Supporting Information

Fabrication of Nanoscale Ni/NiO Heterostructures as Electrocatalyst for Efficient Methanol Oxidation

Juan Wang,[a] Detre Teschner, [b] Yuanying Yao, [a] Xing Huang,* [b] Marc Willinger, [b] Lidong Shao,* [a] and Robert Schlögl [b]

[a]Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, China. E-mail: lidong.shao@shiep.edu.cn

[b]Department of Inorganic Chemistry, Fritz-Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany.E-mail: xinghuang@fhi-berlin.mpg.de

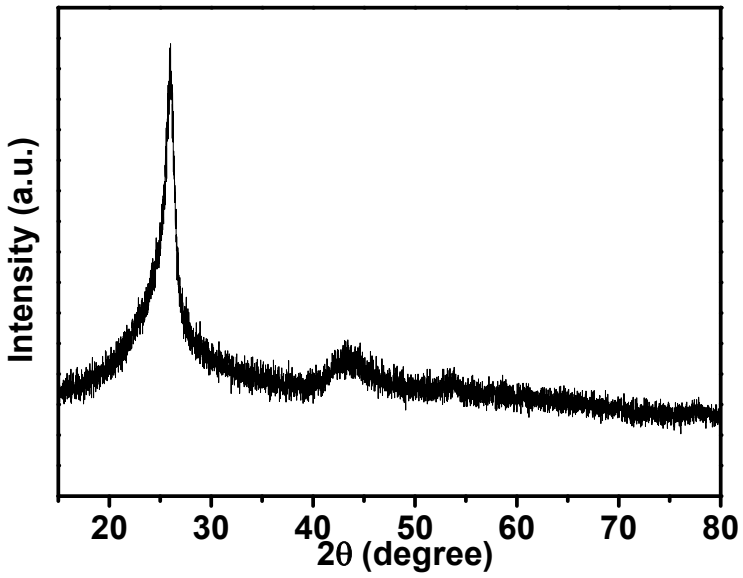
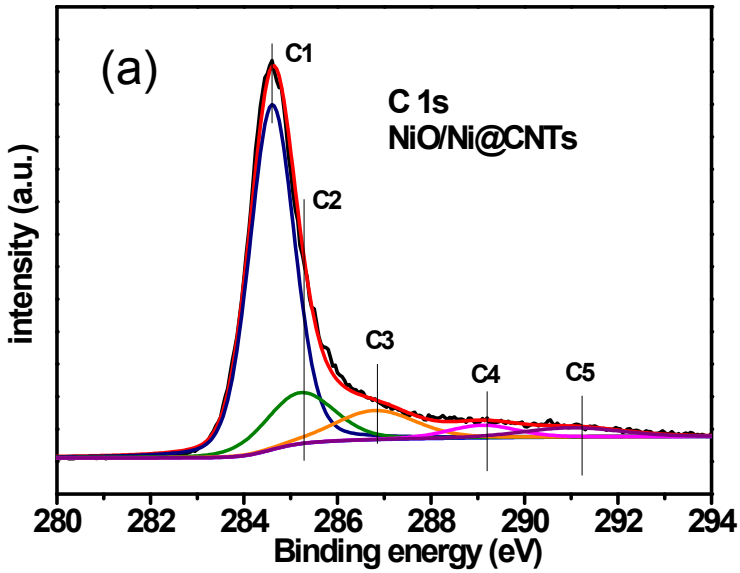
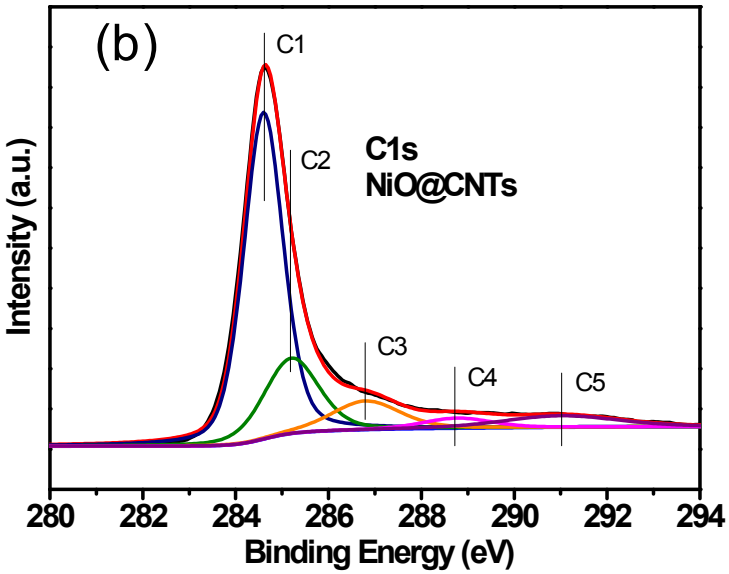


Figure S1. XRD pattern of OCNTs


(a)
C1
C2
C3
C4
C5
C 1s
NiO/Ni@CNTs
intensity (a.u.)
280
282
284
286
288
290
292
294
Binding energy (eV)


(b)
C1
C2
C3
C4
C5
C1s
NiO@CNTs
Intensity (a.u.)
280
282
284
286
288
290
292
294
Binding Energy (eV)

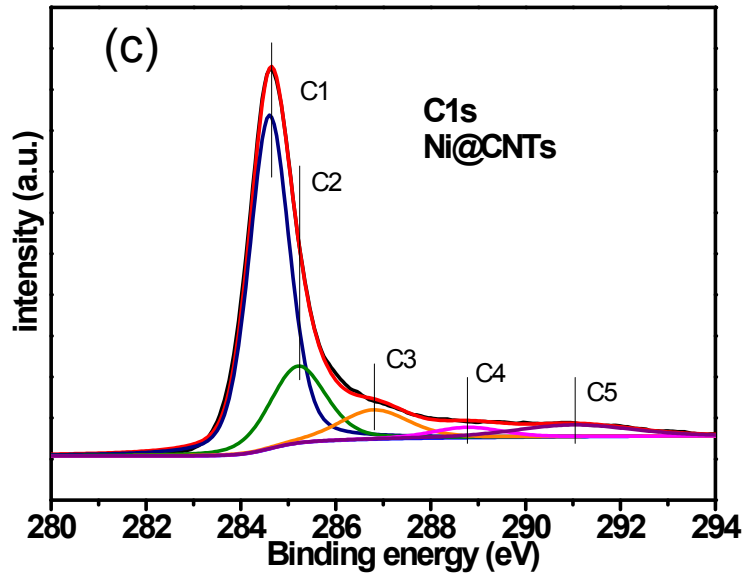
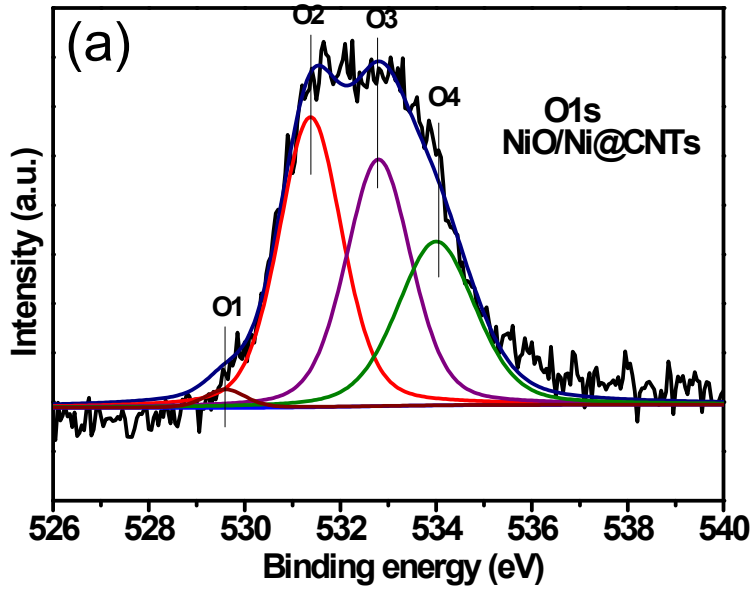


Figure S2. XPS C1s profile of NiO/Ni@CNTs (a), NiO@CNTs (b) and Ni@CNTs (c).



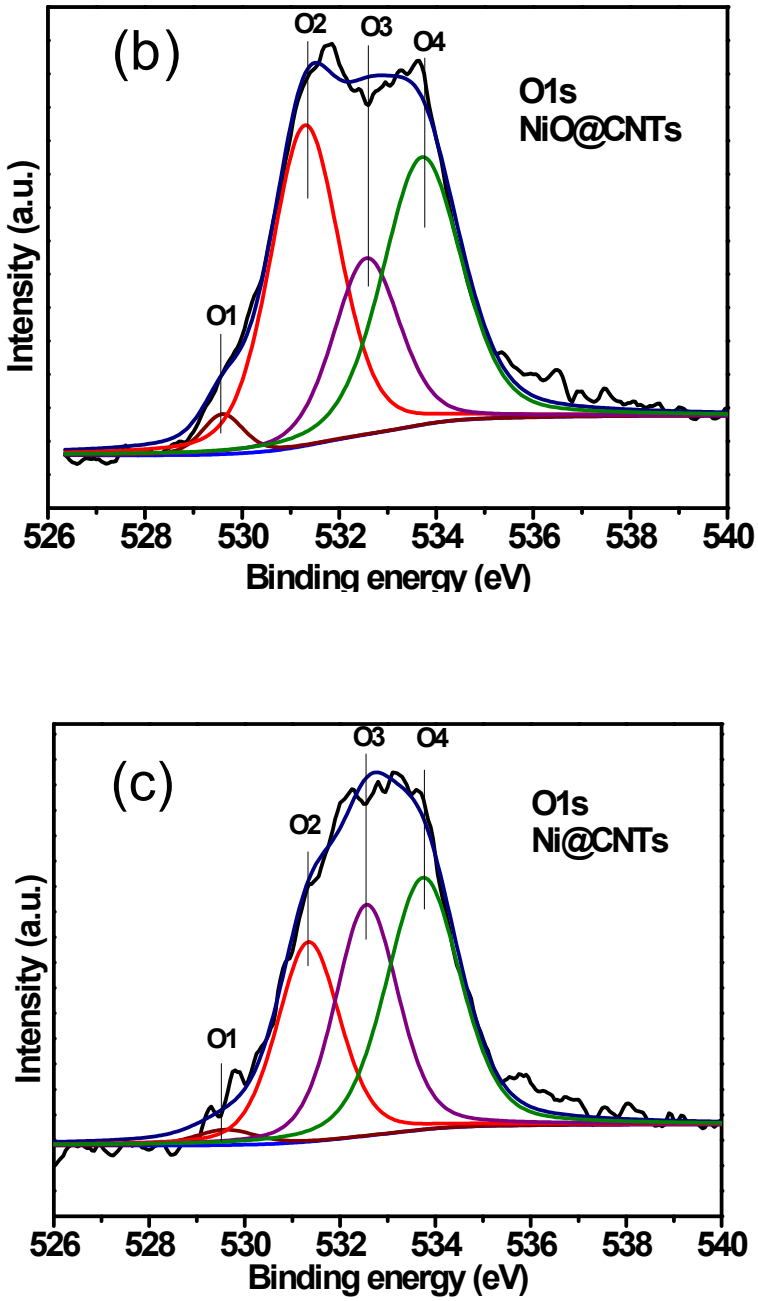


Figure S3. XPS O1sprofile of NiO/Ni@CNTs (a), NiO@CNTs(b) and Ni@CNTs(c).

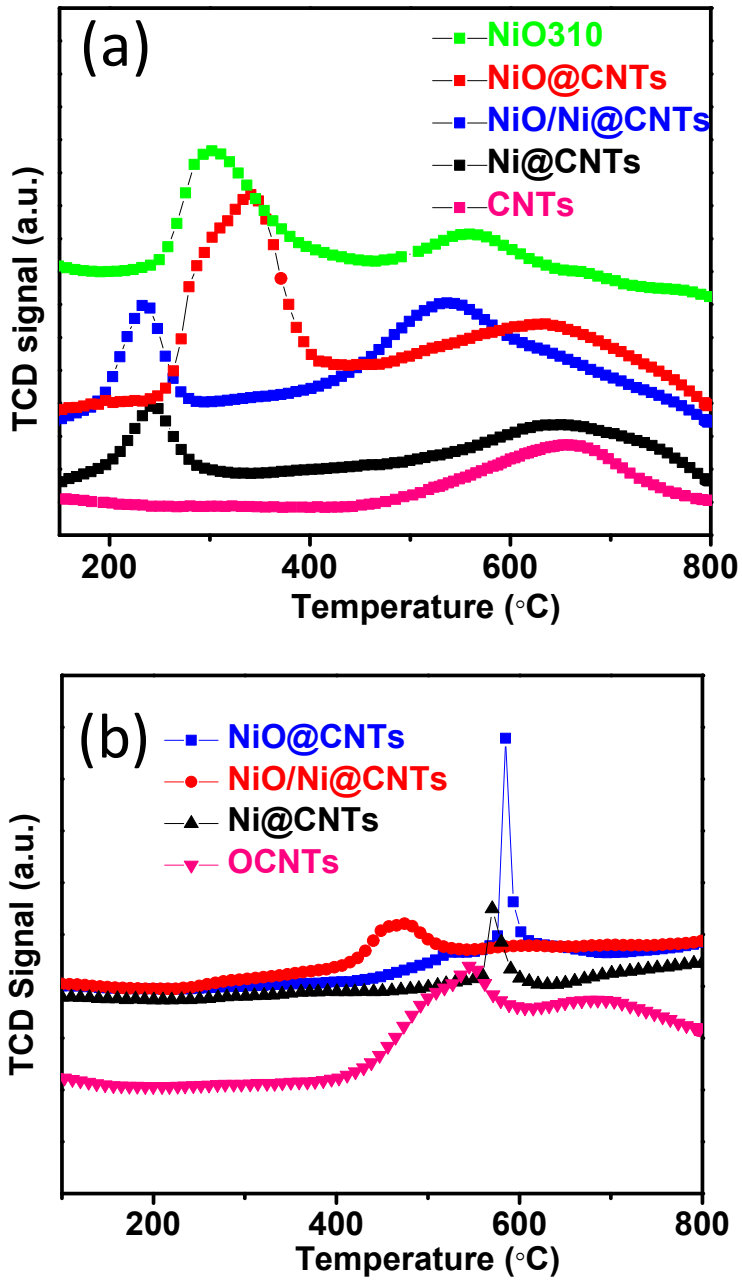
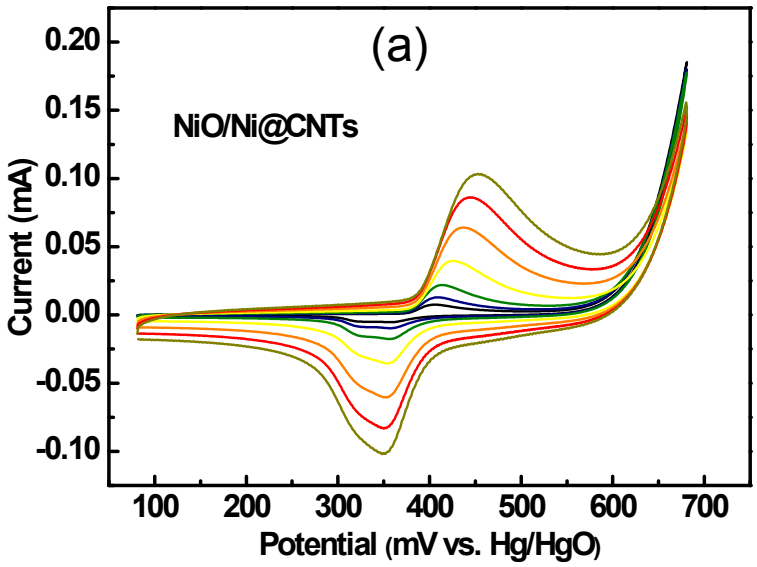
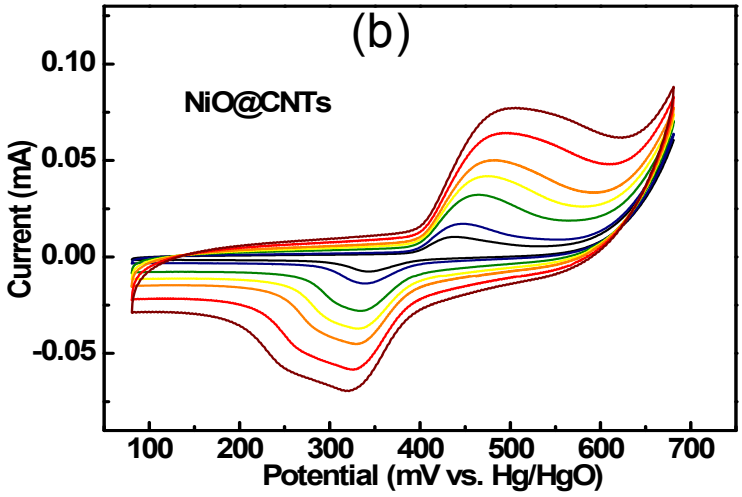


Figure S4. H_2–TPR profiles (a) and CO_2–TPD profiles (b) of the catalysts.


(a)
NiO/Ni@CNTs
Current (mA)
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
100
200
300
400
500
600
700
Potential (mV vs. Hg/HgO)


(b)
NiO@CNTs
Current (mA)
0.10
0.05
0.00
-0.05
100
200
300
400
500
600
700
Potential (mV vs. Hg/HgO)

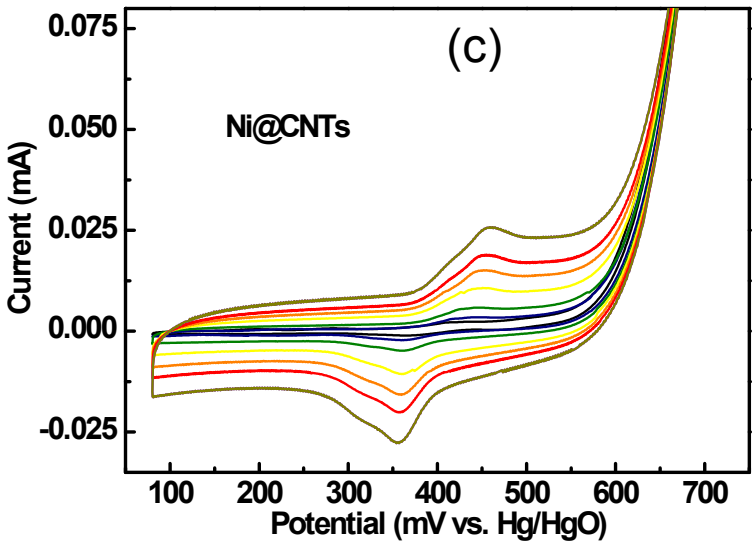


Figure S5. Cyclic voltammograms (CV) of NiO/Ni@CNTs (a), NiO@CNTs (b) and Ni@CNTs (c) in 1M KOH. Scan rate: 5, 10, 20, 50, 100, 150, 200 mV s^{-1}.

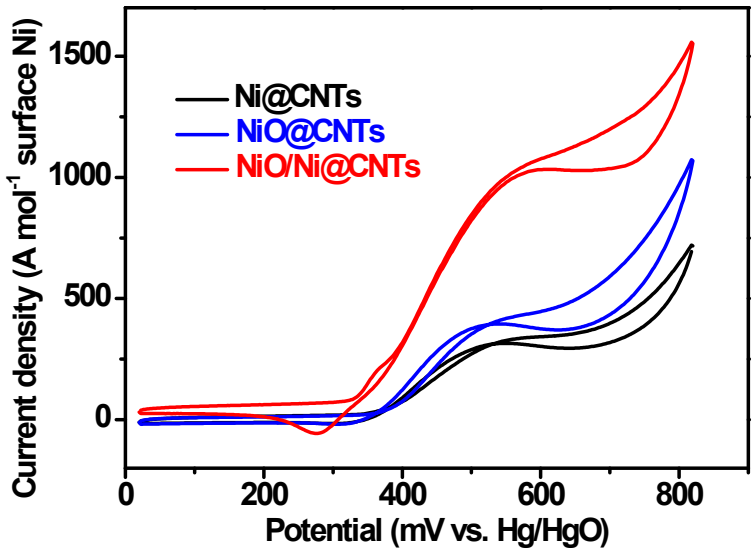


Figure S6. CVs of catalysts normalized to the surface Ni content in 1M KOH+0.5 M CH_3OH. Scan rate: 50 mV s^{-1} .

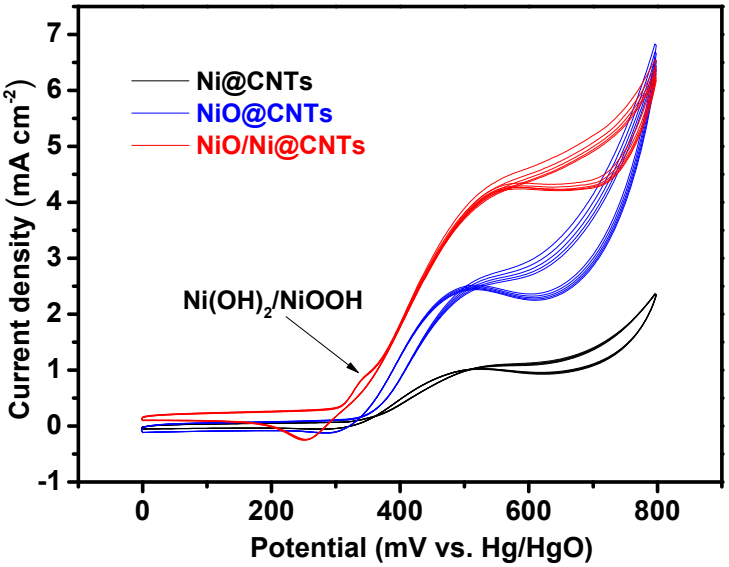


Figure S7. CVs of catalysts in the first five cycles.

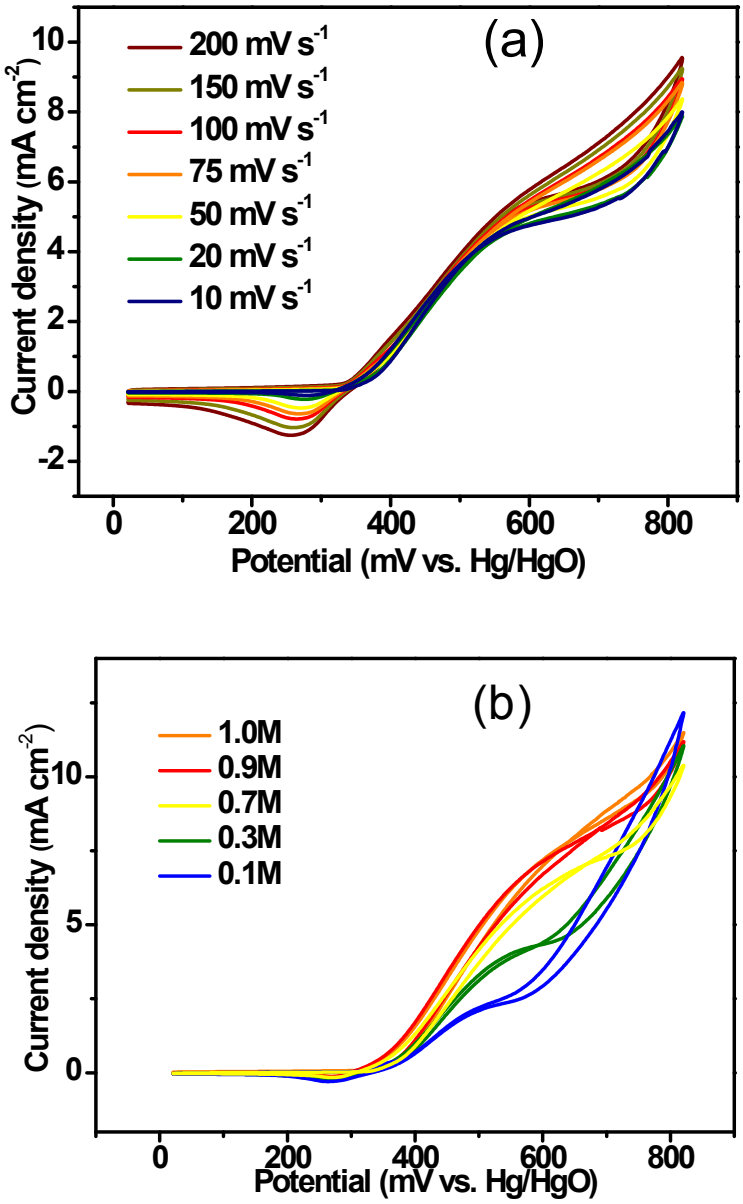


Figure S8. Current response of methanol oxidation of NiO/Ni@CNTs with the increasing scan rates in 1.0 M KOH+0.5 M methanol (a). Scan rate: 10, 20, 50, 100, 150, 200 mV s^{-1}. Current response of methanol oxidation of NiO/Ni@CNTs with the increasing concentration of methanol (b). Scan rate: 20 mV s^{-1}.

Table S1. Structural parameters of various samples.

sample	**content (wt%)[a)]**	**dispersion (%)[b)]**	**surface content (mmol g^{-1}_{cat}) [b)]**	**surface area ($m^2g^{-1}_{cat}$) [b)]**	**Particle size TEM (nm)**	**Particle size XRD (nm)**
Ni@CNTs	3.26	4.21	0.023	0.9141	9.17	9.4
NiO@CNTs	3.76	4.50	0.045	1.1277	4.1	4.0
NiO/Ni@CNTs	3.98	4.38	0.0297	1.1616	7.93	8.0

[a)] values determined by ICP−AES. [b)] values calculated based on pulse chemisorption analysis.

Table S2. Comparison of activity between catalysts in this study and reported Ni based catalysts.

Catalysts	Mass Activity ($mA\ mg^{-1}$)	Testing Conditions		References
		Scanning rate ($mV\ s^{-1}$)	CH_3OH concentration	
NiO/Ni@CNTs	2094	50	1.0 M CH_3OH	This work
NiO @CNTs	1328	50	1.0 M CH_3OH	This work
Ni@CNTs	966	50	1.0 M CH_3OH	This work
NiP	1490	50	1.0 M CH_3OH	[1]
CNT–Ni/SiC-700	1000	50	1.0 M CH_3OH	[2]
NiO	84	20	0.1M CH_3OH	[3]
NiO/CNTs	1900	50	0.5 M CH_3OH	[4]
NiO/N-CNFs	1800	50	1.0 M CH_3OH	[5]
Ni–P/RGO	117	10	0.5 M CH_3OH	[6]
Ni-P	60	10	0.5 M CH_3OH	[6]
Ni-DES	3	10	0.1M CH_3OH	[7]
$Ni(OH)_2$/BDD	600	5	0.47 M CH_3OH	[8]

References

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