

Electronic Supplementary Information

Electrocatalytic activity for protons reduction by covalent non-metal graphene-fullerene hybrid

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1. Experimental section

1.1 Reagents and materials

Fluorinated graphite (GF) (C:F 1:1.1, >61 wt. %F), trimethylamine (Et₃N) and anhydrous 1,2-dichlorobenzene (o-DCB) were purchased from Sigma-Aldrich. All reagents were used as received without further purification. Fullerene derivative C₆₀-pyr-NH₂ (illustrated in Fig. 1) was synthesized according to the literature.¹

1.2 Synthesis of G-C₆₀

15 mg (0.48 mmol) of fluorographene (FG), exfoliated from GF (100 mg), were suspended in 5 mL of anhydrous o-DCB with the aid of sonication for 4 h and the mixture was degassed and flushed with nitrogen. In parallel, 50 mg (0.049 mmol) of ammonium-fulleropyrrolidine salt C₆₀-pyr-NH₃⁺ were dissolved in 3 mL of anhydrous o-DCB and afterwards, 50 μL of Et₃N were added to the solution as a counter-balance agent for the protonated primary amine. Subsequently, o-DCB solution containing the C₆₀-pyr-NH₂ was added to the o-DCB suspension of FG and the reaction mixture was heated at 130 °C and stirred under nitrogen for 72 h. Then, the G-C₆₀ hybrid material was separated using centrifugation and washed consecutively with carbon disulfide, in order to remove any non-covalently bound fullerene moiety, dichloromethane and ethanol.

1.3 Control experiment

15 mg of exfoliated FG were mixed with o-DCB solution containing fullerene C₆₀ and the reaction was carried out according to the above-mentioned process. The reaction did not introduce any functionality onto FG (see Fig. S1).

1.4 Instrumentation

FT-IR spectra were recorded on an iS5 FTIR spectrometer (Thermo Nicolet) using the KBr pellet accessory. Spectra were acquired by summing 64 scans. Pellet made by pure KBr was employed for the background acquisition. Baseline correction was applied to the collected spectra. X-ray photoelectron spectroscopy (XPS) was carried

out with a PHI VersaProbe II (Physical Electronics) spectrometer using an Al K α source (15 kV, 50 W). The obtained data were evaluated with the MultiPak (Ulvac - PHI, Inc.) software package. Raman spectra were recorded on a DXR Raman microscope using the 633 nm excitation line of a diode laser. Thermogravimetric analysis (TGA) with evolved gas analysis (EGA) was performed using a Netzsch STA 449C Jupiter thermo-microbalance coupled with a QMS 403C Aëolos quadrupole mass spectrometer. Measurements were carried out in an α -Al₂O₃ open crucible under N₂ flow. A temperature program from 40 to 950 °C with heating rate of 10 °C min⁻¹ was used. Before each experiment, the crucible was heated to 1300 °C and then cooled to room temperature. Differential pulse voltammograms (DPV) were recorded on an Autolab PGSTAT128 N potentiostat/galvanostat equipped with a dual mode bipotentiostat (BA module) electrochemical analyzer using a three-electrode system. A platinum cloth served as the counter electrode and a platinum wire was used as the reference electrode. A platinum button electrode was used as the working electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All solutions were purged prior to electrochemical measurements using nitrogen gas. 0.1 M TBAPF₆ was used as supporting electrolyte. The potential are vs Fc/Fc⁺ and the scan rate is 100 mV/s. Electron microscopy images were obtained with a High Resolution Transmission Electron Microscope (HRTEM) Titan G2 60-300 (FEI) with image corrector on accelerating voltage 80 kV. Images were taken with BM UltraScan CCD camera (Gatan). AFM images were obtained in the amplitude modulated semicontact mode on an NT-MDT NTegra system equipped with a VIT-P AFM probe with the amplitude set point set to 71% of the free amplitude, a scanning speed of 0.5 Hz per line for all pictures, and using fresh cleaved muscovite mica. The height profile and surface roughness (RMS) was calculated using Gwyddion 2.51 software. All electrochemical measurements were carried out using an Autolab PGSTAT128N potentiostat/galvanostat and were carried out at room temperature in a standard three-compartment electrochemical cell by using a graphite rod as a counter-electrode, an RDE with glassy carbon disk (geometric surface area: 0.0196 cm²) as a working electrode, and Hg/HgSO₄ (0.1 M KOH) as reference electrode. LSV measurements were carried out at room temperature in N₂-saturated aqueous 0.1 M KOH. The catalyst ink was prepared by dispersing 1.0 mg of the catalytic powder in 250 μ L mixture of deionized water, isopropanol and 5% Nafion (v/v/v = 4:1:0.2) and sonicated for 1 h prior use. Before casting the electrocatalytic ink on the electrode's

surface, the working electrode was polished with 3 and 1 mm diamond pastes, rinsed with deionized water, and sonicated in double-distilled water. Afterward, 8.5 μL aliquots of the electrocatalyst were casted on the electrode surface and were left to dry at room temperature. EIS measurements were conducted from 10^5 to 10^{-1} Hz with an AC amplitude of 0.01 V.

References:

1 K. Kordatos, T. Da Ros, S. Bosi, E. Vázquez, M. Bergamin, C. Cusan, F. Pellarini, V. Tomberli, B. Baiti, D. Pantarotto, V. Georgakilas, G. Spalluto and M. Prato, *J. Org. Chem.*, 2001, **66**, 4915–4920.

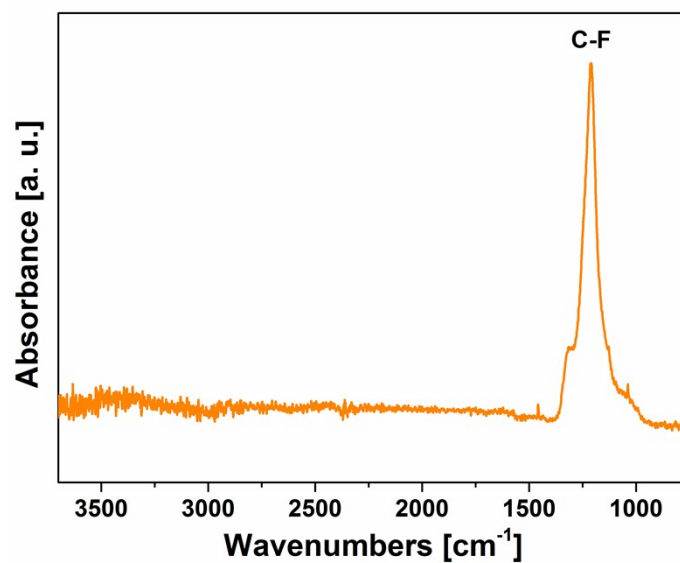


Figure S1. FT-IR spectrum of the produced material after heating of exfoliated FG at 130 °C in a solution of dry o-DCB and C₆₀ (control experiment).

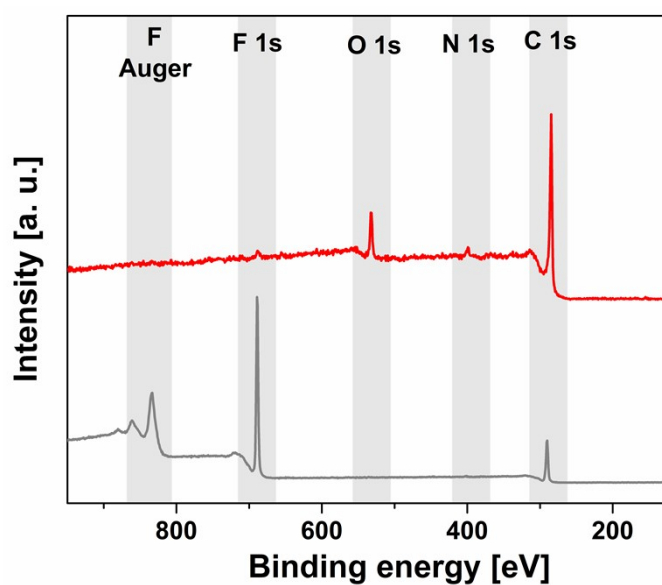


Figure S2. XPS survey spectra of G-C₆₀ (red) and pristine GF (grey).

Table S1. Elemental composition of G-C₆₀ and pristine GF as obtained from the XPS analyses (wide scan XPS spectra).

	Atomic percentage [%]			
	C 1s (284 eV)	N 1s (400 eV)	O 1s (532 eV)	F 1s (688 eV)
G-C ₆₀	85.3	3.0	10.2	1.5
GF	43.5	-	0.8	55.7

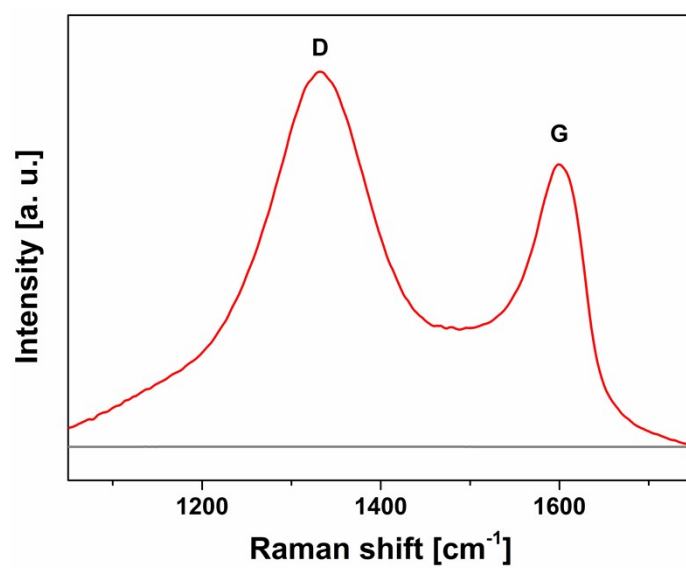


Figure S3. Raman spectra of pristine GF (grey) and G-C₆₀ (red).

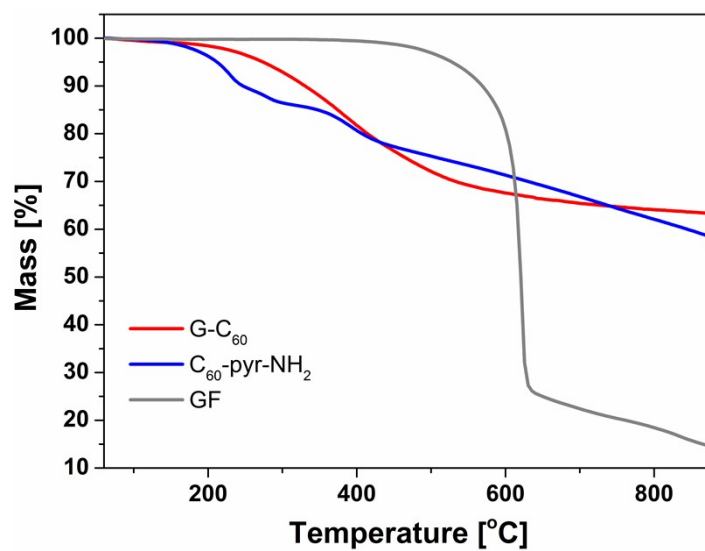


Figure S4. TGA graphs of pristine GF (grey), C₆₀-pyr-NH₂ (blue) and G-C₆₀ (red).

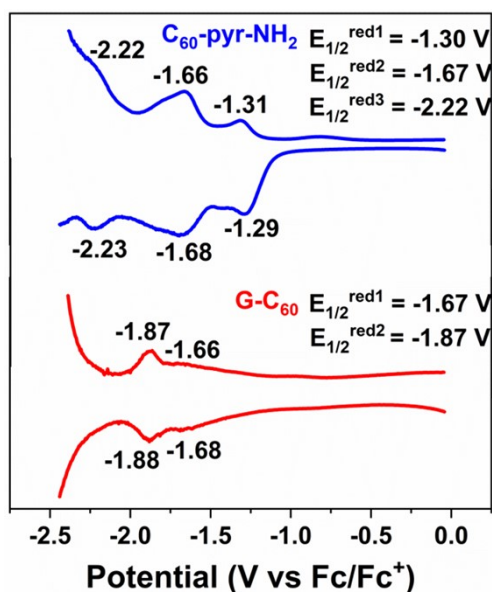


Figure S5. Differential pulse voltammograms of C_{60} -pyr-NH₂ (blue) and G- C_{60} (red) in o-DCB with 0.1 M TBAPF₆ as supporting electrolyte. The potential are vs Fc/Fc⁺ and the scan rate is 100 mV/s.

Table S2. Electrocatalytic HER parameters for G- C_{60} , C_{60} -pyr-NH₂ and GF.

Electrocatalyst	Onset potential (V vs RHE)	Potential (V vs RHE) at -10 mA/cm	Tafel slope (mV/dec ⁻¹)	R_{ct} (Ω)	ECSA (cm ²)
G- C_{60}	-0.562	-0.939	347	73	1.4
C_{60} -pyr-NH ₂	-1.488	-1.819	542	266	0.3
GF	-1.613	-1.853	438	188	1.0

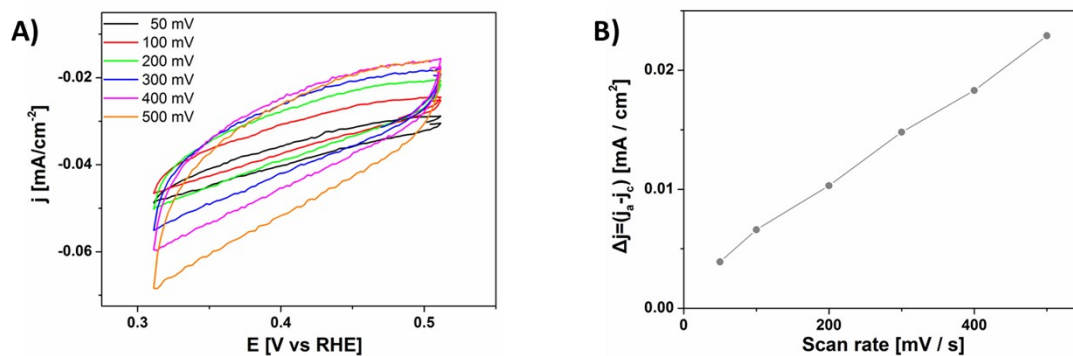


Fig S6: A) Cyclic voltamograms for HER of GF, and B) scan rate dependence of the current densities for GF.

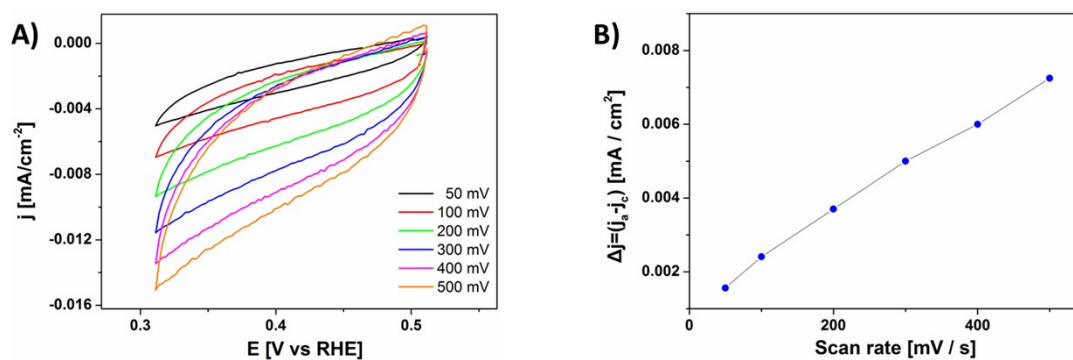


Fig S7: A) Cyclic voltamograms for HER of C₆₀-pyr-NH₂, and B) scan rate dependence of the current densities for C₆₀-pyr-NH₂.

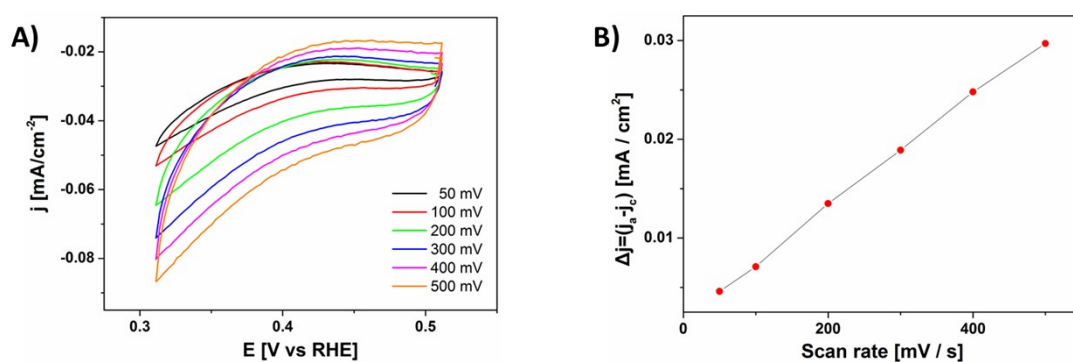


Fig S8: A) Cyclic voltamograms for HER of G-C₆₀, and B) scan rate dependence of the current densities for G-C₆₀.