Electronic Supplementary Information

One-Pot Synthesis of CuNi Nanoparticles with Ni-Rich Surface for Electrocatalytic Methanol Oxidation Reaction

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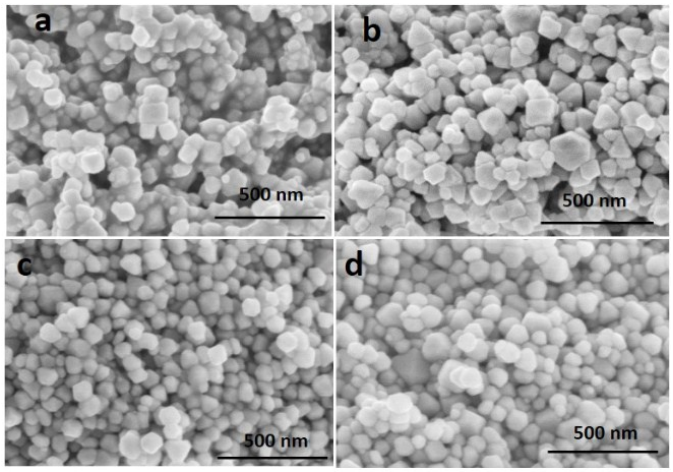

Fig. S1 SEM images of (a) NiCu-200, (b) NiCu-210, (c) NiCu-230 and (d) NiCu-240.

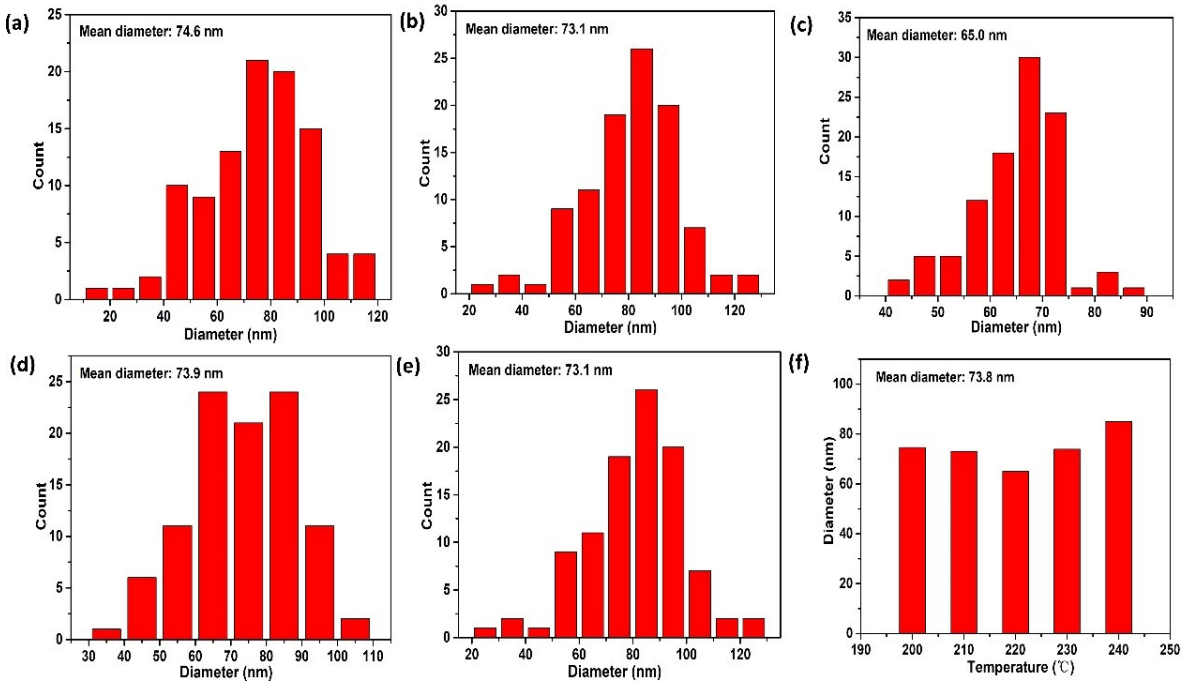

Fig. S2 Histograms showing the diameter distribution of (a) NiCu-200, (b) NiCu-210 (c) NiCu-220, (d) NiCu-230 and NiCu-240,(e) Average size distribution of 5 samples.

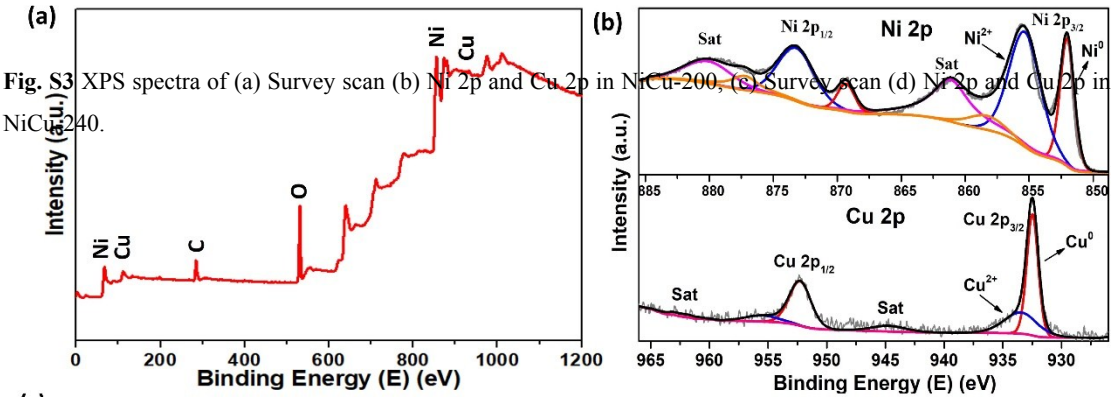

Fig. S3 XPS spectra of (a) Survey scan (b) Ni 2p and Cu 2p in NiCu-200, (c) Survey scan (d) Ni 2p and Cu 2p in NiCu-240.

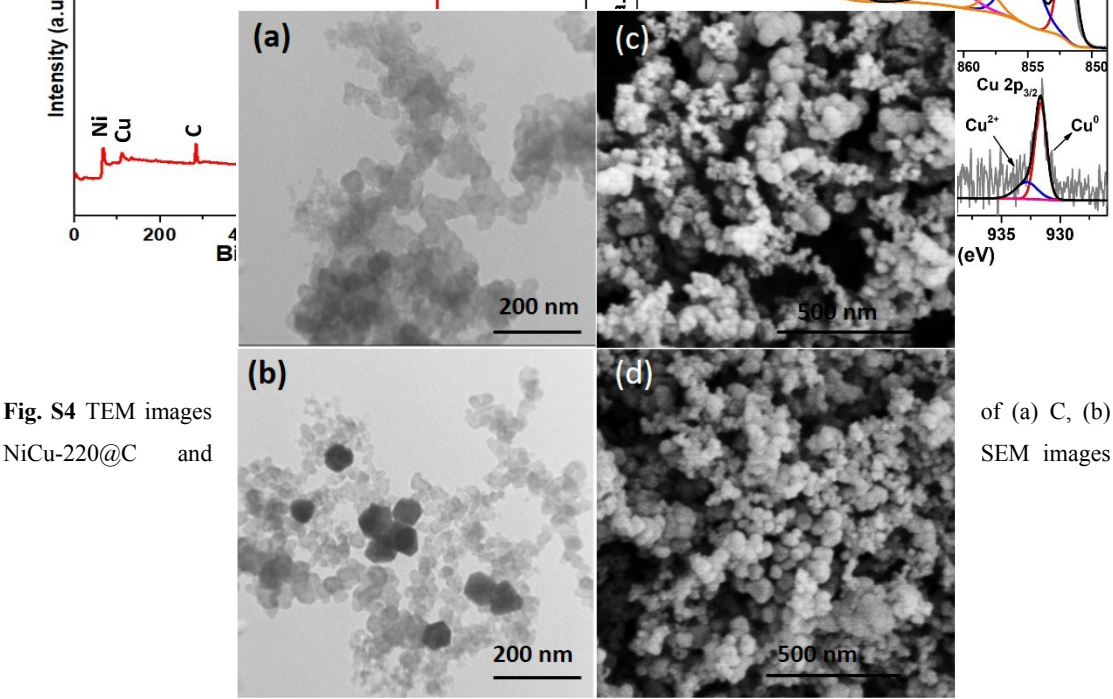

Fig. S4 TEM images of (a) C, (b) NiCu-220@C and SEM images

of (c) C, (d) NiCu-220@C

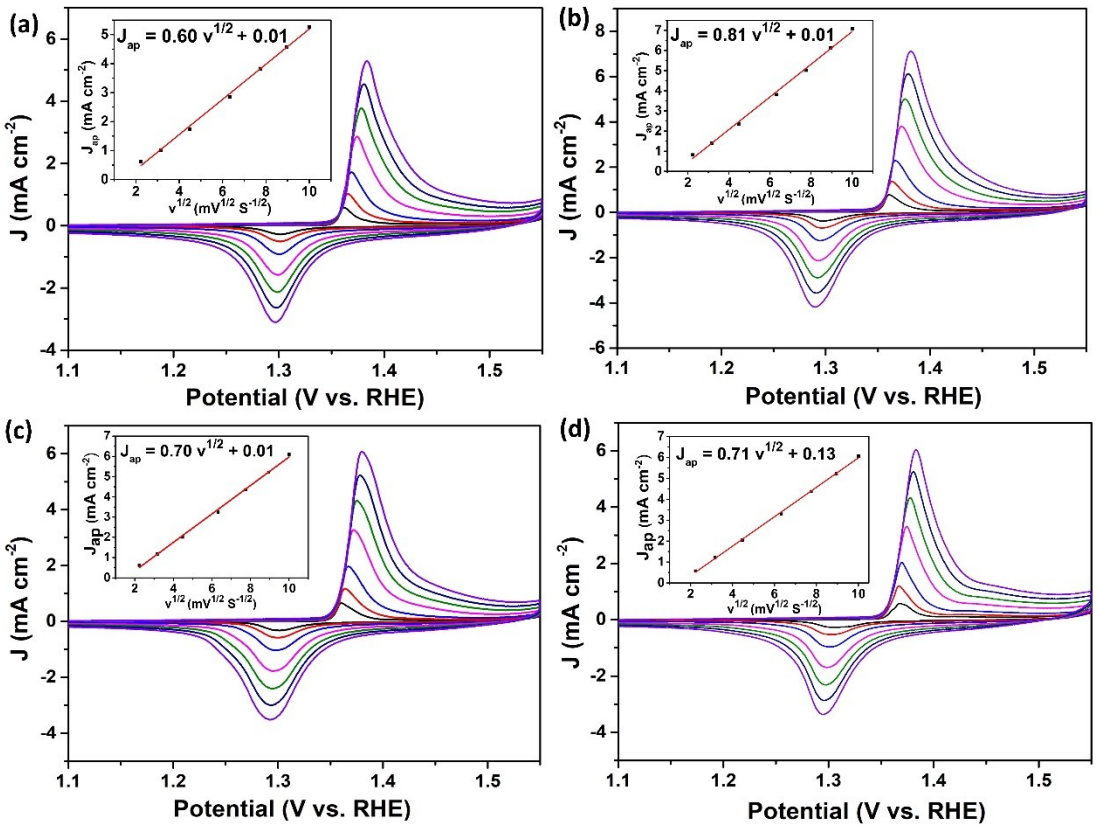

Fig. S5 Cyclic voltammograms of NiCu alloy NP in the presence of 1 M KOH at various scan rates of 5, 10, 20, 40, 60, 80, and 100 mV s^{-1} (inset: $J_{ap} \approx v^{1/2}$ relationship).(a) NiCu-200@C, (b) NiCu-210@C,(c) NiCu-230@C and (d) NiCu-240@C.

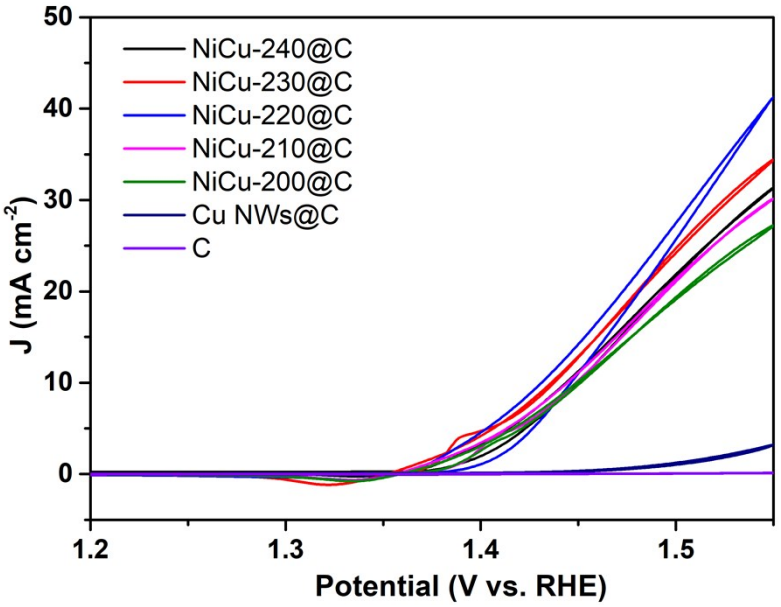

Fig. S6 CVs of C powder, Cu NWs@C, NiCu-200@C, NiCu-210@C, NiCu-220@C, NiCu-230@C and NiCu-240@C electrodes in 1 M KOH solution with 1 M methanol at a scan rate of 50 mV s^{-1}.

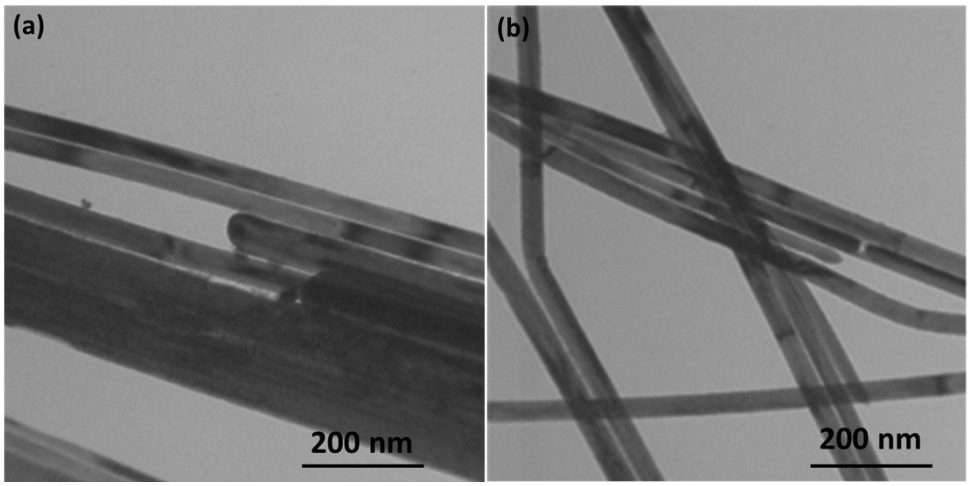

Fig. S7 TEM images of the Cu NWs.

Table S1. ICP analysis about atomic ratio (%) (Cu vs. Ni) of NiCu-200, NiCu-220, NiCu-240.

	NiCu-200	NiCu-220	NiCu-240
Ni	67.40%	68.50%	67.43%
Cu	26.48%	22.55%	25.80%

Table S2. Comparison of electrocatalytical activity of different Ni-based catalysts and commercial catalysts

Catalyst	**Activity**	**Scanning rate ($mV\ s^{-1}$)**	**Condition**	**Reference**
Ni/GC	8.47 mA cm^{-2}	50	1 M NaOH + 0.5 M CH_3OH	(*1*)
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Ni-P/RGO	16.4 mA cm^{-2}	10	1 M KOH + 0.5 M CH_3OH	(*2*)
	117 mA mg^{-1}			
Ni-Cu-P/C	17 mA cm^{-2}	10	0.1 M KOH + 0.5 M CH_3OH	(*3*)
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Cu/NiCuNWs-220/C	34.9 mA cm^{-2}	50	1 M KOH + 1 M CH_3OH	(*4*)
	867.1 mA mg^{-1}			
$NiCo_2O_4$/GCE	15.5 mA cm^{-2}	50	0.1 M NaOH + 1 M CH_3OH	(*5*)
	10.99 mA mg^{-1}			
Ni-Cu/CN	2.7 mA cm^{-2}	50	1 M NaOH + 2 M CH_3OH	(*6*)
	8.7 mA mg^{-1}			
GC/MWCNTs/NiO	20 mA cm^{-2}	100	0.1 M NaOH +0.5 M CH_3OH	(*7*)
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$Ni_{0.75}Cu_{0.25}$	84 mA cm^{-2} 168 mA mg^{-1}	50	1 M NaOH + 0.5 M CH_3OH	(*8*)
Ni/TiO_2NTs	28.3 mA cm^{-2} --	50	1 M NaOH + 0.5 M CH_3OH	(*9*)
GC/NiO_x	5.38 mA cm^{-2} --	50	0.5 M NaOH +0.5 M CH_3OH	(*10*)
NiCu	182.07 mA cm^{-2} --	100	1 M KOH + 2 M CH_3OH	(*11*)
NiCu NP-220@C	41.12 mA cm^{-2} 1028 mA mg^{-1}	50	1 M KOH + 1 M CH_3OH	***This work***
Commercial Pt/C	214.2 mA mg^{-1}	50	0.5M H_2SO_4 + 0.5 M CH_3OH	(12)
Commercial Pt/C	301.7 mA mg^{-1}	50	0.5 M KOH +0.5 M CH_3OH	(13)

References:

1. M. Zhou, P. Xiao, W. Guo, J. Deng, F. Liu, Y. Zhang, Electrochemical synthesis of monodisperse nickel with predominant {111} orientation and high electro-oxidation activity for methanol. *Journal of The Electrochemical Society* **161**, H133-H137 (2014).
2. H. Zhang, GU, ChangDong, HUANG, MeiLing, WANG, XiuLi, TU, JiangPing, Anchoring three-dimensional network structured Ni—P nanowires on reduced graphene oxide and their enhanced electrocatalytic activity towards methanol oxidation. *Electrochemistry Communications* **35**, 108-111 (2013).
3. R. M. Hameed, K. M. El, Ni–P and Ni–Cu–P modified carbon catalysts for methanol electro-oxidation in KOH solution. *International Journal of Hydrogen Energy* **35**, 2517-2529 (2010).
4. D. Wu, W. Zhang, D. Cheng, Facile synthesis of Cu/NiCu electrocatalysts integrating alloy, core-shell and one-dimensional structures for efficient methanol oxidation reaction. *Acs Applied Materials & Interfaces* **9**, acsami.7b03876 (2017).
5. A. Prathap, U. M., SRIVASTAVA, Rajendra, Synthesis of NiCo2O4 and its application in the electrocatalytic oxidation of methanol. *Nano Energy* **2**, 1046 (2013).
6. I. S. Pieta, A. Rathi, P. Pieta, R. Nowakowski, M. Hołdynski, M. Pisarek, A. Kaminska, M. B. Gawande, R. Zboril, Electrocatalytic methanol oxidation over Cu, Ni and bimetallic Cu-Ni nanoparticles supported on graphitic carbon nitride. *Applied Catalysis B: Environmental* **244**, 272-283 (2019).
7. Shamsipur, Mojtaba, Najafi, Mostafa, Hosseini, M. R. Milani, Electrooxidation of alcohols at a nickel oxide/multi-walled carbon;nanotube-modified glassy carbon electrode. *Journal of Applied Electrochemistry* **43**, 1027-1033 (2013).
8. X. Cui, P. Xiao, J. Wang, M. Zhou, W. Guo, Y. Yang, Y. He, Z. Wang, Y. Yang, Y. Zhang, Highly Branched Metal Alloy Networks with Superior Activities for the Methanol Oxidation Reaction. *Angew Chem Int Ed* **56**, 4488 (2017).
9. H. He, X. Peng, Z. Ming, Y. Zhang, Q. Lou, X. Dong, Boosting catalytic activity with a p–n junction: Ni/TiO 2 nanotube arrays composite catalyst for methanol oxidation. *International Journal of Hydrogen Energy* **37**, 4967-4973 (2012).
10. R. H. Tammam, A. M. Fekry, M. M. Saleh, Electrocatalytic oxidation of methanol on ordered binary catalyst of manganese and nickel oxide nanoparticles. *International Journal of Hydrogen Energy* **40**, 275-283 (2015).

11. G. S. Theres, G. Velayutham, P. S. Krishnan, K. Shanthi, Synergistic impact of Ni–Cu hybrid oxides deposited on ordered mesoporous carbon scaffolds as non-noble catalyst for methanol oxidation. *Journal of materials science* **54**, 1502-1519 (2019).

12. Zhou Y, Yang G, Pan H B, et al. Ultrasonic-assisted synthesis of carbon nanotube supported bimetallic Pt–Ru nanoparticles for effective methanol oxidation[J]. *Journal of Materials Chemistry A* **3,** 8459-8465 (2015).

13. Wu S, Liu J, Tian Z, et al. Highly dispersed ultrafine Pt nanoparticles on reduced graphene oxide nanosheets: in situ sacrificial template synthesis and superior electrocatalytic performance for methanol oxidation[J]. *ACS applied materials & interfaces* **7**, 22935-22940 (2015).