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Introduction of W-doped ZnO nanocomposite as a new and efficient nanocatalyst for the synthesis of biscoumarins in water

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Abstract W-doped ZnO nanocomposite (W-ZnO) is easily prepared and characterized using a variety of techniques including XRD, TEM, BET, ICP-OES and SEM. This reagent can be used as an efficient and heterogeneous catalyst for the preparation of biscoumarins in water under mild conditions. Easy preparation of the catalyst, mild reaction conditions, easy work-up procedure, excellent yields and short reaction times are some of the advantages of this work. In addition, in this article and for the first time, the preparation of biscoumarins from the protected derivatives of aldehydes including oximes, hydrazones and 1,1-diacetates is reported.

Keywords Biscoumarins · Aldehydes · Protected aldehydes · W-doped ZnO nanocomposite · Heterogeneous reaction conditions

Background

Biscoumarins are a large group of heterocycles with diverse, interesting and important biological and pharmaceutical activities [1–5] activities. In recent years and because of these important activities, several methods are reported for the synthesis of biscoumarins using a variety of catalysts and reagents [6–14]. These methods although useful but most of them suffer from disadvantages such as long reaction times (e.g., in the presence of piperidine [4], the reactions are performed during 3–4 h), unsatisfactory yields (e.g., when HBF_4 is used as the catalyst the products are obtained in 55–70 % yields [9]), harsh reaction conditions, expensive reagents, hazardous and toxic solvents (e.g., refluxing toluene is used as the solvent in some of these methodologies [13]) or catalysts and tedious work-up. Therefore, introduction of efficient and economical catalysts that solve these drawbacks is desirable.

Oximes and semicarbazones are used not only for the isolation, purification and characterization but also for the protection of carbonyl compounds [15, 16]. Since oximes can be prepared from non-carbonyl compounds [17–19], the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. In addition, oximes can also be used as intermediates for the preparation of nitriles [20–22], nitrones [23], amines [24], amides [25], isoxazoles [26] and chiral α-sulfinyloximes [27]. Because of the remarkable stability of the acylals to neutral and basic conditions, these compounds have been introduced as the other suitable protection group for aldehydes [28]. In addition, they can be converted into other useful functional groups by reaction with appropriate nucleophiles [29] and used as carbonyl surrogates for asymmetric synthesis [30]. 1,1-Diacetates, on the other hand, are ambient substrates containing two types of reactive carbon centers, the carbon atom of the protected aldehyde function and the carbonyl group in the ester moieties [31]. To the best of our knowledge and in spite of the abovementioned important applicabilities of oximes, semicarbazones and acylals, there is no any report about the preparation of biscoumarins using these types of substrates.

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In recent years and because of the unique properties of nanocatalysts, synthetic chemists focused on the preparation and characterization of these types of compounds [32]. Among them nano metal oxides are under considerable attention of many researchers. Nano-ZnO, as a solid acid reagent, is one of these catalysts which have found a wide range of applications in organic transformations [33–41]. One of the most important applicabilities of nano-ZnO is based on its photocatalytic activity which occurs under ultraviolet light excitation [42–46]. In 2008, Ma et al. [47] reported that the catalytic activity of TiO_2 in photocatalytic degradation of methyl orange can be highly improved by doping with tungsten. They attributed this result to the help of the doped W in trapping of photogenerated electrons and the enhancement of the surface acidity of TiO_2. In 2013 and on the basis of the Ma's report, Moafi et al. [48] showed that doping of ZnO with 4 mol % of tungsten, in the same manner, can improve the photocatalytic activity of this reagent in photodegradation of methylene blue.

Methods

General

All chemicals were purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constants and comparison with authentic samples. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

To investigate the morphology of the W-doped sample, scanning electron microscopy (SEM) images were obtained on a Philips, XL30. The particles sizes were obtained by transmission electron microscope (TEM) images on a Philips CM10 instrument with an accelerating voltage of 100 kV. Elemental analyses of the samples were carried out by ICP-OES. Measurements were made on an ICP-OES Vista-Pro (Varian), after dissolution of the samples in a HNO_3:HF:H_2O mixture.

The BET specific surface areas of the synthesized nanocomposite were determined by nitrogen adsorption at liquid nitrogen temperature on a Sibata SA-1100 surface area analyzer. X-ray diffraction measurements were recorded by a Philips PW1840 diffractometer with Cu-Kα radiation, scan rate $0.02 \times 2\theta/s$ and within a range of 2θ of $10°–80°$ at room temperature.

A Perkin Elmer 781 Spectrophotometer was used to record the IR spectra. The ^{1}H NMR spectra were recorded with Bruker Avance 300, 400 and 500 MHz instruments. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. The ^{13}C NMR data were collected on Bruker Avance 100 MHz instrument. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Catalyst preparation

The W-doped ZnO nanocomposite was prepared by sol–gel method using the precursors of zinc and tungsten. Zinc acetate dihydrate [$Zn(Ac)_2 \cdot 2H_2O$] was used as zinc oxide source. In a typical procedure, 0.02 mol of zinc acetate dihydrate was dissolved in 50 mL of methanol and heated at 50 °C with stirring for half an hour. Then, certain amounts of sodium tungstate (8 mol % with respect to zinc acetate dihydrate) was dissolved in a mixture of water/methanol [10 mL (2:8)] under vigorous stirring and then the solution was added dropwise into the mixture of zinc acetate dihydrate and methanol, thus making precursor solution A. Afterwards, 0.04 mol of sodium hydroxide was dissolved in 50 mL of methanol and heated at 50 °C with stirring for 1 h, making precursor solution B. To make ZnO nano-sol, the solution of sodium hydroxide (solution B) was added dropwise into the solution A under constant stirring for half an hour and then the mixture was heated at 50 °C for further half an hour. Subsequently, a homogenous sol was obtained. The obtained solution was precipitated after continuous stirring for 2 h and cooling at room temperature. After 24 h, the colloidal solution was washed several times with methanol. Finally, so obtained precipitate was dried at 80 °C and then calcinated at 300 °C for 3 h. Using the same procedure, 2, 4, 6.0 mol % W-doped ZnO and undoped ZnO samples were obtained. The obtained results clarified that the sample with 8 mol % W has highest catalytic activity.

General procedure

General procedure for the synthesis of biscoumarins

A mixture of the aldehyde and/or the protected derivative of aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol) and W-ZnO (20 mg) in H_2O (3 mL) was stirred at 80 °C for the appropriate time. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the solvent was evaporated. Then the solid residue was dissolved in CH_2Cl_2 (5 mL) and filtered to separate the catalyst. After evaporation of the solvent, the residue was recrystallized from EtOH and water (95:5) to afford the pure product.

Spectral data of the selected products

(a) Biscoumarin derivative of benzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl_3, 300 MHz):

$\delta = 6.12$ (1H, s), 7.24–8.10 (13H, m), 11.33 (1H, s), 11.56 (1H, s) ppm.

(b) Biscoumarin derivative of 4-chlorobenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 6.04$ (1H, s), 8.09–7.17 (12H, m), 11.32 (1H, s), 11.54 (1H, s) ppm.

(c) Biscoumarin derivative of 2-chlorobenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 300 MHz,): $\delta = 6.14$ (1H, s), 8.03–7.22 (12H, m), 10.93 (1H, s), 11.63 (1H, s) ppm.

(d) Biscoumarin derivative of 4-bromobenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 300 MHz,): $\delta = 6.01$ (1H, s), 7.10–8.06 (12H, m), 11.31 (1H, brs), 11.54 (1H, brs)

(e) Biscoumarin derivative of 4-nitrobenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 300 MHz,): $\delta = 6.14$ (1H, s), 7.28–8.22 (12H, m), 11.40 (1H, s), 11.59 (1H, s) ppm.

(f) Biscoumarin derivative of 3-nitrobenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 6.39$ (1H, s), 7.28–8.04 (12H, m), 8.04–9.52 (2H, m) ppm.

(g) Biscoumarin derivative of 2-nitrobenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 300 MHz,): $\delta = 6.6$ (1H, s), 6.72–7.94 (12H, m), 11.24 (2H, brs) ppm.

(h) Biscoumarin derivative of 4-methoxybenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 3.80$ (3H, s), 6.05 (1H, s), 6.85 (2H, d, $J = 8.7$ Hz), 7.13 (2H, d, $J = 8.7$ Hz), 7.30–7.42 (4H, m), 7.63 (2H, t, $J = 8.2$ Hz), 8.03 (2H, dd, $J = 8.4$ Hz), 11.29 (1H, brs), 11.51 (1H, brs)

(i) Biscoumarin derivative of 2-hydroxybenzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 5.41$ (1H, s), 7.10–7.20 (2H, m), 7.23 (2H, d, $J = 8.0$ Hz), 7.30–7.38 (3H, m), 7.40–7.50 (2H, m), 7.53 (1H, td, $J_1 = 7.5$, $J_2 = 1.5$ Hz), 7.67 (1H, td, $J_1 = 7.8$, $J_2 = 1.5$ Hz), 8.07 (1H, dd, $J_1 = 7.9$, $J_2 = 1.5$ Hz), 8.19 (1H, dd, $J_1 = 8.0$, $J_2 = 1.5$ Hz), 10.43 (1H, s) ppm.

(j) Biscoumarin derivative of 4-(N,N-dimethyl)benzaldehyde with 4-hydroxycoumarin: ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 3.2$ (6H, s), 6.31 (1H, s), 7.23–7.84 (12H, m) ppm.

(k) Biscoumarin derivative of cinnamaldehyde with 4-hydroxycoumarin: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 4.9$ (1H, d, $J = 3.5$ Hz) 6.85 (1H, d, $J = 15.4$ Hz), 7.15–7.18 (5H, m), 7.20 (2H, td, $J_1 = 8.0$, $J_2 = 2.5$ Hz), 7.25 (1H, dd, $J_1 = 15.4$, $J_2 = 3.5$ Hz), 7.29 (2H, d, $J = 8.0$ Hz), 7.51 (2H, td, $J_1 = 8.0$, $J_2 = 1.7$ Hz), 7.89 (2H, d, $J = 8.0$ Hz) ppm.

(l) Biscoumarin derivative of pyridine-4-carbaldehyde with 4-hydroxycoumarin: ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 6.49$ (s, 1H, s), 7.23 (2H, t, $J = 7.2$ Hz), 7.28 (2H, d, $J = 8.4$ Hz), 7.5 (2H, t, $J = 7.2$ Hz), 7.81–7.83 (4H, m), 8.6 (2H, d, $J = 6$ Hz), 16.97 (2H, brs) ppm.

(m) Biscoumarin derivative of pyridine-3-carbaldehyde with 4-hydroxycoumarin: ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 6.43$ (1H, s), 7.26 (2H, t, $J = 7.6$ Hz), 7.3 (2H, d, $J = 8$ Hz), 7.56 (2H, td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz), 7. 82 (2H, dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz), 7.94 (1H, td, $J_1 = 7$ Hz, $J_2 = 2$ Hz), 8.37 (1H, d, $J = 8$ Hz), 8.66 (1H, s), 8.72 (1H, d, $J = 5.2$ Hz), 16.93 (2H, brs) ppm.

(n) Biscoumarin derivative of 3-phenylpropanal with 4-hydroxycoumarin: ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 1.89$ (2H, m), 2.67 (2H, m), 5.8 (1H, t, $J = 6.8$ Hz), 6.5–6.8 (5H, m), 7.30 (2H, td, $J_1 = 8.0$, $J_2 = 2.4$ Hz), 7.33 (2H, d, $J = 8.0$ Hz), 7.65 (2H, td, $J_1 = 8.0$, $J_2 = 2.2$ Hz), 7.88 (2H, d, $J_1 = 8.0$ Hz) ppm.

Results and discussion

Catalyst characterization

Powder X-ray diffraction

Figure 1 shows the XRD patterns of W-doped ZnO nanocomposite. The sample showed a hexagonal wurtzite crystal structure and high crystallinity of ZnO. The peaks at $2\theta = 31.7°$, 34.5°, 36.7°, 47.7°, 56.5°, 62.9° and 67.9° are associated with the (100), (002), (101), (102), (110),
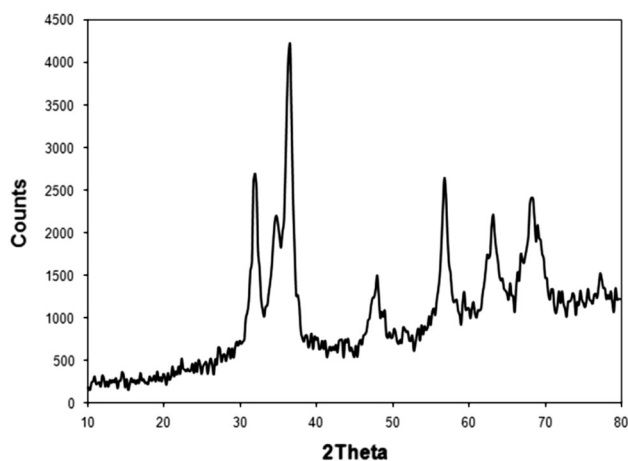

Fig. 1 XRD pattern of W-ZnO

Table 1 Some characteristics of W-ZnO

Sample	Crystalline structure	Contents		BET surface area (m²/g)	Pore volume (cm³/g)	XRD crystal size (nm)	TEM crystal size (nm)
		Nominal (mol %)	ICP W/Zn %				
W-ZnO (8 mol %)	Wurtzite	8	0.228	93.70	0.033	11	10–15

(103) and (112) planes of the ZnO hexagonal wurtzite structure. The diffraction peaks of the W-ZnO are broad, indicating a small crystal size of this sample. The XRD pattern of the W-ZnO catalyst shows that there is no change in the crystal structure upon tungsten doping process. However, it can be indicated that W^{+6} ions are uniformly dispersed on ZnO nanoparticles in the form of highly dispersed WO_3 clusters.

There were no detectable peaks relating to the existence of a separate dopant metal phase in any corresponding pattern. This could be attributed to the fact that the dopant metals/metal oxides were too low in concentration and/or amorphous structure to be seen as a separate phase. The real W content in W-ZnO sample was measured by ICP-OES (Table 1). The weight ratio of W/Zn in the W-ZnO nanocomposite was 0.228 %.

Surface area and pore distribution measurements

The surface area of W-ZnO nanocomposite, which influences the catalytic activity, was determined using the nitrogen gas adsorption method. The BET surface area of the prepared W-ZnO yielded relatively high surface area (93.70 m²/g). The average grain size are calculated using the Scherrer's equation based on the full width at half maximum (FWHM) of the (101) peak of the compounds. The results are summarized in Table 5.

SEM analysis

The surface morphology and dispersion of the sample were determined by scanning electron microscopy (SEM). Figure 2 shows SEM micrographs of 8 mol % W-ZnO. The image reveals that the particles in this sample have relatively a sphere-like morphology and the nano particles were composed of agglomerates of fine W-doped ZnO nanoparticles and particle size less than 100 nm. The small and uniform size of the prepared reagent can be affected by its catalytic performance.

TEM analysis

Figure 3 depicts transmission electron micrograph of 8 mol % W-ZnO. The TEM image of W-ZnO shows that
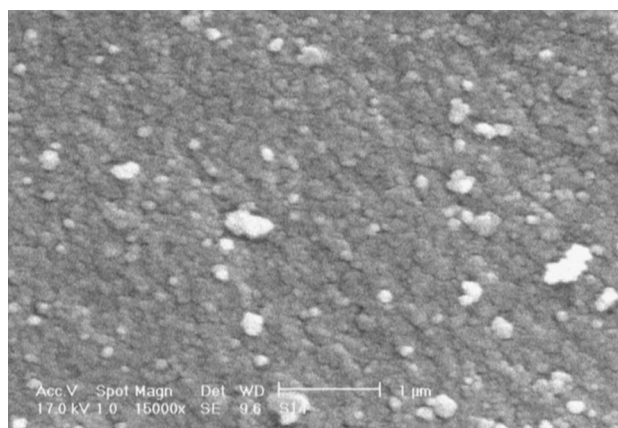
Fig. 2 SEM image of W-ZnO
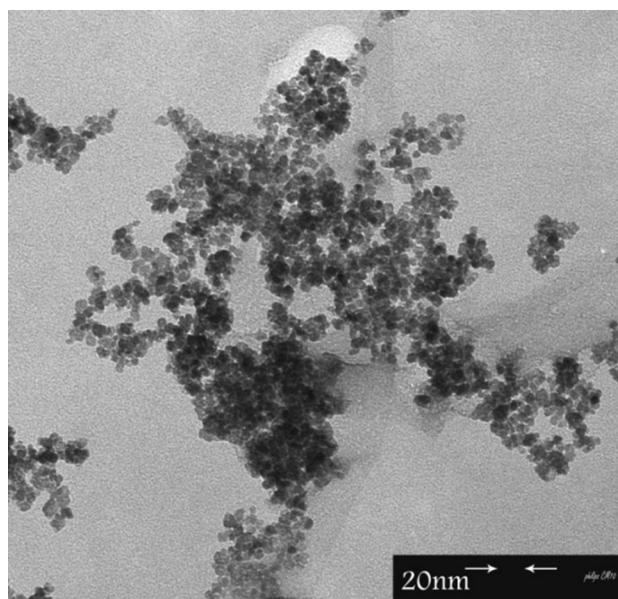
Fig. 3 TEM image of W-ZnO

the sample consists of fine particles with diameters less than 20 nm in size.

Catalytic activity

In recent years, preparation and use of nanocatalysts in organic transformations became an important part of our ongoing research program [32, 49–51]. In continuation of

Table 2 The effect of different solvents and different amounts of the catalyst on the model reaction

Entry	Solvent	W-ZnO (mg)	Time (min)	Conversion (%)[a]
1	H_2O	20	32	100
2	H_2O	10	44	100
3	H_2O[b]	20	60	80
4	H_2O[c]	20	60	80
5	EtOH	30	85	100
6	CH_3CN	30	115	40
7	CH_2Cl_2	30	100	30
8	CCl_4	30	130	20
9	*n*-Hexane	30	80	10
10	Solvent-free	30	80	0

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), 4-hydroxy-coumarin (2 mmol), 80 °C

[a] GC

[b] 6 mol % W-ZnO

[c] 4 mol % W-ZnO

these studies, and on the basis of the Fallah Moafi's report [48], we anticipated that W-doped ZnO nanocomposite can be used as an efficient solid acid catalyst for the acceleration of the reactions which need the use of an acidic catalyst to speed up. So we were interested to investigate the applicability of this reagent in the promotion of the synthesis of biscoumarins.

Our initial studies clarified that to obtain the best results the amounts of tungsten should be enhanced to 8 mol %. So we have prepared, identified and studied the role of the 8 mol % W-doped ZnO nanocomposite in the synthesis of biscoumarins.

At the first step and to optimize the reaction conditions, the prepared catalyst was used for the promotion of the condensation of 4-chlorobenzaldehyde with 4-hydroxy-coumarin and compared the effect of different solvents and solvent-free conditions and also the effect of the catalyst load on the reaction yield and time at thermal conditions. The results are shown in Table 2. On the basis of these
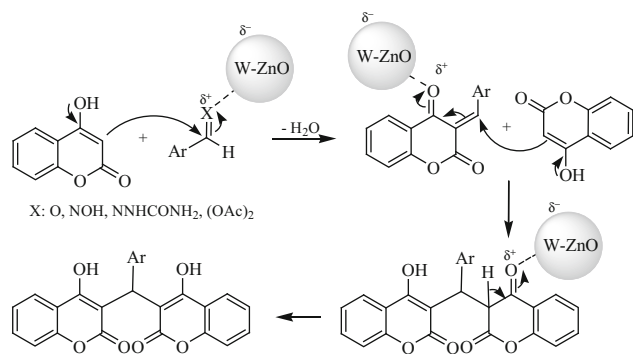
Scheme 1 Synthesis of biscoumarins using W-ZnO as the catalyst

X: O, NOH, NNHCONH$_2$, (OAc)$_2$
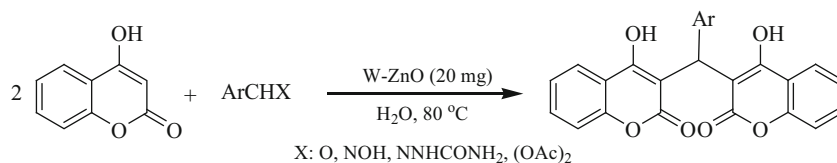
Table 3 Preparation of biscoumarins using W-ZnO as the catalyst

Entry	Aldehydes	Time (min)	Yield (%)[a]	mp (°C) Found	mp (°C) Reported [References]
1	C_6H_5CHO	15	98	226–229	229–231 [51]
2	$4\text{-}ClC_6H_4CHO$	32	98	248–250	250 [53]
3	$2\text{-}ClC_6H_4CHO$	60	97	200–202	201–203 [54]
4	$4\text{-}BrC_6H_4CHO$	41	98	263–266	264–266 [7]
5	$4\text{-}NO_2C_6H_4CHO$	37	98	232–233	230 [53]
6	$3\text{-}NO_2C_6H_4CHO$	68	98	231–233	229–231 [7]
7	$2\text{-}NO_2C_6H_4CHO$	15	95	196–198	198–200 [53]
8	$4\text{-}MeOC_6H_4CHO$	45	98	248–250	250–252 [53]
9	$3\text{-}MeOC_6H_4CHO$	37	95	232–234	238–240 [7]
10	$2\text{-}MeOC_6H_4CHO$	20	95	252–254	258–260 [54]
11	$4\text{-}OHC_6H_4CHO$	60	98	222–225	228–230 [55]
12	$4\text{-}NMe_2C_6H_4CHO$	75	90	215–218	222–224 [12]
13	Cinnamaldehyde	20	95	226–228	230–232 [11]
14	Pyridine-4-carbaldehyde	90	90	263–265	261–263 [56]
15	Pyridine-3-carbaldehyde	75	90	270–272	274–276 [56]
16	$PhCH_2CH_2CHO$	45	98	182–185	190 [4]
17	2-Naphthaldehyde	45	98	262–263	263–265 [56]
18	$1,4\text{-}C_6H_4(CHO)_2$	120	98	310–312	313–315 [57]

[a] Isolated yield

Table 4 Preparation of biscoumarins from the reaction of protected aldehydes and 4-hydroxycoumarin in the presence of W-ZnO

Entry	Protected aldehydes	Time (h)	Yield (%)[a]	mp (°C)	
				Found	Reported [References]
1	$4\text{-}ClC_6H_4CH=NOH$	3	70	248–250	250 [53]
2	$4\text{-}NO_2C_6H_4CH=NOH$	2	90	232–233	230 [53]
3	$2\text{-}NO_2C_6H_4CH=NOH$	3	70	196–198	198–200 [52]
4	$4\text{-}BrC_6H_4CH=NOH$	1.2	80	263–266	264–266 [7]
5	Pyridine-4-carbaldehyde oxime	2.6	80	262–263	261–263 [56]
6	$4\text{-}NO_2C_6H_4CH=NNHCONH_2$	2.5	90	232–233	230 [53]
7	$4\text{-}MeOC_6H_4CH=NNHCONH_2$	3.6	80	248–250	250–252 [52]
8	$2\text{-}OHC_6H_4CH=NNHCONH_2$	2	90	250	250–252 [58]
9	$2\text{-}MeOC_6H_4CH(OAc)_2$	2.5	95	252–254	258–260 [54]
10	$4\text{-}BrC_6H_4CH(OAc)_2$	1.6	90	263–266	264–266 [7]

[a] Isolated yield

Scheme 2 A plausible mechanism for the synthesis of biscoumarins in the presence of W-ZnO

results it can be concluded that the best results can be obtained under the conditions shown in Scheme 1. It is interesting to note that using lower amounts of the catalyst (Table 2, entry 2) and/or lower amounts of W in the preparation of the catalyst (Table 2, entries 3, 4) resulted the products' longer reaction times and/or lower yields.

To study the efficiency of W-ZnO in the preparation of biscoumarin derivatives, a wide range of aromatic, aliphatic and heterocyclic aldehydes were reacted with 4-hydroxycoumarin under the optimal reaction conditions and the obtained results are tabulated in Table 3.

It was observed that under the selected conditions, aromatic aldehydes containing electron-withdrawing groups as well as electron-donating groups were easily reacted in short reaction times with good to excellent isolated yields (Table 3, entries 1–12). α,β-Unsaturated aldehydes were also reacted in high yields using this procedure without the formation of any by-products (Table 3, entry 13).

After the abovementioned studies and for the first time, we have studied the applicability of the same method in the preparation of biscoumarins from the protected aldehydes (e.g., oximes, semicarbazones and 1,1-diacetates). The obtained results showed that under the same reaction conditions, the protected derivatives of aldehydes were efficiently converted to the requested biscoumarins during short reaction times in high yields (Table 4).

A plausible mechanism of the reaction is shown in Scheme 2 [60].

To show the efficiency of the present method, we have compared our results obtained from the synthesis of biscoumarins catalyzed by W-ZnO with some of the other results reported in the literature. As it can be seen in Table 5, some of the previously reported methods are performed in the presence of toxic reagents (Table 5, entry 2) or solvents (Table 5, entries 4–6). It should be noted that

Table 5 Comparison of our results with some of the other catalysts in the preparation of biscoumarins

Entry	Catalyst (mol %)	Reaction conditions	Time (h)	Yield (%)	References
1	On-water	H_2O, 90 °C	4–5	93–98	[6]
2	I_2 (10)	H_2O, 100 °C	0.33–0.53	91–99	[59]
3	$RuCl_3 \cdot nH_2O$ (5)	H_2O, 80 °C	0.42–0.58	75–95	[60]
4	$[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ (7)	**Toluene**, 90 °C	0.5–0.8	90–96	[13]
5	$NaHSO_4 \cdot SiO_2$ (150 mg)	**Toluene**, 100 °C	0.5	85–91	[8]
6	Indion 190 resin (150 mg)	**Toluene**, 100 °C	0.5	87–93	[8]
7	SDS (20)	H_2O, 60 °C	2.5–3	80–96	[12]
8	Phosphotungstic acid (15)	H_2O, 80 °C	0.23–0.42	90–98	[11]
9	W-ZnO(22.4)	H_2O, 80 °C	0.25–2	90–98	This work

Bold represents the usage of toxic solvent (Toluene)

in the absence of the catalyst, the reaction is completed during much longer times (Table 5, entry 1).

Conclusion

In summary, we have introduced W-doped ZnO nano-composite as a highly efficient nanocatalyst for the acceleration of the synthesis of biscoumarins under mild and completely heterogeneous reaction conditions. This method has several advantages such as ease of preparation and handling of the catalyst, easy work-up procedure, high reaction rates and excellent yields. Also, and for the first time different types of protected aldehydes were successfully employed in these types of reactions and the corresponding products were obtained in high to excellent yields.

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