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Short Communication

Synthesis and characterization of CdS and Mn doped CdS nanoparticles and their catalytic application for chemoselective synthesis of benzimidazoles and benzothiazoles in aqueous medium

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ABSTRACT

CdS and Manganese doped CdS nanoparticles of ~2 nm have been prepared at room temperature by a wet chemical technique. The heterogeneous catalysts were fully characterized by XRD, TEM, EDAX, ICP-AES and UV/VIS. These nanoparticles were exploited to study their catalytic activities towards the chemoselective aqueous mediated synthesis of 2-aryl benzimidazoles and benzothiazoles. Doping of Mn promotes the activity and selectivity of CdS nanoparticles indicated by high TOF value, providing the products in good to excellent yields, and with good chemoselectivity. The catalyst could also be recovered easily and used repetitively four times without significantly affecting the catalytic activity.

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1. Introduction

Exciting new opportunities are emerging in the field of catalysis based on nanotechnology approaches. Nanoparticles have attracted considerable attention in catalysis: their unique properties, intermediate between those of the bulk and the single particles, combine the advantages of heterogeneous catalysis (recovery and recyclability) with those of homogeneous catalysis (low loadings and good selectivity) [1].

To speak of bioactive molecules, 2-aryl benzimidazoles and benzothiazoles behold an arena in diverse array of such compounds. Various pharmacophores bearing these heterocyclic units have revealed broad spectrum of biological activities in past [2,3] as well as recent medicinal chemistry applications [4,5]. The potentialities of these compounds have led to them being encountered through the development of various synthetic protocols, several approaches for the synthesis of these compounds were developed [6–9]. Most widely used protocol involves the direct condensation of o- phenylenediamine/o-aminothiophenols with aryl aldehydes using variety of oxidative and catalytic reagents [10–12] e.g. sulfamic acid, DDQ, Oxone, FeCl₃· $6H_2O$, In(OTf)₃, Yb(OTf)₃, Sc(OTf)₃, KHSO₄.

However, all of these procedures suffer from one or more of the following disadvantages such as long reaction times, low yields of the products, harsh reaction conditions, use of excess amounts of reagents, tedious workup procedures, and co-occurrence of several side reactions with less selectivity of the process. In addition, some of the catalysts and reagents are expensive, toxic, and air sensitive. Therefore,

* Corresponding author. E-mail address: dranshudandia@yahoo.co.in (A. Dandia). there is still a need to search for better catalysts that could be superior to the existing ones regarding toxicity, handling, and operational simplicity. To meet the requirement of recyclability, nanoparticles as a catalyst is opted which has unique properties such as high stability, ease of recyclability, easy preparation, possible processability. Mn based catalysts has attracted a great deal of attention in the past as oxidation catalysts. Particular for oxidation reactions, redox active transition metals such as Co, Fe and Mn have been investigated as promoter elements [13]. Nonetheless, the outcome of the promoting effect of the Mn depends on its concentration and its location within the catalyst [14]. It has also been reported that MnO acts as a structural promoter, increasing the stability of the catalyst [15]. As a part of our continuing activities to explore the novel protocols for heterocyclic frameworks [16–18] and nanoparticles synthesis by wet chemical method [16,19], we report herein the synthesis, characterization and catalytic application of CdS and Mn doped CdS nanoparticles for selective oxidative synthesis of 2-aryl benzimidazoles and benzothiazoles by the cyclocondensation reaction of aldehydes and o- phenylenediamine or o-aminothiophenols in aqueous medium respectively (Scheme 1).

2. Results and discussion

2.1. Synthesis and characterisation of catalyst

CdS NPs and Mn doped CdS nanoparticles were synthesized through the wet chemical precipitation method, which is a promising technique for synthesis of these NPs with excellent catalytic properties and high stability. The advantages of this method lie in its simplicity, cost effectiveness, environment friendliness, easier



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Scheme 1. Chemoselective synthesis of 2-aryl benzimidazoles and benzothiazoles.

scaling up for large scale synthesis while avoiding the use of high pressure, temperature and toxic chemicals as required in earlier method [20]. The nanostructure of the nanoparticles has been characterized by XRD, TEM, EDAX, ICP-AES and UV/VIS (See Supporting Information).The diffraction peaks appearing for all the samples at 20 values of about 26.55, 44.03 and 52.08 correspond to the (111), (220) and (311) planes of cubic phase of CdS and the addition of Mn to CdS nanoparticles does not create any change in the CdS matrix (Fig. 1). The average particle size of Mn doped CdS nanoparticles and pure CdS is ~2 nm, which is confirmed from TEM image. It shows abundance of spherical particles (Fig. 2).

EDAX has been employed to confirm the Mn doping in the soprepared samples of nanoparticles (Fig. 3). In UV a slight blue shift is observed with doping of Mn (Fig. 4). This slight blue shift in the absorption edge is the outcome of the quantum confinement effect produced due to increased nucleation rate with increase in doping concentration [21].

The surface Lewis acidity of this material was confirmed through the adsorption of pyridine vapour [22] on the surface of the NPs. FT-IR spectra of pyridine adsorbed on the catalysts are shown in Fig. 5 (See Supporting Information).

2.2. Catalytic performance in chemoselective synthesis of benzimidazoles and benzothiazoles

To examine the feasibility of CdS NPs catalysed reaction in aqueous medium, an initial experiment was performed



Fig. 1. XRD patterns of nanoparticles.

with 4-chlorobenzaldehyde (1 mmol) and o-phenylenediamine/ aminothiophenol (1 mmol) as the model substrate. With 4chlorobenzaldehyde (1 mmol), o-phenylenediamine/aminothiophenol (1 mmol) and CdS nanoparticles (10 mol%) the condensation gave a yield of 79% at 90 °C for 2.5 h. Further the study of catalytic ability of Mn doped CdS nanoparticles showed that doping increase the product yield to 95% and reducing the reaction time (1.5 h) with decrease the catalyst loading(5 mol%). These nanoparticles were used in water as obtained by wet chemical method. Additionally, water served as a suitable solvent for the currently probed transformation as well, based on the solubility difference of the product from the starting materials, leading to separation of product from the reaction mixture upon completion, thereby facilitating easy isolation of solid product from the reaction mixture.

Literature reveals that in the oxidative cyclization of aldehyde and o-phenylenediamine the formation of the required 2-aryl-1Hbenzimidazole is accompanied by the occurrence of 1-benzylated 2-aryl-1H-benzimidazoles as side products [23], and sometimes these disubstituted derivatives have been isolated as the main product [24,25]. The present protocol gives 2-aryl-1H-benzimidazole selectively. Further we extended our studies on oxidative reactions of aldehydes with o-aminothiophenol. Although thiols are good nucleophiles and SET agents [26], in present studies, no substitution of the halogen atom or the nitro group, dealkylation/debenzoylation took place as reported earlier [27–29]. Further the dithioacetal formation is a common reaction of aldehydes with thiols [30], no competitive dithioacetal formation was observed under the present conditions.

Under these reaction conditions, we performed a series of experiments for reactions of o-phenylenediamine/aminothiophenol with different aldehydes. The results are summarized in Table-1, aldehydes bearing both electron-donating and electron-withdrawing substituents afforded desired products in excellent yields. Heterocyclic aldehydes were well tolerated under these conditions. It was found that only 43% yield was observed under similar conditions in the absence of catalyst, even after 4 h. It was proved that the catalyst did play an important role in this reaction. The effect of catalyst concentrations on the reaction rate and yield of the product was also investigated. It was found that the optimum reaction rate and yield could be achieved at the catalyst concentration of 5 mol%. Elemental analysis (by ICP-AES) of the product after completion of the reaction showed that there was no nanocatalyst present in the final product.

2.3. Catalysis and comparison of catalytic activity of Mn doped CdS nanoparticles with other catalysts

A comparison of efficiency of catalytic activity of Mn doped CdS NPs with CdS and several other catalysts is presented in Table 2. It was found that the best result in terms of turnover frequency ($602 h^{-1}$) could be achieved by using Mn doped CdS NPs catalyst (5 mol% loading), as compared to undoped CdS NPs ($TOF = 142 h^{-1}$). This result is in agreement with our working hypothesis that a higher concentration of acidic sites gives more products in the reaction. Therefore, lower catalyst loading required for this transformation as compared to many other catalytic systems. These results show that this method is superior to the other methods in terms of yield and reaction time.

Based on the above observations, a plausible mechanism for the formation of 3 is depicted in Scheme 2. The Lewis acid sites of NPs were coordinated to the oxygen of carbonyl groups. The coordination of NPs with the carbonyl oxygen of 2 induces electrophilic activation of aldehyde, which benefits the initial condensation of 1 with 2 to give an imine A, the subsequent intramolecular nucleophilic cyclization of A afforded B, which subsequently undergoes an oxidation promoted by Mn(IV) to give 3 as the final product (Mn (IV) species formed *in situ* by oxidation of Mn (II) with air). At the same time, the *in situ* formed Mn (IV) could be reduced to regenerate Mn(II) for the next catalytic cycle.



Fig. 2. TEM image of nanoparticles.

2.4. Recyclability

3. Experimental

3.1. Catalyst preparation

After the completion of the reaction, the nanoparticles were recycled by separating them from the reaction mixture by sonication and used as a catalyst for the same reaction again (Table 3). Powder XRD of reused nanoparticles is also recorded which shows that the structural integrity remains unaltered after the reaction and thus proves the efficiency of nanoparticles as a recyclable catalyst.

Nanoparticles of CdS were prepared at room temperature by dropping simultaneously 50 ml of 1 M solution of $CdSO_4$ and 50 ml of 1 M solution of Na_2S into 200 ml of distilled water containing 50 ml of 0.1 M solution of EDTA, which was vigorously stirred using a magnetic stirrer under Ar



Fig. 3. EDX spectrum of the nanoparticles.



Fig. 4. UV spectrum of the nanoparticles.

 Table 1

 Synthesis of benzimidazoles and benzothiazoles.

S. No.	R	Х	Time (h)	Product	Yield (%) [*]	Mp (°C)
1.	C ₆ H ₅	NH	1.5		93	292–294
2.	3-NO ₂ C ₆ H ₅	NH	2.5		92	203–205
3.	3-ClC ₆ H ₅	NH	1.5		97	235–237
4.	2-ClC ₆ H ₅	NH	1.5		94	231-233
5.	4-NO ₂ C ₆ H ₅	NH	2.0		91	313-315
6.	4-MeC ₆ H ₅	NH	1.5		98	274–276
7.	4-ClC ₆ H ₅	NH	1.5		95	287–289
8.	4-OMeC ₆ H ₅	NH	1.5		95	224–227
9.	2- Thienyl	NH	2.5		87	330-331
10.	C ₆ H ₅	S	1.5		94	110-111
11.	4-OMeC ₆ H ₅	S	1.5		96	124–125
12.	2-OHC ₆ H ₅	S	1.5		98	225-227



* Isolated yield.

atmosphere. The role of EDTA was to stabilize the particles against aggregation which may lead to an increase in the particle size. The doping of Mn has been done by adding 2 wt.% of metal sulphate (MnSO₄) to CdSO₄ (at the starting of the reaction) for the formation of CdS:Mn NPs. The precipitate was separated from the reaction mixture and was dried at room temperature. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle.

3.2. Determination of surface acidity

To check the nature of acid sites present in NPs, the material was kept in contact with pyridine vapor in a closed container for 24 h. Pyridine adsorbed material was analyzed with FT-IR spectra.

3.3. Catalyst activity measurement:

In a 50 ml round bottom flask, o-phenylenediamine/aminothiophenol (1 mmol) and aromatic aldehydes (1 mmol) in water (4 ml) were mixed and stirred at 90 °C. To this, catalyst was added. The progress of the reaction was checked on TLC. After completion, the reaction mixture was cooled at room temperature. Then, it was extracted with ethyl acetate; the organic layer was dried over sodium sulphate and concentrated in a vacuum to afford the crude products. The pure products were obtained by recrystallization from ethanol. The structure of the products was

Table 2			
Comparison	of catalytic	activity	of catalys

Entry	Condition	Time (h)	Yield $(\%)^*$	$TOF(h^{-1})$
1.	MeSO ₃ H (10 mol%), H ₂ O,	3.5	74	95
2.	PTSA (10 mol%), H ₂ O,	3.5	80	103
3.	CAN (10 mol %), H ₂ O,	3.0	77	116
4.	ZnS powder (10 mol%), H ₂ O,	3	65	98
5.	CdS powder (10 mol%), H ₂ O,	2.5	67	118
6.	CdS NPs (10 mol%), H ₂ O,	2.5	79	142
7.	Mn:CdS NPs(5 mol%), H ₂ O,	1.5	95	602

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), o-phenylenediamine / aminothiophenol (1 mmol) in water as a solvent at 90 °C. * Isolated yield.



Scheme 2. Plausible mechanism.

Table 3	
Recyclability of the catalyst.	

No of cycles	Yield $(\%)^*$
1	95
2	94
3	93
4	93

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), o-phenylenediamine/ aminothiophenol (1 mmol) in water as a solvent at 90 $^\circ\text{C}.$

* Isolated yield.

unambiguously established on the basis of their spectral analysis (IR, ¹H NMR, ¹³C NMR and GC–MS mass spectral data).

4. Conclusions

In this study, CdS and Mn doped CdS nanoparticles have been prepared, characterized and used as efficient and chemoselective catalysts for the synthesis of 2-aryl benzimidazoles and benzothiazoles. The enhanced catalytic activity and product yield by Mn doping could be attributed to the increase of surface acidity. Overall, this methodology offers competitive advantages such as recyclability of the catalyst without further purification or without using additives or cofactors, low catalyst loading, broad substrate applicability, and high yields. The application of this new nanocatalyst in organic synthesis will provide a novel pathway for the synthesis of pharmaceutically pertinent compounds.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.08.020.

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