Electronic Supplementary Material (ESI) for RSC Advances.
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Supporting Information

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_3N_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_3N_4, the g-C_3N_4 surface with nitrogen atom vacancy was modelled to study the N_2 adsorption properties.

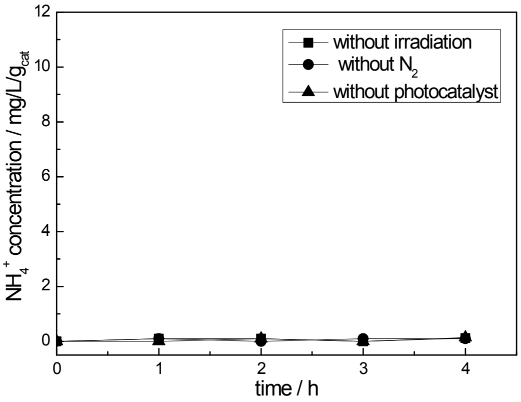

Figure S1. The N_2 photofixation ability of CN_{520} in the absence of irradiation, N_2 or photocatalyst.

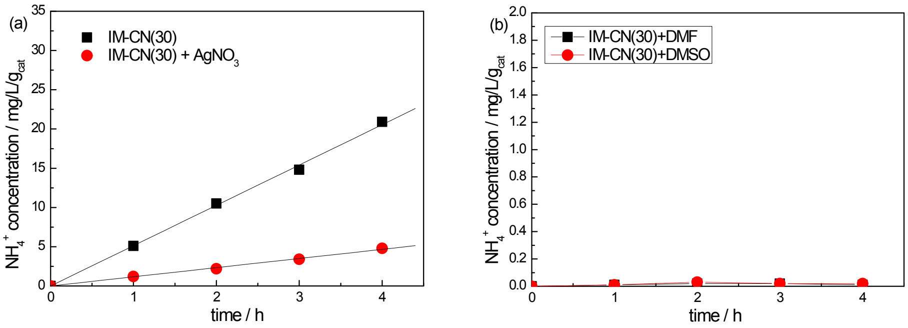

Figure S2. Nitrogen photofixation ability of IM-CN(30) using $AgNO_3$ as the electron scavenger (a) or in aprotic solvents DMF and DMSO (b).

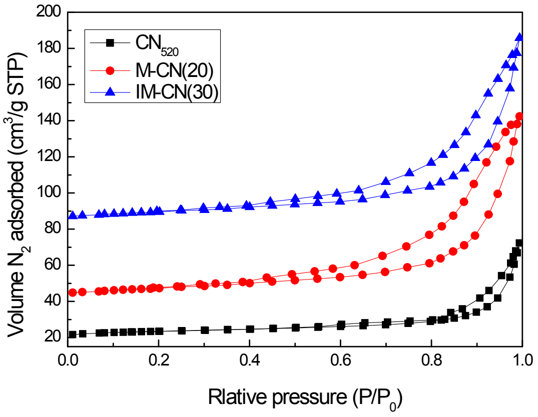

Figure S3. N_2 adsorption-desorption isotherms of as-prepared CN$_{520}$, M-CN(20) and IM-CN(30).

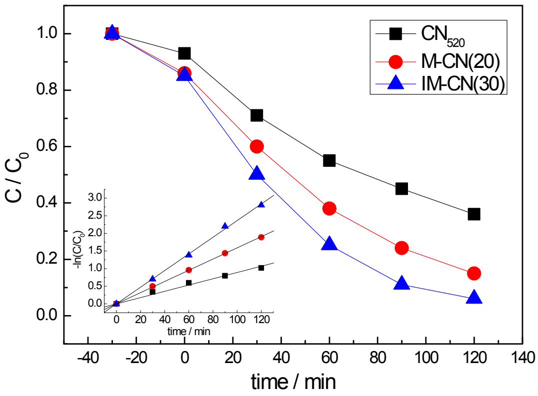

Figure S4. The RhB degradation performance over as-prepared CN_{520}, M-CN(20) and IM-CN(30) under visible light.

Table S1. Photocatalytic H_2 production ability of as-prepared catalysts

Catalyst	CN_{520}	M-CN(20)	IM-CN(30)
H_2 production ($\mu mol \cdot h^{-1}$)	0.40	0.52	0.55

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 ($\lambda > 420$ 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 $cm^3 \cdot min^{-1}$. All runs were conducted at ambient pressure and 30 °C.