

Supporting information

Porifera-like Nickel Nanodendrite for Efficient Electrosynthesis of C-N Compounds from Carbon Dioxide and Nitrate Anions

Shivaraj B. Patil,^{1#} Chang-Ru Lee,^{1#} Swathi M. Gowdru,^{1#} Chun-Chih Chang,^{2*} Shu-Ting Chang,¹ Yi-Chia Chen,¹ Kuan-Chang Wu,¹ Chia-Che Chang,¹ Shu-Chih Haw,³ Di-Yan Wang^{1*}

¹ Department of Chemistry, Tunghai University, Taichung 40704, Taiwan

² Department of Chemical and Materials Engineering, Chinese Culture University, Taipei 11114, Taiwan

³ National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

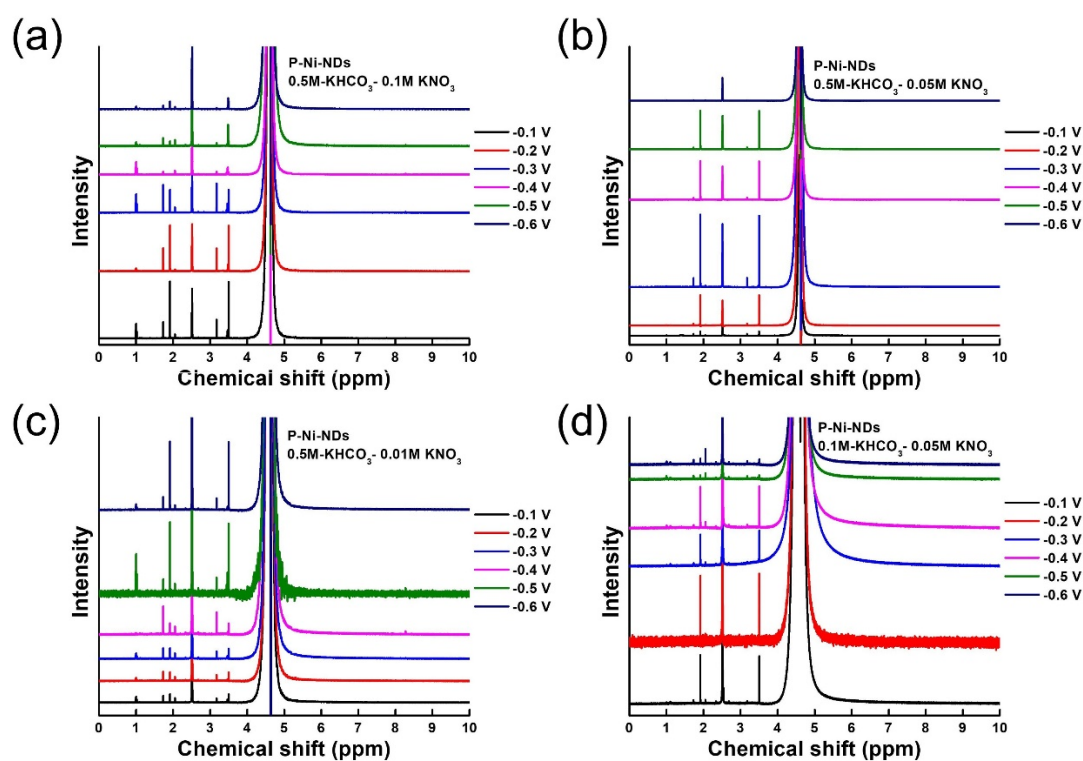


Figure S1. NMR spectra of test samples in different electrolytes at different potentials on p-Ni NDs surface. (All the voltages are provided against RHE.) The peaks at 1.0, 1.7, 1.9, 2.1, 3.1 and 3.5 are indexed to ethanol, acetate, acetamide, acetone, methanol, and ethylene glycol, respectively. The peaks at 4.5 and 2.5 ppm are ascribed to water and dimethyl sulfoxide-d₆ (DMSO), respectively. DMSO was added as an internal reference.

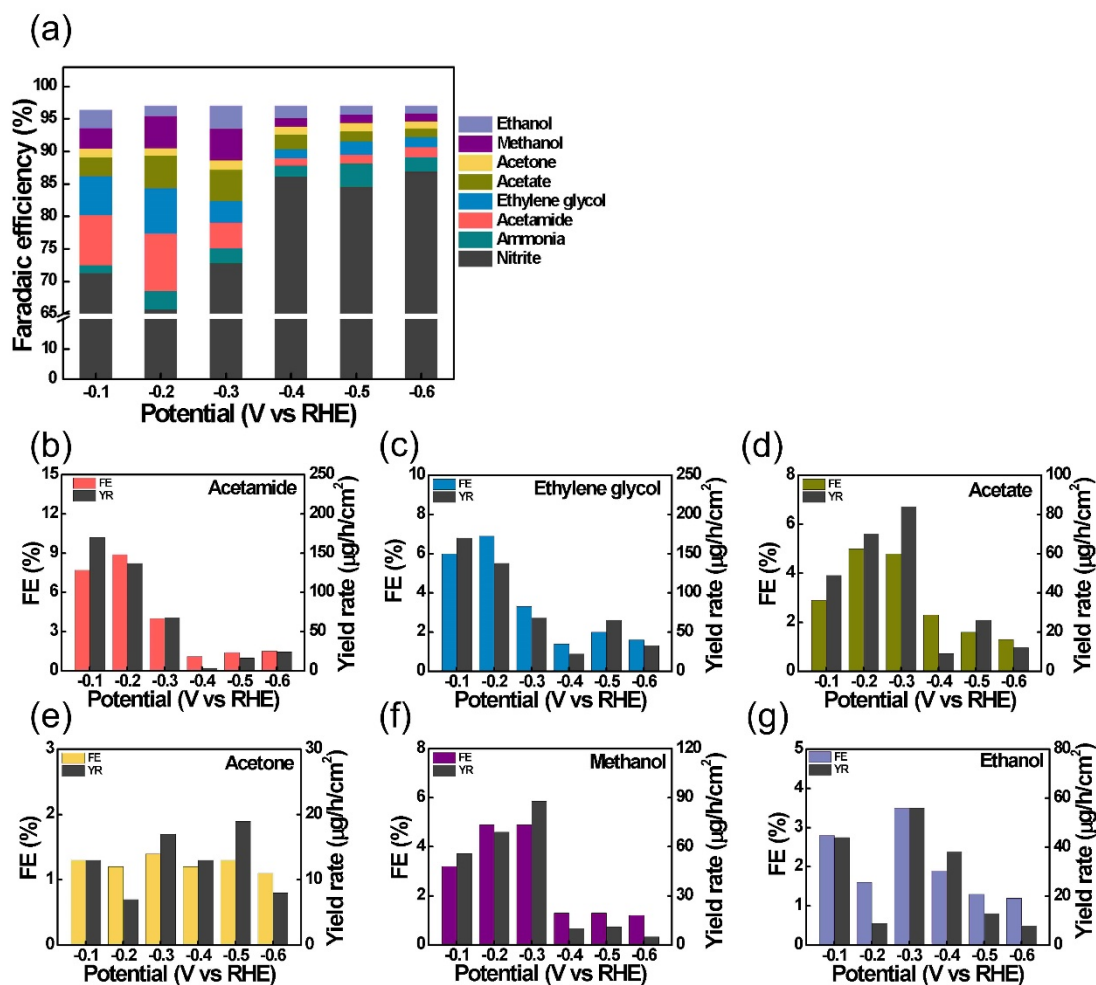


Figure S2. Product distribution, Faraday efficiency and yield rates of products formed at p-Ni NDs when 0.1 M KNO_3 + 0.5 M KHCO_3 was employed as electrolyte.

To further investigate the relation between FE and yield rate of acetamide, the concentration of electrolyte was varied. Maintaining the constant concentration of KHCO_3 (0.5 M), the higher concentration of KNO_3 (0.1M) was opted as the electrolyte. **Figure S2 (a)** shows the FE of all compounds produced at different potentials in the electrolyte of KHCO_3 (0.5 M) and KNO_3 (0.1M) when p-Ni NDs was used as a working electrode. However, FE and yield rates of acetamide (9.0%, 140 $\mu\text{g/h/cm}^2$), ethylene glycol (7.0%, 150 $\mu\text{g/h/cm}^2$), and acetone (1.2%, 20 $\mu\text{g/h/cm}^2$) have diminished, whereas FE and yield rates of acetone (4.7%, 85 $\mu\text{g/h/cm}^2$), methanol (5.0%, 90 $\mu\text{g/h/cm}^2$), and ethanol (3.5%, 57 $\mu\text{g/h/cm}^2$) have improved.

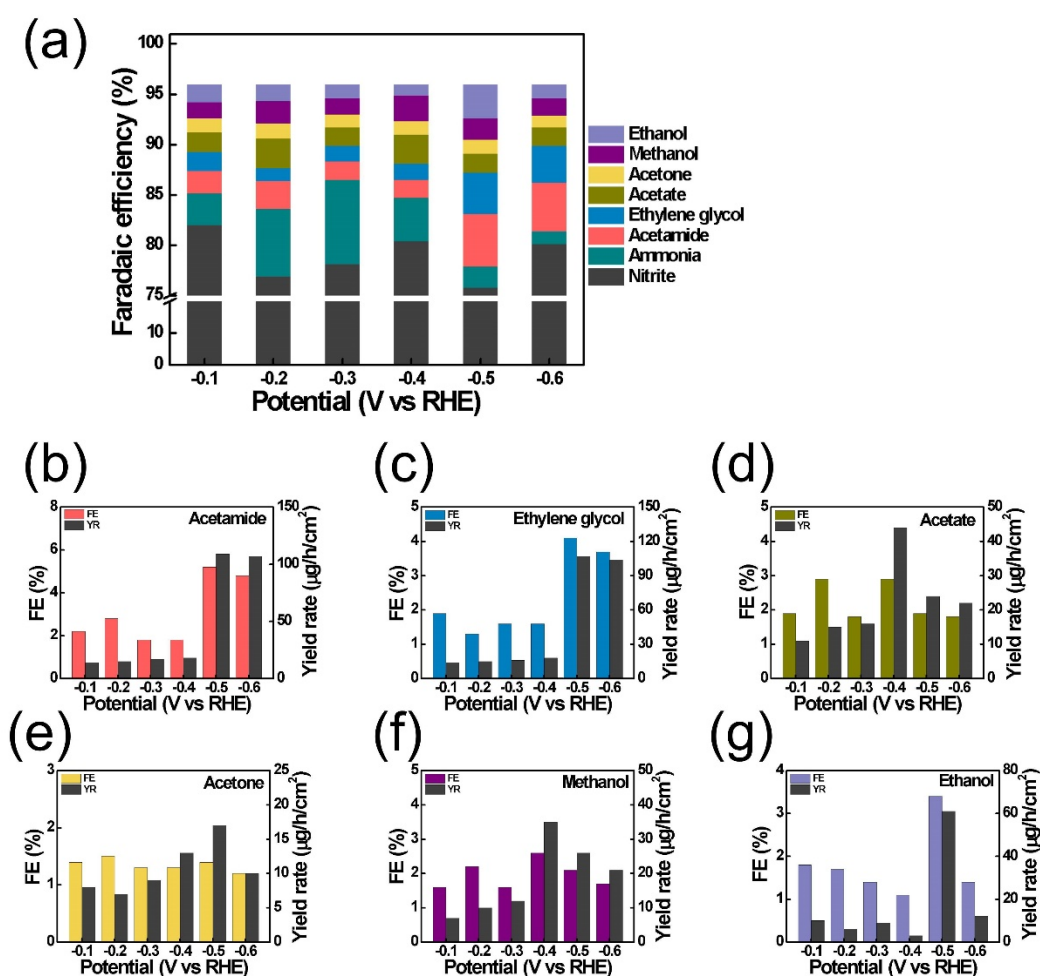


Figure S3. Product distribution, Faraday efficiency and yield rates of products formed at p-Ni NDs when 0.01 M KNO_3 + 0.5 M KHCO_3 was employed as electrolyte.

Furthermore, the concentration of KNO_3 was reduced to 0.01 M maintaining the concentration of KHCO_3 constant (0.5 M) that is 0.5 M KHCO_3 + 0.01 M KNO_3 . **Figure S3a** shows the product distribution at different potentials when p-Ni NDs was used as a working electrode. Acetamide, ethylene glycol, acetate, acetone, methanol, and ethanol were found to be formed at the rate of $109 \mu\text{g/h/cm}^2$ (-0.5 V), $104 \mu\text{g/h/cm}^2$ (-0.2 V), $44 \mu\text{g/h/cm}^2$ (-0.4 V), $17 \mu\text{g/h/cm}^2$ (-0.4 V), $35 \mu\text{g/h/cm}^2$ (-0.4 V), $61 \mu\text{g/h/cm}^2$ (-0.5 V) with FE of 5.2%, 4.1%, 2.9%, 1.4%, 2.6%, and 3.4%, respectively. FE and yield rate of the acetamide and most of C_{2+} compounds found to reduce significantly when the concentration of KNO_3 was varied from the ideal concentration. Therefore, 0.05 M is considered as ideal concentration of KNO_3 for p-Ni NDs.

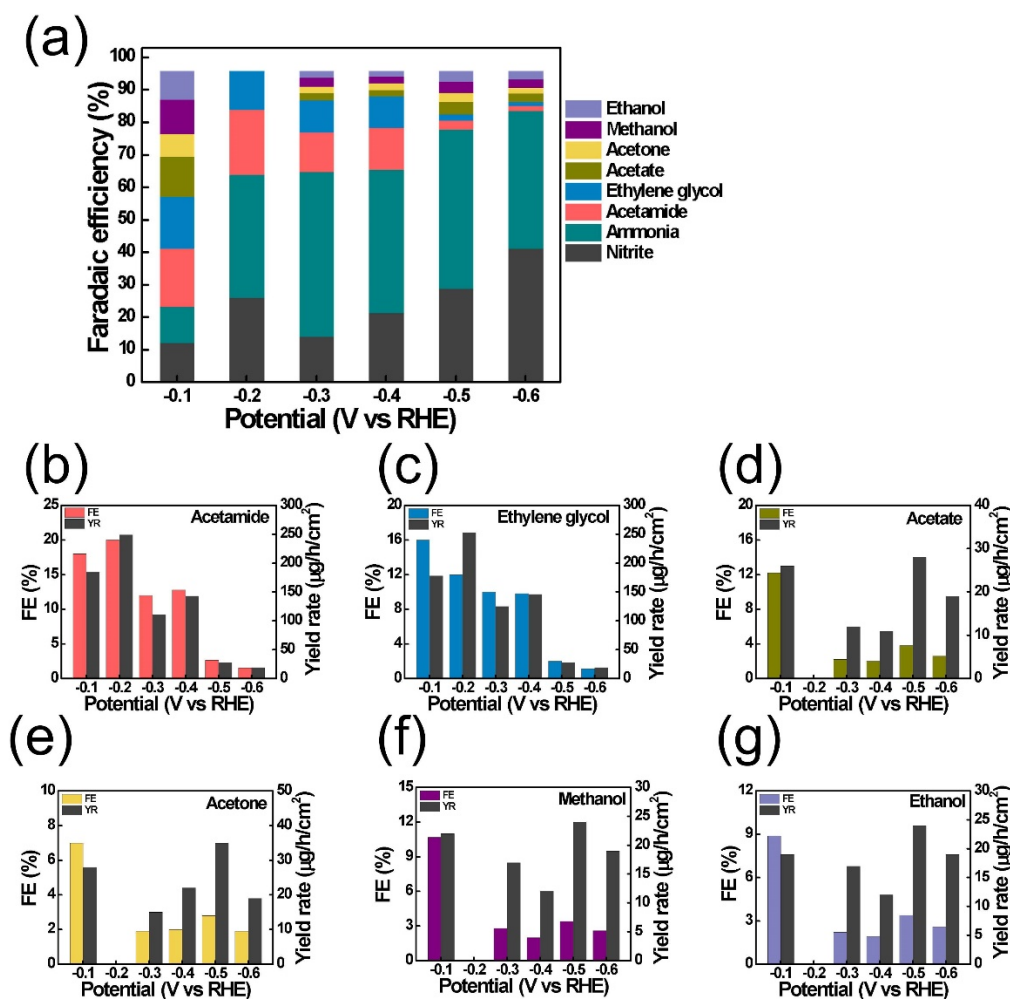


Figure S4. Product distribution, Faraday efficiency and yield rates of products formed at p-Ni NDs when 0.01 M KNO_3 + 0.1 M KHCO_3 was employed as electrolyte.

To further improve the FE and formation rate, the concentration of KHCO_3 was reduced from 0.5 to 0.1 M maintaining the concentration of KNO_3 constant (0.05 M) that is 0.1 M KHCO_3 + 0.05 M KNO_3 . **Figure S4a** shows the product distribution at different potentials when p-Ni NDs was used as a working electrode. Acetamide, ethylene glycol, acetate, acetone, methanol, and ethanol were found to be formed at the rate of $249 \mu\text{g/h/cm}^2$ (-0.2 V), $253 \mu\text{g/h/cm}^2$ (-0.2 V), $26 \mu\text{g/h/cm}^2$ (-0.1 V), $28 \mu\text{g/h/cm}^2$ (-0.1 V), $22 \mu\text{g/h/cm}^2$ (-0.1 V), $19 \mu\text{g/h/cm}^2$ (-0.1 V) with FE of 20.0%, 12.0%, 12.2%, 7.0%, 10.7%, and 8.9%, respectively. Interestingly, FE of acetamide and ethylene glycol were reduced while FE of acetate, acetone, methanol, and ethanol found to increase. Thus, 0.5 M KHCO_3 + 0.05 M KNO_3 is considered as the ideal electrolyte condition for p-Ni NDs to produce acetamide and ethylene glycol with very high FE and yield rate.

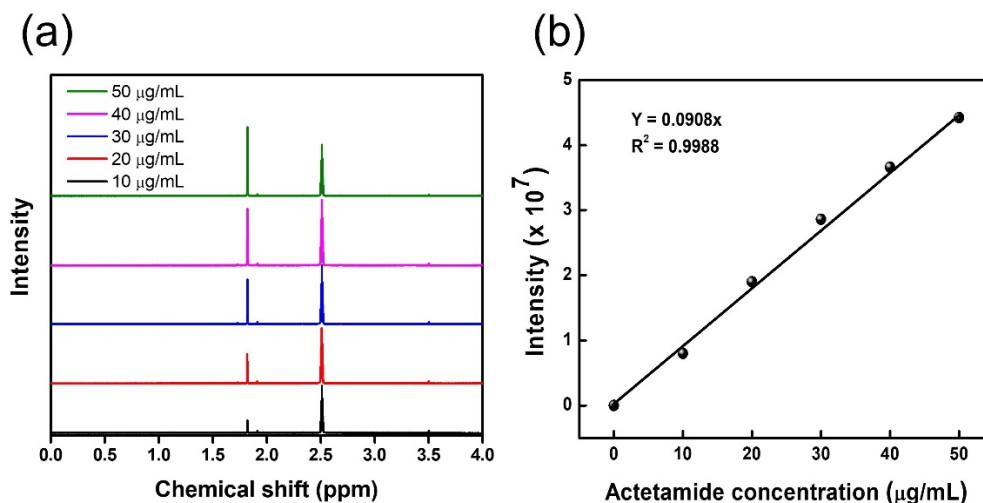


Figure S5. (a) H-NMR spectra and (b) calibration graph of acetamide, respectively. (D6-DMSO was added as an internal reference)

Yield rate (Y) calculation

Yield rate of each product is calculated as following

$$\text{Yield rate}_{\text{mass}}(\text{product}) = (c(\text{product}) \times V) / (t \times A) \quad \text{Eq. 1}$$

Where $c(\text{product})$ is the measured the concentration of the product, V is the volume of electrolyte, t is the duration time of the reduction reaction, and A is the geometric area of the cathode ($1 \times 1 \text{ cm}^2$).

Faradic efficiency (FE) Calculations

Faradaic efficiency of each product is calculated as following

$$\text{FE} = (nF \times C_{\text{product}} \times V) / (MW \times Q) \quad \text{Eq. 2}$$

Where n stands number of electrons involved, F stands for Faradaic constant (96485 C/mol), MW stands for molecular weight of the product, and Q stands for total quantity of supplied coulomb. The number of electrons involved, and molecular weight of each product is given in **Table S1**.

Table S1. The number of electrons involved, and molecular weight of different products formed during the reaction.

	Compound Name	Number of electrons involved (n)	Molecular weight (g/mol)
1	Acetamide	16	59.07
2	Ethylene glycol	10	62.07
3	Acetate	8	59.04
4	Acetone	16	58.08
5	Ethanol	12	46.07
6	Methanol	6	32.04
7	Ammonia	8	17.03
8	Nitrite	2	46.00

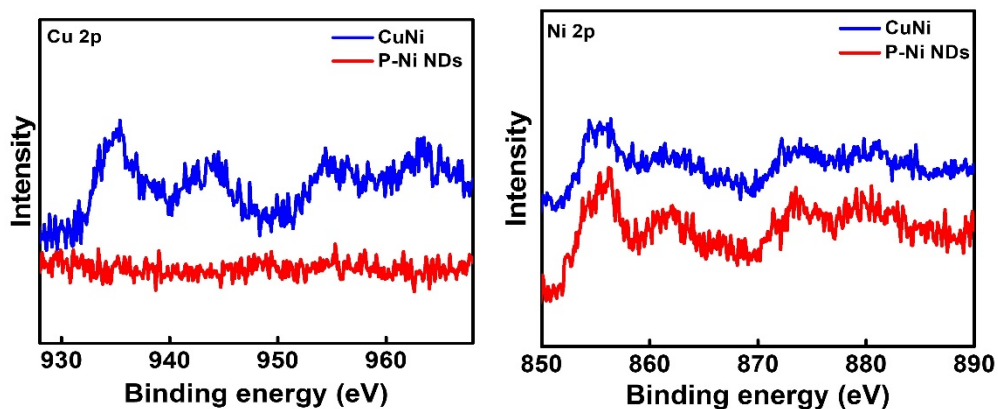


Figure S6. X-ray photoelectron spectra (XPS) of (a) Cu and (b) Ni, respectively.

Figure S6a shows the X-ray photoelectron spectra (XPS) of Cu. The peaks at 933 and 953 eV are attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The peaks next to these peaks are recognized as satellite peaks of Cu. These peaks confirm the presence of Cu in the metallic state in CuNi NDs. A slight shift in the peaks' position can be ascribed to surface oxidation. However, these peaks disappeared

from p-Ni NDs' Cu spectrum implying the complete removal of Cu from the matrix and formation of highly porous Ni NDs. **Figure S6b** shows the XPS spectra of Ni. The peaks at 853 and 873 eV are attributed to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively. These results also indicate that Ni is present in metallic state. Likewise, the peaks next to these peaks are recognized as satellite peaks and slight shift in the peaks is ascribed to surface oxidation. After removing Cu, the peaks corresponding to Ni remain unchanged signifying the formation of pure Ni P-NDs. XPS results further substantiate the formation of CuNi NDs and p-Ni NDs (by complete removal of Cu).

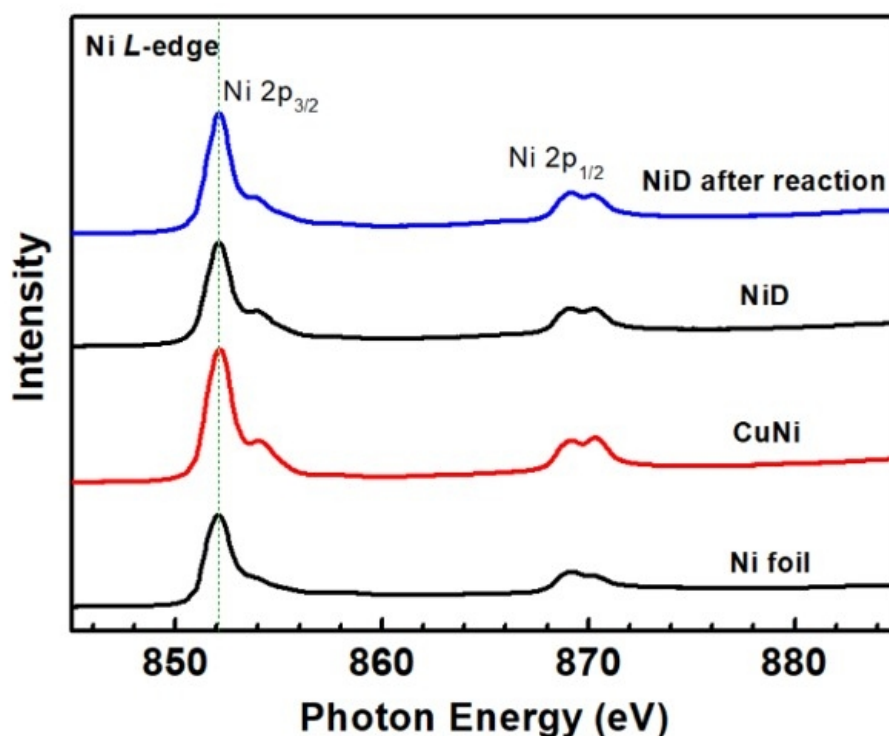


Figure S7. Soft X-ray absorption spectra (XANES) of Ni foil, CuNi NDs, Ni NDs (before and after reaction) by measuring the Ni L-edges.

The CuNi, NiD and NiD after reaction were characterized with *ex situ* soft X-ray absorption spectra by measuring the Ni L-edges. The spectra (**Figure S7**) were measured in the method of surface sensitive total electron yield. The Ni L-edge shape was attributed to the dipole transitions from 2p to 3d which was split into two regions for the core–hole spin–orbital interaction. two peaks at 852 eV and 870 eV are contributed from 2p_{3/2} to 3d and 2p_{1/2} to 3d, respectively. The results indicated that The features in both L₃ and L₂ edges of The CuNi, NiD and NiD after reaction samples are very similar to that of Ni foil, meaning that the typical features of Ni in the CuNi, NiD and NiD after reaction are belonged to metallic state.

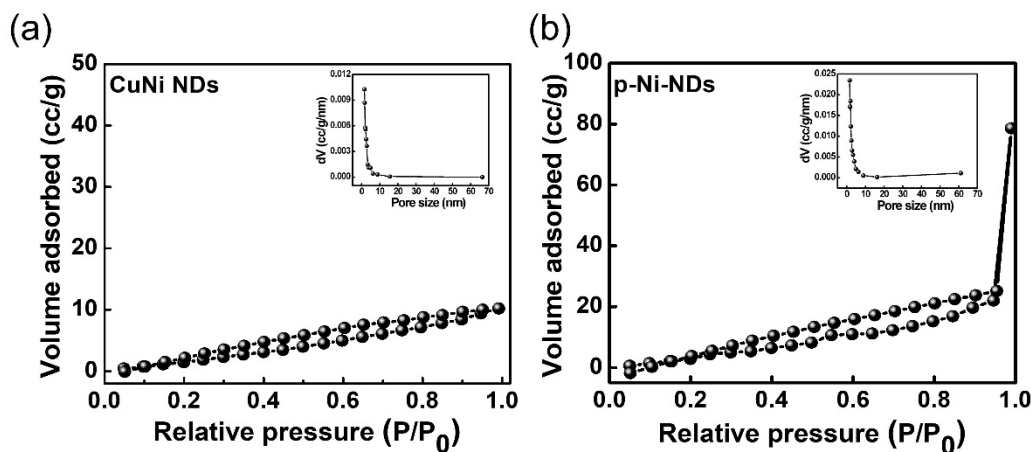


Figure S8. N₂-adsorption isotherms of (a) CuNi NDs and (b) p-Ni NDs, respectively. Insets show pore size distribution in CuNi NDs and p-Ni NDs, respectively.

The surface area and pore size of CuNi and Ni were calculated using N₂ adsorption isotherms and BJH pore size distribution. **Figure S8a and S8b** show the N₂-adsorption isotherms of CuNi NDs and p-Ni NDs, respectively. The Brunauer-Emmett-Teller (BET) specific surface area of CuNi NDs and p-Ni NDs were found to be 12 and 68 m²/g, respectively. **Insets of Figure S8a and S8b** show pore size distribution in CuNi NDs and p-Ni NDs, respectively. The BJH pore volume of CuNi NDs and p-CuNi NDs were calculated to be 0.015 and 0.123 cc/g, respectively. BET study revealed that p-Ni NDs exhibit larger surface area and higher pore volume value compared to CuNi NDs. It should be noted that removal of Cu by CV method to yield p-Ni NDs played an important role in enhancing the surface area and pore volume. Thus, overall characterization results confirm the successful removal of Cu and creation of highly porous, and large surfaced porifera structured Ni NDs.

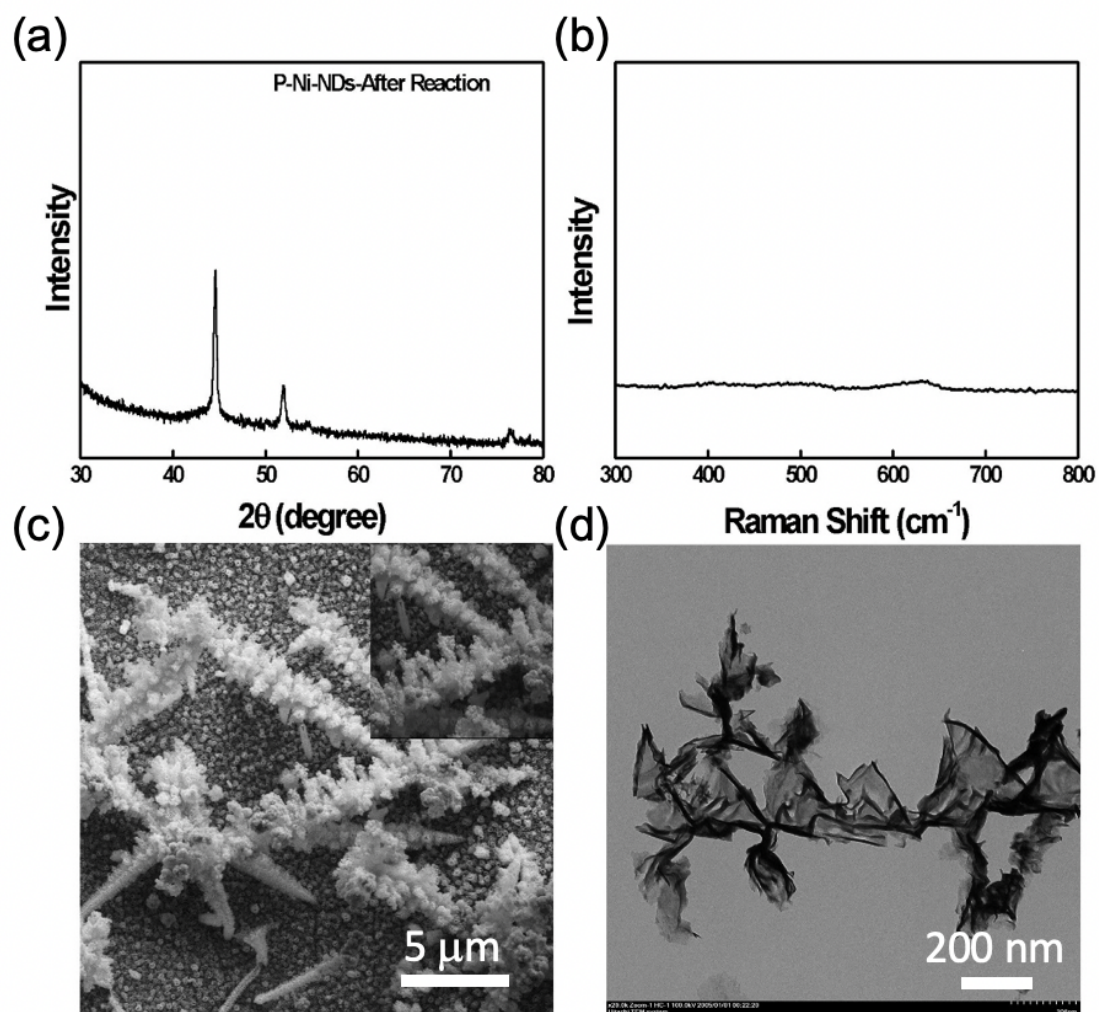


Figure S9. (a) XRD pattern, (b) Raman spectroscopy, (c) HRSEM and (d) TEM images of p-Ni NDs after reaction.

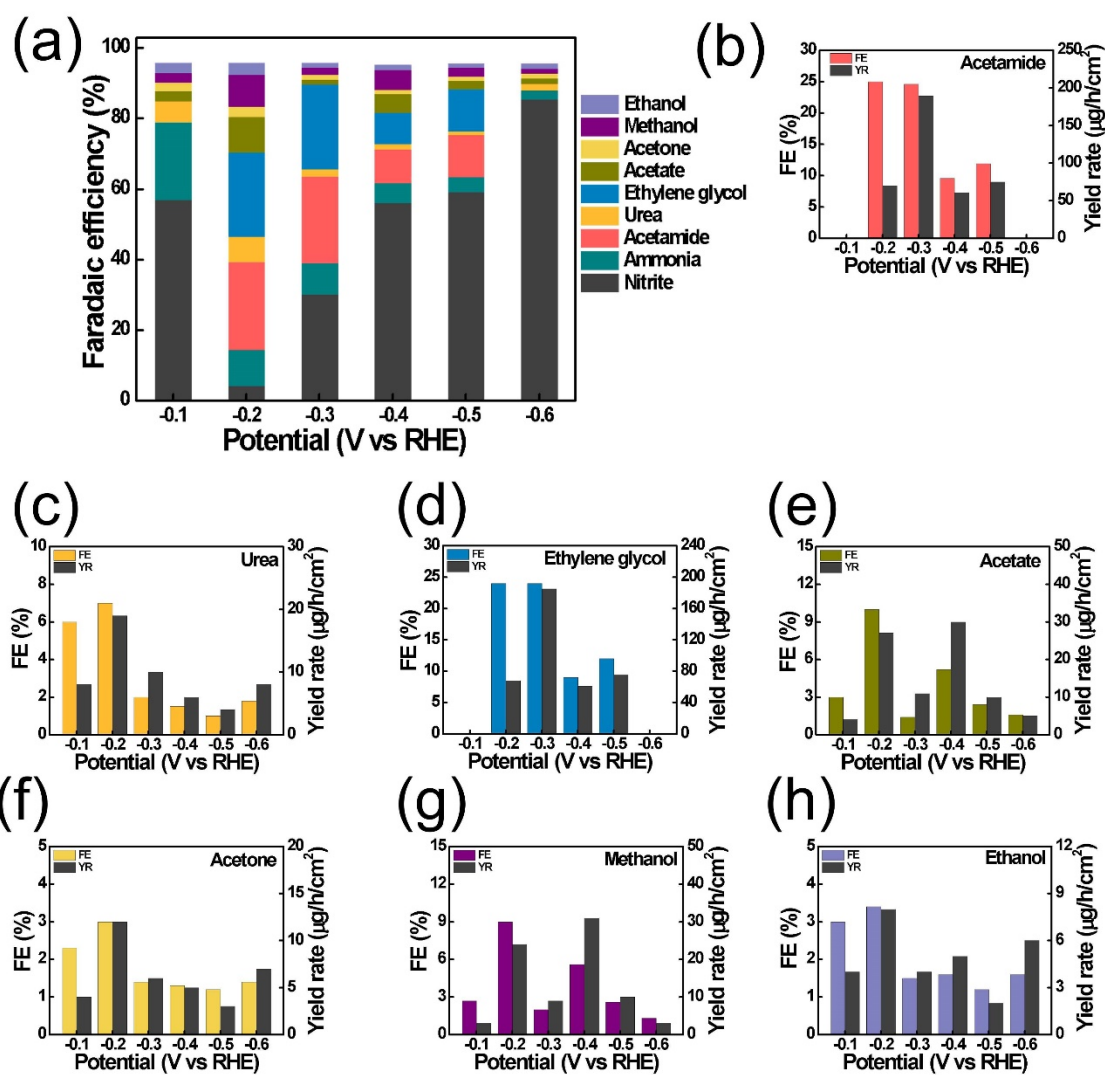


Figure S10. Product distribution, Faraday efficiency and yield rates of products formed at CuNi NDs when 0.01 M KNO_3 + 0.5 M KHCO_3 was employed as electrolyte.

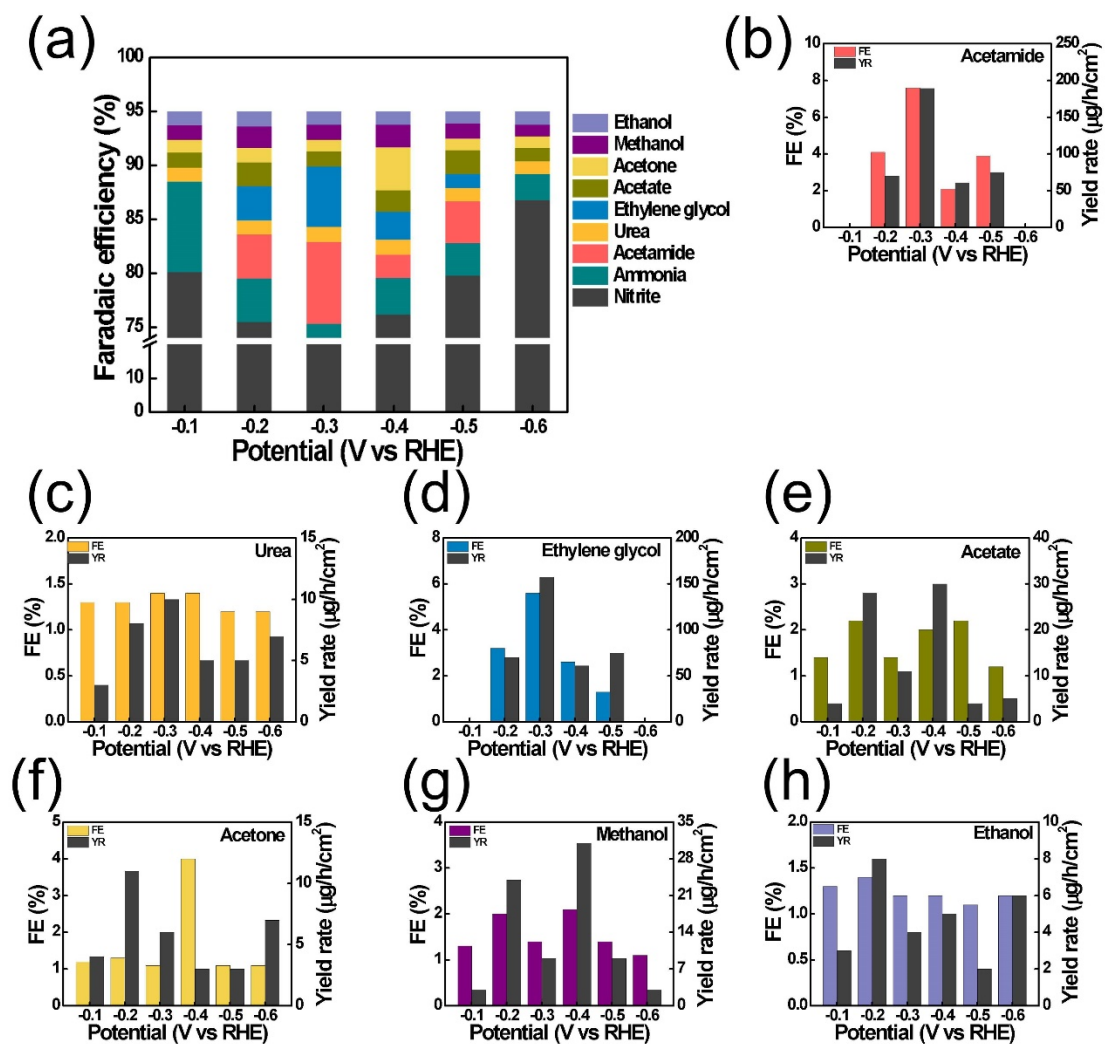


Figure S11. Product distribution, Faraday efficiency and yield rates of products formed at CuNi NDs when 0.1 M KNO_3 + 0.5 M KHCO_3 was employed as electrolyte.

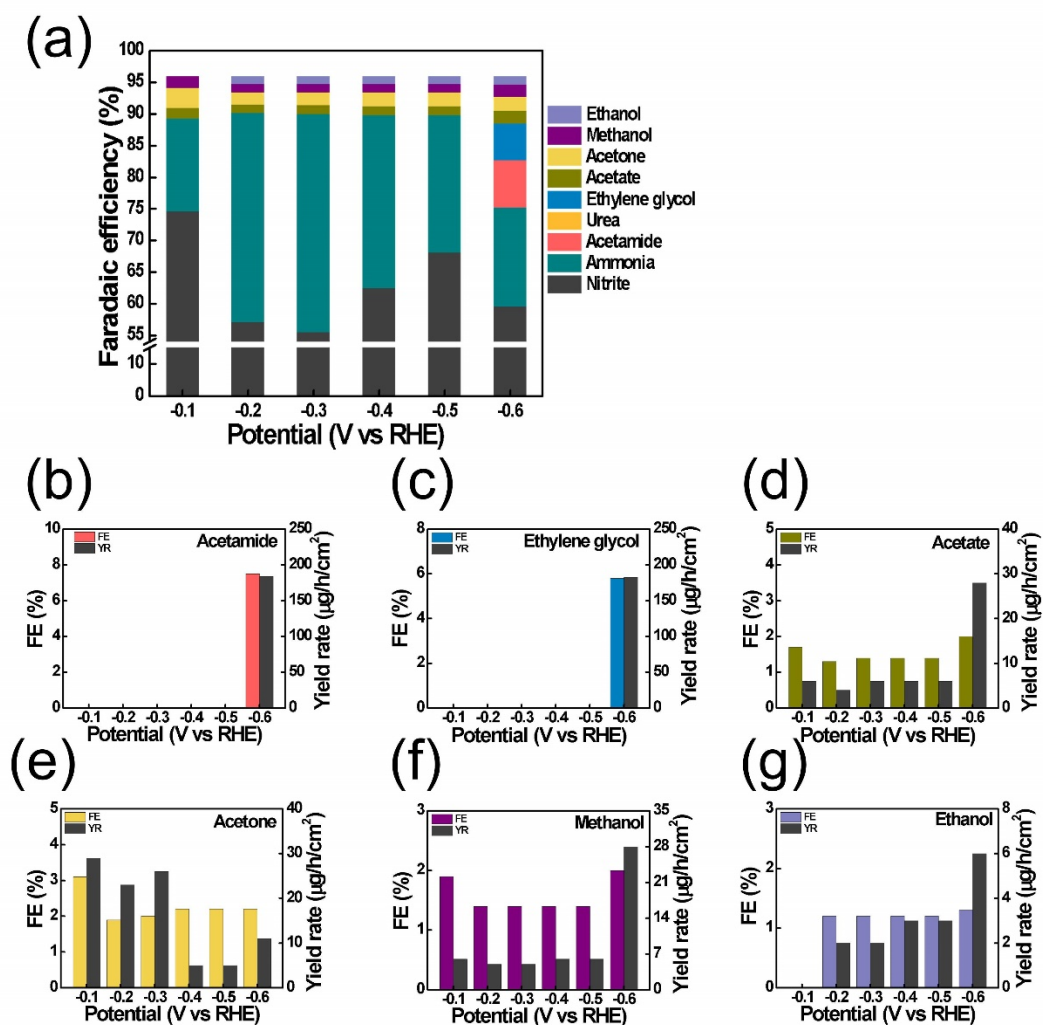


Figure S12. Product distribution, Faraday efficiency and yield rates of products formed at CuNi NDs when 0.05 M KNO₃ + 0.5 M KHCO₃ was employed as electrolyte.

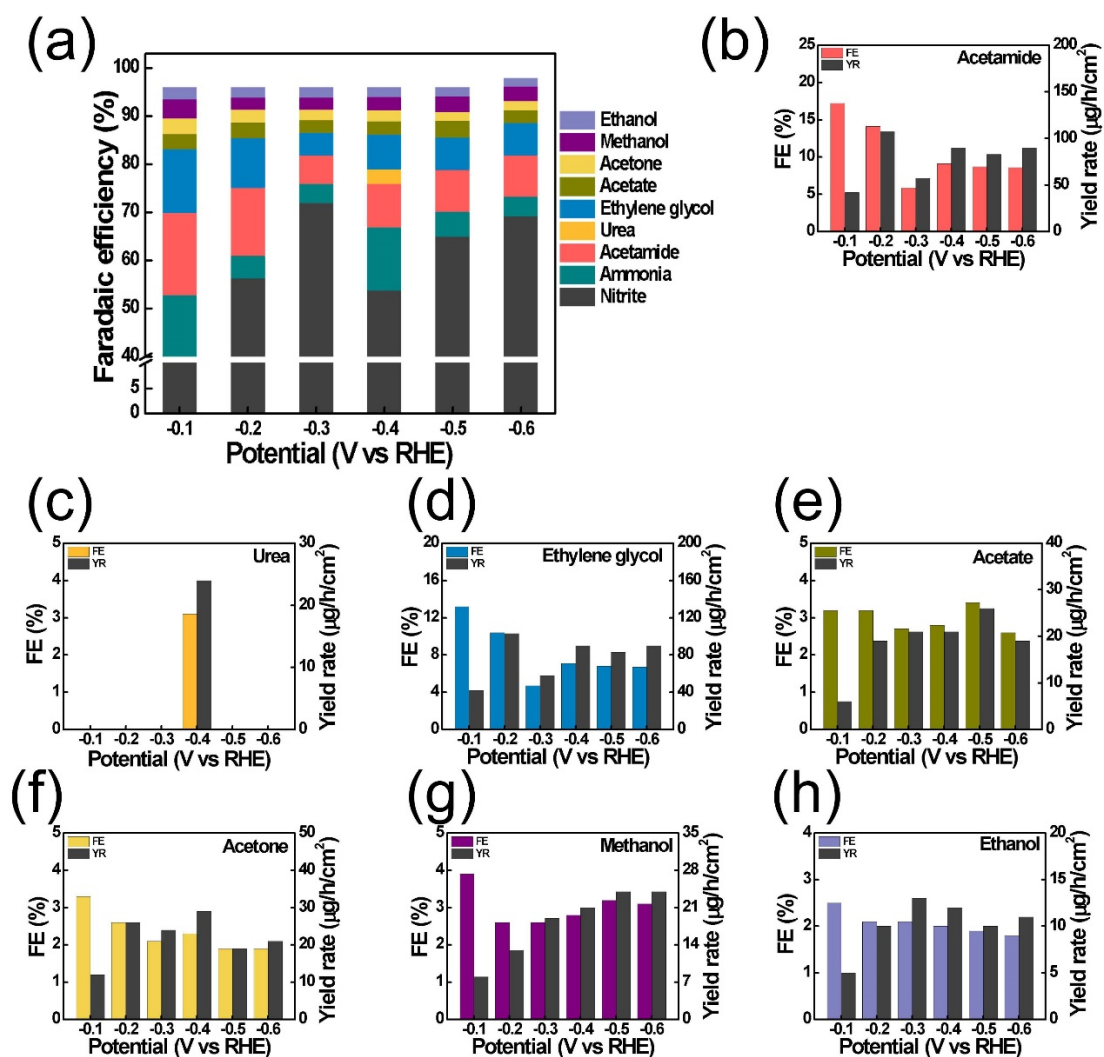


Figure S13. Product distribution, Faraday efficiency and yield rates of products formed at CuNi NDs when 0.05 M KNO₃ + 0.1 M KHCO₃ was employed as electrolyte.

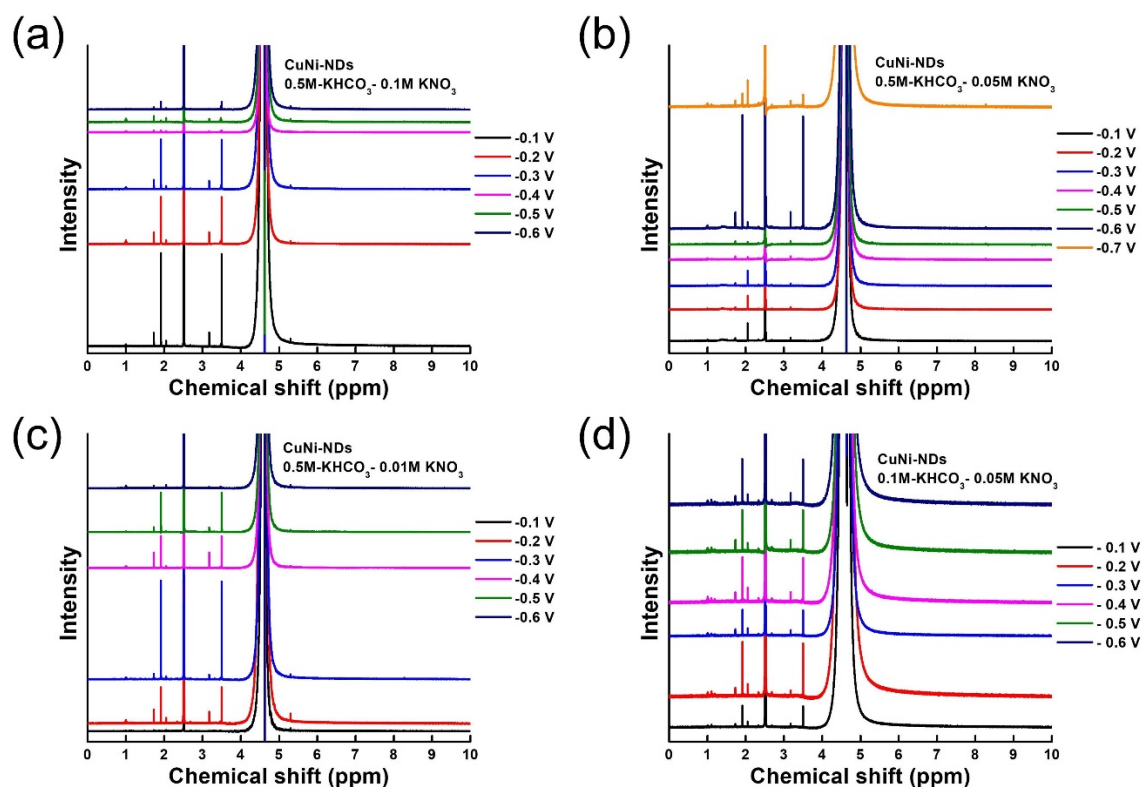
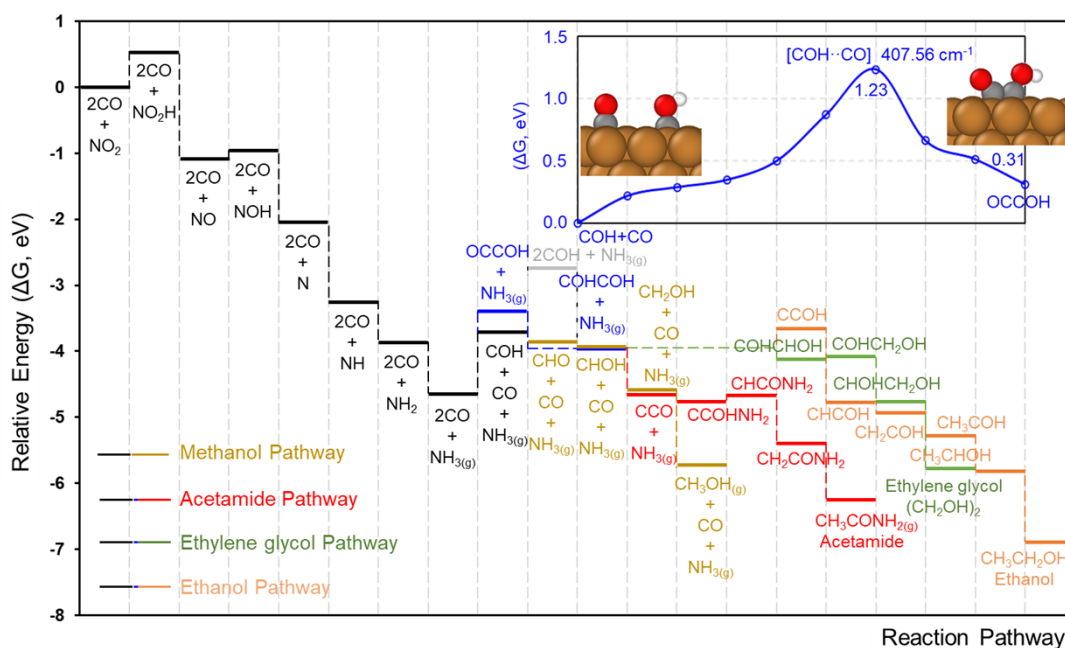


Figure S14. NMR spectra of test samples in different electrolytes at different potentials on CuNi NDs surface. (All the voltages are provided against RHE.) The peaks at 1.0, 1.7, 1.9, 2.1, 3.1 and 3.5 are indexed to ethanol, acetate, acetamide, acetone, methanol, and ethylene glycol, respectively. The peaks at 4.5 and 2.5 ppm are ascribed to water and dimethyl sulfoxide-d₆ (DMSO), respectively. DMSO was added as an internal reference.

To further clarify the catalytic activity for forming N-HC compounds on the Ni(111) surfaces, we have compared the reduction reaction of CO_x and NO_x on Cu(111) and NiCu(111) surfaces by using DFT calculation. The calculation results are shown in Figure S15 and S16 below. Our calculation results show that the NO_x can be preferentially reduced to NH_3 with a thermodynamically favorable process on Cu(111), NiCu(111) and Ni(111) surfaces. Notably, Compared to the Cu(111) surface, the formation of COH intermediate along the CO_2RR pathway would suppress the C1 production¹⁻³ and possible yield more C2 products on NiCu(111) and Ni(111) surfaces. It is well known that the interaction between CO and the catalyst has a critical correlation with the activity of CO_2RR .⁴ Therefore, according to the electronic analysis results of NiCu(111) and Ni(111) surfaces (Figure S17), we observed that when a small amount of Cu remains on the Ni(111) surface, the activity of Ni will be improved (d-band center (ϵ_d) increases from -1.61 eV to -1.42 eV), which would lead the adsorption energies of CO on NiCu(111) is possible larger that of Ni(111). With adsorption energies of -2.23 eV for NiCu(111) and -1.81 eV for Ni(111). However, the high adsorption energy of CO on NiCu(111)



will lead to a thermodynamically unfavorable trend of the $\text{CO} \rightarrow \text{COH}$ step.

Figure S15. Potential energy diagrams for the formation of representative compounds including acetamide, ethylene glycol, and ethanol on Cu(111) surface.

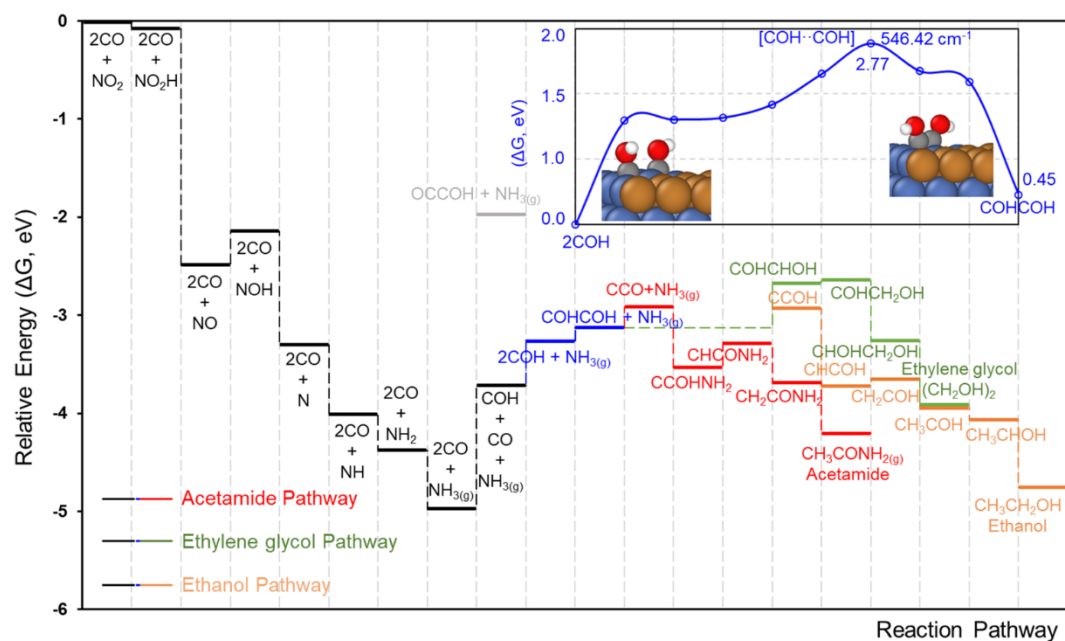


Figure S16. Potential energy diagrams for the formation

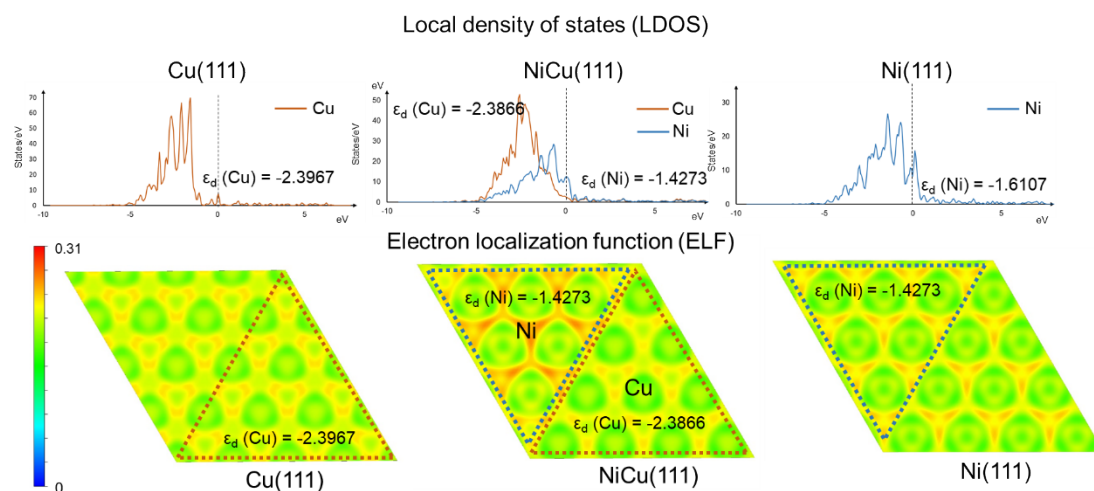


Figure 17. Local density of states (LDOS) diagram and Electron localization function (ELF) plots on Cu(111), CuNi(111) and Ni(111) surfaces.

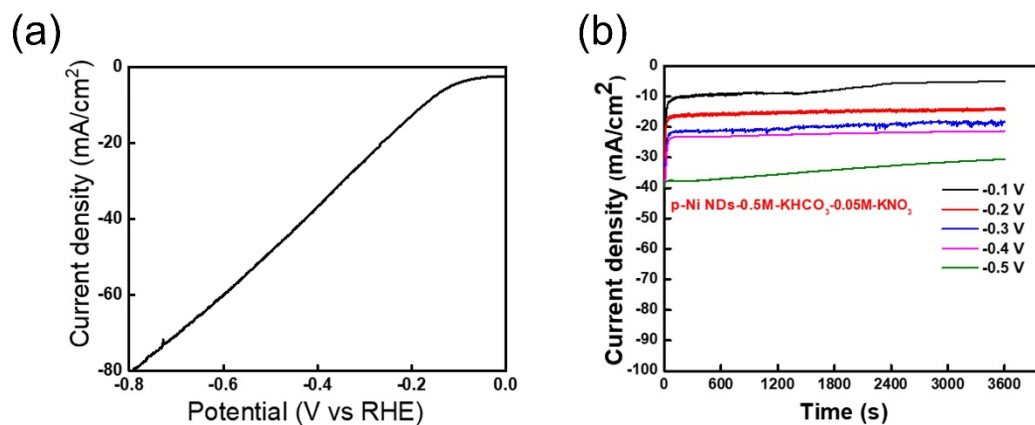


Figure S18. (a) LSV and (b) IT curves of p-Ni NDs for C-N and C-C coupling reactions.

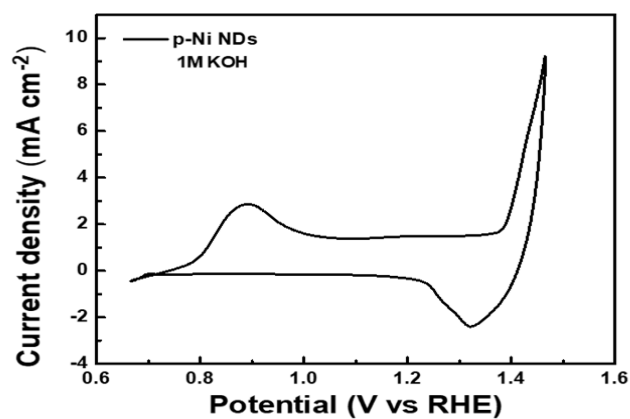


Figure S19. CV plot of electrochemical active surface area of p-Ni NDs. We have carried out electrochemical active surface area of p-Ni NDs and it was found to be 73.28 cm².

Table S2. Comparative table of electrocatalytic C – N coupling reactions yielding acetamide and urea.

Catalyst	Carbon source	Nitrogen source	Product	Potential (V vs RHE)	Faradaic efficiency	Yield rate (mmol/g/h)	Quantification method	Ref
p-Ni NDs	CO ₂ (KHCO ₃)	NO ₃ ⁻ (KNO ₃)	Acetamide	-0.3	23.2 %	11.13	¹ H NMR	This work
Cu NPs	CO (KOH)	NH ₃	Acetamide	-0.68	38.0 %	-	¹ H NMR GCMS	5
In(OH) ₃ -S	CO ₂	NO ₃ ⁻ (KNO ₃)	Urea	-0.6	53.4 %	8.87	Diacetyl monoxime	6
Cu-TiO ₂ -Vo	CO ₂ (KHCO ₃)	NO ₃ ⁻ (KNO ₂)	Urea	-0.4	43.1 %	20.8	Urease	7
Te-doped Pd	CO ₂ (KHCO ₃)	NO ₃ ⁻ (KNO ₂)	Urea	-1.1	12.2 %		Urease	8
BiFeO ₃ / BiVO ₄	CO ₂ (KHCO ₃)	N ₂	Urea	-0.4	17.18 %	4.94	¹ H NMR Diacetyl monoxime	9
CuPc NTs	CO ₂ (KHCO ₃)	N ₂	Urea	-0.6	12.99 %	2.39	Diacetyl monoxime	10
Bi/BiVO ₄	CO ₂ (KHCO ₃)	N ₂	Urea	-0.4	12.55 %	5.91	¹ H NMR Diacetyl monoxime	11
Zn NBs	CO ₂ (KHCO ₃)	NO	Urea	-0.92	11.16 %	15.13	¹ H NMR HPLC	12
Pd ₁ Cu ₁ /TiO ₂	CO ₂ H ₂ O	N ₂	Urea	-0.4	8.92 %	3.36	¹ H NMR Diacetyl monoxime	13

References

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