Materials

Unless otherwise stated, all solvents and chemicals used were of commercially available analytical grade and used without further treatment.

General methods

N_2 sorption analysis was performed at 77 K using a QUADROSORB SI, equipped with automated surface area and pore size analyzer. Before analysis, samples were degassed at 150 ^{o}C for 20 h using a masterprep degassing system. The material morphology was visualized using a Gemini scanning electron microscope (SEM). Elemental analysis was obtained on a Vario El elemental analyser. Optical absorption at the range of 300-800 nm was recorded with the T70 UV/VIS spectrometer (PG Instruments LTD). A mercury lamp (100 W) together with a 420 nm cut-off filter was used as a visible light source for the irradiation of reaction system. All GC experiments were carried out and recorded using a SHIMADZU GC-2010 with FID detector. The structure of products and by-products was identified using HP6890 GC-MS spectrometer by comparing retention times and fragmentation patterns with authentic samples.

Synthesis of mpg-C_3N_4 material

5 g cyanamide was dissolved in a 40% dispersion of 12 nm SiO_2 particles (Ludox HS40, Aldrich) in water (12.5 g) with stirring at 60 ^{o}C overnight. The resulting transparent mixtures were then heated to 550 ^{o}C in 4 h and then kept at this temperature for another 4 h within an air oven. The resulting yellow powder was treated with 4 M NH_4HF_2 for 2 days to remove the silica template. The powders were then filtered and thoroughly washed with distilled water. The final product was obtained by drying overnight at 100 ^{o}C under vacuum.

Post-carbonization of the mpg-C_3N_4 material

In a typical synthesis, the original dried mpg-C_3N_4 (300 mg), α-amino acid N-methylglycine (3 mmol) and the corresponding aldehyde (2 mmol) were added into 150 mL toluene, and the reaction mixture was performed at 120 ^{o}C for 21 h. The resulting products were then cooled to room temperature. After filtration and thoroughly washing, functionalized products from yellow to dark brown were obtained and dried at 80 ^{o}C for 24 h.

Typical procedure for the catalytic oxidation of 3, 5, 5-trimethylcyclohex-3-en-1-one (β-IP) by carbon nitrides

In a typical oxidation, 0.5 mmol β-IP, 75 μL n-decane (internal standard), 50 mg carbon nitride catalyst, additives as described in the paper and 3 mL pyridine were added into a 5 mL glass-reactor, which was fitted with a magnetic stirrer. The glass-reactor was then put into a water bath (25 or 60 ^{o}C) with magnetic stirring. A mercury lamp (100 W) together with a 420 nm cut-off filter was placed at a distance of ~10 cm from the reactor as a visible light source for the irradiation of this reaction system. After completion of the reaction, carbon nitride catalysts were filtered and the reaction mixture was then analyzed by GC and GC-MS.

Figures

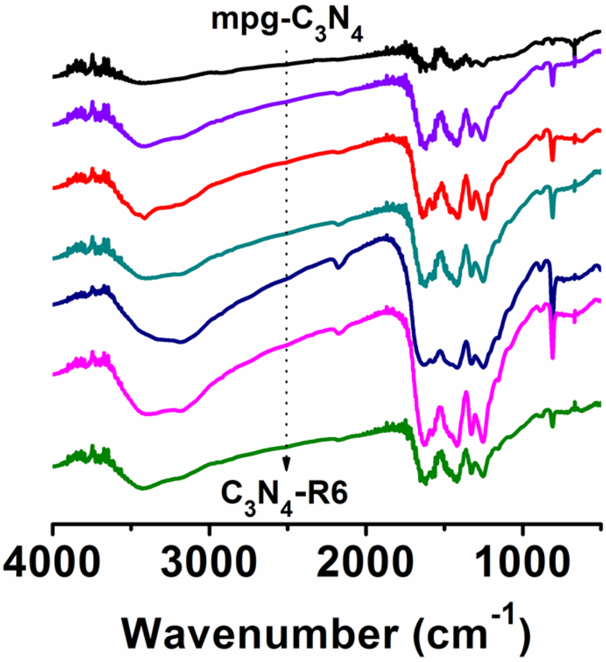

Figure S1. FTIR spectra of carbon nitrides.

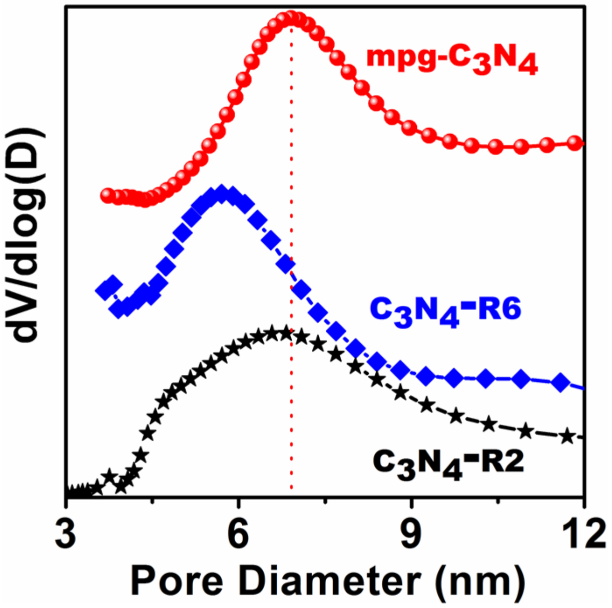

Figure S2. Pore size distributions of carbon nitrides.

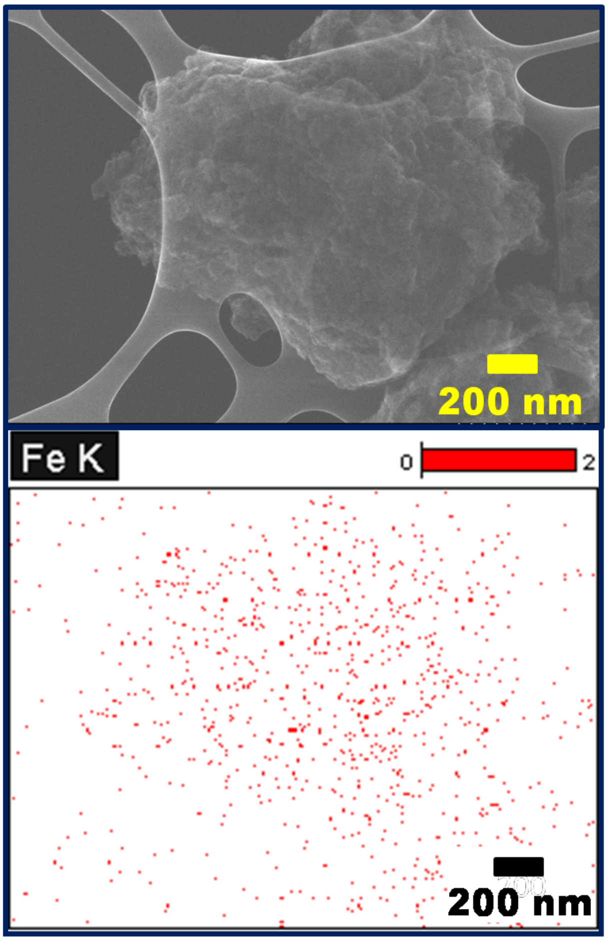

Figure S3. SEM image of C_3N_4-R6 and corresponding Fe elemental mapping image.

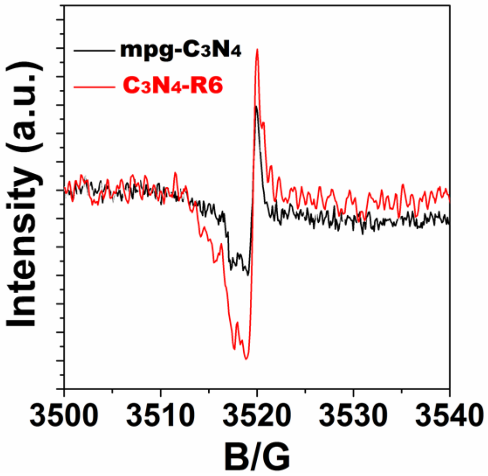

Figure S4. Room temperature electron paramagnetic resonance spectra of mpg-C_3N_4 and C_3N_4-R6.

Table S1. Characterization of those prepared carbon nitrides.

Sample	Weight Loss (%)[a]	Grafting density (mmol/g)	C/N molar ratio	S_{BET} (m^2/g)	APS (nm)[b]
Mpg-C_3N_4	-	-	0.74	148	9.4
C_3N_4-R1	6.3	0.47	0.81	26	9.7
C_3N_4-R2	4.6	0.26	0.77	95	7.6
C_3N_4-R3	2.9	0.22	0.76	106	9.0
C_3N_4-R4	5.3	0.19	0.77	91	8.9
C_3N_4-R5	7.4	0.16	0.81	21	10.8
C_3N_4-R6	6.8	0.26	0.80	52	9.1
Meso-Carbon [c]	-	-	-	712	7.0
Meso-Carbon-R2[c]	5.9	0.29	-	392	6.9
Meso-Carbon-R3[c]	3.7	0.22	-	446	6.9

[a] Based on the weight loss in N_2 between 100 °C to 550 °C with mpg-C_3N_4 as blank sample. [b] APS: average pore size. [c] Data from reference (*Chem. Mater.*, 2008, 20, 4800-4802).