Supporting Information

$NiAg_{0.4}$ 3D porous nanoclusters with epitaxial interfaces exhibiting Pt like activity towards hydrogen evolution in alkaline medium

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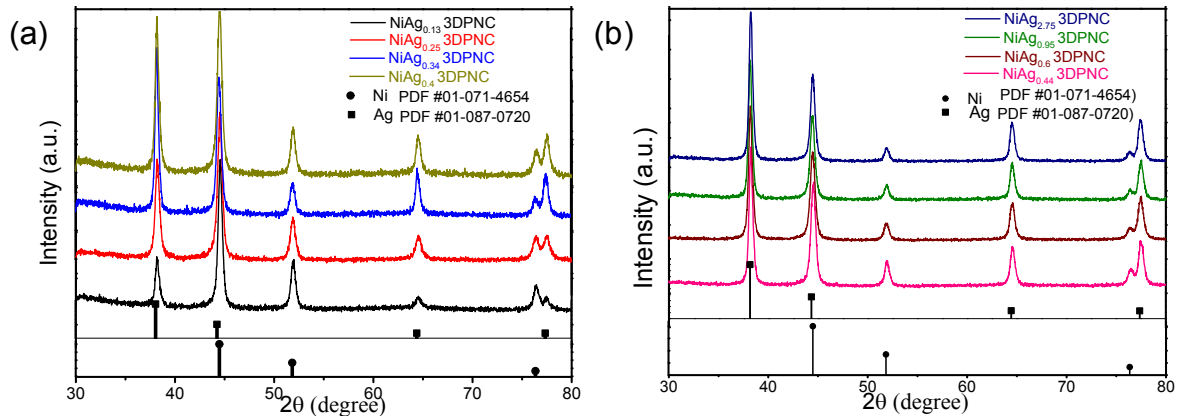

Fig. S1 XRD patterns of (a) $NiAg_{0.13}$ 3DPNC, $NiAg_{0.25}$ 3DPNC, $NiAg_{0.34}$ 3DPNC, and $NiAg_{0.4}$ 3DPNC, and (b) $NiAg_{0.44}$ 3DPNC, $NiAg_{0.6}$ 3DPNC, $NiAg_{0.95}$ 3DPNC, and $NiAg_{2.75}$ 3DPNC.

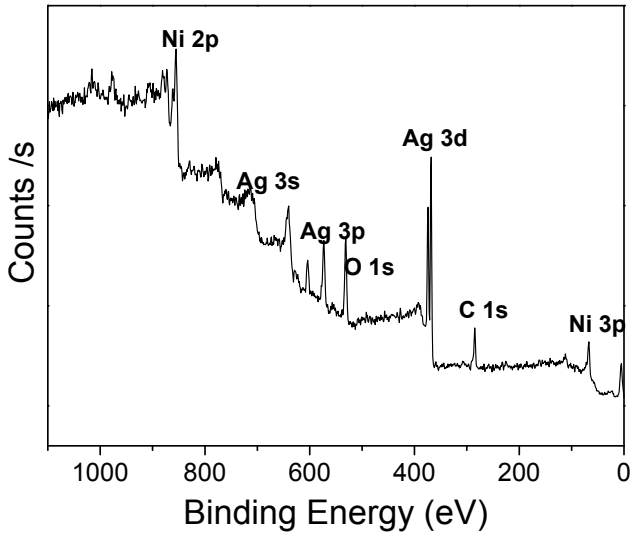

Fig. S2 XPS survey spectrum of $NiAg_{0.4}$ 3DPNC.

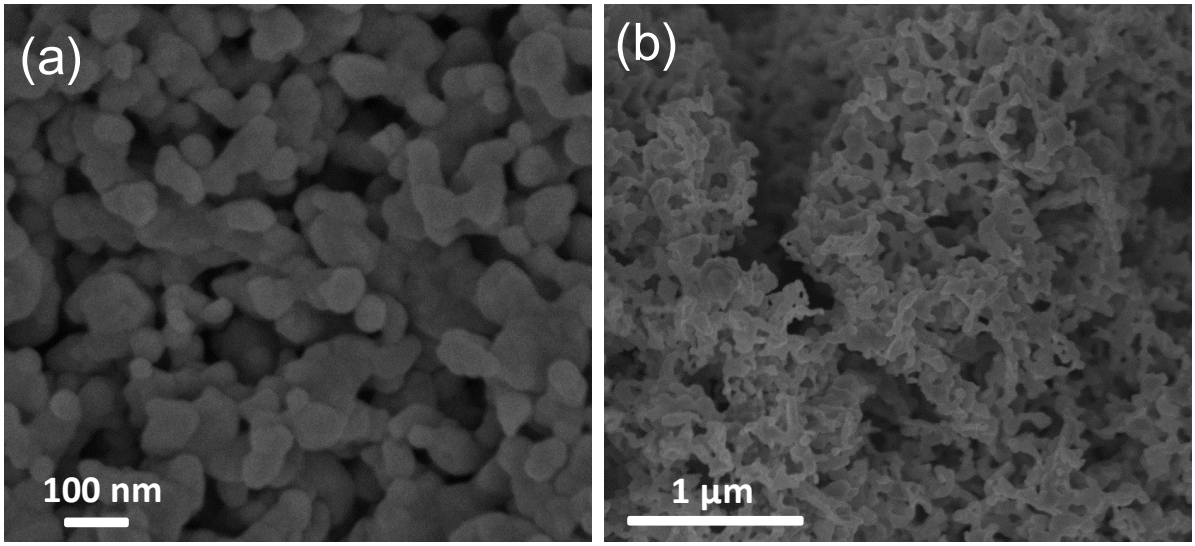

Fig. S3 FESEM images of (a) Ag NPs, (b) Ni 3DPNC.

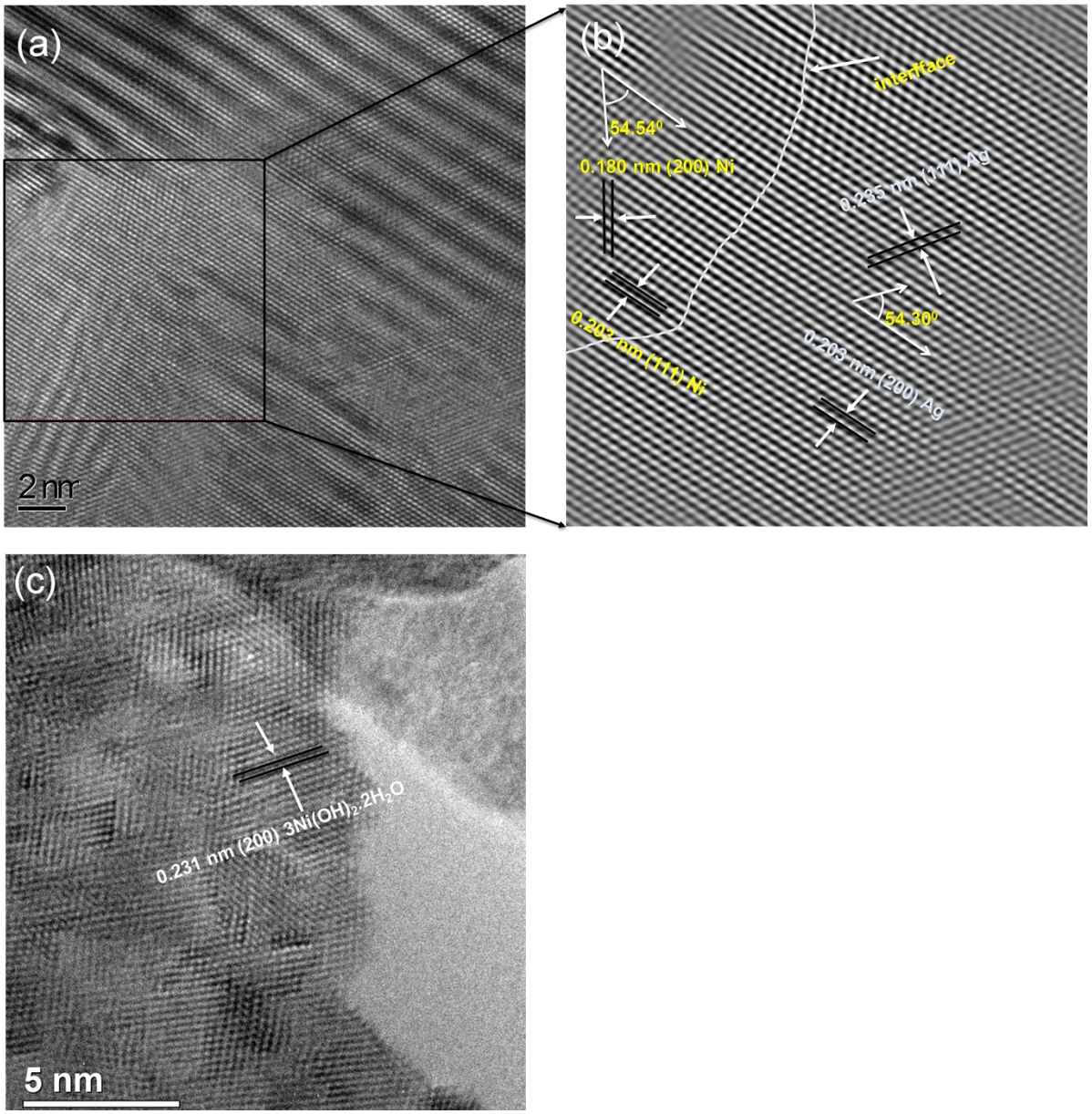

Fig. S4 HRTEM image of (a) $NiAg_{0.4}$ 3DPNC, (b) FFT analyzed image of $NiAg_{0.4}$ 3DPNC, and (c) HRTEM image of $Ag/Ni(OH)_2.2/3H_2O$ precursor.

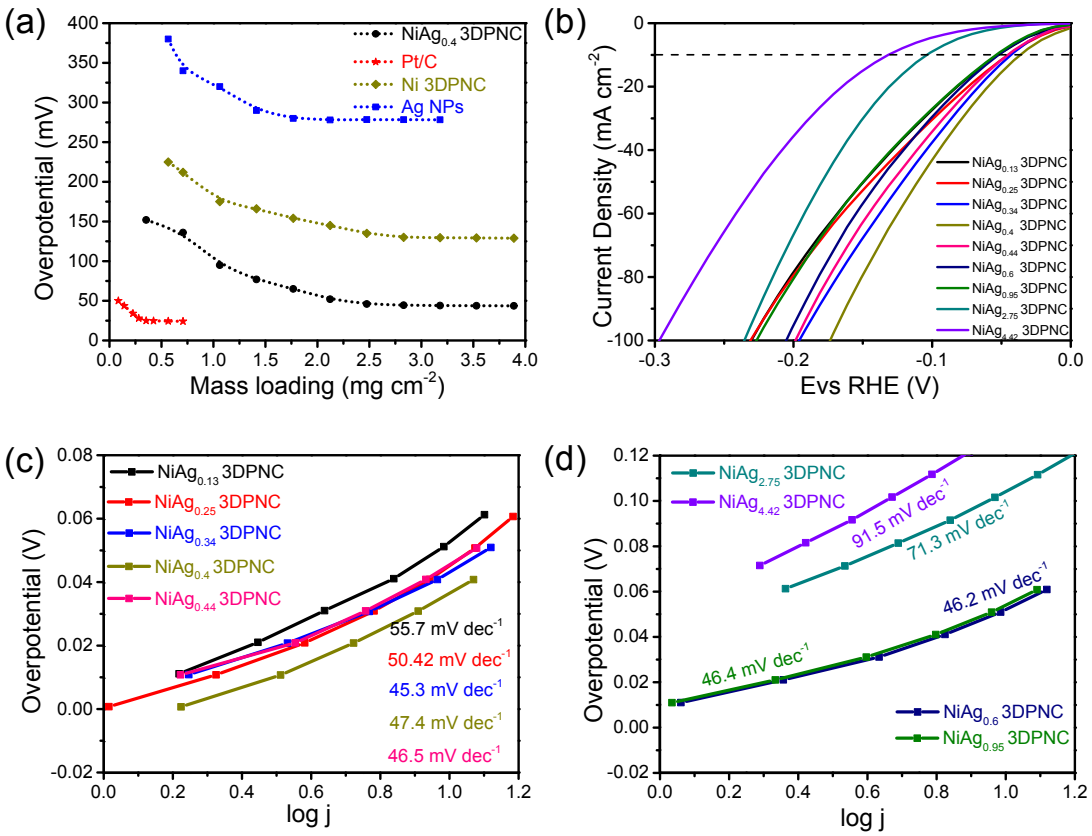

Fig. S5 (a) Variation of overpotential with catalyst loading for Ni 3DPNC, Ag NPs, $NiAg_{0.4}$ 3DPNC, and Pt/C catalysts. (b) HER polarization curves of $NiAg_x$ 3DPNC with varying Ni to Ag ratios without iR correction and their corresponding (c-d) Tafel plots.

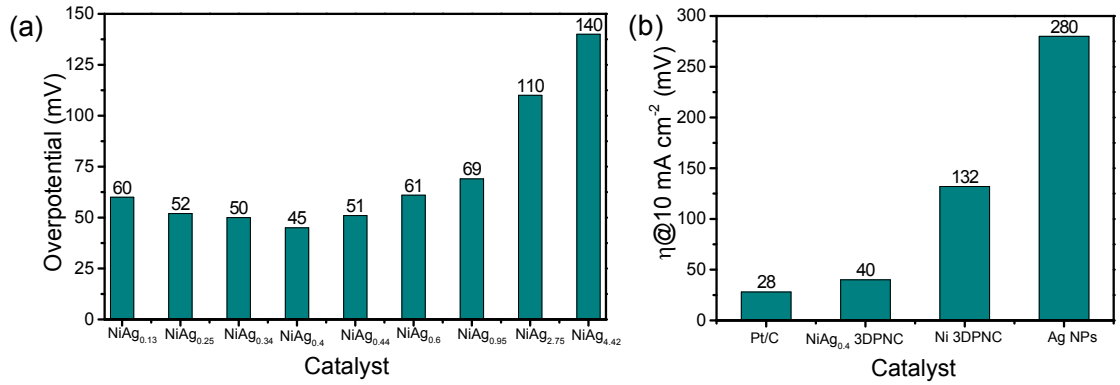

Fig. S6 Variation of overpotential at 10 mA cm^{-2} for (a) synthesized catalysts with varying Ag composition, (b) Pt/C, $NiAg_{0.4}$ 3DPNC, Ni 3DPNC and Ag NPs.

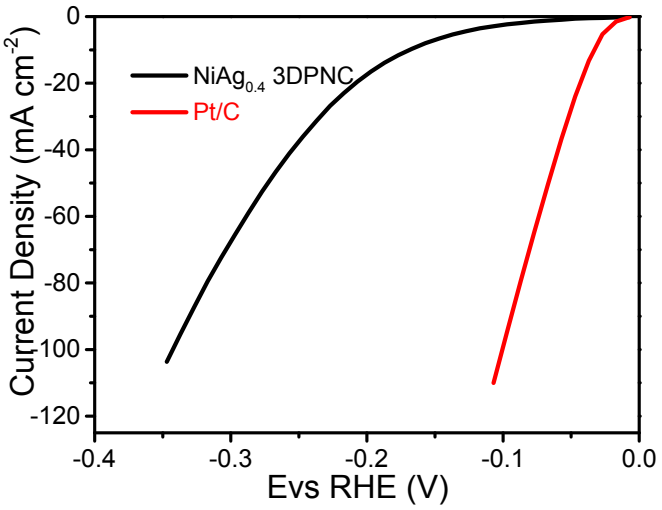

Fig. S7 HER polarization curves for $NiAg_{0.4}$ 3DPNC and Pt/C in 0.5 M H_2SO_4.

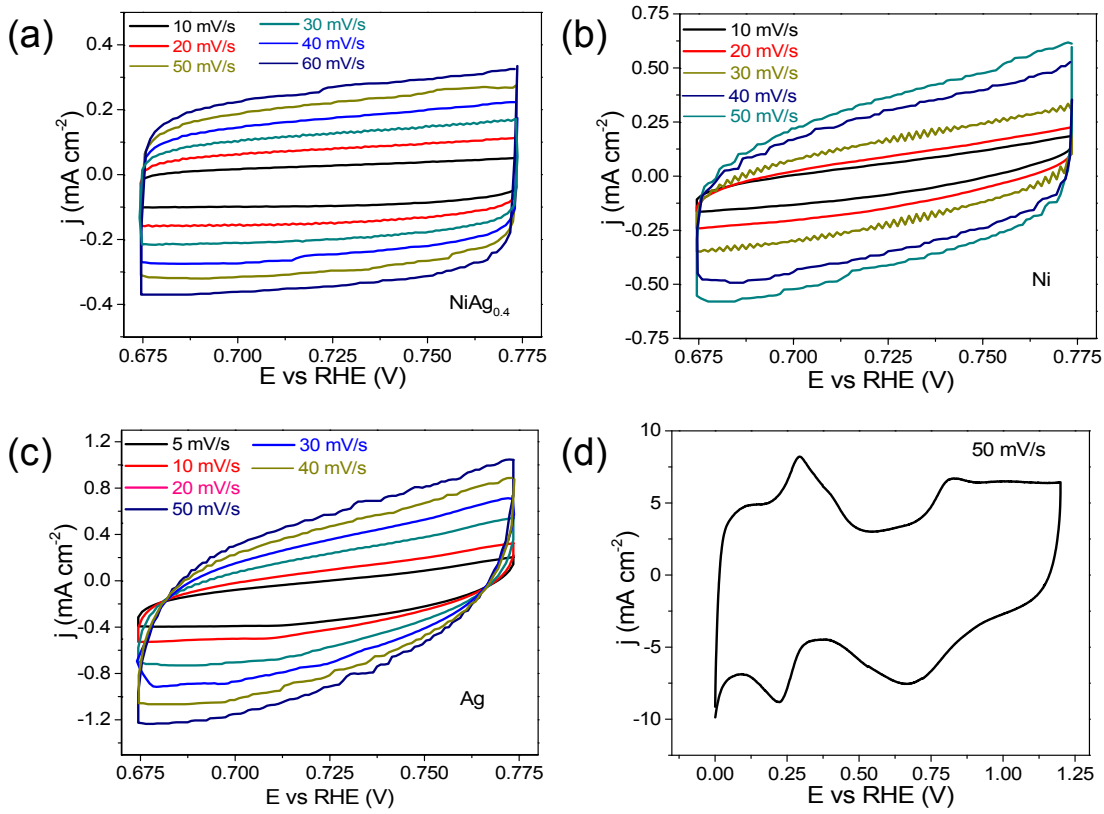

Fig. S8 Cyclic voltagram (CV) curves for (a) $NiAg_{0.4}$ 3DPNC, (b) Ni 3DPNC, (c) Ag NPs, and (d) CV curve for underpotential deposition for Pt/C 20% wt. catalyst.

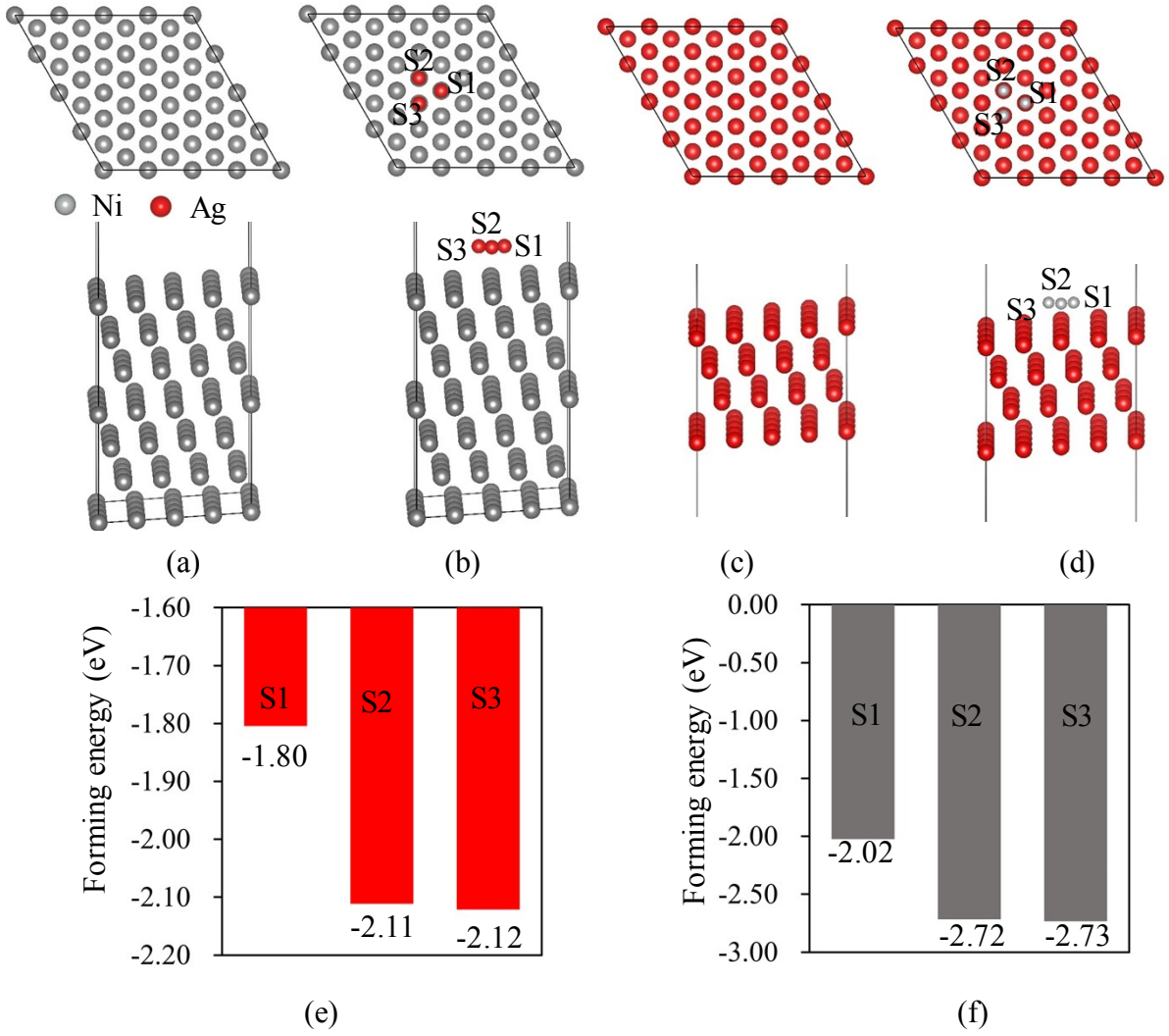

Fig. S9 The top and side view of crystal structures of: (a) pristine Ni (111) surface, (b) Ag/Ni (111) surface where the adsorption sites: top of Ni (S1), the Ni fcc sites (S2) and Ni hcp sites (S3); the top and side view of crystal structures of (c) pristine Ag (111) surface, (b) Ni/Ag (111) surface where the adsorption sites: top of Ag (S1), the Ag fcc sites (S2) and Ag hcp sites (S3); (e) the forming energy of Ag adsorbed on Ni (111) surface; (f) the forming energy of Ni adsorbed on Ag(111) surface.

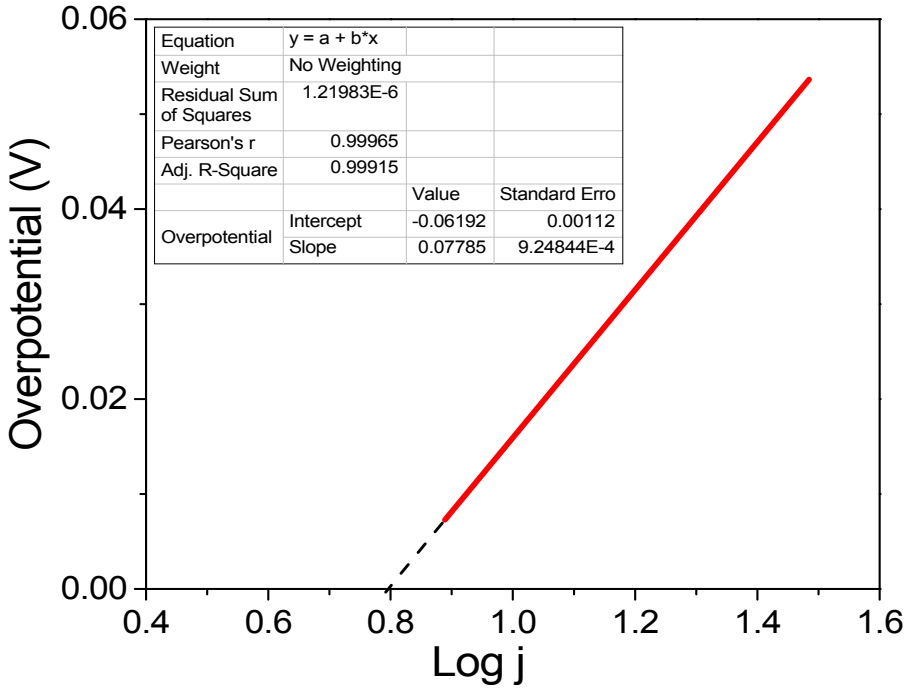

Fig. S10 Tafel plot of $NiAg_{0.4}$ 3DPNC to evaluate the exchange current density. Exchange current density was computed from the Tafel equation.

The exchange current density of the $NiAg_{0.4}$ 3DPNC based on the geometric surface area was computed from the Tafel equation as shown below:

$$\eta = -0.062 + 0.077 \log j$$

$$0 = -0.062 + 0.077 \log j$$

$$\text{Log } j = 0.8052$$

$$j_{0\text{geometric}} = 6.3856 \text{ mA cm}^{-2}{}_{\text{geometric}}$$

$$j_{0\ (\text{ECSA})} = 6.3856/125 \text{ mA cm}^{-2}{}_{(\text{ECSA})}$$

$$j_{0\ (\text{ECSA})} = 5.10 * 10^{-5} \text{ A cm}^{-2}{}_{(\text{ECSA})}$$

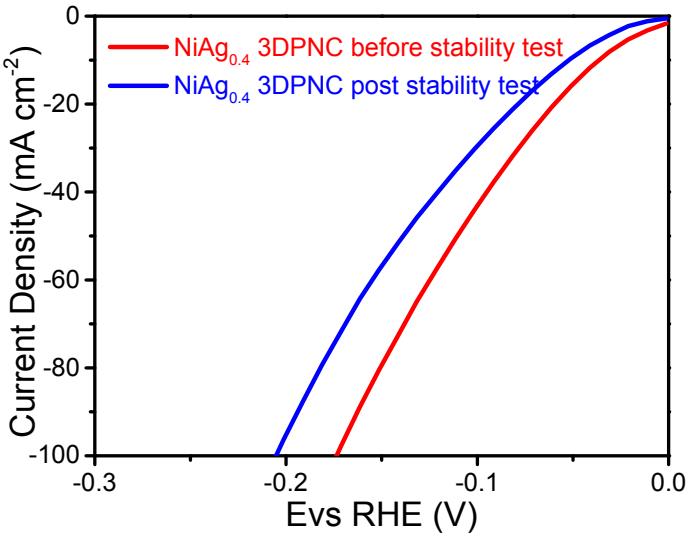

Fig. S11 Comparison of HER polarization curve of $NiAg_{0.4}$ 3DPNC after 80 hours chronoamperometry test with the initial catalyst.

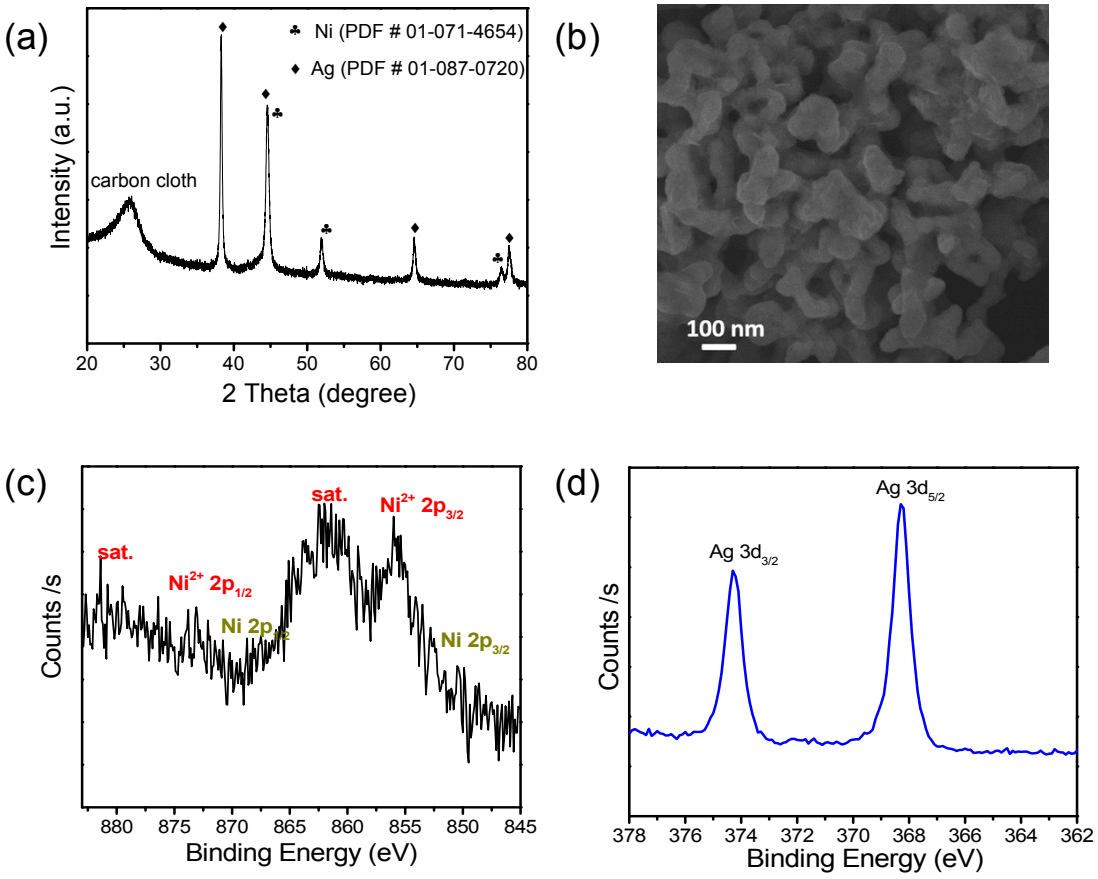

Fig. S12 (a) XRD pattern of $NiAg_{0.4}$ 3DPNC after 80 hours chronoamperometry test. (b) FESEM image of the $NiAg_{0.4}$ 3DPNC after chronoamperometry test. XPS spectra of $NiAg_{0.4}$ 3DPNC after 80 hours chronoamperometry test in the (c) Ni 2p region, (d) Ag 3d region.

Table S1. Inductive couple plasma- atomic emission spectroscopy results for the synthesized samples with different Ni/Ag ratios.

Ni : Ag ratio in the precursor solution	Expected molar concentration from synthesis	Measured molar concentration from ICP-OES	Expected molar concentration from synthesis	Measured molar concentration from ICP-OES	Sample name in the report
	Ni (%)	Ni (%)	Ag (%)	Ag (%)	
1 : 0.1	90.9	88.43019	9.1	11.56981	$NiAg_{0.13}$ 3DPNC
1 : 0.2	83	80.20356	17	19.79644	$NiAg_{0.25}$ 3DPNC
1 : 0.3	76.9	74.63433	23.1	25.36567	$NiAg_{0.34}$ 3DPNC
1 : 0.4	71.5	71.89	28.5	28.11	$NiAg_{0.4}$ 3DPNC
1 : 0.5	66.67	69.57572	33.33	30.42428	$NiAg_{0.44}$ 3DPNC
1 : 0.6	62.5	62.55256	37.5	37.44744	$NiAg_{0.6}$ 3DPNC
1 : 0.8	55.55	51.37111	44.45	48.62889	$NiAg_{0.95}$ 3DPNC
1 : 2	33.33	26.63245	66.67	73.36755	$NiAg_{2.75}$ 3DPNC
1 : 3	25	18.4579	75	81.5421	$NiAg_{4.42}$ 3DPNC
		68.5		31.5	$NiAg_{0.4}$ 3DPNC Post chronoamperometry test

Table S2. Roughness factor values for different catalysts which was evaluated from the double layer capacitance.

Catalyst	C_{dl} (mF cm^{-2})	Roughness factor (cm^2 per $cm^2_{(geometric)}$)
Ni 3DPNC	7	175
Ag NPs	12.8	320
Pt/C	20.4738 mC cm^{-2}	97.5
$NiAg_{0.4}$ 3DPNC	4.9	125

Table S3. HER activity of the $NiAg_{0.4}$ 3DPNC in comparison with other recently reported catalysts with good activity.

Catalyst	HER overpotential (mV@mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	Stability	Reference
Boron doped RhFe alloy	25 mV @ 10 mA cm^{-2}	32	0.5 M H_2SO_4	8 hours	[1]
$Ni_{20}Fe_{20}Mo_{10}Co_{35}Cr_{15}$ high entropy alloy	172 mV @ 10 mA cm^{-2}	41	1 M KOH	8 hours	[2]
Pt_3Ni_3 NWs	70 mV @ 19.8 mA cm^{-2}	NA	1 M KOH	3 hours	[3]
Micro-nano MoS_2 spheres	214 mV @ 10 mA cm^{-2}	74	0.5 M H_2SO_4	24 hours	[4]
Pt_3Co nanoparticles	32.6 mV @ 10 mA cm^{-2}	28.6	0.5 M H_2SO_4	5000 CV cycles	[5]
np-CoP_3 on Ti mesh	76 mV @ 10 mA cm^{-2}	50	1 M KOH	60 hours	[6]
PtCo–Co/TiM	70 mV @ 46.5 mA cm^{-2}	35	1 M KOH	50 hours	[7]
$Fe_{1.89}Mo_{4.11}O_7$/ MoO_2	197 mV @10 mA cm^{-2}	79	1 M KOH	1000 CV cycles	[8]
V-doped Ni_3S_2 Nanowires on Ni foam	68 mV @ 10 mA cm^{-2}	112	1 M KOH	7000 cycles	[9]

CrO*x*/Ni–Cu	48 mV @ 10 mA cm^{-2}	64	KH_2PO_4 + K_2HPO_4 buffer (pH = 7)	24 hours	[10]
FeP nanoparticles	154 mV @ 10 mA cm^{-2}	65	0.5 M H_2SO_4	1.66 hours	[11]
IrAg nanotubes	20 mV @ 10 mA cm^{-2}	61.1	0.5 M H_2SO_4	6 hours	[12]
$NiAg_{0.4}$ 3DPNC	**40 mV @ 10 mA cm^{-2}**	**39.1**	**1 M KOH**	**80 hours and 5000 CV cycles**	**This work**

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