Electronic Supplementary Information

Single-stage functionalization and exfoliation method for the production of graphene in water: stepwise construction of 2D-nanostructured composites with iron oxide nanoparticles

Dris Ihiawakrim,a Ovidiu Ersen,a Frédéric Melin,b Petra Hellwig,b Izabela Janowska,c Dominique Begin,c Walid Baaziz,c Sylvie Begin-Colin,c Cuong Pham-Huu,c and Rachid Baati*d

aInstitut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg, CNRS UMR 7504, 23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France.

bLaboratoire de Bioelectrochimie et Spectroscopie, UMR 7140, Chimie de la matière complexe, Université de Strasbourg-CNRS, 67070 Strasbourg, France

cLaboratoire des Matériaux Surfaces et Procédés pour la Catalyse, UMR 7515 CNRS, European Laboratory for Catalysis and Surface Sciences, 25 rue Becquerel, 67087 Strasbourg, France

dUniversité de Strasbourg, Faculté de Pharmacie, UMR/CNRS 7199, 74 Route du Rhin 67401 Illkirch

corresponding author : rachid.baati@unistra.fr
Content

1. Non-covalent functionalization and exfoliation of graphene from graphite with NH$_2$-His$_6$-pyrene I and TEM analysis  p. S3
2. Raman analysis of His$_6$@GN  p. S5
3. X-ray photoelectron spectroscopy (XPS) spectra of GN  p. S6
4. UV-absorption of NH$_2$-His$_6$-pyrene and His$_6$@GN in water  p. S7
5. Electrical resistance measurements  p. S7
6. Hierarchical self-assembly of His$_6$@GN with magnetic Fe$_3$O$_4$ nanoparticles  p. S7
1. Non-covalent functionalization and exfoliation of graphene from graphite with His$_6$-pyrene 1 and TEM analysis

(See Methods in the manuscript)

TEM analysis

The conventional TEM, high-resolution TEM (HRTEM) analysis have been performed on a JEOL 2100F (FEG) TEM/STEM electron microscope operating at 200 kV, equipped with a Cs probe corrector and a TRIDIEM post-column GATAN imaging filter. In order to minimize the irradiation damages, the specimen has been maintained at low temperature during the measurements by using a cryo-holder.

![TEM images](image1.png)

**Figure S1. Top:** TEM images recorded on typical fragments obtained by: a) simple sonication of expanded graphite without amphiphilic molecule; b) assisted-exfoliation of expanded graphite by NH$_2$-His$_6$-pyrene. **Bottom:** optical images of the samples containing the solution; c) non functionalized expanded graphite in water, d) stable colloidal dispersion of His$_6$@GN.

1a. Time stability of the colloidal dispersion of His$_6$@GN and reproducibility of the exfoliation-functionalization process:
Figure S2. TEM (a) and b)) and optical images (c) and d)) of representative His₆@GN obtained by assisted-exfoliation of expanded graphite by NH₂-His₆-pyrene as-prepared (left) and after 6 months of another sample (d) prepared in the same manner (right), respectively.
1b. His$_6$@FLGs with a size of few tenths of nanometer to large micrometer sized species demonstrating the efficiency of the process:

![TEM images at different magnifications of His$_6$@FLGs obtained by assisted-exfoliation of expanded graphite by NH$_2$-His$_6$-pyrene 1.](image)

**Figure S3.** TEM images at different magnifications of His$_6$@FLGs obtained by assisted-exfoliation of expanded graphite by NH$_2$-His$_6$-pyrene 1.

2. **Raman analysis of His$_6$-@GN**

Raman spectra were recorded on a Renishaw Invia Raman Microscope with the 514-nm emission line of an Ar-laser. One drop of the sample suspended in water was deposited on a silicon window and allowed to dry before measurement. Typically, 5 spectra obtained with 15 s irradiation time and 25 mW laser power were averaged.
Figure S4: Full Raman spectra of the natural and expanded graphite samples before and after treatment with peptides (414 nm excitation).

3. X-ray photoelectron spectroscopy (XPS) spectra of GN

Figure S5. C1s XPS spectrum, analyzed in components corresponding to the graphene sheets and the oxygen containing species
This peak is analyzed in components related to non-oxygenated carbon (C-C/C=C) at 284.6 eV, oxygenated carbon (C-O, C=O and O-C=O) at higher binding energies, and the $\pi-\pi^*$ transition loss peak at $\sim$291 eV.\textsuperscript{1} It is evident that the amount of oxygenated functional groups on the FLG surface is relatively low as indicated by the above mentioned Raman Analysis.


4. UV-absorption of NH$_2$-His$_6$-pyrene and His$_6$@GN in water

Absorption spectra were recorded on a Cary 4 (Varian) spectrophotometer.

![Absorption spectra](image)

\textbf{Figure S6:} a) Absorption spectra of NH$_2$-His$_6$-pyrene. B) Absorption spectra for stable aqueous dispersion of His$_6$@GN. Concentration of 1 = 10 µM. Concentration of functionalized graphene $\approx$ 50 µg/mL.

5. Electrical resistance measurements

The FLG obtained by exfoliation was dispersed for 5 min. in ultrasonication bath at low power in ethanol. A low concentrated suspension (0.05mg. ml$^{-1}$) was then sprayed by air-brush system onto Si/SiO$_2$ substrate with the gold circuit prepared before by lithography (Fraunhofer) (figure1A in the manuscript). A deposition of the FLG flakes between gold electrodes with the gap of 2.5, 5 and 10 µm was controlled before and after measurements by SEM microscopy. Two points measurements were then applied in the r.t. with the at the voltage range of $\pm$ 1V.

6. Hierarchical self-assembly of His$_6$@GN with magnetic Fe$_3$O$_4$ nanoparticles

(Protocol: See Methods in the manuscript)
Figure S7: Size distribution of Fe$_3$O$_4$ NPs used for the self-assembly

Additional images of the nanostructured assemblies of His$_6$@GN/Fe$_3$O$_4$ hybrids.
Figure S8. TEM images at different magnifications of Fe₃O₄ NPs homogeneously and densely packed on the multivalent platform His₆@GN obtained by assisted-exfoliation of expanded graphite by NH₂-His₆-pyrene 1.

7. Magnetic properties of iron-oxide/graphene composite

Figure S9. Magnetization curves of nanoparticles NPs/FLG as a function of applied magnetic field at 300 K and 5 K. Insert: Magnetic interaction between the NPs/FLG sample and the external magnet allowing the easy separation of the solid from the solution.