

SUPPORTING INFORMATION FOR

Improving carbon nitride photocatalysis by supramolecular preorganization of monomers

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Synthesis of CM-C₃N₄: The CM complexes were prepared by using 1:1 molar ratio of Cynauric acid and Melamine (1g total weight) in 40ml of ethanol, water and chloroform. Then the complexes were mixed for 4 hours using automatic shaker. After that white CM complexes were precipitated by filtration of the solutions. The white powders were washed several times with the original solvent used. The resulting powders were dried at 60°C in vacuum oven and calcined at 550°C under nitrogen condition with heating rate of 2.3°C per minute. The one which were precipitated from ethanol calcined for 2, 4, 8 and 12 hours. The powders which were precipitated from water and chloroform and the C₃N₄ prepared from DCDA calcined for 4 hours.

Characterization: X-ray diffraction-patterns were measured on a Bruker D8 Advance instrument using Cu- K α -radiation. Nitrogen sorption measurements were accomplished with N₂ 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 LS-50B, Perkin Elmer instrument.

Time-resolved fluorescence measurements were performed by using a single photon counting setup (TCSPC) with a Becker&Hickl PML-spectrometer (modified Oriel MS-125) with a laser repetition rate of 2 MHz. The detector comprises a Becker&Hickl PML-16-C-1 (modified Hamamatsu) multi-alkaline photomultiplier. The excitation wavelength was 405 nm. Raw decay data presented as logarithm of photon counts versus time were analyzed with data analysis software of PicoQuant GmbH (Germany). The decay times were extracted by means of a reconvolution fit

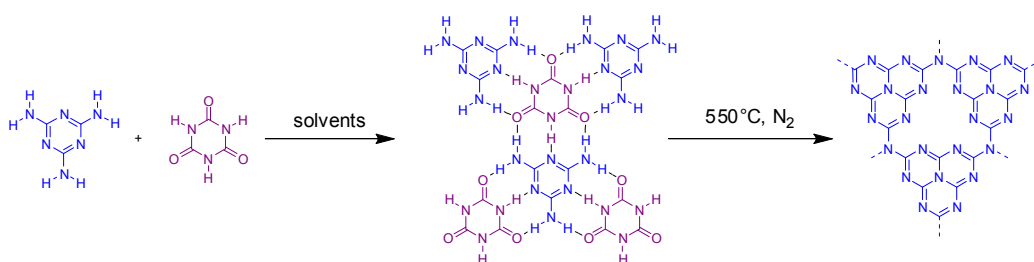
based on a double or triple exponential model. Considering that $I_{PL}(t) = \sum_{i=1}^{i=n} a_i e^{-t/\tau_i}$,

where τ_i is the lifetime and a_i is the amplitude of the i^{th} component, the intensity-averaged fluorescence lifetime $\langle \tau \rangle$ was calculated as

$$\langle \tau \rangle = \frac{\sum_{i=1}^{i=n} a_i \tau_i^2}{\sum_{i=1}^{i=n} a_i \tau_i} \quad (1)$$

PL quantum efficiencies (ϕ) were determined with a Hamamatsu C9920 set-up, including an integrating sphere combined with a photonic multi-channel analyzer. The nonradiative decay rate (k_{nr}) was determined according to $k_{nr} = 1 - \phi / \langle \tau \rangle$.

LED module emitting at 420 nm with 12 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 5mg of carbon nitride in 5ml of RhB solution (10 $\mu\text{g/ml}$) 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 the concentration of RhB which was adsorbed to the C_3N_4).



Scheme S1. Hydrogen bonds supramolecular structure of is the cyanuric acid-melamine (refers here as CM) complex. The formation of C_3N_4 is achieved after calcination in 550°C under nitrogen.

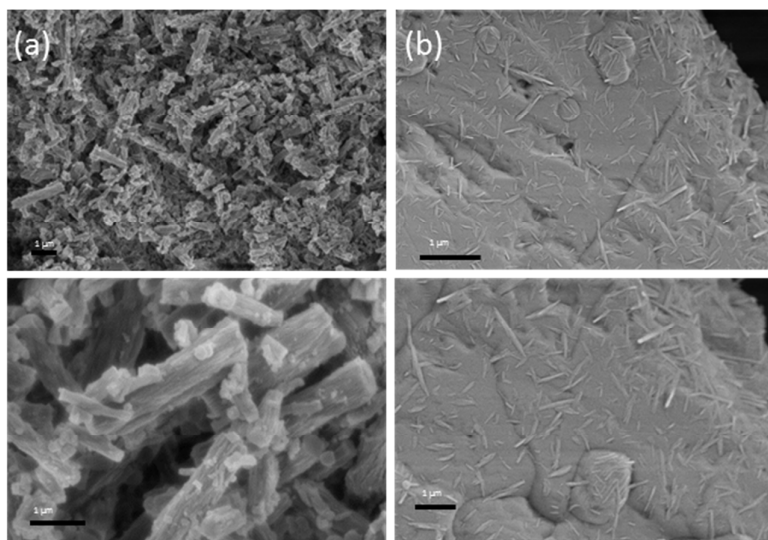


Figure S1. SEM images of the CM complex prepared in water (a) and chloroform (b)

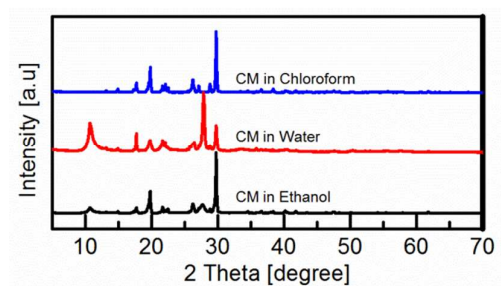


Figure S2. X-ray diffraction patterns of the CM complex prepared in water, ethanol and chloroform.

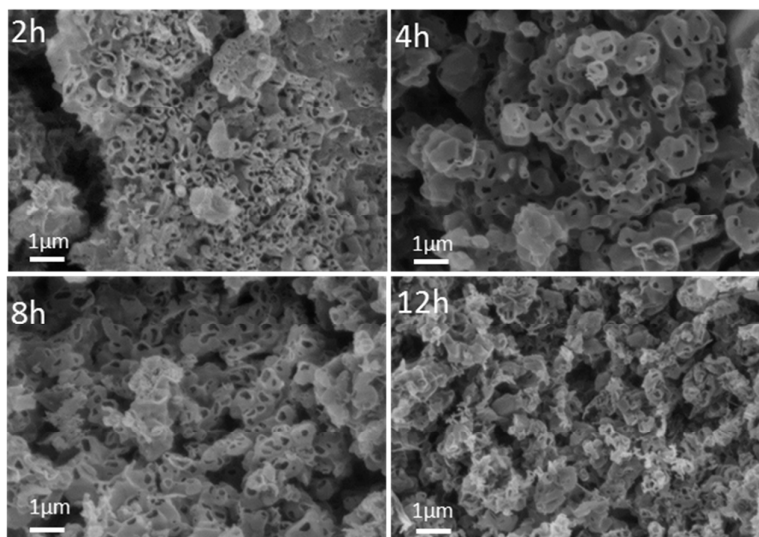


Figure S3. SEM images of CM that was prepared in ethanol obtained after different condensation times.

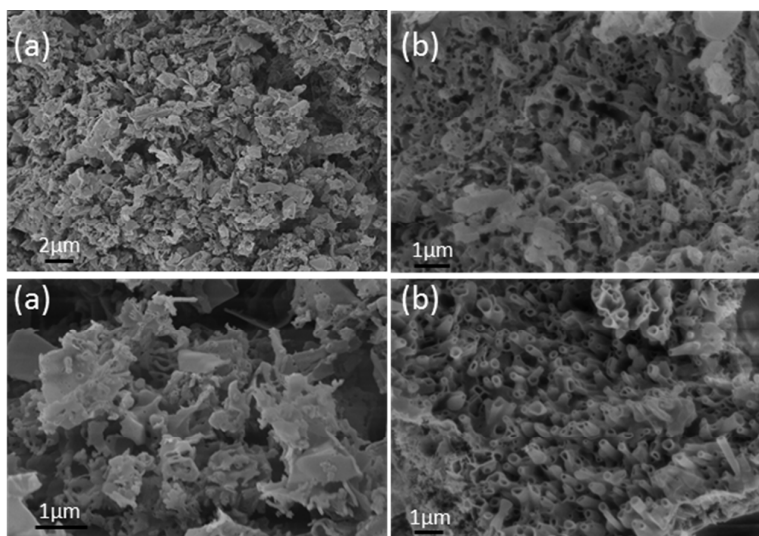


Figure S4. SEM images of CM-C₃N₄ that was prepared in water (a) and chloroform (b) obtained after condensation in 550°C.



Figure S5. Pictures of the CM aggregate (~1cm length) which was prepared in water before and after condensation in 550°C.

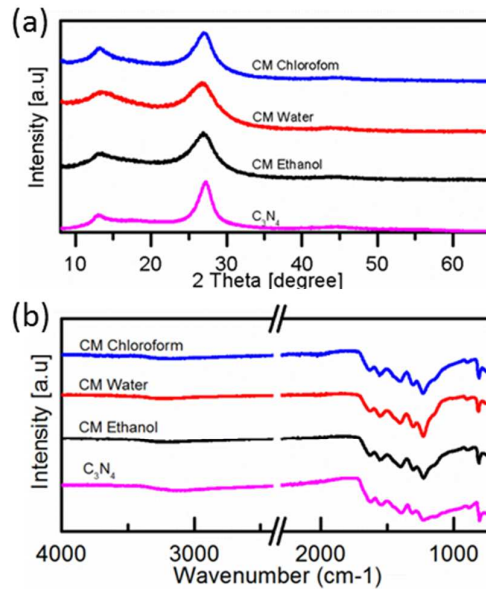


Figure S6. FT-IR spectra (a) and X-ray diffraction pattern (b) of CM which condensed from different solvents, indicating the formation of C₃N₄.

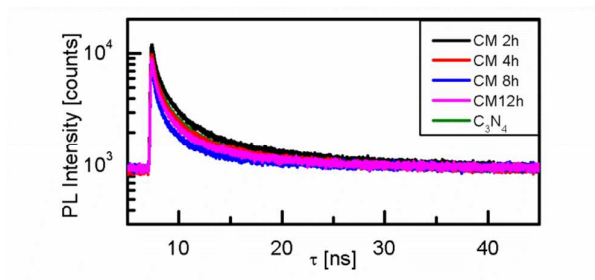


Figure S7. Fluorescence intensity decay curves of CM-C₃N₄ which condensed for different hours. The samples were excited at 405 nm and the emission at 475 nm was collected.

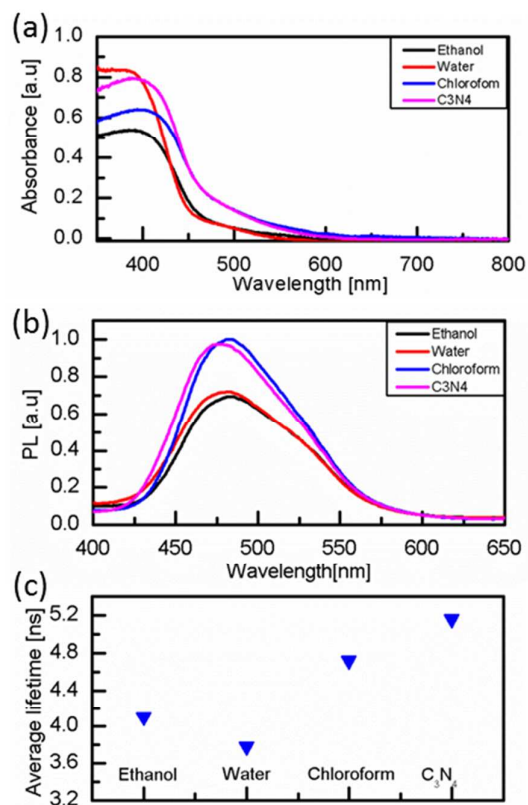


Figure S8. Diffuse reflectance absorption spectra (a) emission spectra (b) and the intensity-averaged fluorescence lifetimes (c) of CM-C3N4 which condensed from different solvents and DCDA-C3N4.

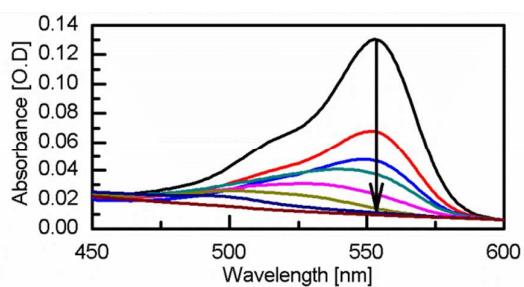


Figure S9. UV-vis spectra of RhB after different illumination time in the presence of CM-C3N4 which was condensed for 8 hours. The black arrow indicates the decrease of RhB absorption at 554 nm with time.

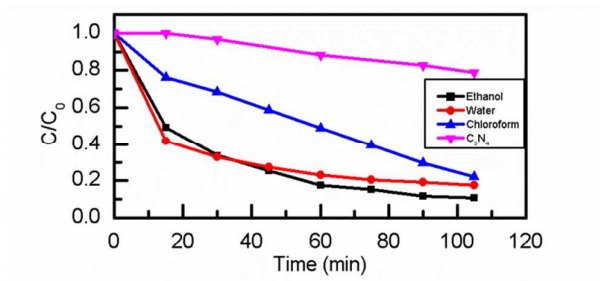


Figure S10. Concentration changes of RhB as a function of illumination time for all the CM-C₃N₄s which condensed from different solvents compared to the bulk C₃N₄.

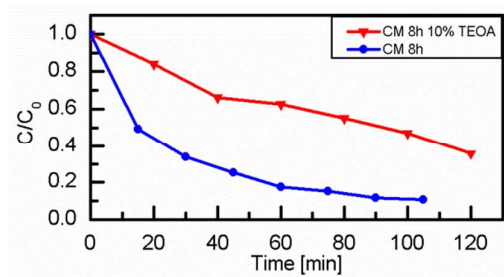


Figure S11. Concentration changes of RhB as a function of illumination time for the CM-C₃N₄ which was condensed for 8 hours with and without TEOA as a hole scavenger.