Dysprosium Incorporated Into Balsalazide Trapped Between the Functionalized Halloysite and $g\text{-C}_3\text{N}_4$ as an Efficient and Heterogeneous Catalyst for the Synthesis of Chromene Derivatives

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Abstract

An efficient and heterogeneous novel Dy complex of balsalazide, trapped between the functionalized halloysite and $g\text{-C}_3\text{N}_4$, was successfully synthesized by post-synthetic modification approach ($\text{Dy@Hal-BS-}g\text{-C}_3\text{N}_4$). It was characterized by several advanced analytical methods including, FT-IR, SEM, EDX, elemental mapping, XRD, ICP-OES and TGA. The as-synthesized material was catalytically explored as a novel recoverable nanocatalyst in the synthesis of an array of biologically active pyran derivatives, i.e., the 2-amino-5,10-dioxo-4-aryl-5,10-dihydro-4H-benzo[*g*]chromene-3-carbonitriles. Excellent yields of the desired products and facile reusability of the catalyst are the two advantageous factors in the introduction of this novel catalytic system.

1. Introduction

In recent times, supported nanomaterials have garnered global attention as novel nanocatalyst due to their unique role in performing catalytic reactions, which is completely different from that of their homogeneous or bulk counterparts [1–4]. Although there are numerous reports on the precious noble metal catalysis in diverse organic transformations, in supported catalysis, the support play a vital role in properly distributing the active metal sites in order to operate the special function of over the reactive substrates [5–9]. The main object in most of the academia research and industrial organic reactions remains to develop a designed or functionalized novel catalyst to explore it in the preparation of target molecules – in higher selectivity and lower energy necessities – and also to improve the reaction rate [10]. In this sense, the utilization of organic biomolecules or functionalized ligand modified catalysts can convert these manufacturing methods to safer, greener and viable procedures, with minimal waste for a variety of organic reactions [11–15]. The progress of sustainable and green catalytic procedures, coupled with the design of unique and environmental-friendly ways, relies pronouncedly on the improvement of catalyst achievement [16, 17]. Transition metal-based nanocatalysts have been established to be competent for the organic transformations. Despite the widespread use of these nanocatalysts, the leaching of expensive or toxic metals into the desired product is one of the negative aspects of employing heterogeneous metal-based catalysts in green catalysis [16, 18]. In this regard, the involvement of high surface area carbonaceous materials in the heterogeneous catalytic core seems to be a suitable sustainable solution [19–24]. 2D-layered Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) with s-triazine core has been considered as one of the most important class of materials with unique physicochemical properties and attracted the attention of a wide variety of researchers [25–29]. Regarding the carbon-based materials, these polymeric compounds have great potential in industry and technology as metal-free green heterogeneous catalysts in various organic transformations [30–35].

In recent times, tubular halloysite (Hal) clay, a member of kaolinite group, has garnered great attention in catalysis science owing to a variety of important advantages, viz., thermal and chemical stability, tubular morphology, simplicity and ease of synthesis, low toxicity, ability to facile functionalization and ease of separation from the reaction medium [36–43]. Therefore, the synthesis of complex modified and heterogenized Hal has received great priority, as potential catalytic support, to be used in several novel

approaches[42, 44–49]. Now, with these inputs we would like to introduce a hybrid metal doped modified Hal supported over high surface carbon matrix ($\text{Dy@Hal-BS-g-C}_3\text{N}_4$) as a novel nanocomposite in the synthesis of biologically active chromene derivatives [50–51].

In our protocol, we approached a three component coupling between 2-hydroxynaphthalene-1,4-dione, an active methylene compound and diverse aldehydes to synthesize a polycyclic chromene scaffold following Knoevenagel Condensation–Michael Addition–Cyclization sequence. In this multicomponent pathway, water is only produced as the by-product. In addition, it possesses a chiral center at the phenyl-substituted carbon that can have significant stereochemical utilities [52–54]. Recently, chromenes and their derivatives have received great attention due to a broad spectrum of biological and pharmacological activities. In addition, some of these scaffolds construct the backbone of a wide range of natural products [55–56].

Considering the interesting benefits of heterogeneous catalysts with the use of natural raw materials, herein, we propose the synthesis of an efficient and heterogeneous novel $\text{Dy@Hal-BS-g-C}_3\text{N}_4$ and its application in the synthesis of such an interesting molecule by condensing various aldehydes, lawsone and ethyl 2-isocyanoacetate or malononitrile derivatives in high yield and under mild conditions.

2. Experimental

2.1. Materials and instruments

All of the materials were obtained from Sigma-Aldrich and Merck and applied as received. To investigate the properties of the catalyst, SEM analysis was performed on a FESEM-TESCAN MIRA3 microscope with EDX attachment (TSCAN). The FT-IR spectrum was obtained using the PERKIN-ELMER-Spectrum 65 device. An ICP analyzer (Vista-pro, Varian) was used to perform ICP analysis. The XRD pattern was investigated using Cu K α radiation (wavelength 1.78897 Angstrom, 40 keV and 40 Ma). Mettler Toledo TGA was used to perform TGA using nitrogen atmosphere. NMR spectra of organic compounds were measured with the BRUKER spectrometer.

2.2. Typical procedure for the synthesis of $\text{Dy@Hal-BS-g-C}_3\text{N}_4$:

2.2.1. Fabrication of Hal-Cl

The CPTES shell was grafted on the surface of Hal layers to generate Hal-Cl according to our previously reported method [57].

2.2.2. Synthesis of Hal-BS

1.5 g of Hal-Cl was dispersed in 50 ml deionized water by sonication for 30 min. Then, 1.5 g of balsalazide (BS) and 2 g of NaOH were added to the dispersion and stirred at 110°C for 24 h. After

completion of the reaction, the Hal-BS product was isolated out by centrifuge, washed with distilled water several times and dried at 100°C for 24 h.

2.2.3. Typical procedure for the synthesis of $g\text{-C}_3\text{N}_4$:

The $g\text{-C}_3\text{N}_4$ was prepared by our previously reported method [58]. 5 g of urea was heated at 550°C for 3 hours in a semiclosed reactor. The yellow-colored product ($g\text{-C}_3\text{N}_4$) was then powdered.

2.2.4. Synthesis of Hal-BS- C_3N_4

1.5 g of $g\text{-C}_3\text{N}_4$ was dispersed in deionized water (100 mL) by sonication for 30 min. Subsequently, Hal-BS was added to the reaction mixture and dispersed for another 15 min. Then, 5 mg of Na_2CO_3 was poured into the reaction mixture and stirred at 50°C for 24 h. Eventually, the precipitated product was collected by simple filtration, washed with EtOH to remove the adhered substances and dried overnight.

2.2.5. Synthesis of Dy@Hal-BS- $g\text{-C}_3\text{N}_4$

Finally, 1.2 g of Hal-BS- $g\text{-C}_3\text{N}_4$ was taken in 15 mL deionized water followed by the addition of 0.03 g of dysprosium (III) nitrate into that. Then catalytic amount of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was added to the reaction mixture and stirred for 12h at ambient temperature. The final product Dy@Hal-BS- $g\text{-C}_3\text{N}_4$ was isolated by filtration, washed thrice with methanol and dried at 60°C in an oven for 24 h (Scheme 1).

2.3. General procedure for the synthesis of 2-amino-5,10-dioxo-4-aryl-5,10-dihydro-4H-benzo[*g*]chromene-3-carbonitrile (2a–j)

A mixture of aromatic aldehydes (1 mmol), 2-hydroxy-1,4-naphthoquinone (1.0 mmol), active methylene compounds (malononitrile or ethyl cyanoacetate) (1.5 mmol) and Dy@Hal-BS- $g\text{-C}_3\text{N}_4$ (20 mg) was refluxed in water at 100°C (Scheme 2). After completion (by TLC), the reaction mixture was diluted with hot ethanol to dissolve the organic substances and the catalyst was isolated by simple filtration. The pure product was recrystallized from the hot ethanolic solution and dried to obtain a pure solid. All products were known and identified by comparing their melting points with authentic literature.

3. Result And Discussion

3.1. Characterization of catalyst

The successful synthesis of Dy@Hal-BS- $g\text{-C}_3\text{N}_4$ was affirmed using different techniques like FT-IR, FE-SEM, EDX, elemental mapping, XRD, ICP-OES, and TGA.

FT-IR technique has been used to identify various functional groups of Dy@Hal-BS- $g\text{-C}_3\text{N}_4$ and its stepwise building. Fig. 1 illustrates the FT-IR spectra of a) Hal-Cl, b) $g\text{-C}_3\text{N}_4$, c) Balsalazide, and d)

Dy@Hal-BS-*g*-C₃N₄. In Fig. 1a, the absorption bands at around 539, 1631, and 3620–3698 cm⁻¹ are related to the stretching vibrations of Si–O–Al, Si–O, and inner -OH groups, respectively [58]. In Fig. 1b, as expected, the strong absorption at 807 cm⁻¹ is due to the special bending vibration of triazine moiety [59]. The FT-IR spectrum of BS is in good accordance with the reported data [60] and exhibited some characteristic bands at 3371, 3039 cm⁻¹, (OH, NH stretching), 1699, 1631 cm⁻¹ (acid and amide carbonyl stretching), 1579 cm⁻¹ (C=C stretching), 1219 cm⁻¹ (C–N stretching) and 1073 cm⁻¹ (C–O stretching) (Fig. 1c). The FT-IR spectrum of Dy@Hal-BS-*g*-C₃N₄ is presented in Fig. 1d. All the expected absorption peaks of Hal-Cl, BS and *g*-C₃N₄ can be detected in this spectrum, which indicates the successful trapping of BS complex in Dy@Hal-BS-*g*-C₃N₄.

The structural morphologies, particle size and shape of the Dy@Hal-BS-*g*-C₃N₄ were determined using FE-SEM analysis. The corresponding image (Fig. 2) displays a tubular morphology indicating that Hal structure remained unchanged even after successful surface coating with BS and incorporation of Dy NPs (Fig. 2).

The elemental composition and their corresponding weight% was ascertained by EDX analysis (Fig. 3). The existence of Al, Si, and O elements are ascribed to the Hal structure in Dy@Hal-BS-*g*-C₃N₄. In addition, the presence of carbon, oxygen and nitrogen elements confirm the attachment of balsalazide molecule in the targeted structure. The occurrence of Dy element peak in the EDX spectrum clearly indicates the loading of Dy on the Hal-BS-*g*-C₃N₄.

The elemental analysis study was further extended via elemental mapping of the Dy@Hal-BS-*g*-C₃N₄ (Fig. 4). The outcome clearly confirms the presence of the mentioned elements in the catalyst with a suitable dispersity. The uniform distribution of active sites over the catalyst surface is very significant in its catalytic activity. The obtained result from elemental mapping analysis therefore agreed well with EDX data (Fig. 4).

The crystalline phase structure of Dy@Hal-BS-*g*-C₃N₄ nanocomposite was examined by XRD analysis. As shown in Fig. 5, the Dy@Hal-BS-*g*-C₃N₄ exhibits seven sharp and strong diffraction peaks at 2θ = 8°, 12°, 22.6°, 28.2°, 31.5°, 57°, and 68° which are in good agreement with XRD pattern of tubular Hal (JCPDS card no. 29-1487) [61, 62]. The *g*-C₃N₄ phase is represented by a peak at 2θ = 28° (JCPDS card no. 87-1526). These results certainly validates that the tubular structure of Hal is not destroyed during the functionalization and stabilization of Dy complex. The diffraction peaks of Dy nanoparticles were not observed in the XRD pattern due to the high dispersion and low loading (1.9 wt% as determined by ICP-OES) and strong attachment onto the support [63].

Thermal stability and the quantitative estimation of the trapped organic groups were investigated by TGA analysis of Dy@Hal-BS-*g*-C₃N₄ over the temperature range of 25-800°C (Fig. 6). The thermograph displays three decomposition breaks and confirms the structure of Dy complex trapped between Hal and *g*-C₃N₄ with various layers. As can be seen, the first weight loss of the catalyst (~4%) occurred at about

50–120°C, related to the removal of the adsorbed water or surface hydroxyl groups. The second weight loss occurred nearly between 330–410°C (~10%), which can be assigned to the destruction of the chloropropyl groups coated on the Hal support. Again, the third and major weight loss (~50%) occurred at 450–675°C, attributed to the removal of the chemisorbed water and BS molecule. Finally, at the end of decomposition till 700°C, the total loss in weight was about 64.23. These results show good thermal stability of Dy@Hal-BS-*g*-C₃N₄.

3.2. Catalytic study

After the detailed structural characterization of the nanocomposite material (Dy@Hal-BS-*g*-C₃N₄), its catalytic activity was investigated in the synthesis of 4H-benzo[*g*]chromenes. However, prior to generalizations, optimization of reaction conditions appeared very important and thus the reaction of 2-hydroxy-1,4-naphthoquinone (1.0 mmol), benzaldehyde (1.0 mmol) and malononitrile (1.5 mmol) was selected as model. Subsequently, the influence of various reaction parameters including solvent, reaction temperature and catalyst loading were examined (Table 1). It's worthy to mention that the reaction failed in the absence of Dy@Hal-BS-*g*-C₃N₄ catalyst. After optimizing the catalyst loading, the effect of a number of solvents and temperature were explored. The results indicated that the presence of solvent and catalyst were very important to succeed the reaction. After comprehensive experiments, 10 mol% of Dy@Hal-BS-*g*-C₃N₄ catalyst in refluxing water was considered as the optimal reaction conditions (Table 1).

Table 1
Optimization of the reaction conditions for the synthesis of 4H-benzo[*g*]chromene derivatives.

Entry	Reaction condition	Catalyst (mol%)	Time (min)	Yield (%)
1	H ₂ O/ r.t.	10	60	85
2	H ₂ O/ 50°C	10	40	90
3	H ₂ O/ 80°C	10	20	96
4	H ₂ O/ reflux	10	14	98
5	H ₂ O/ reflux	–	60	10
6	EtOH, r.t	10	65	80
7	EtOH, reflux	10	35	90
8	CH ₃ CN, reflux	10	40	87
9	CHCl ₃ , reflux	10	75	80
10	Toluene, 80°C	10	20	87
11	H ₂ O/ 80°C	15	14	98
12	H ₂ O/ 80°C	5	25	88
Reaction conditions: Dy@Hal-BS- <i>g</i> -C ₃ N ₄ as catalyst, Solvent (5 ml)				

After optimization the reaction parameters, immediately we had to investigate the scope and generality of those conditions by involving diverse substrates in the reaction. Thus, we examined various electron-withdrawing and electron-releasing benzaldehydes in the Dy@Hal-BS-*g*-C₃N₄ catalyzed multicomponent cyclocondensation reaction for the preparation of 4H-benzo[*g*]chromene derivatives. The results have been documented in Table 2. It is evident from the results that the different aldehydes are very much compatible under the reaction conditions, providing excellent yields irrespective of the functional character and geometry in positions in aromatic ring (o, m, p). Evidently, our catalytic system is very suitable in terms of the efficiency of reactions, reaction time and yields. All the derivatives were obtained in excellent yields (90-98%) and short reaction times (10-30 min). Noticebaly, the substrates with electron-withdrawing groups (NO₂, Cl, Br and F) reacted faster than that with electron-donating substrates (Me, OMe, OH and NMe₂). In addition to malononitrile, ethyl cyanoacetate was also employed in the reaction, showing comparable efficacy. After isolating the pure products, they were dried and the melting pints were recorded to compare with authentic samples.

Table 2
One pot, three-component synthesis of 4H-chromenes using Dy@Hal-BS-*g*-C₃N₄ as the catalyst.

Entry	R	R'	Time (min)	Yield (%)	M.P.	
					Obs.	Lit. [52, 64, 65]
1	C ₆ H ₅	CN	14	98	262-263	260-262
2	4-FC ₆ H ₄	CN	11	96	242-245	244-246
3	4-ClC ₆ H ₄	CN	14	97	231-233	230-232
4	4-BrC ₆ H ₄	CN	15	95	248-250	249-251
5	4-NO ₂ C ₆ H ₄	CN	22	96	232-234	230-232
6	4-CH ₃ C ₆ H ₄	CN	25	95	241-245	240-242
7	4-OCH ₃ C ₆ H ₄	CN	20	95	244-245	244-246
8	4-OHC ₆ H ₄	CN	30	90	257-260	258-260
9	4-NMe ₂ C ₆ H ₄	CN	32	91	249-252	250-252
10	2-ClC ₆ H ₄	CN	25	95	248-250	248-250
11	2,4-Cl ₂ -C ₆ H ₃	CN	30	94	281-283	280-282
12	C ₆ H ₅	CO ₂ Et	20	95	185-188	185-187
13	4-FC ₆ H ₄	CO ₂ Et	15	94	209-210	209-211
14	4-NO ₂ C ₆ H ₄	CO ₂ Et	25	91	198-200	197-199
15	4-CH ₃ C ₆ H ₄	CO ₂ Et	30	90	207-209	207-210
16	4-OCH ₃ C ₆ H ₄	CO ₂ Et	25	92	222-225	224-226
17	3-NO ₂ C ₆ H ₄	CO ₂ Et	28	93	196-199	198-200

3.3. Reaction mechanism

Scheme 3 demonstrates a plausible transformation mechanism for the catalysis over Dy@Hal-BS-*g*-C₃N₄ nanocomposite [66]. Initially, the Dysprosium complex led to the activation of the carbonyl group on the aldehyde based on its high Lewis acidity. Subsequent nucleophilic addition by the active methylene compounds (malononitrile or ethyl cyanoacetate) generated the intermediate (I) following Knoevenagel condensation. Now, enolic Michael addition by 2-hydroxy-1,4-naphthoquinone molecule to I produces the intermediate (II). An intramolecular cyclocondensation takes place being activated by the catalyst and final enolization of the intermediate (III) affords the target 4H-benzo[*g*]chromene derivative [8].

3.5. Catalyst recyclability

Catalysts, having metal complexes in their structure, play an important and effective role in industries and other applications in laboratory scale. Hence, recyclability of the catalyst to prevent waste generation is one of the most important factor in catalysis. Nevertheless, recoverability of Dy@Hal-BS-*g*-C₃N₄ was evaluated on the model reaction and it was recycled up to 8 runs by simple filtration with a gradual decrease in activity from 96 to 82% in the corresponding product (Fig. 7).

3.6. Uniqueness of our protocol

In order to demonstrate the exclusivity of Dy@Hal-BS-*g*-C₃N₄ as a heterogeneous catalyst in the synthesis of 4H-benzo[*g*]chromene derivatives, our results in the optimized model reaction conditions was compared with the reported ones, being displayed in Table 3. Evidently, as depicted there, Dy@Hal-BS-*g*-C₃N₄ is the most efficient catalyst among them in terms of reaction time and yield. Significantly, most of the reported methods toil from the absence of commonness for the condensation reactions of the deactivated aldehydes. In addition, the reported synthetic paths have some limitations, such as requires extreme temperature or long duration, large amounts of the catalyst and, most importantly, the use of hazardous solvents.

Table 3
Comparison of the catalytic activity of Dy@Hal-BS-*g*-C₃N₄ with reported results in the literature.

Entry	Catalyst	Time (min)	Yield (%)	Ref
1	Fe ₃ O ₄ /(PEG)	20	85	[67]
2	Imidazole	30	93	[68]
3	Piperidine	15	85	[69]
4	[PySO ₃ H]BF ₄	25	89	[70]
5	FeCl ₃	40	65	[70]
6	Dy@Hal-BS- <i>g</i> -C ₃ N ₄	14	97	This work

4. Conclusion

In conclusion, herein, we have demonstrated an effective and successful preparation of Dy incorporated balsalazide immobilized between the functionalized halloysite and $g\text{-C}_3\text{N}_4$ (Dy@Hal-BS- $g\text{-C}_3\text{N}_4$). The novel material was characterized using various advanced analyses. Towards its application, the catalyst showed high catalytic efficiency in the synthesis of 4*H*-benzo[*g*]chromenes over a variety of aromatic aldehydes, active methylene compounds (malononitrile or ethyl cyanoacetate) and 2-hydroxy-1,4-naphthoquinone in refluxing water. Easy work-up procedure, using green solvent, excellent yield, short reaction time, good tolerance of various functional groups in the introduced conditions, easy isolation of products without the involvement of tedious column chromatography and catalyst reusability up to 8 successive runs with only an insignificant loss in the product yields are the advantages of this method.

Declarations

Conflicts of interest

There are no conflicts of interest with this research work.

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Author contributions

G.R. and M.D. designed and performed the experiments, M.T contributed materials/analysis tools, M.T. and M.M. wrote the paper and M.D. prepared figures. All authors reviewed the manuscript.

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Scheme

Scheme 1, 2 and 3 is available in supplementary section

Figures

Figure 1

FT-IR spectra of a) Hal-Cl, b) $g\text{-C}_3\text{N}_4$, c), BS and d) $\text{Dy@Hal-BS-}g\text{-C}_3\text{N}_4$.

Figure 2

FE-SEM images of Dy@Hal-BS-*g*-C₃N₄

Figure 3

EDX analysis of Dy@Hal-BS-*g*-C₃N₄

Figure 4

EDX-mapping study of Dy@Hal-BS-*g*-C₃N₄

Figure 5

XRD pattern of Dy@Hal-BS-*g*-C₃N₄ nanomaterials

Figure 6

The TGA curve of Dy@Hal-BS-*g*-C₃N₄

Figure 7

Reusability of Dy@Hal-SS-*g*-C₃N₄.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme01.png](#)
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