Supporting Information

Highly dispersive Pt atoms on the surface of RuNi nanoparticles with remarkably enhanced catalytic performance for ethanol oxidation

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Experimental Section

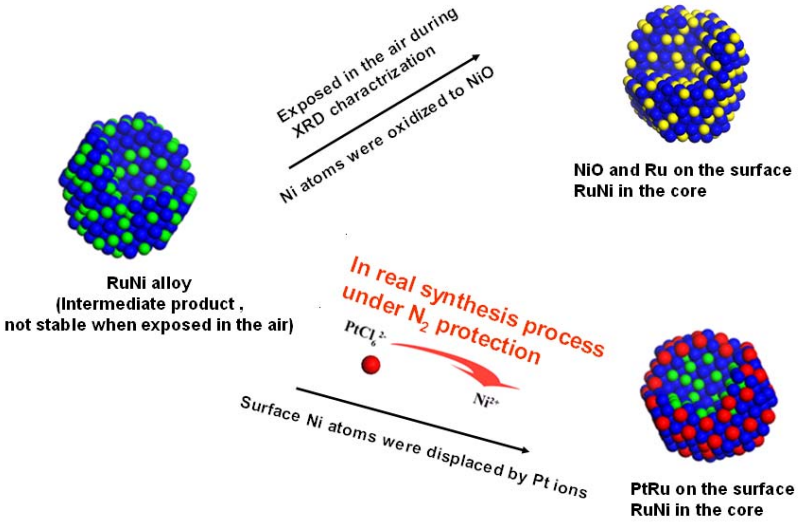
RuNi/SWCNT was prepared by the $NaBH_4$ reduction of $RuCl_3$ and $NiCl_2$ onto the SWCNTs in methanol and ethanol solution. Briefly, 7.4 mL $RuCl_3$ (0.037086 mmol/mL), $NiCl_2{\cdot}6H_2O$ (97.5 mg) and SWCNTs (30.6 mg) were mixed in 30 mL methanol and 30 mL ethanol solution and co-deposited at room temperature by the $NaBH_4$ reduction. Prior to the experiment, all the solvents used were degassed using an ultrasonicator and purged with N_2 for at least 0.5 h to ensure that the solvents are free from dissolved O_2. Upon mixing, freshly prepared $NaBH_4$ solution in ethanol was added directly and quickly under vigorous stirring. Thirty minutes later, the mixed

solution was refluxed for 0.5 h at 80 ^{o}C to decompose any remaining $NaBH_4$. Then, the mixed solution was cooled down to room temperature. RuNi@PtRu/SWCNT catalyst was synthesized by simply mixing the resulting RuNi/SWCNT with the Pt precursor. Briefly, 2 mL H_2PtCl_6 was added dropwise to the above solution. After overnight stirring, the resulting suspension was filtered, and the residue was soaked in 1.0 M H_2SO_4 solution to remove surface Ni. Then, the acidic solution was filtered and washed several times with ethanol and deionized water, and the flake was dried at 60 ^{o}C over night in a vacuum oven. The entire reaction process was carried out under an N_2 atmosphere to prevent oxidation of Ni and Ru.

For structural analysis and chemical composition, the as-synthesized catalyst was characterized by transmission electron microscopy (TEM, Philips Tecnai F20, 200 kV), powder X-ray diffraction (XRD, Rigaku D/max-2500 X-ray generator, Cu Kα radiation), inductively coupled plasma emission spectroscopy (ICP), and X-ray photoelectron spectroscopy (XPS). Electrochemical measurements were performed in a conventional three-compartment glass cell using a CHI660C electrochemical working station (CH Instrument, Inc.).

It should be pointed out that the RuNi alloy is only the intermediate product. It is not stable when exposed in the air (XRD measurement) or in the acidic medium (ethanol oxidation). The scheme below indicated different behavior of the

intermediate product RuNi alloy when exposed in the air during the XRD measurement or in the real synthesis process under N_2 protection.



The catalyst ink was prepared by mixing the catalyst, ethanol, and perfluorsulfonic acid solution (5 wt%, Aldrich) ultrasonically. Before use, the glassy carbon electrode was polished and rinsed ultrasonically with double-distilled water. The slurry was spread on the glassy carbon-disk electrode using syringe, and it was used as the working electrode. A piece of Pt foil was used as the counter electrode, and a mercury sulfate electrode was used as the reference electrode. Before the experiments, a 0.5 M H_2SO_4 or 1.0 M CH_3CH_2OH + 0.5 M H_2SO_4 solution was purged with ultrapure N_2 gas for 20 min to expel oxygen. Due to slight contamination, the working electrode was cycled at 50 mV s^{-1} until stable cyclic voltammograms were obtained in the 0.5 M H_2SO_4 solution. In all experiments, analytical grades and deionized water were

used, and the test electrolyte cell was placed in a water bath at 26± 0.2 ^{o}C. For comparison, commercial Pt/C was also studied.

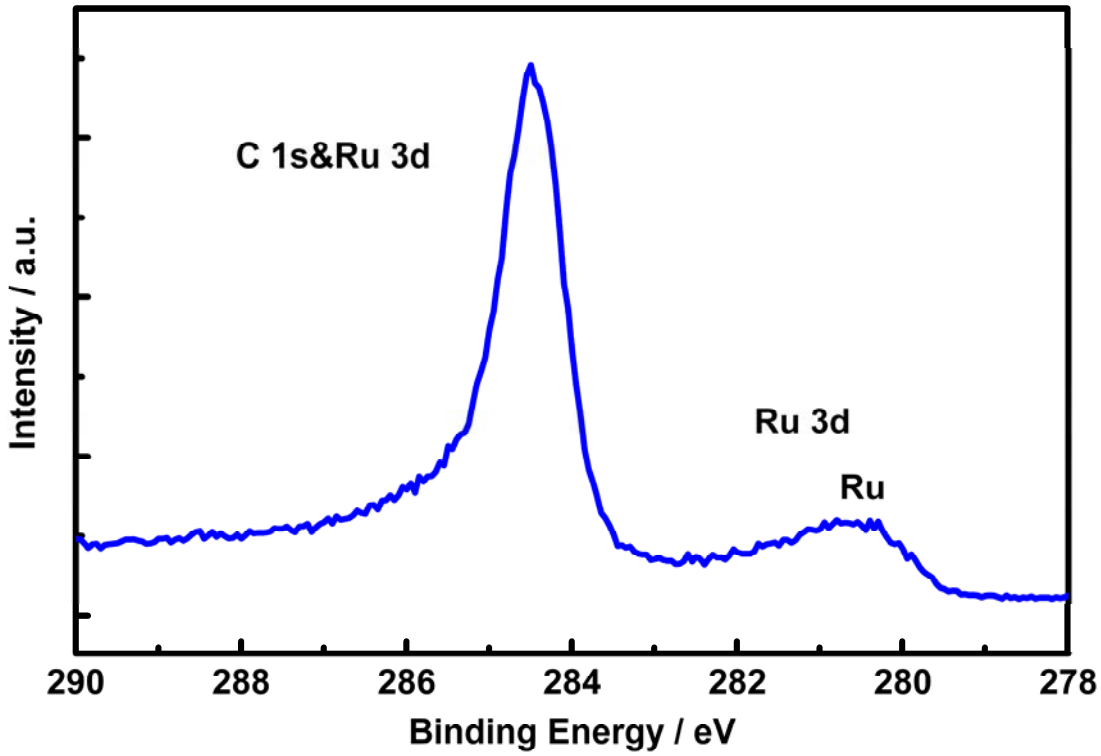


Figure S1 XPS core level spectra for the Ru 3d photoemission from RuNi@PtRu/SWCNT nanoparticles.

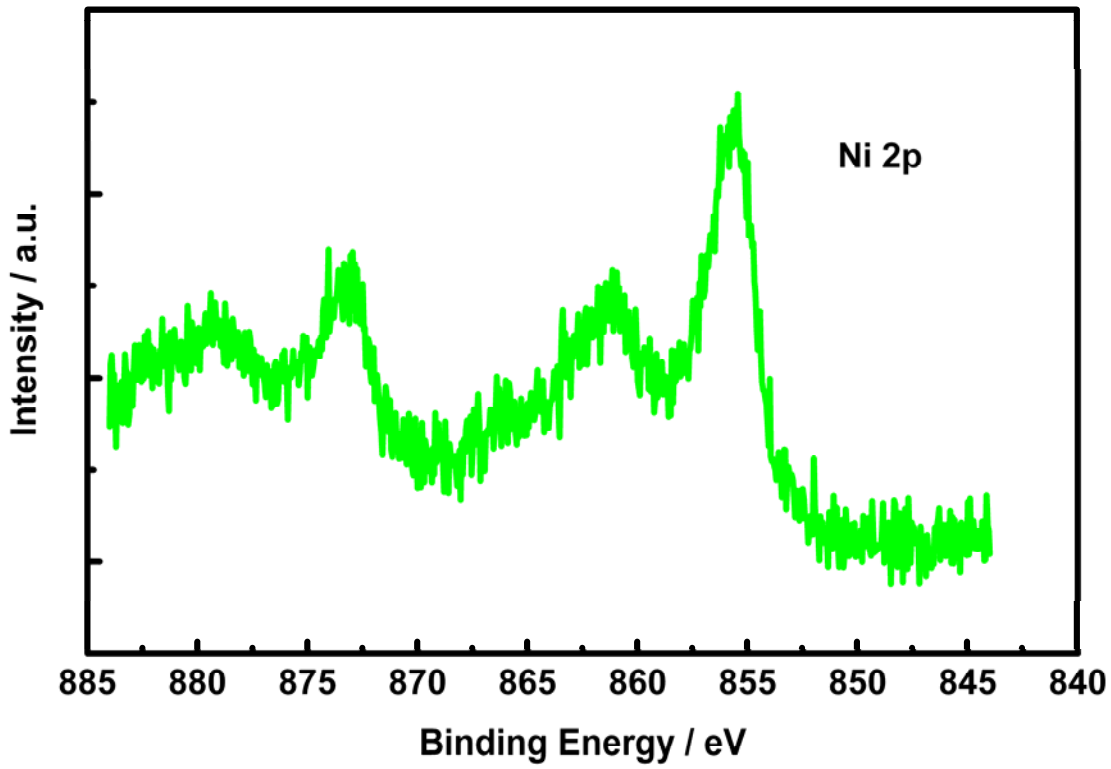


Figure S2 XPS core level spectra for the Ni 2p photoemission from RuNi@PtRu/SWCNT nanoparticles.

The Ru spectrum is overlapped with that of C 1s, and the Ru 3d5 peak is located at 280.8 eV, which are characteristic of metallic Ru (see Figure S1).[S1] As can be seen from Figure S2, the Ni 2p spectrum of the RuNi@PtRu/SWCNT shows a complicated structure by the presence of high binding energy satellite peaks adjacent to the main peaks, which can be attributed to multi-electron excitation.[S2] The four peaks may be ascribed to Metallic Ni, NiO, $Ni(OH)_2$ and NiOOH.[S3]

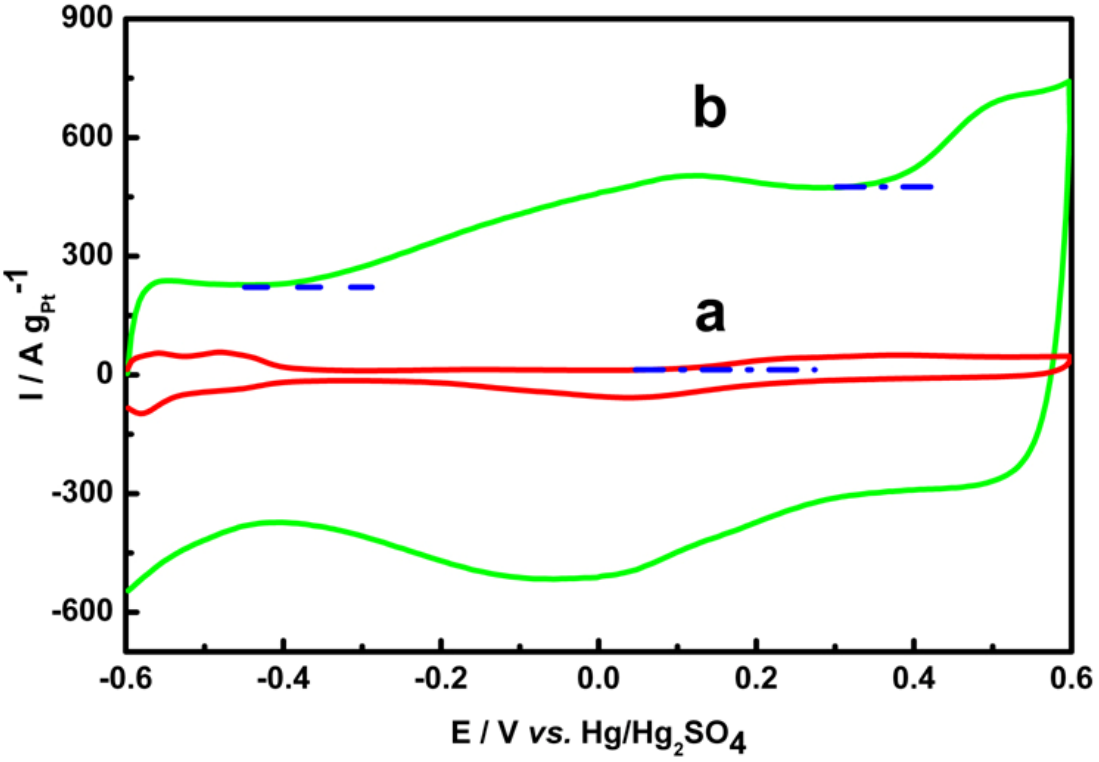


Figure S3. Cyclic voltammograms on RuNi@PtRu/SWCNTs and commercial Pt/C at 50 mV s^{-1} in 0.5 M H_2SO_4. Mercury sulfate electrode was used as the reference one (0.62V versus SHE).

Seeing from the CV curve without CO, the RuNi@PtRu/SWCNT generates oxygen-containing species at -0.4 V. The result shows that the surface of RuNi@PtRu/SWCNT has abundant Ru atoms, which generate Ru-OH at lower potential. So the RuNi@PtRu/SWCNT is in good accord with oue design requirements. The difference of onset potential with CO oxidation and without CO oxidation may be due to hydrogen adsorption/desorption on Pt, which decreases the OH coverage on Ru through the repulsion between the H adsorbed on Pt.[S4] An excellent electrocatalyst for ethanol requires lower onset potential and lower onset

potential needs oxygen-containing species (for example, Ru-OH) at lower potentials. Though oxygen-containing species help Pt oxidize CO, oxygen-containing species at lower potentials also generate current. So we cannot analyze the current composition.[S5] But without a doubt, oxygen-containing species make the RuNi@PtRu/SWCNT have quite lower onset potential. Because when CO is adsorbed on Pt, the onset current and the onset potential are lower than those without CO oxidation. However, when H is adsorbed on Pt, the onset current and the onset potential are higher than those with CO oxidation. At the same time, the onset potential of Pt/C for CO oxidation occurs at around 0.03V. Hence, Ru makes Pt have quite lower onset potential for CO oxidation. The result also shows that the RuNi@PtRu/SWCNT has abundant surface Pt and Ru, and the RuNi@PtRu/SWCNT is in accordance with our design requirements.

References

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