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# Water enabled self-healing polymeric coating with reduced graphene oxide-reinforcement for sensors

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## ABSTRACT

Intrinsic self-healing materials have received significant attention due to the characteristic recovery after damage properties through reversible dynamic covalent and non-covalent interactions. Furthermore, functional recovery with reliable mechanical properties are highly keen as protective coatings, specifically for devices and sensors vulnerable to abrasion in severe environments. Here, we present a functional hierarchical nanostructure capable of multiple micro-sized healings, with enhanced mechanical hardness due to the incorporation of graphene oxide (rGO) nanoplatelets. A self-healing multilayered nanocomposite formed by poly(ethylene imine) (PEI) and poly (acrylic acid) (PAA) was easily assembled by the layer-by-layer (LbL) technique. The addition of the rGO nanoplatelets in the LbL nanostructure resulted in a 13-fold increase in hardness ( $0.4 \pm 0.1$  GPa) when compared to the (PEI/PAA) architecture ( $0.03 \pm 0.01$  GPa). In addition, the nanocomposite presents an enhanced insulating electrical behavior ( $\sim 4.10^{-8}$  S/cm) despite the addition of the rGO nanoplatelets. Raman and Zeta Potential analysis indicated a possible wrapping of the rGOs by PEI, justifying the observed insulating electrical characteristics. The nanocomposite presents good hydrophobicity with a water contact angle of  $136^\circ$ , interesting to extend the lifetime and protect underlying layers from humidity, degradation, and encrustation. Therefore, we propose an attractive hydrophobic, electrically insulating, and mechanically resistant multifunctional coating for high-performance electronic interfaces from minor cuts and abrasions, dispensing maintainer intervention.

## 1. Introduction

Nature-inspired, and first defined by Scott R. White, self-healing materials can restore properties/functions after mechanical damage by using available inner resources [1]. They are tailored to increase lifetime and reduce waste, degradation, maintenance, and costs of devices, with potential application in protective coatings [2–4], health-monitoring systems [5–8], and flexible electronics [9–11]. Briefly, extrinsic self-healing materials need an integrated healing agent (microcapsules, nanocapsules embedded in a polymeric matrix) to restore the damaged area, being unable of multiple regenerations at the same damaged region [12–14]. Intrinsic self-healing materials are mainly based on

reversible dynamic covalent and non-covalent interactions, without healing agents to perform the regeneration process, although sometimes it may require external stimuli such as water, heat, or light [13,15]. Nowadays, the ultimate goal is the development of multifunctional coatings having high durability even in severe environments, which may demand, for example, efficient control of mechanical resistance, healing ability, and wettability of the coating.

Within this framework, the LbL technique provides an elegant, facile way to design and fabricate hierarchical nanostructures with well-defined thickness, composition, and structure, regardless the substrate morphology [16–19]. In the LbL assembly the intrinsic self-healing occurs with the migration of molecules from the deposited layers to the

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damaged area [20,21]. Wang et al. [22] demonstrated that a high pH difference between oppositely charged polyelectrolytes leads to a better healing ability of the LbL structures. Qi et al. [23] fabricated a quasi-linear LbL self-healing film made of poly(vinyl alcohol) (PVA), tannic acid (TA), and graphene oxide (GO) in a (PVA-GO/TA) structure having an epidermis-like morphology and a tooth enamel hardness, with the healing mechanism based on hydrogen bonding and electrostatic interactions. Zhu et al. [24] reported the preparation of graphene-reinforced self-healing LbL films having improved electrochemical performance. Fan et al. [25] incorporated GO with branched poly(ethyleneimine) (bPEI)/poly(acrylic acid) (PAA) multilayers to improve the corrosion resistance of interfaces. Overall, a general challenge for polymeric self-healing materials is to overcome the vulnerability to abrasion by increasing the mechanical resistance of the self-repairing coatings. However, the healability decreases with increasing loading of materials used to elevate the mechanical resistance of interfaces [26].

Here, we present a reinforced composite incorporating functionalized rGO nanoplatelets (NPLs) in a PEI/PAA LbL self-healing matrix. The rGO NPLs were functionalized with poly(allylamine hydrochloride) (PAH) or poly(sodium 4-styrenesulfonate) (PSS), thus forming rGO nanoplatelets wrapped by PAH or PSS molecules. rGO NPLs wrapped by PAH are named here as GPAH, analogically for GPSS. Previous studies on GPAH and GPSS report non-covalent intermolecular bonding interactions between rGO and the polymers, preserving good chemical stability, mechanical stiffness, and electrical conductivity [27–32]. However, the formed  $(\text{GPAH-PEI/GPSS-PAA})_n$  nanocomposite presented conductivity values ( $\sim 4.10^{-8} \text{ S/cm}$ ) four times lower than that observed for  $(\text{PEI/PAA})_{60}$ . Raman and Zeta Potential analysis indicated a physical interaction between GPAH and PEI molecules, thus hampering electric conduction pathways between rGO nanoplatelets in the composite LbL film. We also observed a water contact angle of  $136^\circ$ , a hydrophobicity that can be favorably used in the protection from humidity, degradation, and fouling. If in contact with water, this multifunctional LbL assembly can quickly recover from damages within 15 min, together with better mechanical hardness of the composite. Its high electrical resistivity can also be further explored to tailor the electrical anisotropy of multilayered nanostructures in FET devices [33].

## 2. Material and methods

### 2.1. Materials

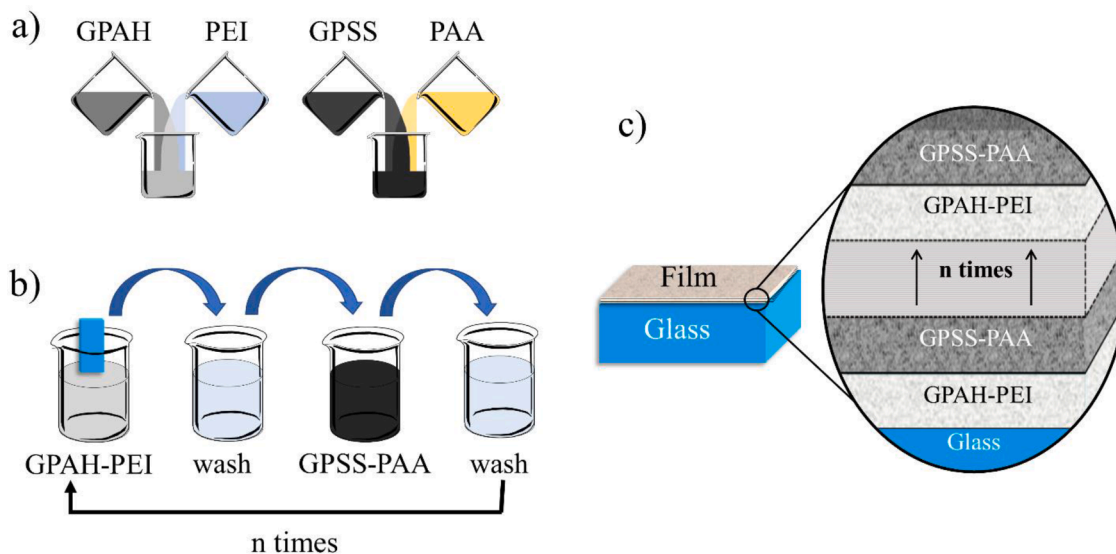
Poly(acrylic acid) ( $M_w \sim 8000$ , 45 wt.% in  $\text{H}_2\text{O}$ ), poly(ethylene imine) ( $M_w \sim 2000$ ), poly(allylamine hydrochloride) ( $M_w \sim 250,000$ , 35 wt.% in  $\text{H}_2\text{O}$ ), poly(sodium 4-styrenesulfonate) ( $M_w \sim 200,000$ , 30 wt.% in  $\text{H}_2\text{O}$ ) and graphene oxide (GO) are acquired from Sigma-Aldrich. GO is then chemically reduced to rGO and functionalized with PSS or PAH molecules similarly to literature [27], thus forming, respectively, GPSS and GPAH. All solutions are prepared with deionized water acquired from a Sartorius Arium Comfort system.

### 2.2. LbL film

A homemade setup automatically controlled by Arduino is used to fabricate the LbL structures [34]. Glass slides are previously cleaned with ammonium hydroxide, hydrogen peroxide and water (1:1:5 v/v/v) at  $\sim 80^\circ \text{C}$  for 10 min. A mixture of PEI (4 mg/mL) + GPAH (0.1 mg/mL), (1:1 v/v) at  $\text{pH} = 10.5$  is used as the positive polyelectrolyte, and PAA (4 mg/mL) + GPSS (0.1 mg/mL), (1:1 v/v) at  $\text{pH} = 3.0$  is used as the negative polyelectrolyte (Fig. 1a). When necessary, the pH is adjusted by adding 1 M solutions of HCl or NaOH. Briefly, a cleaned glass slide is immersed 15 min [24,35] in the positive polyelectrolyte and then washed in ultrapure water at  $\text{pH} = 10.5$  to remove the excess of material loosely bound. In the sequence, the glass slide is immersed 15 min in the negative polyelectrolyte, followed by another washing step in ultrapure water at  $\text{pH} = 3.0$  (Fig. 1b), thus forming  $(\text{GPAH-PEI/GPSS-PAA})_n$  LbL films as illustrated in Fig. 1.  $(\text{GPAH/GPSS})_{50}$  and  $(\text{PEI/PAA})_{60}$  LbL films are used as control experiments, with all assembly parameters listed in Table 1.

### 2.3. Analyses

Zeta Potential experiments are performed on GPAH and GPSS solutions to investigate the electrical charge of the polyelectrolytes in a broad pH range, using a Zetasizer Nano ZS ZEN 36,000 (Malvern Instruments). The LbL films are analyzed by Raman Spectroscopy with a Micro Raman XploRA from Horiba Scientific using a 532 nm laser excitation source and a 100X objective. The scattered light is dispersed with an 1800/mm grating through a 10% filter, with an exposure time of 8 s and 8 accumulations. Atomic Force Microscopy (AFM)



**Fig. 1. LbL film fabrication.** (a) Preparation of the polyelectrolytes mixing GPAH with PEI, and GPSS with PAA, both (1:1) in volume; (b) Fabrication of the multilayered LbL nanostructure, and (c) Schematic illustration of the  $(\text{GPAH-PEI/GPSS-PAA})_n$  LbL film.

**Table 1**

LbL nanostructures assembled in this work, with the parameters used for the film formation.

LbL architecture	material	Concentration (mg/mL)	pH	Immersion Time (min)
(GPAH-PEI/GPSS-PAA) <sub>60</sub>	GPAH	0.1	10.5	15
	PEI	4		
	GPSS	0.1	3.0	15
	PAA	4		
(PEI/PAA) <sub>60</sub>	PEI	4	10.5	15
	PAA	4	3.0	15
(GPAH/GPSS) <sub>50</sub>	GPAH	0.1	3.5	10
	GPSS	0.1	3.5	10

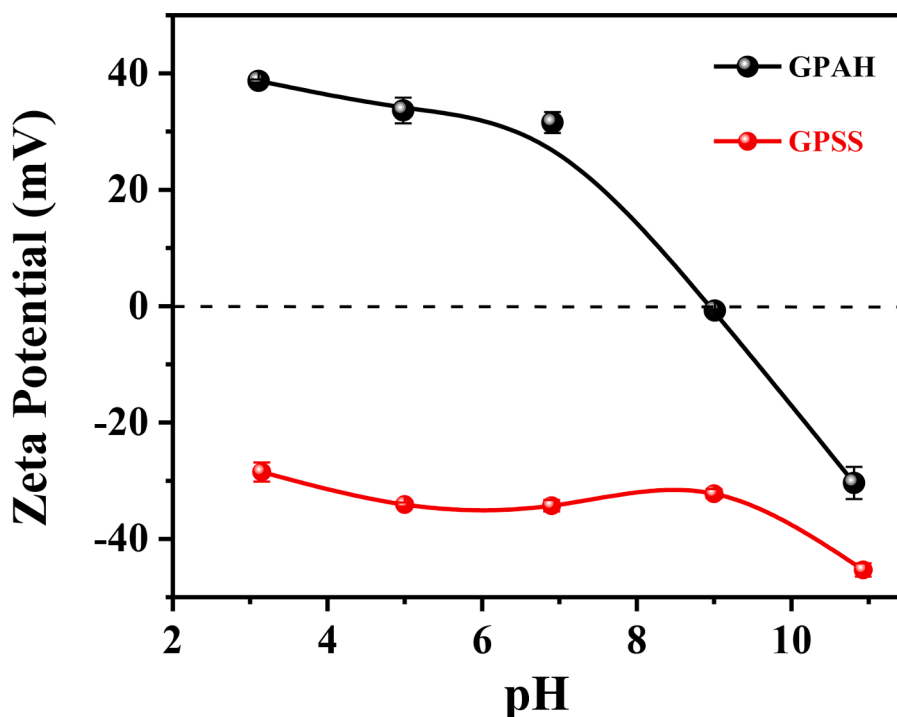
measurements are taken on a Bruker Dimension ICON equipment with a rectangular-shaped silicon tip set to intermittent contact mode, with 42 N/m spring constant and 330 kHz free oscillation. The healing ability of the LbL films is checked with a Dino Lite USB microscope AM7515MT4A. A profilometer Dektak 150 is used to determine quantitatively the depth of the mechanical damage made in the films with an STM tip. Once the scratch is healed, the image is registered with the film dried at ambient conditions. The wettability of the films is analyzed with an optical tensiometer DSA 100 Standard and software Drop Shape Analyzer from Krüss. The hardness of the LbL nanostructures is investigated using a NanoTest, Berkovich diamond indenter from Micro Materials. For hardness data analysis it is adopted the Oliver-Pharr model [36]. Nanoindentation depths are fixed at 500 nm, corresponding to less than 20% of the estimated film thickness. Current (I) vs voltage (V) measurements are acquired at each deposition step of LbL films deposited on gold interdigitated electrodes (IDEs) having 30 pairs of fingers with 150 nm height, 3 mm of length (L), 40  $\mu$ m width (W) and separated 40  $\mu$ m from each other (L). The (I - V) curves are obtained coupling the homemade automated LbL setup controlled by Arduino with a Keithley 6487 Picoammeter [34].

### 3. Results and discussion

#### 3.1. Component analyses

Fig. 2 illustrates the Zeta potentials for GPAH and GPSS solutions. The PAH response prevails for GPAH solutions, as the allylamine hydrochloride group is positively charged below pH 9 and presents an isoelectric point around pH 9 [37]. On the other hand, GPSS keeps a negative zeta potential in the whole pH range studied, as PSS is a strong and not pH dependent polyanion [38]. The literature indicates that the best pH for the LbL film fabrication are, respectively, pH  $\sim$  10 for PEI and  $3 < \text{pH} < 5$  for PAA [22,25]. That led us to prepare the polyelectrolytes as follows: (PEI + GPAH) aqueous solutions at pH = 10, and (PAA + GPSS) aqueous solutions at pH = 3.5. It is worth mentioning the stability of the GPAH and GPSS ( $\pm$  40 mV) aqueous suspensions [27–29], with the literature indicating a tendency of PEI become deprotonated around pH  $\sim$  10 [39–42], which may interfere on the molecular vibration of the GPAH-PEI mixture. In addition, this method represents a non-covalent approach based on supramolecular complexation using PEI (PAA) to wrap GPAH (GPSS) nanoplatelets, i.e., the driving force between polymers and rGO can be van der Waals forces,  $\pi$ – $\pi$  interactions, and hydrogen bonding, as will be discussed in the Raman section.

Raman spectra of the (GPAH-PEI/GPSS-PAA)<sub>60</sub>, (GPAH/GPSS)<sub>50</sub>, and (PEI/PAA)<sub>60</sub> LbL films are illustrated in Fig. 3, with the last one used for comparison and better comprehension of the composite system. It is observed the characteristic vibrational bands of graphene at 1583  $\text{cm}^{-1}$  (G-band) due to the  $\text{sp}^2$  bond stretching of atoms in both rings and chains, and at 1343  $\text{cm}^{-1}$  (D-band) attributed to defects of the rGO nanoplatelets owing to the breathing modes of  $\text{sp}^2$  atoms in rings [43]. The  $I_D/I_G$  ratio for (GPAH/GPSS)<sub>50</sub> is 1.1, in good agreement with the literature [20,27,28] where the increase of the  $I_D/I_G$  ratio also indicates a successful transformation of GO in rGO together with a degradation of the overall size of the formed  $\text{sp}^2$  domains [44]. Regarding the polymers, it is noticed in (PEI/PAA)<sub>60</sub> bands at 1106  $\text{cm}^{-1}$  due to the stretching of the C–COO<sup>–</sup> groups from PAA molecules and at 1560  $\text{cm}^{-1}$  due to the



**Fig. 2.** Zeta potential measurements. Zeta potential for GPAH (black line) and GPSS (red line) solutions prepared in different pH. Some error bars are too small to be observed.

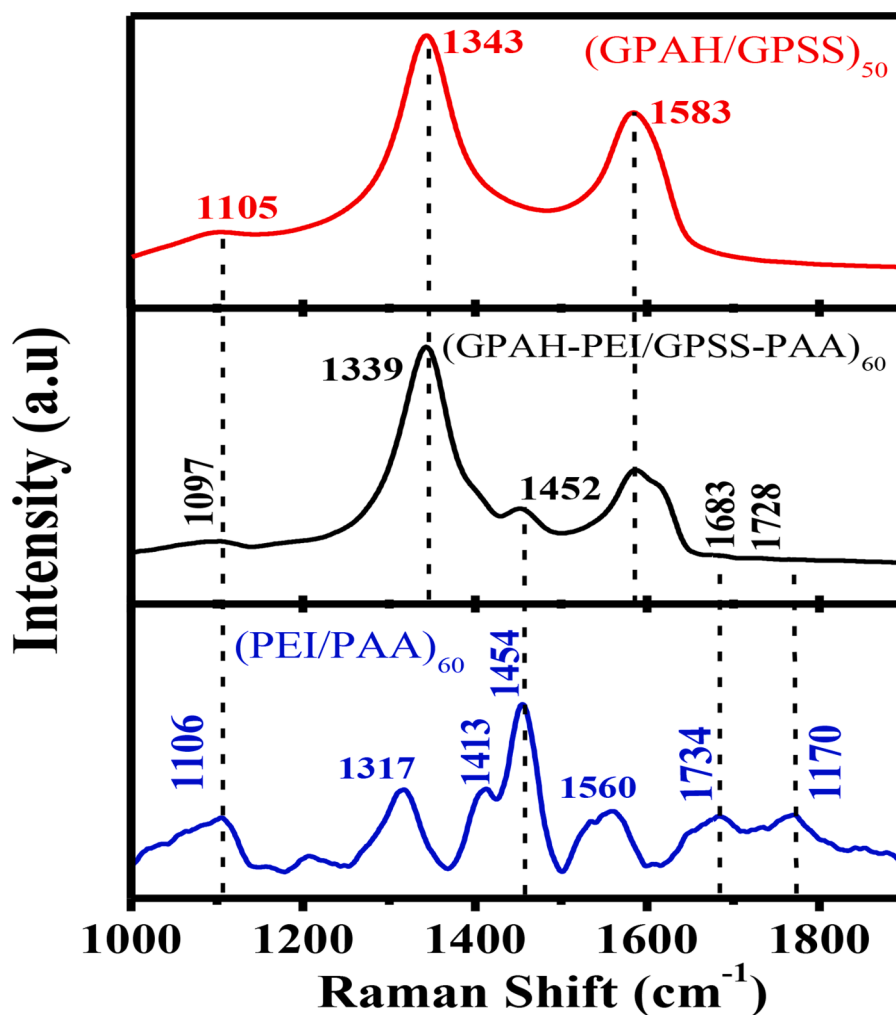


Fig. 3. Raman spectra. Raman spectra of (GPAH-PEI/GPSS-PAA)<sub>60</sub>, (GPAH/GPSS)<sub>50</sub> and (PEI/PAA)<sub>60</sub> LbL films.

N—H bending vibration of NH<sub>2</sub> groups from PEI [45]. The composite (GPAH-PEI/GPSS-PAA)<sub>60</sub> spectrum presents the main bands from both (GPAH/GPSS)<sub>50</sub> and (PEI/PAA)<sub>60</sub>, thus indicating that the (GPAH-PEI/GPSS-PAA)<sub>60</sub> LbL film is a hybrid system preserving the main molecular vibrations discussed above. It is worth mentioning the decrease of the G band intensity at 1583 cm<sup>-1</sup> in the (GPAH-PEI/GPSS-PAA)<sub>60</sub> LbL film compared to (GPAH/GPSS)<sub>50</sub>, and also the non-appearance of an expected vibrational peak at 1560 cm<sup>-1</sup> from PEI, suggesting an electrostatic interaction between PEI and GPAH. Such hypothesis agrees with the previous Zeta Potential analysis and others arguments in the literature [39–42], once the NH<sub>2</sub> group from PEI may be deprotonated at the pH value used here. Therefore, our results suggest the wrapping of the GPAH nanoplatelets by PEI molecules in solution before the LbL assembly and van der Waals forces as a driving interaction between PEI (PAA) molecules and GPAH(GPSS).

### 3.2. Electrical analyses

The electrical properties illustrated in Fig. 4 derive from the wrapping in solution between PEI and GPAH nanoplatelets. Consequently, a low electrical conduction is observed for the (GPAH-PEI/GPSS-PAA)<sub>60</sub> film, considering the separation of rGO conducting islands in the composite LbL structure. It is a direct evidence of physical interactions between GPAH and PEI as discussed above, with the conductivity of (GPAH/GPSS)<sub>50</sub> (~ 1.10<sup>-4</sup> S/cm) orders of magnitude higher than that measured for (GPAH-PEI/GPSS-PAA)<sub>60</sub> (~ 4.10<sup>-8</sup> S/cm) and (PEI/

PAA)<sub>60</sub> (~ 2.10<sup>-7</sup> S/cm). The electrical characteristics of (GPAH/GPSS)<sub>50</sub>, (GPAH-PEI/GPSS-PAA)<sub>60</sub> and (PEI/PAA)<sub>60</sub> structures (Fig. 4) are calculated from the I-V curves acquired during the LbL assembly [27]:

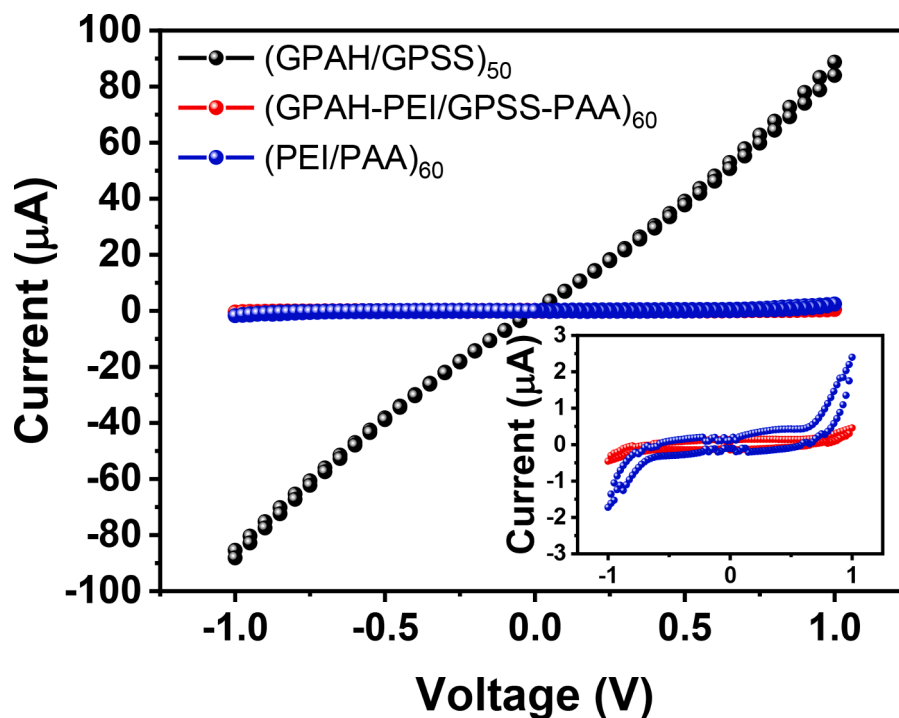
$$\sigma_{dc} = (R.K_{cell})^{-1} \quad (1)$$

where K<sub>cell</sub> is the cell constant of the IDEs. A simplified equation can be obtained for K<sub>cell</sub> when L = W:

$$K_{cell} = (N - 1)L/2 \quad (2)$$

(GPAH/GPSS)<sub>50</sub> displays a current orders of magnitude higher than (PEI/PAA)<sub>60</sub> and (GPAH-PEI/GPSS-PAA)<sub>60</sub> (Fig. 4), with a thermally activated hopping conduction [27]. Although we initially expected higher conduction for (GPAH-PEI/GPSS-PAA)<sub>60</sub> due to the increase of rGO nanoplatelets dispersed in the polymeric matrix, the composite (GPAH-PEI/GPSS-PAA)<sub>60</sub> film presented a conductivity 4 times lower than that observed for (PEI/PAA)<sub>60</sub>. This result corroborates both Raman and Zeta Potential analyses indicating a physical interaction between GPAH and PEI molecules, which hinders conductive pathways in the LbL film structure, resulting in the observed high resistive in-plane electrical behavior. This is particularly interesting to control electric anisotropy in multilayered structures for field-effect or flexible electronic devices. One final remark on the blue curve in the inset at -1 V and 1 V is that it is ruled by the presence of water molecules trapped in the LbL structure, as previously reported in [20].





**Fig. 4.** Electrical analyses. I-V measurements from  $-1$  V to  $1$  V for (PEI/PAA)<sub>60</sub>, (GPAH/GPSS)<sub>50</sub> and (GPAH-PEI/GPSS-PAA)<sub>60</sub> LbL films. Inset: Zoom at the low current region.

### 3.3. Healability and hydrophobicity tests

The healing ability of the nanocomposite is checked through cuts having tens of microns that were completed restored after immersing the damaged area 15 min. in water, illustrated in Fig. 5. The results are in the average healing efficiency (recovery time, cut depth) values reported for (PEI/PAA) LbL films in the literature. Table 2 brings the detailed information of similar works for reference and comparison [22,25,46, 47]. It is often observed in the literature an increase in hardness with the addition of other materials in a self-healing matrix, which can seriously compromise the healing performance. Here, we have successfully maintained the self-healing capability of the LbL composites, as the optimized rGO reinforcement did not bring significant changes to the healing process of scratched coatings when compared to PEI/PAA films.

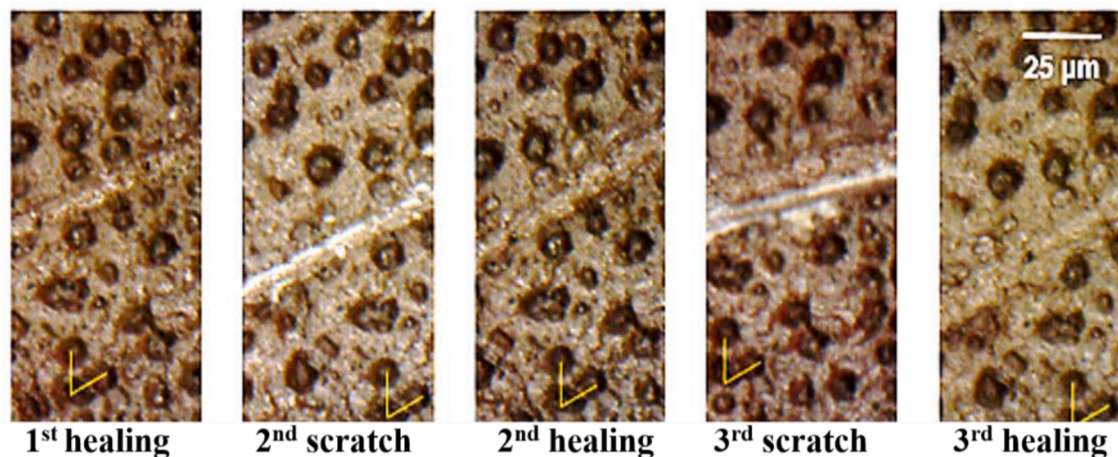
What happens in the studied coating is that the positive GPAH-PEI composite interacts with the negative GPSS-PAA part by electrostatic

**Table 2**

Demonstration of the healability of several PEI/PAA based self-healing films in literature and in this work.

Structure	Immersion time	Cut dimensions	Ref.
PEI/PAA	5 min	50 $\mu$ m	[22]
Ce(IV)/GO/PEI/PAA	10 min	10 $\mu$ m	[25]
MoS <sub>2</sub> /(PAA-AD/PEI- $\beta$ -CD)	30 min	20 $\mu$ m	[46]
PAA-AD/PEI- $\beta$ -CD	30 min	50 $\mu$ m	[47]
GPAH-PEI/GPSS-PAA	15 min	10 $\mu$ m	this work

forces. The water stimulus causes the swelling effect that saturates after a certain time, thus favoring higher mobility to the polymer chains that migrate to the damaged region separated by micrometers of distance. As the rGO nanoplatelets are isolated in the polymer matrix and also present in smaller quantities, it is expected that they do not interfere with



**Fig. 5.** Healability tests. (GPAH-PEI/GPSS-PAA)<sub>60</sub> fil scratched by a STM tip. The damaged area had  $\sim 10$   $\mu$ m width and 30  $\mu$ m depth, followed by immersion in water for 15 min for the healing process. The yellow V mark at the bottom of Fig. 5 is a reference to prove that the damages occurred in the same region.

the swelling and healing processes, enriching only the mechanical properties of our films. The corresponding schematic is illustrated in Fig. 6.

The water contact angle (WCA) for the (PEI/PAA)<sub>60</sub> film is ( $130^\circ \pm 2^\circ$ ), with a slight increase observed in the (GPAH-PEI/GPSS-PAA)<sub>60</sub> structure ( $CA = 136^\circ \pm 5^\circ$ ), being both LbL assemblies hydrophobic. A comparative AFM analysis in a ( $2 \times 2$ )  $\mu\text{m}^2$  scanned area is performed (see in Support Information Figure S1), indicating differences in the surface roughness by AFM and profilometry analyses are distinct each other due to the dimension (1D vs. 2D) and extension (1.5 mm vs.  $2 \times 2 \mu\text{m}^2$ ) of the scanned regions. A rougher surface is obtained with the addition of rGO nanoplatelets, resulting in average root mean square roughness values of 55 nm for (GPAH-PEI/GPSS-PAA)<sub>60</sub> film, 16 nm for (GPAH/GPSS)<sub>50</sub>, and 13 nm for (PEI/PAA)<sub>60</sub>. The higher surface roughness in (GPAH-PEI/GPSS-PAA)<sub>60</sub> is the reason for the increased WCA, resembling the hierarchical structure observed in nature [48–50]. The average thickness of the (PEI/PAA)<sub>60</sub> and (GPAH/GPSS)<sub>50</sub> films in a ( $2 \times 2$ )  $\mu\text{m}^2$  area are  $\sim 6 \mu\text{m}$  and  $\sim 100 \text{ nm}$ , respectively. The thickness of (GPAH-PEI/GPSS-PAA)<sub>60</sub> film is measured by profilometry as the cut region presented a quite irregular surface for AFM analysis, with an average thickness of  $\sim 15 \mu\text{m}$  in a 1.5 mm measured profile line. The regeneration illustrated in Fig. 7 indicates an effective migration of the molecules to the damaged area, with the measured profile along with the healed scratch ( $\sim 13 \mu\text{m}$  thick) comparable to the average surface roughness of the analyzed extension ( $\sim 15 \mu\text{m}$ ).

### 3.4. Hardness test

Fig. 8 illustrates the load-depth curve as a result of the hardness test by nanoindentation for both (GPAH-PEI/GPSS-PAA)<sub>60</sub> and (PEI/PAA)<sub>60</sub> structures. Up to the same depth profile it is necessary ten times more load for the (GPAH-PEI/GPSS-PAA)<sub>60</sub> structure, which quantitatively imply in a hardness ( $H$ ) of ( $0.4 \pm 0.1$ ) GPa for the nanocomposite that is indeed 13 times higher than that presented by the (PEI/PAA)<sub>60</sub> film ( $H = (0.03 \pm 0.01) \text{ GPa}$ ). Hummod et al. [51] also investigated the nano-mechanical behavior of PEI/PAA film using nanoindentation, obtaining a hardness of  $H = (0.44 \pm 0.06) \text{ GPa}$  at similar humidity condition. It is worth mentioning that their films were deposited on silicon and ours on glass. Our system consists of a soft film deposited on a hard substrate, a case where the influence of the substrate on the hardness of the film should be negligible according to the literature [52]. What could be considered on the LbL film growth on different substrates is the influence of the substrate used in the formation of the first LbL layers, thus

altering structural properties and influencing the film hardness.

Xiang et al. [26] fabricated a self-healing LbL film composed by PAA with branched PEI grafted with ferrocene (bPEI-Fc) and rGO nanosheets modified with  $\beta$ -cyclodextrin (RGO-CD). The as-prepared PAA/bPEI-Fc & RGO-CD presented a hardness of 1.0 GPa, which is by far the highest hardness value of all reported self-healing LbL films in the literature. Experimental results showed that the mobility of the bPEI-Fc polyelectrolytes within the (PAA/bPEI-Fc&RGO-CD<sub>0.04</sub>)<sub>45</sub> films is significantly suppressed by the rGO nanofillers due to their strong host–guest interactions. Consequently, the healability is no longer efficient in water being necessary the immersion of the LbL film in H<sub>2</sub>O<sub>2</sub> solution, which increase processing steps, costs and may be eventually harmful depending on the application. However, in our work the polymeric wrapping of the rGO NPLs did not compromise the mobility of the materials in the healing process, enabling multiple regenerations of the composite (GPAH-PEI/GPSS-PAA)<sub>60</sub> structure with water addition at room temperature. Therefore, the (GPAH-PEI/GPSS-PAA)<sub>60</sub> structure also presented improved hardness when compared to (PEI/PAA), good hydrophobicity and electrical insulation.

## 4. Conclusions

We demonstrated an rGO reinforced coating that increases the mechanical hardness of LbL coatings without compromising the self-healing ability of the formed composite. Hierarchical multilayered nanostructures were easily prepared allowing functional films presenting multiple regenerations at the same damaged area after contact with water. The LbL (GPAH-PEI/GPSS-PAA)<sub>60</sub> composite also presented higher hydrophobicity, surface roughness, and electrical resistivity than (PEI/PAA)<sub>60</sub> due to the wrapping of GPAH nanoplatelets by PEI molecules in solution, previous to the LbL assembly deposition. It forms an attractive insulating LbL framework where minor cuts and abrasions are difficult and time-consuming to locate and repair, becoming a valuable tool to form new transistor architectures where the film can both act as a channel and insulating layer, paving the way for future field effect devices or organic electronics.

### Associated content

#### Supporting information

I-V measurements and AFM analysis of the LbL films (file type: PDF)

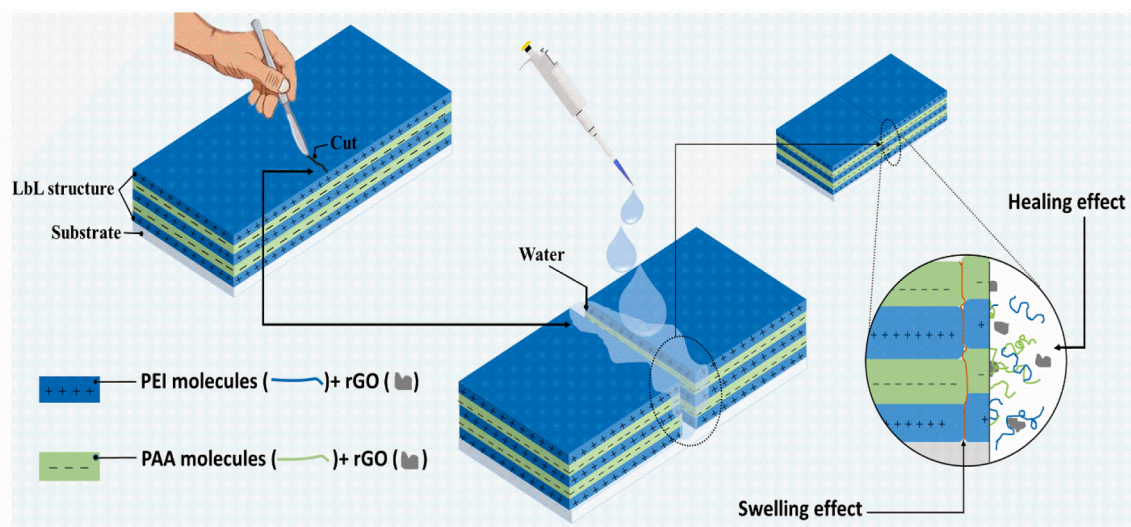


Fig. 6. Schematic diagram of the involving interactions of the self-healing process.

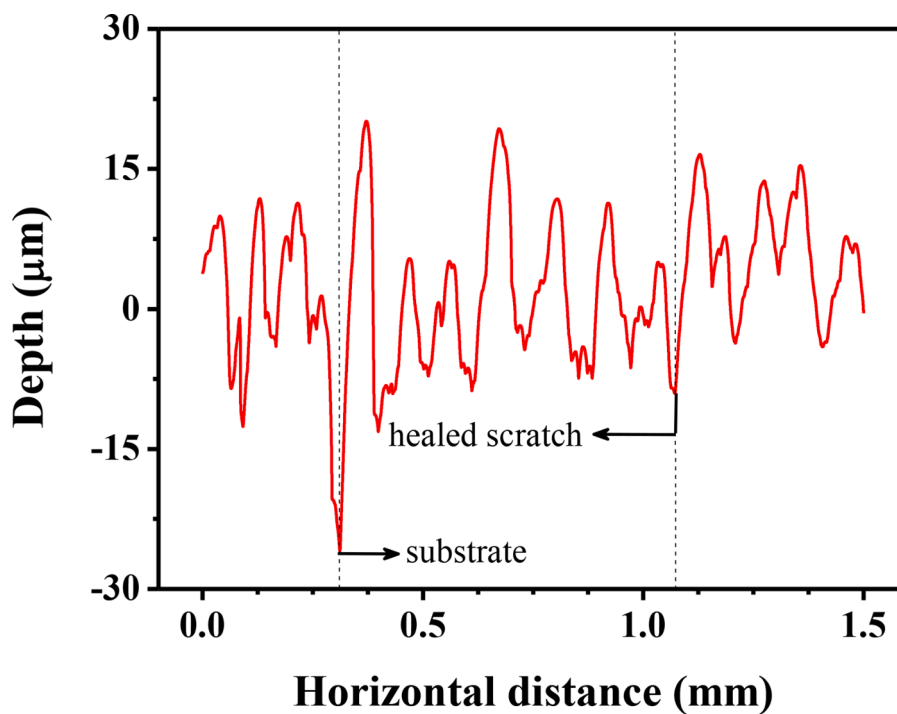


Fig. 7. Profilometry measurements of the (GPAH-PEI/GPSS-PAA)<sub>60</sub> film. The first depth demarcated by the left vertical line represents a scratch on the LbL film, with the second line on the right representing the healed area after damage occurred in the same region.

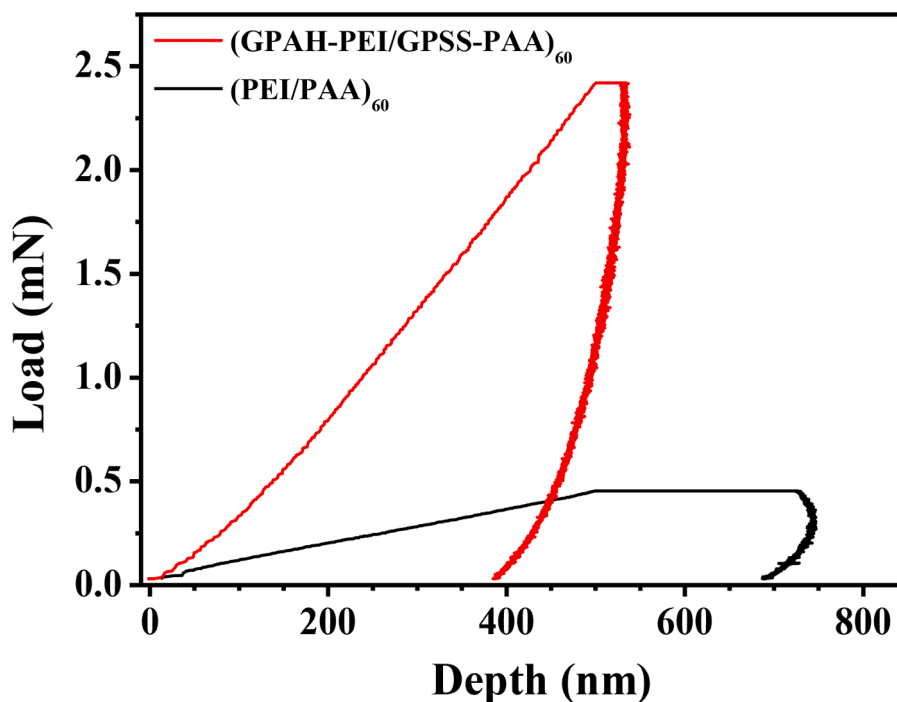


Fig. 8. Hardness tests. Load vs. depth obtained from the nanoindentation measurements for the films (PEI/PAA)<sub>60</sub> e (GPAH-PEI/GPSS-PAA)<sub>60</sub>.

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#### Declaration of Competing Interest

The authors declare no conflict of interest.

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## Supplementary materials

Supplementary material associated with this article can be found in the online version at doi:[10.1016/j.snr.2021.100059](https://doi.org/10.1016/j.snr.2021.100059).

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