

Supporting information for:

**Thermite-Driven Melamine Condensation to $C_xN_yH_z$ Graphitic Ternary Polymers:
Towards an Instant, Large-Scale Synthesis of $g-C_3N_4$**

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Materials and Characterization techniques

Iron oxide ($Fe_2O_3 \cdot FeO$), obtained directly from a steel producer (ArcelorMittal, Warsaw), aluminum powder (Al, Benda-Lutz Skawina), aluminum oxide (Al_2O_3 , POCH Gliwice), and 2,4,6-triamino-*s*-triazine (melamine, $C_3H_6N_6$, Fluka) were used as received. An elemental analysis (EA) was performed using a Vario ELIII analyzer. A thermogravimetric analysis (TGA) was performed using a Labsys TG/DTA (Setaram) thermal analyzer in a flowing Ar atmosphere (99,999%; AirProducts) from room temperature up to 1000 °C. The XRD patterns of the powders were collected within a 2θ range from 10 to 60° on a D500 Diffractometer (Siemens) in conjunction with $CuK\alpha$ radiation. To precisely monitor the temperature of the melamine condensation reaction, type K thermocouples with 0.50 mm diameter, (Omega) were used. A computer-assisted data logger (NI 9219, National Instruments) recorded the thermoelectric power continuously with a sampling frequency of 10 Hz. Fourier transform infrared spectroscopy (ATR/FT-IR) data was obtained using the Nicolet iS10 (Thermo Scientific) apparatus. The X-ray photoelectron spectra (XPS) were performed using a PHI 5000 VersaProbe (ULVAC-PHI) spectrometer with monochromatic Al $K\alpha$ radiation ($h\nu = 1486.6$ eV) as the X-ray excitation source. A scanning electron microscope (SEM) operating at an accelerating voltage of 2kV (LEO 1530 apparatus) was used to study the morphology of the condensation products. The Brunauer–Emmett–Teller specific surface area (S_{BET}) was calculated from the nitrogen adsorption isotherm in the p/p_0 range of 0.05 – 0.25. The N_2 physisorption measurements were performed at -196 °C using an ASAP 2020 Surface Area and a Porosimetry Analyzer (Micromeritics). The $C_xN_yH_z$ materials' skeletal density was

measured using an AccuPyc II 1340 helium pycnometer (Micromeritics, helium purity of 99,999%).

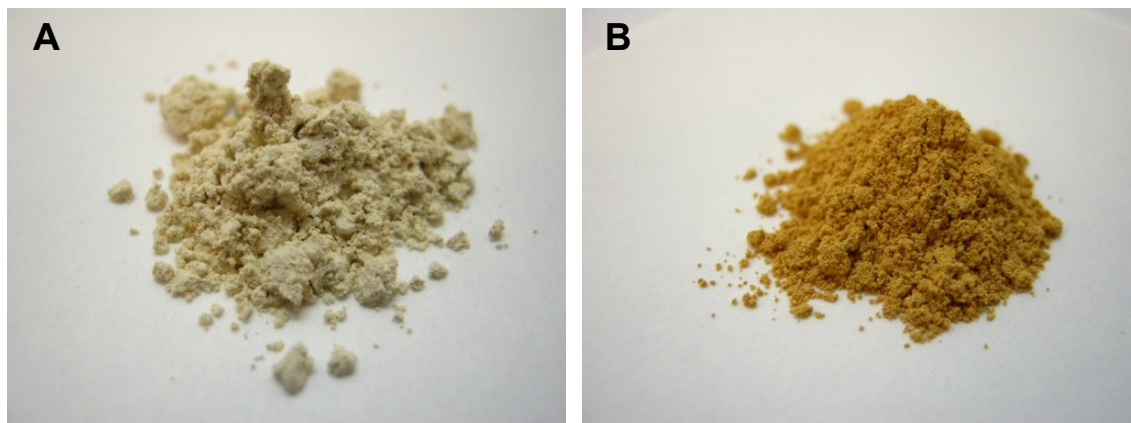


Fig. S1. Raw products of melamine condensation heated by $\text{Fe}_2\text{O}_3 \cdot \text{FeO}/\text{Al} + 15 \text{ wt } \%$ of Al_2O_3 , Sample I (A), and by $\text{Fe}_2\text{O}_3 \cdot \text{FeO}/\text{Al} + 5 \text{ wt } \%$ of Al_2O_3 , Sample II (B).

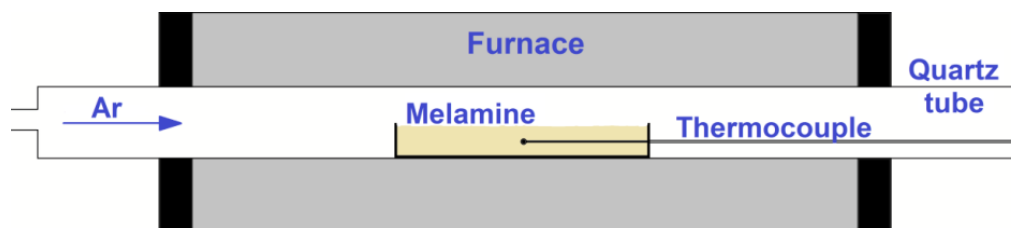


Fig. S2. Scheme of the experimental system using resistance tube furnace.

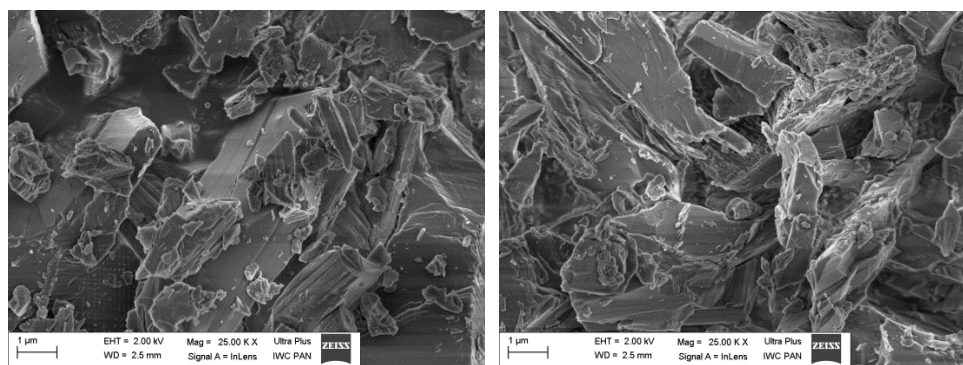


Fig. S3. SEM microphotographs of the condensation products; melamine heated by $\text{Fe}_2\text{O}_3 \cdot \text{FeO}/\text{Al} + 15 \text{ wt } \%$ of Al_2O_3 , Sample I.

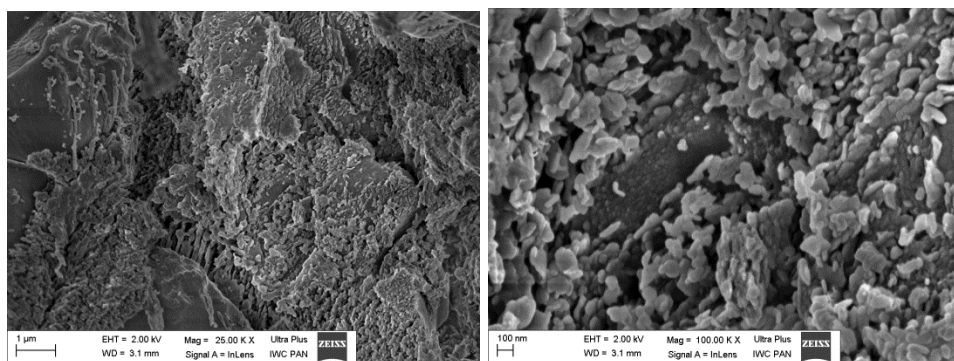


Fig. S4. SEM microphotographs of the condensation products; melamine heated by $\text{Fe}_2\text{O}_3 \cdot \text{FeO}/\text{Al} + 5 \text{ wt } \% \text{ of } \text{Al}_2\text{O}_3$, Sample II.

Table S1. Physical parameters of the $\text{C}_x\text{N}_y\text{H}_z$ graphitic ternary polymers.

Sample no.	S_{BET} (m^2/g)	Density (g/cm^3)
Melamine	-	1.57
Sample I	4.1	1.75
Sample II	13.3	1.90
Sample III	7.0	1.81
Sample IV	9.9	1.85

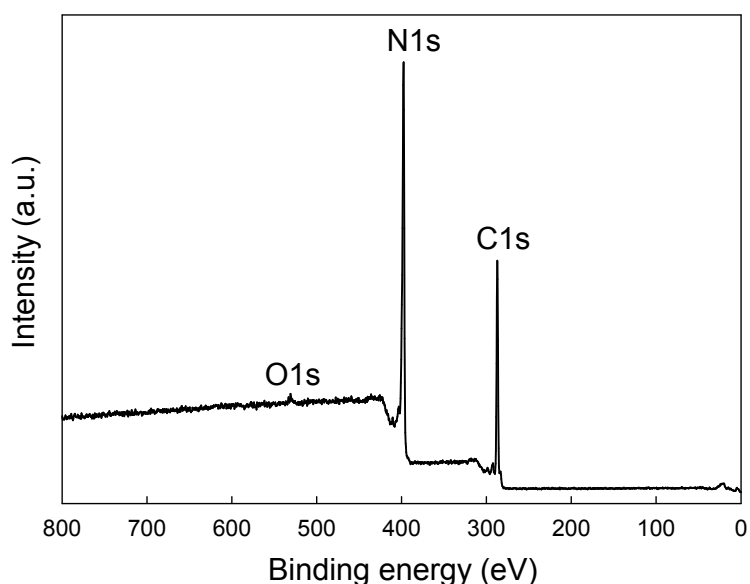


Fig. S5. X-ray photoelectron full survey spectrum of condensation product obtained by thermite-heated condensation ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}/\text{Al} + 5 \text{ wt } \% \text{ of } \text{Al}_2\text{O}_3$, Sample II).

Evaluation of the photocatalytic properties

The photograph of the reactor set-up used for evaluating $C_xN_yH_z$ photocatalyst activity towards degradation of rhodamine B (RhB) is presented in Fig. S6. A 150 W tungsten-halogen lamp (Osram) was placed in a cylindrical glass vessel with a glass jacket filled with flowing water to keep the system cool and at constant temperature. The lamp was immersed inside the beaker with the RhB/ $C_xN_yH_z$ mixture to assure maximum, uniform irradiation. The emission property (intensity as a function of wavelength) of the tungsten lamp with the cooling system was estimated using a USB2000+ (Ocean Optics) general-purpose UV-Vis-NIR spectrometer (Fig. S7). The RhB degradation efficiency was determined by dividing C/C_0 , where C is the RhB concentration after a particular time of illumination and C_0 is the starting concentration of RhB (after subtracting the fraction of RhB, that was adsorbed by the $C_xN_yH_z$ polymer surface by stirring the catalyst with RhB for 60 minutes in the dark). In each test 75 mg of $C_xN_yH_z$ ternary polymer was dispersed in RhB aqueous solution (150 mL, 10 mg/L). At 15 min intervals, 4 mL of the suspension was collected and centrifuged at 4000 rpm for 3 minutes to remove the catalyst. A Cary 3E UV-Visible spectrophotometer (Varian) was used to monitor the changes of RhB concentration. The RhB concentration was calculated using a calibration curve. The maximum absorption was recorded at 553 nm and used for evaluating the decreasing concentration (Fig. S8).

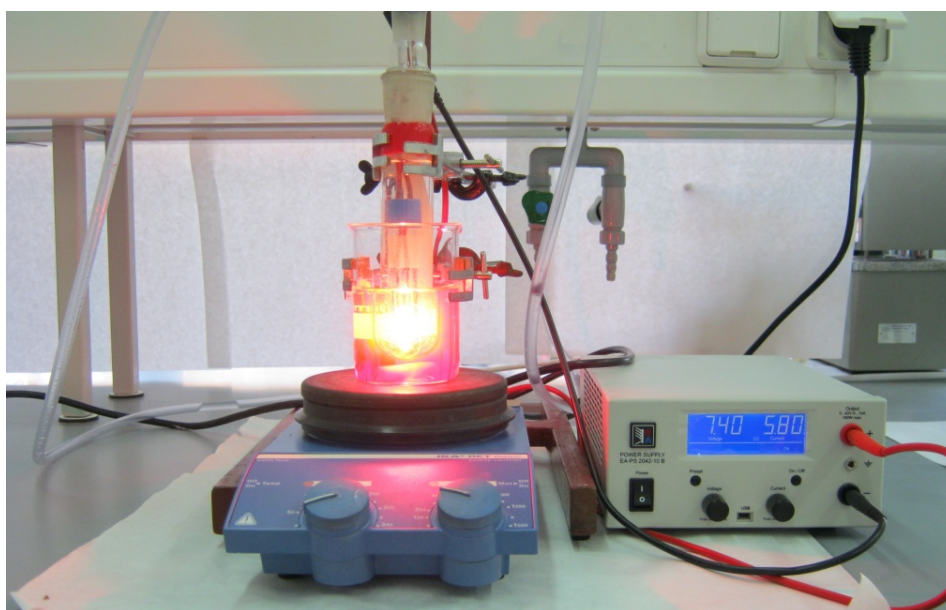


Fig. S6. Reactor set-up used for evaluating $C_xN_yH_z$ photocatalyst activity towards degradation of rhodamine B.

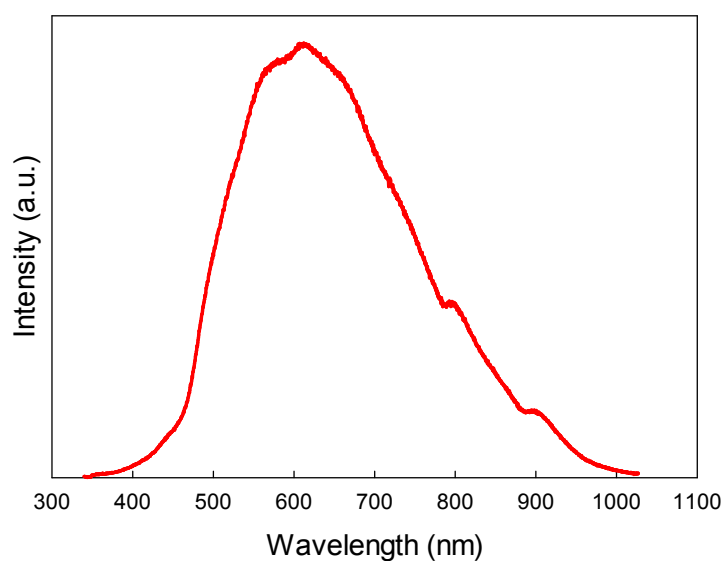


Fig. S7. Emission properties of the tungsten-halogen lamp with the cooling water jacket.

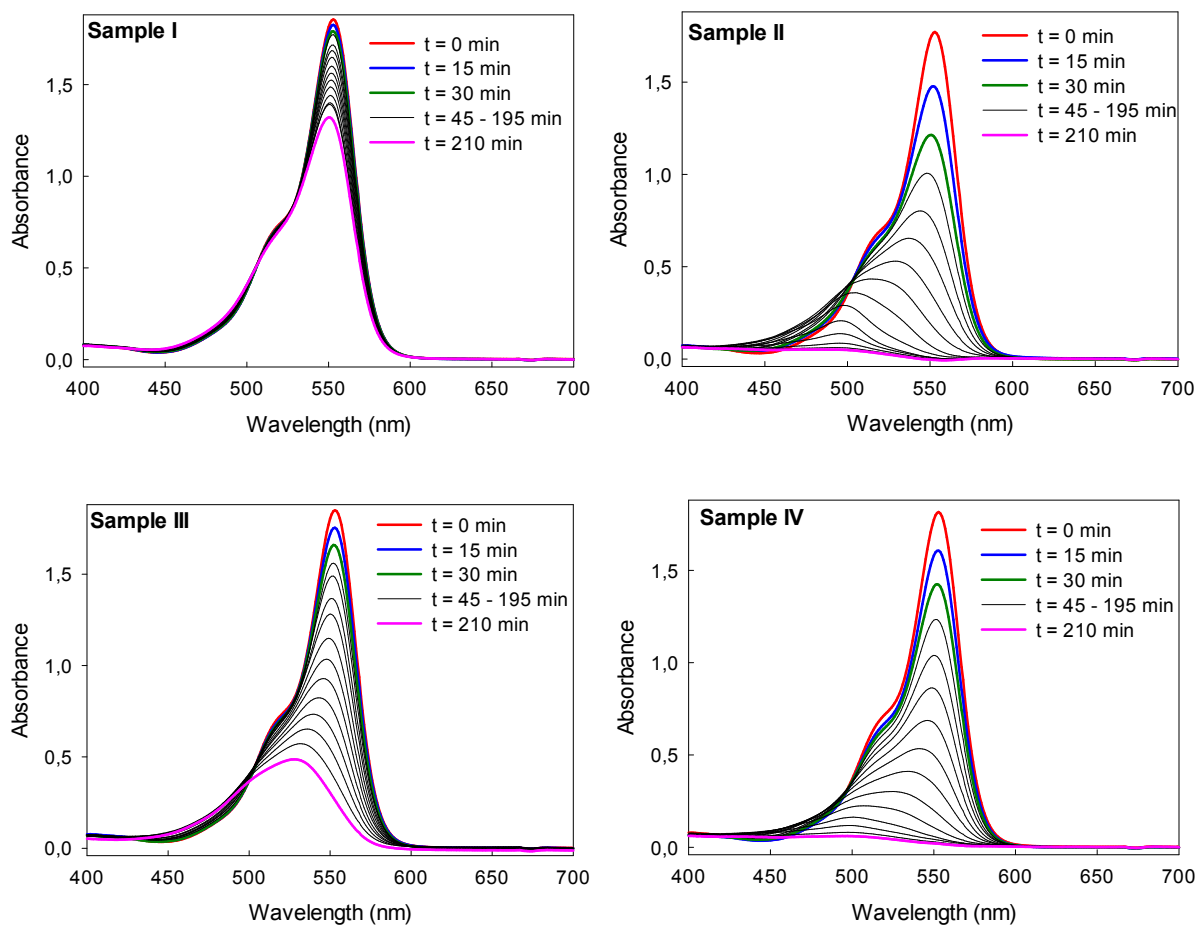


Fig. S8. Absorption spectra of RhB aqueous solutions after different illumination times.