Supporting Information

3D ternary Ni_xCo_{2-x}P/C nanoflower/nanourchin arrays grown on HCNs: as Highly Efficient Bi-functional Electrocatalyst for Boosting Hydrogen Production via Urea Electrooxidation Reaction.

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1. EXPERIMENTAL SECTION

1.1. Materials

Pyrrole and aniline (Merck) were purified by the distillation under the reduced pressure and stored in a refrigerator before utilization. Ammonium persulfate (APS), TX-100, Cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), Nickel (II) chloride (NiCl₂), N,N-dimethylformamide (DMF), ethanol, Sodium hypophosphite (NaH₂PO₂.H₂O), potassium hydroxide (KOH), and urea were purchased from Merck. Nafion (5 wt%) and 1,4-Benzene dicarboxylic acid (H₂BDC, 95%) was obtained from Aldrich. All aqueous solutions were prepared using ultra-pure deionized water (18.2 MΩ, Zolalan Sharif Company, Tehran, Iran).

1.2. Instruments and Materials Characterizations

Tube furnace (ATE 1100L, Atra, Iran) was used for the thermal pyrolysis of PPCA and also for the carbonization/phosphorization of NiCo/MOF@HCNs, NiCo/MOFs, Ni/MOFs, and Co/MOFs samples. The crystalline structures of the as-prepared samples were characterized by using X-ray diffraction (XRD, X'Pert MPD, PHILIPS, equipped with Co Ka radiation, 1.78897 Å, at 40 kV and 40 mA with a step size of 0.02 s^{-1}). Field emission scanning electron microscope (FE-SEM, model VEGATescan, Razi Metallurgical Research Center, Tehran, Iran) equipped with energy-dispersive X-ray spectroscopy (EDX) were used to evaluate the structure, morphology, chemical composition and elemental quantitative analysis of the prepared samples. The transmission electron microscopy (TEM) investigations were carried out on a PHILIPS CM 200 instrument. X-ray photoelectron microscopy (XPS) measurements were made on (X-Ray 8025, Bestec, Germany) with Mg K α radiation (hv = 1253.6 eV). The specific surface area was calculated by using the Brunauer-Emmett-Teller (BET) formula based on the N₂ adsorptiondesorption isotherms measured on a Builder SSA-4200 instrument. Raman spectra were collected using Raman spectrometer (Senterra-Bruker) with a 785 nm laser excitation. Fouriertransform infrared spectroscopy (FT-IR) data were obtained using an ABB Bomem MB-100 FT-IR spectrophotometer using KBr pellets. The Ni and Co loading on the prepared composites were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Vista-Pro, Varian Australia) after dissolution with aqua regia.

1.3. Electrochemical Measurements

Electrochemical studies were performed in a three-electrode cell containing glassy carbon electrode (GCE) (d = 2.0 mm and 0.0314 cm^2 geometric surface area, Azar electrode Co., Urmia, Iran) and carbon cloth (CC), a Pt wire and Ag/AgCl (saturated KCl) as, working, counter and reference electrodes, respectively. Electrochemical experiments including, cyclic voltammetry and chronoamperometry were performed by using a Potentiostat/Galvanostat (SAMA 500-C Electrochemical analysis system, Sama, Iran) coupled with a personal computer. Electrochemical impedance spectroscopy (EIS) measurements were performed by means of an electrochemical workstation (Autolab PGSTAT 204, Metrohm, Netherlands) in the frequency range from 1 Hz to 100 kHz with a bias potential of 1.45 V (vs. RHE). For HER, all electrochemical experiments were performed in 50 mL aqueous solution of 1.0 M KOH as the electrolyte. Since the urea concentration in human urine is around 0.33 M and the most published papers have chosen this concentration as the benchmark, therefore, this concentration was used for UOR tests. Hence, all electrochemical experiments were also carried out in aqueous solutions containing 1.0 M KOH and 0.33 M urea. The apparent surface area of the electrode was used to calculate the current

density (j mA cm⁻²). Moreover, the overpotential at the current density of 10 mA cm⁻² (η_{10}) was selected as an index for comparison of the obtained results. Also, the potentials reported in this work were calibrated to RHE, using the following equation: E (RHE) = E (Ag/AgCl) + (0.197 + 0.059 pH) V. The linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV s⁻¹. All experiments were carried out at 25 °C. The electrical double layer capacitance (C_{dl}) of the samples was obtained from CV plots in a small potential range of 0.06 – 0.16 V (vs. Ag/AgCl).

1.4. Preparation of PPCA and HCNs

HCNs were successfully prepared by the direct carbonization of hollow copolymer nanospheres, according to the reported work [33], without any tedious templating and activation procedures. In this regard, poly (pyrrole-co-aniline) (PPCA) was obtained through the in-situ emulsion polymerization of a mixture of aniline and pyrrole using TX-100, as a non-ionic emulsifier and APS as an oxidant in an aqueous solution. In a typical protocol, 0.38 mL aniline and 0.29 mL pyrrole were added to 60 mL deionized water containing a certain amount (0.02, 0.04, 0.06 and 0.08 g) of Triton X-100. In the following, the prepared solution was kept in ice-bath at 5 °C under magnetic stirring for 30 min to gain a homogeneous mixture. Then, for the chemical oxidative polymerization process, a precooled aqueous solution of APS (1.9 g APS dissolved in 15 mL deionized water) at 0 °C was added to the mentioned solution in one portion and allowed the solution stirred for another 0.5 min to make sure for perfect mixing. Finally, the solution was kept at 0 °C for 24 h without agitation and after that, the resulting PPCA was washed by double-distilled water until the filtrate became colorless and dried under vacuum at 60 °C for 24 h. Then, the carbonization process of as obtained PPCA was carried out in a furnace under Ar flow

at 800 °C for 2 h with a heating rate of 2 °C min⁻¹. The solids were cooled to ambient temperature to obtain the HCNs black powder.

1.5. Preparation of Urchin-Like and Flower-Like NiCo/MOF@HCNs and Ni_xCo_{2-x}P/C@HCNs

In this work urchin-like and flower-like NiCo/MOF were synthesized through adjusting the Ni/Co ratio and a simple hydrothermal process according to the previously reported approach with this difference that the as-prepared HCNs was employed as the core for the growth of MOFs [1, 2]. At first, a homogenous solution containing 20 mg HCNs and 30 mL equal portions of ethanol and DMF prepared with vigorous magnetic stirring and sonication for 1 h. Then, $Co(NO_3)_2 \cdot 6H_2O$ (x mmol), NiCl₂ (y mmol) (x + y = 5) and 1.0 mmol H₂BDC were added to HCNs solution with vigorous magnetic stirring for 10 min at room temperature to form a homogeneous mixture solution. In the next step, the solution was transferred into a Teflon-lined autoclave and the autoclave was kept at 135 °C for 15 h. Then, the sample was removed from the oven and allowed to cool to room temperature. The resulting precipitate was thoroughly washed several times with ethanol and then drying at 60 °C for 12 h. It should be noted that for flowerlike and urchin-like NiCo/MOF@HCNs, the molar ratios of Ni²⁺/Co²⁺ were adjusted to be (4:1) and (1:4), respectively. The corresponding products were labeled as flower-like NiCo/MOF@HCNs (4-1), and urchin-like NiCo/MOF@HCNs (1-4). Also, for comparison, NiCo/MOF with Ni²⁺/Co²⁺ (4:1) and (1:4) metal ratio, Ni-MOF, Co-MOF were synthesized with the same procedure as described above without the presence of HCNs. The corresponding products were denoted as petal-like NiCo/MOF (4-1), and needle-like NiCo/MOF (1-4), sheetlike Ni-MOF, break-like Co-MOF, respectively. In the following, the Ni_xCo_{2-x}P/C@HCNs (4:1,

1:4) and Ni_xCo_{2-x}P/C (4:1, 1:4), Ni₂P/C, Co₂P/C composite materials were prepared through the carbonization and phosphorization of precursors. In a typical synthesis, 100 mg of the prepared samples were transferred to a ceramic boat in a quartz tube, which was fixed in the center of the tube furnace. Then, 200 mg NaH₂PO₂.H₂O was put in another ceramic boat and placed in the tube furnace with the distance from the samples. The steady flow of Ar was used to exhaust air for 30 min, and the temperature of the furnace was raised to 400 °C with a heating rate of 2 °C min⁻¹ for 2 h. After cooling to room temperature, the prepared samples were collected.

Preparation of Working Electrodes

The homogeneous suspension (1.0 mg/mL) of electrocatalyst inks were prepared by mixing 4 mg of the MOF-derived prepared catalysts with 20 μ L Nafion solution (5 wt%) and 980 μ L of aqueous ethanol solution (1:1) under ultrasonic agitation over 1 h. Prior to the GCE modification, its surface was hand-polished successively with alumina slurry in water by using a polishing cloth until the electrode surface had a mirror finish and then ultrasonically cleaned for 2.0 min in ethanol. Then, the electrode was rinsed thoroughly with distilled water. A 4 μ L portion of the electrocatalyst ink was loaded on the electrode surface by a microliter syringe and then dried at 60 °C for up to 10 min to evaporate the water. The catalyst loading density on the working electrode surface was 0.5 mg cm⁻².

Preparation of Alkaline Urea Electrolyzer

For performing this experiment, the commercial CC was used as the substrate. Prior to the modification, commercial CC cut to 1×2 cm⁻² and then cleaned by sonication sequentially in acetone, 3 M HCl solution, deionized water, and ethanol, respectively. After being dried, a 100

 μ L portion of catalyst ink (described in section 2.6) was carefully dropped onto the CC electrode surface (1 × 1 cm⁻²). Also, similar to GCE, the catalyst loading density was kept at 0.5 mg cm⁻². For more clarity, the sequential synthesize processes applied for the mentioned electrocatalysts are shown in scheme 1.



Scheme 1. Schematic illustration of the synthetic process of HCNs, NiCo/MOF@HCNs, and Ni $_xCo_{2-x}P/C@HCNs$



Fig. S1. SEM images with different magnification (A, C) PPCA and (B, D) HCNs.



Fig. S2. TEM image of PPCA (A) and HCNs (B).



Fig. S3. SEM images of PPCA with different TX-100 concentration, (a) 0.02 g; (b) 0.04 g; (c)

0.06 g; (d) 0.08 g.



Fig. S4. Energy dispersive spectra and elemental mapping of PPCA and HCNs.



Fig. S5. Raman spectra of HCNs (A), TGA curves of PPCA and HCNs (B, C), N₂ adsorption and desorption isotherms of PPCA and HCNs (D) and the pore size distributions of the PPCA and HCNs (E).



Fig. S6. Energy dispersive spectra and elemental mapping of NiCo/MOF@HCNs (1:4),

NiCo/MOF@HCNs (4:1) , $Ni_{0.4}Co_{1.6}P/C@HCNs$ and $Ni_{1.6}Co_{0.4}P/C@HCNs.$



Fig. S7. SEM images of (A) NiCo/MOF (1:4), (B) Ni_{0.4}Co_{1.6}P/C, (C) NiCo/MOF (4:1), (D) Ni_{1.6}Co_{0.4}P/C, (E) Ni/MOF, (F) Ni₂P/C, (G) Co/MOF and (H) Co₂P/C.



Fig. S8. Energy dispersive spectra of Ni/MOF, Co/MOF, NiCo/MOF (4:1), NiCo/MOF (1:4),

Ni₂P/C, Co₂P/C, Ni_{1.6}Co_{0.4}P/C, Ni_{0.4}Co_{1.6}P/C.



Fig. S9. The nitrogen adsorption/desorption isotherms at 77 K: (A) NiCo/MOF@HCNs (1:4), NiCo/MOF@HCNs (4:1), (B) Ni_{0.4}Co_{1.6}P/C@HCNs, Ni_{1.6}Co_{0.4}P/C@HCNs. The BJH pore-size distribution curves of (C) NiCo/MOF@HCNs (1:4), NiCo/MOF@HCNs (4:1), (D) Ni_{0.4}Co_{1.6}P/C@HCNs, Ni_{1.6}Co_{0.4}P/C@HCNs.



Fig. S10. The CV curves of (A) Ni/MOF, NiCo/MOF (4:1) and NiCo/MOF@HCNs (4:1) (B) Ni₂P/C, Ni_{1.6}Co_{0.4}P/C and Ni_{1.6}Co_{0.4}P/C@HCNs, (C) Co/MOF, NiCo/MOF (1:4) and NiCo/MOF@HCNs (1:4), (D) Co₂P/C, Ni_{0.4}Co_{1.6}P/C, and Ni_{0.4}Co_{1.6}P/C@HCNs in 1.0 M KOH solution at v = 50 mVs⁻¹.



Fig. S11. (A) LSV curves of Ni-NiO/C and Co-CoO/C on GCE in 1.0 M KOH with 0.33 M urea at a scan rate of 5 mV s⁻¹. (B) Tafel plots for LSV curves presented in (A). (C) Nyquist plots for Ni-NiO/C and Co-CoO/C measured in 1.0 M KOH with 0.33 M urea electrolyte. (D) Current density as a function of the scan rate to give the double-layer capacitance (C_{dl}). (E) LSV curves of Ni-NiO/C and Co-CoO/C on GCE in 1.0 M KOH at a scan rate of 5 mV s⁻¹. (F) Tafel plots for LSV curves presented in (E).



Fig. S12. (A) LSV curves of Ni_{1.6}Co_{0.4}P/C@HCNs in 1.0 M KOH with 0.05, 0.15, 0.33, 0.5, 0.7, and 0.9 M urea. Inset: Plot of current density at 1.6 V vs. urea concentration (0.05-0.9 M). (B) LSV curves of Ni_{1.6}Co_{0.4}P/C@HCNs at different scan rates (5-50 in 1.0 mVs⁻¹) M KOH with 0.33 M urea. Inset: Plot of current density at 1.6 V vs scan rate.

Composite	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	
NiCo/MOF@HCNs (4-1)	1597	0.72	0.51	
NiCo/MOF@HCNs (1-4)	1323	0.63	0.52	
Ni1.6Co0.4P/C@HCNs	873	0.43	7.37	
Ni _{0.4} Co _{1.6} P/C@HCNs	730	0.28	6.35	

Table S1. Surface areas and pore distribution of the prepared MOFs and the related composites

Prepared catalysts	Potential at 10 mA cm ⁻² (V vs. RHE)	Current density at 1.6 V (vs. RHE) (mA cm ⁻²)	Tafel Slope mV dec ⁻¹
Ni _{1.6} Co _{0.4} P/C@HCNs	1.331	136.3	74.6
Ni _{0.4} Co _{1.6} P/C@HCNs	1.362	114.2	82.8
Ni _{1.6} Co _{0.4} P/C	1.375	70.2	97.7
Ni _{0.4} Co _{1.6} P/C	1.414	52.9	108.9
Ni ₂ P/C	1.524	23.3	154.4
Co ₂ P/C	1.551	18.1	186.4
Ni-NiO/C	1.532	22.4	190.1
Co-CoO/C	1.562	15.2	198.2

Table S2. Comparison of the UOR activity between prepared composites.

Catalyst	Urea Conc. (M)	Current density (mA cm ⁻²)	Potential (V vs. RHE)	Ref.
Ni ₂ P/Carbon cloth (array)	0.5	10	1.38	[3]
Ni ₃ N/Carbon cloth (array)	0.33	10	1.35	[4]
NiCo ₂ S ₄ NS/Carbon cloth	0.33	10	1.31	[5]
NiCo ₂ O ₄ NS/Carbon cloth	0.33	10	1.35	[5]
Ni-MOF/Glassy carbon	0.33	10	1.36	[6]
Ni(OH) ₂ /Glassy carbon	0.33	10	1.46	[6]
Zn _{0.08} Co _{0.92} P/Ti mesh (array)	0.5	50	1.48	[7]
CE-NiFe/Ni foam (film)	0.33	10	1.39	[8]
MnO ₂ /MnCo ₂ O ₄ /Ni foam	0.5	10	1.33	[9]
Ni-Co/Glassy carbon	0.33	10	1.53	[10]
NiMoS/Ti mesh (array)	0.5	10	1.38	[11]
Graphene-Ni(OH) ₂ /Glassy carbon	0.33	10	1.52	[12]
LaNiO ₃	0.33	10	1.39	[13]
CoS ₂ /Ti mesh (array)	0.30	10	1.4	[14]
Se-Ni(OH)2@NiSe/Ni foam	0.33	10	1.36	[15]
Ni-Cr/Glassy carbon	0.33	10	1.38	[16]
NiO-Fe ₂ O ₃ /Graphene aerogel	0.33	10	1.40	[17]
Ni1.6Co0.4P/C@HCNs/GCE	0.33	10	1.33	This work
Ni _{0.4} Co _{1.6} P/C@HCNs/GCE	0.33	10	1.36	This work

 Table S3. Comparison of the UOR activity between recently reported electrode electrocatalyst

Prepared catalysts	Potential at 10 mA cm ⁻² (V vs. RHE)	Tafel Slope mV dec ⁻¹
Ni _{1.6} Co _{0.4} P/C@HCNs	-0.145	52.3
Ni _{0.4} Co _{1.6} P/C@HCNs	-0.170	62.3
Ni _{1.6} Co _{0.4} P/C	-0.200	70.6
Ni _{0.4} Co _{1.6} P/C	-0.210	75.3
Ni ₂ P/C	-0.229	90.4
Co ₂ P/C	-0.250	96.4
Ni-NiO/C	-0.270	98.4
Co-CoO/C	-0.288	99.4

Table S4. Comparison of the HER activity between prepared composites.

Catalyst	Current density (mA cm ⁻²)	η at corresponding j (mV)	Ref.
NiCo ₂ S ₄ NS	10	181	[5]
Zn _{0.08} Co _{0.92} P/TM	10	67	[7]
Mn-Co-P/Ti	10	76	[18]
Ni-Co-P-300	10	150	[19]
u-CoP/Ti	10	60	[20]
Ni ₂ P	10	205	[21]
FeNi ₃ N	50	202	[22]
Fe _{0.1} -NiS ₂	10	243	[23]
Fe-CoP/Ti	10	78	[24]
CoP hollow polyhedron	10	400	[25]
NiFe LDH	10	251	[26]
EG/Co _{0.85} Se/NiFe-LDH	10	349	[27]
NiFeS	10	180	[28]
CoP/G	10	154	[29]
CNTs@Co-S	10	190	[30]
NiS ₂	10	243	[31]
Ni _{1.6} Co _{0.4} P/C@HCNs	10	145	This work
Ni _{0.4} Co _{1.6} P/C@HCNs	10	170	This work

Table S5. Comparison of HER performance of prepared composites in 1.0 M KOH with othernewly reportedHER electrocatalysts

Current density Urea Conc. **Bifunctional Catalyst** Voltage Ref. (mA cm⁻²) **(M)** Ni₂P NF/CC 0.5 50 1.35 [3] Ni₃N/Carbon cloth (array) 0.33 10 1.44 [4] NiCo₂S₄ NS/Carbon cloth 10 0.33 1.45 [5] [9] MnO₂/MnCo₂O₄/Ni foam 0.5 10 1.55 NiMoS/CC 0.5 10 1.59 [11] CoS_2/Ti mesh (array) 0.3 10 1.59 [14] MnO₂/Ni foam||CoP_x/Ni foam 0.5 10 [32] 1.41 NiCoP NS/CCj 0.33 20 1.25 [33] Ni₂P/CFC 0.33 10 1.44 [34] Ni/C-1 0.33 10 1.60 [35] Ni₂P/Fe₂P/NF 0.5 10 1.47 [36] Ni1.6Co0.4P/C@HCNs/CC 0.33 10 1.47 This work Ni_{0.4}Co_{1.6}P/C@HCNs/CC 0.33 10 1.53 This work

Table S6. Comparison of the overall urea-electrolysis efficiency for prepared composites with other newly-reported highly active bifunctional catalysts

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