Supplementary Information

Defect-rich N-doped CeO$_2$ supported by N-doped graphene as a metal-free plasmonic hydrogen evolution photocatalyst
Apparent quantum yield efficiency calculation:

The apparent quantum yield (AQY) efficiency for HER activity have been performed to understand the effect of the different irradiation wavelengths over the photocatalytic performance of nanocomposite materials. The AQY efficiency, thereby, are calculated based on the amount of hydrogen evolution in the duration $t$ of a single incident wavelength exposure using the following equation:

$$AQY\;efficiency\;[\%] = \frac{\text{Numbers of evolved hydrogen molecules} \times 2}{\text{Number of incident photons}} \times 100$$

$$Number\;of\;incident\;photons = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{PS\lambda_{\text{inc}}t}{hc}$$

Finally, the AQY efficiency is calculated by:

$$AQY\;efficiency\;(%)) = \frac{2n_{H_2}tN_Ahc}{PS\lambda_{\text{inc}}t} \times 100$$

Where, $n_{H_2}$ (mol) represents the amount of hydrogen evolution in the duration time ($t$) of incident monochromatic light exposure, $\lambda_{\text{inc}}$ (m); $N_A$ (mol$^{-1}$) is Avogadro’s constant; $h$ (J s) is Planck’s constant, $c$ (m s$^{-1}$) is the speed of light; $P$ (W m$^{-2}$) presents the power density of the incident monochromatic light; and $S$ (m$^2$) is the irradiation area. The incident light wavelength is controlled by a 300 W xenon lamp (Asahi, Max 303) with an appropriate band pass filter inserted between light source and made reactor.
Table S1. Free energy corrections calculated for H$_2$ molecule and H* adsorbate. All values are in eV.

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<tr>
<th></th>
<th>ZPE</th>
<th>( \int C_p dT )</th>
<th>-T(\Delta S)</th>
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<tr>
<td>H$_2$ (g)</td>
<td>0.267</td>
<td>0.091</td>
<td>-0.554</td>
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<tr>
<td>H*</td>
<td>0.023</td>
<td>0.009</td>
<td>-0.014</td>
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Fig. S1 (a) TEM observation, (b) EDS elemental mapping of as-pyrolyzed 3.9% N-CeO$_2$ nanoparticles, (c) high-resolution TEM image of 3.9% N-CeO$_2$ with lattice fringe of (111) plane, and (d) SAED pattern of assembly 3.9% N-CeO$_2$ nanoparticle.
Fig. S2 (a, b) TEM observation of as-pyrolyzed 1.8 and 7.6% N-CeO$_2$ NPs.

Fig. S3 (a) TEM observation and (b) TEM elemental mapping of as-pyrolyzed undoped CeO$_2$.
**Fig. S4** (a) XRD analysis for as-pyrolyzed undoped CeO$_2$, 1.8% N-CeO$_2$, 3.9% N-CeO$_2$, and 7.6% N-CeO$_2$ nanocomposites. (b, c) Corresponding change in (111) peak positions.

**Fig. S5** Full XPS survey measured by prolonging the integration time to carefully detect the chemical compositions of as-pyrolyzed undoped CeO$_2$, 1.8% N-CeO$_2$, 3.9% N-CeO$_2$, and 7.6% N-CeO$_2$ nanocomposites.
Fig. S6 High-resolution XPS analysis of (a) Ce 3d and (b) O 1s for as-pyrolyzed undoped CeO$_2$.

Fig. S7 High-resolution XPS analysis of (a) N 1s, (b) O 1s, and (c) Ce 3d for as-pyrolyzed 3.9% N-CeO$_2$. 
Table S2. XPS fitting result comparison for as-calcined undoped CeO$_2$ and N-doped CeO$_2$, and 3.9% N-CeO$_2$/N-Gr samples.

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<tr>
<th>Samples</th>
<th>Ce$^{3+}$</th>
<th>Oxygen</th>
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<tr>
<td></td>
<td>Binding energy (eV)</td>
<td>Relative percentage (%)</td>
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<tr>
<td>CeO$_2$</td>
<td>884.83, 903.02</td>
<td>13.11</td>
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<tr>
<td>1.8% N-CeO$_2$</td>
<td>885.84, 903.10</td>
<td>15.32</td>
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<tr>
<td>3.9% N-CeO$_2$</td>
<td>885.05, 903.16</td>
<td>22.47</td>
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<tr>
<td>7.6% N-CeO$_2$</td>
<td>885.29, 903.52</td>
<td>24.92</td>
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<tr>
<td>3.9% N-CeO$_2$/N-Gr</td>
<td>885.31, 903.47</td>
<td>23.08</td>
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Fig. S8 (a) UV-vis absorption spectra of as-calcined CeO$_2$ and N-CeO$_2$ materials and (b) plot of $(\alpha h\nu)^2$ vs. photon energy with estimated bandgap energy ($E_g$) measured by Tauc’s equation.

Fig. S9 Mott-Schottky plots based on impedance measurement at frequency of 20 kHz for as-calcined CeO$_2$ and N-CeO$_2$. 
**Fig. S10** TEM observation of as-pyrolyzed free N-Gr.

**Fig. S11** EDS elemental mapping for as-pyrolyzed 3.9% N-CeO$_2$/N-Gr nanocomposites.
Fig. S12 TEM analysis for as-pyrolyzed 3.9% N-CeO$_2$/Gr nanocomposites.

Fig. S13 Corresponding BET surface area for as-pyrolyzed 3.9% N-CeO$_2$ and 3.9% N-CeO$_2$/N-Gr photocatalysts.
**Fig. S14** XRD analysis for as-pyrolyzed undoped CeO$_2$, 3.9% N-CeO$_2$, and 3.9% N-CeO$_2$/N-Gr nanocomposites.

In case of 3.9% N-CeO$_2$/N-Gr (yellow), ceria XRD peaks are highlighted with (•). The XRD pattern of 3.9% N-CeO$_2$/N-Gr nanocomposites further consists of a small diffraction peak at around 26°, which corresponds to nitrogen-doped graphene, as marked with (*).

**Fig. S15** Full XPS investigation of as-prepared N-Gr and high-resolution XPS analysis of N 1s.
Fig. S16 (a) UV-vis absorption spectra and (b) corresponding plot of $(\alpha h \nu)^2$ vs. photon energy of as-pyrolyzed undoped CeO$_2$ and 3.9% N-CeO$_2$, and 3.9% N-CeO$_2$/N-Gr nanocomposites.

Fig. S17 The local electrostatic potential to calculate the work function values for (a) N-Gr and (b) 3.9% N-CeO$_2$ (111). Red and green horizontal dashed lines correspond to the vacuum level and the Fermi level, respectively.
Fig. S18 A circuit used to fit the Nyquist plots: R1 is the solution resistance, R2 is the charge transfer resistance, and CPE1 is a constant phase element.$^1$

Fig. S19 MOR activity for 3.9% N-CeO$_2$/N-Gr nanocomposites with and without visible-light irradiation.
**Fig. S20** Time-resolved photoluminescence (TRPL) spectra monitored at 500 nm for 3.9% N-CeO$_2$ and 3.9% N-CeO$_2$/N-Gr samples.

**Fig. S21** Time-dependent photocatalytic hydrogen evolution amount for N-Gr, 3.9% N-CeO$_2$, and 3.9% N-CeO$_2$/N-Gr nanohybrids.
**Fig. S22** A comparison of visible light-driven hydrogen evolution reactions based on current advanced photocatalysts reported in recent literatures.$^{2-24}$

![Graph showing the comparison of different photocatalysts.](image)

*This work*

**Fig. S23** TEM analysis for as-used 3.9% N-CeO$_2$/N-Gr nanocomposites after long-term HER stability test over 20 h.
**Fig. S24** (a) Field-emission SEM observation for as-used 3.9% N-CeO$_2$/N-Gr nanocomposites after stability test and (c-e) corresponding SEM-EDS elemental mapping.

**Fig. S25** Possible mechanism of HER over pure CeO$_2$ photocatalyst under visible-light irradiation.
Fig. S26 Free energy diagram of (a) CeO$_2$, (b) 3.9% N-CeO$_2$, (c) 3.9% N-CeO$_2$/N-Gr (two graphene layers), (d) 3.9% N-CeO$_2$/N-Gr (three graphene layers) for HER activity.
References

10. Q. Xiang, F. Cheng and D. Lang, 2016, 9, 996-1002.