Electronic Supplementary Information for:

Bifunctional Catalytic/Magnetic Ni@Ru Core-Shell Nanoparticles

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Chemicals:

Nickel (II) acetylacetonate, ruthenium carbonyl, oleylamine (purity: 70%), oleic acid (purity: 90%), diphenyl ether, Superhydride® (1.0 M lithium triethylborohydride in THF), 1-octadecene (purity: 90%), 1-hexadecylamine (purity: 90%), trioctylphosphine, ammonia borane complex (97%) were purchased from Sigma Aldrich. Electroconductive carbon black Ketjenblack EC-300J was obtained from AkzoNobel company. All chemicals were used as purchased.

Synthesis

All synthetic experiments were carried out using standard airless procedures, using Ar flow as inert gas.

(1)Synthesis of Ni nanoparticles (NPs): The synthesis method was similar to that of PtNi NPs used by Yang et al.[s1] In a typical synthesis, nickel (II) acetylacetonate (64 mg) were dissolved in diphenyl ether (5 ml) containing oleic acid (0.75 ml). The solution was heated to ~120 ^{o}C and kept at this temperature for 20 min to remove humidity and oxygen. Next, the solution was cooled down to ~90 ^{o}C, and 1 ml of Superhydride® was quickly injected into the solution. After 1 min, the as prepared mixture was transferred into a flask containing 15 ml of oleylamine which was preheated to ~300 ^{o}C. The mixture was kept at 250 ^{o}C for 15 min and then cooled down to either 100 ^{o}C for the deposition of Ru or room temperature for NP characterizations. For the latter, the Ni NPs were first purified by adding 40 ml of ethanol and centrifuging at 9000 rpm for 10 min. The precipitated NPs were then dispersed in hexane.

(2)Synthesis of Ni@Ru core-shell NPs: When the colloidal suspension of Ni seeds (1) was cooled down to about 100 ^{o}C, oleylamine solution (4 ml) containing $Ru_3(CO)_{12}$ (53.3 mg) was injected. The as obtained mixture was heated to 180 °C under vigorous stirring, and then slowly brought to 200 °C. The reaction was quenched by removing the reaction flask off the mantle after refluxing for 30 min. Ethanol (40 mL) was added and the product was separated by centrifugation at 9000 rpm for 10 min. The product was then dispersed in hexane.

(3)Synthesis of Ru NPs: $Ru_3(CO)_{12}$ were ultrasonicated in oleylamine (15 ml) for 30 min to get a transparent crimson solution. The as prepared solution was heated to 200 ^{o}C and kept at this temperature for 30 min. The solution was cooled down to room temperature. Ethanol (40 mL) was added and the product was separated by centrifugation at 9000 rpm for 10 min. The product was then dispersed in hexane.

Catalytic hydrolysis of ammonia borane (AB)

The Ketjenblack carbon black was dispersed in the colloidal dispersion of NPs in hexane, and this mixture was stirred until the hexane was completely evaporated. Water (10 mL) was then added to the NPs/carbon powder. Since the NPs and carbon are both hydrophobic, ultrasonication was required to get a uniform dispersion. The hydrolysis of ammonia borane

was carried out at 25 ± 1 ^{o}C. To start the reaction, AB (63 mg) was introduced into the aqueous dispersion of NPs/carbon catalysts under vigorous stirring. The volume of hydrogen gas evolved was measured by recording the displacement of water level in an inverted and graduated water-filled burette (Aldrich® graduated burette). The used catalysts were washed and then re-dispersed in water for the catalyst comparisons and durability.

The Turnover Frequency (TOF) (mol $H_2 \cdot min^{-1} \cdot mol$ Ru^{-1}) of AB hydrolysis was estimated from the average rate at half completion of the reaction (mol H_2 released at ½ completion / time from AB injection). For comparison to Pt-based bimetallic NPs, we converted the values to the same units, and normalized for the amount of noble metal.

Characterizations

Powder X-ray diffraction (XRD) was performed on a Philips X'pert diffractometer using a Cu Kα radiation source (λ = 0.154 nm). X-ray photoelectron spectra (XPS) were taken using a VG Escalab 220i-XL equipped with a polychromatic Al source. The etching was carried out by Ar sputtering under the conditions of a background vacuum of 2.0×10^{-8} mbar, a sputtering acceleration voltage of 3.0 kV and a sputtering current of 100 nA.

Transmission electron microscopy (TEM, JEOL 2100F) and energy-dispersive X-ray spectroscopy (EDS) were applied for a detailed analysis of microstructure and composition. The TEM and EDS samples were prepared by depositing one or two droplets of the NPs colloidal suspension in hexane onto copper grids coated with thin carbon film.

Macroscopic magnetic hysteresis loops were measured at room temperature using a vibrating sample magnetometer (VSM) (Model EV9 from ADE Technologies) with sensitivity of 10^{-6} electromagnetic units (emu). A maximum saturating field of 10 kOe was applied parallel to sample surface, then decreased down to -10 kOe in small steps, and back up to 10 kOe. To measure the hysteresis loops of the Ni@Ru core-shell nanoparticles, the as-prepared NPs dispersed in hexane were dropped onto a silicon substrate and vacuumed before test. To ensure that the samples used for the comparative study of catalysis contained the same amounts of Ru and Ni, neutron activation analysis (NAA, SLOWPOKE) was conducted to analyze the amounts of Ni and Ru in the prepared Ni, Ru and Ni@Ru NP dispersions.
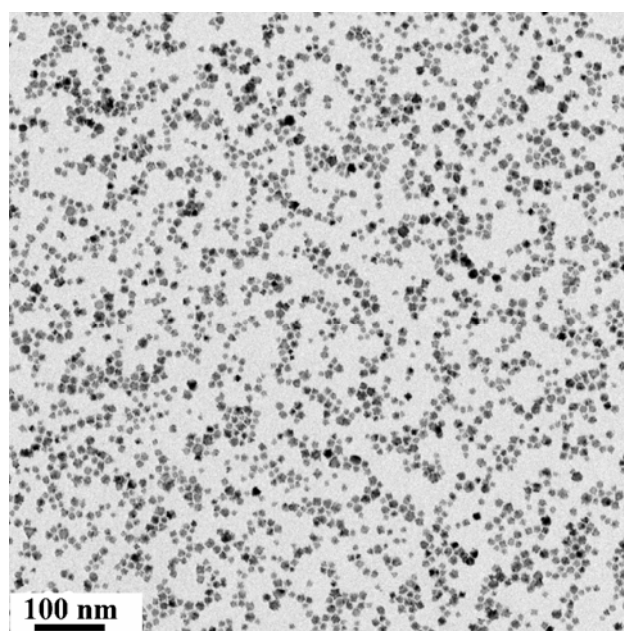
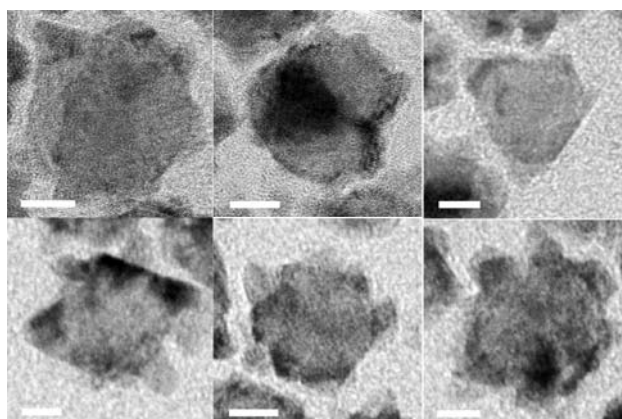**Fig. S1** TEM image of the as-prepared Ni@Ru core-shell NPs.

Fig. S2 TEM images of six Ni@Ru NPs showing the rounded contour of the Ni core adhering to some Ru NPs. The scale bar is 5 nm.
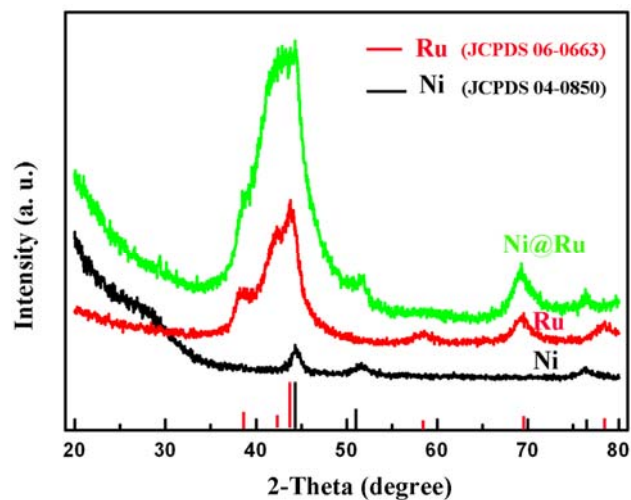
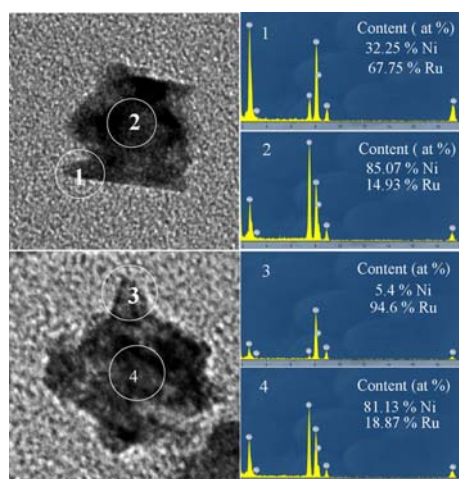**Fig. S3** XRD patterns of Ni, Ru and Ni@Ru core-shell NPs.

Fig. S4 Representative EDS point analyses of two Ni@Ru core-shell NPs comparing the composition in the center and at the surface.
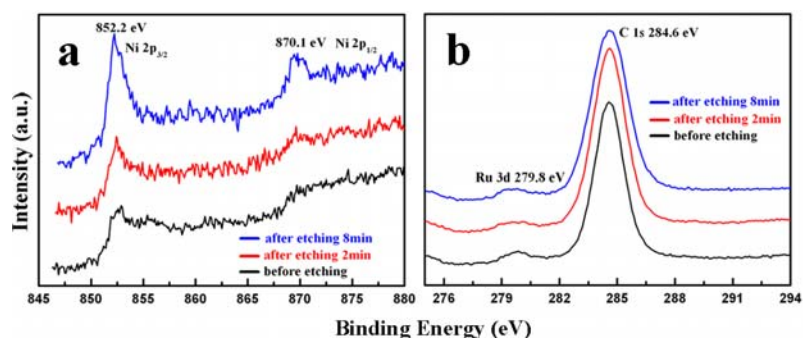
Fig. S5 XPS spectra of Ni@Ru core-shell NPs before and after Ar sputter etching for 2 and 8 min: (a) Ni 2p peaks, and (b) Ru 3d peaks, respectively.
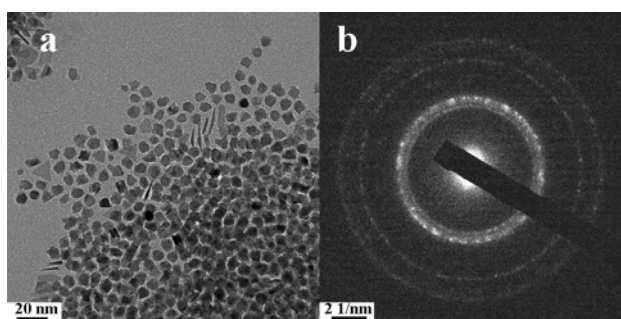

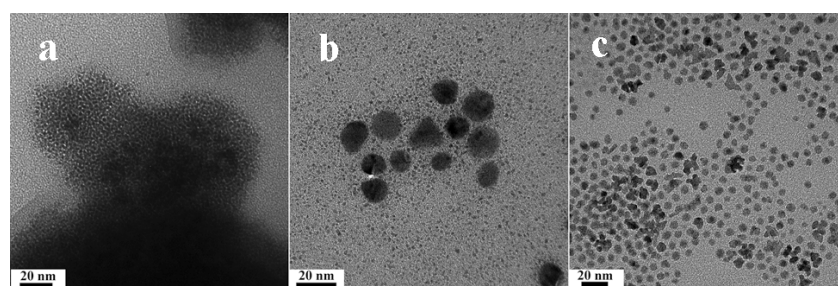**Fig. S6** TEM image and SAED pattern of the Ru NPs.

Fig. S7 TEM images of the Ni-Ru particles synthesized by dispersing the oleic acid-capped Ni NPs in (a) diphenyl ether or (b) 1-octadecene, instead of oleylamine. (c) TEM image of the Ni-Ru NPs synthesized by using TOP, instead of oleic acid, as capping agents for Ni NP seeds.
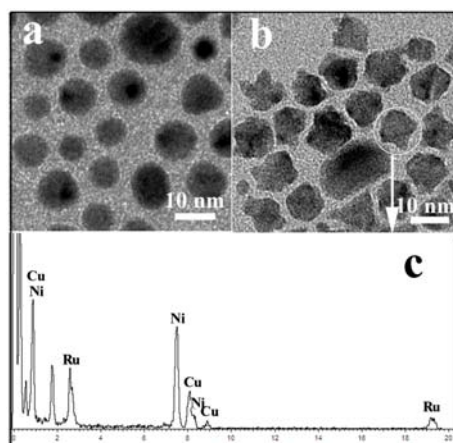
Fig. S8 TEM images of the Ni (a) and Ni-Ru particles (b) synthesized by replacing oleylamine with 1-hexadecylamine. (c) EDS result for the circled NP in (b).
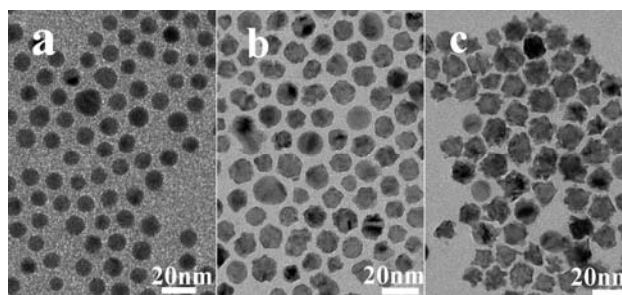

Fig. S9 TEM images of Ni@Ru core-shell NPs collected at different reaction times, (starting when the reaction temperature reaching 200 ^{o}C): (a) 0 min; (b) 10 min; (c) 30 min.
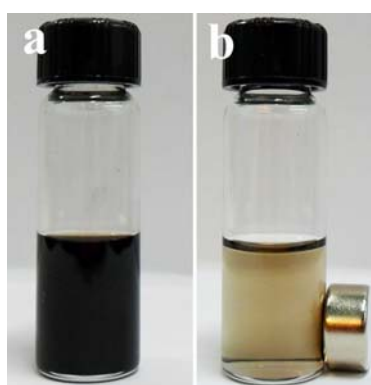

Fig. S10 Photographs of the Ni@Ru core-shell NPs dispersed in hexane (a) and subsequently exposed to a magnetic field (b).

Reference:
[S1]. H. Yang, J. Zhang, S. Kumar, H. Zhang, R. Yang, J. Fang and S. Zou, *Electrochem. Commun.*, 2009, **11**, 2278.