Supporting Information for:

Brand new P-doped g-C$_3$N$_4$: enhanced photocatalytic activity for H$_2$ evolution and Rhodamine B degradation under visible light

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Figure S1: Time course of RhB Photodegradation on (a) Px-550 (x=0, 5, 10, 15, 20), and (b) P10-T (T=550, 600, 650) together with the pure g-C$_3$N$_4$. 
Figure S2: Typical TEM images of (a) pure g-C$_3$N$_4$, and (b) P10-600. The inset images are the corresponding selected area electron diffraction (SAED) patterns. (c) is the EDS spectra of P10-600.

Figure S3. FTIR spectra of pure and P-doped g-C$_3$N$_4$. 

In Figure S4, we can see clearly that the sample P10-600 after catalysis still remains the original functional groups. This phenomenon could identify the RhB absorbed by the catalysis was finally photodegraded.

Table S1. BET specific surface areas and elemental compositions of pure and CP-modified g-C$_3$N$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}^a$ (m$^2$ g$^{-1}$)</th>
<th>C/wt$^b$%</th>
<th>N/wt$^b$%</th>
<th>H/wt$^b$%</th>
<th>C/N$_\text{EA}^c$</th>
<th>P/N$_\text{XPS}^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0-550</td>
<td>26.86</td>
<td>37.67</td>
<td>51.53</td>
<td>1.969</td>
<td>0.85</td>
<td>0</td>
</tr>
<tr>
<td>P10-550</td>
<td>32.80</td>
<td>34.72</td>
<td>49.25</td>
<td>2.152</td>
<td>0.82</td>
<td>0.041</td>
</tr>
<tr>
<td>P10-600</td>
<td>40.50</td>
<td>34.60</td>
<td>51.28</td>
<td>1.652</td>
<td>0.79</td>
<td>0.024</td>
</tr>
</tbody>
</table>

$^a$ BET specific surface area, $^b$ weight percent based on elemental analysis, $^c$ Molar ratio based on elemental analysis, $^d$ Molar ratio based on XPS.
Figure S4. Degradation efficiency and TOC removal of RhB on P10-600.

Figure S5. Survey XPS spectra of pure and P-doped g-C$_3$N$_4$. 

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**Figure S4.** Degradation efficiency and TOC removal of RhB on P10-600.

**Figure S5.** Survey XPS spectra of pure and P-doped g-C$_3$N$_4$. 

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Figure S6. (a) UV-vis absorption spectra, (b) UV-vis DRS corresponding Tauc plots, (c) Valence-band XPS spectra, (d) PL spectra of pure and CP-modified g-C₃N₄.

The UV-Vis absorption spectra of the obtained samples are shown in Figure S6a. Compared to the pure g-C₃N₄, the absorbance band edge of P10-550 demonstrates a little bit blue shift. It is worth noting that the condensation temperature shows stronger influence on their electronic structure, leading to further blue shift of P10-600. The corresponding Tauc plots (Figure S6b) related to the diffuse reflectance spectra are applied to calculate band gaps of the samples. The band gaps of P0-550, P10-550, and P10-600 are 2.69 eV, 2.71 eV, and 2.84 eV, respectively. The incorporation of P atoms and the condensation temperature has effects on their band structure, and consequently their catalytic performance. The wider band gap of the sample obtained at higher temperature leads to decreased utilization efficiency of visible light, and lowered hydrogen evolution rate. The valence band XPS are shown in Figure S6c. The valence band maximum (VBM) edges of P0-550, P10-550, and P10-600 are measured to be about 2.07 eV, 2.12 eV, and 2.03 eV, respectively. The VBM edge of the materials has changed slightly. It is widely known that the VBM edge is dominant in the oxidation ability of the semiconductor. With similar VBM edges, other factors may largely influence the oxidation performance for RhB degradation. The photoluminescence (PL) spectra were conducted to inspect the separation efficiency of charge carriers. In Figure S6d, it is clear that P-doped in g-C₃N₄ can effectively inhibit the recombination of photogenerated charge carriers. The much weakened intensity of the emission peak of P10-550 suggests that the recombination of photogenerated electrons and holes has been maximally suppressed.
We have measured the PL spectra of all the samples prepared at 550 °C, as shown in the figure S7. With more P atoms doped, the electron delocalization will be strengthened and the mobility/separation efficiency of charge carriers can be improved. However, excessive doping of P atoms may produce more defects to trap carriers. P10-550 showed the best photocatalytic activity and this may be attributed to its highest charge mobility and separation efficiency.

**AQE measurement:**

The apparent quantum efficiency (AQE) was measured under the same photocatalytic reaction condition. Monochromatic light through a band-pass filter (central wavelength 435nm, half bandwidth 15nm) emitted from a 300 W Xe lamp was used as light source to trigger the photocatalytic reaction. The intensity of irradiation was measured by a light meter (Thorlabs TES-1339). The reaction solutions were irradiated for 1 h for AQE test on the H₂ production. The AQE was calculated according to the following equation:

\[ \text{AQE} = (2 \times \frac{H}{I}) \times 100\% \]

Where H and I represent the numbers of evolved H₂ molecules and incident photons, respectively. It is assumed that all incident photons are absorbed by the photocatalyst. The AQE of sample P10-550 at 435 nm is ca. 0.7%.