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RESEARCH PAPER

Design and Preparation of Nano-ZnO/Ag Composite for Catalytic Performance in Synthesis of Benzo(g)chromenes

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ABSTRACT

In this current research, the nano-sized ZnO/Ag composite was prepared through hydrothermal method. The as-prepared nano-sized composite was characterized by different methods, such as: FE-SEM (field emission scanning electron microscopy), EDX (Energy Dispersive X-Ray), FT-IR (Fourier transform infrared), and XRD (X-ray diffraction) analysis. The XRD outcome shows that the designed nano-sized ZnO/Ag composite was formed with hexagonal shape and high crystallinity. Also, the FE-SEM images displayed that the average particle size of nano-sized ZnO/Ag composite was obtained about 72 nm. Moreover, FT-IR spectroscopy confirm the presence of ZnO along with silver bands. A three-component reaction of cyanoacetonitrile, different benzaldehydes, and hennatannic acid have been done in the existence of designed nano-sized ZnO/Ag composite as a robust heterogeneous nanocatalyst to prepare benzo(g)chromenes. FT-IR, NMR, and melting point techniques were used to confirm the formation and purity of final products. The obtained compounds were produced with good to excellent yields (75-93 %) in short time (75-95 min) under reflux conditions.

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INTRODUCTION

Today, several products were synthesized in biological and medicinal chemistry. For instance, family of chromenes are substantial members of oxygen-containing heterocyclic products. This family have interesting attributes: antidiabetes, anti-inflammatory, antivirus, antimicrobial, and anticancer [1-5]. Moreover, some reports are published about Alzheimer's cure in recent decades [6]. The outstanding drug structures: acronycine, vitamine E, cromakalim, and uvafzlelin are other samples of chromene scaffolds. These mentioned compounds display prominent properties, prolonged effect, high bioavailability, and no fast-onset [7]. Recent researches presented that chromene scaffolds are seen as important aims in organic synthesis. Because of this, finding effective ways to create various substituted chromenes is an interesting challenge. Several researches have been hitherto reported in the synthesis of chromen compounds using different catalytic conditions, such as: *p*-TsOH [8], diazabicycloundecene [9], trimethylamine [10], $Zn(L\text{-proline})_2$ [11], and [bmim]OH ionic liquid [12].

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Nano-sized metal/ metal oxide composites are unique nanostructures that have been extensively investigated due to their special properties and potential application in diverse issues. Zinc element is a super strategic element in synthesis of metal oxide nanocomposites [13, 14]. Till now, different reports have been published about zinc and zinc oxide composites in various fields: catalyst, chemotherapeutic, and biology [15, 16]. Recent reports show that facile and available methods are fastly developed. One of them is hydrothermal protocol [17]. Hydrothermal method is generally conducted in autoclave system and there are less environmental challenges [18]. Besides, this protocol is a most substantial route to set the shape of nanostructure sample by altering the preparation conditions [19, 20]. Consequently, hydrothermal method as clear, facile, and relatively inexpensive protocol. Moreover, the preparation of metal/metal oxide composites is a more powerful strategy for increasing the synergic effect of nanostructures [21, 22]. For instance, the various ZnO composites with different type of elements: W, Ag, Mg, and Ce have been reported[23-25].

In this report, we herein present the preparation of nano-ZnO/Ag composite as an efficient nanostructure for catalytic performance in the synthesis of benzo(*g*)chromenes through multicomponent reactions.

MATERIALS AND METHODS

Simple route for synthesis of nano-ZnO/Ag composite via hydrothermal method

In water medium (40 mL), zinc sulfate monohydrate (2 g) was completely dissolved. Then, 1 g of silver nitrate was directly added to above solution and stirred for 10 minutes at room temperature. In next step, polyvinylpyrrolidone (PVP) solution (0.75 g in 15 mL of deionized water) was droply added. The caustic soda solution [5 *N*] was added slowly to above medium via burette to give pH=12. The formed mixture was moved to autoclave for 12 hours at 140 °C. At completion, the sediment was filtered and washed with 15 mL of ethanol 90 several times. To give pure nano-ZnO/Ag composite, the dried sediment was calcined at 550 °C for 180 min.

Typical synthesis method for benzo(g)chromenes

A round-bottom flask (25 M), the cyanoacetonitrile, different benzaldehydes, and hennotannic acid in a 1:1:1 mole ratio were mixed together in 10 mL of ethanol medium in the presence of the nano-ZnO/Ag composite as a nanocatalyst. The mixture was then refluxed.

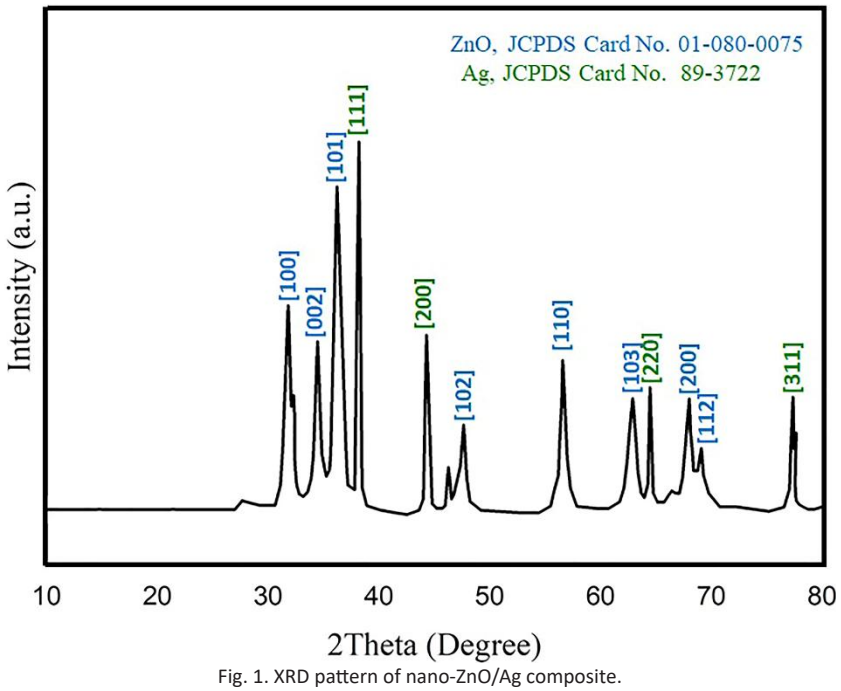


Fig. 1. XRD pattern of nano-ZnO/Ag composite.

The process of the reaction was controlled by TLC (Thin Layer Chromatography). At completion, the nanocatalyst was extracted. The crude product was extracted and then, washed with cold ethanol. To give pure product, the collected sediment was recrystallized. The chemical structure of obtained product was checked by $^{1}H/^{13}C$ NMR and FT-IR.

RESULTS AND DISCUSSION

We fabricated nano-ZnO/Ag composite via facile and available technique: hydrothermal method [13]. The XRD technique was used to investigated

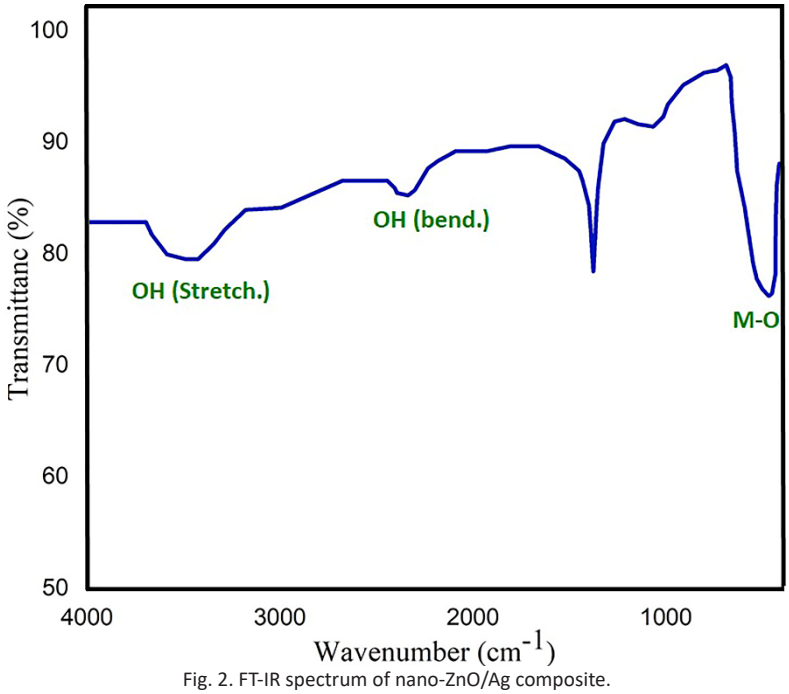


Fig. 2. FT-IR spectrum of nano-ZnO/Ag composite.

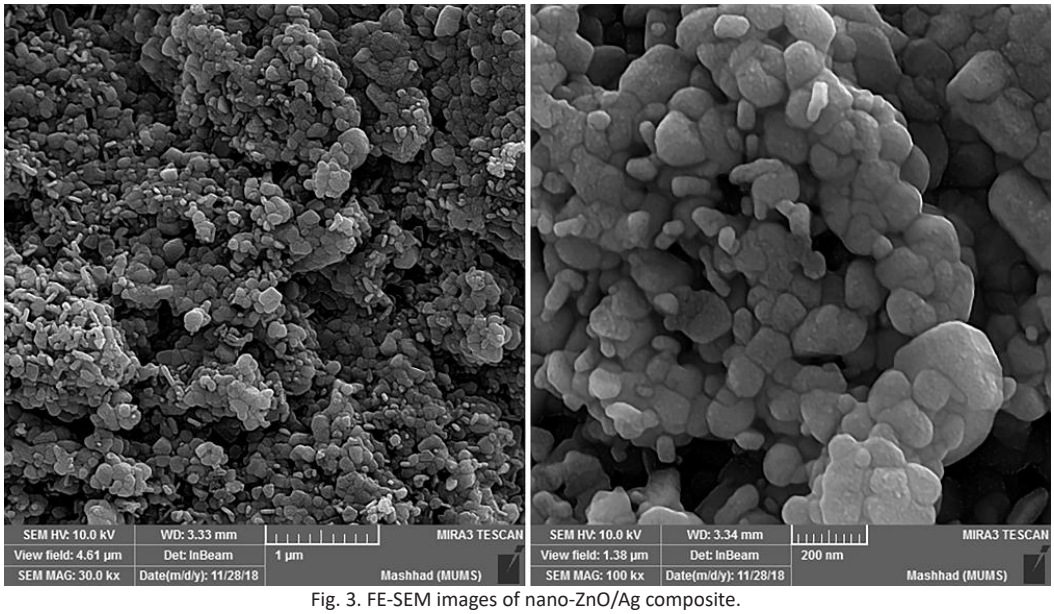


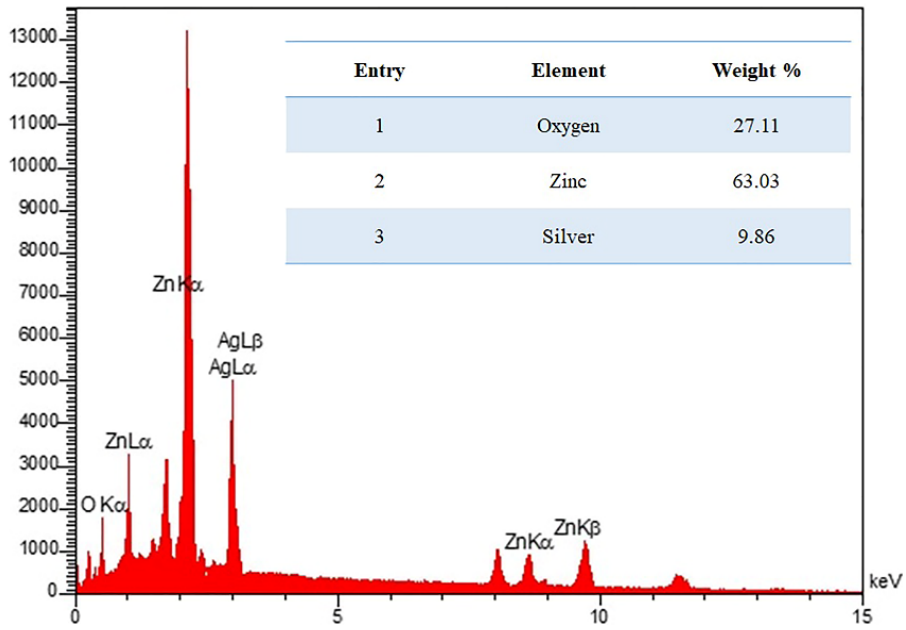
Fig. 3. FE-SEM images of nano-ZnO/Ag composite.

the crystallinity of as-prepared sample. The XRD pattern of nano-ZnO/Ag composite was displayd in Fig. 1. The XRD information prove that there are both elements of zinc (Ref. Card. No. 01-080-0075) [26] and silver (Ref. Card. No. 89-3722) [13, 27] in final structure.

FT-IR analysis was used to study of the functional group of as-prepared nano-sized composite. The FT-IR spectrum was displayed in Fig. 2. Two peaks at 3458 cm^{-1} and 1625 cm^{-1} can be related to hydroxyl stretching and bending vibrations, respectively. The strong peak was located at 540 cm^{-1} which might be related to metal-oxygen bonds (metal: silver and zinc) [28].

FE-SEM analysis was applied to study of the shape and size. The images of FE-SEM of designed nanocomposite are revealed in Fig. 3. Moreover, EDAX spectrum confirm the existence of Zn, O as well as Ag elements in as-prepared nanostructures (Fig. 4).

To study of the synthesis of benzo(*g*) chromenes, the three-component reaction of cyanoacetonitrile, benzoic aldehyde, and 2-hydroxy,1,4-naphthaquinone was chosen as a model reaction. The model reaction was tested in the existence of various catalysts: *p*-TSA, NEt_3, CuO/Ce_2O nanocomposite, and nano-sized ZnO/Ag composite. Different solvents (water,



Entry	Element	Weight %
1	Oxygen	27.11
2	Zinc	63.03
3	Silver	9.86

Fig. 4. EDAX pattern of nano-ZnO/Ag composite.

Table 1. Optimization of catalytic performance in synthesis of benzo(*g*)chromenes. [a]

Entry	Amount of Catalyst	Solvent	Time (min)	Yield (%) [b]
1	$NaHSO_4$ (5 mol%)	Ethanol	360	20
2	*p*-TSA (6 mol%)	Ethanol	380	15
3	NEt_3 (8 mol%)	Ethanol	150	60
4	ZnO NPs (8 mg)	Ethanol	90	70
5	Nano-sized ZnO/Ag composite (4 mg)	Ethanol	80	88
6	Nano-sized ZnO/Ag composite (5 mg)	Ethanol	70	91
7	Nano-sized ZnO/Ag composite (6 mg)	Ethanol	70	91
8	Nano-sized ZnO/Ag composite (5 mg)	Water	100	79
9	Nano-sized ZnO/Ag composite (5 mg)	Acetonitrile	90	82
10	Nano-sized ZnO/Ag composite (5 mg)	Dimethylformamide	120	75
11	No Catalyst	Ethanol	400	N.R.

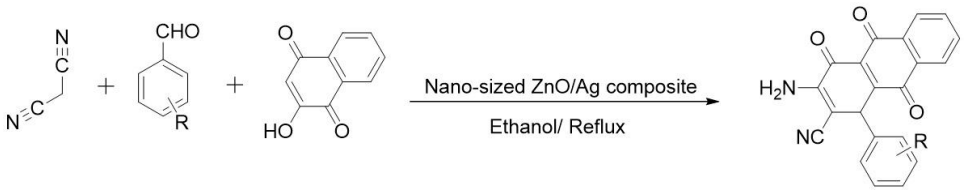
[a] Reaction chemicals: Cyanoacetonitrile (1 mmol), benzaldehyde (1 mmol), and hennotannic acid (1 mmol) under reflux condition.
[b] Isolated Yield.

acetonitrile, and ethanol) were also used. Among all tested solvents and under reflux condition, the best data was observed in ethanol medium and the selected three-component reaction gave satisfying outcomes in the existence of nano-ZnO/Ag composite as a heterogeneous nano-sized catalyst. Moreover, catalyst loading was tested and 6 mg of nano-sized ZnO/Ag composite was selected as an optimized amount (91% reaction yield). The reaction yield was also decrease (85%) when the lower amount of catalyst was used (5 mg) (Table 1). To develop the reaction and investigate the electron-donating/withdrawing groups, various substituted benzoic aldehydes were used. The results show that the excellent reaction yield is related to electron-withdrawing groups. In addition, different substituted benzo(*g*)chromenes were synthesized and their information was summarized in Table 2. To compare the efficiency of our proposed nano-sized catalyst with other reported catalysts, the Table 3 was set. According to Table 3, the designed nano-sized ZnO/Ag composite presented the better results to compared others in terms of conditions, time, and yield.

The recoverability of proposed nano-sized catalyst was examined. The observations revealed that the nano-sized ZnO/Ag composite can be catalyzed for five runs without notable loss in its performance (Fig. 5).

A probable reaction mechanism for the preparation of benzo(*g*)chromene compound in the existence of the nano-sized ZnO/Ag composite as a heterogeneous nanocatalyst is presented in Fig. 6. We proposed that the reaction was started through condensation reaction between benzoic acid and malononitrile. The intermediate (I) was formed in this step. In the following, 2-hydroxy-1,4-naphthoquinone was reacted by intermediate (I) to form intermediate (II). To give intermediate (III), the molecular cyclization reaction was accrued. To form final product, the migration of H atom was done. In addition, the interaction of chemicals on active sites of nano-sized catalyst

Table 2. Preparation of benzo(*g*)chromenes in the presence of nano-sized ZnO/Ag composite (5 mg).



Entry	R	Product	Time (min)	Yield (%)	M.P. (°C) [Reference]	M.P. (°C) [Reported]
1	4-Cl	4a	65	89	249-252 [8]	248-251
2	4-Br	4b	65	88	253-255 [8]	252-254
3	4-NO_2	4c	55	93	234-235 [8]	234-235
4	H	4d	70	91	261-262 [8]	258-260
5	2-Cl	4e	75	85	236-239 [8]	237-240
6	4-OMe	4f	85	82	224-226 [8]	220-222
7	4-Me	4g	90	78	211-214 [8]	210-212
8	4-SMe	4h	85	80	230-233 [8]	228-230
9	3-Me	4i	95	75	212-214 [8]	215-217

[a] Reaction chemicals: Cyanoacetonitrile (1 mmol), benzaldehyde (1 mmol), and hennotannic acid (1 mmol).
[b] Isolated Yield.

Table 3. Comparison of other catalysts with nano-sized ZnO/Ag composite in the preparation of benzo(*g*)chromenes.

Entry	Catalyst (amount) [Ref.]	Conditions	Yield (%)	Time (min)
1	Triethylamine (10 mol%) [29]	Acetonitrile/ r.t.	82	900
2	Diazabicycloundecene (10 mol%) [9]	Water/ Reflux	87	90
3	Ce_2O/CuO@GQDs@NH_2 (6 mg) [7]	Ethanol/ Reflux	90	75
4	Nano-sized ZnO/Ag composite (5 mg) [This Job]	Ethanol/ Reflux	91	70

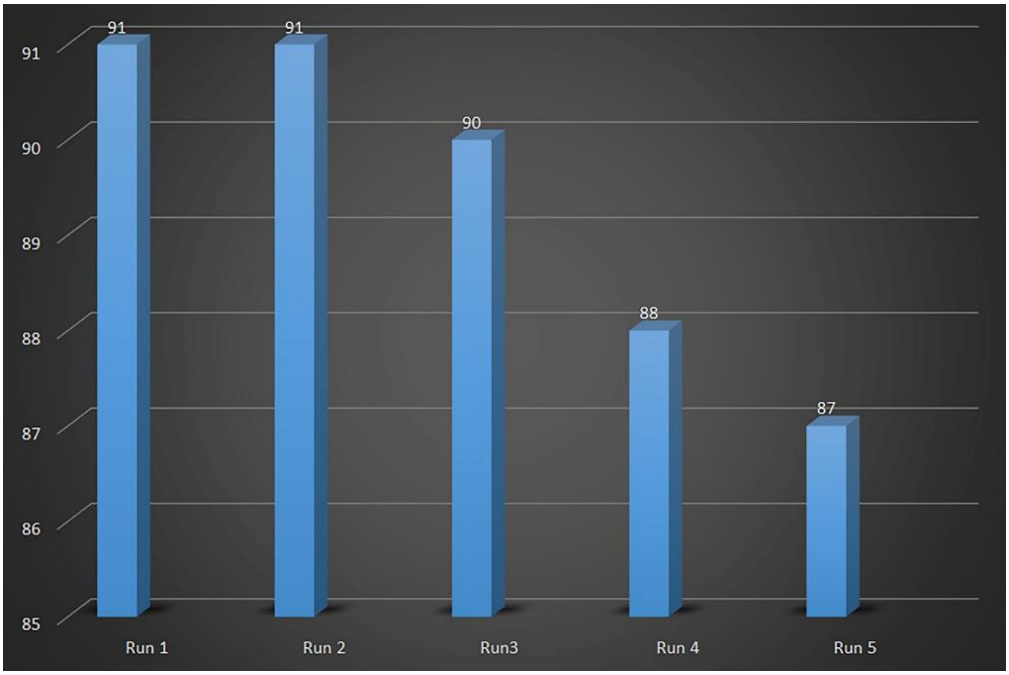


Fig. 5. Reusability of nano-sized ZnO/Ag composite.

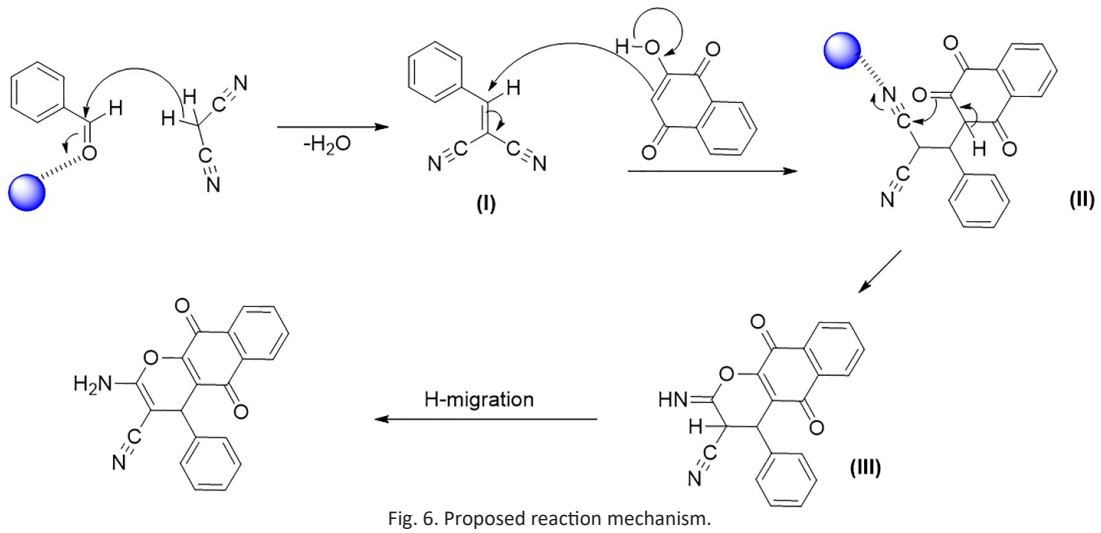


Fig. 6. Proposed reaction mechanism.

was shown during the mechanism.

CONCLUSION

As a result, we have offered a methodical and a facile route for the preparation of different substituted benzo(*g*)chromene compounds in the existence of nano-sized ZnO/Ag composite as a heterogeneous under reflux conditions. The XRD, EDAX, FT-IR, and FE-SEM methods were used to characterize the designed composite. This current report provides obvious advantages: low catalyst loading, recoverability of catalyst, eco-friendly,

and facile workup methodology.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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