Graphene-based polymer nanocomposite, a new and efficient catalyst for synthesis of Benzimidazole derivatives

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Abstract: In this work, we reported the synthesis of benzimidazole derivatives via the condensation of 1, 2-phenylenediamines with benzaldehyde derivatives catalyzed by graphene-based polymer nanocomposites under mild conditions in moderate to good yields. To study the morphology and characterization of the nanocomposite, Fourier Transform Infrared Radiation (FT-IR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) were obtained.

Keywords: Heterocycles, Benzimidazole, Graphene-based polymer nanocomposites.

Introduction

Polymer nanocomposites as hybrid materials are the mixture of polymers and organic-inorganic fillers which at least one dimension of its fillers phases could be less than 100 nm [1]. The addition of nanoscale particles into a matrix material can magnitude improvement in the properties of polymer such as thermal, optical, mechanical and electrical [2].

Recently, different materials have been used to improve the properties of nanocomposites. Regarding to some remarkable characters of graphene and graphene oxide noteworthy these compounds widely considered to use in synthesis of polymer nanocomposites. GO has some reactive groups such as (-COOH, OH) on its surface, it has a respectable compatibility with nanomaterial polymers [3, 4].

Benzimidazole derivatives are among the most significant classes of bioactive molecules in pharmaceuticals. The construction of these heterocycles has received an increasing attention to synthetic organic chemists and biologists [5, 6]. Recently, numerous catalysts such as SDS micelles, glyoxalic acid, $FeBr_2$, $CoCl_2$, Zn-proline, silica sulfuric acid, nano-

In_2O_3, L-proline, $ZnCl_2$ and $FeCl_3/SiO_2$ have been employed for constructing the 1, 2-disubstituted benzimidazoles. On the other hand, graphene-based polymer nanocomposites have attracted strong interest due to their novel properties or enhanced performance [7].

In this research, we synthesized graphene-based polymer nanocomposite. It can be used as a heterogeneous catalysis in direct condensation–aromatization reaction of 1, 2-phenylenediamines with aldehydes for the selective synthesis of 1, 2-disubstituted benzimidazoles.

Experimental

General

All the solvents, chemicals and reagents were purchased from Merck and Aldrich. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectromete. XRD measurements were carried out using a JEOL JDX–8030 (30 kV, 20 mA). FE-SEM images were obtained on a Sigma Zeiss.

Synthesis Graphene Oxide-Lignosulfonate-Polyaniline (GO-LS-PANI) nanocomposite

The GO-LS-PANI nanocomposite was prepared with the LS and GO concentrations of 5 wt % in HCl aqueous solution [4]. GO (0.104 g) was dispersed in an aqueous solution of HCl under ultrasonication for 1 h. In the following, 0.104 g of LS and 20 mmol of aniline was added to the GO suspension and stirred vigorously to form a mixture of LS-GO-aniline. 20 mmol APS was dissolved separately in an aqueous solution of HCl (1.0 mol L^{-1}, 30 mL) to get ready an oxidant solution and placed for 0.5 h in an ice bath. This APS solution was discharged into the mixture of previous GO-LS-aniline and immediately stirred to ensure appropriate mixing. At that time, the polymerization was carried out without stirring for 24 h in an ice bath. The LS-GO-PANI nanocomposite was isolated from the mixture by filtration and washed with an excess amount of deionized water. The product was dried at a 60 °C vacuum for 72 h.

General procedure for the synthesis of 1, 2-disubstituted benzimidazoles 4a–f

A mixture of an *o*-phenylenediamine (1 mmol), an aldehyde (2 mmol), and GO-LS-PANI nanocomposite (20 mg) in 3 mL of EtOH was stirred in a round bottomed flask at room temperature. After completion of the reaction, as indicated by TLC, the resulting reaction mixture

was filtered to separate the catalyst. The filtered solution was allowed to cool to obtain crude products then purified by recrystallization using ethanol.

Results and discussion

First, GO-LS-PANI nanocomposite was prepared as described in the experimental section. To study the morphology and characterization of GO-LS-PANI nanocomposite, Fourier Transform Infrared Radiation (FT-IR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) patterns were used.

FT-IR spectra of the LS-GO-PANI nanocomposite is shown in Fig 1. The spectrum illustrated the stretching peaks of quinoid rings at 1556 cm^{-1}, the stretching of benzenoid rings at 1448 cm^{-1}, C−N stretching vibration at 1294 cm^{-1}, vibration of the −NH− at 1126 cm^{-1}, the vibration of COOH at 1730 cm^{-1}, the vibration of C-O at 1047 cm^{-1} and the S-O symmetric stretching of the $-SO_3$ groups on the LS chains at 1047 cm^{-1}.

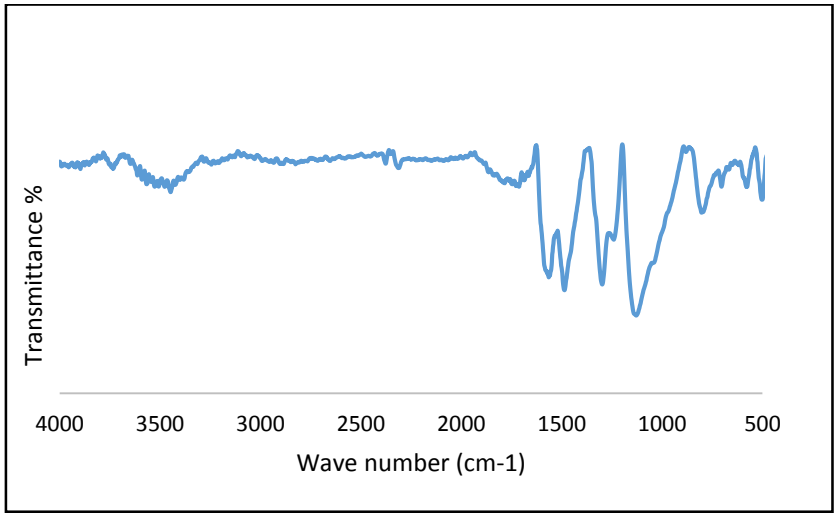


Fig. 1 FT-IR adsorption spectra of GO-LS-PANI.

The occurrence of residual stacked layers of GO with functional groups which was formed during oxidation process understood from the strong peak at 11.8 in the GO pattern. Due to the disturbance by PANI and LS, the inter-planar spacing of the GO-LS-PANI nanocomposite was broadened. The rich functional groups on the GO layers could induce PANI and LS to grow with a reasonably ordered chain structure.

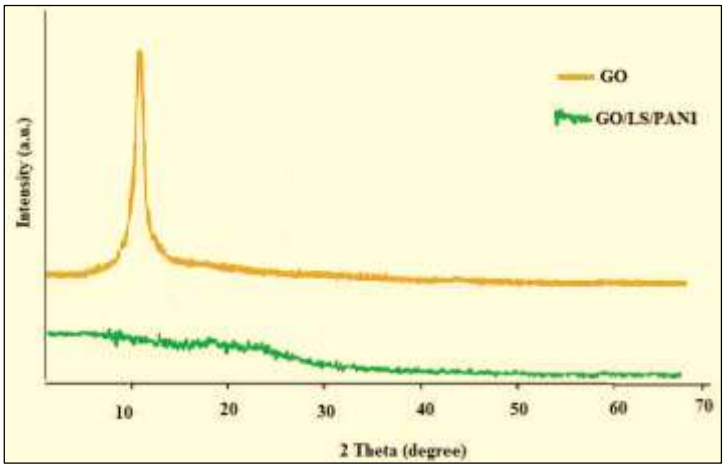


Fig. 2 XRD patterns of GO and GO-LS-PANI.

FE-SEM image of the LS-GO-PANI nanocomposite is shown in Fig 3 that illustrated the GO-LS-PANI nanocomposite has a greater special surface than the pure PANI. Also FE-SEM has shown that surfaces of the GO nanosheets are surrounded with nanofibers with an average diameter of 50 nm.

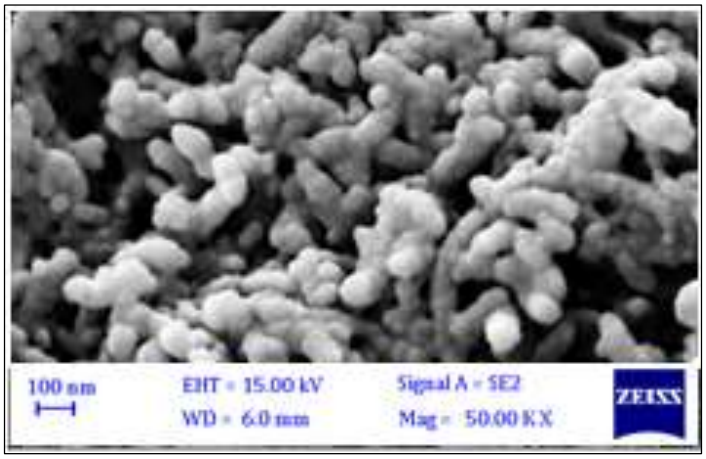
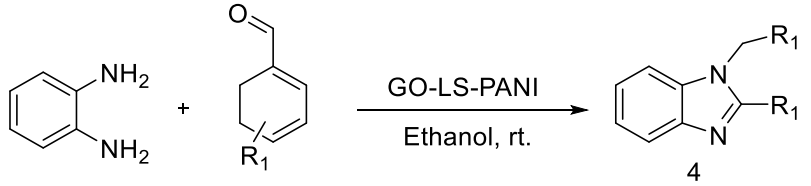


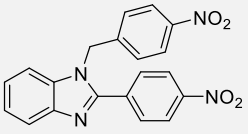
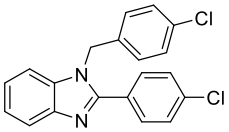
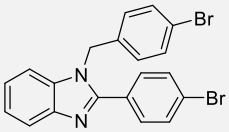
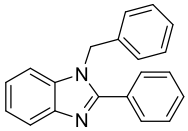
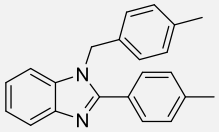
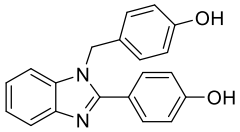
Fig. 3 FE-SEM image of GO-LS-PANI nanocomposite.

To investigate the catalytic ability of GO-LS-PANI nanocomposite, the reaction of benzaldehyde and *o*-phenylenediamine was considered as model reaction. After several tests, we realized that the optimized conditions for the reaction is using 0.02 g of GO-LS-PANI nanocomposite at room

temperature in ethanol. To investigate the generality of this procedure the synthesis was done with various aromatic aldehydes, (Table 1).

Table 1 Synthesis of 1,2- disubstituted benzimidazoles 4a-f via GO-LS-PANI.[a]



Entry	R^1	Products	Time (min)	Yield[b] (%)	Mp (°C)	Mp (°C)
1	4-NO_2	 **4a**	30	96	237-239	240-242[7]
2	4-Cl	 **4b**	60	90	143-144	142-144[7]
3	4-Br	 **4c**	75	94	159-162	163[7]
4	H	 **4d**	40	92	140-141	142-143[7]
5	4-Me	 **4e**	70	90	160-161	159-161[7]
6	4-OH	 **4f**	120	87	248-250	246-248[7]

[a] Reaction conditions: *o*-phenylenediamine (1.0 mmol), aromatic aldehyde (2.0 mmol), GO-LS-PANI (20 mg), ethanol (3 mL), r.t. [b] Isolated yield.

Conclusions

In summary, we synthesized GO-LS-PANI nanocomposite as a biopolymer-based nanocomposite and then we used the prepared nanocomposite as an efficient heterogeneous recyclable

nanocatalyst to preparation of 1, 2- disubstituted benzimidazoles. Short reaction time with moderate to good yields, easy workup procedure, and reusability of the catalyst are outstanding advantages of this work.

Acknowledgements

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