Supporting Information

"Caffeine Doping" of Carbon/Nitrogen-Based Organic Catalysts: Caffeine as a Supramolecular Edge Modifier for the Synthesis of Photoactive Carbon Nitride Tubes

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Supporting Information

Synthesis of the Caffeine-doped CM-C$_3$N$_4$ and CMp-C$_3$N$_4$:

All chemicals were purchased from Sigma-Aldrich and used without further purification. The FTO-electrodes were washed with detergent to remove the pollutants and then sonicated in acetone for 30 min. Afterwards they were rinsed with ethanol and dried using nitrogen flow.

The Caffeine-doped CM complexes were prepared by using a mixture of 10 mmol Cyanuric acid, 10 mmol Melamine and x mol-% Caffeine, with molar ratios of Caffeine of x = 2.5 mol-%, 5 mol-%, 7.5 mol-% and 10 mol-% in 50 ml of water. Then the complexes were mixed for 4 hours using an automatic shaker. After that, the white CM complexes were precipitated by filtration of the solutions. The white powders were washed several times with water. The resulting powders were dried at 60°C in a vacuum oven and calcined at 500°C under nitrogen condition with a heating rate of 2.5 K min^{-1}. The caffeine-doped CMp complexes and C$_3$N$_4$-materials were prepared by the same procedure, but with the use of 2,4-diamino-6-phenyl-1,3,5-triazine instead of Melamine.

For the production of the CMp-C$_3$N$_4$-coated FTO-electrodes, a (2 cm * 1 cm)-piece of FTO-glass was placed at the bottom of a crucible, covered with the powdered Caffeine-doped CMp complex and then calcined as described above. After synthesis, the electrodes were sonicated for 10 min. in water to remove excess C$_3$N$_4$ and then dried in nitrogen flow.

Characterization:

X-ray diffraction-patterns were measured on a Bruker D8 Advance instrument using Cu-K$_\alpha$-radiation. Nitrogen sorption measurements were accomplished with N_2 at 77 K after degassing the samples at 150°C under vacuum for 20 hours using a Quantachrome Quadrasorb SI porosimeter. The apparent surface area was calculated by applying the Brunauer–Emmett–Teller (BET) model to the isotherm data points of the adsorption branch. Elemental analysis was accomplished as combustion analysis using a Vario Micro device. SEM images were obtained on a LEO 1550-Gemini. FT-IR spectra for the characterization of the compounds were recorded on a Varian1000 FT-IR spectrometer. Optical absorbance spectra were measured using a Varian spectrophotometer equipped with an integrating sphere. The emission spectra were recorded on a LS-50B Perkin Elmer instrument.

Time-resolved fluorescence measurements were performed by using a time-correlated single photon counting setup (TCSPC) with a Becker & Hickl SPC-130 acquisition system and a multichannel PML-16-C-1 PMT detector. Excitation at 405 nm was provided by a PicoQuant PDL-800B CW laser with a repetition rate of 2 MHz. The emission was monitored at 500 nm.

LED module emitting at white light ($\lambda > 410$ nm) with 50 W light output (OSA Opto Lights) served as a light source for the photo-degradation of RhB. The photo-degradation of all the materials was tested using 10 mg of carbon nitride in 10 ml of RhB solution (20 mg/l) in distilled water under illumination. The changes in RhB concentration were monitored by using UV-vis absorption spectra to measure the remained RhB. The degradation efficiency was determined by dividing c/c_0, where c is the remained RhB concentration and c_0 is the starting RhB concentration (after subtraction of the concentration of RhB which was adsorbed to the C_3N_4s).
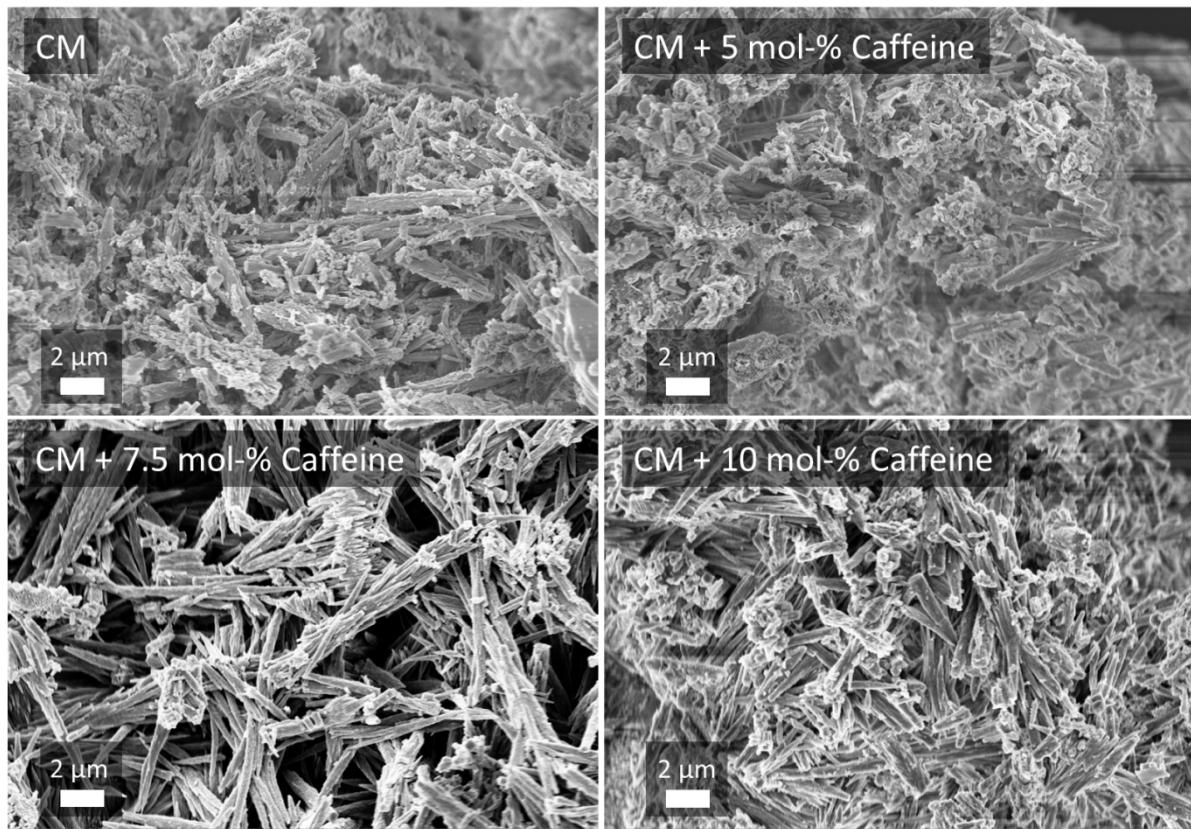
Figure S1. SEM images of the Caffeine–doped CM complexes before calcination.
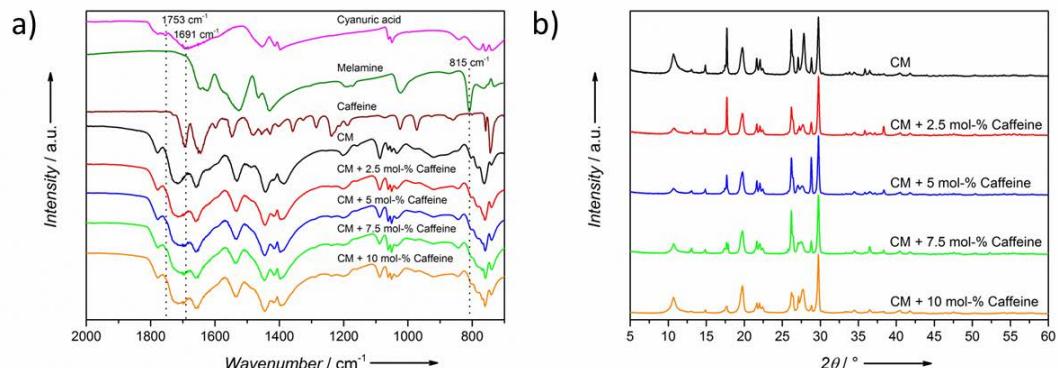
Figure S2. (a) FT-IR spectra and (b) X-ray diffraction patterns of the Caffeine–doped CM complexes, cyanuric acid, melamine and caffeine, before calcination.
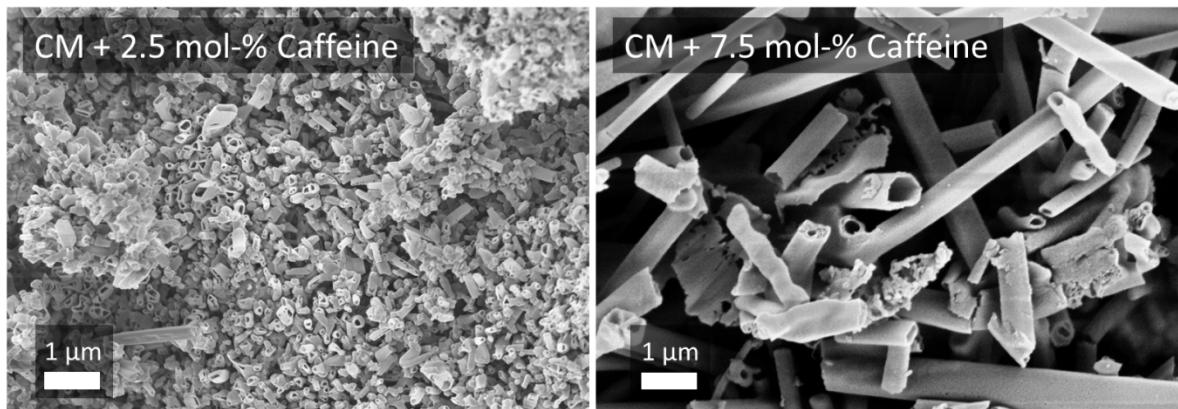
Figure S3. SEM images of the CM carbon nitride-materials obtained at 500 °C.

Amount of caffeine added to the precursors	N [%]	C [%]	H [%]	C/N ratio
0 mol-% (without caffeine)	58.8	34.1	2.2	0.6
5 mol-%	58.8	34.0	2.2	0.6
7.5 mol-%	58.9	34.2	2.2	0.6
10 mol-%	58.9	34.1	2.2	0.6

Table S1. Elemental analysis data for the CM carbon nitride-materials.
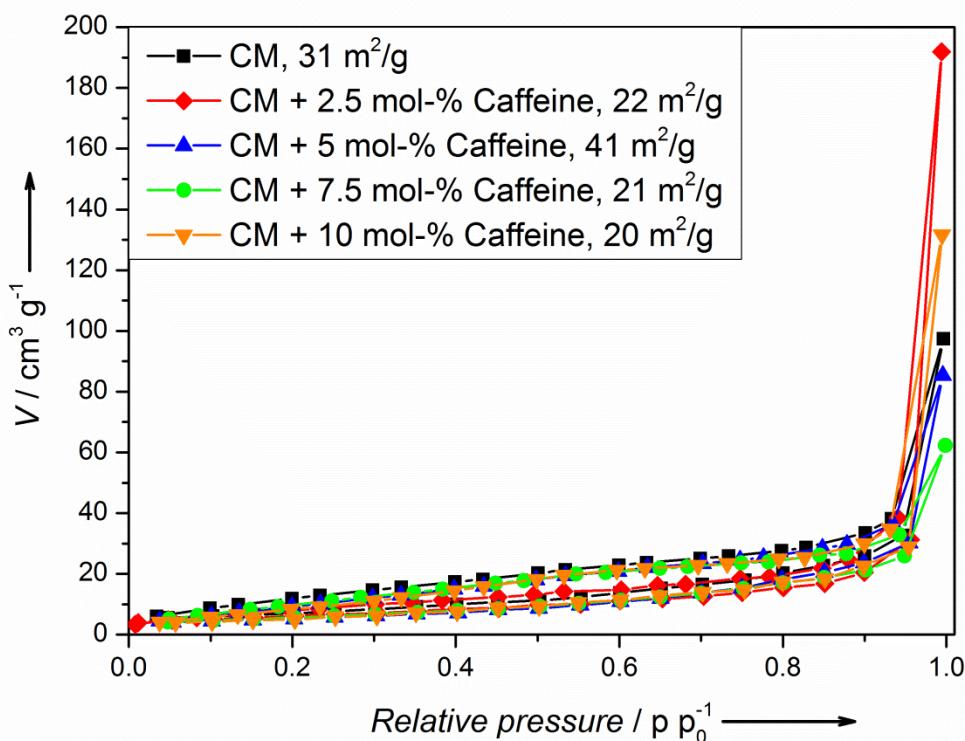
Figure S4. Nitrogen-sorption isotherms and specific BET-surfaces of the CM carbon nitride-materials.
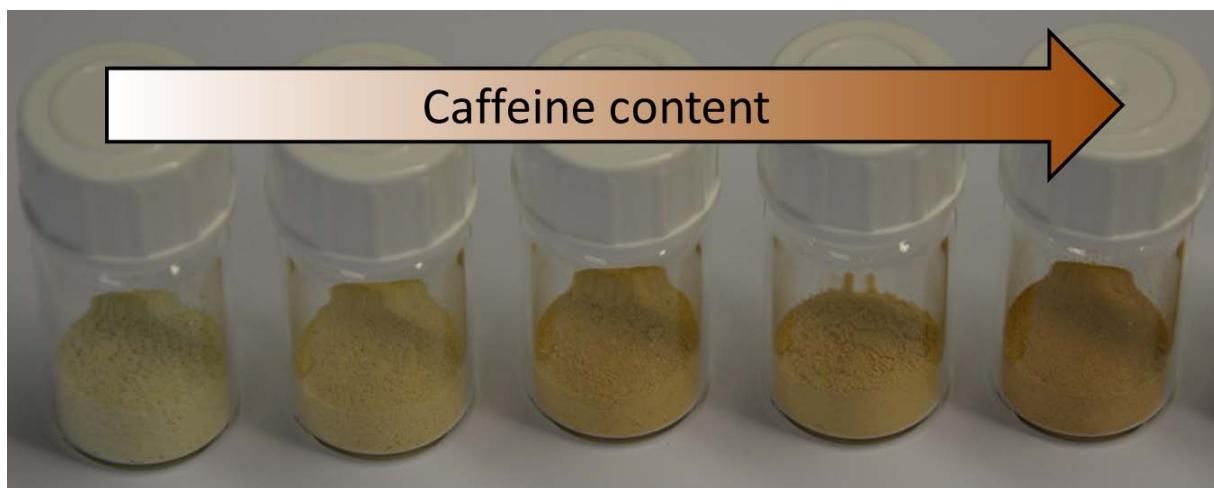
Figure S5. Images of the CM carbon nitride-materials with 0 mol-%, 2.5 mol-%, 5 mol-%, 7.5 mol-% and 10 mol-% caffeine added to the precursor mixtures (from left to right).
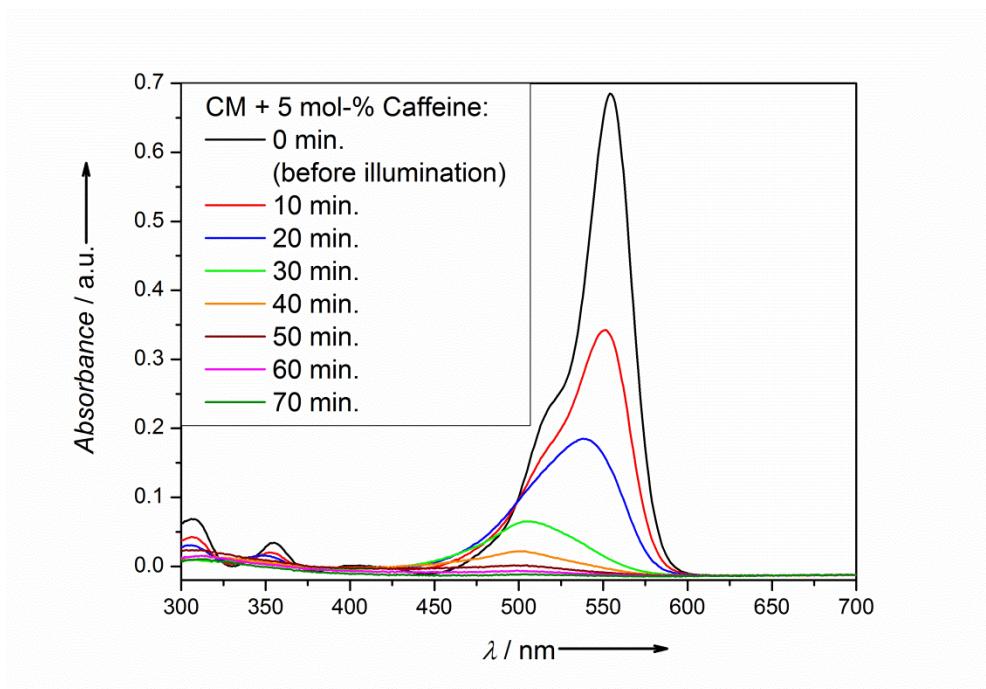
Figure S6. Absorption spectra of RhB as a function of illumination time for the 5 mol-% caffeine based CM-C_3N_4.
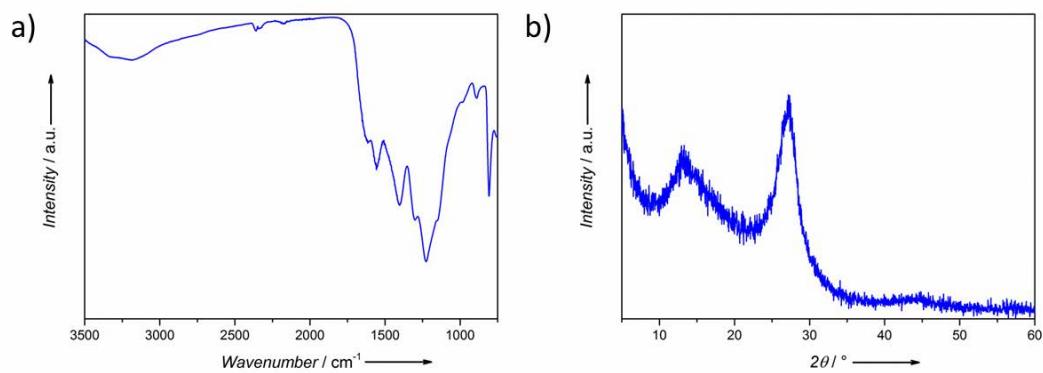
Figure S7. (a) FT-IR spectra and (b) X-ray diffraction patterns for the 5 mol-% caffeine based CM-C_3N_4 after three RhB-degradation cycles.
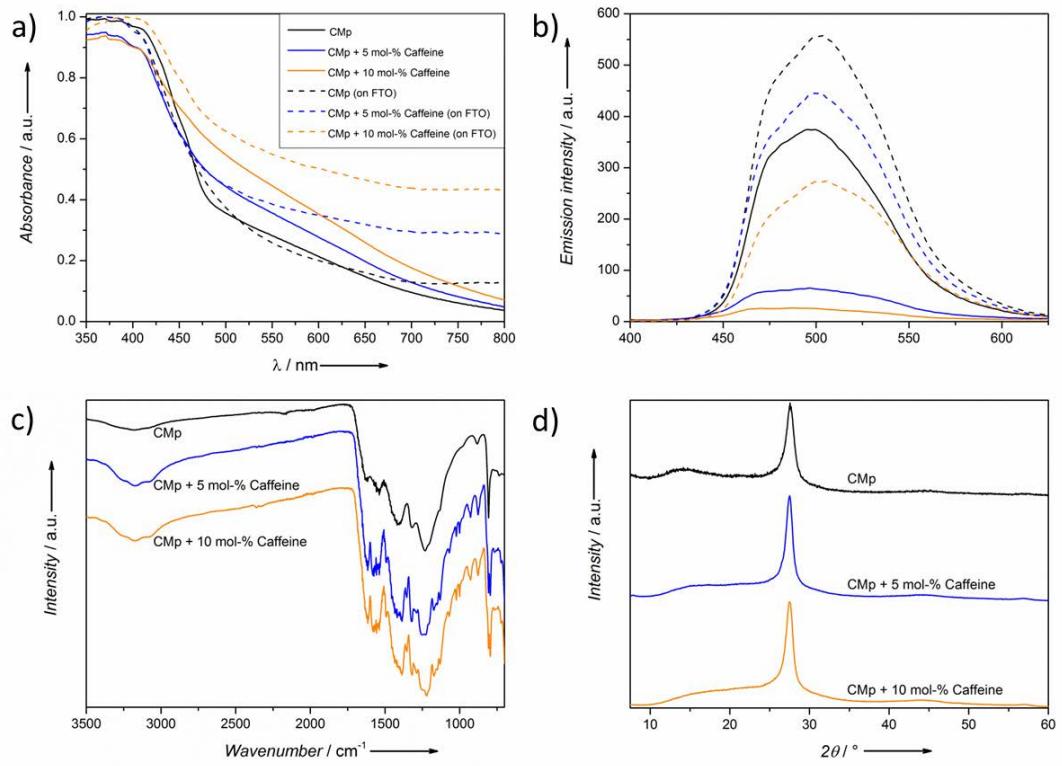
Figure S8. (a) UV-vis spectra , (b) emission spectra (λ_{exc} = 330 nm, same key as in (a)), (c) FT-IR spectra and (d) X-ray diffraction patterns of the CMp-C_3N_4-materials.