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Vertical assembly of few-layer graphene decorated with iron oxide nanoparticles on gold surfaces

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Precise assembly of exfoliated graphene sheets on electrode surfaces plays a major role for next generation electrodes to be used in sensors, batteries, supercapacitors and other types of energy storage devices. Here, we achieve vertical assembly of sulfonated, few-layer graphene on a metal surface. The few layer graphene flakes were extensively decorated with dopamine capped iron oxide nanoparticles utilizing electrostatic interactions between the nanoparticles and the graphene sheets. The attached nanoparticles drived the assembly of the graphene nanosheets into a vertical orientation on a gold surface under the effect of a moderate external magnetic field.

1. Introduction

Graphene has emerged as one of the most prodigious classes of materials due to its superior mechanical strength and interesting electronic properties.[1] Several devices have recently been designed, applying graphene in electronic junctions and electrodes.[2] Particularly in electrochemistry, graphene represents an excellent electrode material for supercapacitors,[3] lithium batteries,[4] and electrochemical sensors.[2a]

The construction of vertically aligned graphene electrodes has been proposed as a possible route to increase the specific surface area, enhancing the charge and power density of a resulting supercapacitor device,[5] or the sensitivity of electrochemical sensors.[5a]

Chemical vapor deposition is commonly applied to grow vertically oriented graphene nanosheets on nickel substrates.[6] This process produces very well defined, vertically oriented graphene structures. However, this method is costly, time-consuming and requires high vacuum conditions as well as high temperatures. Such characteristics impede the usage of chemical vapor deposition methods for growing vertically oriented graphene nanostructures over a broad variety of substrates, and thus limiting the construction of more versatile devices.

Alternatively, top-down processing can be applied. It is known that in high magnetic fields reduced graphene sheets, dispersed in a solvent, align parallel to the magnetic field lines. The graphene sheets can then be deposited on a surface, leading to conducting surfaces with very high specific surface area.[7] While these are very elegant processes; the lack of susceptible magnetic centers per nanosheet requires the application of high power fields for the alignment, impeding a more widespread application of this method and its rapid transfer into industrial manufacturing processes.[7]

Hence, a facile wet-processing technology using moderate field magnets to obtain vertically aligned graphene surfaces would enable low-cost and large area processing for next generation batteries, super capacitors, electrochemical sensors and fuel cells. In this sense, we hypothesize that an extensive decoration of graphene sheets with magnetic nanoparticles will enable the use of commercially available permanent magnets to produce vertically oriented graphene surfaces.

Single layer graphene-iron oxide nanoparticles composites are commonly produced by growing the particles on the surface of graphene oxide with the concomitant reduction of the latter.[8]

In addition; there are a few reports of an alternative procedure for decorating single graphene oxide sheets with previously formed iron oxide nanoparticles (**IONPs**) by taking advantage of electrostatic interactions.[9]

Here we propose the decoration of few-layer graphene (**FLG**) nanosheets with previously formed IONPs utilizing electrostatic interactions to produce a **FLG-IONPs** composite with a large number of magnetic centers. Under the effect of a magnetic field from commercial neodymium iron boron (NIB) permanent magnets, the IONPs should induce a vertical alignment of the graphene nanosheets, thus facilitating the oriented deposition of FLG on metallic substrates.

We deliberately selected FLG for our study on the magnetic manipulation and orientation. Our material of choice exhibits

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

two important advantages over single layer graphene. First, the chemical modification of the outermost layers does not deteriorate the electronic and conductive properties of the entire sheet, and secondly, the edge-on assembled graphene flakes have sufficient mechanical integrity to stand up perpendicularly to the surface and do not fold back onto the surface, which is often the case when using single layer graphene.[10]

The colloidal stability of the graphene-IONP composite material should play an important role during the magnetically guided vertical assembly onto the electrodes as the necessary rotational motion could be hindered for large aggregates. Therefore, two steps were identified to be crucial for producing a well dispersible FLG-IONP nanocomposite: (i) the preparation of FLG and IONPs precursors (with chemical moieties of opposite charges) both with high colloidal stability, and (ii) a method for mixing both components so as to produce stable dispersion of FLG-IONP nanocomposites.

Succinctly, the objectives of the present study were, first, to synthesize and characterize a sulfonated few-layered graphene (Sulf-FLG) material that could be easily dispersed in polar organic solvents; secondly, to produce super paramagnetic iron oxide nanoparticles capped with a positively charged dopamine protective layer (IONP-Dop);thirdly, to decorate Sulf-FLG with IONP-Dop, producing a Sulf-FLG@IONP-Dop nanocomposite with high colloidal stability; and finally, to vertically assemble the Sulf-FLG@IONP-Dop composite over the surface of gold surfaces and electrodes under the effect of a NIB permanent magnet.

2. Experimental

2.1 General

All reagents were purchased from Sigma Aldrich and used as received. Expanded graphite was obtained as described in Ref. 11.

All substrates were created by dividing a Silicon wafer coated with a layer of vaporized gold (from Aldrich) into approximately 1 cm^2 pieces.

TEM measurements were carried out on a 200 kV FEI Tecnai20.

SEM analyses were carried out on a Hitachi UHR FE-SEM SU9000 and on a Hitachi S-4800 field emission microscope, operating between 2.0 kV and 5.0 kV. Elemental mapping was performed by using an energy-dispersive X-ray (EDX) detector from Oxford (model Xmas 80) attached to the Hitachi UHR FE-SEM SU9000 microscope; operating between 10 kV and 15 kV.

Raman Spectra were recorded using a Renishaw Invia Raman microscope equipped with two Peltier-cooled CCD detectors and a Leica microscope with two gratings with 1200 and 1800 lines/mm and band-pass filter optics.

Infrared spectra were recorded using a Rayleigh WQF-510 FT-IR spectrophotometer. Each spectrum was averaged over 32 scans

collected at 2 cm^{-1} resolution. Samples were prepared as of KBr pellets containing approximately 2 wt % of the sample of interest.

Cyclic voltammetric determinations were recorded with a 384B EG&G Princeton Applied Research Polarographic Analyzer Model controlled by home-built software.

Electrochemical measurements of gold substrates were carried out by means of a Teflon cell with a circular hole in the bottom where the gold substrates were in contact with the electrolyte solution. Pictures and details of the construction of such special electrochemical cell can be found in the ESI. Ag/AgCl (sat) was used as reference and a 2 cm^2 platinum sheet linked to a platinum wire was used as counter electrode. Cyclic voltammetry experiments were recorded in a $K_3[Fe(CN)_6]$ solution (0.01 M) containing Na_2SO_4 (0.1 M), at a scan rate of 0,1 V/s.

2.2 Synthesis of Sulf-FLG

Expanded graphite (EG) (50,4 mg) was introduced in a round-bottom flask containing in 1-cyclohexyl-2-pyrrolidone (10 mL) and sonicated for 30 min. Subsequently, 2,5-diaminobenzenesulfonic acid (681.2 mg ; 3.6 mmol) was added to the flask and HCl (0.5 M) was added until pH=1 was achieved. The mixture was sonicated for another 30 minutes. Later, $NaNO_2$ (250 mg; 3.6 mmol), were dissolved in the minimum amount of water, and added to the flask. Sonication was maintained for an hour. The addition of $NaNO_2$ produced the generation of NOx gases and the dispersion changed to a greenish grey colour. After 1h of reaction, acetonitrile was added (20 mL) and the mixture was submitted to centrifugation at 4000 rpm for 15 minutes. Under such conditions, a grey solid precipitated and a yellowish-brown supernatant was discarded. The solid material was then dispersed in DMF (10 ml) assisted by sonication, mixed with ethanol (20 mL) and subsequently submitted to centrifugation (4000 rpm). Each time the yellowish supernatant was discarded and the process was repeated 5-7 times until the supernatant became colorless.

2.3 Synthesis of IONPs

In a 50 mL three-necked round-bottom flask, iron (III) oleate (1.6 mg) was dissolved in oleylamine (10 mL). In order to remove the residual solvents the reactants were heated to 100 °C, under a blanket of N_2 and vigorous stirring for 1 h. Afterwards, the mixture was heated up to 320 °C and maintained for 1.5 h for producing the desired nanoparticles. After that period of time, the dark brown dispersion of IONPs was cooled to room temperature. Acetonitrile (10 mL) was then added to the reaction mixture and the nanoparticles were collected by magnetic concentration and subsequent removal of the solvent. The particles were washed through two cycles of sonication in acetonitrile and magnetic collection followed by drying in vacuum at 60 C°. The well-dried powder was dispersed in dichloromethane under sonication to obtain the stock solution of 5 mg/mL for the ligand exchange process.

2.4 Recapping IONPs with dopamine

In a 30 mL glass bottle, 3 mL of the IONPs dispersion (5 mg/mL) was mixed with 9 mL of an acidic (pH≈4, HCl) DMSO solution containing dopamine hydrochloride (60 mg). The mixture was initially sonicated for 15 min and kept under vigorous magnetic stirring for 24 h. Subsequently, acetone (15 mL) was added to the mixture and the IONPs were collected by magnetic concentration and solvent removal. The collected IONPs were then dispersed in 3 mL of DMSO for a final concentration of 5 mg/mL approximately.

2.5   Decoration of Sulf-FLG with IONP-Dop

A dispersion of Sulf-FLG (6 mg dissolved in 3 mL of DMSO containing approximately 150 mg of tetrabutyl ammonium hydroxide) was added drop wise to a dispersion of IONP-Dop (15 mg in 3 mL of DMSO) under sonication. After the addition was complete the mixture was continuously sonicated for 20 min and shaken for another 20 min. For purification, the mixture was submitted to centrifugation at 4000 rpm. The precipitated Sulf-FLG@IONP-Dop was then separated from the unassociated IONPs, which remained dispersed in the DMSO supernatant. The Sulf-FLG@IONP-Dop composite was then redispersed in DMSO and purified by magnetic extraction. These purification steps were repeated two more times to eliminate all the nonmagnetic contaminants that could sediment together with the Sulf-FLG@IONP-Dop composite during the centrifugation process.

2.6   Vertical assembly of Sulf-FLG@IONP-Dop on gold surface

Previous to the magnetically guided assembly of Sulf-FLG@IONP-Dop, the gold substrates were immersed in piranha mixture (H_2O_2:H_2SO_4 1:1) for 12 h and rinsed with bidistilled water. Subsequently, the gold substrates were immersed and stored in HCl (1 M) for 15 min for eliminating any possible oxide from the surface. After the immersion in HCl solution a gold substrate was copiously rinsed with bidistilled water and introduced in 20 mL of a cysteamine methanolic solution (10^{-2} M) for 24 hours in a closed container. The modified Au substrate was copiously rinsed with bidistilled water before used to assemble the Sulf-FLG@IONP-Dop composite.

The gold substrates modified with a monolayer of cysteamine were introduced in an inclined plastic centrifuge tube containing 10 mL of pure methanol. A commercial permanent magnet (NIB Sintered 1.2 T) was located adjacent to the bottom of the tube in parallel disposition with respect to the plane of the gold substrate (See pictures of the system employed on ESI).

Once the above described system was set up, 100 µL of the Sulf-FLG@IONP-Dop DMSO dispersion were added drop-wise to the methanol containing tube. Under such conditions the Sulf-FLG@IONP-Dop material was deposited on top of the gold substrate within an hour. Subsequently, the methanol inside the tube was removed until the top of the square gold substrate touched the liquid-air interface. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, 50 mg) and N-hidroxosuccinimide (100 mg) were then carefully added to the solution and the container was opened to allow further evaporation of methanol. When the level of solvent decreased below the bottom of the substrate, the magnet was removed. The substrate was then introduced into an open vial containing methanol (15 mL)
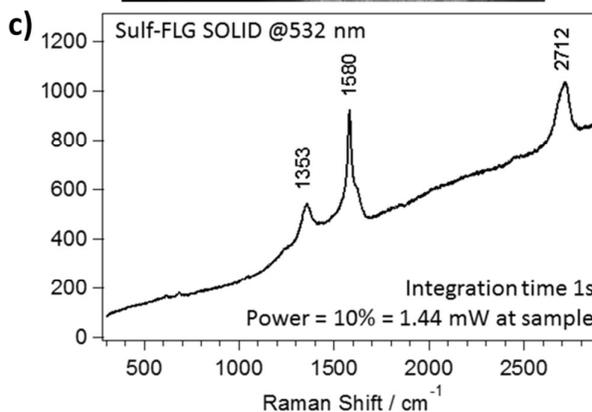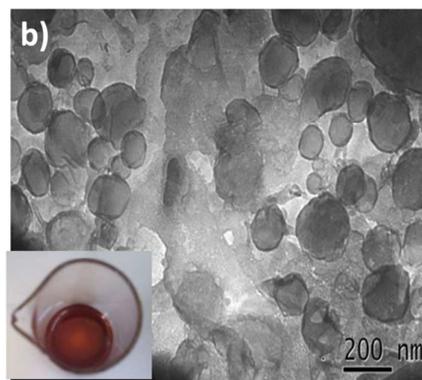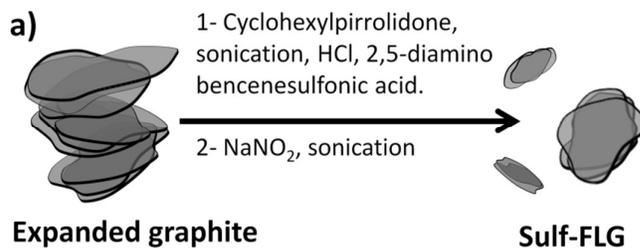
Fig. 1 a) Scheme of synthesis of Sulf-FLG. b) Transmission electron micrographs of a dispersion of Sulf-FLG. Inset, picture of Sulf-FLG dispersions. c) Raman spectrum of Sulf-FLG.

and submitted to gentle manual shaking to remove all molecular contaminants. Methanol was then discarded and the previous procedure was repeated two more times. The substrate was finally dried at room temperature in vacuum.

2.7 Electrodeposition of Pt and electroxidation of methanol.

The electrodes modified with the vertically oriented graphene were introduced into a solution of $K_2[PtCl_6]$ (10 mM), containing H_2SO_4 (0,5 M) and submitted to a potential of -0,25 V for 10 s to electrodeposit metallic platinum. As control experiment a gold electrode was also submitted to the electrodeposition of platinum.

The oxidation of methanol was carried out by immersing each electrode in a methanol aqueous solution (1M), containing H_2SO_4 (0,5 M), and at scan rate of 50 mV/s.
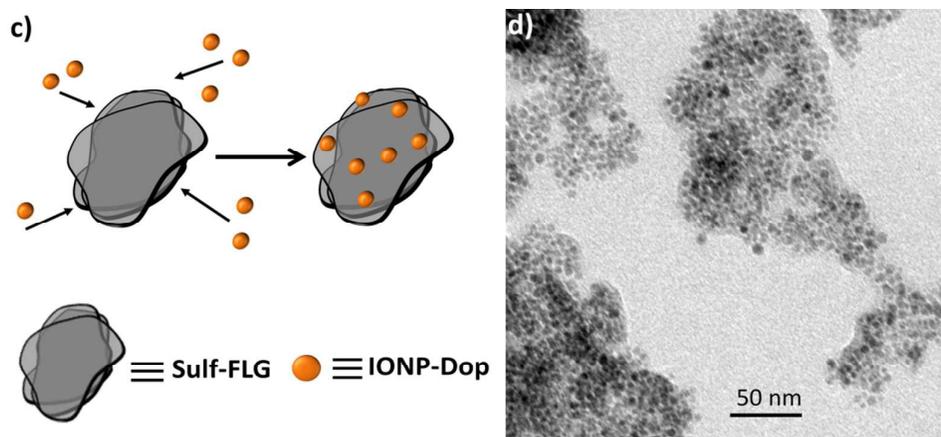
Fig. 2 a) Scheme of synthesis of Sulf-FLG@IONP-Dop; b) TE micrographs of Sulf-FLG@IONP-Dop.

3   Results and discussion

3.1 Synthesis of Sulf-FLG

The scheme of synthesis of Sulf-FLG started by choosing expanded graphite as the precursor material since it can be efficiently used to produce FLG during the sonication treatment in different solvents (Fig. 1).[11, 13] Sonication assisted graphene exfoliation is commonly carried out using high polar aprotic organic solvents like N-alkyl pyrrolidone that are miscible with aqueous solutions. Therefore, we reasoned that the exfoliation process of expanded graphite could be simultaneously carried out with a chemical reaction for the incorporation of negatively charged benzenesulfonic acid groups to the outermost layers of the *in situ* formed FLG. For this, 2,5-diaminobenzenesulfonic acid and HCl were dissolved in 1-cyclohexyl-2-pyrrolidone. During the sonication the solvent became gray colored. With the addition of $NaNO_2$ the diazotization reaction started, the evolution of brown NO_2 gases was observed and the solution started to gain a yellow-brownish color, which is probably due to the formation of 2,5-diaminobenzenesulfonic acid azo-compounds.

The benzenesulfonic acid groups confer solubility to the FLG material in aqueous NaOH solution as well as in DMSO solutions containing tetrabutylammonium hydroxide (see inset of Fig. 1b). These dispersions remained stable over months. TEM analysis reveals Sulf-FLG nanosheets with diameters of 151.30 ± 35.23 nm (Fig. 1b, ESI-1).

In order to obtain information about the final state of Sulf-FLG material a Raman spectroscopic exploration was carried out (Fig. 1-c). The 2D band (commonly denoted as G´) appeared at frequencies above 2700 cm^{-1}, with lower intensity than the G band. This intensity and frequency profile indicates the presence of several graphene layers per FLG platelet.[14] The D band at 1350 cm^{-1} indicates the presence of sp^3 carbons, which can be attributed to the incorporation of sulfonate moieties and some oxygen

containing defects (See FTIR spectra on ESI 1). The ratio between the G and D bands clearly indicates a majority of sp^2 carbons.[14] This observation strongly suggests that only the exposed outermost graphene layers of each FLG platelet turned out to be modified during the process of sulfonic acid functionalization. In a previous report, where a single layer graphene material was submitted to a similar sulfonation process a great amount of sp^3 carbons was generated with the consequent deterioration of the electronic properties.[15]

3.2 Synthesis of IONP-Dop

Solvothermal methods very frequently produce small and monodisperse IONPs. Both properties were identified to be crucial for obtaining the Sulf-FLG@IONP-Dop (see Section 3.3). The IONPs obtained through the solvothermal decomposition of the iron oleate complex resulted of 9.02 ± 1.15 nm as it can be seen in ESI 2. Such particles resulted capped with a hydrophobic oleylamine monolayer that does not form stable interactions with our Sulf-FLG. In order to increase the affinity of such IONPs towards our Sulf-FLG, the IONPs were submitted to a ligand exchange reaction in DMSO with dopamine hydrochloride. After the interaction with dopamine the IONPs displayed a complex set of IR signals corresponding to phenyl deformation, NH vibrations, and so forth. (See ESI 2) Such result clearly indicates the incorporation of dopamine to the surface of the particles.

The X-Ray diffraction pattern and magnetic susceptibility results of our IONP-Dop are consistent with previous analyses of superparamagnetic Fe_3O_4 particles (See ESI 2).

3.3 Synthesis of Sulf-FLG@IONP-Dop nanocomposite

All experiments for decorating Sulf-FLG with IONP-Dop revealed one important conclusion: highly dispersible Sulf-FLG@IONP-Dop composites were almost exclusively obtained when Sulf-FLG dispersions were added to concentrated dispersion of IONP-Dop (5mg/mL or higher). The use of dilute solutions of IONP-Dop, as well as an inversion in the order of addition, produced non-dispersible precipitates.
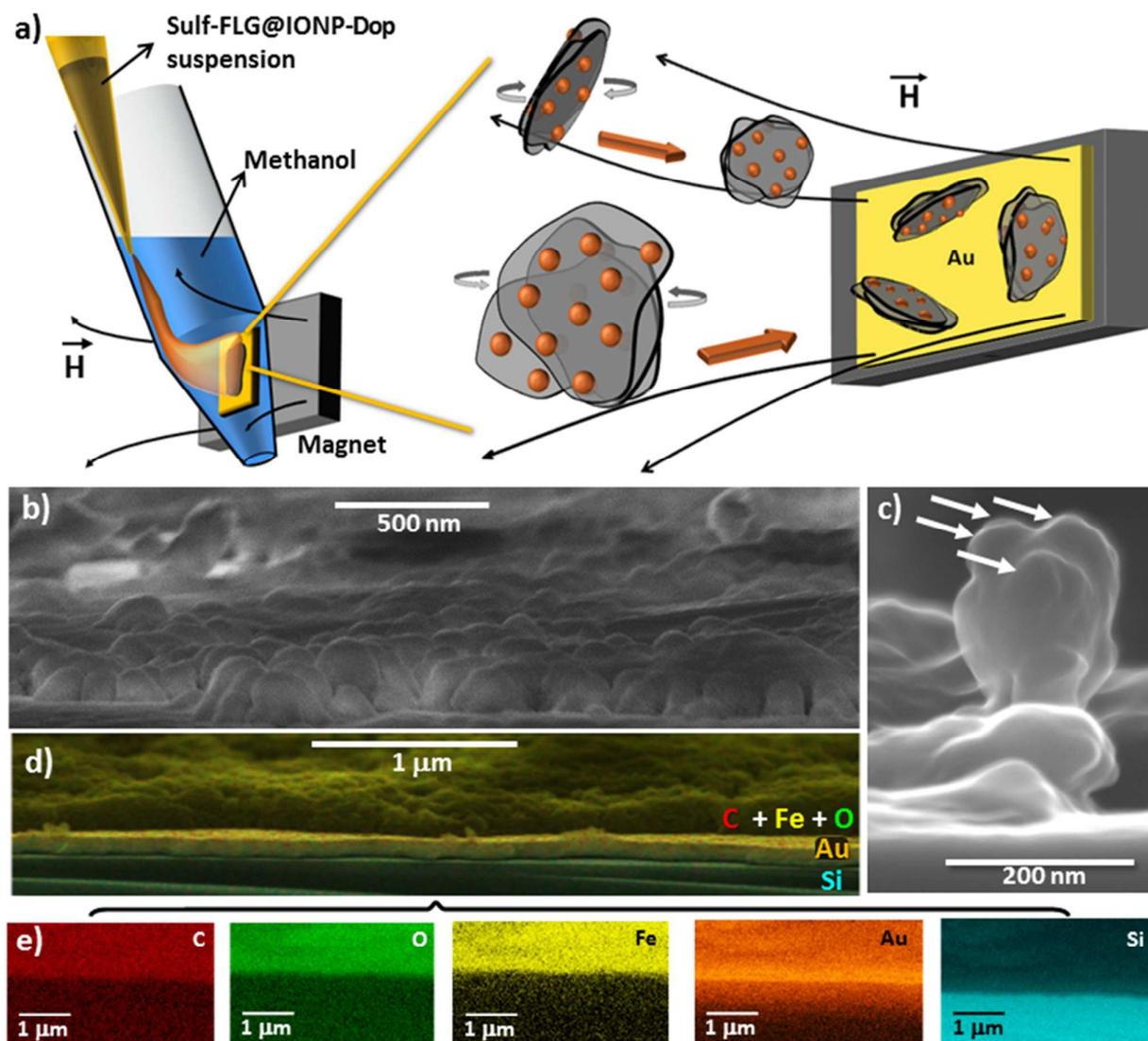
Fig. 3:a) Scheme of the association of the Sulf-FLG@IONP-Dop to the gold substrate. b) Low angle SEM image of vertically assembled Sulf-FLG@IONP-Dop on gold surfaces. c) High resolution SEM of a vertically oriented Sulf-FLG@IONP-Dop sheet. Arrows indicate different graphene layers d) Elemental analysis of gold surfaces modified with vertically assembled Sulf-FLG@IONP-Dop. e). Element distribution of gold surfaces modified with vertically assembled Sulf-FLG@IONP-Dop.

Probably, during mixing, highly concentrated IONP-Dop dispersion quickly saturates the negatively charged surface of Sulf-FLG (Fig. 2a). By contrast, when using low concentration of the positively charged particles the formation of insoluble precipitates can result from the association of IONP-Dop acting as bridge between flakes of Sulf-FLG. Regardless of the precise process of mixing, any possible insoluble precipitates formed was discarded and only the suspended Sulf-FLG@IONP-Dop nanocomposites were used in further procedures.

By TEM analysis, it can be observed that our method produced an extensive decoration of Sulf-FLG with IONP-Dop (Fig. 2b). In addition, it can be observed that all IONP-Dop particles are attached to a Sulf-FLG sheet. The large association of IONP-Dop to the outermost layers of Sulf-FLG, produced a large

mass increase of each flake of the obtained Sulf-FLG@IONP-Dop in comparison to its IONP-Dop precursor. This difference in weight resulted crucial for rapid separation of Sulf-FLG@IONP-Dop from the excess of IONP-Dop by simple centrifugation at 4000 rpm.

The DMSO dispersions of the obtained Sulf-FLG@IONP-Dop remained stable for weeks.

3.4 Magnetically guided vertical assembly of Sulf-FLG@IONP-Dop over Au surfaces.

For the alignment of Sulf-FLG@IONP-Dop in a magnetic field and their assembly onto a substrate, we decided to apply gold substrates carrying a self-assembled monolayer of cysteamine. Graphene edges frequently contain carboxylic acid groups.[16] Therefore, the cysteamine SAM was used to covalently attach

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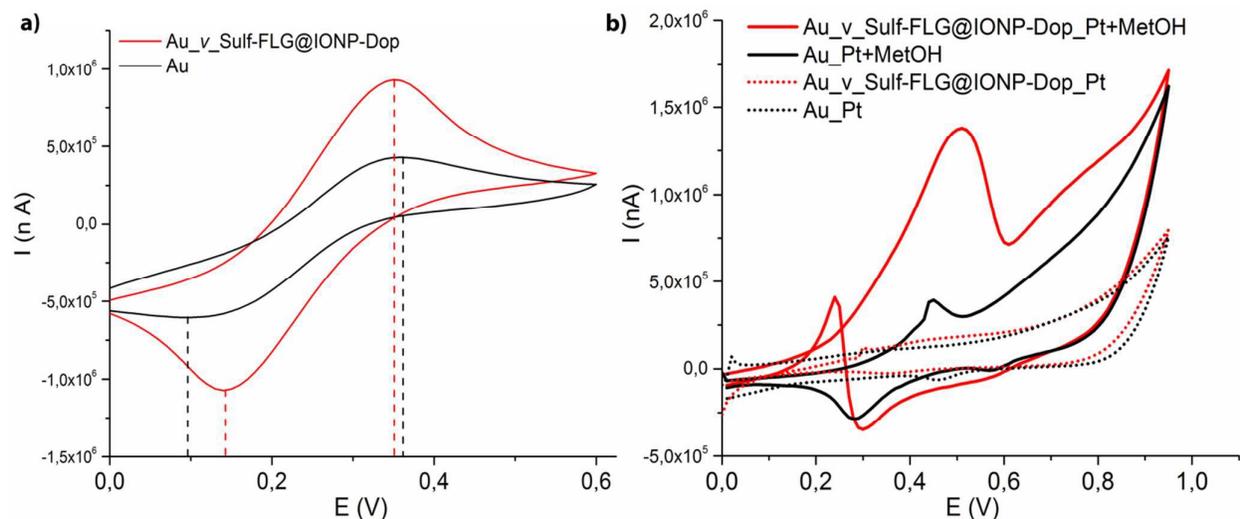
Fig. 4. a)Cyclic voltammetry of a $K_3[Fe(CN)_6]$ solution recorded with a Au and Au_*v*_Sulf-FLG@IONP-Dop electrode. b) Cyclic voltammetry electrooxidation curves of methanol solution using a Au-Pt and Au_*v*_Sulf-FLG@IONP-Dop_Pt electrodes.

the vertically oriented Sulf-FLG@IONP-Dop nanosheets through amide coupling via carbodimide chemistry (See 2.6 section).

To conduct the magnetically guided assembly of Sulf-FLG@IONP-Dop onto the gold surface, the simple setup described in Section 2.6 was utilized. The gold substrate (modified with a SAM of cysteamine) was immersed in methanol to reduce the viscosity of the mixture and thus allow the fast magnetic migration of Sulf-FLG@IONP-Dop to the substrate. The substrate was fixed vertically to prevent the Sulf-FLG@IONP-Dop adhesion to the substrate through sedimentation. The Sulf-FLG@IONP-Dop dispersion in DMSO was added drop wise to the tube, as depicted in Fig. 3a (a photograph of the experimental setup can be found in ESI-3).

During the assembly, two processes are concurrently occurring: 1-) the IONPs attached to each graphene nanosheet orient the FLG along the magnetic field lines, leading graphene flakes perpendicularly aligned with respect to the surface; and 2-) Sulf-FLG@IONP-Dop sheets are drawn towards the gold surface, due to the magnetic field exerted by the permanent magnet, leading to the covalent attachment of vertically aligned FLG on the surface (Fig. 3a).

To analyze this assembly, high resolution SEM and EDX elemental analyses were performed (Fig. 3b-e; also, more images can be found in ESI 4). Vertically oriented graphene nanosheets, with diameters of several hundred nanometers can be observed in the SEM images (Fig. 3b). When a single vertically oriented nanosheet was zoomed-in, its multilayer nature became observable with clearly defined individual edges from each of the stacked graphene sheets (see Fig. 3c). An EDX elemental analysis corroborates that the structures observed in figure 3b-c indeed correspond to vertically oriented nanosheets, with signals for C, Fe and O (See Fig. 3d-

e). The layer of gold and the underlying silicon substrate are also clearly identifiable (see Fig. 3e, ESI 4).

3.5 Electrochemical properties of an Au electrode modified with vertically assembled Sulf-FLG@IONP-Dop electrode

Gold substrates with vertically oriented Sulf-FLG@IONP-Dop (Au_*v*_Sulf-FLG@IONP-Dop) were examined as electrochemical working electrodes by means of a Teflon cell with a circular aperture in its bottom (ESI 5).

A cyclic voltammetry of a $[Fe(CN)_6]^{3-}$ solution recorded by means of Au_*v*_Sulf-FLG@IONP-Dop electrode displayed a 117% increase in current (for the corresponding redox events) when compared to the Au electrodes(Fig 4a). This result clearly indicates the larger electroactive area of the obtained graphene-based electrode due to the vertical disposition of FLG sheets and its conductive nature (since it is mainly composed by sp^2 carbon atoms). Additionally, the electrochemical response of $[Fe(CN)_6]^{3-}$ recorded with our Au_*v*_Sulf-FLG@IONP-Dop electrode displayed a reduction of the peak-to-peak difference (Fig 4a). Such peak-to-peak reduction has been described to occur when the electron transfer processes take place between $[Fe(CN)_6]^{3-}$ and graphene structures through their edges, where the higher density of states near the Fermi level is located.[17]

The electrochemical properties displayed by Au_*v*_Sulf-FLG@IONP-Dop demonstrated the suitability of our method for producing new electrodes for electrochemical applications. In this regard, a simple exploratory experiment was made using our Au_*v*_Sulf-FLG@IONP-Dop electrode for constructing an anode for the oxidation of methanol. For this, such electrode was previously set to electrodeposit Pt (**Au_*v*_Sulf-FLG@IONP-Dop_Pt**). For comparison a gold electrode, previously submitted to the electro-deposition of platinum (Au_Pt), was also used as anode for oxidation of methanol.[18] In figure 4b the voltamograms of the electrooxidation of

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methanol (1M) using the Au_*v*_Sulf-FLG@IONP-Dop_Pt and Au_Pt electrodes are presented. It can be observed that our graphene based electrode displayed a 3,5 fold increment of the current collected during the electroxidation of methanol respect to the gold one. Such result is also the consequence of the greater electroactive area of the vertically oriented graphene based electrode respect the flat gold electrode.

Conclusions

In conclusion we have reported a very simple method for assembling few layer graphene on surfaces with vertical orientation. Here, we employed gold as a conducting surface, which represents a suitable setup for electronic applications; however, by following the adopted procedure (or slight adaptations to it) the attachment to other material surfaces for obtaining novel electrode structures with specific designs, surface areas, conductivities and capacities, will be possible. Additionally, the method employed for the production of Sulf-FLG@IONP-Dop can be easily adjusted for decorating FLG with different nanoparticles for applications in water decontamination, H_2 production and other catalytic processes.

Acknowledgements

Notes and references

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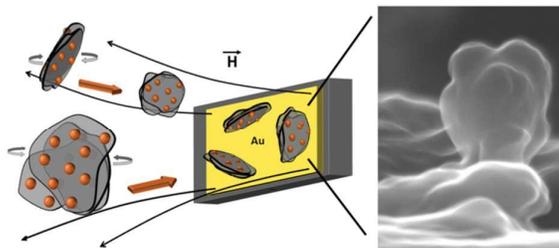
A wet method for producing vertically oriented graphene based electrodes is described.