Polymeric imidazole-derived graphene nanocatalysts: functionalization and one-pot polymerization

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Abstract

The present work shows the route of graphene functionalization with imidazole derivative and its application as catalyst.

Introduction

Nowadays, promising multifunctional materials have been obtained by chemical functionalization, because can both improve existents properties as insert new ones. In this perspective, the oxygenated sites from graphene oxide (**GO**) can be strategically attached to specific functional groups. For example with catalytic activity like the imidazole group, particularly interesting because it is present in many enzymes, exercising catalytic activity in dephosphorylation reactions. Also, when polymerized can become a conductor polymer.

The present study presents the functionalization of GO with 1-(3-aminopropyl)imidazole (**API**), obtaining **GOIMZ**, following by a one-pot chemical polymerization of GOIMZ (**Poli-GOIMZ**). Characterizations were carried out by, thermogravimetric analysis, scattering electron microscopy, Fourrier Transform Infra Red and Raman Spectroscopy. The materials were evaluated as nanocatalysts in the dephoshorylation reaction of diethyl 2,4-dinitrophenyl phosphate (**DEDNPP**).

Results and Discussion

GO was obtained using a modified Hummers method[2]. Functionalization was done following procedure analogous as found in the literature[2] using a GO dispersion, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS) and API, specific for amide bond formation at the carboxylic acid sites of GO. The *in situ* polymerization also follows a literature procedure to polymerize imidazole derivatives, using ammonium persulfate in the same flask where the functionalization occurs,[3] hence comprising a one-pot polymerization (Figure 1). For comparison purposes, API was also polymerized (**Poli-API**).

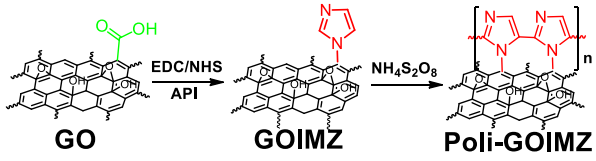

Figure 1. Synthesis of GOIMZ and Poli-GOIMZ.

Figure 2 shows the obtained kinetic profile, with the observed rate constant (k_{obs}) in varying pH for the reaction of **DEDNPP** with **Poli-GOIMZ** and **Poli-API**.

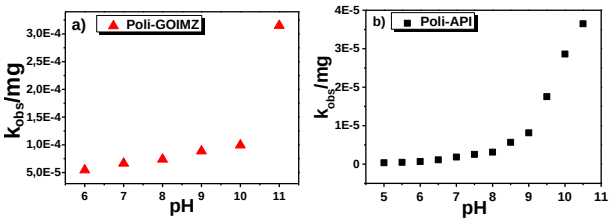

Figure 2. Obtained kinetic profile.

Poli-GOIMZ shows catalytic increments of 10^6 fold compared to the spontaneous reaction of DEDNPP. Poli-API also shows significant catalysis (10^4 fold), which is expected due to the high concentration of reactive imidazole groups, compared to the graphene-derivatives (functionalization degree above 20%). The higher reactivity of Poli-GOIMZ indicates synergistic effect on the surface of GO of the imidazole and other oxygenated moieties. Based on previous studies,[4] GOIMZ is a better nanocatalyst, which can be explained due to higher steric effects in the polymeric cataysts herein, for favorable interactions in the reaction, such as attractive effect.

Conclusions

Results show that Poli-GOIMZ and Poli-API, that were synthezied for the first time, can efficiently catalyze the cleavage of DEDNPP. Thus, the nanocatalysts are promising for detoxification under mild conditions (pH ~7). Also, studies with the toxic pesticide Paraoxon are being carried out. In addition, Poli-GOIMZ has potential for solar cell devices.

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