Electronic Supplementary Information (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Au/Pt and Au/Pt_3Ni nanowires as self-supported electrocatalysts with high activity and durability for oxygen reduction reaction

Yueming Tan,[a] Jingmin Fan,[a] Guangxu Chen,[a] Nanfeng Zheng [a]* and Qingji Xie[b]

[a] State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering，Xiamen University, Xiamen 361005, China

Email: nfzheng@xmu.edu.cn

[b] Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Experimental Section

Reagents: Pt(II) acetylacetonate (Pt(acac)$_2$) was purchased from Alfa Aesar, oleylamine was purchased from Sigma-Aldrich, Ni(II) acetylacetonate (Ni(acac)$_2$), $HAuCl_4 \cdot 4H_2O$, and *n*-butylamine were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All other chemicals were of analytical grade or better quality. Ultrapure water (Millipore, ≥18 MΩ cm) was used throughout.

Instrumentation: Electrochemical experiments were conducted on a CHI760D electrochemical workstation (CH Instrument Co., USA). A conventional three-electrode system included a glassy carbon RDE (diameter 5 mm, Pine Research Instrumentation) coated with catalysts, a Pt auxiliary electrode and a leak-free saturated calomel reference electrode (SCE). All the potentials are reported with respect to the reversible hydrogen electrode (RHE) and all electrochemical data were obtained at room temperature (25 ^{o}C). TEM and HRTEM studies were performed on a TECNAI F-30 high-resolution transmission electron microscopy operating at 300 kV. The samples were prepared by dropping ethanol dispersions of the samples onto 300-mesh carbon-coated copper grids and immediately evaporating the solvent. SEM studies were performed on a Hitachi S4800 scanning electron microscope with a field emission electron gun. The samples were prepared by dropping ethanol dispersions of the samples onto Si substrates and immediately evaporating the solvent. XRD studies were performed on a PANalytical X'pert Pro X-ray diffractometer.

Synthesis of Au nanowires: $HAuCl_4 \cdot 4H_2O$ (0.2 g) in 2 mL hexane and 2 mL oleylamine was added to the mixture of oleic acid (10 mL) and oleylamine (8 mL) at 80 °C under vigorous magnetic stirring. Magnetic stirring was stopped after 5 min, and the solution was kept steady at this temperature for 4 h. The Au nanowires were precipitated out by adding ethanol and then centrifugation for further applications.

Synthesis of Au/Pt nanowires: 10 mg Au nanowires and 20 mg Pt(acac)$_2$ were mixed together with 20 ml oleylamine at room temperature. Then the mixture was heated from room temperature to 220 ^{o}C and kept at this temperature for 1 h with stirring. The resulting products were collected by centrifugation, and washed several times with ethanol and cyclohexane.

Synthesis of Au/Pt$_3$Ni nanowires: 10 mg Au nanowires, 20 mg Pt(acac)$_2$ and 5 mg Ni(acac)$_2$ were mixed together with 20 ml oleylamine at room temperature. Then the mixture was heated from room temperature to 220 ^{o}C and kept at this temperature for 1 h with stirring. The resulting products were collected by centrifugation, and washed several times with ethanol and cyclohexane.

Surface treatment of Au/Pt and Au/Pt$_3$Ni nanowires: The capping agents on the surface of Au/Pt and Au/Pt$_3$Ni nanowires were treated following a reported methodology.[1] The solid product was dispersed in *n*-butylamine and kept under stirring for 3 days and then collected by centrifugation. The precipitate was re-dispersed in methanol by sonicating for 15 min and then separated by centrifugation. This procedure was repeated three times. The final samples were dispersed in ethanol for further characterization and electrochemical studies.

Electrochemical studies: The Pt loadings of Au/Pt$_3$Ni and Au/Pt catalysts modified on the glassy carbon RDE were 10.4 and 11.9 μg cm^{-2}, respectively, based on the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements. For Pt/C catalyst (20 wt%, E-TEK), an aqueous dispersion (1 mg mL^{-1}) was prepared and sonicated for 5 min. 15 μL of the dispersion was then was cast on the glassy carbon RDE and air-dried. Therefore, the Pt loading of Pt/C catalyst was 15.3 μg cm^{-2}. 5 μL of Nafion solution (0.1%) was placed on the surface of the above catalysts modified RDE and air-dried before electrochemical experiments. Prior to electrochemical experiments, the catalysts modified RDE were subjected to continuous potential cycling (0.05 V to 1.1 V vs. RHE, 50 mV s^{-1}) in 0.10 M aqueous $HClO_4$ until cyclic voltammograms became reproducible. For specific electrochemically active surface area (SEASA) measurements, the electrolyte solutions were purged with high-purity N_2 gas before use for 30 min. The ORR measurements were performed in 0.1 M $HClO_4$ solutions under flow of O_2 using the catalysts modified RDE at a rotation rate of 1,600 rpm and a sweep rate of 10 mV s^{-1}. In the ORR polarization curve, current densities (j) were normalized in reference to the geometric area of the glassy carbon RDE (0.196 cm^2). For the ORR at a RDE, the kinetic current (j_k) was calculated based on the Koutecky-Levich equation,[2]

$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{j_\mathrm{d}}$$

where j is the experimentally measured current, j_d is the diffusion-limiting current, and j_k is the kinetic current. The accelerated durability tests were performed at room temperature in O_2-saturated 0.1 M $HClO_4$ solutions by applying cyclic potential sweeps between 0.6 and 1.1 V versus RHE at a sweep rate of 50 mV s^{-1} for 5000 cycles.

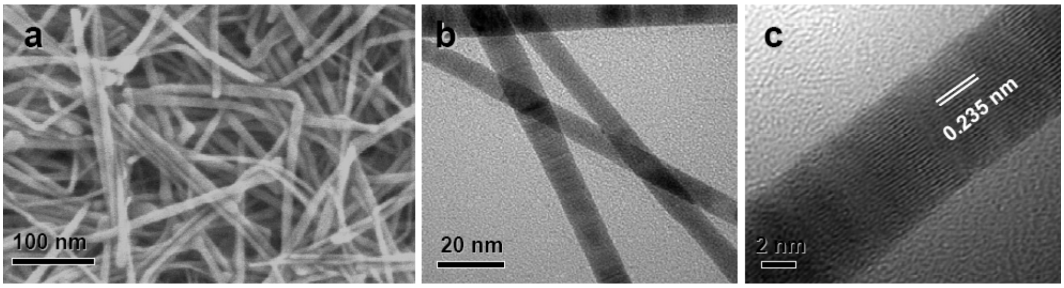

Fig. S1 SEM (a), TEM (b) and HRTEM (c) images of Au nanowires. The Au nanowires exhibit high aspect ratios with an average diameter of ~7 nm and millimeter-scale length. The *d* spacing of the lattice shown in the high resolution TEM (HRTEM) image was 0.235 nm (Fig. S1c), corresponding to (111) lattice spacing (0.23 nm) of the face centered cubic (fcc) Au.

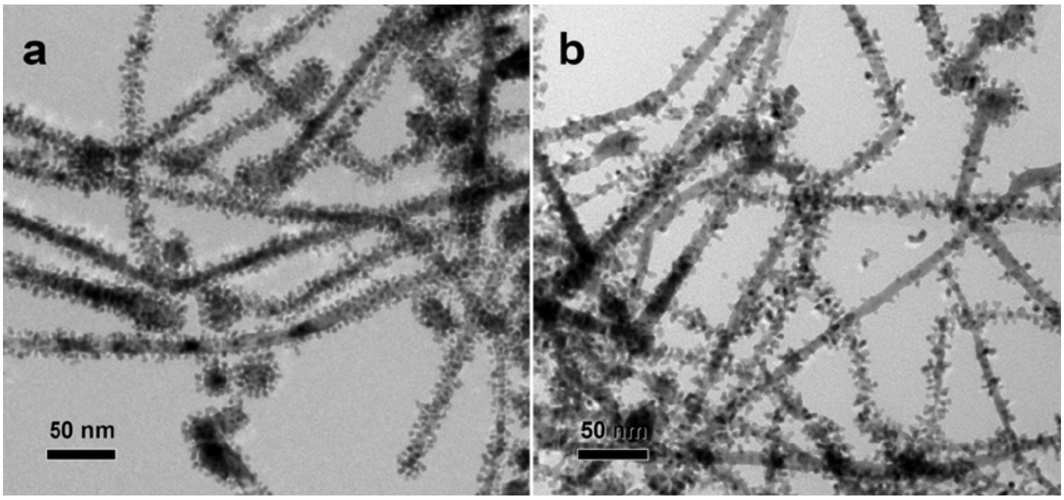

Fig. S2. Large-area TEM images of Au/Pt (a) and Au/Pt_3Ni (b) nanowires.

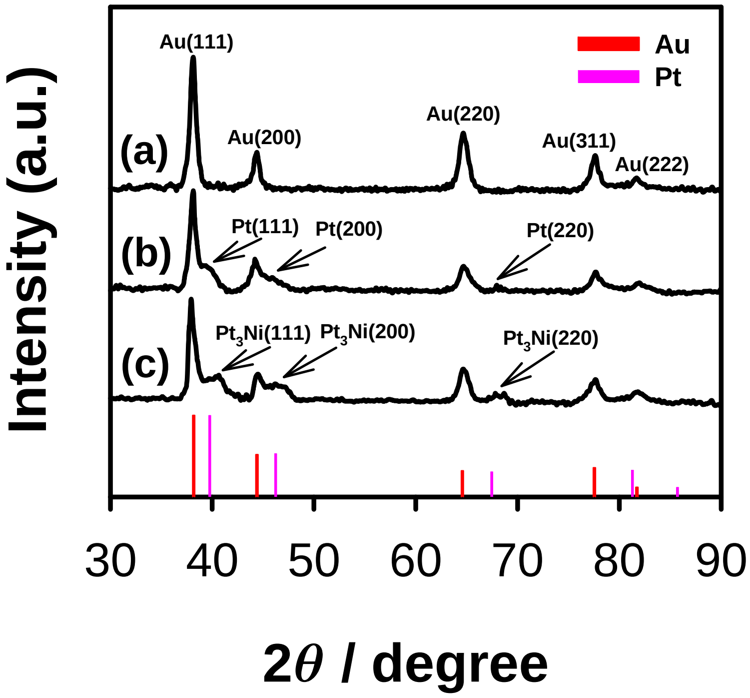

Fig. S3. XRD patterns of Au (a), Au/Pt (b), and Au/Pt_3Ni nanowires (c). The intensity and position for Au and Pt references were taken from the JCPDS database (Au: card no. 04-0784, Pt: card no. 04-0802).

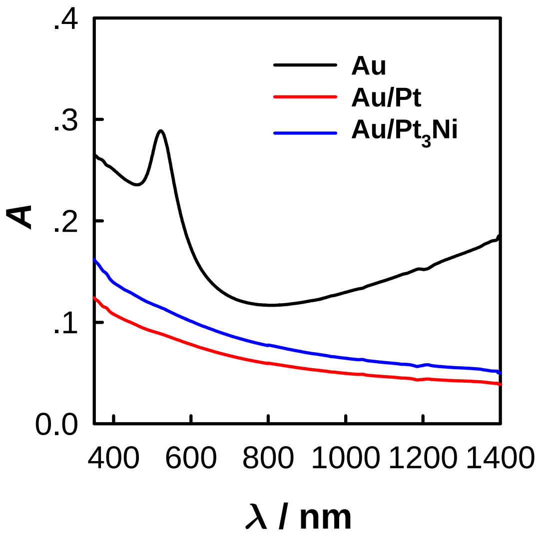

Fig. S4. Absorption spectra of Au, Au/Pt, and Au/Pt_3Ni nanowires.

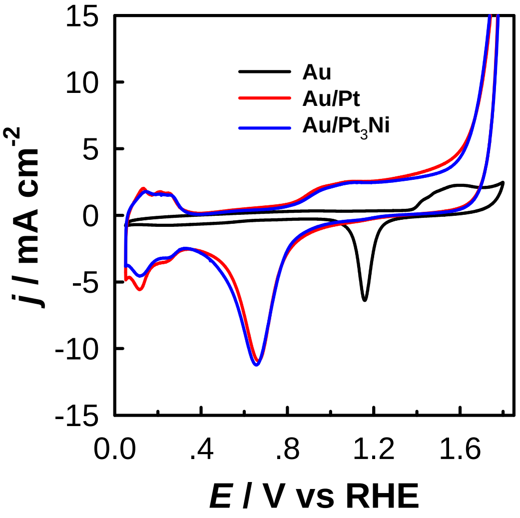

Fig. S5. Cyclic voltammograms of Au, Au/Pt, and Au/Pt_3Ni nanowires modified glassy carbon electrodes in 0.5 M H_2SO_4 aqueous solution at the scan rate of 50 mV s^{-1}.

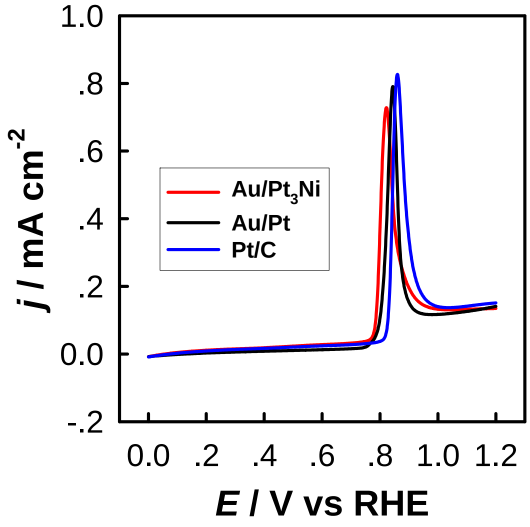

Fig. S6 CO stripping voltammograms of Au/Pt, Au/Pt_3Ni and Pt/C catalysts modified glassy carbon electrodes in 0.5 M H_2SO_4 aqueous solution at the scan rate of 50 mV s^{-1}. The CO oxidation peak in the stripping voltammogram obtained on Au/Pt_3tNi nanowires is only a little more negative than those on Au/Pt nanowires and Pt/C, implying a Pt-enriched surface of Au/Pt_3tNi nanowires. Generally, if there are a significant amount of Ni species on the surface, the CO stripping peak should be much more negative than that on the pure Pt.[3] The formation of Pt-rich surface mainly results from surface segregation in the synthesis.[4]

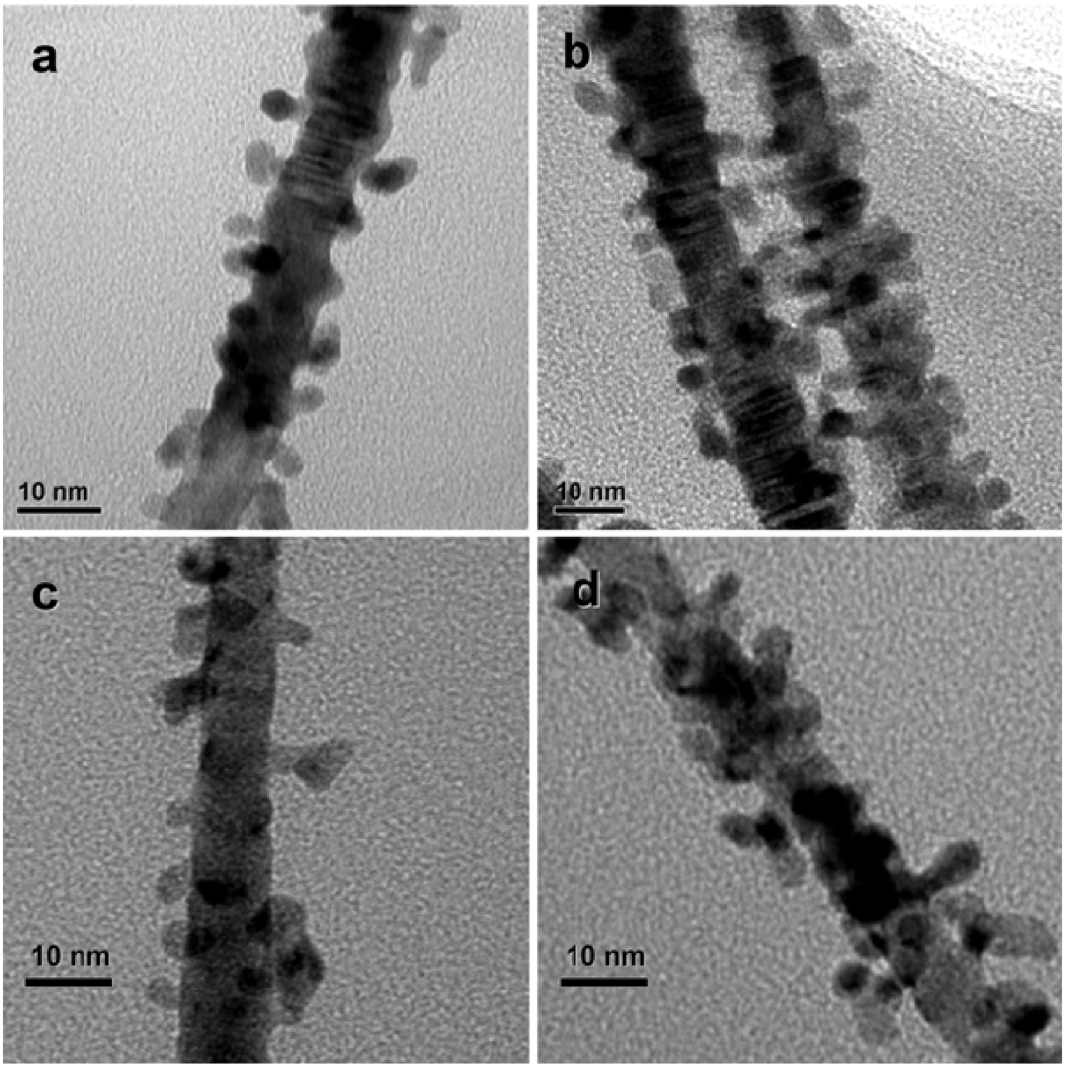

Fig. S7. Typical TEM images of Au/Pt (a, b) and Au/Pt_3Ni (c, d) nanowires with molar ratios of Au nanowires to Pt precursor being 2:1 (left panels) and 1:1 (right panels) in a synthesis.

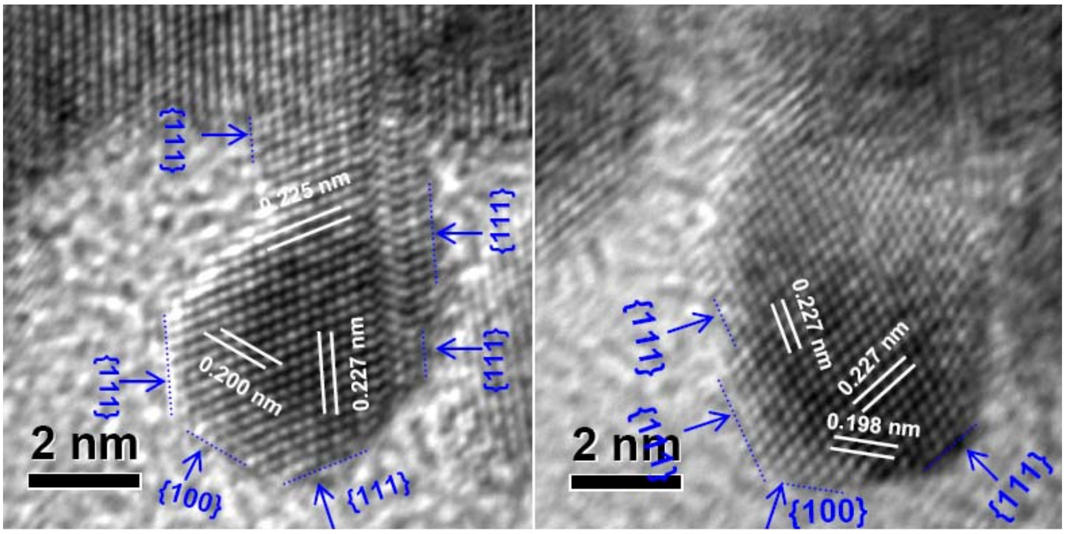

Fig. S8. HRTEM images of Au/Pt nanowires. The images reveal that most of the exposed facets on the Pt nanodendrites were {111} planes, because the nucleation and growth of Pt are strongly influenced by the incorporated metal cores.[5,6] Small-sized Pt nanoparticles are usually covered by a mix of {100} and {111} facets in order to minimize the total interfacial free energy.[7,8] The ORR activity on Pt(111) is far higher than that on Pt(100) in nonadsorbing electrolyte such as perchloric acid.[9,10]

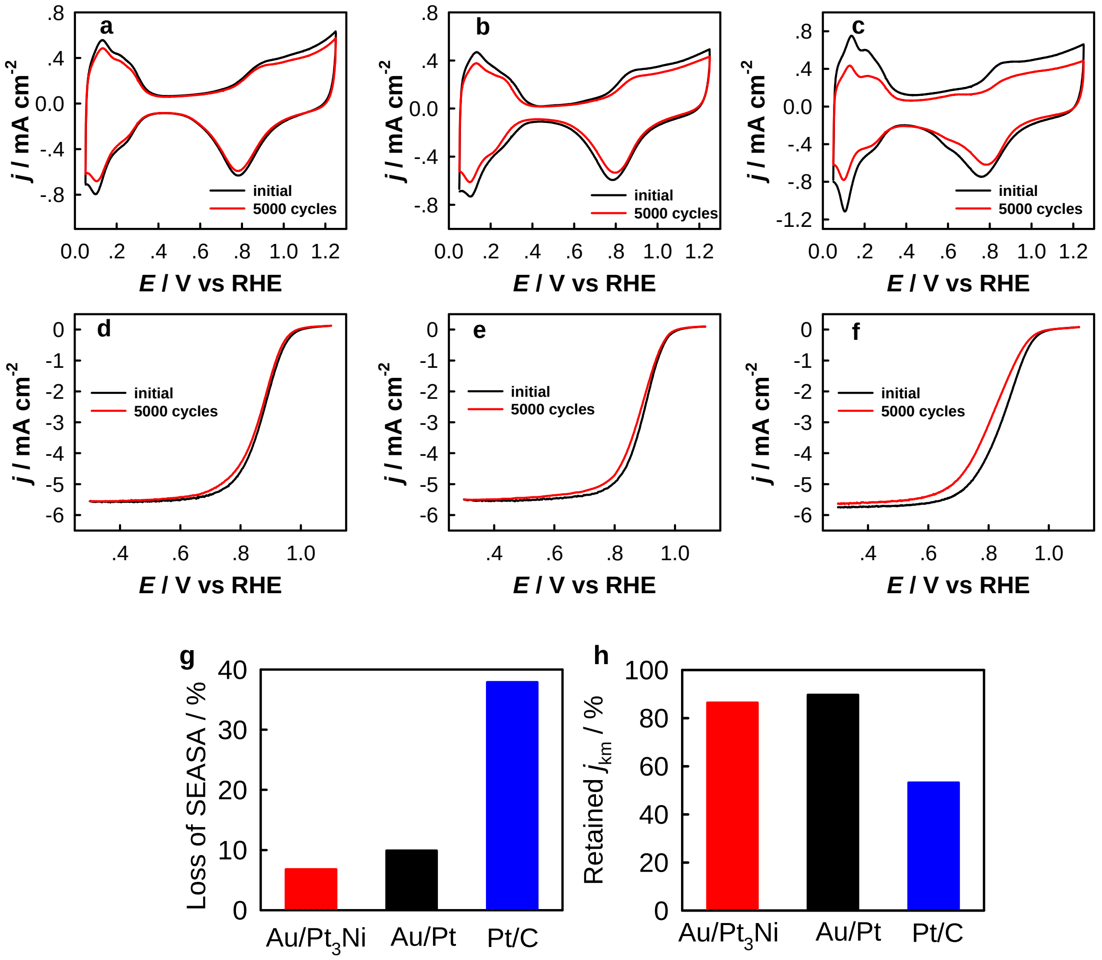

Fig. S9. Cyclic voltammograms for Au/Pt (a), Au/Pt_3Ni (b), and Pt/C (c) catalysts in 0.1 M N_2-saturated $HClO_4$ solution before and after 5,000 potential cycles. Scan rate: 50 mV s^{-1}. ORR polarization curves for Au/Pt (d), Au/Pt_3Ni (e), and Pt/C (f) catalysts in 0.1 M O_2-saturated $HClO_4$ solution before and after 5000 potential cycles. Scan rate: 10 mV s^{-1}. Rotation rate: 1600 rpm. The potential cycles were from 0.6 to 1.1 V in an O_2-saturated 0.1 M $HClO_4$ solution at room temperature at a sweep rate of 50 mV s^{-1}. Losses of SEASAs (g) and retained j_{km} (h) at 0.9 V for the three catalysts after 5000 potential sweep cycles.

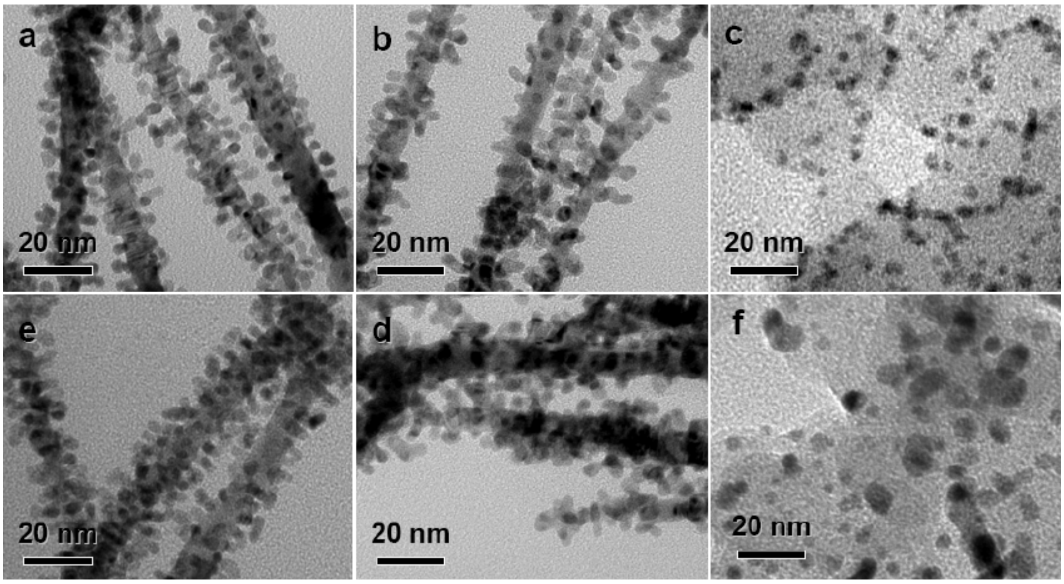

Fig. S10. TEM images of Au/Pt (a, e), Au/Pt_3Ni (b, d), and Pt/C (c, f) catalysts before (top panels) and after (down panels) 5,000 potential sweep cycles between 0.6 and 1.1 V in an O_2-saturated 0.1 M $HClO_4$ solution at 50 mV s^{-1}.

References

1. J. Wu, J. Zhang, Z. Peng, S. Yang, F. T. Wagner and H. Yang, J. Am. Chem. Soc., 2010, 132, 4984.

2. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2000.

3. K. J. J. Mayrhofer, V. Juhart, K. Hartl, M. Hanzlik and M. Arenz, *Angew. Chem., Int. Ed.*, 2009, 48.

4. V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas and N. M. Markovic, *Science*, 2007, **315**, 493.

5. B. Lim, M. Jiang, P. H. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu and Y. Xia, *Science*, 2009, **324**, 1302.

6. Y. Kim, J. W. Hong, Y. W. Lee, M. Kim, D. Kim, W. S. Yun and S. W. Han, *Angew. Chem. Int. Ed.*, 2010, **49**, 10197.

7. C. Wang, H. Daimon, T. Onodera, T. Koda and S. Sun, *Angew. Chem. Int. Ed.*, 2008, **47**, 3588.

8. H. Song, F. Kim, S. Connor, G. A. Somorjai and P. Yang, *J. Phys. Chem. B*, 2005, **109**, 188.

9. N. Markovic, H. Gasteiger and P. N. Ross, *J. Electrochem. Soc.*, 1997, **144**, 1591.

10. N. M. Marković and P. N. Ross, *Surf. Sci. Rep.*, 2002, **45**, 117.