Graphene-based polymer nanocomposite catalyzed one pot multi-component synthesis of Chromene derivatives

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Abstract: We report an efficient procedure for the synthesis of functionalized 2-Amino-4H-Chromenes via the three component reaction catalyzed by graphene-based polymer nanocomposite in an eco-friendly condition with good yields. The characterization of the nanocomposite was investigated by Fourier transform Infrared Radiation (FT-IR), Scanning electron microscopy (SEM).

Keyword: Heterocycles, Benzochromenes, Graphene-based polymer nanocomposites

Introduction

Multicomponent reactions (MCRs) have attracted considerable interest of the synthetic organic chemists for construction functionalized organic molecules and pharmacologically significant heterocyclic compounds [1]. Chromenes have biologically remarkable properties such as antimicrobial, antiviral, and antiproliferation [2]. Functionalized 2-Amino-3-cyano-4H-Chromene derivatives are one of the most important heterocycle compounds which are used as agrochemicals, biological and anticancer agents [3].

Nanocomposites are prepared from two or more materials with different properties which at least one dimension of its fillers phases could be less than 100 nm. The convenient versatility of polymer nanocomposites is due to large available variety of polymers and fillers. The addition of nanoscale particles into a matrix material can magnitude improvement in the properties of polymer like thermal, optical, mechanical and electrical properties [4]. Polymer nanocomposites have unique physicochemical properties and they are used in important applications such as environmental restoration, anti-corrosion, defense system, the absorption of electromagnetic energy storage, information industry and new catalyst [5]. The recent developments are used as energy sources

such as electrochemical capacitors and batteries, anticorrosion and energy saving applications [6]. The discovery of graphene with its combination of extraordinary physical properties and ability to be dispersed in various polymer matrices has created a new class of polymer nanocomposites [7]. In this research, Graphene Oxide -Lignosulfonate-Polyaniline (GO-LS-PANI) was synthesized via an in situ polymerization and used as a catalyst in synthesis of 2-Amino-3-cyano-4H-Chromene derivatives.

2. 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.

Synthesis GO-LS-PANI nanocomposite

The GO-LS-PANI nanocomposite was prepared with the LS and GO concentrations of 5 wt % in HCl aqueous solution [5]. 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. Then, 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.

2.3. Synthesis of 2-amino-3-cyano-4H-chromenes

A mixture of Aldehyde (1mmol), malononitrile (1mmol), barbitoric acid (1mmol) were comboined in ball mill at room temperature. The progress of reaction was monitored by TLC. After completion of reaction, the product was precipitated in EtOH. The final product was obtained after recrystallization with EtOH.

3. Result and discussions

In this research, the characterization and morphology of GO-LS-PANI nanocomposite were considered by FT-IR, Scanning electron microscopy (SEM). In this section, these analysis were explained completely.

3.1. Fourier transform Infrared Radiation (FT-IR) analysis

According to FT-IR spectra of GO-LS-PANI, peak at 1556 cm^{-1} is related to the stretching peak of quinoid ring and the stretching peak of benzenoid ring is at 1448 cm^{-1}, C-N stretching vibration at 1294cm^{-1}, vibration of the N-H at 1126cm^{-1}, the vibration of COOH at 1730cm^{-1}, and the vibration of C-O is appeared at 1047cm^{-1}. S-O symmetric stretching vibration of SO_3 function group in LS chains is appeared at 1047cm^{-1}(Fig1).

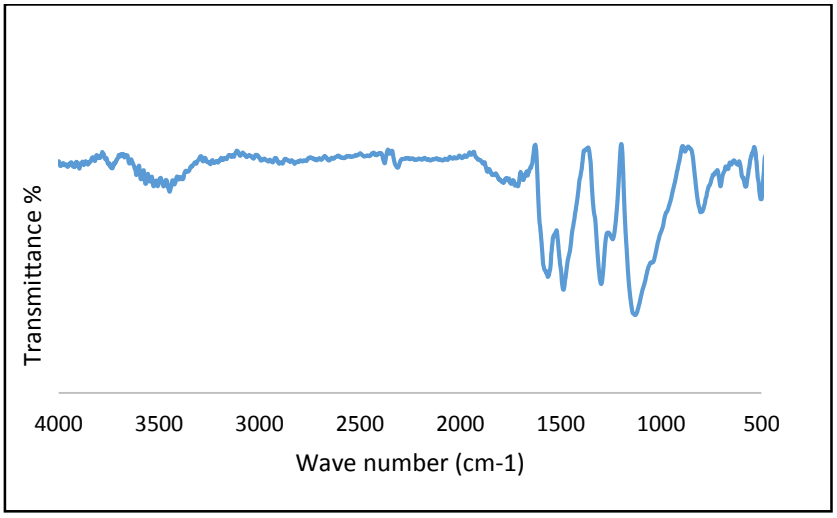


Fig.1. FT-IR Spectra of GO-LS-PANI

3.2. Scanning electron microscopy (FE-SEM)

According to Fe-SEM analysis, there is a broad specific surface in GO-LS-PANI. The size of 50nm has been able to describe that the surface of the GO nanosheet are surrounded by nanofibers.(Fig 2).

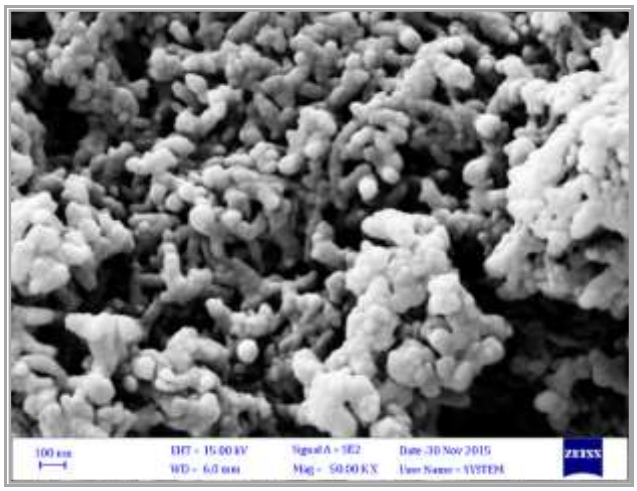
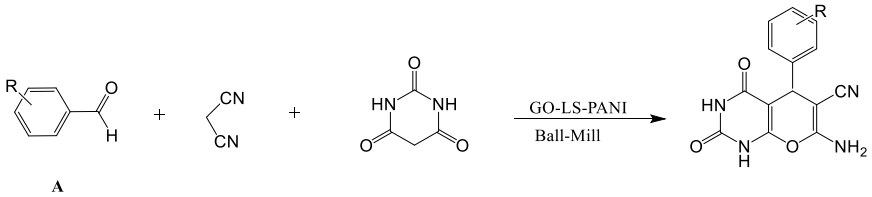
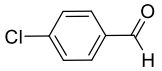
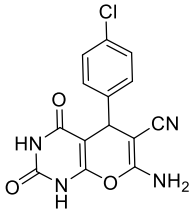


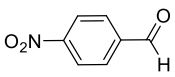
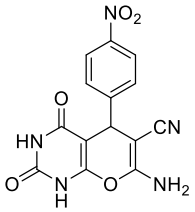
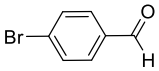
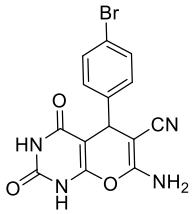
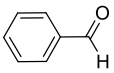
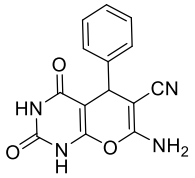
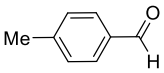
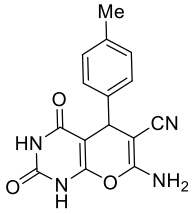
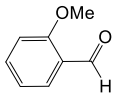
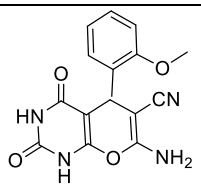
Fig.2. FE-SEM images of GO-LS-PANI nanocomposite

After optimization the reaction conditions, to showing the generality of this procedure the synthesis was done with various aromatic aldehydes (Table 1). As shown in Table 1, aldehydes with withdrawing groups have a great effect on reduction reaction time and increasing yields in presence of 0.03g GO-LS-PANI nanocomposite as a catalyst.

Table 1 Preparation of 2-Amino-4H-Chromenes catalyzed by GO-LS-PANI.



Entry	A	Product	Time (min)	Yield[a] (%)	M.p. (°C)	M.p.[ref] (°C)
1			8	95	278	270 [8]

2			5	96	275	268 [8]
3			10	90	227-229	229-231[9]
4			15	92	225-227	224-225[9]
5			20	90	224	225[10]
6			14	93	249	241[8]

[a] Yield refers to isolated pure product.

Conclusions

In this work, we synthesized GO-LS-PANI nanocomposite and then we used the prepared nanocomposite as a heterogeneous recyclable nanocatalyst to synthesis of 2-Amino-4H-Chromenes. Short reaction time, easy workup procedure, environmentally benign reaction condition, and reusability of the catalyst with excellent yields are outstanding advantages of this work.

Acknowledgements

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