Electronic Supplemental Information for

A Facile Mechanochemical Route to Covalently Bonded Graphitic Carbon Nitride (g-C$_3$N$_4$) and Fullerene Hybrid toward Enhanced Visible Light Photocatalytic Hydrogen Production

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**S1. Raman spectra of products obtained from ball-milling a mixture of pristine g-C₃N₄ and C₆₀ with and without LiOH catalyst.**

![Raman Spectra](image)

**Figure S1.** Raman spectra of pristine g-C₃N₄ (a), products obtained from ball-milling a mixture of pristine g-C₃N₄ and C₆₀ without (b) and with (c) LiOH catalyst, and pristine C₆₀ (d). The excitation laser light wavelengths are 532 nm (A) and 785 nm (B), respectively.

**S2. High-resolution C1s, N1s and O1s XPS spectra.**

![XPS Spectra](image)

**Figure S2.** High-resolution C1s XPS spectra of g-C₃N₄/C₆₀-4 wt% (a) and g-C₃N₄/C₆₀-20 wt% (b).
Figure S3. High-resolution N1s XPS spectra of g-C$_3$N$_4$/C$_{60}$-4 wt% (a) and g-C$_3$N$_4$/C$_{60}$-20 wt% (b).

Figure S4. High-resolution O1s XPS spectra of pristine g-C$_3$N$_4$ (a) and g-C$_3$N$_4$/C$_{60}$-12 wt% (b).

Figure S5. High-resolution N1s XPS spectra of products obtained from ball-milling a mixture of pristine g-C$_3$N$_4$ and C$_{60}$ without (a) and with (b) LiOH catalyst.
S3. XRD patterns of products obtained from ball-milling a mixture of pristine g-C₃N₄ and C₆₀ with and without LiOH catalyst.

Figure S6. XRD patterns of pristine g-C₃N₄ (a), products obtained from ball-milling a mixture of pristine g-C₃N₄ and C₆₀ without (b) and with (c) LiOH catalyst, and pristine C₆₀ (d).

S4. TGA curves.

Figure S7. TGA curves of pristine g-C₃N₄ (a), g-C₃N₄/C₆₀-12 wt% hybrid (b), and C₆₀ (c). The right dotted vertical line was added to aid identifying the last weight loss step (708 - 830 °C) corresponding to the decomposition of C₆₀.
**Figure S8.** TGA curves of pristine g-C$_3$N$_4$ (a), pure g-C$_3$N$_4$ after ball-milling (BM-g-C$_3$N$_4$, b), products obtained from ball-milling a mixture of pristine g-C$_3$N$_4$ and C$_{60}$ without (c) and with (d) LiOH catalyst.

**S5. Schematic illustration of the formation mechanism of the g-C$_3$N$_4$/C$_{60}$ hybrid.**

**Scheme S1.** A schematic illustration of the formation mechanism of the g-C$_3$N$_4$/C$_{60}$ hybrid via the mechanochemical ball-milling in the existence of LiOH as catalyst.
S6. FTIR, Raman spectra and XRD patterns of product obtained by reaction of g-C₃N₄ with C₆₀ in DMF solution.

Figure S9. FTIR spectra (A), Raman spectra (B) and XRD patterns (C) of pristine g-C₃N₄ (a), C₆₀ (b) and product obtained by reaction of g-C₃N₄ with C₆₀ in DMF solution (g-C₃N₄-C₆₀, c).

A mixture of 200 mg pristine g-C₃N₄ and 200 mg C₆₀ was dispersed in N,N-dimethylformamide (DMF) solution and stirred for 24 h under 70 °C, followed by Soxhlet-extraction with CS₂ for 48 h to remove the unreacted C₆₀. No C₆₀ moiety was detected in the final product based on FTIR, Raman and XRD characterizations, revealing that the reaction of C₆₀ with the terminal NHₓ did not occur despite of the high nucleophilicity of the primary amine, and consequently covalent bonding of C₆₀ with the terminal NHₓ at the edge of pristine g-C₃N₄ seems unlikely.

S7. SEM image of product obtained from ball-milling pure g-C₃N₄.

Figure S10. SEM image of product obtained from ball-milling of pure g-C₃N₄.
Figure S11. TEM elemental mapping images of the portion selected for pristine g-C₃N₄ (a, c, e) and g-C₃N₄/C₆₀-12 wt% hybrid (b, d, f). The corresponding C (c, d) and N (e, f) elemental mapping images are also shown.

The C elemental mapping image of g-C₃N₄/C₆₀ hybrid (image d) shows the enrichment of C elements at the edges (marked by arrows), whereas such a phenomenon is not observed for N element in the N elemental mapping image of g-C₃N₄/C₆₀ hybrid (image f). For the case of pristine g-C₃N₄, both C and N elements distribute uniformly without obvious enrichment at the edges (images c and e). This provides further experimental evidence on the C₆₀ bonding to the cleaved edge of g-C₃N₄.
**S9. Quantum efficiency and action spectra of pristine g-C$_3$N$_4$ and g-C$_3$N$_4$/C$_{60}$ hybrid.**

To measure the quantum yield for visible light H$_2$ evolution, 50 mg powder sample was dispersed in 100 mL aqueous solution containing 17.5 mg Eosin Y (EY) and 5 ml triethanolamine (TEOA), which was irradiated by a monochromic light using a bandpass filter (± 5 nm) for 420, 450, 475, 520, and 550 nm, respectively. The quantum efficiency ($\varphi$) is calculated according to the following equation (1):

$$\varphi = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$

$$\varphi = \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$  \hspace{1cm} (1)

Where the number of incident photons ($N_{\text{ph}}$) can be calculated from the power of the incident light ($P_{\text{ph}}$, 0.194, 0.205, 0.202, 0.305 and 0.225 J/s for 420, 450, 475, 520, and 550 nm, respectively), which was calibrated by an irraditometer (FZ-A, Beijing Normal University Optical Instrument), according to equation (2) (see Figure S12):

$$N_{\text{ph}} = P_{\text{ph}} \times \frac{t}{(hc/\lambda)} = P_{\text{ph}} \times t \times \frac{\lambda/\lambda}{(hc)}$$  \hspace{1cm} (2)

Where $t$ is the irradiation time, $\lambda$ is the wavelength of the incident light, $h$ is planck constant, $c$ is the speed of light in vacuum.

**Table S1.** Quantum efficiencies ($\varphi$) of different samples with (w) or without (w/o) Pt cocatalyst and EY photosensitizer measured under irradiation with visible light at $\lambda = 420$ nm.

<table>
<thead>
<tr>
<th>sample</th>
<th>condition</th>
<th>quantum efficiency ($\varphi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine g-C$_3$N$_4$</td>
<td>w/o</td>
<td>0.072%</td>
</tr>
<tr>
<td>g-C$_3$N$<em>4$/C$</em>{60}$-12 wt%</td>
<td>w/o</td>
<td>0.20%</td>
</tr>
<tr>
<td>no (control)</td>
<td>w</td>
<td>6.95%</td>
</tr>
<tr>
<td>pristine g-C$_3$N$_4$</td>
<td>w</td>
<td>6.79%</td>
</tr>
<tr>
<td>g-C$_3$N$<em>4$/C$</em>{60}$-12 wt%</td>
<td>w</td>
<td>6.97%</td>
</tr>
<tr>
<td>pristine g-C$_3$N$_4$</td>
<td>w/o</td>
<td>0.037%</td>
</tr>
<tr>
<td>g-C$_3$N$<em>4$/C$</em>{60}$-12 wt%</td>
<td>w/o</td>
<td>0.051%</td>
</tr>
</tbody>
</table>

Without the existence of Pt cocatalyst, $\varphi$ of g-C$_3$N$_4$/C$_{60}$-12 wt% hybrid is 0.20% (with the existence of EY photosensitizer), which is about 2.8 times of that for pristine g-C$_3$N$_4$ (0.072%). Such an enhancement ratio is consistent with that measured for H$_2$ production rate (about 4.0 times), confirming that covalently bonding of C$_{60}$ onto g-C$_3$N$_4$ can indeed result in enhanced visible light photocatalytic H$_2$ production.
We also measured and compared the quantum efficiencies ($\Phi$) of g-C$_3$N$_4$/C$_{60}$-12 wt% hybrid and pristine g-C$_3$N$_4$ under different conditions with the existence of Pt cocatalyst (measured under irradiation with visible light at $\lambda = 420$ nm). Surprisingly, with the co-existence of both Pt cocatalyst and EY photosensitizer, the measured $\Phi$ of g-C$_3$N$_4$/C$_{60}$-12 wt% hybrid and pristine g-C$_3$N$_4$ (6.97% and 6.79%, respectively) are quite comparable to that obtained for the control sample (only Pt cocatalyst + EY photosensitizer, 6.95%). This suggests that in this case the visible light H$_2$ production is primarily contributed by EY. Furthermore, without the existence of EY photosensitizer, the measured $\Phi$ of g-C$_3$N$_4$/C$_{60}$-12 wt% hybrid and pristine g-C$_3$N$_4$ (0.051% and 0.037%, respectively) with the existence of Pt cocatalyst only dramatically decrease, and are even lower than that measured without Pt cocatalyst (0.072%). This confirms further the importance of EY photosensitizer which plays the role of sensitizer for extending the spectral response region as discussed already in the main text.

Figure S12. UV-VIS diffuse reflectance spectra of EY (a), g-C$_3$N$_4$+EY (b) and g-C$_3$N$_4$/C$_{60}$-12 wt%+EY (c), and action spectra for H$_2$ evolution of g-C$_3$N$_4$+EY (d) and g-C$_3$N$_4$/C$_{60}$-12 wt%+EY (e) from an aqueous triethanolamine (TEOA) solution under visible light irradiation of 300 W Xe-lamp using a bandpass filter for 420, 450, 475, 520, and 550 nm, respectively.
**S10. Typical time courses of \( H_2 \) production based on pristine g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\)/C\(_{60}\)-12 wt% hybrid.**

![Graph showing typical time courses of \( H_2 \) production for pristine g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\)/C\(_{60}\)-12 wt% hybrid.](image)

**Figure S13.** Typical time courses of \( H_2 \) production based on pristine g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\)/C\(_{60}\)-12 wt% hybrid. The measurements were carried out in an aqueous solution (containing TEOA as a hole scavenger and EY as the photosensitizer) evacuated per 3 h without renewing the hole scavenger under visible light (\( \lambda > 420 \text{ nm} \)) irradiation of 300 W Xe-lamp.

**S11. Visible light photocatalytic \( H_2 \) production rates of different control samples.**

![Bar chart showing photocatalytic \( H_2 \) production rates for different control samples.](image)

**Figure S14.** Photocatalytic \( H_2 \) production rates of different samples measured in 5 vol% TEOA aqueous solution in the presence of EY for 3 h under visible light (\( \lambda > 420 \text{ nm} \)) irradiation of 300 W Xe-lamp. 

**Blend-1**: a physical blend of g-C\(_3\)N\(_4\)/C\(_{60}\) (64:9, w/w); **Blend-2**: a mixture of pristine g-C\(_3\)N\(_4\) and C\(_{60}\) powders ball-milled without LiOH catalyst (g-C\(_3\)N\(_4\)/C\(_{60}\)-w/o LiOH). **Comp-1, 2, 3**: C\(_{60}\)/g-C\(_3\)N\(_4\) composites with different C\(_{60}\)/dicyandiamide mass ratios (0.03 wt%, 0.3 wt% and 1.0 wt% for Comp-1, 2, 3, respectively) using the method reported in ref. [27].
S12. Diffuse reflectance UV-vis absorption spectra of pristine g-C₃N₄ and g-C₃N₄/C₆₀-12 wt% hybrid.

Figure S15. Diffuse reflectance UV-vis absorption spectra (A) and ($\alpha h\nu$)$^2$ versus $h\nu$ curves (B) of pristine g-C₃N₄ (a) and g-C₃N₄/C₆₀-12 wt% hybrid (b), and C₆₀ (c).

S13. BET surface areas of pristine g-C₃N₄ and g-C₃N₄/C₆₀ hybrid calculated from the nitrogen adsorption-desorption isotherms.

Table S2. BET surface areas of pristine g-C₃N₄, BM-g-C₃N₄, g-C₃N₄/C₆₀-12 wt% and g-C₃N₄/C₆₀ w/o LiOH.

<table>
<thead>
<tr>
<th>sample</th>
<th>BET Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine g-C₃N₄</td>
<td>12.5</td>
</tr>
<tr>
<td>BM-g-C₃N₄</td>
<td>16.1</td>
</tr>
<tr>
<td>g-C₃N₄/C₆₀-12 wt%</td>
<td>16.6</td>
</tr>
<tr>
<td>g-C₃N₄-C₆₀-w/o LiOH</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Figure S16. Nitrogen adsorption–desorption isotherms of g-C₃N₄ (a) and g-C₃N₄/C₆₀ hybrid (b).
S14. Electrical Conductivities of pristine g-C₃N₄ and g-C₃N₄/C₆₀ hybrid.

Figure S17. Electrical conductivities of the pristine g-C₃N₄, g-C₃N₄/C₆₀-12 wt% and a physical blend of g-C₃N₄:C₆₀ (g-C₃N₄ + C₆₀). Samples were pressed into tablets with the same thickness of approximately 1 mm.

S15. Mott–Schottky plots of pristine g-C₃N₄ and g-C₃N₄/C₆₀ hybrid.

Figure S18. Mott-Schottky (MS) plots of pristine g-C₃N₄ (a) and g-C₃N₄/C₆₀-12 wt% hybrid (b) film electrodes. The MS plots were obtained in a 0.1 M Na₂SO₄ aqueous solution at a frequency of 1 kHz. The flat band potentials of g-C₃N₄ (a) and g-C₃N₄/C₆₀-12 wt% hybrid (b) are determined to be -1.15 and -0.92 V vs. Ag/AgCl, which correspond to -0.95 and -0.72 V vs. NHE, respectively, according to an equation E(NHE) = E(Ag/AgCl) + 0.198.
**S16. PL spectra of pristine g-C₃N₄ and g-C₃N₄/C₆₀ hybrid.**

![Figure S19](image-url)

**Figure S19.** (A) PL spectra of pristine g-C₃N₄ (a) and g-C₃N₄/C₆₀-12 wt% hybrid (b) under the excitation wavelength of 360 nm. (B) PL spectra of EY (a) and EY + g-C₃N₄ (b) under the excitation wavelength of 520 nm.