

Hydrogenated Fluorographene: A 2D Counterpart of Graphane with Enhanced Nonlinear Optical Properties

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Supporting Information. *Fluorographene (CF) dispersion in DMF:* 1 g fluorinated graphite (grey-white powder, C/F=1:1 ratio, Aldrich) was suspended by 3 h sonication in 200 mL DMF. The suspension was left in rest at room temperature for 3-4 days. The supernatant fluorographene colloid (0.1 mg mL^{-1}) was collected for further reaction with NaBH_4 towards hydrogenated fluorographene.

Hydrogenated fluorographene (CFH derivative): 550 mg NaBH_4 (Aldrich, 99.99 %) were dissolved in 150 mL CF dispersion in DMF. The reaction mixture was stirred for 3 days at room temperature in sealed vial. Then it was centrifuged at 5000 rpm for 10 min and the collected solid was washed five times with 80 mL water ($5 \times 80 \text{ mL}$) and three times with 40 mL acetone ($3 \times 40 \text{ mL}$). The black residue was exfoliated in 12 mL acetone by 1 h sonication. The sonicated mixture was left standing for one day in order to allow most of the insoluble particles to precipitate and then was centrifuged at 1000 rpm for 25 min to get a dark-brown colloidal dispersion (CFH in acetone, 1 mg mL^{-1}).

Graphene (G) dispersion in DMF: 250 mg graphite (synthetic powder, Aldrich) was suspended by 2 h sonication in 50 mL DMF. The suspension was left standing at room temperature for 1 day. The supernatant colloid was collected for further centrifugation at 1500 rpm for 20 min prior to collecting the graphene colloid (0.1 mg mL^{-1}).

Characterization: X-ray photoelectron spectroscopy (XPS) was carried out with a PHI VersaProbe II (Physical Electronics) spectrometer using an Al $K\alpha$ source (15 kV, 50 W). The obtained data were evaluated and deconvoluted with the MultiPak (Ulvac - PHI, Inc.) software package. Spectral analysis included a Shirley back-ground subtraction and peak deconvolution employing mixed Gaussian-Lorentzian functions. FT-IR spectra were recorded on an iS5 FTIR spectrometer (Thermo Nicolet) with the Smart Orbit ZnSe ATR technique. A drop from an

ethanol dispersion of the materials was left to form a film over the ZnSe crystal. Spectra were the sum of 52 scans, using nitrogen flow in the ATR accessory. ATR and baseline correction was applied on the collected spectra. Raman spectra were recorded on a DXR Raman microscope using the 532 nm excitation line of a diode laser. Atomic force microscopy images were obtained in tapping mode with a 3D Multimode Nanoscope, using Tap-300G silicon cantilevers with a tip radius < 10 nm and a force constant of 75 N m^{-1} . Samples were deposited onto silicon wafers (P/Bor, single side polished) from dispersions by drop casting. Thermal gravimetric analysis with evolved gas analysis was performed using a Netzsch STA 449 C Jupiter instrument with adapted quadrupole mass spectrometer QMS 403 C Aëolos, with a measurement range 0-300 AMU. The experiments were carried out in an open $\alpha\text{-Al}_2\text{O}_3$ crucible under dynamic Ar atmosphere ($80 \text{ cm}^3 \text{ min}^{-1}$) and they were performed in the temperature range of 40-1000 °C, at a heating rate of 5 °C min^{-1} .