Electronic Supplementary Material (ESI) for Nanoscale.

THIOGRAPHENE IMMOBILIZED BIOCATALYSTS
for
WATER REMEDIATION

Jiri Sturala, Soňa Hermanová, Lucie Artigues, Zdeněk Sofer, and Martin Pumera*

Contents

Experimental Procedures

Graphene oxide (HOGO)[1]

98% H_2SO_4 (87.5 mL) and 68% HNO_3 (27 mL) were added to a reaction flask (Pyrex beaker with a thermometer) containing a magnetic stir bar. The mixture was then cooled by immersion in an ice bath for 30 min. Graphite (5.0 g, 0.417 mol) was added to the mixture with vigorous stirring motion. While keeping the reaction flask in the ice bath, $KClO_3$ (55.0 g, 0.449 mol) was slowly added to the mixture. Upon the complete dissolution of $KClO_3$, the reaction flask was then loosely capped to allow the escape of the gas evolved and the mixture was continuously stirred for 96 hours at room temperature. The mixture was poured into deionized water (3 L) and decanted. Graphite oxide was then redispersed in 5% aqueous HCl solution (3 L) to remove sulfate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on chloride and sulfate ions was achieved. HOGO slurry was then dried in a vacuum oven.

Reduced graphene oxide (TRG)[1]

HOGO (1 g) was placed in a quartz glass microwave reactor. The reactor was repeatedly evacuated and filled with high purity nitrogen. Exfoliation was performed using 2.45 GHz/1 kW power for 3 minutes. The exfoliation was performed under a nitrogen atmosphere (50 $mL \cdot min^{-1}$) at reduced pressure 10 mbar. During the exfoliation was formed nitrogen plasma, which further accelerated exfoliation and reduction of graphite oxide. Reduced graphite oxide (TRG) was further used for the fluorination.

Fluorographene[2]

Fluorination was performed in Teflon lined autoclave using F_2/N_2 mixture (20 vol.% F_2). 0.5 g of TRG was placed into an autoclave, which was evacuated and filled with N_2/F_2 mixture (5 bar). The TRG was fluorinated at 180 °C for 72 h at 5 bar pressure and the F_2/N_2 mixture was exchanged every 24 hours. Fluorographene used for further reactions is termed as FG.

Analytical Techniques

FT-IR spectroscopy

Fourier transform infrared spectroscopy (FT-IR) measurements were performed on an iS50R FTIR spectrometer (Thermo Scientific, USA). The measurement was performed diamond ATR crystal, DLaTGS detector and KBr beamsplitter in the range 4000 – 400 cm^{-1} at a resolution of 4 cm^{-1}.

Raman Spectroscopy

inVia Raman microscope (Renishaw, England) in backscattering geometry with CCD detector was used for Raman spectroscopy. DPSS Nd-YAG laser (532 nm, 50 mW) with an applied power of 1% and 50x magnification objective. The spectra were referenced according to a laser peak position at 0 cm^{-1}. Prior to the measurements, pure silicon was measured and the Raman shift was set to 521 cm^{-1} corresponding to silicon Raman peak. The samples were deposited on a metal plate as a powder and measured immediately after the deposition.

X-ray Photoelectron Spectroscopy

High-resolution X-ray photoelectron spectroscopy (XPS) was performed using an ESCAProbeP spectrometer (Omicron Nanotechnology Ltd, Germany) with a monochromatic aluminium X-ray radiation source (1486.7 eV). Wide-scan surveys of all elements were performed, with subsequent high-resolution scans of the C 1s, N 1s, O 1s, F 1s and S 2p. Relative sensitivity factors were used to evaluate the element ratios from the survey spectra. The samples were placed on a conductive carrier made from a high purity silicon coated with gold used as a reference (Au 4f$_{7/2}$ peak, 84.0 eV). An electron gun was used to eliminate sample charging during measurement (1 – 5 V).

Zeta Potential

The measurements of zeta-potential were performed on Malvern Zetasizer Nano ZS. The measurements were performed at pH = 7.0 in 56 mM PBS solution. A suspension of sample concentration 1 mg·mL^{-1} in PBS was used for the measurements.

XPS Spectra

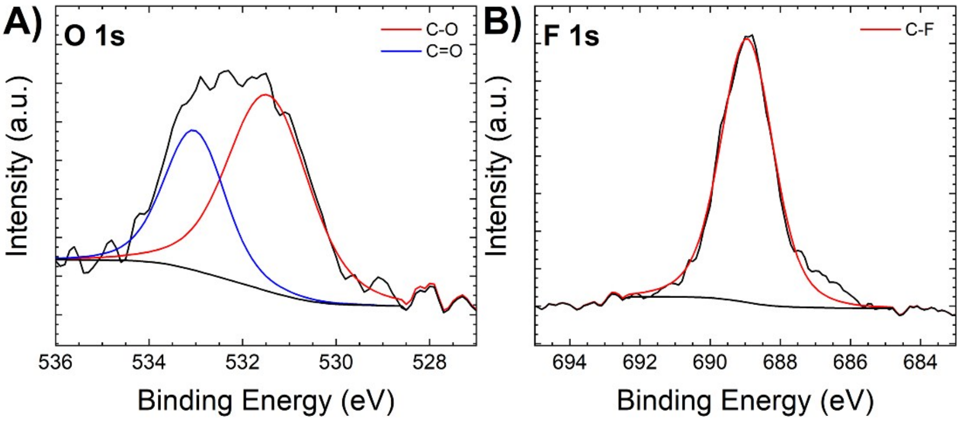

Figure S1. *GrSH1 high resolution XPS spectra for (A) O 1s and (B) F 1s.*

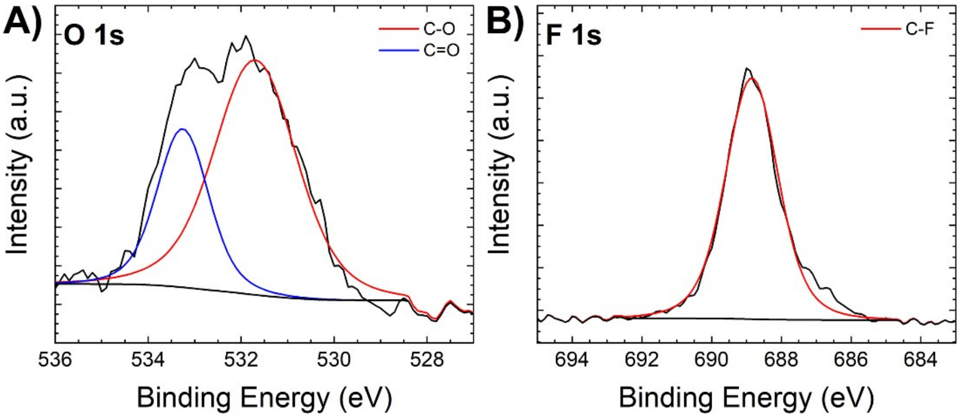

Figure S2. *GrSH2 high resolution XPS spectra for (A) O 1s and (B) F 1s.*

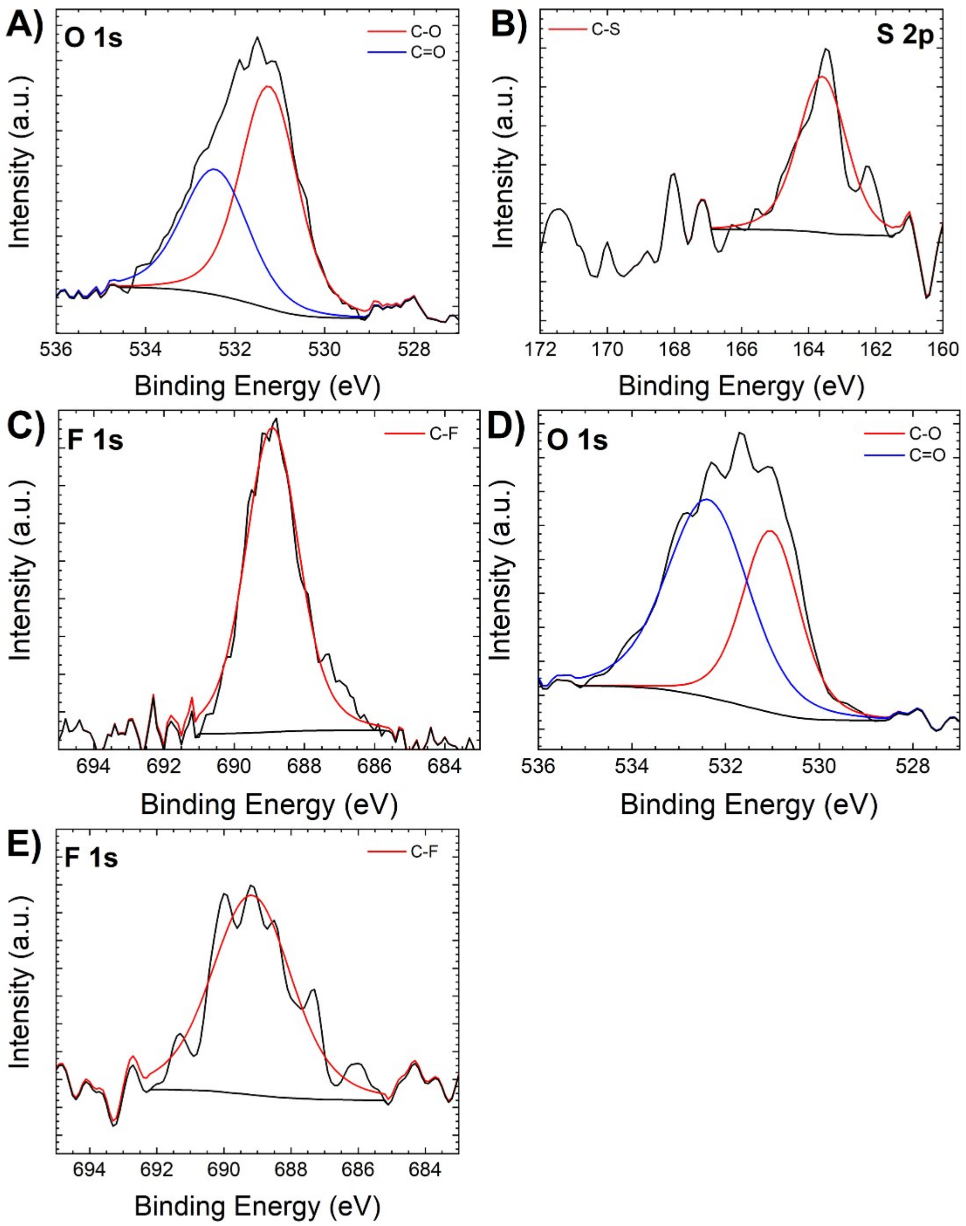

Figure S3 *High resolution (A) O 1s, (B) S 2p and (C) F 1s XPS spectra for lipase modified thiographene GrSH1 and high resolution (D) O 1s, (E) F 1s XPS spectra for catalase modified GrSH1.*

Figure S4. *High resolution (A) O 1s, (B) S 2p and (C) F 1s XPS spectra for lipase modified thiographene GrSH2 and high resolution (D) O 1s, (E) F 1s XPS spectra for catalase modified GrSH2.*

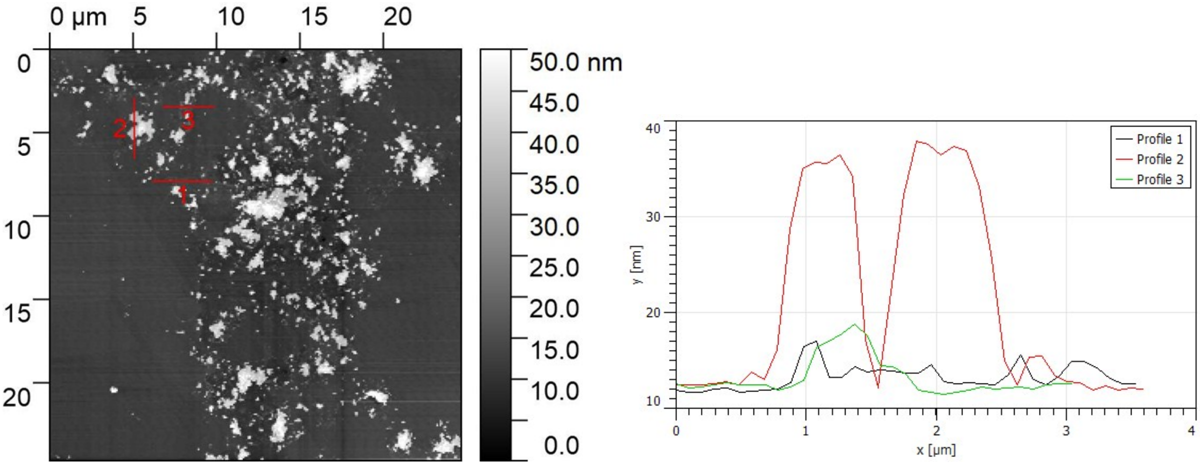

Figure S5. *AFM image of GrSH2 sample with corresponding height profiles.*

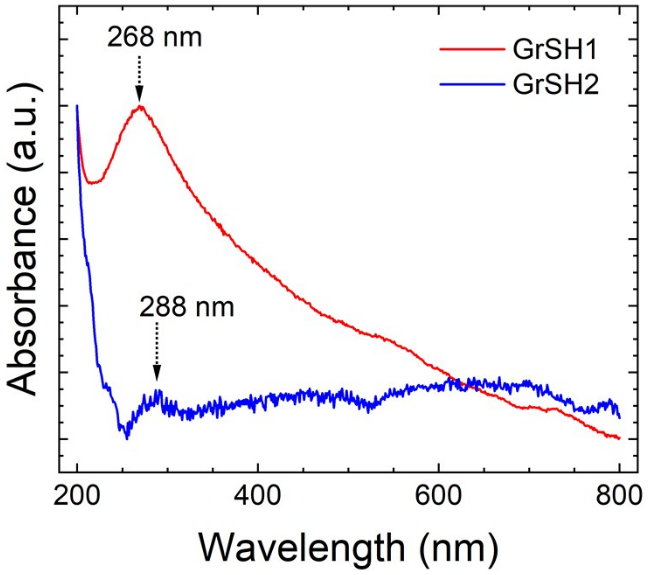

Figure S6. *UV-Vis spectra of thiographene samples in acetonitrile suspension (1 mg/mL).*

Literature:

1. Jankovský, O.; Marvan, P.; Nováček, M.; Luxa, J.; Mazánek, V.; Klímová, K.; Sedmidubský, D.; Sofer, Z., Synthesis procedure and type of graphite oxide strongly influence resulting graphene properties. *Applied Materials Today* **2016,** *4*, 45-53.

2. Mazanek, V.; Jankovsky, O.; Luxa, J.; Sedmidubsky, D.; Janousek, Z.; Sembera, F.; Mikulics, M.; Sofer, Z., Tuning of fluorine content in graphene: towards large-scale production of stoichiometric fluorographene. *Nanoscale* **2015,** *7* (32), 13646-13655.