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Synthesis of Benzimidazole and Benzothiazole Derivatives using Reusable Waste Stem of *Trigonella Foenum-graecum* Assisted Zinc Sulphide Nanoparticles: A Green and Efficient Solid Acid Catalyst

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ABSTRACT

In this study, the simple and rapid methods for the preparation of benzimidazole and benzothiazole by the condensation of o-phenylenediamine with the aromatic aldehyde in presence of the zinc sulphide nanoparticles derived from the waste stem of the Trigonella foenum-graecum. The catalyst was prepared by using the waste stem of the Trigonella foenum-graecum. Most of the reaction carried under the mild condition with very high excellent yield. The method is used for the aromatic, unsaturated and heteroaromatic aldehyde. The main advantage of this method is that it takes very short reaction time, solvent free reaction condition, reusable catalyst, milder reaction, easy workup and waste stem of the plant was used.

1. Introduction

Naturally occurring nucleotides, i.e., adenine base of the DNA, as well as a component of vitamin B12 have extensively been used in drug synthesis and medicinal chemistry containing the benzimidazole or 1H-1,3-benzothiazole-based heterocyclic compounds (shown in fig.) [1–6]. Due to the presence of aromatic ring and nitrogen present in the ring of Benzimidazoles, it can show the large number of the biological activity such as antiviral activities [7–8], anticancer [9–11], antidiabetics [12,13], level modulators [14], antimicrobial [15–17], anti-inflammatory [18–20], and antioxidant [21].

There are various methods for the synthesis of benzimidazole derivatives. The most common traditional methods are coupling of the nitriles, amides, esters, chlorides, carboxylic acids with the o-phenylenediamine [22–23]. There are several methods in which thermal, microwave or the sonication method was used, most of time the benzimidazoles synthesized using the condensation of orthophenyl diamine with 2-nitroamines [24], aldehydes [25], carboxylic acids [26], carbonitriles, [27], arylamino oximes [28], cyclization of o-bromoaryl derivatives [29] and orthoesters [30].

The second route involves condensation reactions between o-phenylenediamine and aldehyde or alcohols via a dehydrogenated coupling, followed by oxidative cyclode hydrogenation [24,25], but in many of these methods, a stoichiometric number of oxidizing agents is a prerequisite [26–29].

Other important method which involves the direct regioselective C-2 arylation of imidazole with aryl halides using Pd(II)/Cu(I) catalytic amount at the high temperature, or pressure with low yield. There are several green catalyst like the inorganic salts zeolites [31–33], micelles [34], heterogeneous ionic liquid gel [35], metal oxides [36–40] p-toluenesulfonic acid/graphite and N,*N*-dimethyl aniline/graphite [41], benzimidazoles using various catalysts such as rose bengal [42], NH_4Cl [43] ytterbium perfluorooctane sulfonates ($Yb(OPf)_3$) [44] and base or metal catalysts [45] produces benzimidazoles. Generally, the condensation of o-phenylenediamines with aldehydes in the presence of acid [20], the dehydration of *N*-acylated, o-phenylenediamines using acetic acid [46], p-TSA [47] or amberlyst-15 Other methods include condensation of o-phenylenediamines with carboxylic acids, nitriles and *ortho*-esters under dehydrating conditions [48].

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Benzothiazole derivatives are known for different biological properties, including antitubercular, antimalarial, anticonvulsant, antihelmintic, analgesic, antidiabetic, antimicrobial, antibacterial, antifungal, herbicidal, antiproliferative and anti-inflammatory activities [49–52]. These compounds have shown antitumor activity against a range of human breast, ovarian, and colon cancers [53,54]. They are also useful for the *in-vivo* diagnosis of Alzheimer's disease [55,56].

Conventionally, 2-substituted benzothiazoles are synthesized by condensation of 2-aminothiophenol with aldehyde derivatives in different conditions. Various catalysts such as ZnO-beta zeolite [56], solid silica supported ferric chloride (SiO_2-$FeCl_3$) [57], glucose oxidase (GOX)/chloroperoxidase (CPO) [58], perchloric acid–doped polyaniline ($HClO_4$/PANI) [59], $Sc(OTf)_3$ [60], YCl_3 and mixed metal oxide nano crystals of Al_2O_3-Fe_2O_3, Al_2O_3-V_2O_5 and Al_2O_3-CuO were used in the synthesis of benzothiazoles. However, there is still room for improvement in the present methods to overcome the limitations and disadvantages of using organic solvents, long reaction times, lower yields and tedious work-up procedures. In this paper, we have reported the development of an environmental friendly protocol for the synthesis of 1,3-benzothiazole derivatives.

Nowadays, ZnS is an important member of this family as it has been extensively investigated [26]. ZnS nanoparticles have attracted a tremendous amount of attention because of their remarkable properties such as low cost, easy synthesis, high stability, small size etc [27]. Because of the importance of benzimidazoles and the catalytic ability of ZnS nanoparticles in the organic reactions, we wish to report a facile and efficient method for the synthesis of benzimidazole derivatives in the presence of catalytic amounts of ZnS nanoparticles in ethanol as solvent at 70°C.

2. Experimental

Chemicals are used of the S.D.Fine chemicals and Loba Chemicals products were characterized by their physical constant via the comparison with the authentic samples. Samples are purified by using column chromatography and progress of the reaction was monitored by using thin layer chromatography. Thin layer chromatography was performed using the aluminium plates with silica coating.

2.1. Synthesis of ZnS nanoparticles

ZnS nanoparticles were prepared by chemical method [5]. The reactants used for synthesis of ZnS nanoparticles were sodium sulphide ($Na_2S{\cdot}7H_2O$) and Zinc sulphate ($ZnSO_4{\cdot}5H_2O$). Using stoichiometric ratio in grams, 1 M solution of each reactant was prepared in distilled water. Freshly prepared aqueous solutions of these chemicals were used for the synthesis of nanoparticles at room temperature. The ZnS nanoparticles were prepared in the following sequence: First the extract prepared from waste stem of the Trigonella foenum-graecum (0.25 g) was added to the Zinc sulphate solution. The solution containing sodium sulphide was then added drop wise in solution of zinc sulphate and extract under continuous stirring until the white precipitates were formed. Stirring was done for 20 min to complete the reaction.

These precipitates were washed several times with distilled water to remove the impurities of sodium. After washing, the precipitates were centrifuged and dried at 100°C for 24 h. After drying, nanoparticles were grinded to achieve fine powder for characterization.

2.2. General procedure for the synthesis of benzimidazole derivatives

o-phenylenediamine (1 mmol) was added to a mixture of plant assisted nanoparticles (30 mg) and aldehyde (1 mmol) and the resulting mixture was sonication on the probe sonicate. After completion of the reaction, as monitored by TLC (EtOAc: hexane 5:5), ethyl acetate (20 mL) was added and the catalyst was separated by filtration. The solvent was then removed under reduced pressure and the resulting solid product was recrystallized from ethanol, producing the pure product in good to high yields.

2.3. General procedure for the synthesis of benzothiazole derivatives

o-phenylenediamine (1 mmol) was added to a mixture of Plant assisted nanoparticles (30 mg) and aldehyde (1 mmol) and the resulting mixture was sonication on the probe sonicate. After completion of the reaction, as monitored by TLC (EtOAc: hexane 8:2), ethyl acetate (20 mL) was added and the catalyst was separated by filtration. The solvent was then removed under reduced pressure and the resulting solid product was recrystallized from ethanol, producing the pure product in good to high yields.

2.4. UV–visible spectrum for ZnS nanoparticles

The UV–Visible spectrum of the prepared ZnS nanoparticles is shown in the Fig. 1. It shows a strong absorption peak around 265–270 nm which is large blue shifted from the bulk absorption. From the absorption peak the optical energy band gap of ZnS nanostructure has been calculated using the formula, Egn = hνgn = hc/λgn where h is plank's constant and Eg is energy band gap of the semiconducting nanoparticles in the optical spectra.

2.5. XRD study

X-ray diffraction patterns of the synthesized ZnS colloidal powders have been depicted in Fig. 2. The XRD traces shows that the prepared zinc sulphate is crystalline having zinc blende type structure. The cubic zinc blende structure was confirmed from the agreement of 2θ values with standard data. Fig. 2, showed three diffraction peaks at 2θ values of 28.96, 48 and 56.52. The peaks were identified to originate from (111), (220) and (311) planes of the cubic zinc-blende phase of ZnS, respectively.

The particle size calculated using Debye Scherer formula was 2.8 nm. The Debye Scherer formula is $D = 0.9\,\lambda/(\beta\cos\theta)$ (2) where D is the mean grain size, λ is the X-ray wavelength, θ is the diffraction angle and β is full width at half maximum.

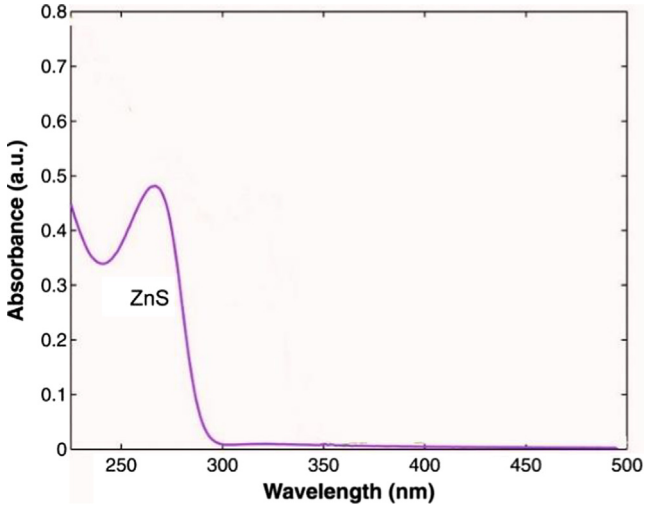


Fig. 1. UV spectrum of prepared ZnS nanoparticles.

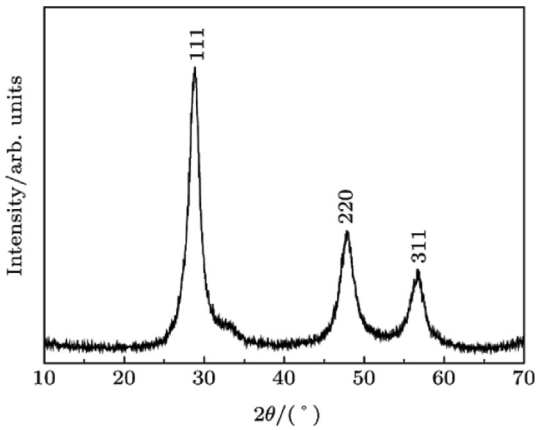


Fig. 2. X-ray diffraction patterns of the synthesized ZnS colloidal powders.

2.6. FTIR

The FTIR spectrum of ZnS nanoparticles at room temperature is shown in Fig. 3. This spectrum shows the IR absorption due to the various vibration modes. The characteristic major peaks of ZnS can be observed at about 1060, 1236, 1404, 788, 592, which are in good agreement with the reported results. The observed peaks at 1538 cm^{-1} – 1659 cm^{-1} are assigned to the C═O stretching modes, and also the broad absorption peaks in a range of 3434 cm^{-1} – 3965 cm^{-1} correspond to O—H stretching modes arising from the absorption of water on the surface of nanoparticles via – COOH group.

2.7. SEM

The SEM microstructural analysis shows that the synthesized ZnS contains mainly the grains of ZnS particles (crystallite) with regular shape (Fig. 4). One can see that nearly spherical nanoparticles have an almost homogenous size distribution with a mean size of 80–90 nm. In the absence of EDTA, a bulk ZnS sample is formed (not shown here). In the synthesis process, the usage of EDTA causes the stabilization of the small particles and the inhibition of this agglomeration. Due to the existence of – COOH group in EDTA molecules which absorbed on the particle surface, EDTA-capped ZnS sample is formed. The maximum particle size does not exceed 70 nm.

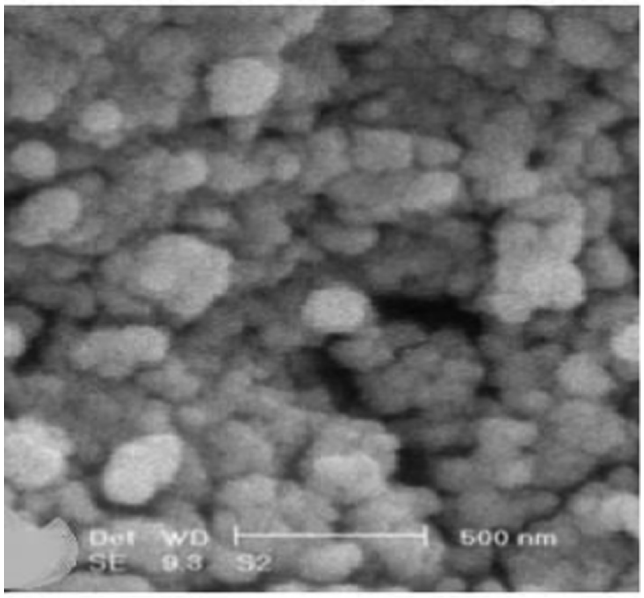


Fig. 4. The SEM image of ZnS nanoparticles.

In order to establish the better catalytic activity of nano-ZnS, the reaction in the presence of other catalysts in ethanol at 70°C was investigated. The results showed that the nano-ZnS, as compared to other catalysts, gave the better yield of the desired product.

To determine the optimum quantity of nano-ZnS, the reaction of benzaldehyde and *o*-phenylenediamine was carried out in ethanol at 70°C using different quantities of nano-ZnS. The results showed that 0.03 g for benzimidazole and for benzothiazole 0.09 of the catalyst gave the excellent yield of the product. (See Tables 1–6).

3. Results and discussion

On the basis of the research information obtained on the applicability of plant assisted nanoparticles in the promotion of different types of organic reactions, we expected that this reagent

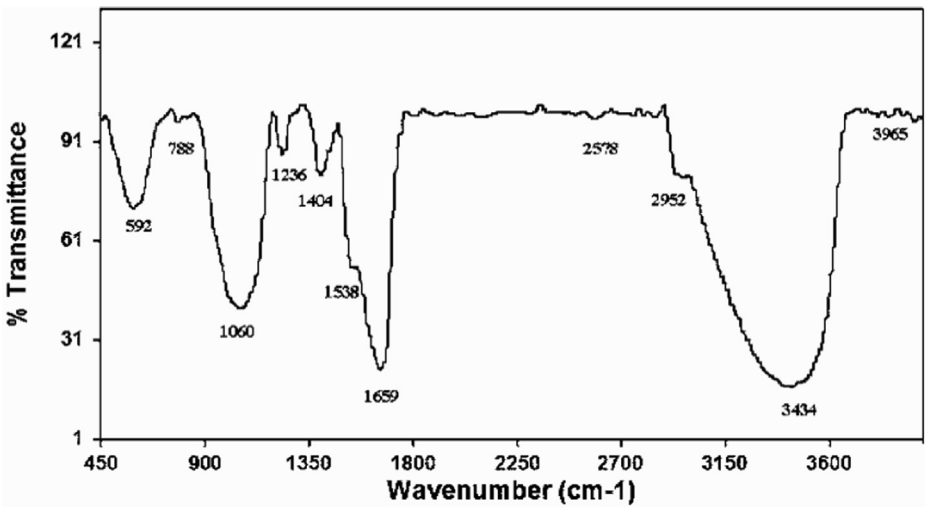


Fig. 3. The FTIR spectrum of ZnS nanoparticles.

Table 1
Evaluation of the activity of different catalysts for the synthesis of 2-phenyl-1*H*-benzimidazole.

Entry	Catalyst	Time (min)	Yield (%) (Benzimidazole)	Yield (%) (Benzothiazole)
1	–	60	25	35
2	Zinc Oxide	60	70	45
3	Alum	60	65	67
4	Hydrochloric Acid	60	65	55
5	Para-toluene Sulphonic Acid	60	67	54
6	NH_4Cl	60	87	86
7	Nano ZnS	60	97	96

Table 2
Optimization amount of nano-ZnS for the synthesis of 2-phenyl-1*H*-benzimidazole.

Entry	Catalyst (g)	Time (min)	Yield (%) (Benzimidazole)	Yield (%) (Benzothiazole)
1	–	60	40	43
2	0.01	60	56	67
3	0.03	60	98	56
4	0.09	60	78	97
5	0.20	60	67	78

Table 3
Optimization of the reaction temperature in the synthesis of 2-phenyl-1*H*-benzimidazole using nano-ZnS.

Entry	Temperature (°C)	Time (min)	Yield (%) (Benzimidazole)	Yield (%) (Benzothiazole)
1	70	60	97	95
2	60	60	70	80
3	40	60	78	70
4	25	60	67	45

Table 4
Reaction between *o*-phenylenediamine and different aldehydes catalyzed by nano-ZnS (0.03 g) in EtOH at 70 °C.

Entry	Ar	Time (min)	Yield (%) (Benzimidazole)	Yield (%) (Benzothiazole)
1	$2\text{-}NO_2C_6H_4$	60	95	92
2	$3\text{-}NO_2C_6H_4$	60	95	94
3	$4\text{-}NO_2C_6H_4$	60	96	91
4	$4\text{-}NHCH_3C_6H_4$	60	91	89
5	$2\text{-}OH\text{-}3CH_3OC_6H_4$	60	85	81
6	$4\text{-}ClC_6H_4$	60	87	86
7	$4\text{-}OHC_6H_4$	60	98	95
8	$3,4(CH_3O)_2C_6H_3$	60	89	92

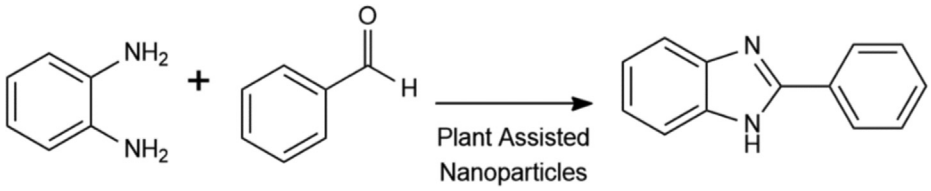
Table 5
Catalyst Reusable for Benzimidazole.

Entry	Catalyst (g)	Time (min)	Catalyst Cycle	Yield (%) (Benzimidazole)
1	0.03	60	1	96
2	0.03	60	2	82
3	0.03	60	3	78
4	0.03	60	4	56
5	0.03	60	5	40

Table 6
Catalyst Reusable Benzothiazole.

Entry	Catalyst (g)	Time (min)	Catalyst Cycle	Yield (%) (Benzothiazole)
1	0.03	60	1	94
2	0.03	60	2	78
3	0.03	60	3	67
4	0.03	60	4	56
5	0.03	60	5	45

could also be efficiently used in promoting the synthesis of benzimidazole and benzothiazole; these compounds function as acidic catalysts and speed up the reaction. Initially, optimize reaction conditions were studied by investigating the effect of various reactant molar ratios and solvents. and also, solvent-free conditions, on the reaction of substituted benzaldehyde (10 mmol) and o-phenylenediamine (10 mmol) in terms of time and the product yield. The obtained results showed that the reaction using 30 mg



Scheme 1. Organic transformation using plant assited nanoparticles.

of the catalyst at room temperature under a solvent-free condition in sonication produced the highest yield during a very short time.

Any further increase of the temperature or the catalyst amount did not improve the reaction time and yield. After optimizing the reaction conditions and in order to show the general applicability of this method, the preparation of benzimidazoles derivatives with a variety of simple, readily available substrates under the optimal conditions was investigated. Several aldehydes having electron donating and electron withdrawing groups underwent the conversion to form a series of aryl benzimidazoles in good to excellent yields. As can be seen, o-phenylenediamines with electron-withdrawing groups gave the desired products in higher yields within longer times in excellent yields.

After the successful synthesis of benzimidazoles, the preparation of benzothiazole derivatives, as the other useful heterocyclic compounds, in the presence of plant assisted nanoparticles, was nominated for further study.

Our investigations clarified that by using this method, the best results can be obtained when the reaction proceeded using lower amounts of the catalyst (90 mg) under solvent-free conditions at ambient temperatures. It is important to note that this reaction was not completed in different types of solvents even after a long time under reflux conditions. The selected conditions are shown in Scheme 1. To assess the efficiency of plant assisted nanoparticles in the preparation of benzothiazole derivatives, various aromatic aldehydes were subjected to the optimal conditions. It was observed that under the selected conditions, all the substrates containing electron-withdrawing groups, as well as electron-donating groups, were easily reacted in short reaction times with good to excellent isolated yields.

To check the reusability of the catalyst, the reaction of o-phenylenediamine with benzaldehyde or aromatic aldehyde under the optimized reaction condition was studied again. When the reaction was completed, ethyl acetate was added and the catalyst was separated by filtration. The recovered catalyst was washed with dichloromethane, dried and reused for the same reaction. The recovered catalyst was reused five times with a slight decrease in reusability in comparison to fresh catalyst. In order to show the efficiency of the present method, our result obtained from the reaction between o-phenylenediamine and benzaldehyde in the presence of plant assisted nanoparticles was compared with some of the other results reported in the literature for the same reaction. This method avoids the disadvantages of other procedures such as long reaction times, excess reagents and organic solvents.

4. Conclusion

We have used plant sasisted nanoparticles as a highly catalyst for the simple and efficient synthesis of benzimidazole and benzothiazole and their derivatives. The procedure has several advantages, such as ease of preparation and handling of the catalyst, being a simple experimental procedure, having high reaction rates, producing excellent yields and the use of inexpensive and reusable catalyst. Furthermore, this process avoids problems associated with the use of organic solvents and liquid acids, which makes it a useful and attractive strategy in view of these economic and environmental advantages.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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