



# Imidazole-derived graphene nanocatalysts for organophosphate destruction: Powder and thin film heterogeneous reactions



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## ABSTRACT

Promoting efficient organophosphate (OP) destruction has been of increasing interest, mainly due to their highly toxic nature and broad use as agrochemicals and chemical warfare. It is known that OP destruction can only be accomplished in the presence of catalysts, since they are kinetically stable. Hence, multifunctional materials have been targeted for this purpose since they can combine catalytic sites with features that enable easy handling, sensor projection for monitoring misuse and even large-scaled detoxification methods. Herein, we developed nanocatalysts derived from graphene oxide, which comprises reactive imidazole groups anchored by covalent functionalization. Two approaches were adopted: (i) a mild aqueous reaction leading to a powder, namely GOIMZ1; and (ii) a liquid/liquid interfacial functionalization, resulting in the thin film GOIMZ2. The nanocatalysts were applied in the destruction of OP and in the case of the toxic pesticide Paraoxon, impressive rate enhancements were obtained (10<sup>8</sup>-fold). Both catalysts were consecutively recycled, maintaining overall characteristics. We highlight the feasible handling of the nanocatalysts, that in the case of the powder, it can be easily filtered, washed and reused. For the thin film, the handling is even more practical, since it can be immersed in the contaminated media and separated easier than the powder. Overall, we show novel imidazole-derived nanocatalysts with promising catalytic efficiency towards OP destruction, which have potential for projecting sensors and detoxification processes, especially with the thin films.

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## 1. Introduction

The high growth of world agricultural production is intrinsically linked to an increasing dependence of its products. This number is directly proportional to the use of toxic agrochemicals, resulting in many environmental and health problems [1]. In this context, organophosphates (OP) stands out since it constitutes many pesticides, insecticides and even chemical warfare, justified by its high toxicity. In spite of its prohibited usage in many countries, OP alarms many worries nowadays due to the eminent threat of the large stocks available (agrochemicals and chemical warfare). Albeit, the OP allowed for agriculture are used abusively which knowingly leads to concerning side effects (e.g. cancerogenic), requiring efficient monitoring devices [2].

Moreover, destruction of OP has become of increasing interest as a tool for solving many issues addressed above. In this context, the high P–O bond stability of OP is noteworthy which assures it to

be potentially active in the environment for a long time, without degrading. Bioinspired by enzymes that promote dephosphorylation processes efficiently (*i.e.* cleave P–O bond) [3], many studies have tried to mimic their action using complex backbones, e.g. biopolymers [4], ionic liquids [5], polyhydroxamate [6] and functionalized fatty acids [7]. Recently a new possibility has aroused by using graphene-derived materials as nanocatalysts for degrading OP. Indeed, the unique physical and chemical properties of graphene materials have been improved by functionalization. Specifically, graphene oxide (GO) has attracted attention due to the several functional groups available for featured covalent functionalization [8,9]. Some promising applications by this means include water treatment [10], catalysis [11], adsorption [12], sensor [13], energy storage [14], solar cells [15], Surface Enhancement Raman Spectroscopy (SERS) substrates [16], among others [8,17]. Previously, we reported the functionalization of GO with cysteamine groups, targeted at the carboxylic acid sites through stable amide bonds. The thiolated nanocatalyst showed high rate enhancements for the cleavage of the OP diethyl 2,4-dinitrophenyl phosphate (DEDNPP), nearly 10<sup>5</sup>-fold compared to

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the spontaneous reaction [18]. This efficiency was attributed to an enzymatic-like mechanism by reactive thiol groups towards phosphorus atom, which regenerates the catalyst and also to synergism between the graphene backbone (*i.e.* functional groups and hydrophobic moieties).

Imidazole (IMZ) group is particularly interesting given its high reactivity against OP as shown by its presence in many enzymatic active sites such as in acetylcholine esterase [19], chymotrypsin [20] and trypsin [21]. Indeed, IMZ can act by multiple catalytic pathways: nucleophilic, basic and acid, and under fairly mild conditions (*i.e.* aqueous pH 7) [22]. Innumerable studies described the functionalization of different materials with IMZ pursuing artificial enzymes (*e.g.* peptide amphiphiles [21], poly(ethylenimine) derivatives [23], polymer lattices [24]), but no study with graphene-based nanocatalysts is reported. Hence, herein we focused on obtaining novel IMZ-derived nanocatalyst derived from GO for OP destruction. Compared to the previous reported thiolated nanocatalyst [18], IMZ has the advantage of having significantly higher chemical stability and catalytic versatility in contrast to thiol groups.

In addition, we aimed to produce the materials as both powder and thin film deposited over several substrates. In fact, graphene-based materials presented as powder is commonly reported, although, to the best of our knowledge, not with IMZ groups. Furthermore, pursuing facile applications of the nanocatalyst, we aimed thin film production by a novel approach developed in our group. Most techniques described for graphene-based thin films rely on layer by layer [25,26], spin [27] and dip coating [28], all which require several steps and are hard to control thickness and/or heterogeneity. A simple one-pot alternative is the liquid/liquid interfacial method, where homogenous self-assembled thin films are obtained from liquid/liquid (L/L) interfaces (aqueous/organic solvent) [29], that has potentiated many applications *e.g.* transparent and flexible electrodes [30], batteries [31], electrochromism [31,32], sensors [30,31], SERS substrates [16], supercapacitor [33], among others. The L/L interfacial method was applied before by our group in the synthesis of several materials, however recently we related two novel approaches to obtain GO directly thiolated followed by the synthesis of a nanocomposite with silver nanoparticle. The film was applied for the cleavage of the toxic pesticide diethyl 4-nitrophenyl phosphate (Paraoxon) showing a high catalytic activity ( $10^6$  fold) and was also applied as SERS substrates for nitrophenols and for 4-aminothiophenol. The multiple functions of this material allowed a new class of sensors and catalyst for dephosphorylation reactions [34].

Recently we reported a synthetic approach based on the chemical functionalization of GO with 1-(3-aminopropyl)imidazole (API) through amide bonds, using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) for activating the carboxylate sites of GO, Fig. 1 [35]. The powder material obtained by that route (GOIMZ1) was employed for a specific study focused on the  $pK_a$  determination of different graphene-based materials, demonstrating a novel tool to validate chemical functionalization [35]. Herein, we developed an innovative route to

directly obtain the IMZ-functionalized GO also as thin film easily transferable to different substrates (GOIMZ2), and demonstrate for the first time the expressive application of both materials (GOIMZ1 and GOIMZ2) as nanocatalysts for OP destruction. Specifically, we evaluated degradation of the model DENDPP and the toxic pesticide Paraoxon.

## 2. Experimental details

GO was synthesized following a modified Hummers method [36]. Paraoxon was obtained commercially, while DEDNPP was synthesized according to a previous report [37]. The synthesis of GOIMZ1 was carried out as previously reported [35].

### 2.1. Synthesis of GOIMZ2

GOIMZ2 was prepared by the liquid-liquid interface route as represented in Fig. 2 [29,36,38]. Initially, a thin film of GO was obtained by mixing an aqueous dispersion (20 mL) of GO ( $0.031 \text{ g mL}^{-1}$ ) with toluene (10 mL) in a round-flask 50 mL, subsequently subjected to magnetic stirring (1000 rpm) during 12 h. The system was kept under ice bath, followed by the addition of 30.0 mmol of NHS and EDC, that was kept under magnetic stirring for 1 h. After removing the ice bath, the system was kept for 1 h in room temperature ( $23.0 \text{ }^\circ\text{C}$ ) before the addition of 3.52 mmol of API and left the mixture under stirring for 12 h. Upon interruption of the magnetic stirring, an emulsion was formed at the liquid-liquid interface. The aqueous phase was repetitively substituted (5 times), with the assistance of micropipette, replacing it with deionized water. The same proceed was repeated for the organic phase replacing it by fresh toluene. In the following, the emulsion was transferred to a beaker containing deionized water, toluene and the target substrate. The film immediately self-assembled at the interface and the deposition consisted of pulling the substrate (glass, quartz, Si;  $7.5 \text{ cm}^2$ ) toward the liquid-liquid interface, using a homemade dip-coating equipment that controls the pulling velocity and guarantees steadiness [39]. The transfer occurred automatically on the surface allowing the deposition of a thin, continuous, and transparent film. Deposition was carried on both sides of a substrate, in a vertical position, as shown in Fig. 2. After the deposition, the thin film GOIMZ2 was dried at  $70 \text{ }^\circ\text{C}$  during 1 h.

### 2.2. Characterization

Raman spectra were recorded on a Renishaw Raman Imaging Microprobe System 3000 spectrophotometer using  $\text{Ar}^+$  laser He-Ne laser ( $632.8 \text{ nm}$  and  $1.96 \text{ eV}$ ) in at least 8 different regions of the samples. Fourier Transform Infrared Spectra (FTIR) were done on a FTIR Bio-Rad spectrophotometer over the range of  $4000\text{--}400 \text{ cm}^{-1}$ , using the KBr pellet method for GOIMZ1 and using a substrate of zinc selenide for GOIMZ2. X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer using  $\text{Cu K}\alpha$  radiation ( $1.5418 \text{ \AA}$ ), at  $40 \text{ kV}$  and  $30 \text{ mA}$ , at  $0.02^\circ$  scan rate (in  $2\theta$ ), with a step of  $5 \text{ s}$  per point. For GOIMZ1, aluminum and

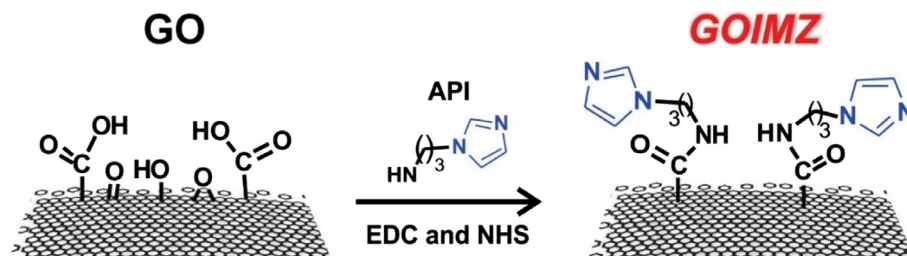


Fig. 1. Schematic representation of the targeted chemical functionalization of GO with API.

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