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Supporting Information Available

Facile synthesis of Pd-Co-P ternary alloy network nanostructures and their enhanced electrocatalytic activity towards hydrazine oxidation

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1. Experimental

Materials

Potassium tetrachloropalladite(II) (K_2PdCl_4), potassium hexacyanocobaltate(III) ($K_3Co(CN)_6$), sodium hypophosphite (NaH_2PO_2), sodium borohydride ($NaBH_4$), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other reagents were of analytical reagent grade and used without further purification. Commercial Pd black and Pd/C were purchased from Johnson Matthey Corporation.

Synthesis of Pd-Co-P ternary alloy network nanostructures (Pd-Co-P TANNs)

Light yellow $K_2PdCl_4/K_3Co(CN)_6$ cyanogel was obtained by mixing 2 mL of 50 mM K_2PdCl_4 and 1 mL of 50 mM $K_3Co(CN)_6$ aqueous solutions at room temperature. Then, 10 mL of mixture of 200 mM NaH_2PO_2 and 475 mM $NaBH_4$ was added into $K_2PdCl_4/K_3Co(CN)_6$ cyanogel and the resulting mixture was stood for an additional 24 h. After reaction, the black Pd-Co-P TANNs were separated by centrifugation at 15000 rpm for 5 min, washed consecutively with water, 0.1 M $HClO_4$ solution and water, and then dried at 40 ^{o}C in a vacuum oven for 12 h. The acid wash process could ensure the removal of unalloyed Co.[1]

Electrochemical measurements

All electrochemical experiments were carried out on a CHI 660 C electrochemical workstation (CH Instruments, Shanghai, Chenghua Co.). A Pt wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used. All potentials refer to SCE. For the preparation of working electrode, 4 mg catalyst and 4 mL H_2O were mixed and sonicated for 30 min to generate an evenly distributed suspension. Then 8.0 μL of the resulting suspension was laid on the surface of the glassy carbon electrode (3 mm diameter, 0.07 cm^2). After drying at 40 ^{o}C, the working electrode was obtained, and the specific loading of metal on the electrode surface was about 8 μg. Electrochemical tests were performed in 0.1 M N_2-saturated $HClO_4$ solution with or without 0.05 M N_2H_4. All the electrochemical measurements were carried out at 30±1 ^{o}C.

Instruments.

Scanning electron microscopy (SEM) images were captured on a Hitachi S-4800 scanning electron microscope, operating at 5 kV. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F electron microscope operating at 200 kV. X-ray diffraction (XRD) data were collected on a Model D/max-rC X-ray diffractometer, operating at 40 kV and 100 mA, using CuKα radiation source (1.5406 Å). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al Kα radiator. The binding energy was calibrated with respect to C1s at 284.6 eV. The composition of the catalysts was determined using the energy dispersive spectrum (EDS) technique. The zeta potential measurements were performed with a Malvern Zetasizer Nano ZS90 analyzer at room temperature.

2. Figures

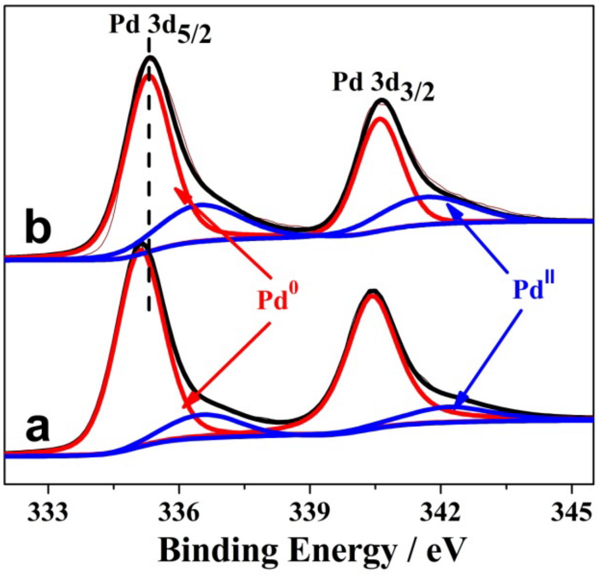

Fig. S1 XPS spectra of (a) Pd-Co-P TANNs and (b) Pd-Co BANNs in the Pd 3d region.

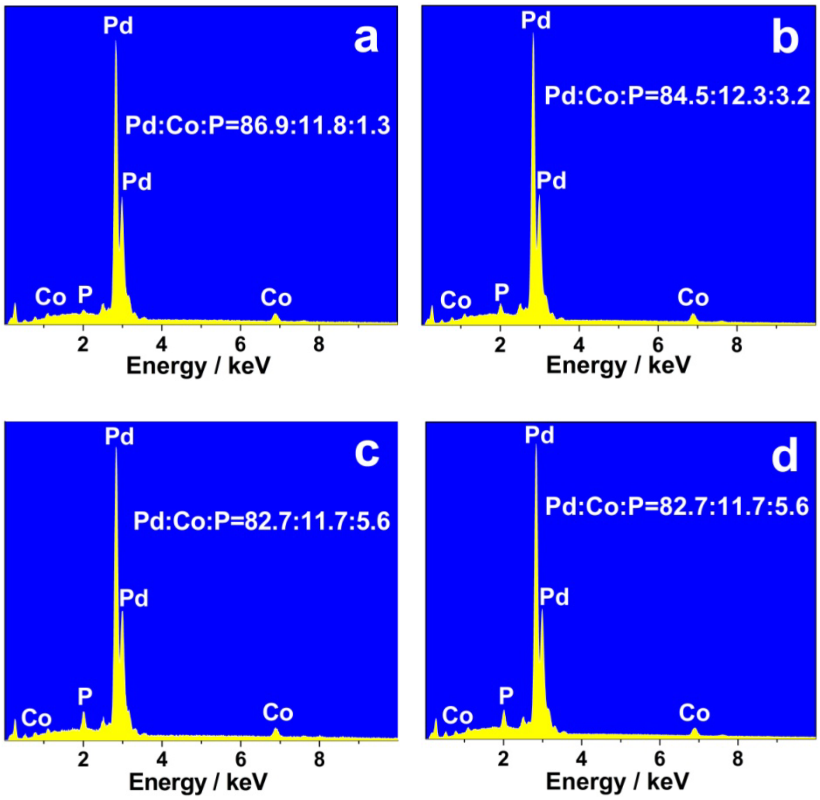

Fig. S2 EDS spectra of Pd-Co-P TANNs prepared at different NaH_2PO_2/ $NaBH_4$ molar ratio. (a) 0.017:1, (b) 0.084:1, (c) 0.42:1 and (d) 0.84:1.

EDS measurements show the P amount of Pd-Co-P TANNs increases with the increasing the molar ratio of $NaH_2PO_2/NaBH_4$ in the range of 0.017:1~0.42:1 and then keep constant with further increasing $NaH_2PO_2/NaBH_4$ molar ratio to 0.84:1. The corresponding P amount of Pd-Co-P TANNs prepared at different $NaH_2PO_2/NaBH_4$ molar ratio is also listed in Table S1.

Table S1. Particle size, lattice constant and P amount of Pd-Co-P TANNs prepared at different $NaH_2PO_2/NaBH_4$ molar ratio.

$NaH_2PO_2/NaBH_4$ molar ratio	Catalysts	Particle size (nm)	Lattice constant (nm)	P amount (Atom %)
0:1	Pd-Co BANNs	3.9	0.3875	0
0.017:1	Pd-Co-P-0.017:1	3.2	0.3864	1.3
0.084:1	Pd-Co-P-0.084:1	2.6	0.3845	3.2
0.42:1	Pd-Co-P-0.42:1	2.1	0.3817	5.6
0.84:1	Pd-Co-P-0.84:1	2.1	0.3817	5.6

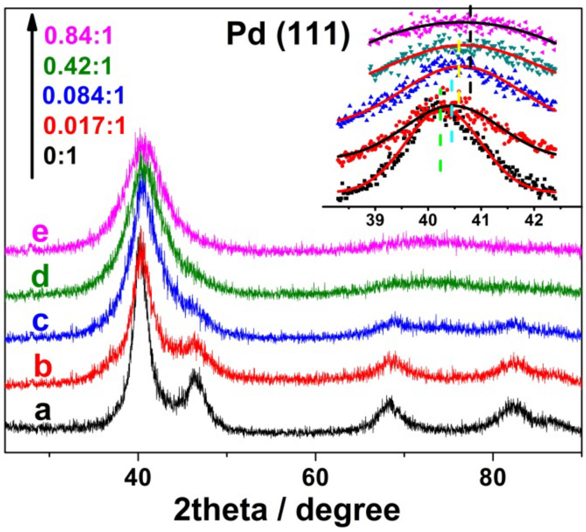

Fig. S3 XRD patterns of Pd-Co-P TANNs prepared at different $NaH_2PO_2/NaBH_4$ molar ratio. (a) 0:1, (b) 0.017:1, (c) 0.084:1, (d) 0.42:1 and (e) 0.84:1. Insert: XRD patterns of Pd(111) peak.

According to Scherrer equation, the average particle size of Pd-Co-P TANNs prepared at different $NaH_2PO_2/NaBH_4$ molar ratio are calculated and listed in Table S1. As shown in Table S1, the particle sizes of Pd-Co-P TANNs decrease with the increasing the molar ratio of $NaH_2PO_2/NaBH_4$ in the range of

0.017:1~0.42:1 and then keep constant with further increasing $NaH_2PO_2/NaBH_4$ molar ratio to 0.84:1 (Table S1).

Moreover, the diffraction peak of Pd(111) of Pd-Co-P TANNs shifts to higher angle with increasing $NaH_2PO_2/NaBH_4$ molar ratio and then remains unchanged at the critical point of $NaH_2PO_2/NaBH_4$ molar ratio = 0.42:1. According to Vegard's law, the lattice parameter value (*a*) of Pd-Co-P TANNs prepared at different $NaH_2PO_2/NaBH_4$ molar ratio is calculated and listed in Table S1.

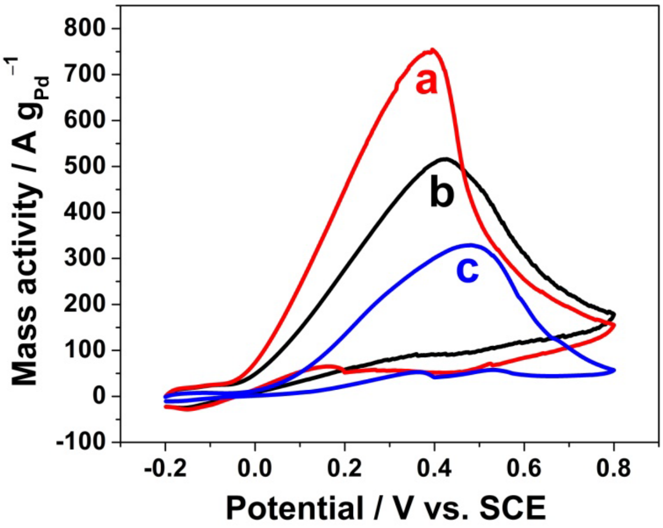

Fig. S4 Mass activity of (a) Pd-Co-P TANNs, (b) Pd-Co BANNs and (c) commercial Pd in N_2-saturated 0.1 M $HClO_4$ + 0.05 M N_2H_4 solutions at the scan rate of 50 mV s^{-1}.

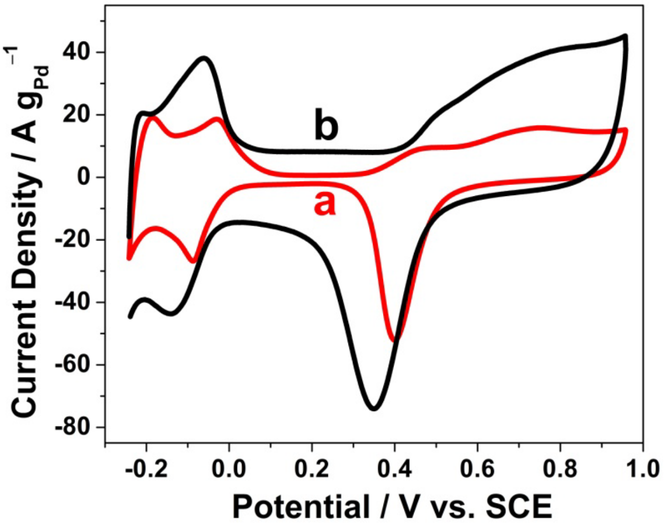

Fig. S5 Cyclic voltammograms of (a) Pd-Co-P TANNs and (b) commercial Pd/C catalyst in N_2-saturated 0.1 M $HClO_4$ solution at the scan rate of 50 mV s^{-1}

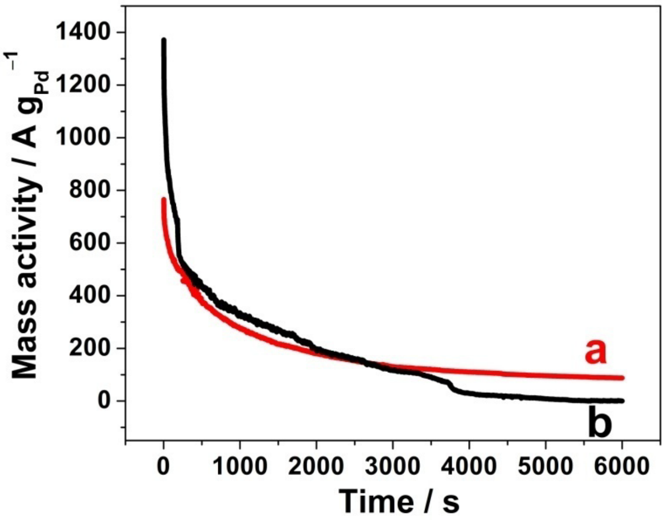

Fig. S6 Chronoamperometric curves of (a) Pd-Co-P TANNs and (b) commercial Pd/C in the N_2-saturated 0.1 M $HClO_4$ + 0.05 M N_2H_4 solutions at 1000 rpm rotation rate at 0.30 V.

1. (a) Xu, J., Liu, X., Chen, Y., Zhou, Y., Lu, T. and Tang, Y., *J. Mater. Chem.* 2012, **22**, 23659-23667; (b) Zhang, L., Wan, L., Ma, Y., Chen, Y., Zhou, Y., Tang, Y. and Lu, T., *Appl. Catal.s B: Environ.* 2013, **138-139**, 229-235.