Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

Few-layer graphenes from ball-milling of graphite with melamine

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Experimental section

Techniques

The thermogravimetric analyses were performed with a TGA Q50 (TA Instruments) at 10 ºC/min under nitrogen atmosphere. Raman spectra were recorded with an Invia Renishaw microspectrometer equipped with a He–Ne laser. Raman samples were prepared by immersion of silicon oxide surfaces (Si-Mat silicon wafers, CZ) into stable diluted dispersions of graphene/melamine; after evaporation of solvent, surfaces were washed with boiling water. For the TEM analyses concentrated dispersions of graphene/melamine were filtrated on a Millipore membrane (PTFE, 0.45 μm), paying special attention to keep the samples wet during the filtration processes. Graphene samples were redispersed in fresh DMF forming stable dispersions. 25 μL of these dispersions were placed on a copper grid (3.00 mm, 200 mesh, coated with carbon film), after being washed with boiling water and dried under vacuum, the sample was investigated by TEM Philips EM 208, accelerating voltage of 100 kV. The milling treatments were carried out in a Retsch PM100 Planetary Mill under different atmospheres (air or nitrogen) and using the reaction conditions described in Table 1. In sample 2, Graphite and melamine were weighted in a glovebox workstation with N_2 gas system. UV-vis-NIR spectra were recorded in 1cm quartz cuvettes on a Jasco FP-6500/6600 spectrofluorometer. Photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser with a pass energy of 50 eV and a Mg K α ($h\nu$ = 1254.6 eV) X-ray source, powered at 120 W. Binding energies were calibrated relative to the C 1s peak at 284.8 eV. High-resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software " *XPS peak.* " Symmetric Gaussian–Lorentzian curves were used to approximate the line shapes of the fitting components. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors.

Solvents were purchased from SDS and Fluka. Chemicals were purchased from Sigma-Aldrich and used as received without further purification. Graphite was purchased from Bay Carbon, Inc. (SP-1 graphite powder, www.baycarbon.com) and used without purification.

Synthesis of Sample 1-5

Sample 1-3. Graphite (5 mg) and melamine (2,4,6-triamine-1,3,5-triazine) (25 mg, 0.20 mmol) were introduced in stainless steel grinding bowl with ten stainless steel balls (1 cm diameter). The ball milling frequencies, atmosphere conditions and reaction times are detailed in Table 1. The bowl was closed and placed within the planetary mill. After the corresponding treatment, the resulting solid mixture was suspended in 20 mL of DMF and sonicated for 1 min. The as-prepared dispersions are stable at room temperature within weeks. Only for sample **2**, a precipitate (4.4 mg) was observed after 5 days.

Sample 4. Graphite (15 mg) and melamine (2,4,6-triamine-1,3,5-triazine) (15 mg, 0.12 mmol) were introduced in a stainless steel grinding bowl with ten stainless steel balls (1 cm diameter). The ball milling frequencies, atmosphere conditions and milling times are detailed in Table 1. The bowl was closed and placed within the planetary mill. After the corresponding treatment, the resulting solid mixture was suspended in 20 mL of DMF and sonicated for 1 min. The as-prepared dispersion is stable at room temperature within weeks.

Sample 5. Graphite (7.5 mg) and melamine (2,4,6-triamine-1,3,5-triazine) (22.5 mg, 0.18 mmol) were introduced in a stainless steel grinding bowl with ten stainless steel balls (1 cm diameter). The ball milling frequencies, atmosphere conditions and reaction times are detailed in Table 1. The bowl was closed and placed within the planetary mill. After the corresponding treatment, the resulting solid mixture was suspended in 20 mL of DMF and sonicated for 1 min. The as-prepared dispersion is stable at room temperature within weeks.

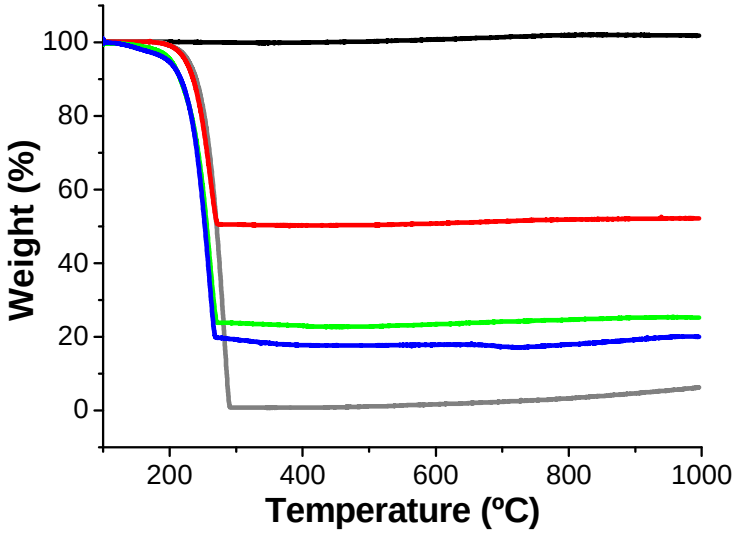

Figure S1. TGA thermograms of Graphite (black), Sample 4 (red), Sample 5 (green), Sample 1 (blue), Melamine (grey)