Supporting Information

Arginine-assisted synthesis of Pd nanochain networks and their enhanced electrocatalytic activity for the borohydride oxidation

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Experimental

Reagents and chemicals

Arginine was purchased from Shanghai Kayon Biological Technology CO., Ltd. (Shanghai, China). Polyvinyl pyrrolidone (PVP, MW = 30000) and palladium chloride ($PdCl_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Commercial Pd black was purchased from Johnson Matthey Corporation. All reagents were of analytical reagent grade and used without further purification.

Preparation of the Pd-NCNs

In a typical synthesis, 0.5 mL of 0.05 M $PdCl_2$ solution, 2.0 mL of 0.05 M arginine, and 50 mg PVP (MW = 30000) were added into 6.0 mL deionized water with continuous stirring for 10 minutes at room temperature. After adjusting the solution pH to 12.0, the mixture was transferred to a 20 mL Teflon-lined stainless steel autoclave and heated at 140 ^{o}C for 3 h. After being cooled to room temperature, the obtained Pd-NCNs were separated by centrifugation at 20 000 rpm for 10 min, washed several times with water solution, and then dried at 60 ^{o}C for 5 h in a vacuum dryer. Finally, the Pd-NCNs were treated with UV irradiation (wavelength at 185 and 254 nm in air for 4 h) to remove the most capping agent (i.e., PVP) prior to electrochemical test.[1, 2]

Physical characterizations

Transmission electron microscopy (TEM) measurements were made on a JEOL JEM-2100F transmission electron microscopy operated at an accelerating voltage of 200

kV. Scanning electron microscopy (SEM) images were taken on a JSM-2010 microscopy at an accelerating voltage of 20 kV. Energy dispersive X-ray (EDX) analysis of the samples was carried out on a JEOL JSM-7600F SEM. X-ray diffraction (XRD) patterns of the samples were obtained with Model D/max-rC X-ray diffractometer using Cu Ka radiation source (λ=1.5406 Å) and operating at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al Ka X-ray source (1486.6 eV photons). The binding energy was calibrated by means of the C1s peak energy of 284.6 eV.

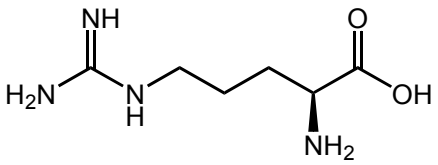
Electrochemical measurements

All electrochemical tests were performed on a CHI 660 D electrochemical analyzer at 30 ±1 ^{o}C. A standard three-electrode system was used, which consisted of a platinum wire as the auxiliary electrode, a saturated calomel reference electrode protected by Luggin capillary with KCl solution as the reference electrode, and a catalyst modified glassy carbon electrode as the working electrode. Potentials in this study were reported with respect to the SCE.

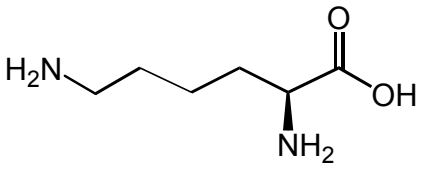
An evenly distributed suspension of catalyst was prepared by ultrasonic the mixture of 10 mg catalyst and 5 mL H_2O for 30 min. Then, 6 μL of the resulting suspension was drop-cast onto the surface of the glassy carbon electrode. After drying at room temperature, 3 μL of Nafion solution (5 wt. %) was covered on the modified electrode surface and allowed drying again. Thus, the working electrode was obtained, and the specific loading of metal on the electrode surface was about 170 μg cm^{-2}. Cyclic

voltammetry (CV) measurements were carried out in N_2-saturated 3.0 M NaOH solution at a sweep rate of 50 mV s^{-1}. The electrochemically active surface area (ECSA) of Pd catalysts was calculated from the following equation (ECSA=Q/mC, m was the loading amount of Pd metal) by integrating the reduction charge of surface $Pd(OH)_2$ (Q) and assuming a value of 420 μC cm^{-2} (C) for the reduction charge of a $Pd(OH)_2$ monolayer on the Pd surface because ECSA of Pd catalysts cannot be precisely assessed by coulometry in the "hydrogen region" due to the interference of hydrogen absorption in bulk Pd. Electrochemical measurements were conducted in N_2-saturated 3.0 M NaOH solution or N_2-saturated 3.0 M NaOH solution with 0.03 M $NaBH_4$.

Figures



Scheme S1. Structure of Arginine Molecule.



Scheme S2. Structure of L-lysine Molecule.

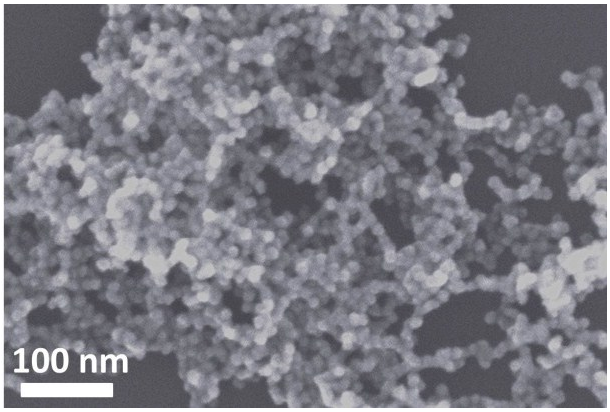


Fig. S1 Large-area SEM image of as-prepared Pd-NCNs.

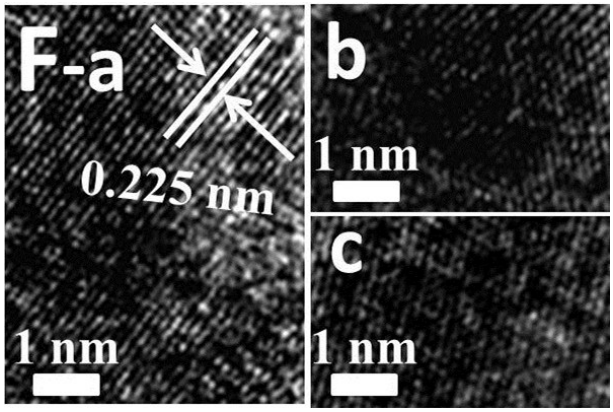


Fig. S2 Magnified HRTEM image taken from regions a, b and c (marked by the squares in Fig. 1D), which correspond to E-a, E-b and E-c, respectively.

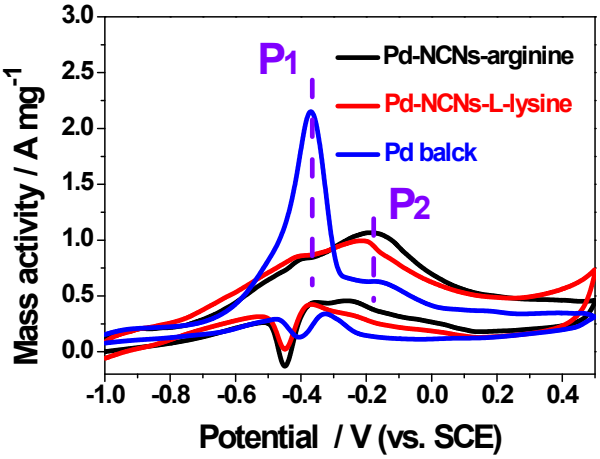


Fig. S3 The mass-normalized cyclic voltammograms for arginine-directed Pd-NCNs, L-lysine-directed and commercial Pd black in N_2-saturated 3.0 M KOH + 0.03 M $NaBH_4$ solution at the scan rate of 50 mV s^{-1}.

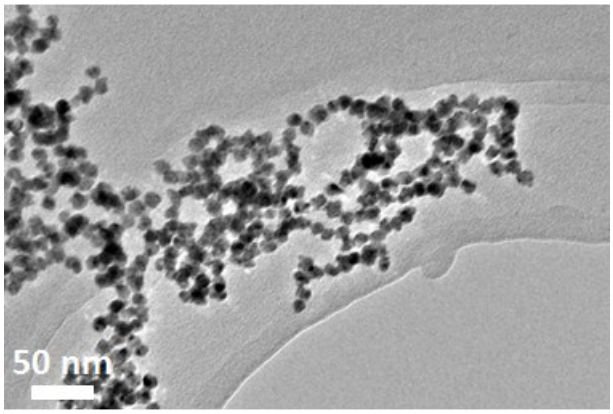


Fig. S4 TEM image of Pd-NCNs after the long-term stability test.

1. M. Crespo-Quesada, J. M. Andanson, A. Yarulin, B. Lim, Y. Xia and L. Kiwi-Minsker, *Langmuir*, 2011, **27** 7909–7916.

2. A. X. Yin, X. Q. Min, W. Zhu, W. C. Liu, Y. W. Zhang and C. H. Yan, *Chem. Eur. J.*, 2012, **18**, 777-782.