Bimetallic NiIr nanoparticles supported on lanthanum oxy-carbonate as highly efficient catalysts for hydrogen evolution from hydrazine borane and hydrazine

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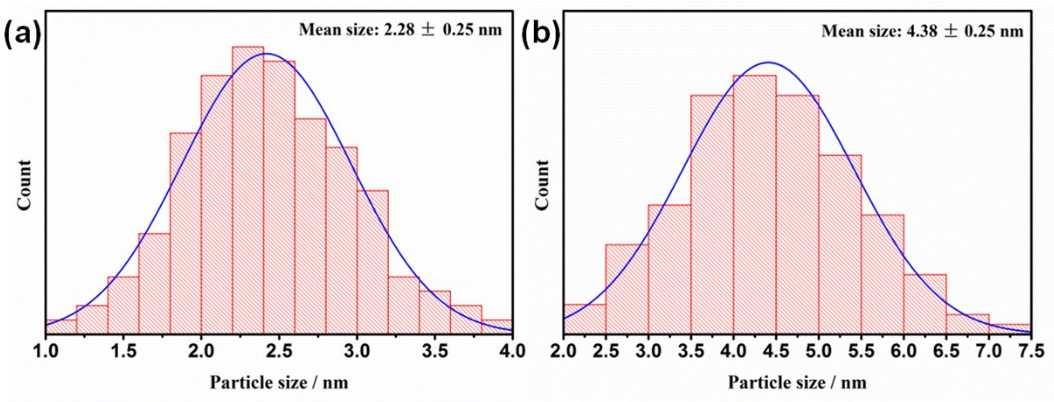

Fig. S1 The particle size distributions of (a) $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ and (b) $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$-N NCs.

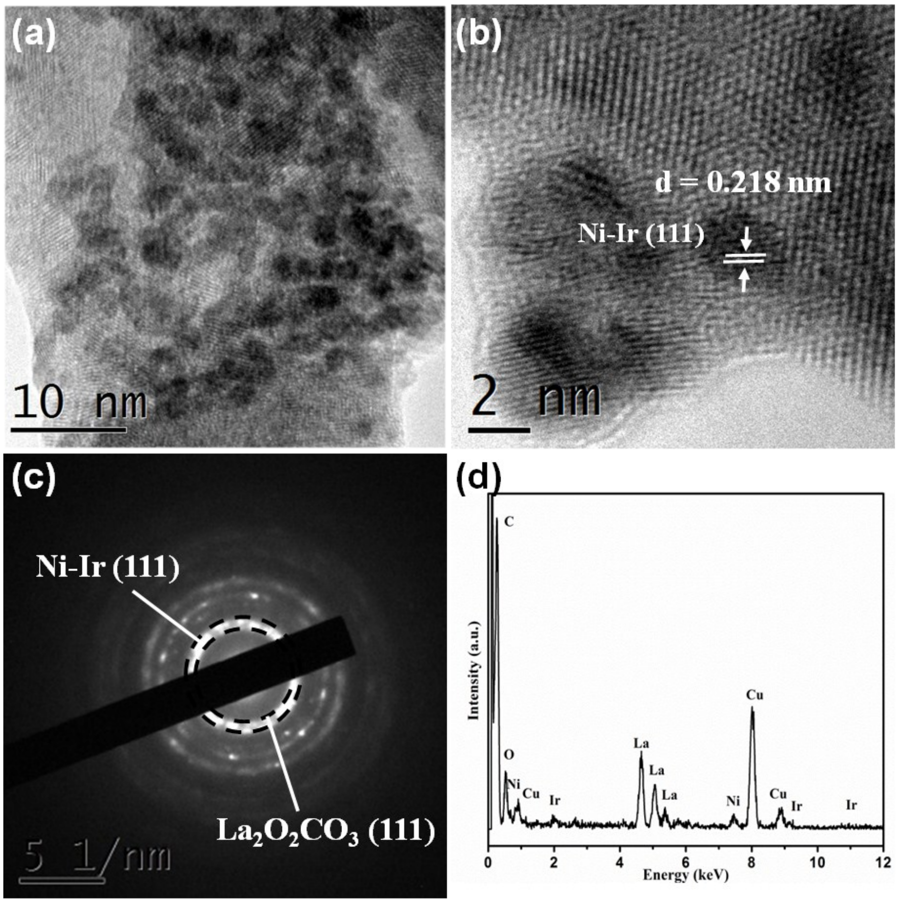

Fig. S2 (a) Typical TEM image, (b) high-resolution TEM image, (c) SAED pattern, (d) EDX pattern of $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ NCs.

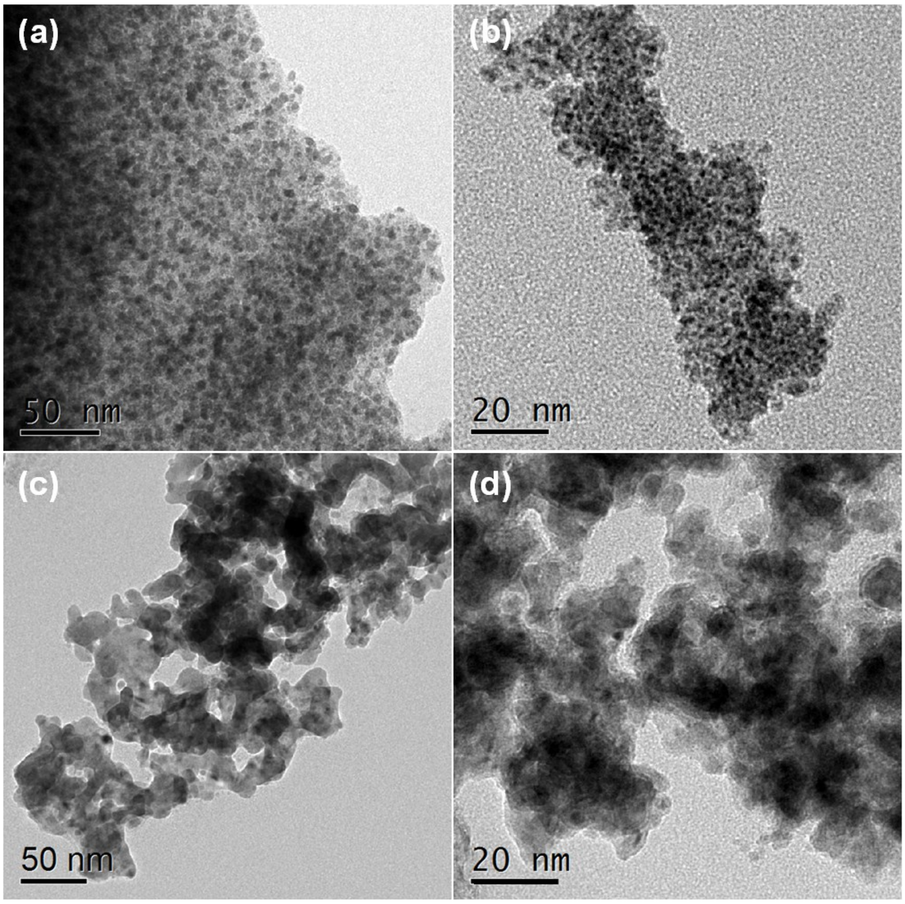

Fig. S3 Typical TEM images of (a,b) $Ni_{0.75}Ir_{0.25}$ and (c,d) $Ni_{0.75}Ir_{0.25}$-N samples.

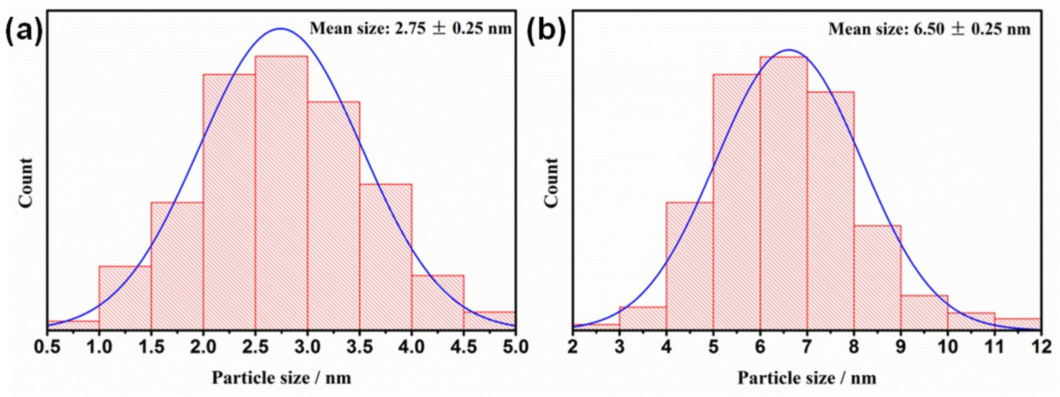

Fig. S4 The particle size distributions of the catalysts (a) $Ni_{0.75}Ir_{0.25}$ and (b) $Ni_{0.75}Ir_{0.25}$-N samples.

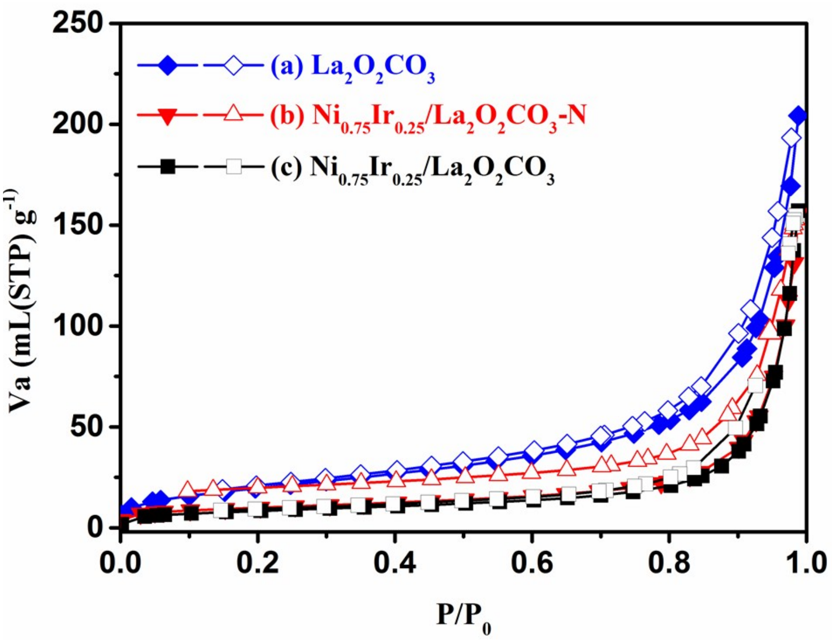

Fig. S5 N_2 adsorption-desorption isotherms of (a) $La_2O_2CO_3$, (b) $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$-N and (c) $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ catalysts.

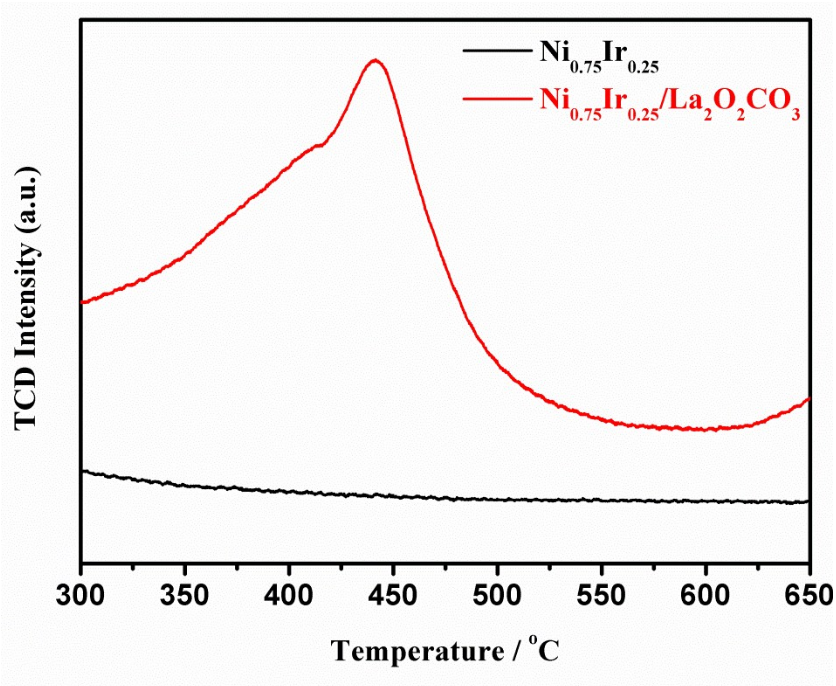

Fig. S6 CO_2-TPD mass spectra of the pure $Ni_{0.75}Ir_{0.25}$ NPs and $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ catalysts.

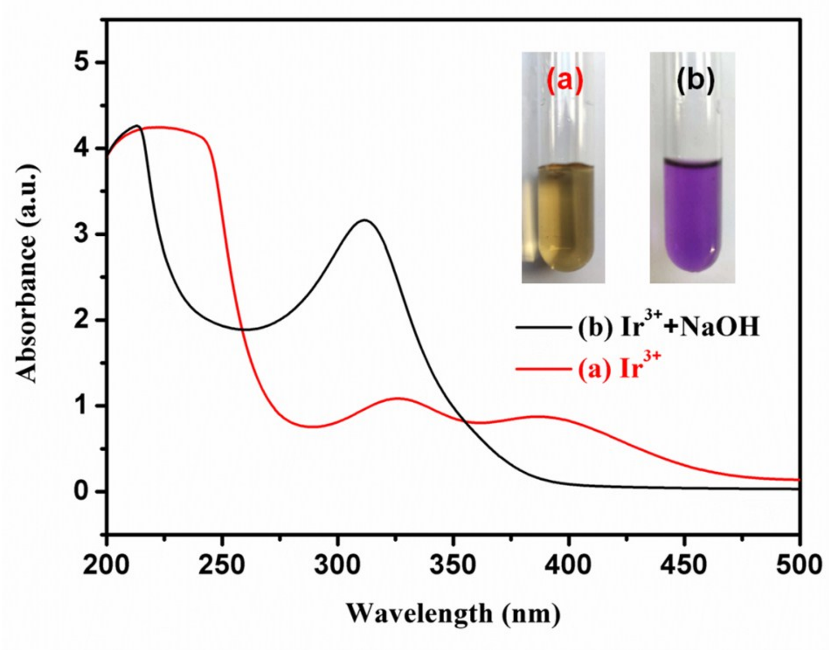

Fig. S7 UV-Vis spectra and the corresponding photos of (a) $IrCl_3{\cdot}xH_2O$ aqueous solution and (b) $IrCl_3{\cdot}xH_2O$ with NaOH mixture aqueous solution.

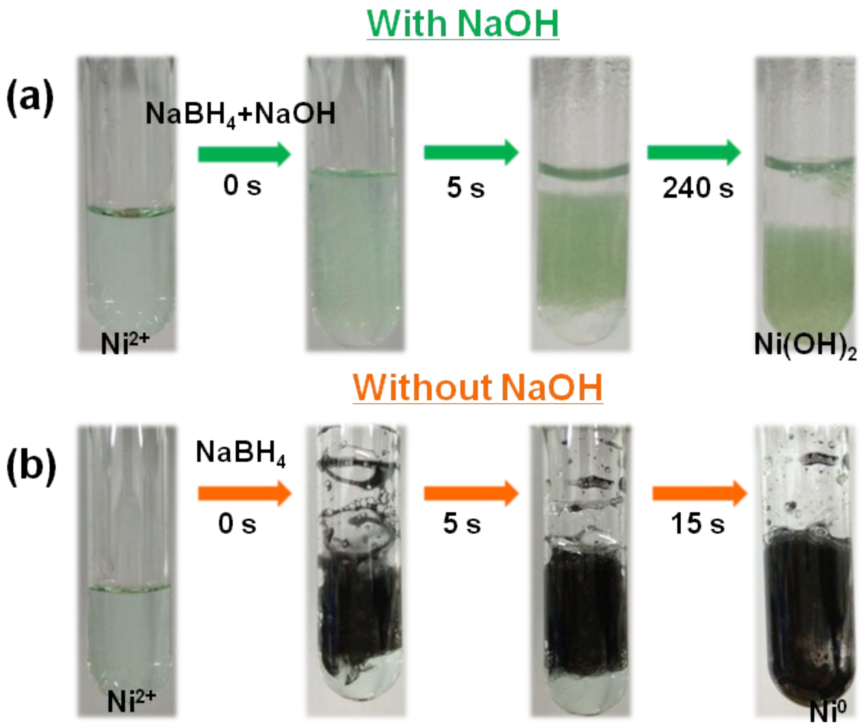

Fig. S8 The color changes of the aqueous solution of $NiCl_2$ during the reduction processes in the (a) presence and (b) absence of NaOH added.

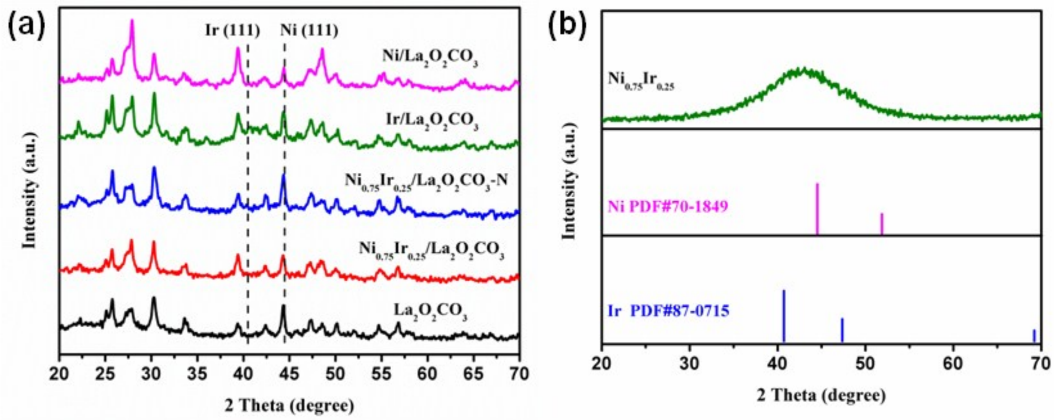

Fig. S9 Powder XRD diffraction patterns of the as-synthesized (a) $La_2O_2CO_3$, $Ni/La_2O_2CO_3$, $Ir/La_2O_2CO_3$, $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$-N, $Ni_{0.75}Ir_{0.25}$, and $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ samples. (b) Powder XRD diffraction patterns of $Ni_{0.75}Ir_{0.25}$ NPs.

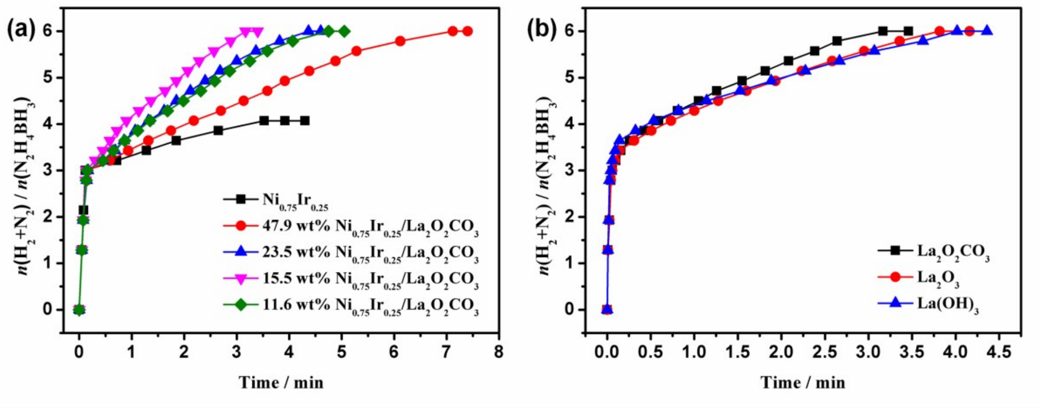

Fig. S10 Time course plots for H_2 generation from aqueous solution of $N_2H_4BH_3$ (200 mM, 5 mL) (a) over $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ with different amount of $La_2O_2CO_3$ at 323 K ($n_{(Ni+Ir)}/n_{(N_2H_4BH_3)}$ = 0.1) and (b) over $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$, $Ni_{0.75}Ir_{0.25}/La_2O_3$ and $Ni_{0.75}Ir_{0.25}/La(OH)_3$.

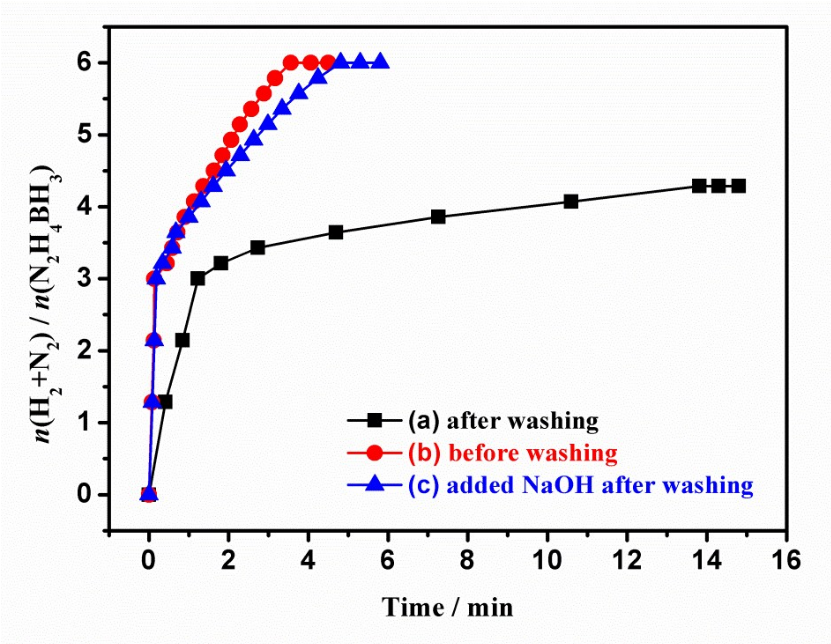

Fig. S11 Time course plots for H_2 generation from aqueous solution of $N_2H_4BH_3$ (200 mM, 5 mL) over $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ (a) after washing, (b) before washing and (c) added NaOH after washing ($n_{(Ni+Ir)}/n_{(N_2H_4BH_3)} = 0.1$).

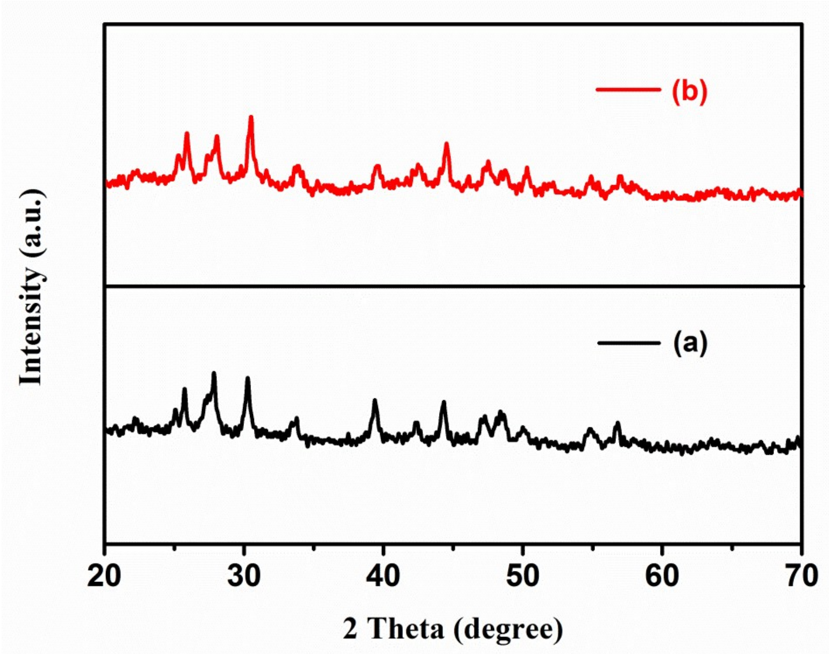

Fig. S12 Powder XRD diffraction patterns of in the $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ (a) before and (b) after the durability test.

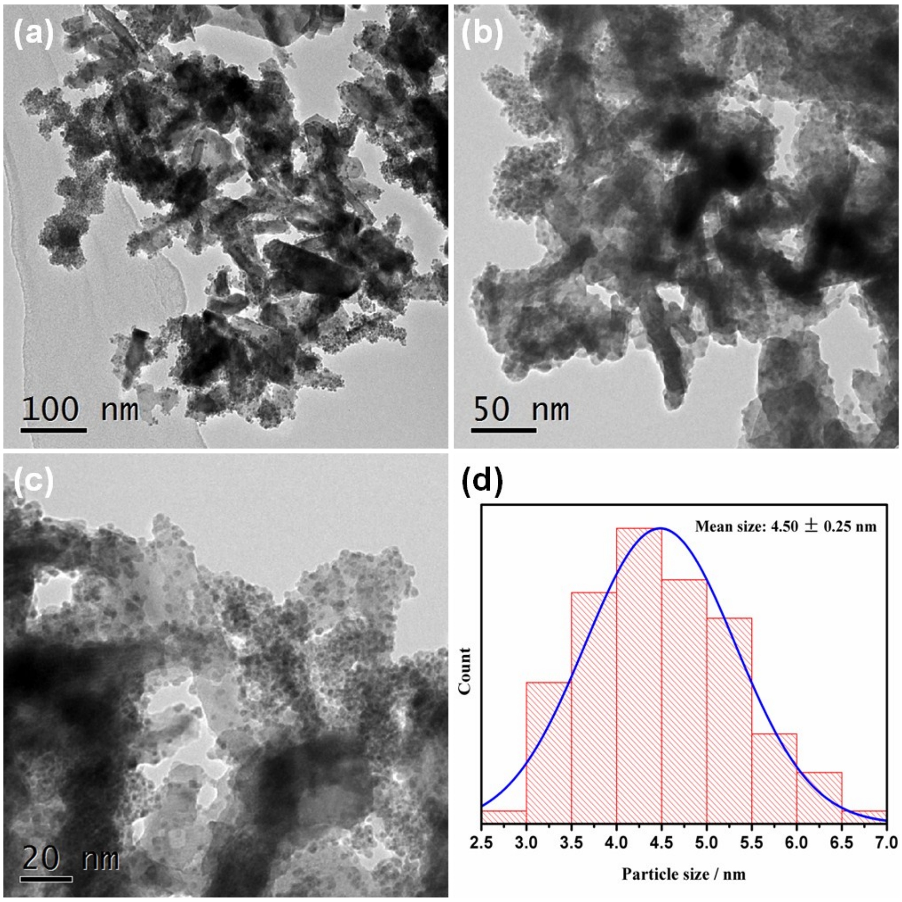

Fig. S13 (a-c) Typical TEM images and (d) the particle size distribution of the $Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$ after the durability test.

Table S1 Comparison of the catalytic performance of different catalysts for H_2 generation from $N_2H_4BH_3$.

Catalyst	T/K	NaOH/M	*n*($H_{2+}N_2$)/ *n*(HB)	TOF/h^{-1}	Ref.
$Rh_{0.5}(MoO_x)_{0.5}$	323	2.0	6.0	2000[b]	S1
$Ni_{0.9}Pt_{0.1}$/MIL-101	323	0.5	6.0	1515[b]	S2
$Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$	**323**	**1.2**	**6.0**	**1250.0**	**This work**
Raney Ni	298	1.0	6.0	892[b]	S3
$Rh_{0.8}Ni_{0.2}$@CeO_x/rGO	323	0.5	6.0	666.7[b]	S4
Ni-MoO_x/BN	323	1.0	6.0	600.0[b]	S5
$Ni_{0.5}Fe_{0.5}$-CeO_x/MIL-101	343	0.5	6.0	351.3[b]	S6
NiIr/Cr_2O_3	323	0.5	6.0	247.9[a]	S7
$Ni_{0.6}Pt_{0.4}$/MSC-30	303	0.6	6.0	240[a]	S8
$Ni_{0.9}Pt_{0.1}$/graphene	323	0.5	6.0	240[b]	S9
$Ni_{0.9}Pt_{0.1}$-CeO_2	323	0.5	5.74	234[b]	S10
$Cu_{0.4}Ni_{0.6}Mo$	323	2.0	6.0	108[b]	S11
Ni@(RhNi-alloy)/Al_2O_3	323	without	5.74	72.0[a]	S12
Ni_5@Pt	323	without	4.4	2.3[a]	S13

[a]*The total TOF values were calculated according to the original data provided by the reports.*

[b]*The inital TOF values and NaOH concentration were provided by the reports.*

Table S2 Comparison of the catalytic performance of different catalysts for H_2 generation by $N_2H_4{\cdot}H_2O$ decomposition.

Catalyst	**T/K**	**NaOH/M**	***n*(H$_{2+}$N$_2$)/ *n*(N$_2$H$_4$)**	**TOF/h^{-1}**	**Ref.**
$CoPt/La(OH)_3$	323	3.5	3.0	2400[b]	S14
$Ni_{0.6}Pt_{0.4}/g\text{-}C_3N_4$	323	0.75	3.0	2194[b]	S15
$Rh_{0.5}(MoO_x)_{0.5}$	323	2.0	3.0	725[b]	S1
$Ni_{0.9}Pt_{0.1}$/MIL-101	323	0.5	3.0	621[b]	S2
$Ni_{0.75}Ir_{0.25}/La_2O_2CO_3$	**323**	**1.2**	3.0	**487.3**	**This work**
$Ni_{0.85}Ir_{0.15}$@MIL-101	323	0.5	3.0	464[b]	S16
$Rh_{55}Ni_{45}/Ce(OH)CO_3$	323	0.5	3.0	395[b]	S17
$Rh_{0.8}Ni_{0.2}@CeO_x$/rGO	323	0.5	3.0	210.5[b]	S4
$Ni_{87}Pt_{13}$/MA	323	0.5	2.97	160[b]	S18
$Rh_{55}Ni_{45}/Ce(OH)CO_3$	303	0.5	3.0	150[b]	S17
$Ni_{0.9}(PtRh)_{0.05}/La_2O_3$	298	0.5	3.0	66.7[a]	S19
Rh-Ni-B	303	1.0	3.0	54.5[a]	S20
$Ni\text{-}0.080CeO_2$	303	without	2.97	51.6[b]	S21
RhNi/graphene	323	1.0	3.0	37.5[a]	S22
Ni/CeO_2	323	0.5	3.0	34.0[b]	S23
$Ni_{0.9}Pt_{0.1}/Ce_2O_3$	298	0.5	3.0	28.1[b]	S24
$NiMoB/La(OH)_3$	323	2.0	3.0	13.3[b]	S25
$NiIr_{0.059}/Al_2O_3$	303	without	2.8	12.4[b]	S26
Rh_4Ni NPs	298	without	3.0	6.0[a]	S27
$Ni\text{-}Al_2O_3$-HT	303	without	3.0	4.8[a]	S28
$Ni_{0.95}Ir_{0.05}$-CTAB	298	without	3.0	3.1[a]	S29

[a]*The total TOF values were calculated according to the original data provided by the reports.*

[b]*The inital TOF values were provided by the reports.*

Calculation method for TOF

The total turn-over frequency (TOF) reported in this work was an apparent TOF value based on the number of metal (Ir+Ni) atoms in catalysts, which was calculated from the equation as follows:

$$\text{TOF} = \frac{n_{\text{H}_2}}{n_{\text{metal}} \cdot t}$$

Where n_{H2} was the mole number of generated H_2, n_{metal} was the total mole number of Ni and Ir in catalyst and t was the completed reaction time in hour.

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