

Electronic Supplementary Information

Experimental

Fabrication of Pd/Ni NWs electrode

The chemical reagents in this work were obtained from Enterprise Group Chemicals Reagent Co. Ltd. China. Polycarbonate membrane coated with polyvinylpyrrolidone as wetting agent was purchased from Whatman Ltd. Cerro-Bismuth alloys with a low melting point of 65 °C were obtained from Si Knight welding material manufacture Co. Ltd. All chemicals were analytical grade and were used as-received without further purification. Ultra-pure water (Millipore, 18 MΩ cm) was used throughout the study.

The Ni nanowires substrate was obtained by a polycarbonate membrane (PM) template-assisted method. In short, primarily, low-melting Cerro-Bismuth (C-B, melting point: 65 °C) alloys were covered by PM template and placed in a drying oven at 100 °C. The C-B alloys transformed to liquid state at 100 °C that higher than their melting point and afterwards brushed onto the one side of PM. After cooling to ambient temperature, the prepared solid C-B alloys combined with PM template were adopted as the cathode for over-plating of Ni metal in the pores of PM at -40 mA cm^{-2} in 0.2 M NiCl₂ + 0.6 M H₃BO₃ + 1 M Ni₂SO₄ + 0.15 mM C₁₂H₂₅SO₄Na + 5 mM C₇H₅O₃NS for 4 h. The concentration unit of mol L⁻¹ was denoted as M. The electrolyte was kept stirring under flowing nitrogen at a water bath temperature of 55 °C during the electrodeposition. After that, the PM template contained Ni metal was removed from the surface of C-B alloys. Later on, the PM template was chemically dissolved by CH₂Cl₂ solvent and subsequently the nickel nanowires were successfully obtained after rinsing in acetone and ethanol for several times and drying in air. Finally, the Pd decorated Ni nanowires (Pd/Ni NWs) electrode was fabricated via the galvanic displacement of Pd nanoparticles on the Ni nanowires surface, as presented in Fig. 1. The Pd catalysts were spontaneously formed on Ni NWs by placing the nickel nanowires substrate in the 1.0 mM Na₂PdCl₄ solution for 5 minutes to acquire the Pd/Ni NWs electrodes. According to some literatures,^{s1-s3} the substitution reaction between nickel and palladium can be described as Eq. (3).



Characterization

The surface morphology and elemental analysis were examined by a scanning electron microscope (SEM, VEGA3 TESCAN) combined with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscope (TEM, FEI Teccai G2S-Twin) equipped with EDX mapping and high-resolution transmission electron microscopy (HRTEM) was used to study the detailed structure of a single composite nanowire and its element distribution. The structure of synthesized samples was conducted by an X-ray diffractometer (XRD, Rigaku TTR III) with Cu-Kα radiation ($\lambda=0.1514178 \text{ nm}$). The loadings of Pd were analyzed by an inductive coupled plasma emission spectrometer (ICP, Thermo Scientific Xseries II). Pd in the 1.0 cm² Pd/Ni NWs electrode was first dissolved in aqua regia solution and subsequently diluted to 1000 mL solution for the ICP tests. The catalysts that used for TEM measurement were obtained as follows: the Ni and Pd/Ni nanowires were firstly scratched down from the supported substrate and then dispersion in the 10 mL ethanol, followed by dropping the 10 mL suspension onto the lacey support film and dried in air.

Electrochemical measurements

Catalytic tests of NaBH_4 electrooxidation were analyzed by chronoamperometry and cyclic voltammetry using computer-controlled Autolab PGSTAT302 potentiostat (Eco Chemie) with GPES software in the conventional 3-electrodes electrochemical cell. The as-obtained Ni NWs (1 cm^2) and Pd/Ni NWs (1 cm^2) electrodes were used as working electrodes, and the Pt plate (4 cm^2) was applied as the auxiliary electrode. The reference electrode was placed in a separate compartment and connected to the electrochemical cell by a Luggin capillary. An Hg/HgO electrode was used as reference electrode in alkaline media and all potentials are changed and reported with respect to reversible hydrogen electrode (RHE) in this work. The NaBH_4 electrooxidation was examined in the NaBH_4 and NaOH solution. All tests were measured at environmental temperature ($20 \pm 1 \text{ }^\circ\text{C}$) in N_2 atmosphere.

Results and discussion

XRD analysis was invoked to investigate the as-prepared electrodes structures. Fig. S1 presents the XRD patterns of Ni nanowires (NWs) and Pd decorated Ni nanowires (Pd/Ni NWs) electrodes obtained by a spontaneous deposition. As seen, the three apparent diffraction peaks were discovered on the Ni NWs at $2\theta = 44.5^\circ$, 51.9° and 76.4° , corresponding to the (111), (200) and (220) planes of Ni metal (JCPDS No. 04-0850), respectively. Differently from the Ni NWs pattern, the diffraction peak of characteristic palladium was appeared at 40.1° on the Pd/Ni NWs electrode, which was coincided well with the (111) plane of palladium metal (JCPDS No. 65-2870). The amplified pattern of palladium diffraction peak on Pd/Ni NWs electrode was apparently shown in Fig. S1b. It is noteworthy that the intensity of Pd diffraction peak was much weaker than that of the Ni NWs substrate, implying that the formed amount of palladium was very low.

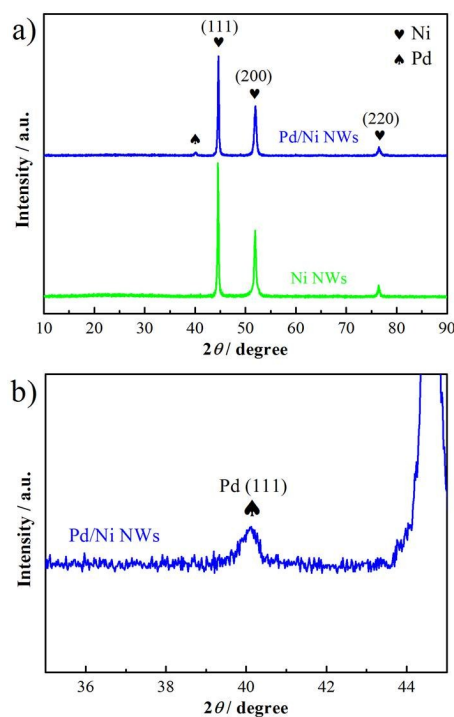


Fig. S1 XRD patterns of the Ni NWs and Pd/Ni NWs electrodes (a); the enlarged XRD pattern of Pd diffraction peak on Pd/Ni NWs electrode (b).

The commercial Pd/C (Hesen electric Co. Ltd.) was employed as a commercial baseline for the comparison of NaBH₄ electrooxidation activity. In order to compare the catalytic performance of the Pd/Ni NWs electrode with the electrode made with conventional Pd, the commercial Pd/C (the Pd loading is 20 wt % and the carbon support is Vulcan XC72R) was applied to carbon fiber cloth to obtain an electrode with the Pd loading same as the Pd/Ni NWs electrode (0.0358 mg). The geometric area of commercial Pd/C electrode (1 cm²) is the same as that of the Pd/Ni NWs electrode. Fig. S2 shows the comparative CVs of commercial Pd/C and Pd/Ni NWs electrodes for NaBH₄ electrooxidation in 1.00 M NaOH and 0.12 M NaBH₄ solutions. The oxidation current on the Pd/Ni NWs electrode was obviously higher than that on the commercial Pd/C electrode at the same potential, demonstrating a benefit to the nanowires over the traditional approach.

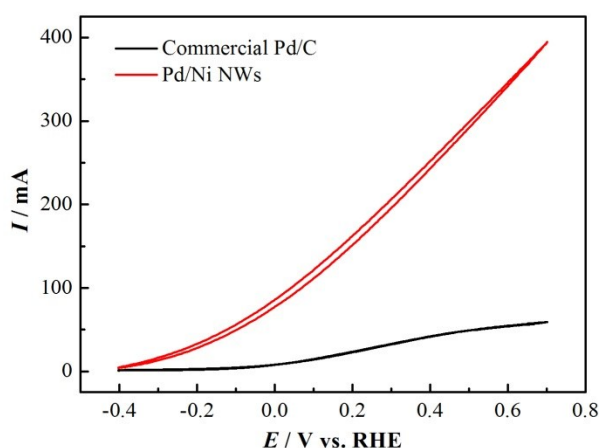


Fig. S2 Comparative CVs for NaBH₄ electrooxidation in 1.00 M NaOH and 0.12 M NaBH₄ solutions at the Pd/Ni NWs electrode and the electrode made with commercial Pd/C. Scan rate: 5 mV s⁻¹.

The chronoamperometric examination was used for investigating the electrocatalytic stability of Pd/Ni NWs electrode towards NaBH₄ oxidation. Fig. S3 represents the chronoamperometric plots of Pd/Ni NWs electrode in 0.12 M NaBH₄ + 1.00 M NaOH solution at various potentials. Clearly, the anodic currents of NaBH₄ oxidation maintained a durably steady-state condition at Pd/Ni NWs electrodes during the 1800 s testing time at all the fixed potentials (0.3, 0.1 and -0.1 V), testifying that the Pd/Ni NWs electrodes own an excellent electrocatalytic stability for NaBH₄ oxidation in alkaline media. In addition, the anodic current densities significantly improved with positively changing the applied potential, which was in keeping with the results of Fig. 4d. The anodic current density at 0.3, 0.1 and -0.1 V finally reached 4.4, 2.6 and 1.2 mA cm⁻² (normalized to ESA), respectively.

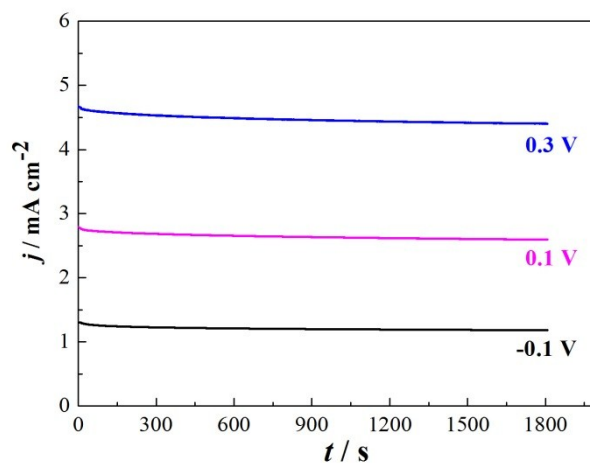


Fig. S3 Chronoamperometric plots of NaBH₄ oxidation in 0.12 M NaBH₄ and 1.00 M NaOH solution on Pd/Ni NWs electrodes at various fixed potentials.

References

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