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Electronic Supplementary Information

Highly Stable Pt_3Ni Nanowires Tailored by Trace Au for the Oxygen Reduction Reaction

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Experimental Section

Preparation of the 1D Pt_3Ni and Au-decorated Pt_3Ni nanowires: All chemicals in analytical level were purchased commercially (Aladdin, China) and used without further purification. In a typical synthesis of Pt_3Ni nanowires, platinum (II) acetylacetonate ($Pt(acac)_2$, 10 mg), nickel (II) acetylacetonate ($Ni(acac)_2$, 2.42 mg), dodecyltrimethylammonium dromide (CTAB, 100 mg) and oleylamine (OAm, 10 mL) were added into a 25 mL vial and ultrasonicated for 1 h to obtain a homogeneous solution. Consequently, the mixture was heated to 180 °C in 40 min and maintained at 180 °C for 1 h in an oil bath, then the system was cooled naturally. The products were collected by centrifugation and cleaned five times with an ethanol/cyclohexane mixture (volume 3/1), and then then products were dried at 40 °C in an oven for other tests. The synthesis processes for Au-Pt_3Ni NWs with various Au/Pt content (0.01, 0.1 and 1) were the same with that of Pt_3Ni NWs except for the different amount of chloroauric acid ($HAuCl_4$) was added to the solution after the reaction has lasted for 2h, and then the reaction was continued for another 1h. In detail, $HAuCl_4$ of 84 μg (atomic ratio of Au/Pt=0.01), 0.84 mg and 8.4 mg was dissolved in 1.5 mL OAm solution and ultrasonicated for 1 h before adding to the reaction systems. The resultant products with different Au/Pt ratio were labelled as $Au_{0.01}$-Pt_3Ni, $Au_{0.1}$-Pt_3Ni and Au_1-Pt_3Ni, respectively, regardless the Ni/Pt ratios.

Characterizations: X-ray diffraction (XRD) patterns was conducted using a powder diffractometer (X'Pert-Pro) with a Cu radiation source (Cu Kα, λ=0.15406 nm). The size and morphology was studied by scanning electron microscope (SEM, JEOL JSM-6510LV) and transmission electron microscopy (TEM, Hitachi H-800). High-angle annular dark field (HAADF) images and the corresponding energy dispersive spectrometer (EDS) elemental mapping were collected by an aberration-corrected TEM (FEI Titan G2 60-300, USA). X-ray photoelectron spectroscopy (XPS) spectra were obtained by the spectroscopy (Thermo

Scientific, ESCALAB 250 XI). The actual compositions were determined by analyzing the inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer Elan-6000).

Electrochemical test: The electrochemical tests are all collected on Metrohm PGSTAT302N workstation equipped with rotating measurements (Pine Research Instruments, USA). The glassy carbon electrode (GCE, 0.196 cm^2) was adopted as the working electrode. A platinum wire and Ag/AgCl (3 M NaCl) electrode was adopted as the counter and reference electrode, respectively. All potential data were corrected with reversible hydrogen electrode (RHE).

Before the electrochemical tests, the catalysts were obtained by loading the prepared samples on the commercial carbon support (Cobalt, XC-72R), and the Pt loading amount was kept at roughly 20 wt%. In detail, desirable amount of Pt_3Ni nanowires (11 mg) and carbon (40) was mixed in cyclohexane under ultrasonicating and stirred overnight. Afterwards, the resultant products were dried at an oven at 80 °C for 12 h. Au-Pt_3Ni/C catalyst with different Au content was synthesized with the same processes as above except different amount of based nanowires were added. The amount of $Au_{0.01}$-Pt_3Ni, $Au_{0.1}$-Pt_3Ni and Au_1-Pt_3Ni NWs was 11.0, 11.3 and 14.4 mg, respectively, was loaded on the carbon support to obtain $Au_{0.01}$-Pt_3Ni/C, $Au_{0.1}$-Pt_3Ni/C and Au_1-Pt_3Ni/C catalysts. JM Pt/C (Vulcan XC-72R carbon as the support, 20 wt%, Johnson Matthey) was used as the counterpart. The catalyst ink was prepared by sonicating the mixture of deionized water (1 mL), catalyst (4 mg), enthanol (0.9 μmL) and nafion (5 wt% in enthanol, 0.1 mL) for 30 min, and then 5 μL of the solution was dropped onto the GCE surface and dried under ambient conditions. The Pt loadings were determined by ICP-MS and kept at 10.2 μg cm^{-2} for all the tested samples.

Cyclic voltammetry (CV) characterization of the catalysts was collected in the scope from 0.1 to 1.1 V in N_2-saturated 0.1 M $HClO_4$ solution at a scanning rate of 50 mV s^{-1}. The electrochemical active area (ECSA) was derived both from the CV by integrating the area of the hydrogen under potential desorption and the CO stripping curves. The CO stripping curves of the samples were collected as follows: The working electrode was firstly immersed into the CO-saturated 0.1 M $HClO_4$ solution, and in order to make sure that all the exposed Pt atoms were covered by CO, the CO gas flow (20 sccm) was bubbled to the solution for 30 minutes with the electrode was kept at 0.1 V (VS RHE). Then the dissolved CO was driven away by bubbling N_2 flow (50 sccm) for 20 min, and the first forward current scan was recorded. Linear sweep voltammetry (LSV) measurements were conducted at a scan rate of 10 mV s^{-1} under the rotation rate of 1600 rpm. Accelerated durability test (ADT) is performed in O_2-saturated 0.1 M $HClO_4$ solution for lasting 20000 cycles (0.6–1.1 V).

Computational details: Spin-polarized calculations within the density-functional theory framework were carried out as implemented in the Vienna *ab initio* simulation package (VASP).[1] The ion-electron interactions were represented by the projector-augmented wave (PAW) method[2] and the electron exchange-correlation by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.[3] The Kohn-Sham valence states were expanded in a plane-wave basis set with a cut-off energy of 400 eV. The empirical DFT-D3 correction was contained for the weak van der Waals interaction,[4] and the dipole correction was also adopted for all calculations.[5] For $Pt_3Ni(111)$ skin, the model was a monolayer Pt(111) covered on a periodic four-layer slabs with a (2×2) surface unit cell of Pt_3Ni. One surface Pt atom was removed to mimic the defective Pt_3Ni skin. The optimized lattice constant of Pt_3Ni bulk is 3.83 Å. For the Brillouin zone integration, a 11×11×1 Monkhorst-Pack mesh was used. The atoms in the bottom two layers were frozen to their bulk position and the rest of the atoms were allowed to relax. The geometry optimization was performed when the convergence criterion on forces became smaller than 0.05 eV/Å and the energy difference was $<10^{-4}$ eV.

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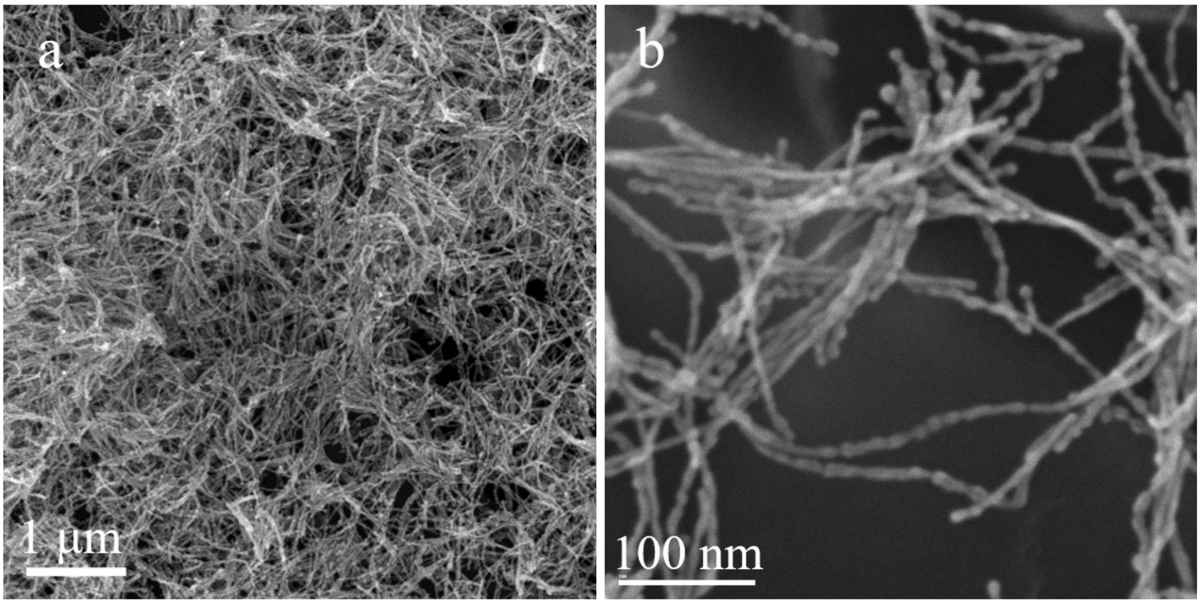

Figure S1. (a) Low resolution and (b) high resolution SEM image of as-synthesized Pt_3Ni nanowires.

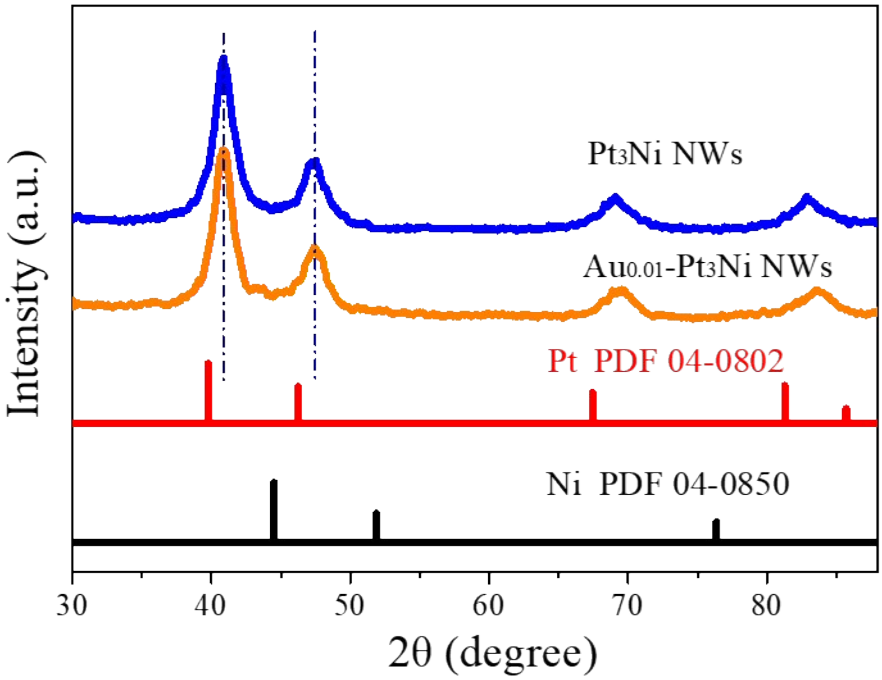

Figure S2. XRD patterns of Pt_3Ni and $Au_{0.01}$-Pt_3Ni nanowires.

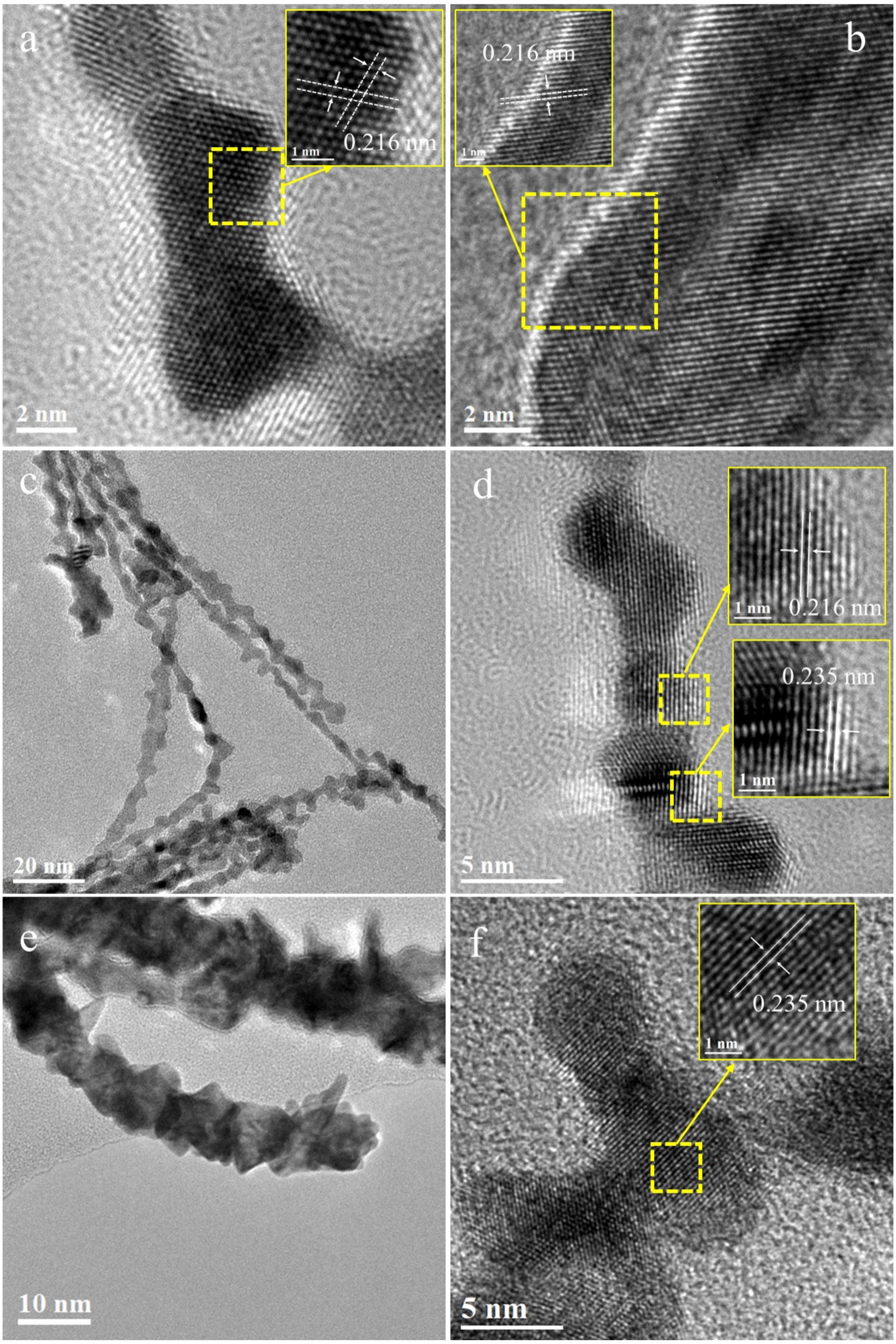

Figure S3. (a, b) STEM image of $Au_{0.01}$-Pt_3Ni, TEM images of (c, d) $Au_{0.1}$-Pt_3Ni and (e, f) Au_1-Pt_3Ni nanowires, and the insets are the corresponding enlarged image marked in the yellow square. The lattice spacing of 0.235 nm, corresponding to the fcc Au (111) facet can be observed with increasing the Au content.

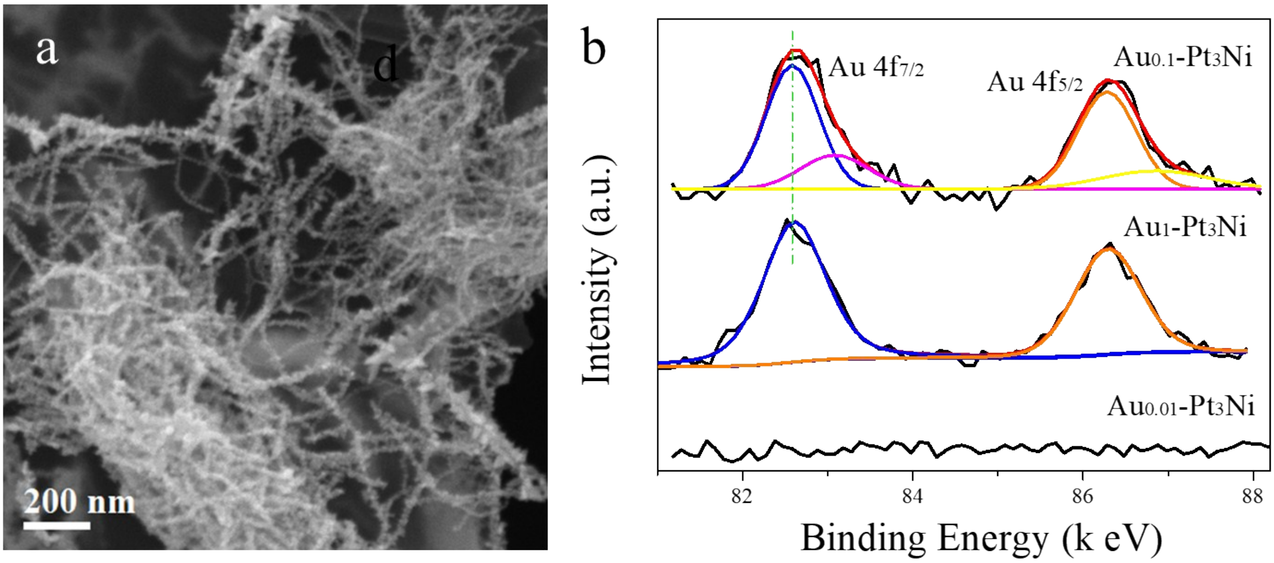

Figure S4. (a) SEM image of Au_1-Pt_3Ni/C and (b) Au 4f pattern peaks of $Au_{0.01}$-Pt_3Ni/C, $Au_{0.1}$-Pt_3Ni/C and Au_1-Pt_3Ni/C.

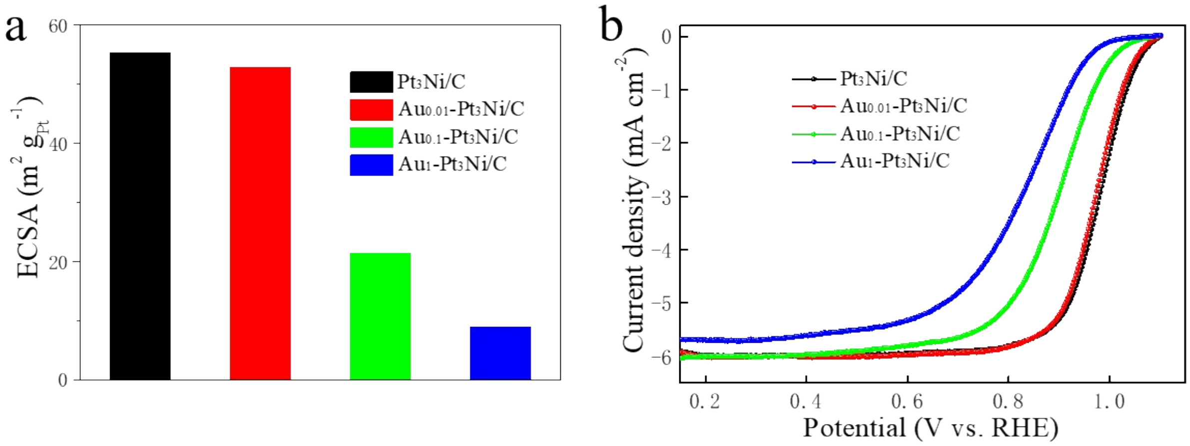

Figure S5. Comparisons of ECSAs and LSV curves of Pt_3Ni/C, $Au_{0.01}$-Pt_3Ni/C, $Au_{0.1}$-Pt_3Ni/C and Au_1-Pt_3Ni/C catalysts.

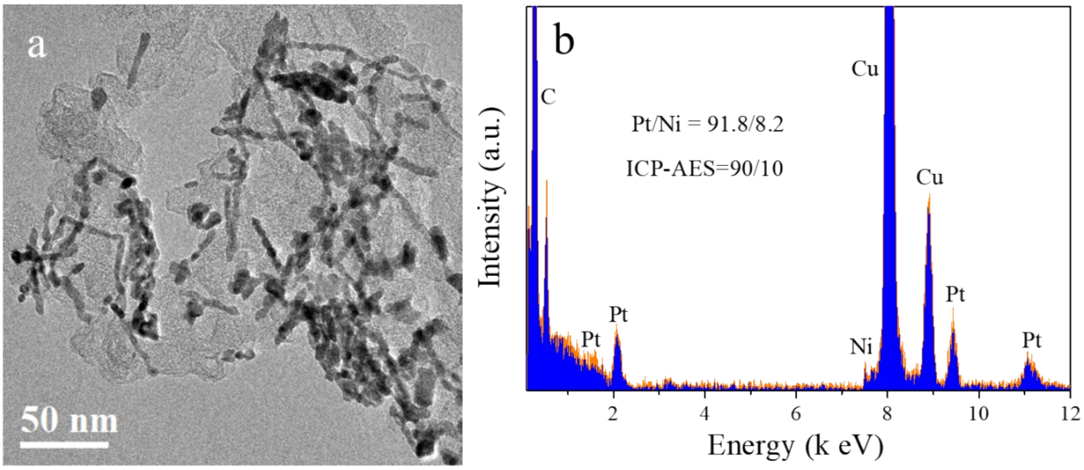

Figure S6. (a) TEM image and (b) TEM-EDX profile of Pt$_3$Ni/C after the durability test.

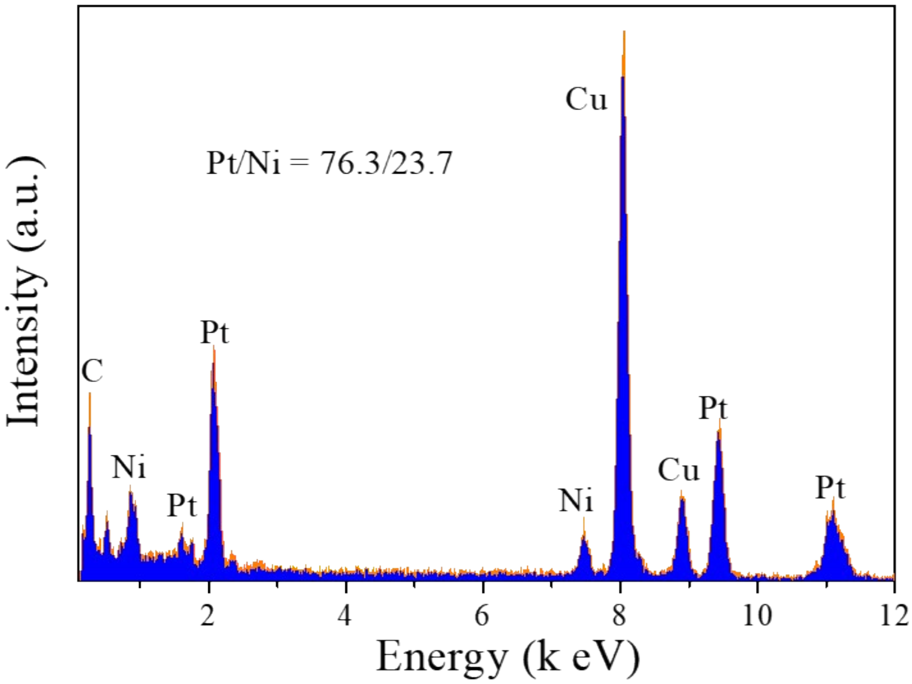

Figure S7. TEM-EDX profile of $Au_{0.01}$-Pt_3Ni/C after the durability test.

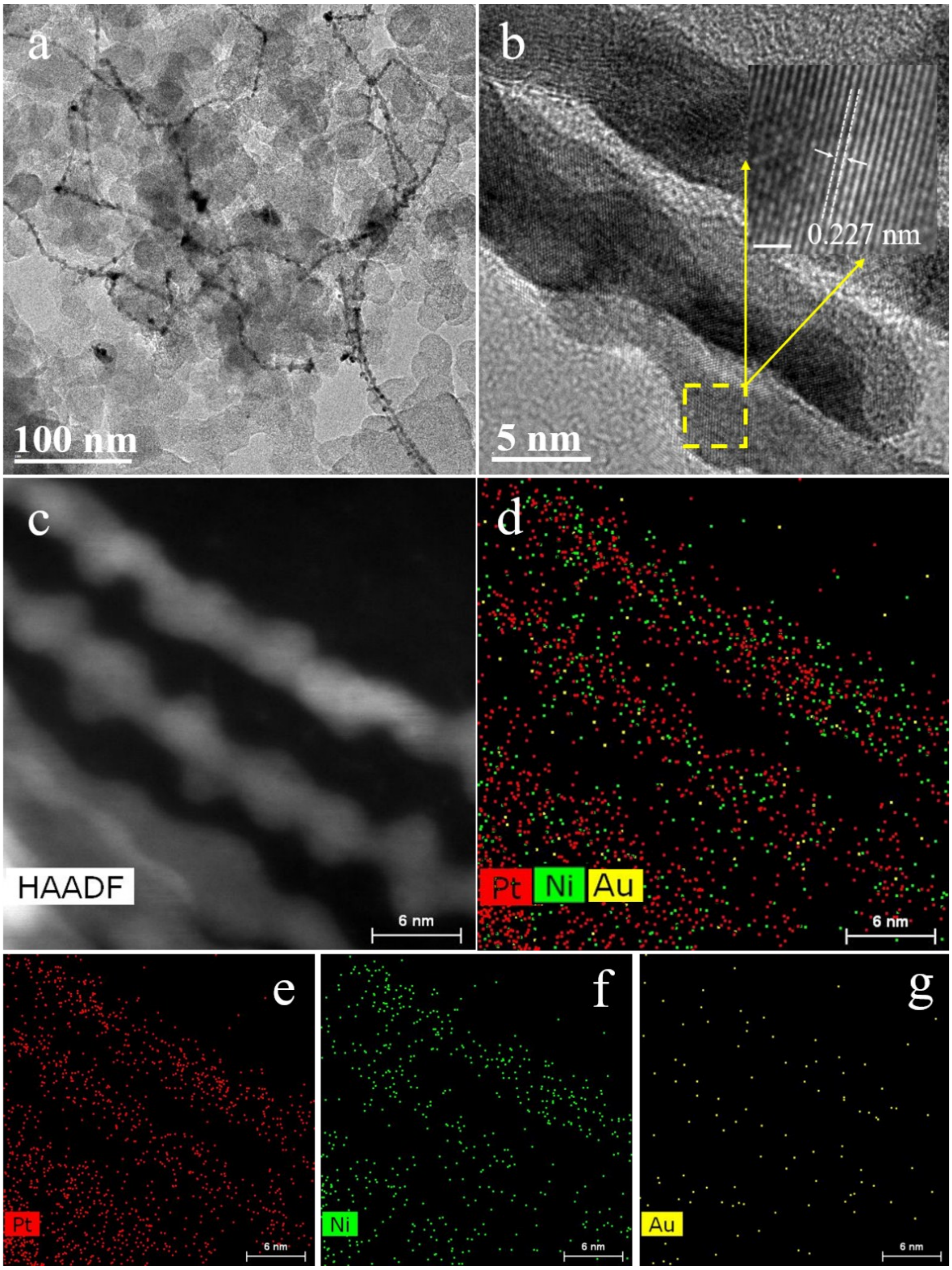

Figure S8. (a,b) TEM images of $Au_{0.01}$-Pt_3Ni/C after the durability test, and the inset of (b) is the magnified image marked in the yellow square, and the scale bar is 1 nm. (c-g) HAADF-STEM image of two $Au_{0.01}$-Pt_3Ni nanowires, and the corresponding elemental mapping of Pt (red), Ni (green) and Au (yellow).

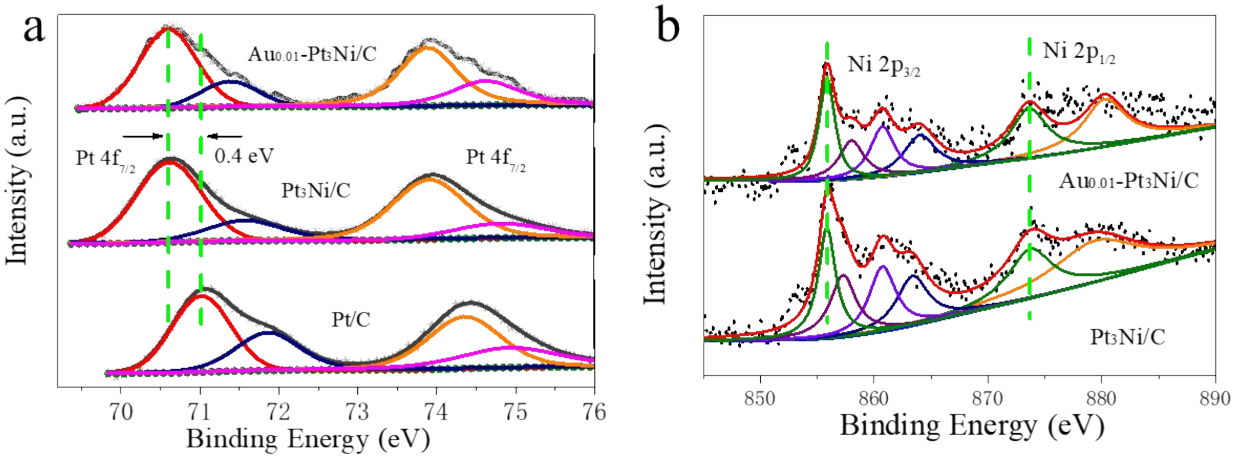

Figure S9. Pt 4f spectra of Pt/C, Pt_3Ni/C and $Au_{0.01}$-Pt_3Ni/C, (b) Ni 2p spectra of Pt_3Ni/C and $Au_{0.01}$-Pt_3Ni/C catalysts.