Supporting Information

Transparent and conductive thin films of graphene/polyaniline nanocomposites prepared through interfacial polymerization

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1. Experimental

1.1. Synthesis of graphite oxide (GO)

An amount of 46 mL of H_2SO_4 (Vetec) was added to a 500 mL round-flask containing 2,0 g of graphite (Nacional de Grafire, Brazil) and 1,0 g of $NaNO_3$ (Vetec). The mixture was maintained under ice-bath and strong magnetic stirring for 15 min. After this, 6 g of $KMNO_4$ (Merck) were slowly added to the system, and the mixture was maintained under strong magnetic stirring for 75 min. In the following 92 mL of distilled water were added, the system was stirred for more 10 min followed by the addition of 280 mL of hot distilled water (~ 100 ^oC). Finally, 10 mL of an aqueous solution of H_2O_2 30% w/w (Vetec) have been added and the system was maintained under stirring for 30 min. The resulting solid was separated by filtration, washed several with distilled water until pH neutral and dried at 60 ^oC for 24 h.

1.2. Synthesis of graphene

An aqueous dispersion of GO (1 $mg.mL^{-1}$) was prepared in a dark flask and maintained under ultrasound bath (Unique, 37 KHz) during 30 min. The resulting dispersion was subsequently submitted to centrifugation (3000 rpm) for 30 min, and the solid was rejected. To the resulting stable brow dispersion a suitable amount of sodium borhidride (Merck) was added (4,0 mg $NaBH_4$/mL dispersion), and the system was maintained under reflux for 3 h. So, the resulting black solid was separated by centrifugation, washed several times with distilled water and dried at 100 ^oC for 24h.

1.3. Synthesis of nanocomposites

Five graphene/PANI nanocomposites were prepared by varying the graphene/PANI ratio, as summarized in Table S1. All experiments were conducted at room temperature (between 21 and 24°C). The different graphene/aniline weight ratios were estimated by fixing the graphene amount and varying the aniline volume: 1/100, 1/32, 1/16, 1/8, and 1/4. For comparison, samples of neat polyaniline were also prepared according to exactly the same experimental procedure as that of the nanocomposites but without the graphene. In all syntheses, the aniline/ammonium persulfate weight ratio was fixed at 1.6.

Table 1. Experimental conditions to the synthesis of samples.

Sample	**m Graphene (mg)**	**V ani (μL)**	**m APS (mg)**
Graphene / PANI - 1/100	0,63	60	38,6
Graphene / PANI - 1/32	0,63	20	12,8
Graphene / PANI - 1/16	0,63	10	6,4
Graphene / PANI - 1/8	0,63	5	3,2
Graphene / PANI - 1/4	0,63	2,5	1,6

ani = aniline, APS = ammonium persulfate.

The preparation of the graphene/PANI nanocomposite was as follows: the correct amount of graphene was dispersed in 20 mL of toluene in an ultrasound bath for 40 min. Subsequently, the aniline is mixed in this dispersion using a micropipette, and the system remains under ultrasound for an additional 30 min. Then, the resulting mixture was transferred to a 50-mL round-flask containing 20 mL of a 1 mol L^{-1} HCl aqueous solution in which a suitable amount of ammonium persulphate was previously dissolved (Table S1). The two-phase system was maintained under strong magnetic stirring (at 1500 rpm, using a magnetic stirrer from Corning and a stirrer bar of 5 mm in diameter × 15 mm in length) for 22 h. After a period of time, depending on the aniline concentration, a blue colour appears, followed by a green colour typical of the conducting form of polyaniline, emeraldine salt. After 22 h the magnetic stirring was stopped, and immediately a green and transparent film was spontaneously formed at the interface. To remove the excess acid and side-products from the polymerization, the aqueous phase was partially removed, and amounts of a diluted aqueous solution of HCl were added to the system. This process in which the aqueous phase is constantly changed was repeated 10 times. In the same manner, the organic phase was constantly changed by successive removal of the toluene followed by additions of novel portions of toluene.

To deposit the nanocomposite films on substrates, cleaned substrates were put into the flask containing the biphasic system in which the film is at the interface. Then, using tweezers, the film was directly transferred to the substrate surface, followed by drying in air. The process of deposition of the graphene/PANI films is summarized in Figure S1 below.

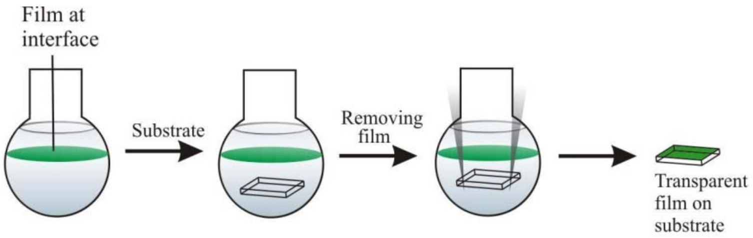


Figure S1 - Schematic representation of the deposition of the graphene/PANI films.

1.4. Characterization techniques

UV-Vis spectra were collected directly from the films deposited on glass slides in a Shimadzu UV-2450 spectrophotometer, using air as the reference, in the range of 190–1100 nm.

The Raman spectra were obtained in a Renishaw Raman Image spectrophotometer coupled to an optical microscope that focused the incident radiation down to a spot of approximately 1 μm. A He-Ne laser (emitting at 632.8 nm) were used with an incidence potency of 0.2 mW over the 3000–200 cm^{-1} range.

The resistivity of the samples was measured directly from the films by the four-points technique using JANDEL Universal Probel equipment. The distance between the points was fixed at 1.0 mm.

The thickness of the films was measured using a scanning perfilometer Veeco DekTak 150 with resolution of 1 nm and tip of 12.5 μm. Measurements have been done in quintuplicate for each sample.

Transmission electron microscopy (TEM) was performed in a JEOL JEM 120 KV instrument. The samples were prepared by depositing the films on standard copper grids exactly as reported before (Figure S1).

Cyclic voltammetry measurements were obtained using a micro-Autolab potentiostat (Eco-Chimie) that was interfaced to a PC computer and GPES 4.9 software. A one-compartment cell was used, with a Pt wire as counter electrode, an Ag/AgCl reference electrode and a 0.5 mol.L^{-1} H_2SO_4 aqueous solution as the electrolyte. The work electrode was built by depositing the films obtained as described earlier over a ITO covered glass slide (active area = 1×1 cm). The scan speed was 50 mV.s^{-1}, and the potential ranged from -200 to 1000 mV.

The AFM images have been collected directly on the films deposited over ordinary glass substrates, using a Shimadzu SPM 9500 J3 microscope using dynamic tip. The samples have been treated in the mode standard, using the SPM Shimadzu software.

2. Some electrical and optical properties of the films

Table S2 – conductivity, sheet resistance, transmittance at 550 nm and thickness of the films

Sample	**Conductivity (S cm^{-1})**	**Sheet resistance (Ω sq^{-1})**	**Transmittance at 550 nm (%)**	**Thickness (nm)**
GR/PANI-1/4	152	4.6	70	153
GR/PANI-1/8	90	67.2	82	71
GR/PANI-1/16	56	42.5	87	66
GR/PANI-1/32	33	60.6	89	129
GR/PANI-1/100	14	18.9	78	208

For comparison, the sheet resistance of both neat graphene and neat polyaniline films obtained by similar way was 28.2 Ω sq^{-1} and 50.1 KΩ sq^{-1} respectively.

3. Cyclic voltammetry of the films

The films were deposited on transparent electrodes and studied by cyclic voltammetry as shown in Fig. S2. The voltamoggram of the neat graphene film does not present any response in the potential window studied. The cyclic voltammograms of the nanocomposites films show the well-defined reversible redox processes characteristic of polyaniline (due to the leucoemeraldine/emeraldine and emeraldine/pernigraniline conversion), confirming that the polymer maintains its electroactivity in the nanocomposites. This is an interesting result because indicates that besides their obvious application as transparent electrodes in optoelectronic devices, this materials can also take advantage of the electroactivity of the polymer to be applied in different fields as electrosensors, electrochromic materials, electrochemical devices, among others.

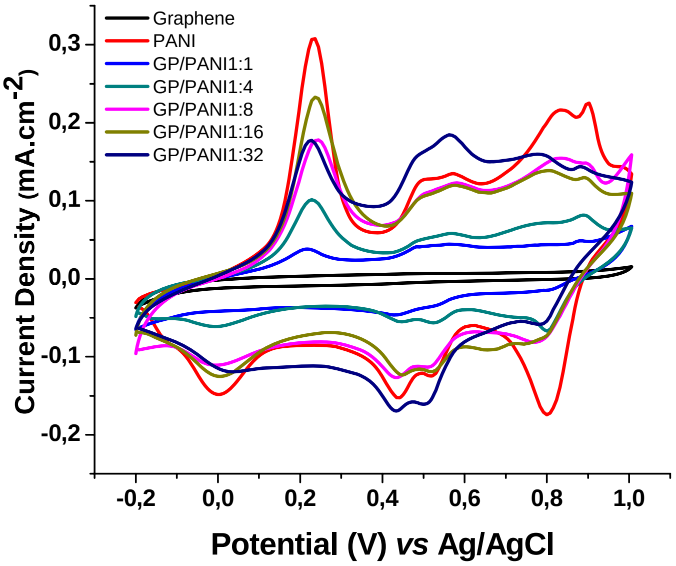
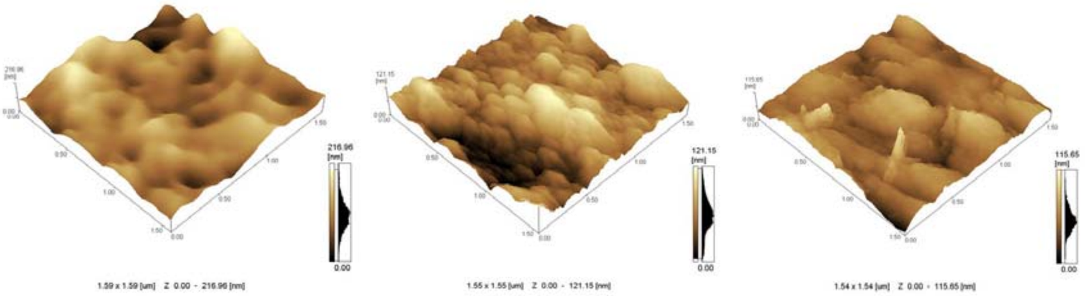


Fig. S2 – Cyclic voltammograms (0.5 mol.L^{-1} H_2SO_4 aqueous solution as the electrolyte, 50 mV.s^{-1}) of the samples.

4. AFM images of the films

Figure S3 show the AFM images of the samples GR/PANI-1/100 (Fig. S3-a), GR/PANI-1/16 (Fig. S3-b) and GR/PANI-1/4 (Fig. S3-c). To collect these images, the films have been deposited over glass substrates, with no previous treatment. The images indicate homogeneous and continuous films.



(a) (b) (c)

Fig. S3 – AFM images: (a) GR/PANI-1/100, (b) GR/PANI-1/16 and (c) GR/PANI-1/4.