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Short communication

Nanochitosan: A biopolymer catalytic system for the synthesis of 2-aminothiazoles

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ABSTRACT

A convenient and efficient method is described for the synthesis of 2-aminothiazoles by one-pot reaction of ketone and thiourea using chitosan nanoparticles under mild condition. Nanochitosan was used as a biodegradable and green catalyst for this reaction in satisfactory yields. The attractive advantages of the present process include easy isolation of products, milder and cleaner conditions, higher purity and yields and easier work-up procedure.

1. Introduction

Thiazole as a core structural element plays an important role in nature and has a wide range of applications in the field of agriculture and medicinal chemistry [1]. Thiazole heterocycle is a main structural motif of many natural compounds such as vitamin B_1 (thiamine), penicillin and carboxylase [2]. On the other hand, 2-aminothiazoles are one of the most important classes of heterocyclic scaffolds in the field of pharmaceutical and medicinal chemistry, such as hypertension [3], bacterial [4], schizophrenia [5], inflammation [6], HIV infections [7], and the treatment of allergies [8].

Therefore, in recent times, increasing attention has been paid for the synthesis of this class of heterocycles. The most straightforward synthesis of this heterocyclic compounds involves condensation of α-bromoketone with thiourea [9], the reaction of α-thiocyanato carbonyl compounds with aromatic or aliphatic amine hydrochlorides [10], treatment of styrene and thiourea with NBS [11] and the condensation of aromatic ketone and thiourea with homogeneous and heterogeneous catalysts [12]. Although these protocols reported by others find certain merits of their own, still they suffer from a number of demerits such as the use of expensive or toxic catalysts, tedious workup, high reaction temperatures, harsh reaction conditions, reagents in stoichiometric amounts, low yields and high catalytic loading [13]. Therefore, the development of an environmentally benign and efficient procedure for the synthesis of 2-aminothiazoles has become particularly fascinating and remains a great challenge.

Recently, biopolymers such as chitosan (CS) [14], starch [15] and cellulose [16] have been used as heterogeneous green catalysts in the chemical transformations. Chitosan can be explored as a basic heterogeneous catalyst in the chemical reactions [14,17]. The presence of both hydroxyl and amino groups in chitosan makes this polymer as an efficient catalyst for base catalyzed reactions [17]. Chitosan as a natural material has been used as a solid catalyst in Ullmann reaction [18], Suzuki cross-coupling [19], [3 + 2] aldol and Knoevenagel reaction [20], Heck reaction [21] and pyridazine synthesis [22]. Chitosan nanoparticles have received a great deal of attention because of their nano-size, large surface area, biodegradable, and good biocompatibility. These characteristics favor the employment of nanochitosan in a wide range of various applications, including drug delivery systems [23], sensors [24], protein carriers [25], removal of pollution [26] and catalysts [27].

However, despite extensive studies on synthesis of 2-aminothiazoles reported in the literature, to the best of our knowledge, there is no report focusing on the development of one-pot synthesis of 2-aminothiazoles using nanocatalyst. Moreover, having the above facts, herein we would like to introduce nanochitosan as a heterogeneous basic catalyst for the effective synthesis of 2-aminothiazole *via* the one-pot reaction of different ketones and thiourea in EtOH under reflux conditions (Scheme 1).

2. Experimental

2.1. Chemicals and apparatus

All chemicals were purchased from the Merck, Aldrich and Sigma Chemical Companies. Melting points were determined on an

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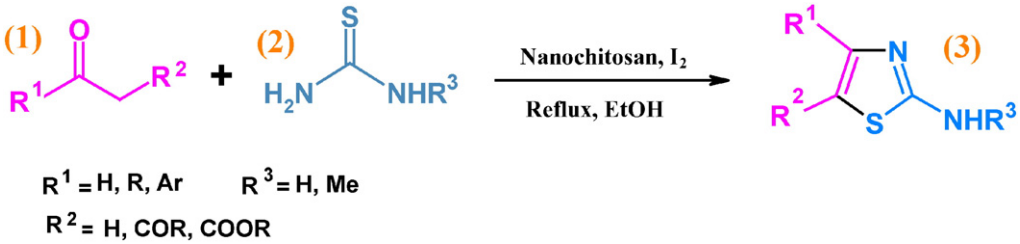

Scheme 1. The synthesis of 2-aminothiazoles catalyzed by nanochitosan.

Electrothermal MK3 apparatus using an open-glass capillary and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. FT-IR spectra were obtained with KBr pellets in the range 400–4000 cm^{-1} with a Perkin-Elmer 550 spectrometer. Nanostructures were characterized using a Holland Philips Xpert X-ray diffraction (XRD) diffractometer (CuK, radiation, $\lambda = 0.154056$ nm), at a scanning speed of 2°/min from 10° to 100° (2θ). The surface morphology of chitosan based material was analyzed by field emission scanning electron microscopy (SEM) (EVO LS 10, Zeiss, Carl Zeiss, Germany).

2.2. Preparation of nanochitosan

Chitosan nanoparticles were prepared through an ionic-gelation method according to reported procedures in the literature [27]. In short, 0.5 g chitosan was dissolved in 2% acetic acid solution at room temperature and 5 mL ammonium heptamolybdate tetrahydrate with a concentration of 2 g L^{-1} to 50 mL of chitosan solution was added dropwise to form a white solution. The product was extensively rinsed with distilled water to remove any ammonium heptamolybdate and then the chitosan nanoparticles were obtained by centrifugation at 16,000 rpm after drying with dried CO_2 for 30 min.

2.3. General procedure for the preparation of 2-aminothiazole derivatives

A mixture of the acetophenone (2 mmol), thiourea (3 mmol) and iodine (2 mmol), in the presence of 0.03 g nanochitosan was refluxed in EtOH. The progress of the reaction was monitored by TLC (petroleum ether–ethyl acetate 4:1). After completion of the reaction, the catalyst was separated by simple filtration. After evaporation of solvent, the crude product was dissolved in boiling water, extracted with ether (3 × 30 mL), and adjusted to pH = 8 with the amount of ammonia to give the solid products. The solid was recrystallized with ethanol–water to give pure 2-aminothiazole.

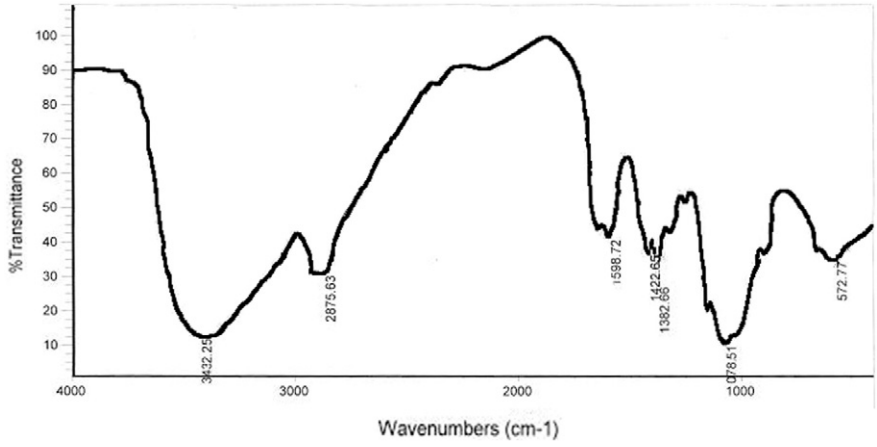

Fig. 1. The FT-IR spectrum of nanochitosan.

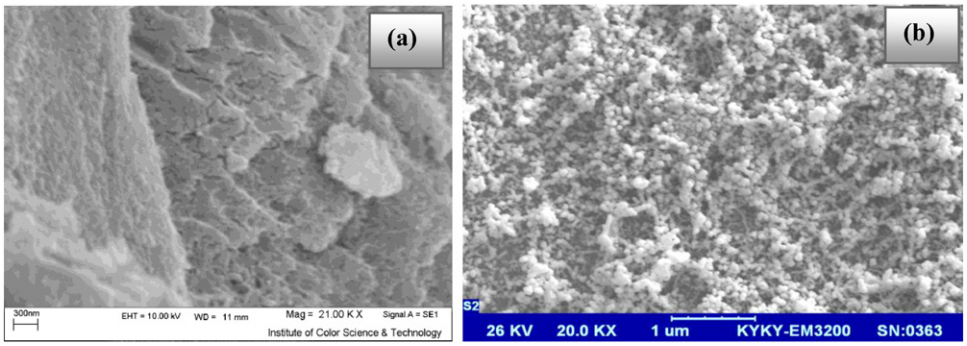

Fig. 2. SEM micrographs of (a) chitosan and (b) nanochitosan.