structural parameters for intermediates involved in CH<sub>3</sub>OH oxidation on NiO(100).

species	site	configurations	E <sub>ads</sub> (eV)	d <sub>C-O</sub> (Å)	d <sub>Ni-O</sub> (Å)	d <sub>Ni-C</sub> (Å)
CH <sub>3</sub> OH	Ni-top	η <sup>1</sup> (O)	-2.14	1.447	2.011	
CH <sub>3</sub> O	Ni-top	η <sup>1</sup> (O)	-2.42	1.411	1.744	
CH <sub>2</sub> OH	Ni <sub>2</sub> -top	η <sup>2</sup> (C, O)	-2.25	1.456	2.019	1.937
CH <sub>2</sub> O	Ni <sub>2</sub> -top	η <sup>2</sup> (C, O)	-1.70	1.326	1.836	1.978
CHO	Ni <sub>2</sub> -top	η <sup>2</sup> (C, O)	-3.79	1.251	1.870	1.809
CO	Ni <sub>2</sub> -bridge	η <sup>1</sup> (C)	-4.20	1.176		1.867, 1.734
HCOOH	Ni <sub>2</sub> -top	η <sup>3</sup> (C, O, O)	-2.85	1.266, 1.402	1.889, 2.075	2.122
COOH	Ni <sub>2</sub> -top	η <sup>2</sup> (C, O)	-2.33	1.268, 1.334	1.908	1.851
HCOO	Ni <sub>2</sub> -top	η <sup>2</sup> (O, O)	-1.88	1.270, 1.275	1.869, 1.914	
CO <sub>2</sub>	Ni <sub>2</sub> -top	η <sup>2</sup> (C, O)	-2.18	1.277, 1.213	1.893	1.919
H <sub>2</sub> O	Ni-top	η <sup>1</sup> (O)	-1.20		2.015	
OH	Ni <sub>2</sub> -bridge	η <sup>1</sup> (O)	-4.54		1.934, 1.939	
H	O-top	η <sup>1</sup> (H)	-1.19			

Table S2: Reaction energies (ΔE), activation energy barriers (E<sub>a</sub>) for the elementary steps involved in the methanol oxidation on NiO(100)

Reactions	ΔE (eV)	E <sub>a</sub> (eV)
CH <sub>3</sub> OH → CH <sub>2</sub> OH + H	-0.05	0.86
CH <sub>3</sub> OH → CH <sub>3</sub> O + H	-0.27	0.54
CH <sub>3</sub> O → CH <sub>2</sub> O + H	-1.27	0.90
CH <sub>2</sub> O → CHO + H	-1.05	0.84
CHO → CO + H	-1.24	0.73
CHO + OH → HCOOH	+0.19	0.58
HCOOH → COOH + H	-0.79	0.72
COOH → CO <sub>2</sub> + 2H	-0.31	0.68
HCOOH → HCOO + H	-1.21	1.16
HCOO → CO <sub>2</sub> + 2H	+1.13	0.97