Supporting Information

Rhodium-nickel bimetallic nanocatalysts: high performance of room-temperature hydrogenation

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Experimental Details

Chemicals: $RhCl_3 \cdot 3H_2O$ and $Ni(acac)_2$ were purchased from Alfa Aesar. ODA, ethanol, cyclohexane, phenol, benzene, cyclohexanone, cyclohexanol, cyclohexene, cyclohexane, styrene, ethylenzene, Benzalacetone, benzylacetone, Nitrobenzene, Aniline, 4-Chloronitrobenzene, 4-Chloroaniline were of analytical grade from the Beijing Chemical Factory of China. All the reagents used in this work were used without further purification.

Synthesis: In a typical synthesis of $Rh_{0.67}Ni_{0.33}$ NCs, 2 mL of $RhCl_3 \cdot 3H_2O$ aqueous solution (0.05 mmol/mL) and 0.0128 g $Ni(acac)_2$ were mixed with 2 g of octadecylamine (ODA) and the resulting mixture was heated to 110 □ with strongly stirring to evaporate the water and form a transparent solution. The mixture was then injected into 6.6 g of ODA preheated at 250 °C with vigorous stirring. The solution turned black immediately with the formation of a precipitate. After reaction at 230 °C for 2 minutes, the precipitate was washed several times with ethanol, and then dispersed in a non-polar solvent such as cyclohexane. Rh_xNi_{1-x} with $0<x<=1$ were prepared using the same procedure of $Rh_{0.67}Ni_{0.33}$ nanocrystals above except that the total molar amount of Rh and Ni was kept at 0.15 mmol.

In the synthesis of Ni NCs, 0.128 g $Ni(acac)_2$ were mixed with 8.6 g of ODA and the resulting mixture was heated to 230 □ and kept at this temperature for 5 min. The precipitate was washed several times with ethanol, and then dispersed in a non-polar solvent such as cyclohexane.

Characterization: Powder XRD patterns were recorded with a Bruker D8 ADVANCE X-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). The particle size and morphology of as-synthesized samples were determined by using Hitachi model H-800 transmission electron microscope and a JEOL-2010F high-resolution transmission electron microscope.

Catalytic measurements: The substrate and Rh_xNi_{1-x} NCs solution (synthesized as described above) were placed in an autoclave. In a typical experiment, H_2 (40 bar) was introduced into the autoclave after the reactor was purged 3 times with H_2. The mixture was stirred at 800 rpm at room temperature (25 ℃) for the required time.

Supplementary Figures

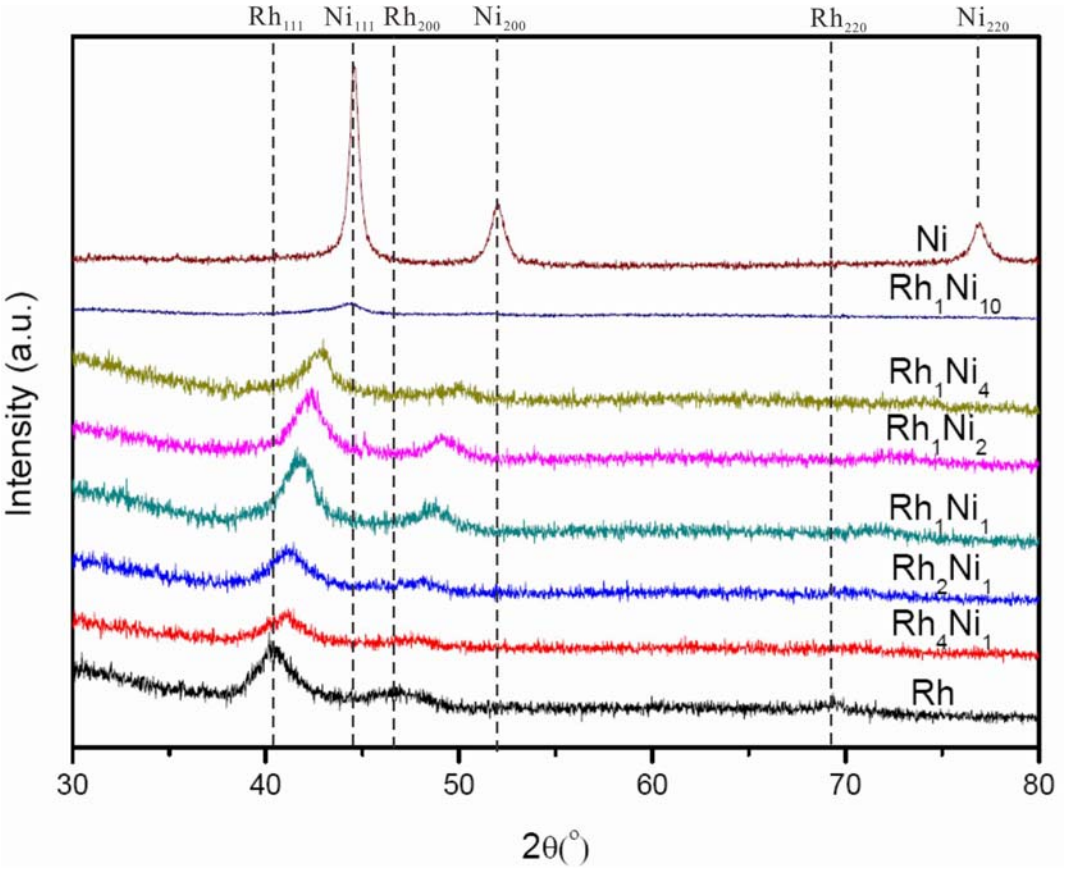


Fig. S1. The powder X-ray diffraction (XRD) patterns of the as-obtained Rh, $RhxNi_{1-x}$, and Ni nanocrystals.

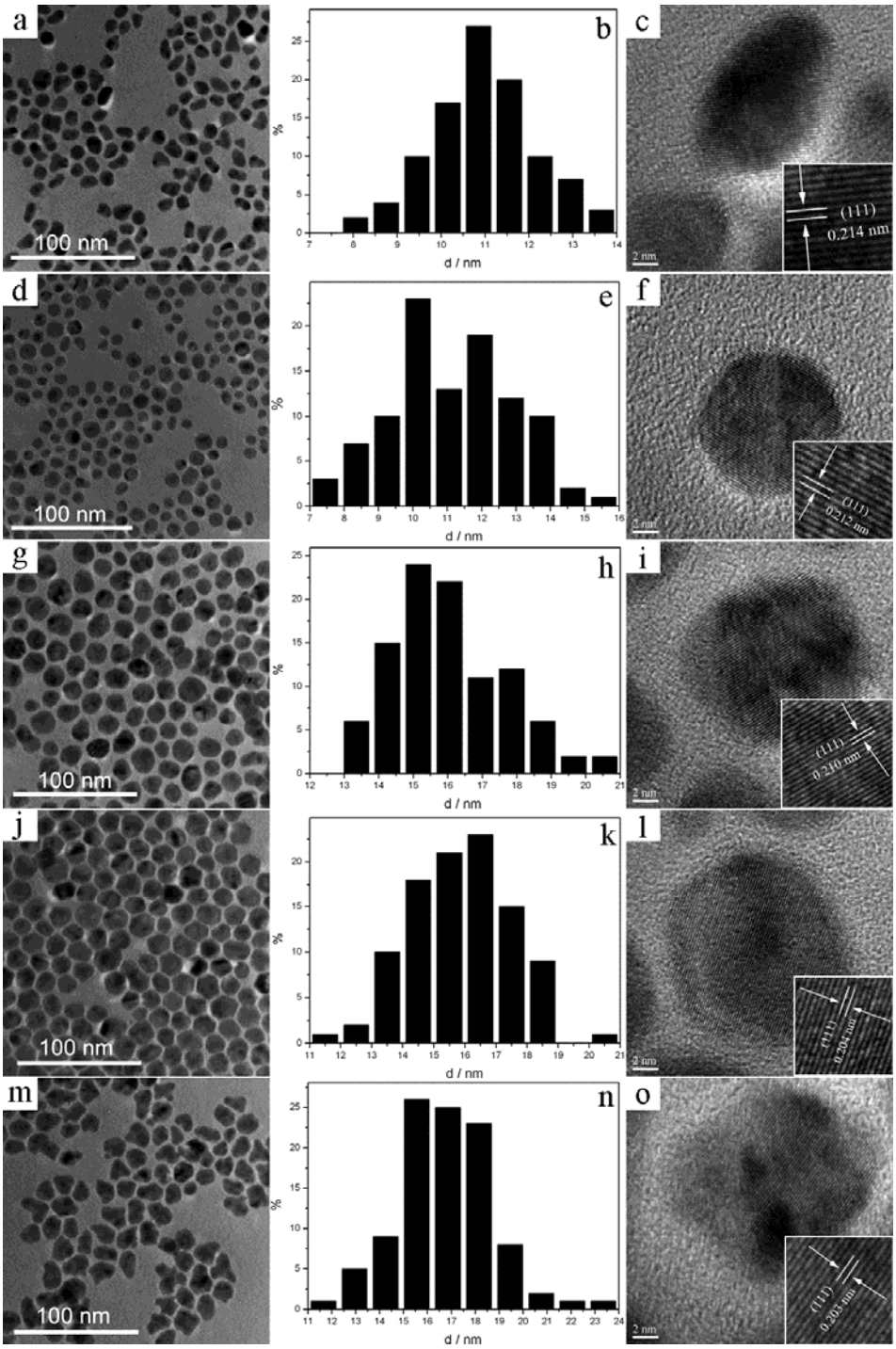


Fig. S2. TEM and HRTEM images as well as the particle size distributions of Rh–Ni NCs with different compositions: (a, b, c) $Rh_{0.45}Ni_{0.55}$; (d, e, f) $Rh_{0.33}Ni_{0.67}$; (g, h, i) $Rh_{0.2}Ni_{0.8}$; (j, k, l) $Rh_{0.12}Ni_{0.88}$; (m, n, o) $Rh_{0.1}Ni_{0.9}$.

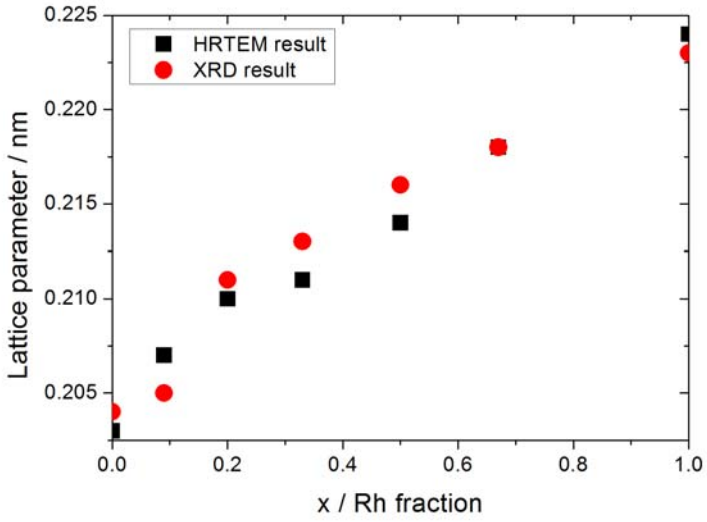


Fig. S3. The variation of lattice parameter of Rh_xNi_{1-x} with composition.

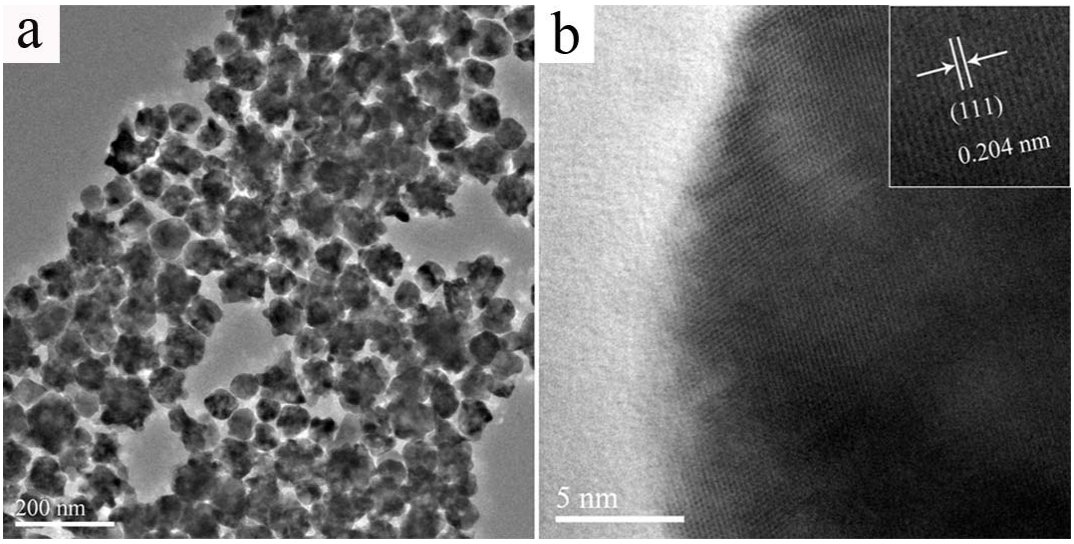


Fig. S4. (a) Representative TEM image of as-obtained Ni NCs. (b) HRTEM image of an individual Ni NC. (Inset, enlarged HRTEM image)

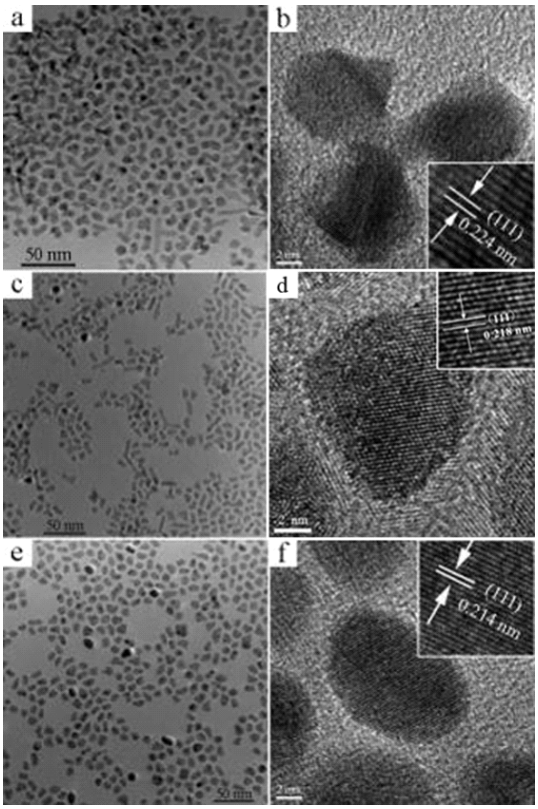


Fig. S5. Representative TEM and HRTEM images of (a, b) Rh, (c, d) $Rh_{0.67}Ni_{0.33}$ and (e, f) $Rh_{0.5}Ni_{0.5}$. (Inset, enlarged HRTEM images)

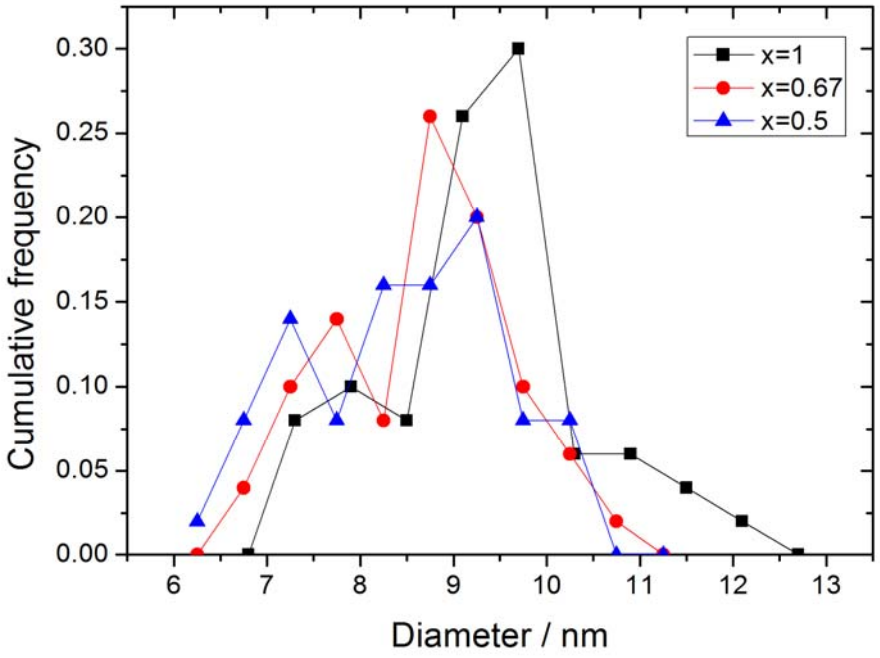
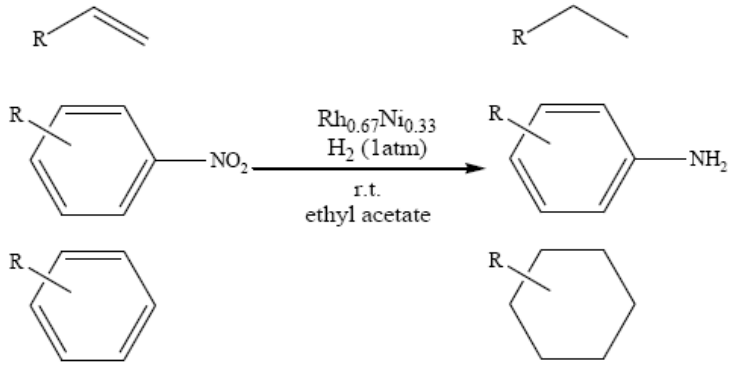


Fig. S6. Size distribution for Rh (black), $Rh_{0.67}Ni_{0.33}$ (red) and $Rh_{0.5}Ni_{0.5}$ (blue).

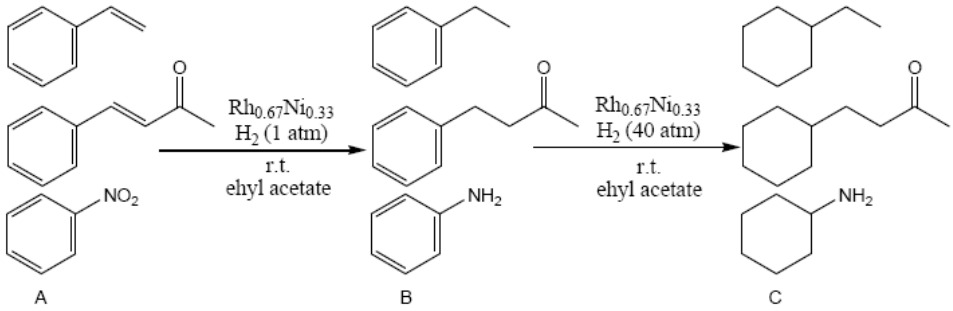
Table. S1 Hydrogenation of alkenes, nitroarenes and arenes in the presence of $Rh_{0.67}Ni_{0.33}$ NCs [a]

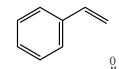
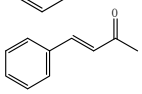
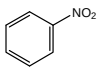


Entry	Substrate	Product	t[h]	Conv[b].[%]	Selectivity[b]	TOF[c] [h^{-1}]
1	Cyclohexene	Cyclohexane	1	>99	>99	3253
2	Styrene	Ethylenzene	0.25	>99	>99	13012
3	Benzalacetone	Benzylacetone	0.5	>99	>99	6506
4	Nitrobenzene	Aniline	16	>99	>99	203
5	4-Chloronitrobenzene	4-Chloroaniline Aniline	24	>99	96.6 3.4	136
6	Phenol	Cyclohexanone Cyclohexanol	24	86.5	63.9 36.1	117
7	benzene	Cyclohexane	24	21.7	>99	29.5

[a]Reaction conditions: 0.5 mmol of substrate and 0.03 mol% of $Rh_{0.67}Ni_{0.33}$ nanocatalyst (based on ICP analysis of Rh metal) in 3 mL ethyl acetate at room temperature (25 ℃) under 1 atm of H_2. [b]Determined by GC-MS. [c]TOF measured in [mol product][mol metal]$^{-1}\cdot h^{-1}$.

Table. S2 Hydrogenation performance using Rh0.67Ni0.33 NCs nanocatalyst under different hydrogen pressure[a]



Entry	Substrate	Pressure (Mpa)	t [h]	Conv.[b] [%]	Selectivity[b] [%]	
					B	C
1		0.1	1	>99	>99	N.D.
2		4	1	>99	91.8	8.2
3		0.1	0.5	>99	>99	N.D.
4		4	0.5	>99	83.7	16.3
5		0.1	24	>99	>99	N.D.
6		4	24	>99	96.2	3.8

[a]0.5 mmol substrates and 0.03 mol% catalyst (based on ICP analysis of Rh metal) in 3 mL ethyl acetate at room temperature (25□) under H_2 (1 atm). [b]Determine by GC-MS.

Table. S3 Recycling of $Rh_{0.67}Ni_{0.33}$ nanocatalyst in the hydrogenation of styrene[a]

Cycle	t [h]	Conv.[b][%]
1	0.5	100
2	0.5	98.8
3	0.5	98.2
4	0.5	97.6
5	0.5	97.4

[a]0.5 mmol styrene and 0.03 mol% catalyst (based on ICP analysis of Rh metal) in 3 mL ethyl acetate at room temperature (25 □) under H_2 (1 atm). [b]Determine by GC-MS.