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

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Content

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.

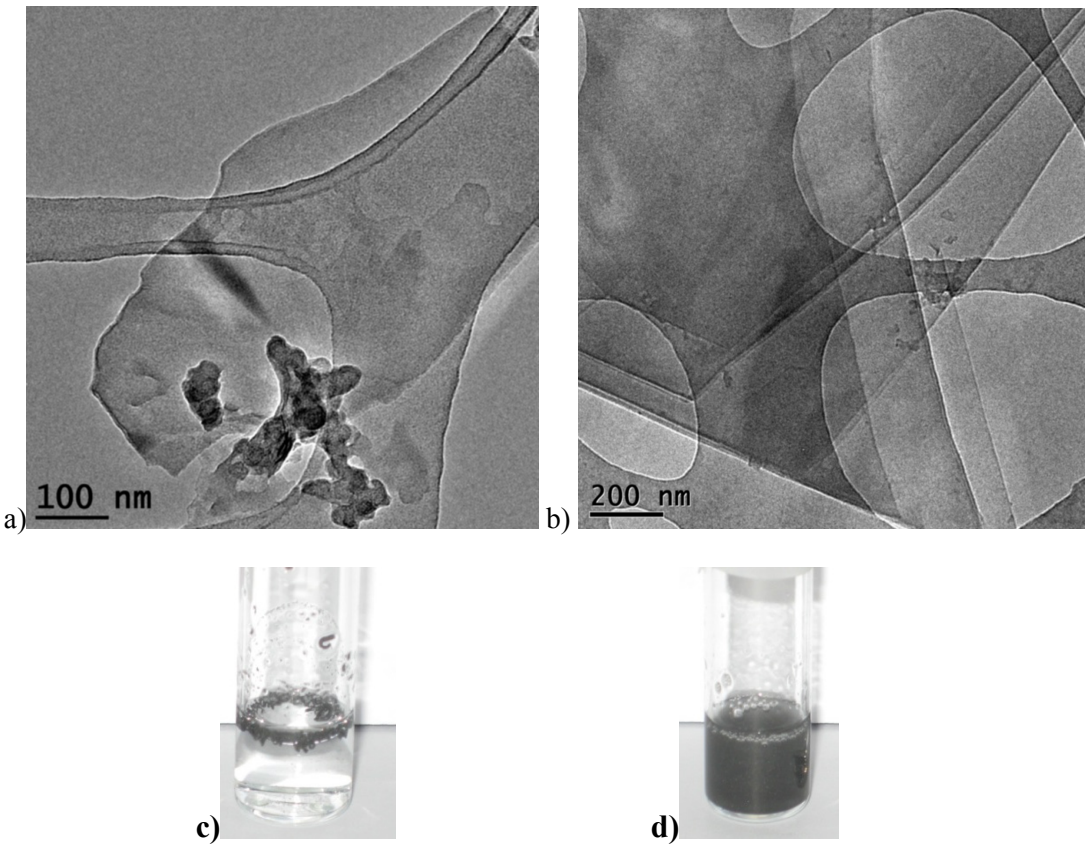


Figure S1. ***Top***: TEM images recorded on typical fragments obtained by: a) simple sonication of expanded graphite without amphiphilic molecule; b) assisted-exfoliation of expanded graphite by NH_2-His_6-pyrene. ***Bottom***: optical images of the samples containing the solution; c) non functionalized 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:

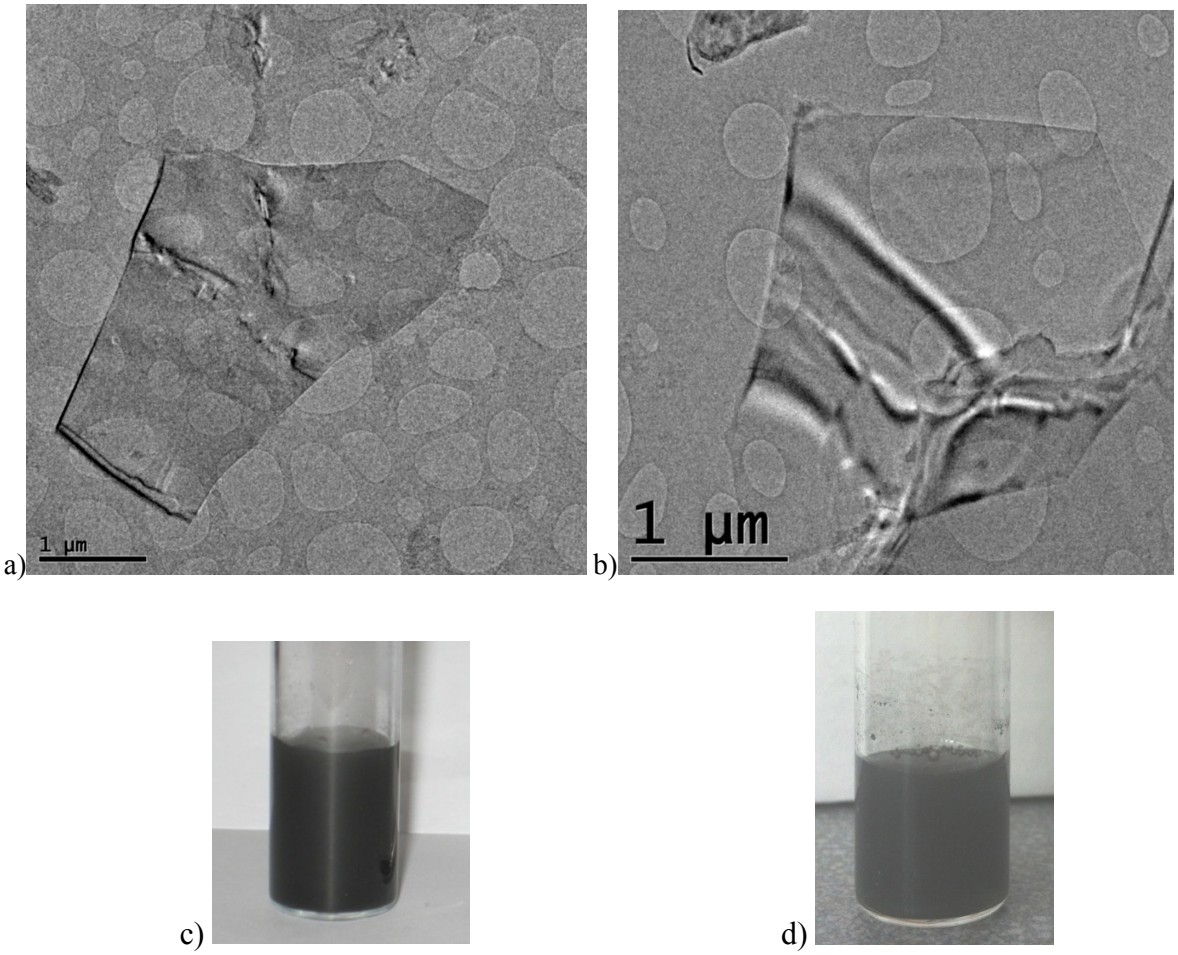


Figure S2. TEM (a) and b)) and optical images (c) and d)) of representative His_6@GN obtained by assisted-exfoliation of expended graphite by NH_2-His_6-pyrene as-prepared (left) and after 6 months of another sample (d) prepared in the same manner (right), respectively.

1b. His_6@FLGs with a size of few tenths of nanometer to large micrometer sized species demonstrating the efficiency of the process:

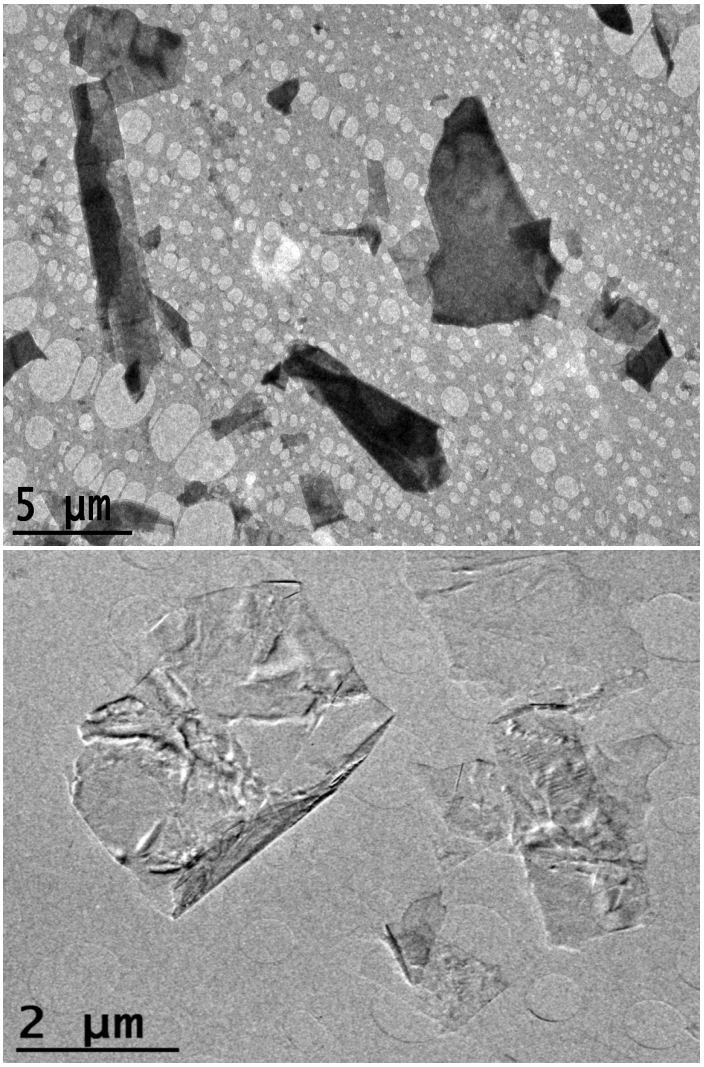


Figure S3. TEM images at different magnifications of His_6@FLGs obtained by assisted-exfoliation of expanded graphite by NH_2-His_6-pyrene **1**.

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.

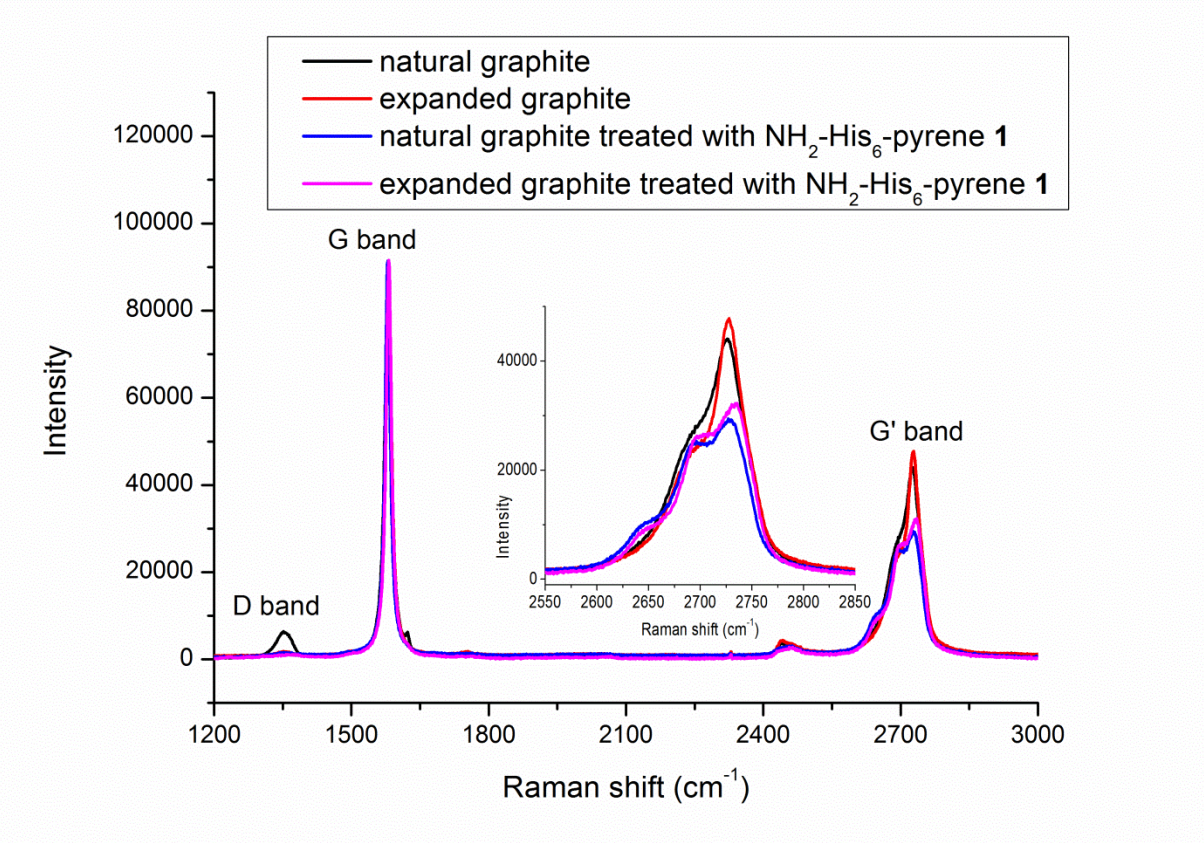


Figure S4 : Full Raman spectra of the natural and expanded graphite samples before and after treatment with peptides (414 nm excitation).

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

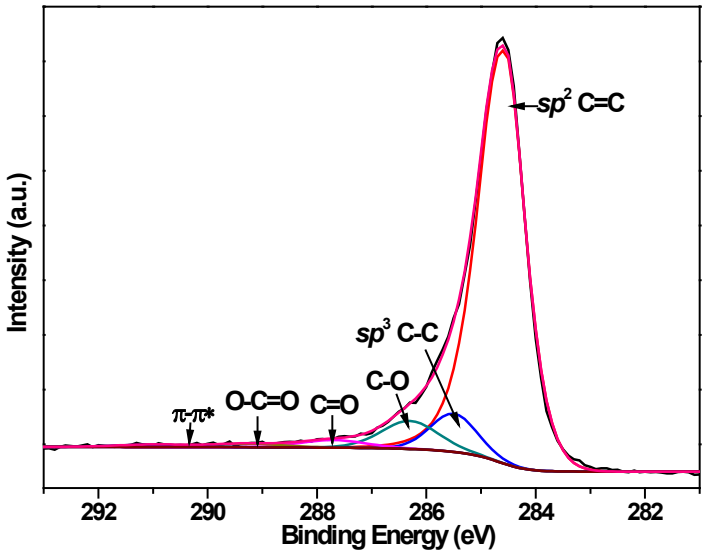


Figure **S5**. C1s XPS spectrum, analyzed in components corresponding to the graphene sheets and the oxygen containing species

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 π-π* transition loss peak at ~291 eV.[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.

(1) Xia, W.; Wang, Y.; Bergstrasser, R.; Kundu, S.; Muhler, M. *Appl. Surf. Sci.* **2007,** 254, 247-250.

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.

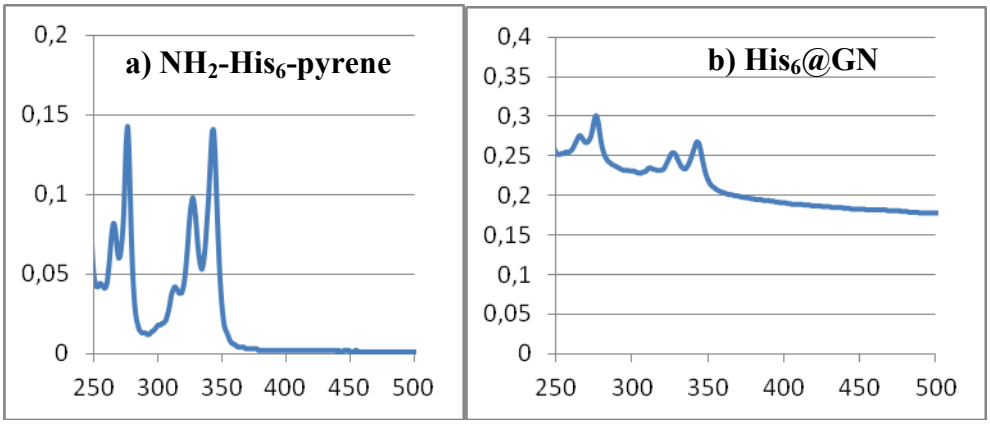


Figure S6 : a) Absorption spectra of NH_2-His_6-pyrene **1**. B) Absorption spectra for stable aqueous dispersion of His_6@GN. Concentration of **1** = 10 µM. Concentration of functionalized graphene ≈ 50 µg/mL.

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 ± 1V.

6. Hierarchical self-assembly of His_6@GN with magnetic Fe_3O_4 nanoparticules

(Protocol: See Methods in the manuscript)

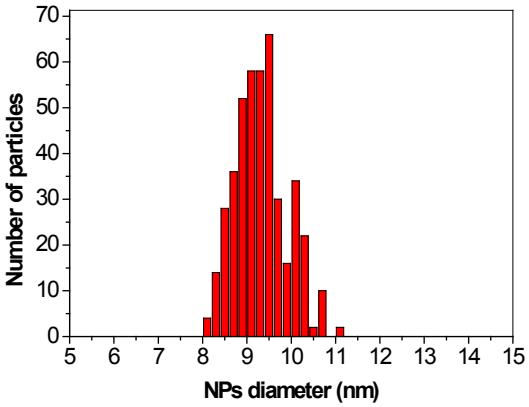
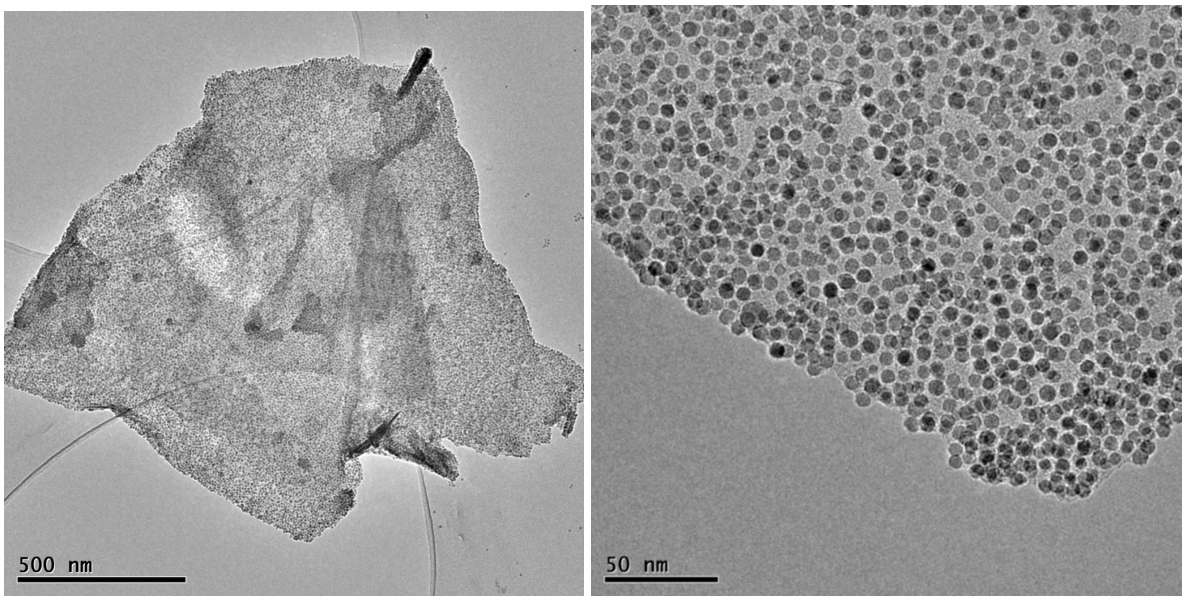


Figure S7 : Size distribution of Fe_3O_4 NPs used for the self-assembly

Additional images of the nanostructured assemblies of His_6@GN/ Fe_3O_4 hybrids.



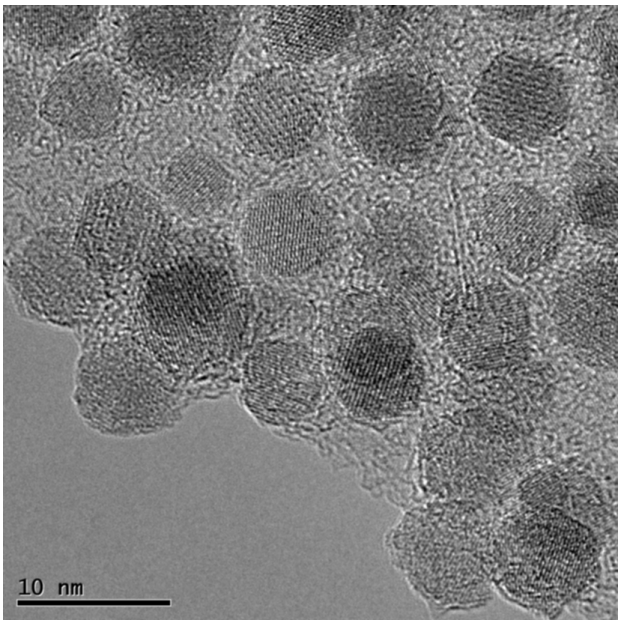


Figure S8. TEM images at different magnifications of Fe_3O_4 NPs *homogeneously and densely packed on the multivalent platform* His_6*@GN* obtained by assisted-exfoliation of expanded graphite by NH_2-His_6-pyrene **1**.

7. Magnetic properties of iron-oxide/graphene composite

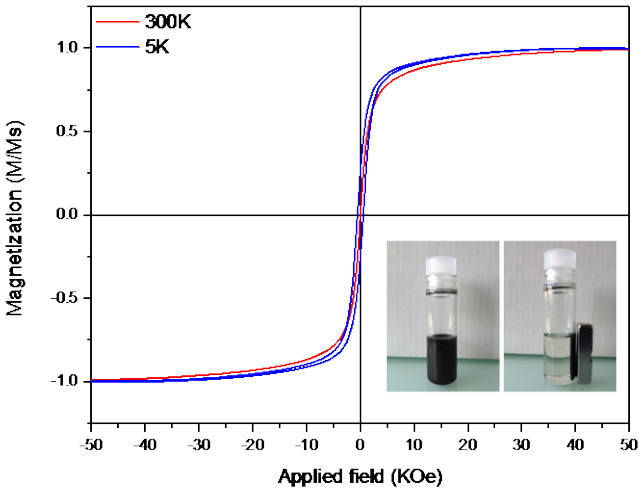


Figure S9. Magnetization curves of nanoparticles NPs/FLG as a function of applied magnetic field at 300 K and 5 K. Insert: Magnetic interaction between the NPs/FLG sample and the external magnet allowing the easy separation of the solid from the solution.