

Unusual synergetic effect of nickel single atoms on the electrocatalytic activity of palladium for alcohol oxidation reactions in alkaline media

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Experimental

Materials and chemicals

Palladium chloride (PdCl₂, Sigma-Aldrich), multi walled carbon nanotubes (MWCNTs, NANOCYL® NC7000™), ethylene glycol (EG, Sigma-Aldrich), L-ascorbic acid (LA, Sigma-Aldrich), sodium hydroxide (NaOH, Sigma-Aldrich), hydrochloric acid (HCl, Sigma-Aldrich), sulfuric acid (H₂SO₄, Sigma-Aldrich), nitric acid (HNO₃, Sigma-Aldrich), Dicyandiamide (C₂H₄N₄, Sigma-Aldrich), methanol (CH₃OH, Sigma-Aldrich), glycerol (H(CH₂OH)₂OH or C₃H₈O₃, Sigma-Aldrich), ethanol (CH₃CH₂OH, Sigma-Aldrich), Nafion solution (5% in isopropanol and water) were used without further purification. The nickel single-atom catalyst supported on carbon nanotubes (NiSA-N-CNTs or NiSA in short) was synthesized by one-pot pyrolysis method as reported recently.¹ The Ni SAC loading was 20.3 wt%.

Synthesis of palladium NPs on NiSA

Palladium NPs supported on NiSA were synthesized using EG assisted with LA as reducing agent. Briefly, 30 mg of NiSA was dispersed in 50 ml of EG for 30 min in an ultrasonic bath before an appropriated amount of PdCl₂ was gradually dropped into the solution. The solution was vigorously stirred by a magnetic stirrer for 3 hr. The pH of the solution was adjusted by NaOH (2M) to below 12 and stirred for another 1 hr. Then, the pH of the solution was adjusted to below 3 by 5M HCl solution, followed by adding an excess amount of LA and then stirred for 8 h. The slurry was washed with ethanol and dried in a conventional oven for 8 h at 100 °C, yielding Pd/NiSA. The Pd loading was designed as 20 wt%, 30 wt% and 40 wt%. In comparison, 20 wt% Pd supported on N-CNT was synthesized following the same procedure as that of NiSA and denoted as Pd/N-CNTs. N-CNTs were prepared by multi-stage pyrolysis method using dicyandiamide as nitrogen source. MWCNT was treated by conventional acid treatment method in mixed acid solution of 1:1 (v/v) 12 M of sulfuric acid and 12 M of nitric acid with the ratio of carbon to acid mixture 70:30 (v/v) before N-doped process (denoted as O-CNT). The slurry was shaken for 8 hours. Afterward, it was washed with deionized water for several times until the pH became 7, followed by filtration and drying overnight at 110 °C in a conventional oven. Then, it was dispersed in ethanol assist with ultrasonic bath. The dispersion was added and grounded until uniformity with mass ratio 1:200 of O-CNT:DCM. The uniformed powder was dried at ambient temperature for overnight and then pyrolyzed in argon-rich condition at 800 °C for 1 h. (denoted as N-CNT). Fig. 1 shows the scheme of synthesis of Pd NPs supported on NiSA.

Characterization

Distributions and morphology of Pd NPs on NiSA and N-CNT electrocatalysts were studied by transmission electron microscopy (TEM) on FEI Talos FS200X. The average particle size of

deposited Pd NPs was obtained by measuring over 100 nanoparticles from the TEM micrographs. X-ray diffraction patterns (XRD) of the electrocatalysts were performed by D8 advance from Bruker AXS using Cu K α as X-ray source ($\lambda=1.5406$ Å) and low background stub holder. Catalyst powder was dispersed in ethanol by ultrasonication technique, subsequently dropped onto the holder. The patterns were reported with 2 theta in the range of 25° to 80° at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD spectrometer using a monochromatic AlK α (1486.6 eV) irradiation source operated at 225 W. The vacuum pressure of the analysis chamber of the spectrometer was maintained a 5×10^{-11} Torr or lower throughout the duration of the analyses.

Electrochemical characterization was accomplished by a conventional three-electrode technique using Gamry potentiostat/galvanostat interface 1000. Glassy carbon rotating disk electrode (RDE) with diameter 5 mm was served as the working electrode. A graphite rod with diameter of 5 mm and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The catalysts was casted onto RDE by dropping 20 μ l of catalyst ink (2 mg catalyst in 1 ml of 0.5% Nafion in isopropanol and water). Cyclic voltammetry (CV) was conducted within the potential window of -0.8 to 0.3 vs. SCE with a scan rate of 50 mV/s.

Chronoamperometry (CA) curves were conducted at -0.3 V vs SCE for 2400 sec. The electrochemical properties of the electrocatalysts for alcohol oxidation reaction were measured in N₂-saturated 1M KOH + 1M CH₃OH, 1M KOH + 1M CH₃CH₂OH and 1M KOH + 1M H(CH₂OH)₂OH solutions.

Table S1. Pd particle size, binding energy of Pd and Ni and the activity of the catalysts for methanol, ethanol and glycerol oxidation in 1M KOH solution.

Material	Size (nm)	Biding energy, eV				Methanol		Ethanol		Glycerol	
		Pd 3d _{5/2}	Pd 3d _{3/2}	Ni 2p _{1/2}	Ni 2p _{3/2}	E _s	I _f	E _s	I _f	E _s	I _f
20%Pd/NiSA	8.1	341.0	355.7	871.9	854.7	-0.47	356	-0.57	1200	-0.35	778
30%Pd/NiSA	9.2	340.7	355.5	872.0	854.7	-0.45	123	-0.55	754	-0.31	247
40%Pd/NiSA	11.8	340.7	355.4	871.9	854.6	-0.43	72	-0.53	86	-0.27	137
20%Pd/N-CNT	8.3	340.6	355.2	-	-	-0.41	30	-0.52	19	-0.26	42
NiSA	-	-	-	872.4	854.9	-	0.0	-	0.0	-	0.0

Reference:

1. Y. Cheng, S. Y. Zhao, B. Johannessen, J. P. Veder, M. Saunders, M. R. Rowles, M. Cheng, C. Liu, M. F. Chisholm, R. De Marco, H. M. Cheng, S. Z. Yang and S. P. Jiang, *Adv. Mater.*, 2018, **30**, 1706287.