

Electronic Supplementary Information for:

Hollow Ruthenium Nanoparticles with Small Dimensions Derived from Ni@Ru core@shell Structure: Synthesis and Enhanced Catalytic Dehydrogenation of Ammonia Borane

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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), 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

The synthetic experiments for Ni and Ni@Ru core@shell NPs were carried out using standard airless procedures with a flow of Ar as the inert gas.

The synthesis procedure of Ni NPs follows our previous paper. To prepare Ni@Ru NPs with complete Ru shell, oleylamine solution (4 ml) containing Ru₃(CO)₁₂ (53.3 mg) was injected into a colloidal suspension of Ni seeds at 100 °C. The mixture was heated to 160 °C (~2°C/min) under vigorous stirring, and then slowly raised to 200 °C (~1°C/min). After refluxing for 60 min, the reaction was quenched by removing the reaction flask off the mantle. Ethanol (40 mL) was added, and the product was separated by centrifugation at 9000 rpm for 10 min. After 3 cycles, the product was dispersed in 5 ml of hexane. To obtain the hollow Ru NPs, 5 ml of HNO₃ (1M) were added in the Ni@Ru NPs dispersion above. Vigorous shaking (30min) was necessary to ensure effective contact between Ni core and HNO₃ and completely remove Ni. Then, the mixture was decanted until two layers of non-polar (hexane) and polar phase (aqueous HNO₃) separate. Next, the aqueous layer was carefully removed using a syringe, followed by addition of an excess of ethanol. Finally, after three cycles of washing with ethanol and centrifugation, the product was dispersed in hexane.

Catalytic hydrolysis of ammonia borane (AB)

Ketjenblack carbon black was dispersed in the colloidal dispersion of the as-prepared hollow Ru NPs, and this mixture was stirred until the hexane was completely evaporated. Water (9 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. To start the reaction, 1 ml of AB in water (2M) was introduced into the aqueous dispersion of NPs/carbon catalysts under vigorous stirring. The data we report on performance comparison and durability refer to catalysts that were used once in a preliminary catalytic run, then washed and re-dispersed in water. The recyclability experiment was conducted under exactly the same conditions as those used in the preliminary catalytic run. Specifically, the used catalyst was washed by water 1

time and then dispersed in 9 mL of water, followed by the addition of 1 mL of AB for the new run. The volume of evolved hydrogen gas was measured by recording the displacement of water level in an inverted and graduated water-filled burette (Aldrich® graduated burette). The hydrogen generation rate at different concentrations and the values of the rate constant k at different temperatures were calculated from the slope of the H_2 release versus time for every experiment.

Characterization

To prepare the samples for XRD and XPS measurements, Si wafers were thoroughly washed 3 times with acetone and ethanol. After dropping the NPs dispersion in hexane on the clean Si wafer, they were dried at room temperature. The as-prepared samples were analyzed by XRD at grazing-angle incidence [X-Pert Pro (PANalytical) Diffractometer]. The angle between sample surface and incident beam was fixed at 3° . The experimental resolution and the integration time per step were 0.05° and 4 s, respectively. XPS was taken using a VG Escalab 220i-XL equipped with a twin anode (Mg/Al) source. Transmission electron microscopy (TEM, JEOL 2100F) and energy-dispersive X-ray spectroscopy (EDX) 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. Neutron activation analysis (NAA, SLOWPOKE) was conducted to analyze the amount of Ru in the hollow Ru NPs. A sequence of FFT, Fourier mask filtering, and IFFT calculation, was applied to the HR-TEM images using the Digital Micrograph™ (DM, Gatan Inc.) software program.

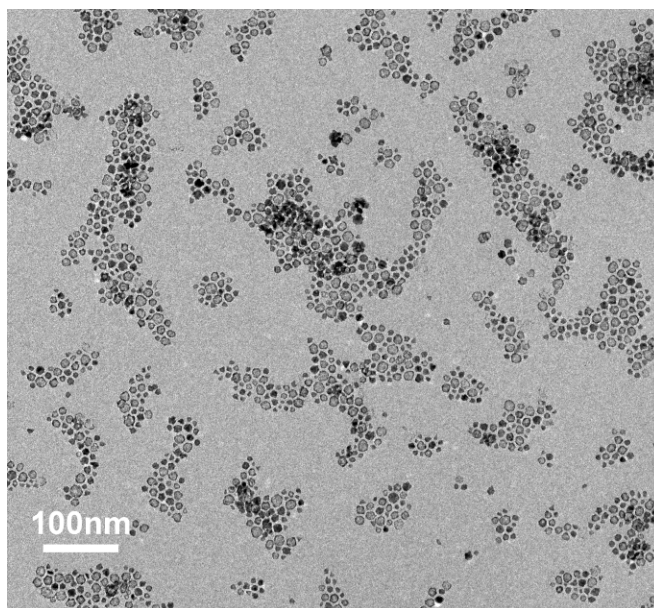


Fig. S1 TEM image of as-prepared hollow Ru NPs at low magnification.

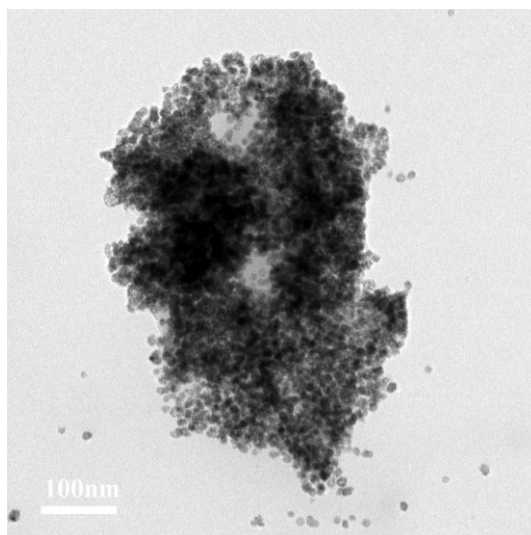


Fig. S2 TEM image of the NPs obtained by dispersing dry Ni@Ru core@shell NPs in HNO₃ aqueous solution, without the addition of hexane.

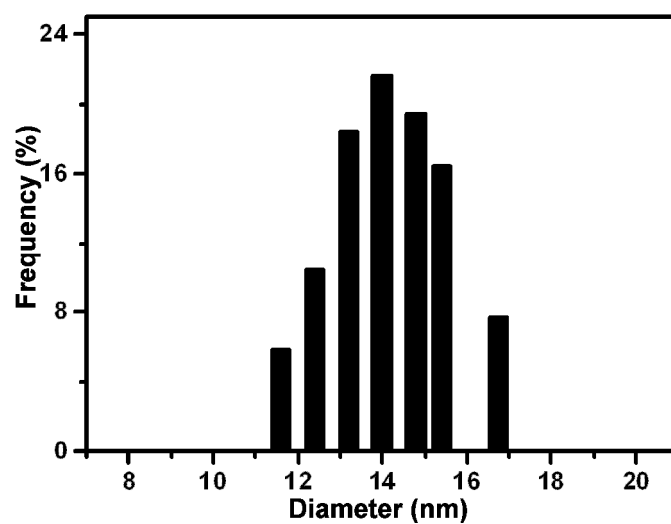


Fig. S3 The histogram of size distribution for as-prepared hollow Ru NPs.

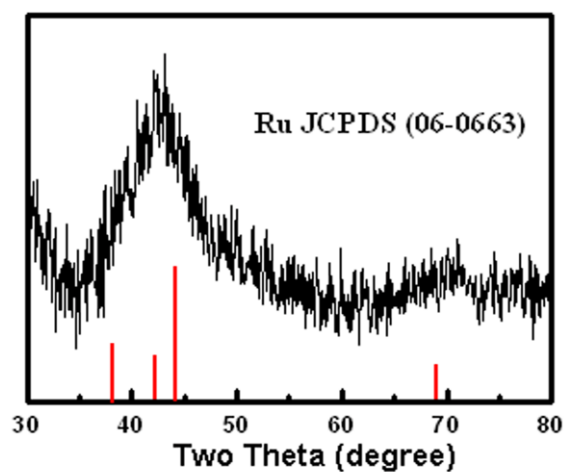


Fig. S4 XRD pattern of as-prepared hollow Ru NPs.

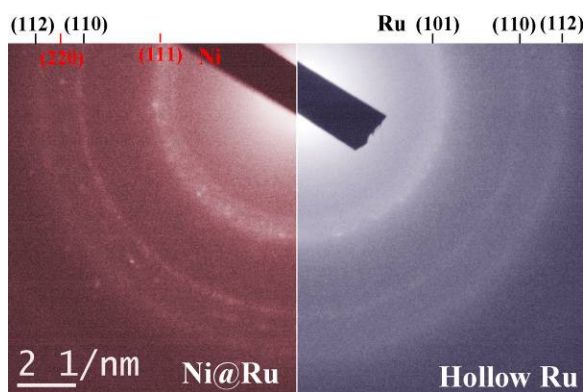


Fig. S5 SAED patterns of Ni@Ru core@shell NPs (left) and hollow Ru NPs (right).

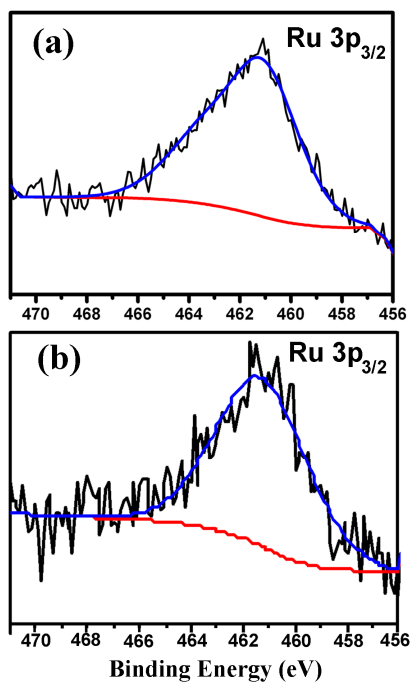


Fig. S6 XPS spectra of Ru 3p_{3/2} of the hollow Ru NPs before (a) and after their deposition onto the carbon black (b).

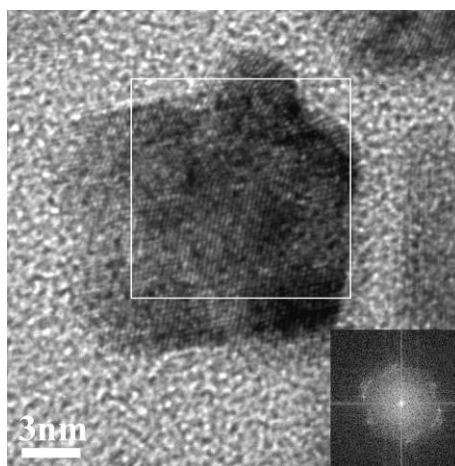


Fig. S7 HR-TEM image of one Ni@Ru core@shell NP. Inset is the Fast Fourier transform(FFT) corresponding to white square part.

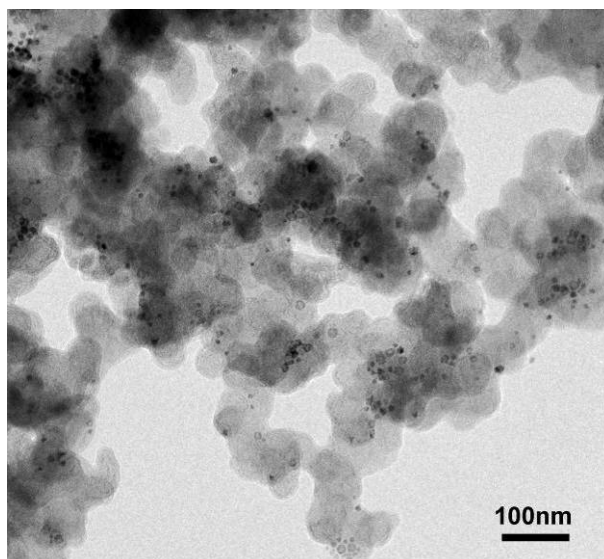


Fig. S8 TEM image of as-prepared hollow Ru NPs deposited on carbon black.

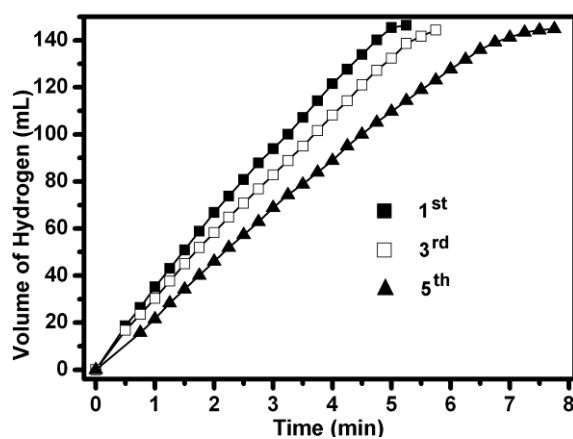


Fig. S9 Plots of the volume of hydrogen versus time during a five-cycle recyclability test at 315K ([Ru]=0.25 mM, [AB]=200 mM).