Noble-metal-free NiFe nanoparticles immobilized on nano CeZrO$_2$

solid solutions for highly efficient hydrogen production from hydrous hydrazine

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**Synthesis of Ce\(_{1-x}\)Zr\(_x\)O\(_2\) solid solutions**

Typically, 1.0 g of Pluronic 123 was dissolved in 10 mL of ethanol with vigorous stirring at 35 °C for 2 h. Then 10 mL quantitative amounts of Ce(NO\(_3\))\(_3\)·6H\(_2\)O and ZrOCl\(_2\)·8H\(_2\)O alcohol solution are dropped slowly into the above solution (total amount of Ce plus Zr is 10 mmol). After being stirred for 4 h, the homogeneous sol was transferred to an oven and underwent solvent evaporation. After aging for 48 h at 40 °C, the gel product were calcined by slowly increasing the temperature from room temperature to 400 °C (1 °C/min ramping rate) and holding at 400 °C for 4 h in muffle furnace to obtain Ce\(_{1-x}\)Zr\(_x\)O\(_2\) solid solutions, where \(x\) is the mole ratio of Zr to (Ce + Zr) in the catalysts. For comparison, with different rare earth groups, La\(_{0.9}\)Zr\(_{0.1}\)O\(_2\) and Nd\(_{0.9}\)Zr\(_{0.1}\)O\(_2\) were also prepared by the same method as Ce\(_{0.9}\)Zr\(_{0.1}\)O\(_2\) replacing Ce(NO\(_3\))\(_3\)·6H\(_2\)O with La(NO\(_3\))\(_3\)·6H\(_2\)O and Nd(NO\(_3\))\(_3\)·6H\(_2\)O, respectively.

**Calculation method for TOF**

The turnover frequency (TOF) reported in this work is an apparent TOF value based on the number of (Ni + Fe) atoms in the catalyst, which is calculated from the equation as follows:

\[
\text{TOF} = \frac{2 P_0 V}{3 RT n_{\text{NiFe}} t}
\]

\(P_0\) is the atmospheric pressure (101325 Pa), \(V\) is the volume of generated gas (H\(_2\) + N\(_2\)) when the conversion reached 50\%, \(R\) is the universal gas constant (8.3145 m\(^3\)·Pa·mol\(^{-1}\)·K\(^{-1}\)), \(T\) is the room temperature (298 K), \(n_{\text{NiFe}}\) is the total number of moles of (Ni + Fe) atoms in the catalyst and \(t\) is the reaction time when the conversion reached 50\%. 

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Fig. S1 TEM images and the corresponding particle size distribution of the as-synthesized (a,b) CeO$_2$ and (c,d) ZrO$_2$.
**Fig. S2** (a,b) TEM images and (c,d) high-resolution TEM images of the as-synthesized NiFe/CeZrO$_2$ catalyst. The inset of (b) shows the corresponding SAED pattern.
**Fig. S3** Powder XRD patterns of the as-synthesized nano Ce$_{1-x}$Zr$_x$O$_2$ solid solutions ($x$ = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0).

The diffraction peaks at $28.52^\circ$, $33.08^\circ$, $47.52^\circ$, $56.40^\circ$, $59.08^\circ$, $69.40^\circ$, $76.70^\circ$, $79.12^\circ$ and $88.38^\circ$ were assigned to the (111), (200), (220), (311), (222), (400), (331), (420) and (422) crystal facets of CeO$_2$. 
Fig. S4 Powder XRD patterns of the as-synthesized catalysts.
**Fig. S5** (a) Nitrogen sorption isotherms and (b) the corresponding pore size distribution curves of CeO$_2$, ZrO$_2$, CeZrO$_2$ and NiFe/CeZrO$_2$ catalysts.
Fig. S6 The survey XPS spectrum of NiFe/CeZrO$_2$ catalyst.
Fig. S7 (a) Time course plots and (b) the corresponding TOF values and H$_2$ selectivity for H$_2$ release from N$_2$H$_4$ aqueous solution (200 mM, 10 mL) over NiFe/CeZrO$_2$ catalysts with different CeZrO$_2$ contents in the presence of NaOH (2.5 M) at 343 K ($n_{\text{NiFe}}/n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}} = 0.1$).
Fig. S8 (a) Time course plots for \( \text{H}_2 \) release from \( \text{N}_2\text{H}_4 \) aqueous solution (200 mM, 10 mL) over NiFe/CeZrO\(_2\), NiFe/CeO\(_2\) and NiFe/ZrO\(_2\) catalysts with NaOH (2.5 M) at 343 K \((n_{\text{NiFe}}/n_{\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}} = 0.1)\). (b) The TOF values and corresponding \( \text{H}_2 \) selectivity for dehydrogenation of \( \text{N}_2\text{H}_4 \) aqueous solution over NiFe/Ce\(_{1-x}\)Zr\(_x\)O\(_2\) with different Ce and Zr contents.
Fig. S9 (a) Time course plots and (b) the corresponding TOF values and H$_2$ selectivity for H$_2$ release from N$_2$H$_4$ aqueous solution (200 mM, 10 mL) over NiFe/CeZrO$_2$ catalyst with different concentration of NaOH at 343 K (m$_{CeZrO_2}$ = 100 mg, $n_{NiFe}$/$n_{N_2H_4\cdot H_2O} = 0.1$).
Fig. S10 Time course plots for H$_2$ release from N$_2$H$_4$ aqueous solution (200 mM, 10 mL) over the NiFe/ReZrO$_2$ catalysts (Re = Ce, La, Nd) with NaOH (2.5 M) at 343 K ($m_{ReZrO_2} = 100$ mg, $n_{NiFe}/n_{N_2H_4H_2O} = 0.1$).
**Fig. S11** Time course plots for H₂ release from N₂H₄ aqueous solution (200 mM, 10 mL) over NiFe supported by different supports with NaOH (2.5 M) at 343 K (n_{NiFe}/n_{N₂H₄·H₂O} = 0.1).
Fig. S12 Time course plots for H₂ release from N₂H₄ aqueous solution (200 mM, 10 mL) over NiCo/CeZrO₂, NiFe/CeZrO₂, NiCu/CeZrO₂, CoFe/CeZrO₂, and CuFe/CeZrO₂ catalysts with NaOH (2.5 M) at 343 K (m_{CeZrO₂} = 100 mg, \(n_{\text{NiFe}}/n_{\text{N₂H₄·H₂O}} = 0.1\)).
Fig. S13 (a) Time course plots (b) arrhenius plots for H$_2$ release from N$_2$H$_4$ aqueous solution (200 mM, 10 mL) over NiFe NPs with NaOH (2.5 M) at different temperatures ($n_{\text{NiFe}}/n_{\text{N$_2$H$_4$·H$_2$O}} = 0.1$).
Fig. 14 (a) Time course plots for H$_2$ release from N$_2$H$_4$ aqueous solution (200 mM, 10 mL) over the NiFe/LaZrO$_2$ catalyst with NaOH (2.5 M) at different temperatures. (b) Arrhenius plots and (inset) the corresponding TOF values ($m_{LaZrO_2} = 100$ mg, $n_{NiFe}/n_{N_2H_4 \cdot H_2O} = 0.1$).
Fig. 15 (a) Time course plots for $H_2$ release from $N_2H_4$ aqueous solution (200 mM, 10 mL) over the NiFe/NdZrO$_2$ catalyst with NaOH (2.5 M) at different temperatures. (b) Arrhenius plots and (inset) the corresponding TOF values ($m_{NdZrO_2} = 100$ mg, $n_{NiFe}/n_{N_2H_4\cdot H_2O} = 0.1$).
Fig. S16 (a) Powder XRD patterns of the as-synthesized NiFe/CeZrO$_2$ catalysts before and after five times used; (b,c) TEM images of the NiFe/CeZrO$_2$ catalyst used five times and (d) the corresponding particle size distribution.
Fig. S17 Stability test for H₂ release from N₂H₄ aqueous solution over the NiFe/LaZrO₂ catalyst with NaOH (2.5 M) at 343 K.
Fig. S18 Stability test for H\textsubscript{2} release from N\textsubscript{2}H\textsubscript{4} aqueous solution over the NiFe/NdZrO\textsubscript{2} catalyst with NaOH (2.5 M) at 343 K.
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Ni (wt%)</th>
<th>Fe (wt%)</th>
<th>Ni/Fe (molar ratio)</th>
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<tr>
<td>Fe</td>
<td>-</td>
<td>10.25</td>
<td>-</td>
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<tr>
<td>N\textsubscript{i}<em>0.3F\textsubscript{e}</em>{0.8}</td>
<td>2.76</td>
<td>9.02</td>
<td>0.23/0.77</td>
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<td>N\textsubscript{i}<em>0.4F\textsubscript{e}</em>{0.6}</td>
<td>4.32</td>
<td>6.83</td>
<td>0.38/0.62</td>
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<td>N\textsubscript{i}<em>0.6F\textsubscript{e}</em>{0.4}</td>
<td>6.96</td>
<td>4.50</td>
<td>0.60/0.40</td>
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<tr>
<td>N\textsubscript{i}<em>0.7F\textsubscript{e}</em>{0.3}</td>
<td>8.06</td>
<td>3.47</td>
<td>0.69/0.21</td>
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<td>N\textsubscript{i}<em>0.8F\textsubscript{e}</em>{0.2}</td>
<td>9.11</td>
<td>2.41</td>
<td>0.78/0.22</td>
</tr>
<tr>
<td>N\textsubscript{i}<em>0.9F\textsubscript{e}</em>{0.1}</td>
<td>10.08</td>
<td>1.39</td>
<td>0.87/0.13</td>
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<tr>
<td>Ni</td>
<td>11.26</td>
<td>-</td>
<td>-</td>
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Table S2. BET surface area, pore volume and pore diameter of different samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m²·g⁻¹)</th>
<th>Pore volume (cm³·g⁻¹)</th>
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<tbody>
<tr>
<td>CeZrO₂</td>
<td>108.6</td>
<td>0.2526</td>
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<tr>
<td>NiFe/CeZrO₂</td>
<td>74.2</td>
<td>0.2614</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>52.2</td>
<td>0.0699</td>
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<tr>
<td>CeO₂</td>
<td>16.9</td>
<td>0.0438</td>
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Table S3. Catalytic activities of as-synthesized catalysts toward the dehydrogenation of N$_2$H$_4$ in aqueous solution compared to other reported catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>T (K)</th>
<th>NaOH (M)</th>
<th>Selectivity (%)</th>
<th>TOF (h$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe</td>
<td>343</td>
<td>0.5</td>
<td>100</td>
<td>6.3</td>
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<tr>
<td>Ni/Al$_2$O$_3$</td>
<td>303</td>
<td>-</td>
<td>93</td>
<td>2.2</td>
<td>S2</td>
</tr>
<tr>
<td>Ni$_{0.080}$/CeO$_2$</td>
<td>303</td>
<td>-</td>
<td>&gt;99</td>
<td>51.6</td>
<td>S3</td>
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<tr>
<td>Ni$<em>{0.5}$/Cu$</em>{0.5}$/MCNS</td>
<td>333</td>
<td>0.5</td>
<td>100</td>
<td>21.8</td>
<td>S4</td>
</tr>
<tr>
<td>Ni$<em>{1.5}$/Fe$</em>{1.0}$/alloy/(MgO)$_{3.5}$</td>
<td>299</td>
<td>-</td>
<td>99</td>
<td>10.9</td>
<td>S5</td>
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<tr>
<td>NiFe/Cu</td>
<td>343</td>
<td>-</td>
<td>100</td>
<td>35.3</td>
<td>S6</td>
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<tr>
<td>Cu@Fe$_8$Ni$_5$</td>
<td>343</td>
<td>0.1</td>
<td>100</td>
<td>18.2</td>
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<tr>
<td>Ni$<em>{0.6}$/Fe$</em>{0.4}$/Mo</td>
<td>323</td>
<td>1.8</td>
<td>100</td>
<td>28.8</td>
<td>S8</td>
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<td>2D NiFe/CeO$_2$</td>
<td>323</td>
<td>-</td>
<td>99</td>
<td>11.5</td>
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<td>Ni$_3$Fe-(CeO$<em>x$)$</em>{0.15}$/rGO</td>
<td>343</td>
<td>1.0</td>
<td>100</td>
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<td>298</td>
<td>-</td>
<td>99</td>
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<td>NiMoB-La(OH)$_3$</td>
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<td>2.0</td>
<td>100</td>
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<tr>
<td>NiFe/CeZrO$_2$</td>
<td>343</td>
<td>2.5</td>
<td>100</td>
<td>119.2</td>
<td>This work</td>
</tr>
<tr>
<td>NiFe/LaZrO$_2$</td>
<td>343</td>
<td>2.5</td>
<td>91</td>
<td>100.3</td>
<td>This work</td>
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<tr>
<td>NiFe/NdZrO$_2$</td>
<td>343</td>
<td>2.5</td>
<td>96</td>
<td>103.7</td>
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References


