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Preparation and catalytic application of graphene oxide-chitosan bionanocomposite

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Abstract: An efficient method for the synthesis of graphene oxide (GO)-chitosan bionanocomposite is demonstrated. Also, GO-chitosan is used as a green nanocatalyst in the synthesis of *tetra*-substituted imidazoles. This protocol has many advantages such as short reaction time, high yield, easy isolation of the catalyst and solvent-free conditions. We put upon Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) analyzes for the confirmation of the nanocomposite production.

Keywords: Graphene oxide, chitosan, bionanocomposite, nanocatalyst, imidazole.

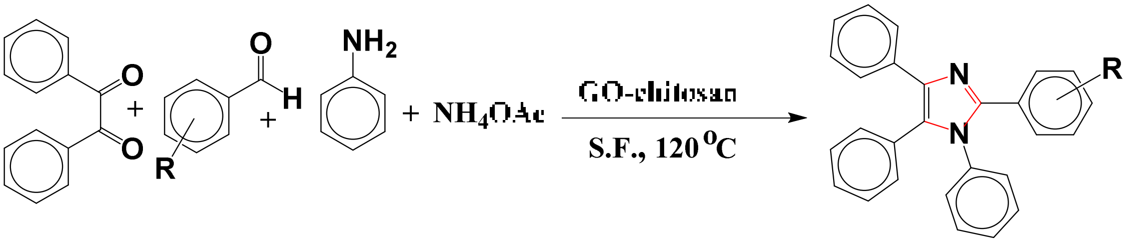
Introduction

Recently, paying attention to “greenness” in the catalyst design and catalytic processes, and thus greener reaction pathways and methodologies has been increased [1].

Graphene is a single atomic layer of sp^2 carbon atoms and lately has attracted tremendous attention due to its exceptional mechanical, thermal, and electrical properties. Graphene and graphene oxide are novel nanomaterials that have significant applications in nanoelectronics, sensors, nanocomposites, batteries, supercapacitors and energy storage. In the recent years, there has been a rush of interest in functionalizing graphene oxide materials with various polymers and biopolymers for various applications [2].

Chitosan, as a partially deacetylated derivative of chitin, is a linear polysaccharide consisting of β(1,4)-linked D-glucosamine residues with a variable randomly located *N*-acetyl-glucosamine groups on it [3].

Herein, we want to show that GO can be readily dispersed in chitosan matrix through the formation of amide linkages between them. Chitosan as a natural polymer has attracted considerable attention due to its unique properties such as biological renewability, biodegradability, non-antigenicity and biocompatibility. Accordingly, functionalization of GO with chitosan for reaching the exceptional properties of the both materials said on the above seems smart [4]. We have prepared and characterized GO-chitosan as a green nanocatalyst and used it in the convenient and effective synthesis of *tetra*-substituted imidazoles through a one-pot four-component reaction of benzyl, benzaldehyde, aniline and NH_4OAc under solvent-free conditions at 120 °C (Scheme 1).



Scheme 1. GO-chitosan-catalyzed synthesis of substituted imidazoles.

Experimental

General

All the solvents, chemicals and reagents were purchased from Merck, Fluka and Aldrich. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellet.

Preparation of GO-chitosan nanocomposite

100 mg GO and 2 g chitosan were poured into a 200 mL round-bottom flask charged with 100 mL DMF. The mixture was sonicated for 1 h, 0.9 g N,N'-dicyclohexylcarbodiimide (DCC) and 0.6 g 4-dimethylaminopyridine (DMAP) were then added into the above suspension and the resulting solution was kept at room temperature for 48 h. The resulting solid was isolated by centrifugation and then washed with *ortho*-dichlorobenzene (ODCB) (3×100 mL) to remove unreacted chitosan. The mixture was subsequently washed completely with water (100 mL), methanol (100 mL) and acetone (100 mL), sequentially. Finally, it was dried at 60 ^{o}C for 24 h under vacuum conditions.

General procedure for the synthesis of tetra-substituted imidazoles

The mixture of benzil (1 mmol), benzaldehyde (1 mmol), aniline (1 mmol) and ammonium acetate (1 mmol) was heated at 120 ^{o}C (bath temperature) in the presence of GO-chitosan (0.012 g) under solvent-free conditions. After the completion of the reaction, as indicated by TLC, the resulting reaction mixture was dissolved in 10 mL of EtOH and filtered to separate the catalyst. The filtered solution retaining product was placed in the refrigerator to obtain pure crystalline products in good-to-high yields.

Results and discussion

Functionalization of GO with chitosan was first prepared by our described procedures [5]. FT-IR spectroscopy was used for the confirmation of amid bond formation between GO and chitosan. In the spectrum of GO-chitosan, the peak presented at 1594 cm^{-1} is attributed to stretching vibration of C=O of NHCO and the peak located at 1038 cm^{-1} is attributed to N-H bending of NH_2 (Fig. 1).

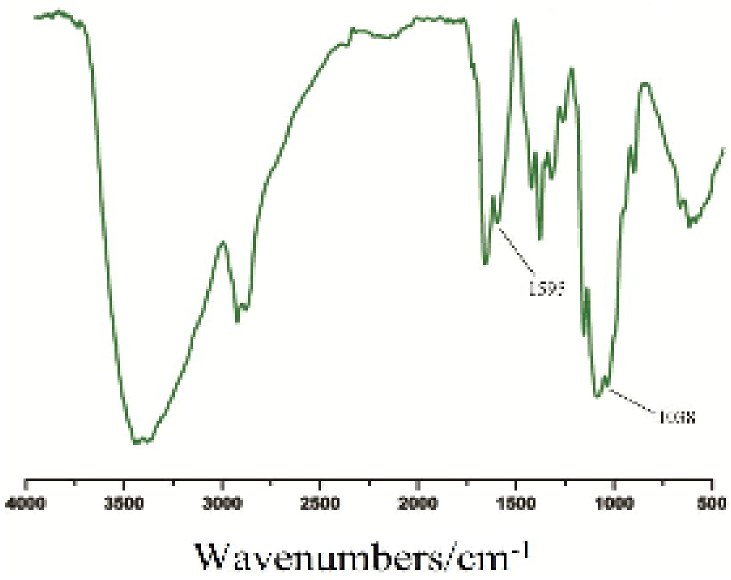


Fig. 1: FT-IR spectra of GO-chitosan.

Fig. 2 shows a scanning electron microscopy (SEM) image of GO-chitosan as obtained, where it is obvious to observe nanoscale structure of GO-chitosan biocomposite.

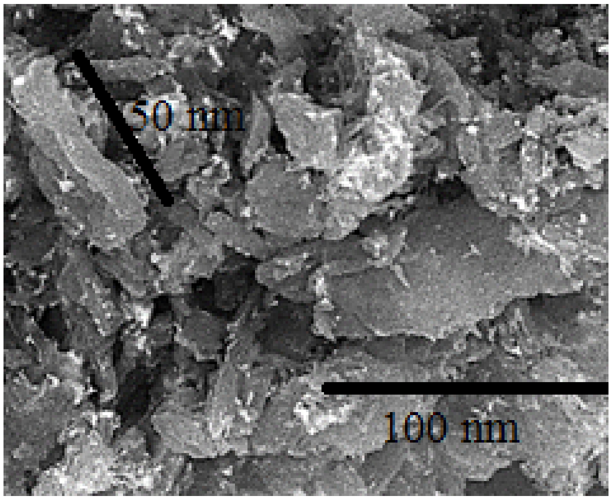


Fig. 2: SEM image of GO-chitosan nanocomposite.

To investigate the catalytic ability of GO-chitosan, a pilot experiment was carried out from the reaction of benzil, benzaldehyde, aniline and ammonium acetate to produce tetra-phenyl imidazole (Scheme 1). After several tests, we realized that the optimized conditions for the reaction was using 0.012 g of GO-chitosan at 120 ^{o}C under solvent-free conditions in a reasonable and short reaction time (20 minutes) and high yield (94%) to produce tetra-phenyl imidazole (Table 1, entry 1). It is noteworthy that, considered product with such efficiency could not be obtained under similar reaction conditions, neither in the absence of any catalyst nor other catalysts which have been used by now.

Subsequently, to investigate the efficiency and applicability of this catalyst the reaction was extended to other substituted benzaldehyde at 120 ^{o}C under solvent-free conditions (Table 1).

Table 1. Synthesis of *tetra*-substituted imidazoles using GO-chitosan nanocatalyst under solvent-free conditions.

Entry	R	Time (min)	Yield (%)
1	phenyl	20	94
2	2-chloro phenyl	30	90
3	4-methyl phenyl	25	92
4	4-methoxy phenyl	35	91
5	3-hydroxy phenyl	30	90

Conclusions

In summary, we have introduced GO-chitosan nanocomposite as a biocompatible and biodegradable heterogeneous nanocatalyst applicable in the synthesis of organic compounds. Then, efficient synthesis of *tetra*-substituted imidazoles were carried out starting from simple and readily available precursors including benzil, benzaldehyde, aniline and NH_4OAc in the presence of a catalytic amount of GO-chitosan.

Acknowledgements

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