Electronic Supplementary Information (ESI)

Room-temperature synthesis with inert bubble templates to produce "clean" PdCoP alloy nanoparticle networks for enhanced hydrazine electro-oxidation

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Table S1. Synthesis conditions and the mass of different precursors.

Sample	$CoCl_2 \cdot 6H_2O$ (mg)	$NaBH_4$ (mg)	Bubbled N_2	Initial atom ratio Pd:Co:P	Actual atom ratio Pd:Co:P
PdCoP-1	160	70.3	√	1:6:14	1:5.6:11
PdCoP-2	215	76.4	√	1:8:14	1:7.5:11
PdCoP-3	270	80.6	√	1:10:14	1:9.2:11
PdCoP-4	325	92.0	√	1:12:14	1:11.5:11
PdCoP-5	380	120	√	1:14:14	1:13.4:11
PdCoP GA	270	80.6	×	1:10:14	1:9.5:11
PdCo ANN	270	71.2	√	1:10:14	1:5.5

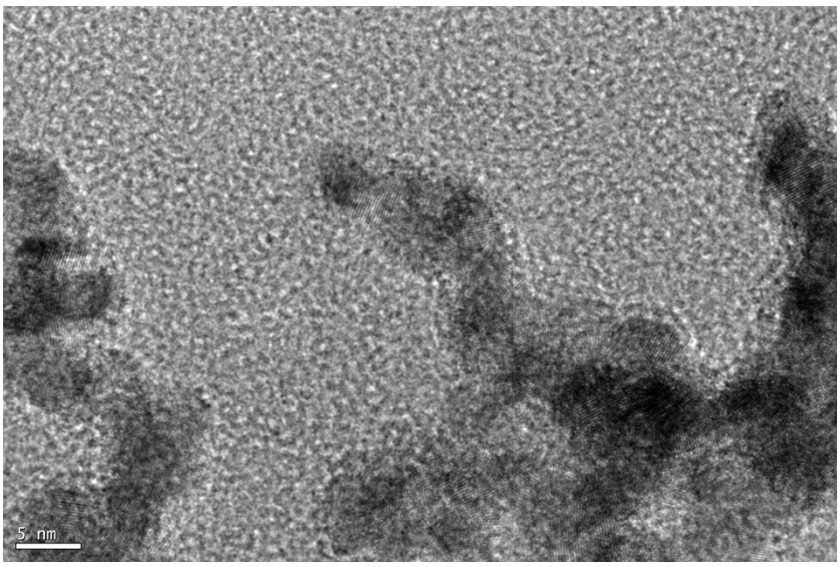

Figure S1. HRTEM image of PdCoP-3.

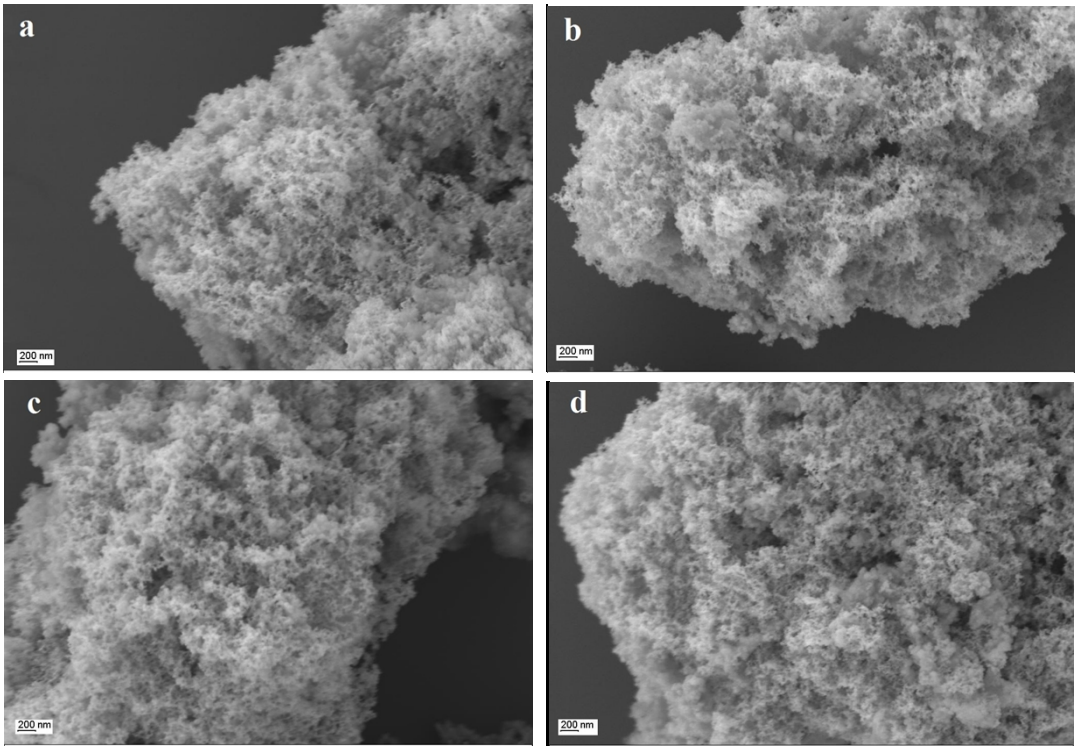

Figure S2. SEM images of the PdCoP-1(a), PdCoP-2(b), PdCoP-4(c), PdCoP-5(d) samples.

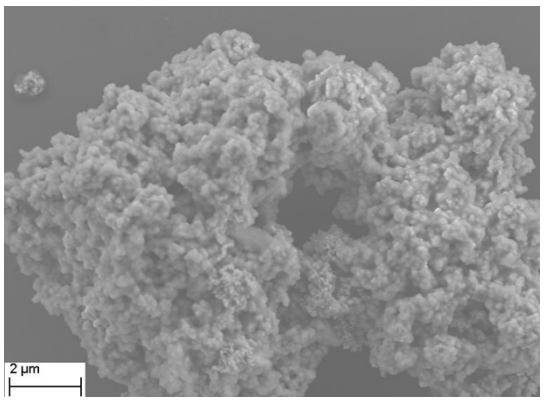

Figure S3. SEM image of the PdCoP grain aggregates (GA).

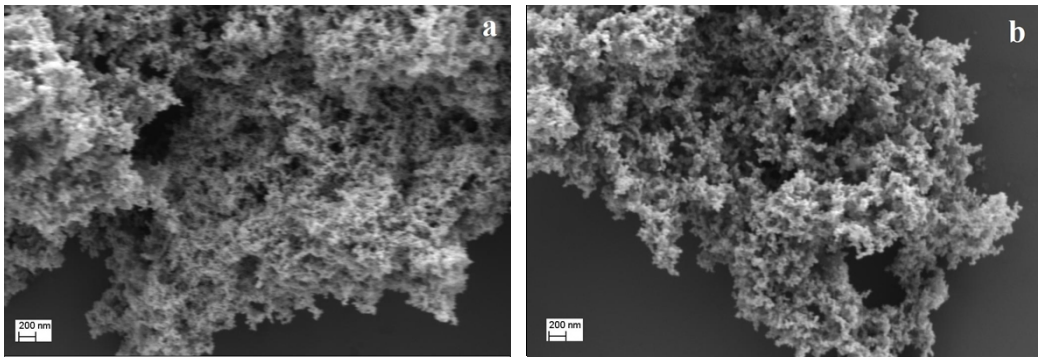

Figure S4. SEM images of PdCoP samples with a molar ratio of Pd:Co:P=1:10:14 prepared by bubbling Ar (a) and He (b) gas.

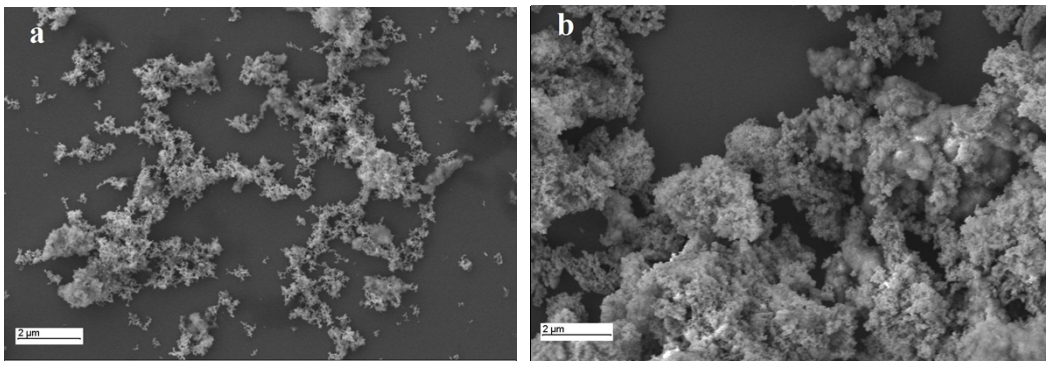

Figure S5. SEM images of the growth intermediates of the PdCoP samples with a molar ratio of Pd:Co:P=1:10:14 produced after (a) 0.5 h, and (b) 1.5 h.

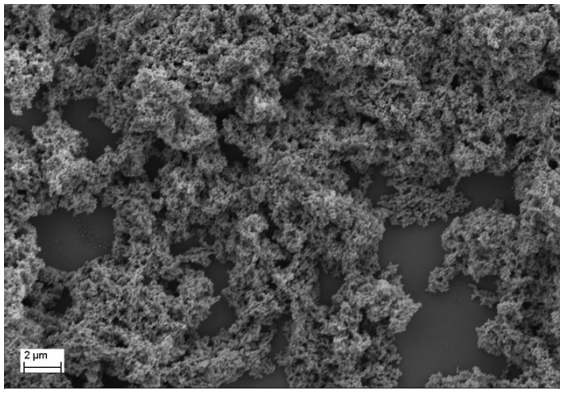

Figure S6. SEM image of the PdCo ANN.

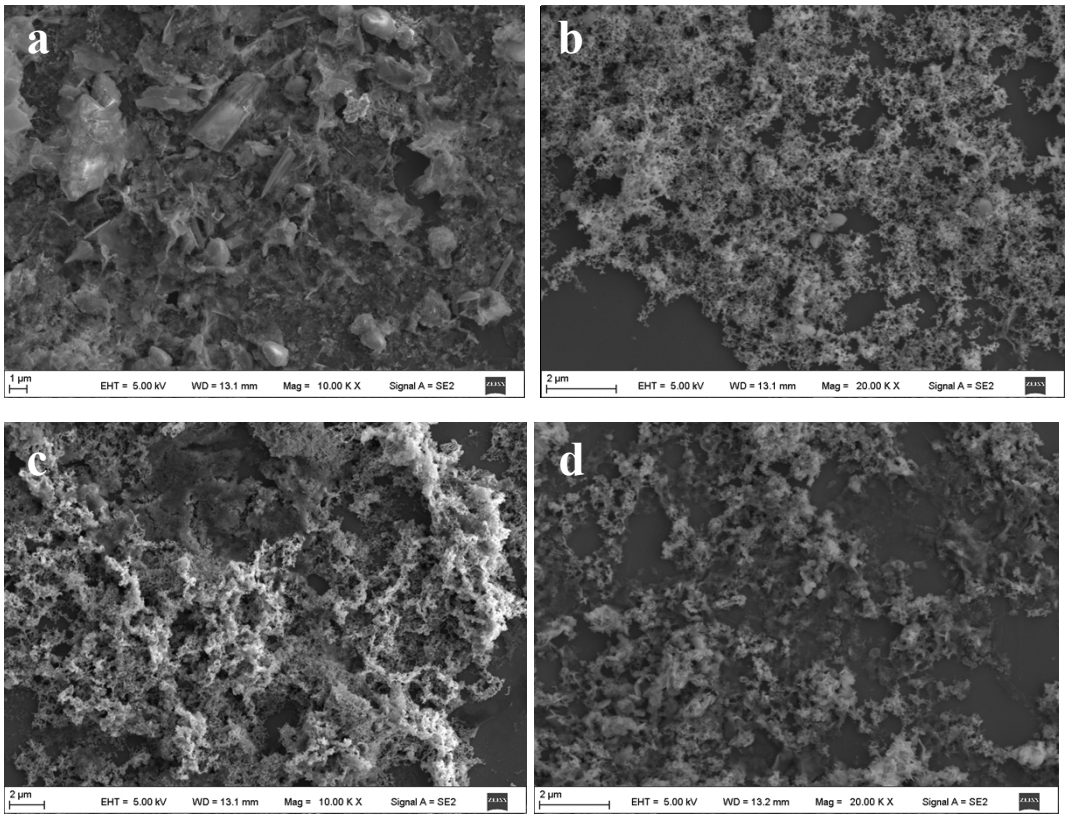

Figure S7. SEM images of PdCoP (a-d) samples. These samples were prepared by solvethermal synthesis as follows: 160 mg of $NaH_2PO_2 \cdot H_2O$ and 480 mg of hexadecyl trimethyl ammonium bromide (CTAB) were dissolved in 30 mL water. 10 mL aqueous solution containing 20 mg of $PdCl_2$ with pH ~ 9 (NaOH) was added into the above solution. Sequently, 20 mL of aqueous solution

containing 80.6 mg of $NaBH_4$ was added into the mixture under stirring, and the obtained solution was transferred to 100 mL Teflon-lined autoclaves, sealed and heated at 120 °C for 12 h, and allowed to cool naturally to ambient temperature. The resulting solid products were collected by centrifugation, washed with distilled water and ethanol. The final products, PdCoP-a were obtained. For PdCoP-b, PdCoP-c, and PdCoP-d, the above procedure and materials were used but with replacement of solvent and surfactant as shown in Table S2:

Table S2. The kinds of solvent and surfactant used in solvothermal synthesis.

Sample	Solvent	Surfactant
PdCoP-a	H_2O	CTAB
PdCoP-b	C_2H_5OH	CTAB
PdCoP-c	H_2O	SDS[a]
PdCoP-d	C_2H_5OH	SDS[a]

[a] sodium dodecyl sulfate

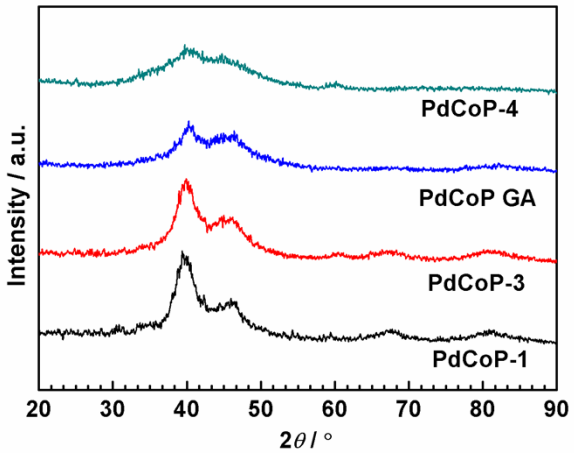

Figure S8. (a) XRD patterns of PdCoP-1, PdCoP-2, PdCoP-4, and PdCoP GA.

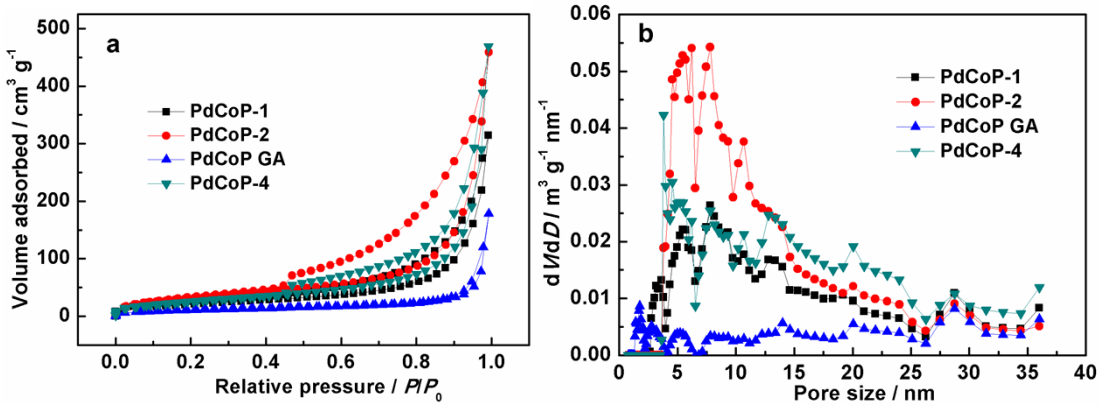

Figure S9. (a) N_2 adsorption-desorption isotherms, and (b) pore size distribution of PdCoP-1, PdCoP-2, PdCoP-4, and PdCoP GA.

Table S3. Porous structure of six samples obtained from its N_2 isotherms.

Samples	BET surface area (m^2 g^{-1})	The range of pores	Pore volume (cm^3 g^{-1})
PdCoP-1	76.2	mesopore	0.486
PdCoP-2	115.4	mesopore	0.710
PdCoP-3	73.1	mesopore	0.446
PdCoP-4	94.7	mesopore	0.725
PdCoP GA	38.6	micropore and mesopore	0.275
PdCo	49.5	mesopore	0.390

Table S4. Assignments, Binding energies (BEs) and concentrations of Pd 3d species in PdCoP-3 and PdCo ANN obtained from XPS results.

Sample	Pd 3d	BE[a]	Concentration[b]
PdCoP-3	0	340.9&335.5	92.0
	2	342.5&336.8	8.0
PdCo ANN	0	340.7&335.3	87.2
	2	342.9&336.5	12.8

[a] Binding energy (in eV). [b] Per species (in at %).

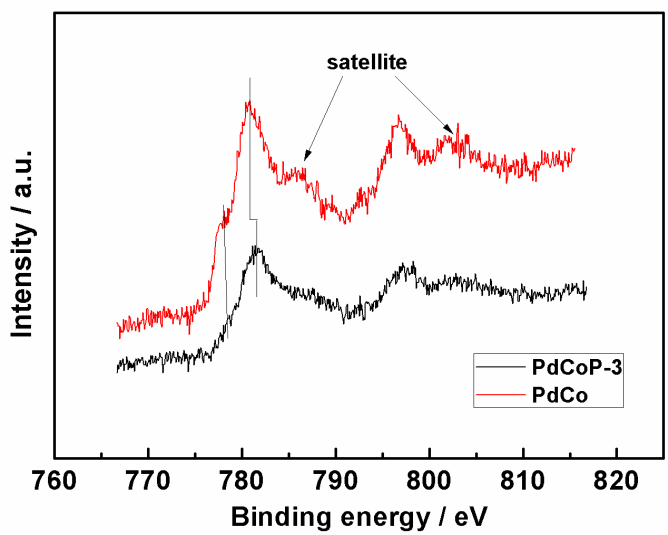

Figure S10. Co 3p XPS spectra of PdCoP-3 and PdCo ANN.

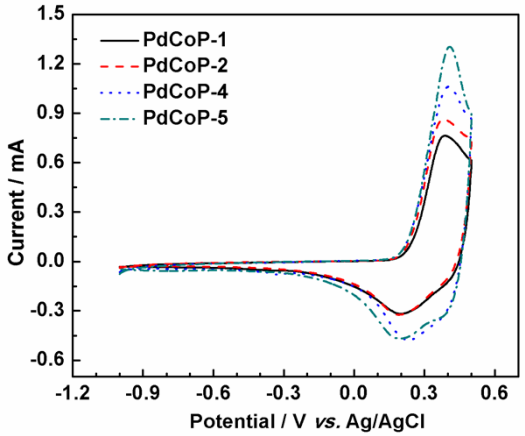

Figure S11. (c) CVs on PdCoP-1, PdCoP-2, and PdCoP-4 electrodes in N_2-saturated 0.1 mol L^{-1} KOH solution at a scan rate of 20 mV s^{-1}.

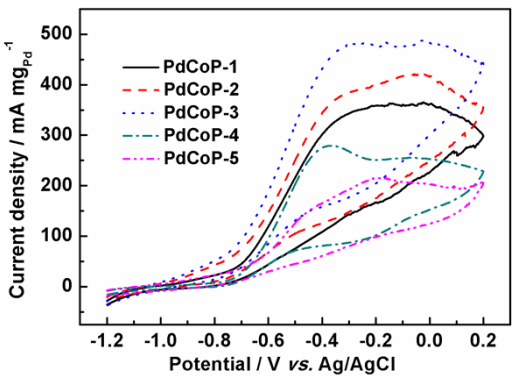

Figure S12. CVs on a series of PdCoP ANN electrodes in N_2-saturated 0.1 mol L^{-1} N_2H_4 + 0.1 mol L^{-1} KOH + 0.1 mol L^{-1} KOH solution at a scan rate of 100 mV s^{-1}.

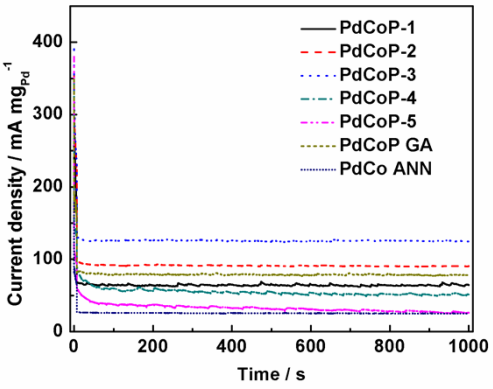

Figure S13. Chronoamperometry curves of the all samples in N_2-saturated 0.1 mol L^{-1} N_2H_4 + 0.1 mol L^{-1} KOH + 0.1 mol L^{-1} KCl solution at a fixed potential of -0.3 V.

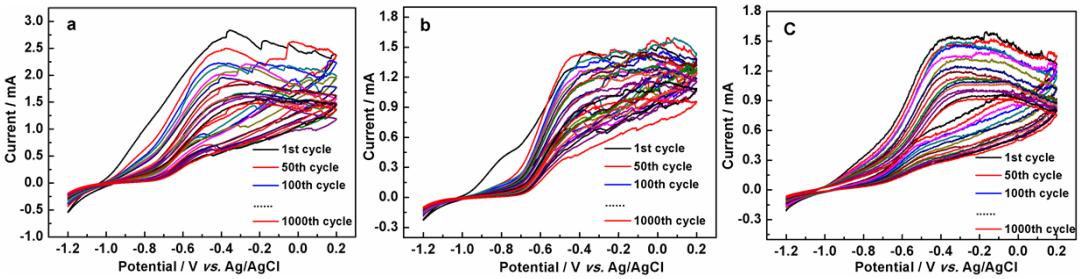

Figure S14. (c) CVs on PdCoP-3 (a), PdCoP GA (b) and PdCo ANN electrodes in N_2-saturated 0.1 mol L^{-1} N_2H_4 + 0.1 mol L^{-1} KOH + 0.1 mol L^{-1} KCl solution at a scan rate of 20 mV s^{-1}.