Supporting Information for

Increasing Oxygen Vacancy of CeO₂ Nanocrystals by Ni Doping and reduced Graphene Oxides Decoration towards the Electrocatalytic Hydrogen Evolution

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As can be seen, the pristine rGO is composed of layered thin platelets in a large scale in Figure S1A, and after the incorporation of the uniform CeO$_2$ NCs (Figure S1B), the almost uniform distribution of CeO$_2$ NCs upon rGO sheets is obtained (Figure S1C, D).
Figure S2 The STEM images of CeO$_2$/rGO NCPs and elemental analysis: (A) HADDF-STEM, B) ABF-STEM, C) SEI-STEM, E-G) separate elemental maps of carbon $K$ edge (red), cerium $L$ edge (cyan), and oxygen $K$ edge (yellow), respectively.
Figure S3. XRD spectra of as-synthesize CeO$_2$ NCs, the pristine rGO, the CeO$_2$/rGO NCPs, and Ni-CeO$_2$/rGO NCPs.

The XRD spectrum of the as-synthesized CeO$_2$ NCs shows the good crystallinity of with four major peaks located around 28.4º, 32.8º, 47.5º, 56.2º, which can be assigned to the 111, 200, 220 and 311 diffraction of the fluorite-cubic structure of CeO$_2$ (JCPDS, 34-0394).

Subsequently, the peak strength and peak width of rGO around 22.1º is degenerated in the large extent, comparing to that of the pristine rGO, while the the good crystallinity of the CeO$_2$ NCs is retained.
Figure S4 Raman spectra of the pristine rGO, CeO$_2$ NCs, and rGO/CeO$_2$ NCPs, respectively.
Figure S5. EELS spectra of the $M$ edge of Ce for pristine CeO$_2$, physically mixed CeO$_2$/rGO and CeO$_2$/rGO-0.05.
Figure S6. The split spectrum of O 1s of the CeO$_2$/rGO and Ni-CeO$_2$/rGO NCPs
Figure S7. Typical cyclic voltammetry curves of (A) the pristine CeO$_2$, (B) CeO$_2$/rGO-0.05, and (C) Ni-CeO$_2$/rGO-0.05 NCPs in 1M KOH with different scan rates.
Figure S8. LSV curves of CeO$_2$/rGO NCPs with different addition of rGO.
Figure S9. LSV curves of all the electrodes related to this study.
Figure S10. The structure models of (A) pristine CeO$_2$ after the removal of one O at the top surface layer, (B) CeO$_2$/rGO constructed by combining the graphene layer with the oxygen end from the CeO$_2$, and (C) Ni-CeO$_2$ with a $V_O$. 
Figure S11. The PDOS of (A) CeO₂, (B) CeO₂ with $V_O$, and (C) Ni-CeO₂.
Table S1. Comparison of HER catalytic activity in alkaline solutions with high-performance catalyst materials reported in the literature

<table>
<thead>
<tr>
<th>Catalytic materials</th>
<th>Electrolyte</th>
<th>Overpotential (mV)</th>
<th>Current density (mA cm(^{-2}))</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Ni-rGO/CeO(_2)</td>
<td>1M KOH</td>
<td>113</td>
<td>10</td>
<td>This work</td>
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<td>rGO-MoS(_2)</td>
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<td>146</td>
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<td>α-Ni(_3)S(_8)</td>
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<td>RGO/MoS(_2)/Pd</td>
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<td>2D Mo-ReS(_2)</td>
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<td>10</td>
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<tr>
<td>Ni(_3)P-Co(_2)P</td>
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<td>NiCoP/NF</td>
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<td>131</td>
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References


