Supplementary Information

for

Playing Peekaboo with Graphene Oxide: A Scanning Electrochemical Microscopy Investigation

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Experimental

Scanning Electrochemical Measurements

All measurements were accomplished using a CHI 410B Scanning ElectroChemical Microscope. Pt microelectrode was used as the probe (10 μm diameter and with a glass to platinum radius ratio of 10) and was approached before the images using the feedback mode of SECM to ca. 8 μm above the Au or SiOx surfaces in 1 mM FcMeOH, $Ru(NH_3)_6Cl_3$, $Fe(CN)_6K_4$, FcCOOH and $Na_3(IrCl_6)$ in phosphate buffer saline solutions. The images were performed in constant height mode. After each image the redox solution was replaced with one of the others in order to image the same area of the gold (SiOx) surface. The applied potentials were +0.4 V for all the approaches and images performed in presence of FcMeOH and $Fe(CN)_6K_4$, and -0.3 V for those performed in $Ru(NH_3)_6Cl_3$, reference electrode was Ag/AgCl (3M KCl), counter electrode was a Pt wire. All the chemicals for the redox solution preparations were purchased by Sigma Aldrich and used without any further purification.

Fitting Procedures, Heterogeneous Rate Constants and Image Plotting

MIRA software by Prof. Wittstock (http://www.uni-oldenburg.de/chemie/pc2/pc2forschung/secm-tools/mira/) was used for fitting all current approach curves and for plotting all the images. Approach curves were fitted by Cornut-Lefrou equations for purely negative feedback, purely positive feedback and for finite sample kinetics, tip/substrate separations and heterogeneous rate constants were accordantly evaluated. A first order heterogeneous rate constant in cm per second (k_{eff}) can be determined using the dimensionless constants, obtained in the fitting procedures and reported in the text, accordingly to the following equation:

$k=k_{eff}\, r_T/D$

where r_T is the electrode radius and D the diffusion coefficient of the redox specie.

1. Preparation of GO

Preparation of GO and RGO adsorbed substrates

Graphene oxide was prepared using a method that relies on previously described procedures (ref. 7 of the main text) and it is based on a modified Hummers method starting from graphite flakes.

The GO powder, dissolved in water, was spin coated at 2000 rpm on the Au and SiOx substrates. (ref. 7 main text)

The reduced GO flakes were obtained by thermal reduction of the GO deposited substrates at 700°C in vacuum. The detailed reduction procedure is reported in our reference 7 of the main text.

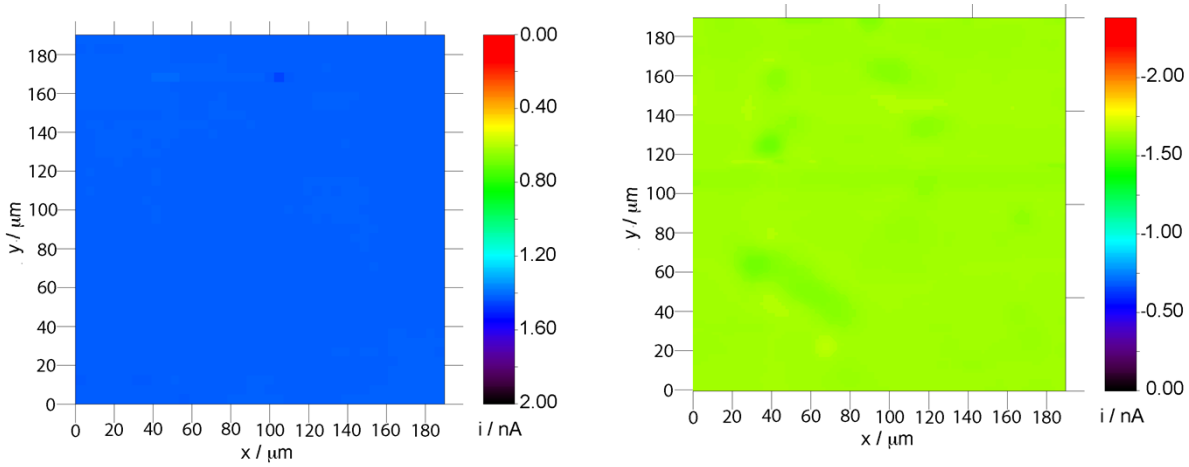

Fig. S1 SECM image of GO sheets on Au in presence of I and III. Image size 200 µm. E=0.4 V (I) and E=-0.3V (III) vs Ag/AgCl/KCl 3M in PBS pH 7.4.

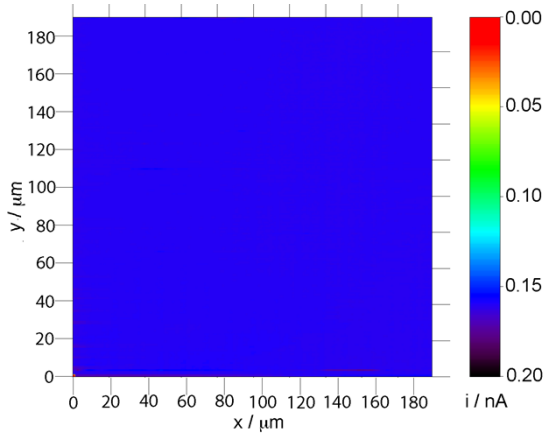

Fig. S2 SiO_x surface with adsorbed reduced GO in presence of III. Image size 200 µm. E=0.4 V vs Ag/AgCl/KCl 3M in PBS pH 7.4.

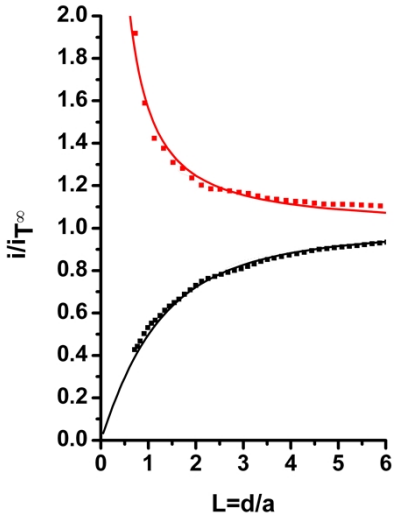

Fig. S3 Theoretical positive (red solid line) and negative (black solid line) feedback approach curves. Experimental approach curves to SiO_x surface in presence of **I** (dashed black line) and to Au surface in presence of **I** (dashed red line).

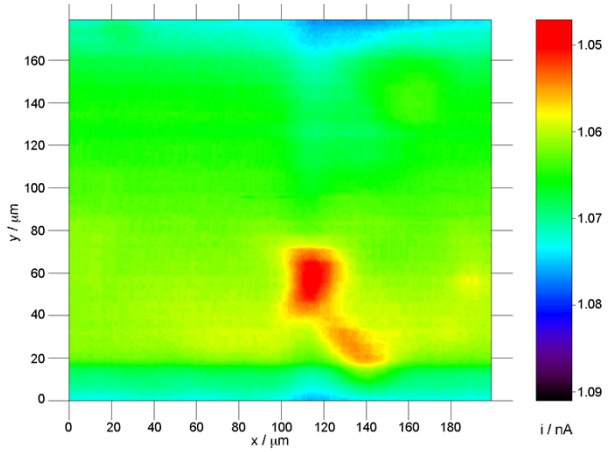

Fig. S4 GO adsorbed on Au surface in presence of FcCOOH. Image size 200 µm. E=0.5 V vs Ag/AgCl/KCl 3M in PBS pH 7.4.

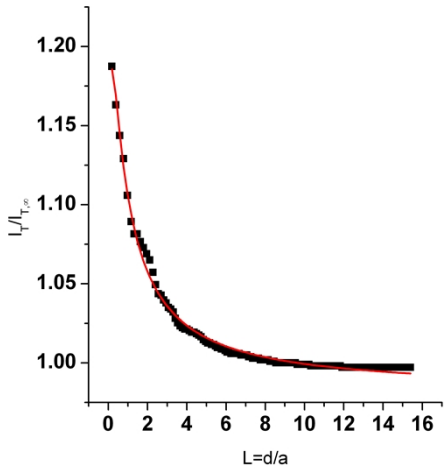

Fig. S5 Experimental approach curve (dotted black line) and fitted curve (solid line) of the tip to GO adsorbed on gold in the presence of FcCOOH 1mM in PBS**.**

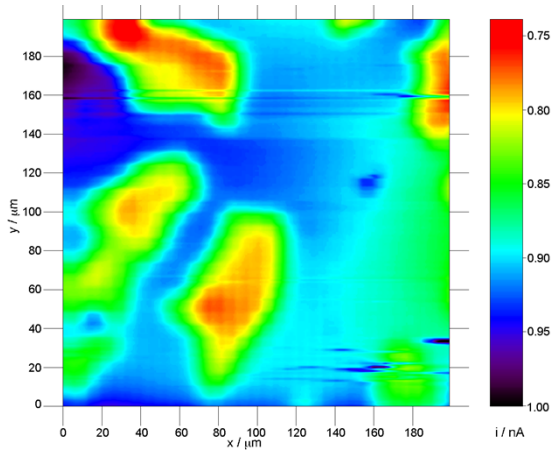

Fig. S6 GO adsorbed on Au surface in presence of $Na_3[IrCl_6]$. Image size 200 µm. E=0.9 V vs Ag/AgCl/KCl 3M in PBS pH 7.4.

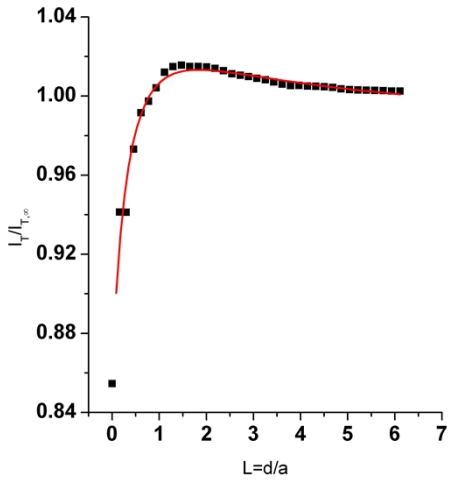

Fig. S7 Experimental approach curve (dotted black line) and fitted curve (solid line) of the tip to GO adsorbed on gold in the presence of $Na_3(IrCl_6)$ 1mM in PBS**.**

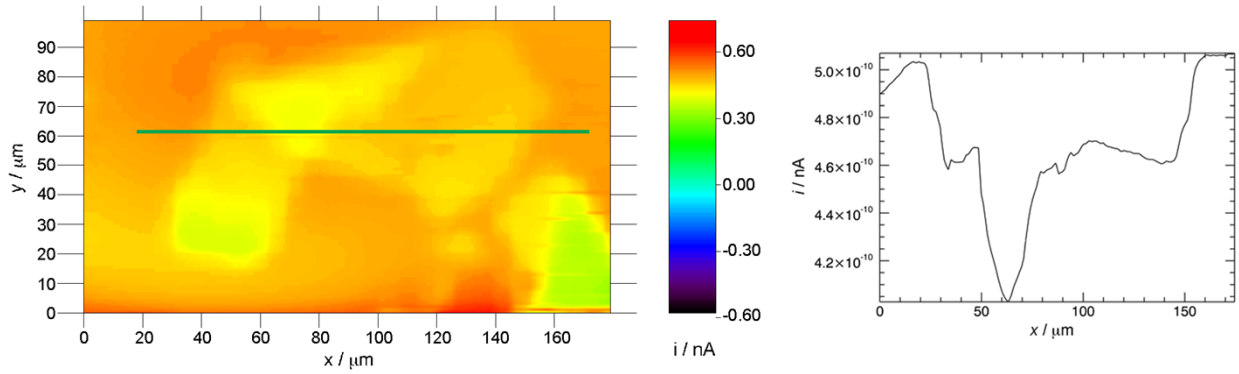

Fig. S8 Left: SECM image of GO on Au using $Na_3[IrCl_6]$ 1 mM in PBS. The folded structure is in green. Right: Current along the line drawn in figure S8 left. Lower currents correspond to higher repulsion and therefore to the presence of a folded GO sheet.

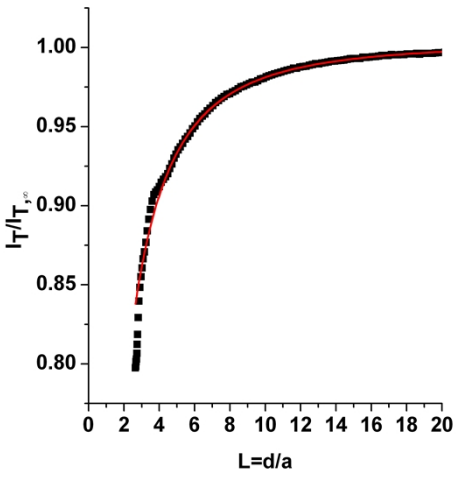

Fig. S9 Experimental approach curve (dotted black line) and fitted curve (solid line) of the tip to RGO adsorbed on SiOx in the presence of FcMeOH 1mM in PBS**.**

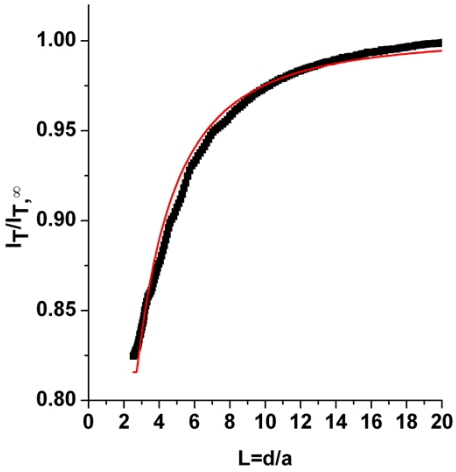

Fig. S10 Experimental approach curve (dotted black line) and fitted curve (solid line) of the tip to RGO adsorbed on SiOx in the presence of $[Ru(NH_3)_6]Cl_3$ 1mM in PBS**.**

Table S1 Summary of the feature of III, IV and V in the experiments. GO on gold.

CONDUCTOR/METAL	RGO/Au		
Molecule:	IV	V	III
	FcCOOH	Na_3 $[IrCl_6]$	Fe(CN)6K4
Molecule charge	NEGATIVE -1	NEGATIVE -3	NEGATIVE -4
GO charge	NEGATIVE	NEGATIVE	NEGATIVE
Substrate	Metal		
Charge Transfer rate to GO	MEDIUM/HIGH K=1.42	LOW K=0.47	LOW K=0.69
Charge Transfer rate to Au	HIGH	HIGH	HIGH
CONTRAST	POOR RESOLUTION	YES	YES

Table S2 Summary of the feature of I, II and II in the experiments. Reduced GO on gold.

CONDUCTOR/METAL	RGO/Au		
Molecule:	I	II	III
	FcMeOH	$Ru(NH_3)_6Cl_3$	Fe(CN)6K4
Molecule charge upon oxidation/reduction	POSITIVE	POSITIVE	NEGATIVE
RGO charge	NEGATIVE	NEGATIVE	NEGATIVE
Substrate	Metal		
Charge Transfer rate to RGO	HIGH	HIGH	HIGH
Charge Transfer rate to Au	HIGH	HIGH	HIGH
CONTRAST	NO	NO	NO

Table S3 Summary of the feature of I, II and II in the experiments. GO sheets on insulating SiOx.

INSULATOR/INSULATOR	GO/SiOx		
Molecule:	I	II	III
	FcMeOH	$Ru(NH_3)_6Cl_3$	Fe(CN)6K4
Molecule charge upon oxidation/reduction	POSITIVE	POSITIVE	NEGATIVE
GO charge	NEGATIVE	NEGATIVE	NEGATIVE
Substrate	Insulator		
Charge Transfer rate to GO	LOW	LOW	LOW
Charge Transfer rate to SiOx	LOW	LOW	LOW
CONTRAST	NO	NO	NO

References

G. Wittstock, T. Asmus and T. Wilhelm, *Fresenius J Anal Chem*, 2000, **367**, 346-351.

R. Cornut and C. Lefrou, *Journal of Electroanalytical Chemistry*, 2007, **608**, 59-66.

R. Cornut and C. Lefrou, *Journal of Electroanalytical Chemistry*, 2008, **621**, 178-184.