Supporting Information for

Ni-doped hyperbranched PdCu nanocrystals for efficient electrocatalytic borohydride oxidation

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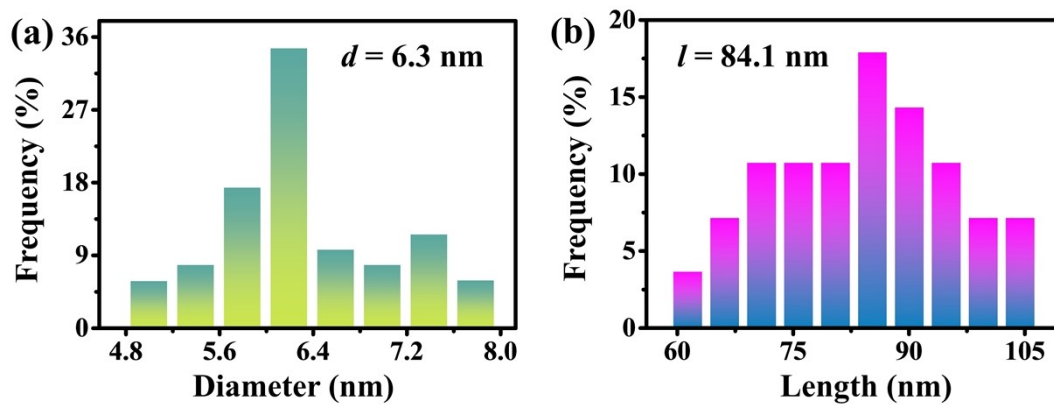E-mails: zqwang@zjut.edu.cn, hjw@zjut.edu.cn, wangliang@zjut.edu.cn.

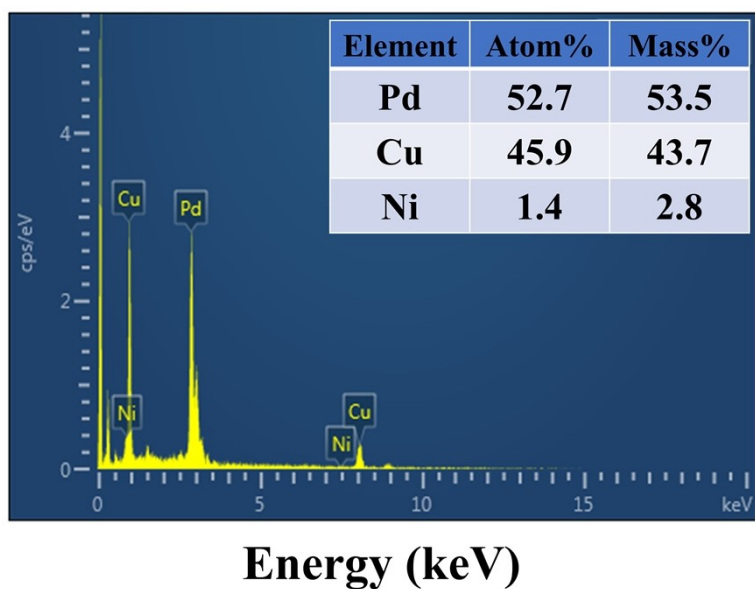**Fig. S1.** Histograms of (a) the diameter and (b) length distribution of branches for Ni-PdCuNi NCs.

Element	Atom%	Mass%
Pd	52.7	53.5
Cu	45.9	43.7
Ni	1.4	2.8

Energy (keV)

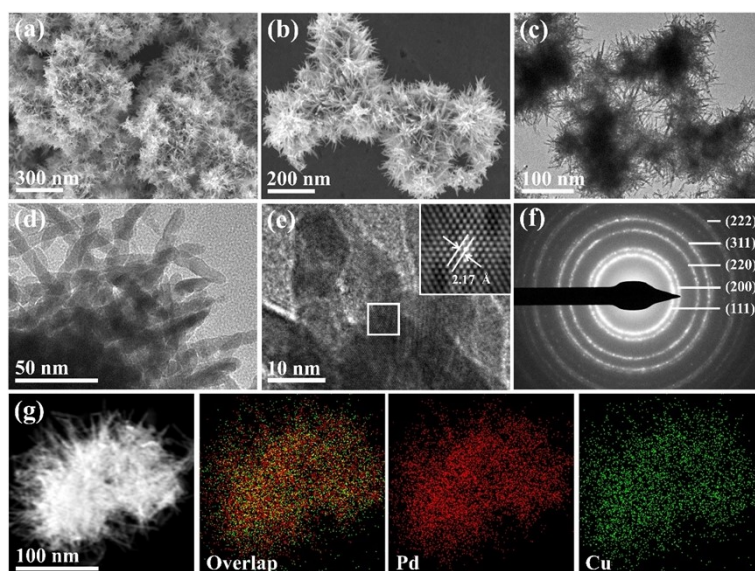**Fig. S2.** The EDS spectrum of Ni-PdCu NCs.

Fig. S3. (a, b) SEM, (c, d) TEM, and (e) HRTEM images of PdCu NCs, (f) corresponding SAED pattern. (g) HAADF-STEM image and the corresponding elemental mapping images of PdCu NCs. Inset of (e) is the corresponding the Fourier filtered lattices.
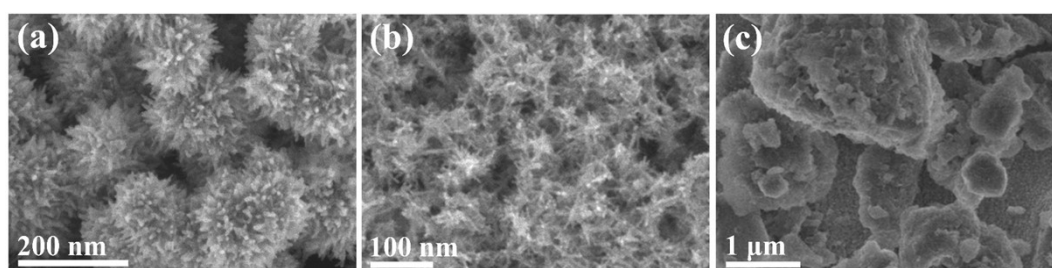

Fig. S4. (a) SEM images of samples obtained without surfactant, and SEM images of samples obtained with (b) F127 and (c) PVP.
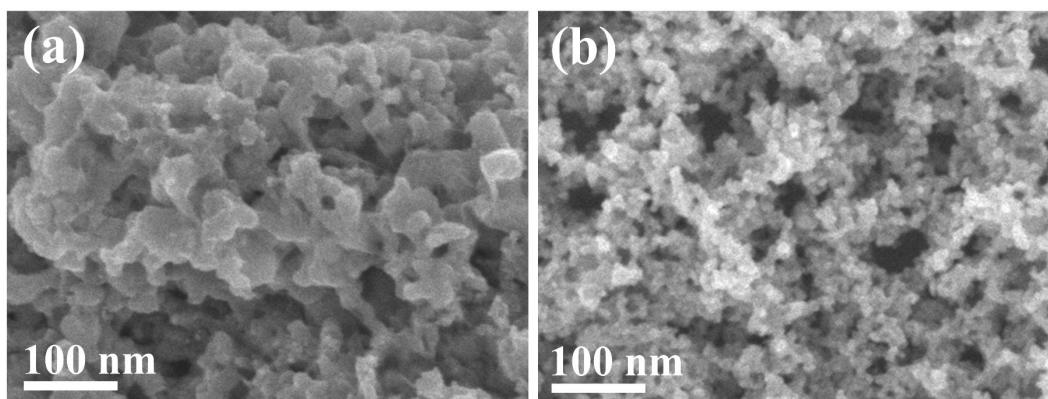
Fig. S5. SEM images of samples obtained with different reducing agents: (a) NaBH$_4$ and (b) DMAB.
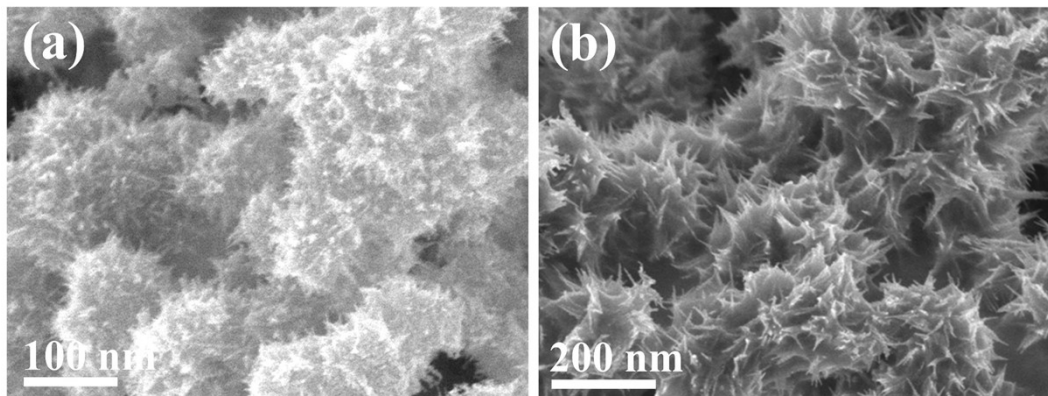

Fig. S6. SEM images of samples prepared with different amounts of KBr under the typical synthesis: (a) 0 mg and (b) 400 mg.
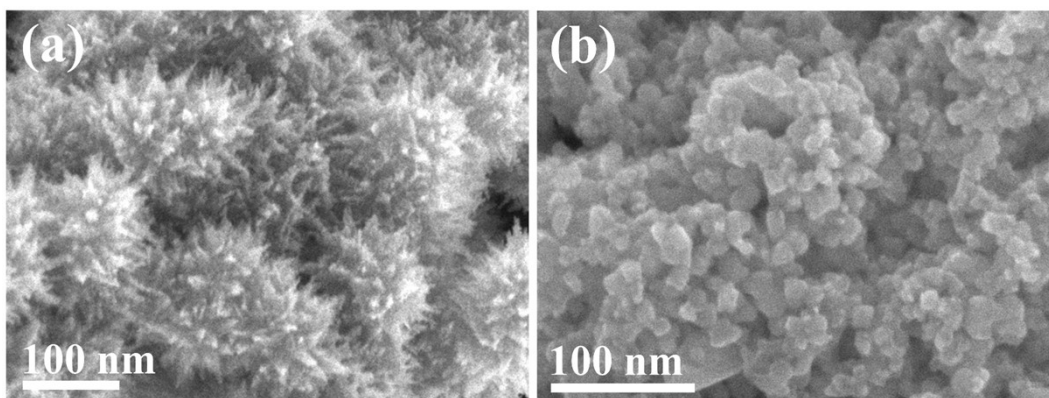
Fig. S7. SEM images of samples prepared by replacing KBr with (a) KCl and (b) KI under the typical synthesis.
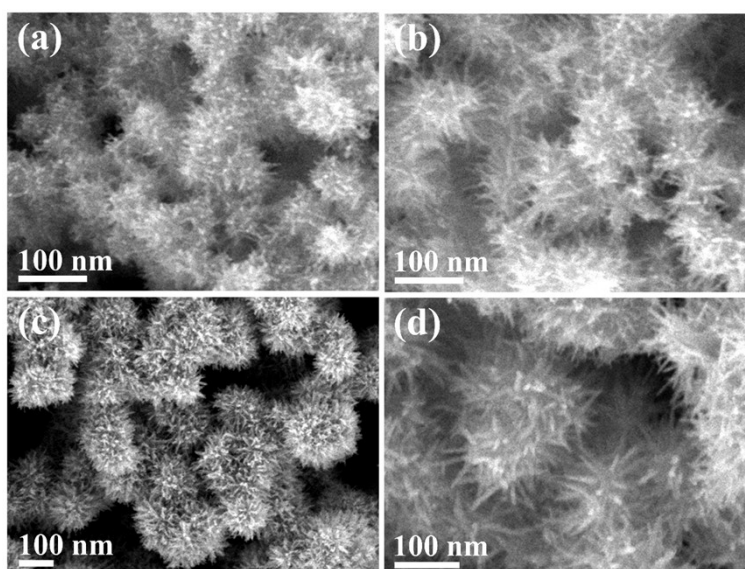

Fig. S8. SEM images of samples prepared with the different molar ratios of Pd/Cu/Ni precursors under the typical synthesis. The added metallic precursor amounts of Na_2PdCl_4, $CuCl_2$, and $NiCl_2$ are (a) 1.0 mL, 4.0 mL and 0.5 mL, (b) 1.5 mL, 3.5 mL and 0. 5 mL, (c) 2.5 mL, 2.5 mL and 0.5 mL, and (d) 3.5 mL, 1.5 mL and 0.5 mL.
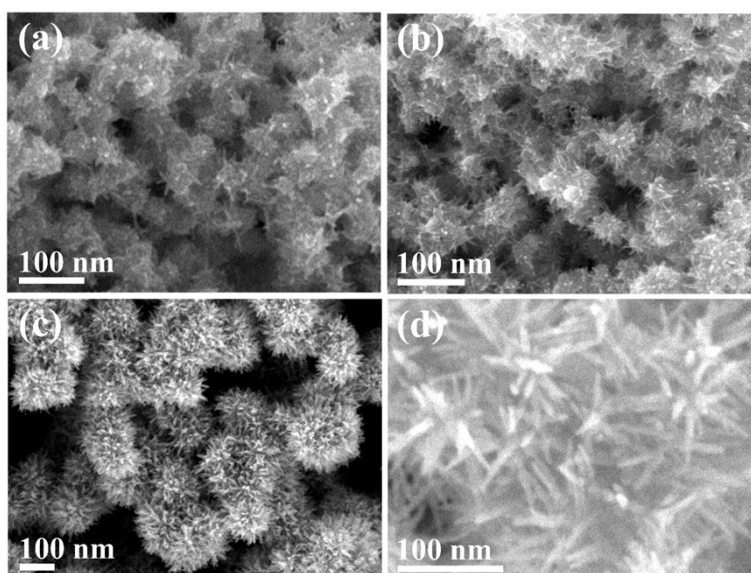
Fig. S9. SEM images of the samples prepared with different amounts of HCl under the typical synthesis: (a) 0 mL, (b) 0.05 mL, (c) 0.1 mL (d) 0.2 mL.
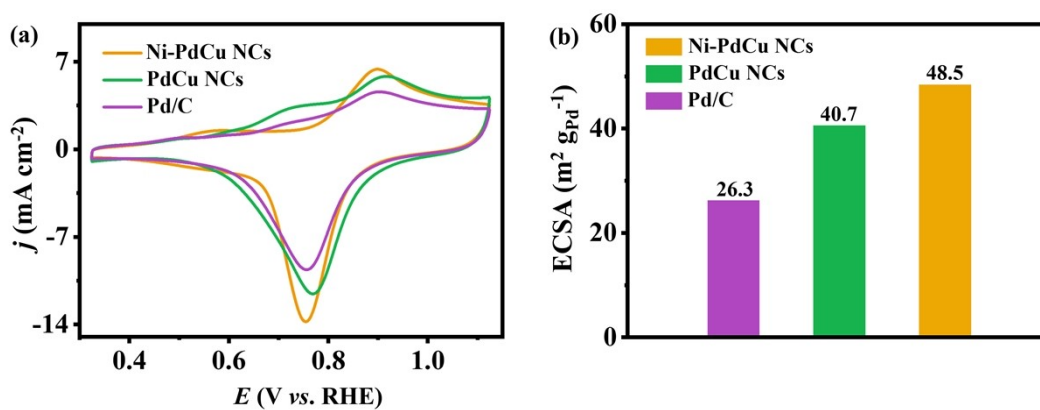

Fig. S10. (a) CV curves of the various catalysts in a N_2-saturated 1.0 M KOH at a scan rate of 50 mV s^{-1}. (b) ECSAs of Ni-PdCu NCs, PdCu NCs and commercial Pd/C.

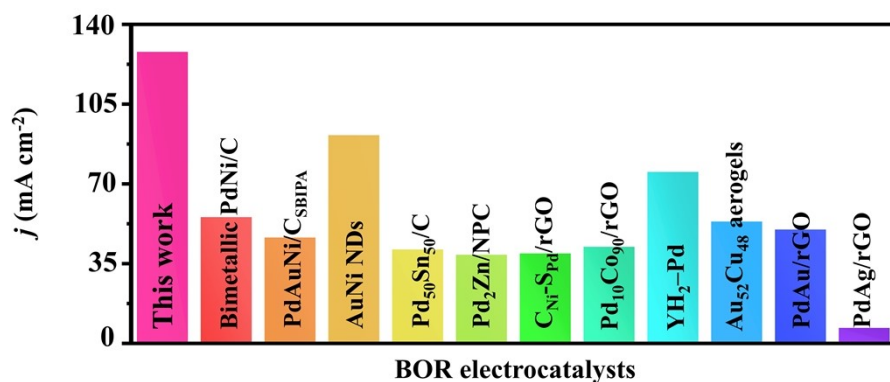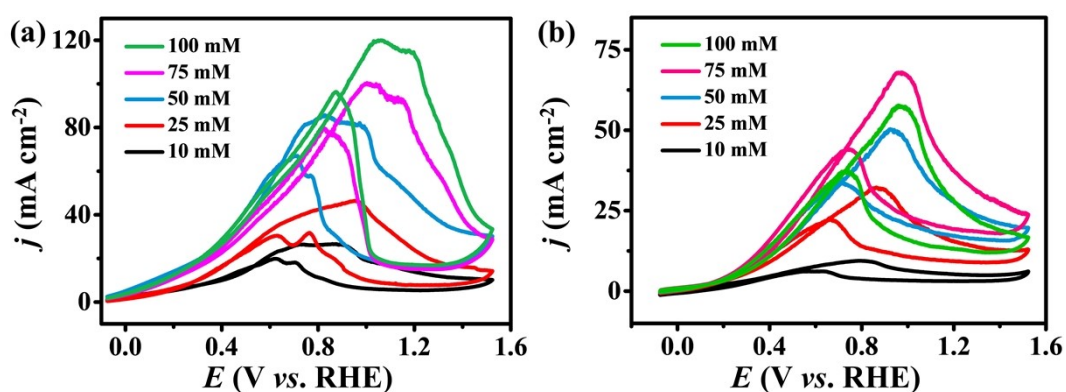**Fig. S11.** BOR current densities on various reported catalysts.

Fig. S12. CV curves of (a) PdCu NCs and (b) Pd/C in 1.0 M KOH solution with different concentrations of NaBH$_4$ at a scan rate of 50 mV s^{-1}.
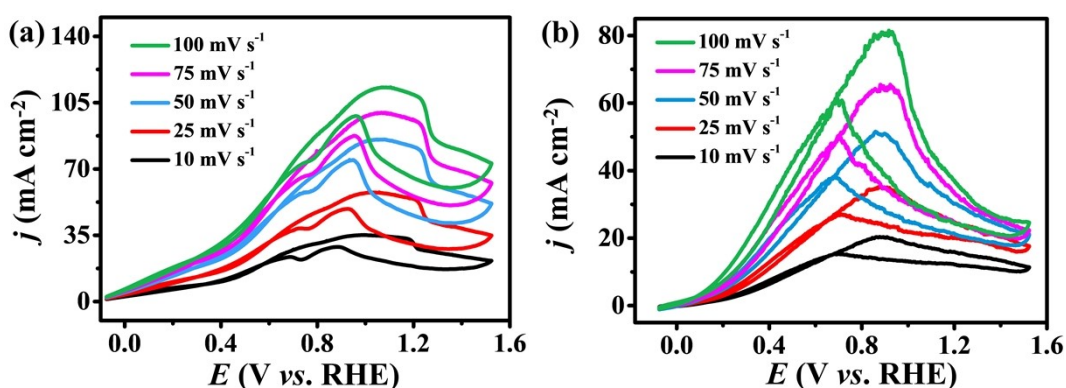

Fig. S13. CV curves of (a) PdCu NCs and (b) Pd/C in 1.0 M KOH containing 50 mM NaBH$_4$ solution with different scan rates.
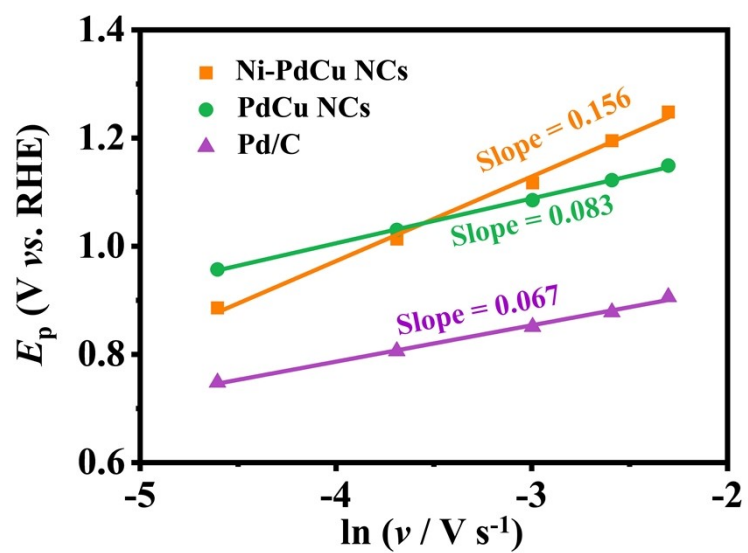
Fig. S14. The fitted E_p *vs.* ln v plot for all electrocatalysts.

Table S1. The current density comparison of BOR on recently reported various electrocatalysts.

Catalysts	Condition	Sweep rate (mV s^{-1})	Current density (mA cm^{-2})	Ref.
Ni-PdCu NCs	**50 mM NaBH$_4$ containing 1.0 M KOH**	**50**	**127.8**	**This work**
Bimetallic PdNi/C	50 mM NaBH$_4$ containing 1.0 M KOH	20	55	1
PdAuNi/C$_{SBIPA}$	30 mM NaBH$_4$ containing 2.0 M NaOH	50	46	2
AuNi NDs	30 mM NaBH$_4$ containing 2.0 M NaOH	50	91	3
Pd$_{50}$Sn$_{50}$/C	100 mM NaBH$_4$ containing 3.0 M NaOH	50	40.9	4
Pd$_2$Zn/NPC	100 mM NaBH$_4$ containing 3.0 M NaOH	20	38.4	5
C$_{Ni}$-S$_{Pd}$/rGO	100 mM NaBH$_4$ containing 1.0 M NaOH	100	39.1	6
Pd$_{10}$-Co$_{90}$/rGO	100 mM NaBH$_4$ containing 1.0 M KOH	50	42	7
YH$_2$–Pd	50 mM NaBH$_4$ containing 2.0 M NaOH	50	75	8
Au$_{52}$Cu$_{48}$ aerogels	100 mM NaBH$_4$ containing 3.0 M NaOH	20	53	9
PdAu/rGO	30 mM NaBH$_4$ containing 2.0 M NaOH	10	49.6	10
PdAg/rGO	30 mM NaBH$_4$ containing 2.0 M NaOH	10	6.2	10

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