Isotopic labeling experiments are carried out as follow. Labeled $^{15}$N$_2$ gas was purchased from Sigma-Aldrich Chemical Company. In the experimental process, reaction mixture was firstly purged with Ar for 30 min to eliminate air and some possible adsorbed ammonia. Then, $^{15}$N$_2$ was passed through the reaction mixture for 30 min. After that, the reactor was sealed and irradiated under visible light. Other experiment conditions were the same as those for $^{14}$N$_2$ photofixation. Indophenol method was used to examine the obtained $^{15}$NH$_4^+$, owing to the low mass of $^{15}$NH$_4^+$ for LC-MS studies. The sample for LC-MS analysis was prepared as follows. 0.5 ml of the reaction reacted with 0.1 ml of 1% phenolic solution in 95% ethanol. Then, 0.375 ml of 1% NaClO solution and 0.5 mL of 0.5% sodium nitroprusside solution were added into above solution. MS studies were carried on an Ultimate 3000-TSQ (LCMS-ESI).

The simulations were performed using the program package Dmol3. The substrate is modelled by one layer of g-C$_3$N$_4$ separated by a vacuum layer of 12Å. All the atoms in the layer and the N$_2$ molecule are allowed to relax. The Brillouin zones of the supercells were sampled by the Gamma points. Based on the structures of g-C$_3$N$_4$, the g-C$_3$N$_4$ surface with nitrogen atom vacancy was modelled to study the N$_2$ adsorption properties.
Figure S1. The N₂ photofixation ability of CN₅₂₀ in the absence of irradiation, N₂ or photocatalyst.
Figure S2. Nitrogen photofixation ability of IM-CN(30) using AgNO$_3$ as the electron scavenger (a) or in aprotic solvents DMF and DMSO (b).
Figure S3. N$_2$ adsorption-desorption isotherms of as-prepared CN$_{520}$, M-CN(20) and IM-CN(30).
Figure S4. The RhB degradation performance over as-prepared CN$_{520}$, M-CN(20) and IM-CN(30) under visible light.
Table S1. Photocatalytic H$_2$ production ability of as-prepared catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CN$_{520}$</th>
<th>M-CN(20)</th>
<th>IM-CN(30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ production (μmol·h$^{-1}$)</td>
<td>0.40</td>
<td>0.52</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The photocatalytic H$_2$ production were performed in an outer-irradiation and air-tight Pyrex glass reactor, connected to a water-cooling system. In a typical run, 0.2 g photocatalyst was suspended in 100 ml deionized water with methanol (10 vol.%, used as the hole scavenger) under stirring. Prior to the photocatalytic reaction, the suspension was purged with Ar gas for 20 min to get rid of O$_2$. A 250 W high-pressure sodium lamp with UV cutoff filter (λ > 420 nm) were used as light source. A continuous magnetic stirrer was applied at the bottom of the reactor in order to keep the photocatalyst particles in suspension status during the whole experiment. The reaction products were analyzed on-line by thermal conductivity detectors on a micro-gas chromatography (Model Agilent P200 Series) equipped with a thermal conductivity detector (TCD) and a stainless steel column (2 m) packed with molecular sieves (5A) at 323 K. Ar was used as the carrier gas at a flow rate of 20 cm$^3$·min$^{-1}$. All runs were conducted at ambient pressure and 30 ºC.