ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Graphene Membranes as Novel Preconcentration Platforms for Chromium Speciation by Total Reflection X-ray Fluorescence

Vanesa Romero, Isabel Costas-Mora, Isela Lavilla and Carlos Bendicho*

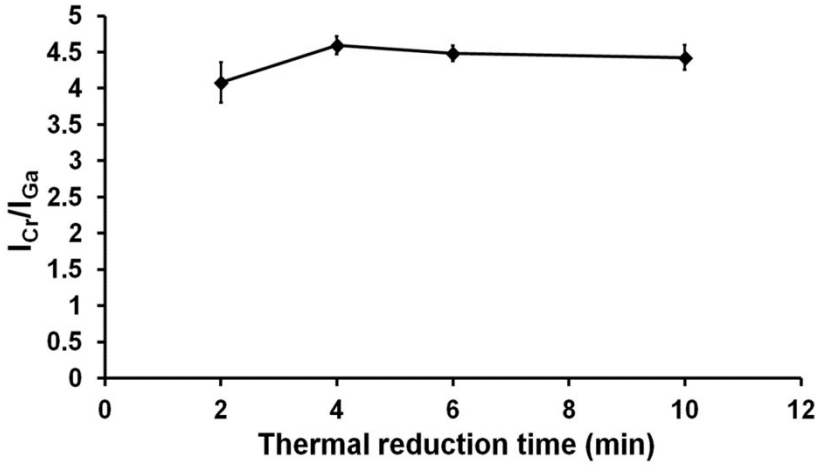
Departamento de Química Analítica y Alimentaria, Área de Química Analítica; Facultad de Química, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain. E-mail: bendicho@uvigo.es; Fax: +34-986-812556; Tel: +34-986-812281

Contents:

The electronic supplementary information (ESI) contains an additional figure (Fig. S1) which show the effect of thermal treatment time for graphene membrane preparation.

ESI also contains the full description for the characterization of graphene membranes including five additional figures, *i.e.,* Fig. S2, Fig. S3, Fig. S4, Fig. S5 and Fig. S6, which show the gel electrophoresis results for GO buffered at pH 1.5, TEM image for synthesized GO, results for AFM characterization of graphene membrane, results for XPS characterization of graphene membrane and GO, and results for TOF-SIMS measurements of graphene membrane with retained Cr (VI), respectively.

Fig. S1. Influence of thermal treatment time for GO reduction and synthesis of graphene membranes



Characterization of graphene membranes

Gel electrophoresis studies

In order to test the charge of the functional groups present in graphene membranes used under sorption conditions, gel electrophoresis was applied. By assuming that functional groups in graphene membranes come from GO (precursor), we used aqueous GO colloids for analysis. The agarose gel containing GO aliquots was buffered at pH 1.5 and a voltage of 90 V was applied for 30 min. We observed that GO moves to negative terminal, hence indicating the presence of positive charge on GO (Fig. S2). We can assume that functional groups are positively charged under sorption conditions, which facilitates the electrostatic interaction with the dichromate anion.

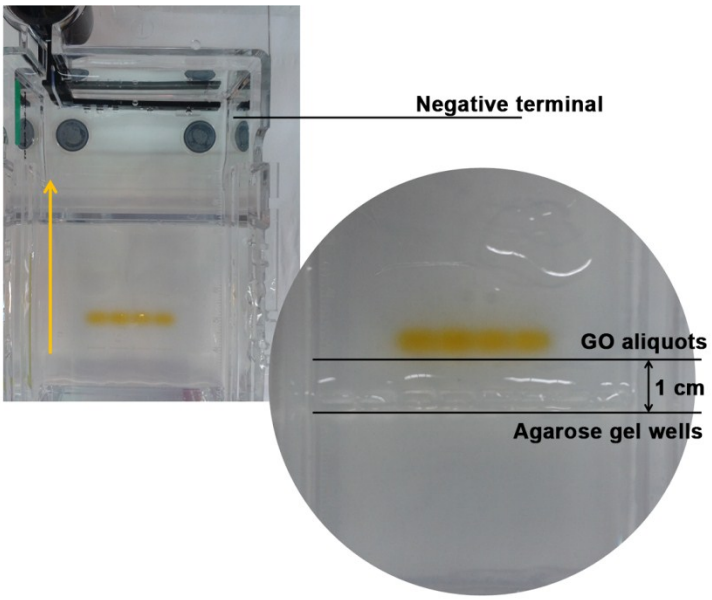


Fig. S2. Gel electrophoresis result for GO sample buffered at pH 1.5

TEM and AFM studies

The synthesized GO was characterized by TEM. As can be see in Fig. S3, GO is well-exfoliated giving rise to irregularly-shaped nanosheets (60 nm in length on average).

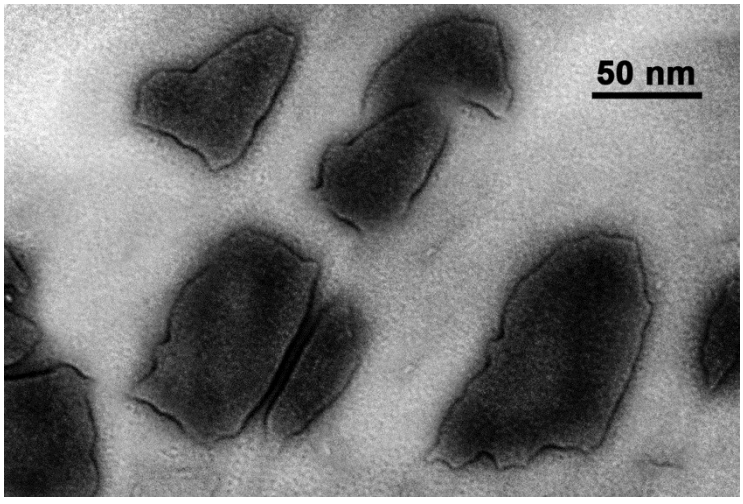


Fig. S3. TEM image for synthesized GO (precursor for graphene membrane preparation)

Besides, graphene membranes were characterized by mechanical profilometry and AFM. Analyses provided suitable information about surface morphology, thickness and

roughness (Fig. S4). Two different graphene membranes using different GO mass, *i.e.* 200 μg GO (M1) and 400 μg GO (M2), were characterized. As expected, membrane thickness increases on increasing GO mass used as precursor. Thickness for M1 and M2 was 122 nm and 193 nm, respectively. Taking into account that the apparent thickness of a graphene monolayer is 0.33 nm,[1] we can consider that a multilayer membrane is fabricated following our approach, which facilitates its handling without the need for a solid substrate as support. Since the drop-casting strategy is used for preparation of membranes, graphene monolayers may be randomly distributed, *i.e.* upon thermal reduction, monolayers are formed and stacked resulting in thicker multilayer membranes. In addition, roughness was also evaluated, a surface nanoroughness of 22.14 and 31.38 nm being obtained for M1 and M2, respectively.

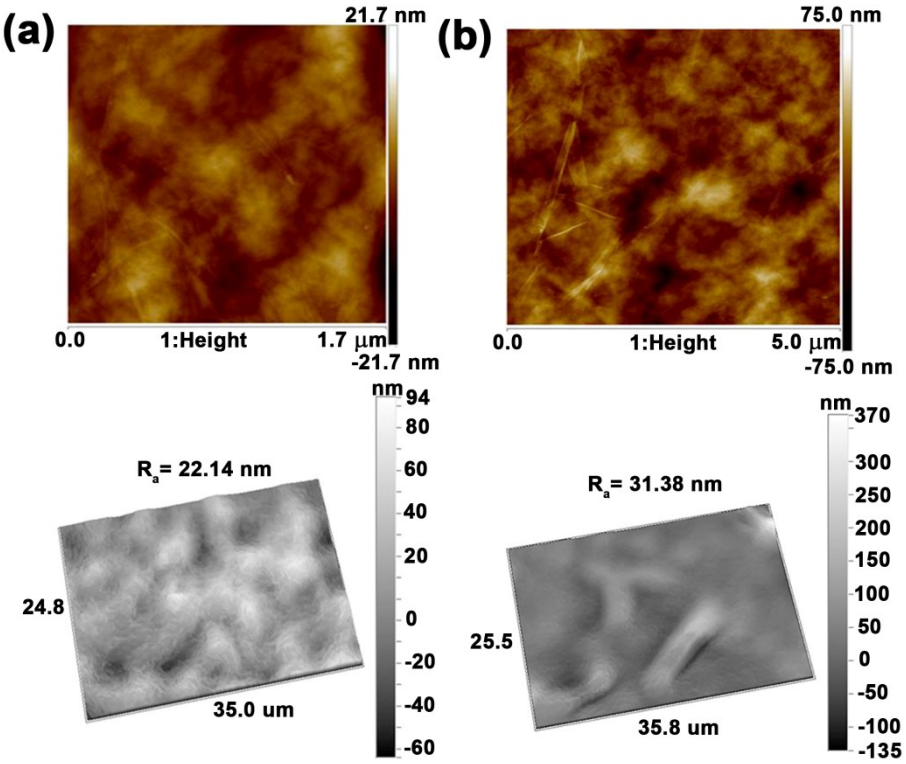
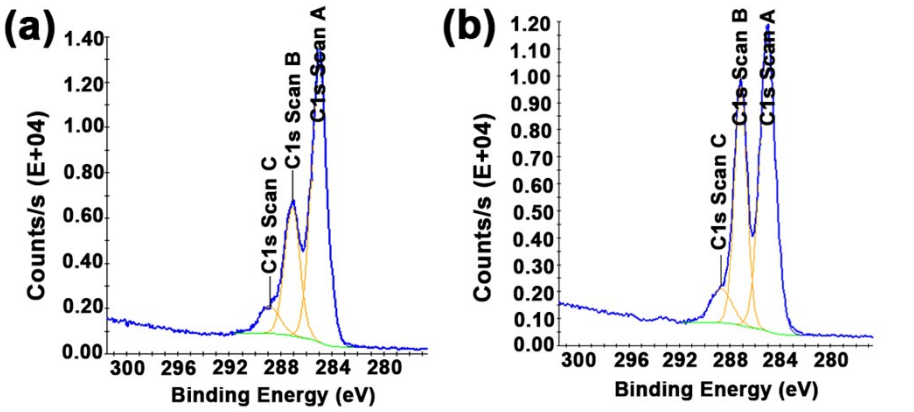


Fig. S4. AFM and mechanical profilometry characterization. (a) Graphene membrane (M1) prepared using 200 μg GO as precursor. (b) Graphene membrane (M2) prepared using 400 μg GO as precursor.

This fact is remarkable, since it accounts for sample permeability through the membrane and interaction of Cr (VI) with functional groups. For highly smooth surfaces with very low surface roughness, water cannot permeate and interact with graphene, which acts as a barrier.[2] Using the drop-casting strategy followed by mild thermal reduction, complete reduction to pristine graphene is not achieved. Nanoroughness graphene membranes with lattice defects that promote the occurrence of holes along the layers of the membrane are obtained, which are suitable for interaction with aqueous samples.

XPS studies

In order to ensure the presence of non-reduced functional groups in graphene membranes, characterization by XPS was performed. Fig. S5 shows XPS results for M1 and GO.



Name	Peak BE	Bond
C1s Scan A	285.00	C-H/C-C
C1s Scan B	287.09	C-OH/C-O-C
C1s Scan C	288.84	C=O/O-C=O

Name	Peak BE	Bond
C1s Scan A	285.00	C-H/C-C
C1s Scan B	287.15	C-OH/C-O-C
C1s Scan C	288.69	C=O/O-C=O

Fig. S5. High resolution C1s XPS spectrum (a) Graphene membrane prepared using 200 µg GO as precursor (M1) (b) GO

The high resolution C1s spectrum of graphene membrane (Fig. S5a) shows a strong peak at 285.00 eV, which can be attributed to graphitic carbon (C-C and C-H bonds). A peak at 288.84 eV can be ascribed to carboxyl functional groups, *i.e.* O-C=O and C=O. In addition, a peak at 287.09 eV is assigned to C-OH and C-O-C groups, thus showing the presence of non-reduced functional groups coming from GO. Furthermore, the high resolution C1s spectrum for GO is also evaluated (Fig. S5b). Results show three main peaks at 285.00, 287.15 and 288.69 eV, which are assigned to C-C/C-H, C-OH/C-O-C and C=O/O-C=O, respectively.[3,4,5] In order to compare both samples, results for the relative percentage (Rel%) of functional groups present were evaluated. The Rel% of C-C/C-H increases for graphene membranes (64%) compared to GO (56%), thus indicating that thermal reduction occurs to some extent. Besides, the Rel% of C-OH/C-O-C is 36% and 28% for GO and graphene membranes, respectively. This result shows that complete reduction to pristine graphene is not achieved, so residual non-reduced functional groups are present in the as-prepared graphene membranes.

TOF-SIMS studies

Finally, graphene membrane characterization by TOF-SIMS was performed. Results provided information about the distribution of Cr (VI) onto the graphene membrane.

Two samples, *i.e.* graphene membrane without analyte (as blank) and graphene membrane after sorption of Cr (VI) (20 μg L^{-1}), were analyzed. Results showed that after sorption, the Cr (VI) content was ten times higher as compared to the blank (Fig. S6a).

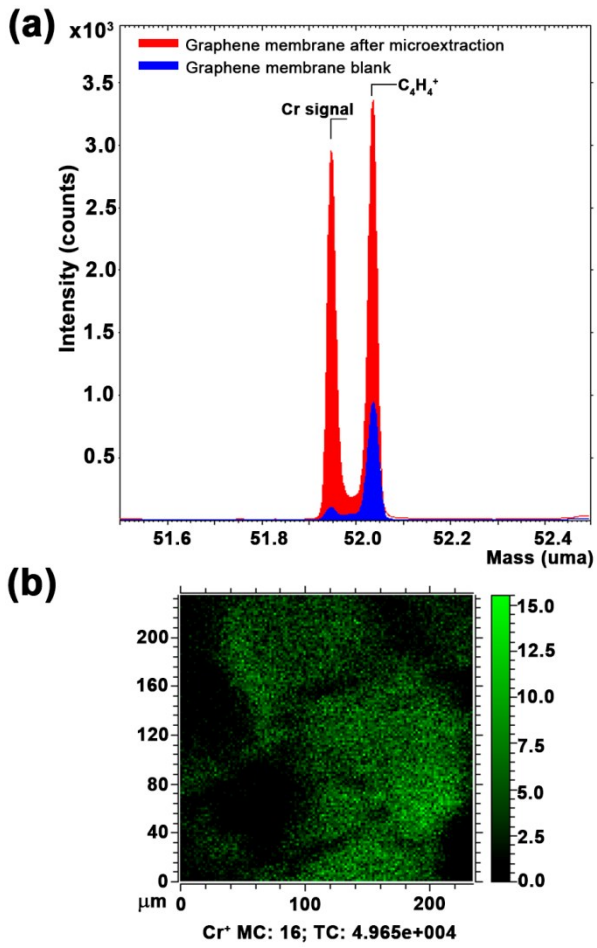


Fig. S6. (a) TOF-SIMS spectrum for graphene membrane after sorption of Cr (VI) and graphene membrane blank (b) 2D Map-Chemical image for chromium distribution onto graphene membrane

The signal for Cr (VI) in graphene membranes used as blank can be attributed to impurities from the reagents used for synthesis of GO, which is used as precursor in the thermal reduction process. Besides, 2D maps show that Cr (VI) is well-distributed (Fig. S6b), thus supporting the results from adsorption isotherm studies, where a better adjustment using the Langmuir model is found. It can be concluded that functional groups are uniformly distributed and bind Cr (VI) in the whole surface.

REFERENCES

1 A. Gupta, G. Chen, P. Joshi, S. Tadigadapa and P. C. Eklund, *Nano Lett.*, 2006, **6**, 2667–2673.

2 T. Kim, J. H. Kang, S. J. Yang, S. J. Sung, Y. S. Kim and C. R. Park, *Energy Environ. Sci.*, 2014, **7**, 3403–3411.

3 T. Kuila, S. Bose, A. K. Mishra, P. Khanra, N. H. Kim and J. H. Lee, *Prog. Mater. Sci.*, 2012, **57**, 1061–1105.

4 R. Sitko, P. Janik, B. Zawisza, E. Talik, E. Margui and I. Queralt, *Anal. Chem.*, 2015, **87**, 3535–3542.

5 B. Dai, L. Fu, L. Liao, N. Liu, K. Yan, Y. Chen and Z. Liu, *Nano Res.*, 2011, **4**, 434–439.