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Bi_2O_3 nano-particles as an efficient catalyst for the multi-component, one-pot, aqueous media preparation of benzo[h]pyrano[3,2-c]chromene-2-carbonitriles and pyrano[3,2-g]chromene-7-carbonitriles

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ABSTRACT

Bi_2O_3 nano-powder was prepared from the reaction of a watery solution of $Bi(NO_3)_3$ with a thin solution of amino ethanol in water *via* a simple precipitation method. The as prepared nanopowder was used for the one-pot synthesis of benzo[h]pyrano[3,2-c]chromene-2-carbonitriles and pyrano[3,2-g]chromene-7-carbonitriles by three-component reacting of aromatic aldehydes, malononitrile and 4-hydroxy-2H-benzo[h]chromen-2-one / 5,7-dihydroxy-4-methyl-2H-chromen-2-one/7-hydroxy-5-methoxy-4-methyl-2H-chromen-2-one under reflux condition in aqueous media and afforded good to excellent yields of product.

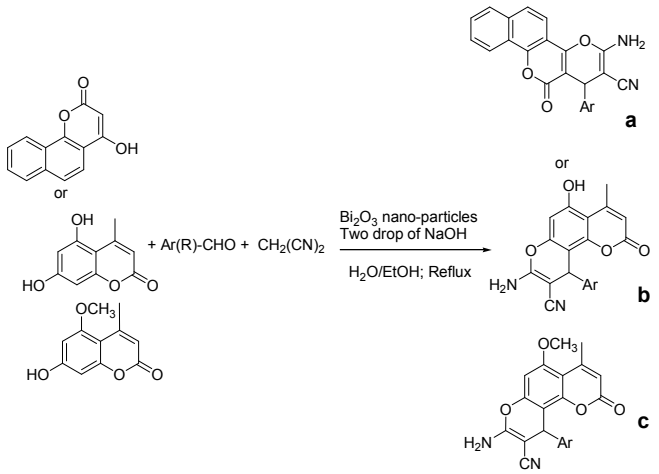
Keywords: *Bi_2O_3 nanopowder; 2-amino-4H-chromene; benzo[h]pyrano[3,2-c]chromene-2-carbonitriles; pyrano[3,2-g]chromene-7-carbonitriles; 4-hydroxy-2H-benzo[h]chromen-2-one.*

1. INTRODUCTION

Heterocyclic compounds containing chromene moieties are of considerable interest as they are a class of natural and synthetic compounds that possess a great variety of biological and pharmaceutical activities [1-5]. These scaffolds are more privileged when they joined with rigid hetero ring systems and / or other chemical functional groups. Obviously, functionalization of chromene derivatives have played an ever increasing role in the synthetic approaches to promising compounds in the field of medicinal chemistry [1-5]. On the other hand, functionalized chromenes appeared as an important structural component in both biologically active and natural compounds [1-5]. For example, some of interesting molecules with chromene framework joined with different functional groups displaying rich medicinal chemistry and numerous applications such as anti-inflammatory, antioxidant, anti-HIV, antibacterial, and analgesic properties [6-11]. Amongst of them chromenes with cyano-functionality has potential applications in the treatment of rheumatoid, psoriasis and cancer [12]. In addition, they are applicable as laser dyes [13], optical brighteners [14] and Pigments [15].

Consequently, several methods have been reported for the preparation of chromene derivatives involve multi-component reaction of aldehydes, malononitrile and β-keto esters, diverse enolizable C-H activated acidic compounds, phenols and α- and β-naphthols [16-26]. To achieve this aim several methods using different homogeneous and heterogeneous catalysts were explored. These methods have the advantages of high yields, and mild reaction conditions and some disadvantages of using toxic solvents and expensive catalysts. However the discovery of new synthetic methodologies that facilitate the preparation of organic compounds is of great interest. One approach to address this challenge involves the development of new synthesized environmentally friendly catalysts to catalyze the reaction.

Therefore, as a part of our incessant efforts on the using of heterogeneous catalysts in multi-component reactions [27-35], the scope of the present work was extended for the multi-component condensation reaction of aldehydes, 4-hydroxy-2H-benzo[h]chromen-2-one / 5,7-dihydroxy-4-methyl-2H-chromen-2-one/7-hydroxy-5-methoxy-4-methyl-2H-chromen-2-one and malononitrile to afford benzo[h]pyrano[3,2-c]chromene-2-carbonitriles and pyrano[3,2-g]chromene-7-carbonitriles using Bi_2O_3 nanopowder as a green, environmentally friendly catalyst (Scheme 1).



Scheme 1. Preparation of benzo[h]pyrano[3,2-c]chromene-2-carbonitriles and pyrano[3,2-g]chromene-7-carbonitriles using Bi_2O_3 nano-particles.

2. EXPERIMENTAL SECTION

All reagents were purchased from Merck and Aldrich and used without further purification. Field Emission Scanning Electron Microscope (FE-SEM) images were obtained on HITACHI S-4160. N_2 adsorption measurements of the catalyst were carried out using micro metrics adsorption equipment (Quantachrome instrument, model Nova 2000, USA), N_2 (99.99%) as the analysis gas and the catalyst samples were slowly heated to 120 °C for 3h under nitrogen atmospheric. The total pore volume was obtained from the maximum amount of nitrogen gas adsorbed at partial pressure P/P0=0.999. Dynamic light scattering (DLS) measurement was done using a Malvern Zetasizer Nano ZS (ZEN 3600) instrument. The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica gel Polygram SIL G/UV 254 plates.

2.1. Preparation of Bi_2O_3 nanopowder.

To a solution of $Bi(NO_3)_3$ (20 mmol) in 200 ml of deionized water was added drop-wise a solution of 2-aminoethanol (150 mmol in 50 ml of water) under vigorous magnetic stirring. The mixture was continuously stirred for another 60 min. The resulting precipitate was filtered, washed with water several times and dried in an oven at 100 °C for 5 h and finally calcined at 600 °C for 3 h.

2.2. General procedure.

A mixture of aldehydes (1 mmol), 4-hydroxy-2H-benzo[h]chromen-2-one /5,7-dihydroxy-4-methyl-2H-chromen-2-one/7-hydroxy-5-methoxy-4-methyl-2H-chromen-2-one (1 mmol), malononitrile (1 mmol), two drop of NaOH (1M), and Bi_2O_3 (0.25 mmol) in H_2O/EtOH (50% v/v) was refluxed (80 °C) for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was dissolved in hot ethanol. The catalyst was removed by simple filtration. The solvent was concentrated and the crude product was purified by crystallization from EtOH. The spectral data of compounds **a, b** and **c** is given below:

3-Amino-12-oxo-1-(phenyl)-1,12-dihydrobenzo[h] pyrano[3,2-c]chromene-2-carbonitrile **(Table 1, Product a_1):** Melting point: 282-284 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.67 (s, 1H, CH), 7.21-7.33 (m, 7H), 7.53 (t, *J* = 8.0, 1H), 7.61-7.85 (m, 4H), 8.27 (d, *J* = 8.0, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 37.3, 58.0, 103.1, 114.9, 120.3, 121.1, 126.9, 127.3, 127.5, 127.7, 127.9, 128.0, 128.3, 128.9, 129.2, 133.5, 145.4, 159.3, 153.9, 161.5, 165.4 ppm. [Found: C, 75.65; H, 3.98; N, 7.84% $C_{23}H_{14}N_2O_3$; requires: C, 75.40; H, 3.85; N, 7.65%].

3-Amino-1-(4-methylphenyl)-12-oxo-1,12-dihydrobenzo[h]pyrano[3,2-c]chromene-2-carbonitrile **(Table 1, Product a_2):** Melting point: 251-253 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.27 (s, 3H, CH_3), 4.71 (s, 1H, CH), 7.07-7.18 (m, 4H), 7.33 (s, 2H, NH_2), 7.49-7.68 (m, 4H), 7.86 (d, *J* = 8.2, 1H), 8.27 (d, *J* = 8.0, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 21.4, 37.1, 58.1, 103.4, 114.9, 120.5, 120.9, 126.8, 126.9, 127.3, 127.4, 127.8, 128.0, 128.4, 129.5, 133.4, 139.9, 145.5, 153.9, 159.6, 161.3, 165.4 ppm. [Found: C, 75.94; H, 4.42; N, 7.44% $C_{24}H_{16}N_2O_3$; requires: C, 75.78; H, 4.24; N, 7.36%].

3-Amino-1-(4-chlorophenyl)-12-oxo-1,12-dihydrobenzo[h]pyrano[3,2-c]chromene-2-carbonitrile **(Table 1, Product a_3):** Melting point: 248-250 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.84 (s, 1H, CH), 7.45-7.63 (m, 9H), 7.70 (d, *J* = 7.9, 1H), 7.86 (d, *J* = 8.1, 1H), 8.26 (d, *J* = 7.9, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 37.6, 58.3, 103.5, 114.7, 120.9, 121.2, 126.8, 127.2, 127.4, 127.9, 128.2, 128.5, 128.9, 129.3, 133.6, 135.9, 145.7, 153.9, 159.4, 161.3, 165.6 ppm. [Found: C, 69.04; H, 3.40; N, 7.09% $C_{23}H_{13}ClN_2O_3$; requires: C, 68.92; H, 3.27; N, 6.99%].

3-Amino-1-(3-nitrophenyl)-12-oxo-1,12-dihydrobenzo[h]pyrano[3,2-c]chromene-2-carbonitrile **(Table 1, Product a_4):** Melting point: 280-282 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 5.03 (s, 1H, CH), 7.46 (t, *J* = 7.9, 1H), 7.51 (s, 2H. NH_2), 7.53-7.94 (m, 6H), 8.17 (s, 1H), 8.20-8.27 (m, 2H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 37.7, 58.1, 103.7, 114.9, 120.6, 120.9, 122.8, 125.6, 126.8, 127.2, 127.4, 127.8, 128.1, 128.4, 130.1, 133.3, 134.5, 148.2, 148.4, 153.8, 159.3, 161.4, 165.5 ppm. [Found: C, 67.34; H, 3.41; N, 10.31% $C_{23}H_{13}N_3O_5$; requires: C, 67.15; H, 3.19; N, 10.21%].

3-Amino-1-(2,4-dichlorophenyl)-12-oxo-1,12-dihydrobenzo[h]pyrano[3,2-c]chromene-2-carbonitrile **(Table 1, Product a_5):** Melting point: 267-269 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.83 (s, 1H, CH), 7.16 (d, *J* = 7.8, 1H), 7.50-7.77 (m, 8H), 7.86 (d, *J* = 8.2, 1H), 8.27 (d, *J* = 7.9, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 37.7, 58.2, 103.4, 114.6, 120.6, 120.9, 126.6, 127.0, 127.1, 127.5, 127.8, 127.9, 128.2, 128.5, 129.3, 133.2, 133.5, 135.4, 142.2, 153.7, 159.3, 161.2, 165.5 ppm. [Found: C, 63.59; H, 2.89; N, 6.57% $C_{23}H_{12}Cl_2N_2O_3$; requires: C, 63.47; H, 2.78; N, 6.44%].

8-amino-5-hydroxy-1,10-dihydro-10-(phenyl)-2-oxo-4-methyl-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product b_1):** Melting point: 257-259 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.45 (s, 3H, CH_3), 4.85 (s, 1H, CH), 5.99 (s, 1H), 6.47 (s, 1H), 6.99 (s, 2H, NH_2), 7.19-7.33 (m, 5H), 11.02 (s, 1H, OH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 20.3, 44.6, 57.5, 102.6, 107.4, 111.7, 115.9, 119.7, 128.8, 128.9, 130.2, 141.7, 145.0, 153.7, 156.4, 160.5, 161.0, 163.7 ppm. [Found: C, 69.49; H, 4.19; N, 8.21% $C_{20}H_{14}N_2O_4$; requires: C, 69.36; H, 4.07; N, 8.09%].

8-amino-10-(4-chlorophenyl)-5-hydroxy-1,10-dihydro-2-oxo-4-methyl-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product b_2):** Melting point: 245-247 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.46 (s, 3H, CH_3), 4.96 (s, 1H, CH), 6.03 (s, 1H), 6.48 (s, 1H), 7.03 (s, 2H, NH_2), 7.38 (d, 2H, *J* = 7.9 Hz), 7.48 (d, 2H, *J* = 7.9 Hz), 11.07 (s, 1H, OH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 20.4, 45.7, 57.8, 101.9, 108.1, 112.1, 116.1, 120.1, 128.9, 129.5, 136.1, 142.1, 145.3, 153.7, 156.1, 160.2, 160.6, 163.6 ppm. [Found: C, 63.27; H, 3.64; N, 7.57% $C_{20}H_{13}ClN_2O_4$; requires: C, 63.08; H, 3.44; N, 7.36%].

8-amino-10-(4-bromophenyl)-5-hydroxy-1,10-dihydro-2-oxo-4-methyl-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product b_3):** Melting point: 295-297 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.44 (s, 3H, CH_3), 4.89 (s, 1H, CH), 5.98 (s, 1H), 6.47 (s, 1H), 7.01 (s, 2H, NH_2), 7.36 (d, 2H, *J* = 7.8 Hz), 7.45 (d, 2H, *J* = 7.8 Hz), 10.98 (s, 1H, OH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 20.4, 44.9, 57.5, 102.1, 107.6, 111.9, 115.9, 119.9, 124.3, 130.8, 132.1, 141.8, 145.1, 153.8, 156.2, 160.3, 160.6, 163.4 ppm. [Found: C, 56.67; H, 3.29; N, 6.77% $C_{20}H_{13}BrN_2O_4$; requires: C, 56.49; H, 3.08; N, 6.59%].

8-amino-1,10-dihydro-5-methoxy-4-methyl-2-oxo-10-(phenyl)-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product c_1):** Melting point: 239-241 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.44 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 4.95 (s, 1H, CH), 5.99 (s, 1H), 6.67 (s, 1H), 6.98 (s, 2H, NH_2), 7.19-7.33 (m, 5H) ppm; ^{13}C-

NMR (100 MHz, DMSO-d_6): δ = 20.4, 45.9, 56.1, 57.3, 101.9, 107.9, 112.6, 115.9, 120.3, 128.6, 128.8, 128.9, 142.1, 144.7, 153.8, 156.1, 159.4, 159.7, 163.4 ppm. [Found: C, 70.16; H, 4.63; N, 7.92% $C_{21}H_{16}N_2O_4$; requires: C, 69.99; H, 4.48; N, 7.77%].

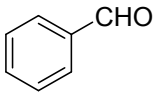
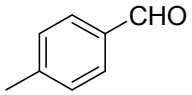
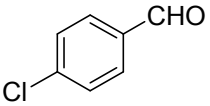
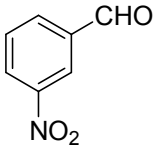
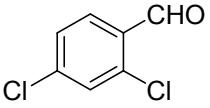
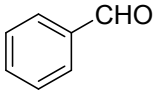
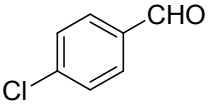
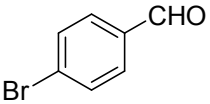
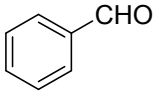
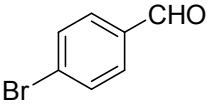
8-amino-10-(4-bromophenyl)- 1,10-dihydro-5-methoxy-4-methyl-2-oxo-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product c_2):** Melting point: 281-283 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.46 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 4.98 (s, 1H, CH), 6.00 (s, 1H), 6.69 (s, 1H), 7.05 (s, 2H, NH_2), 7.36 (d, 2H, *J* = 8.0 Hz), 7.45 (d, 2H, *J* = 8.0 Hz) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 20.7, 46.7, 56.5, 57.3, 102.2, 108.6, 112.9, 116.4, 120.3, 124.7, 130.5, 131.7, 142.4, 145.3, 153.7, 156.2, 159.7, 159.9, 163.5 ppm. [Found: C, 57.63; H, 3.61; N, 6.59% $C_{21}H_{15}BrN_2O_4$; requires: C, 57.42; H, 3.44; N, 6.38%].

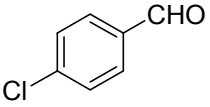
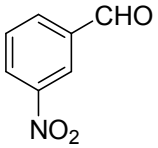
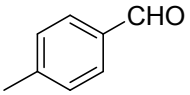
8-amino-10-(4-chlorophenyl)- 1,10-dihydro-5-methoxy-4-methyl-2-oxo-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product c_3):** Melting point: 229-231 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.45 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 5.03 (s, 1H, CH), 6.02 (s, 1H), 6.70 (s, 1H), 7.03 (s, 2H, NH_2), 7.38 (d, 2H, *J* = 7.9 Hz), 7.49 (d, 2H, *J* = 7.9 Hz) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 20.6, 47.4, 56.3, 57.5, 102.6, 108.4, 113.0, 116.9, 120.1, 128.9, 129.7, 136.2, 142.1, 144.8, 153.9, 156.2, 159.6, 159.8, 163.5 ppm. [Found: C, 63.97; H, 3.96; N, 7.33% $C_{21}H_{15}ClN_2O_4$; requires: C, 63.89; H, 3.83; N, 7.10%].

8-amino- 1,10-dihydro-5-methoxy-4-methyl-10-(3-nitrophenyl)-2-oxo-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product c_4):** Melting point: 276-278 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.45 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 5.28 (s, 1H, CH), 6.03 (s, 1H), 6.71 (s, 1H), 7.11 (s, 2H, NH_2), 7.45 (t, 1H, *J* = 8.0 Hz), 7.94 (d, 1H, *J* = 8.0 Hz), 8.22 (m, 2H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 20.5, 48.1, 56.4, 57.6, 102.9, 108.6, 113.1, 116.2, 120.4, 122.9, 125.3, 127.9, 130.1, 141.7, 144.7, 148.3, 153.8, 156.2, 159.7, 159.9, 163.5 ppm. [Found: C, 62.39; H, 3.96; N, 10.55% $C_{21}H_{15}N_3O_6$; requires: C, 62.22; H, 3.73; N, 10.37%].

8-amino-1,10-dihydro-5-methoxy-4-methyl-10-(4-methylphenyl)-2-oxo-pyrano[2,3-h]chromene-9-carbonitrile **(Table 1, Product c_5):** Melting point: 217-219 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.27 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 4.90 (s, 1H, CH), 6.00 (s, 1H), 6.69 (s, 1H), 6.98 (s, 2H, NH_2), 7.08 (d, 2H, *J* = 7.8 Hz), 7.17 (d, 2H, *J* = 7.8 Hz) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 20.4, 21.7, 46.4, 56.3, 57.5, 102.8, 108.6, 112.8, 116.1, 120.1, 126.8, 129.4, 140.3, 141.8, 145.2, 153.9, 156.1, 159.5, 159.7, 163.3 ppm. [Found: C, 70.77; H, 5.03; N, 7.71% $C_{22}H_{18}N_2O_4$; requires: C, 70.58; H, 4.85; N, 7.48%].

Table 1: Preparation of benzo[h]pyrano[3,2-c]chromene-2-carbonitriles and pyrano[3,2-g]chromene-7-carbonitriles using Bi_2O_3 nano-particles (0.25 mmol)

Entry	Aldehyde	Product	Time (h)	Yield (%)[a]
1		a_1	20	85
2		a_2	24	80
3		a_3	20	89
4		a_4	18	87
5		a_5	25	74
10		b_1	15	89
11		b_2	18	90
12		b_3	18	92
13		c_1	15	88
14		c_2	17	91

Entry	Aldehyde	Product	Time (h)	Yield (%)[a]
15		c_3	17	90
16		c_4	20	92
17		c_5	15	92

[a]Isolated yield; All product were characterized on the basis of their NMR and elemental analysis (CHN).

3. RESULTS SECTION

The XRD pattern was used to identify the phase of the Bi_2O_3 nano-powder (Figure 1). The XRD pattern can be indexed to monoclinic α-Bi_2O_3 (00-027-0053) phase. The diffraction peaks related to α-Bi_2O_3 are 25.75, 26.91, 27.39, 28.01, 33.03, 33.23, 35.04, 37.57, 46.29, 48.59, 52.38 and 54.80 [2theta degree] which are matched well with monoclinic α-Bi_2O_3. An average crystal size of α-Bi_2O_3 particles was estimated using Scherrer equation as 58 nm.

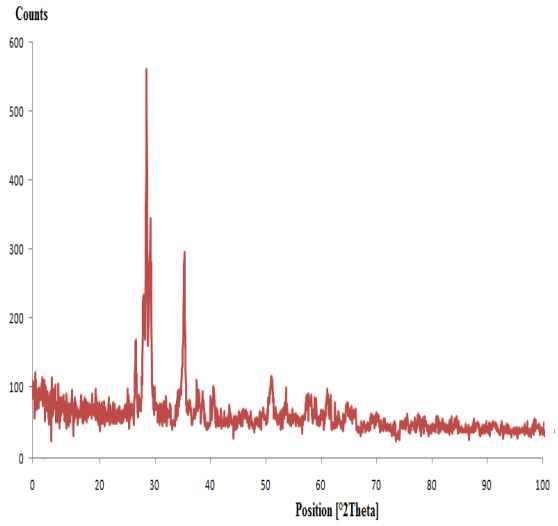


Figure 1. XRD pattern of Bi_2O_3 nanopowder calcined in 600 °C.

The morphological evolution of the Bi_2O_3 nano-powder was further studied using FE-SEM images of calcined powder and the results are revealed in Figure 2. As shown in Figure 2 the particles are relatively homogeneous in size and shape and are uniform spheres.

The specific surface area measurements of the Bi_2O_3 nano-powder were evacuated by BET method and also total pore volume and average pore diameter were determined at 200 °C for 300 min. The results are given in Table 2. These results show that the catalyst have a good specific surface area. The average diameter of the nanoparticles is comparable with those obtained from XRD and FE-SEM techniques.

The dynamic light scattering (DLS) analysis was used to determine the particle size distribution of Bi_2O_3 nano-powder. Before analysis the sample was diluted in water (0.5 gL^{-1}) and sonicated for 2h

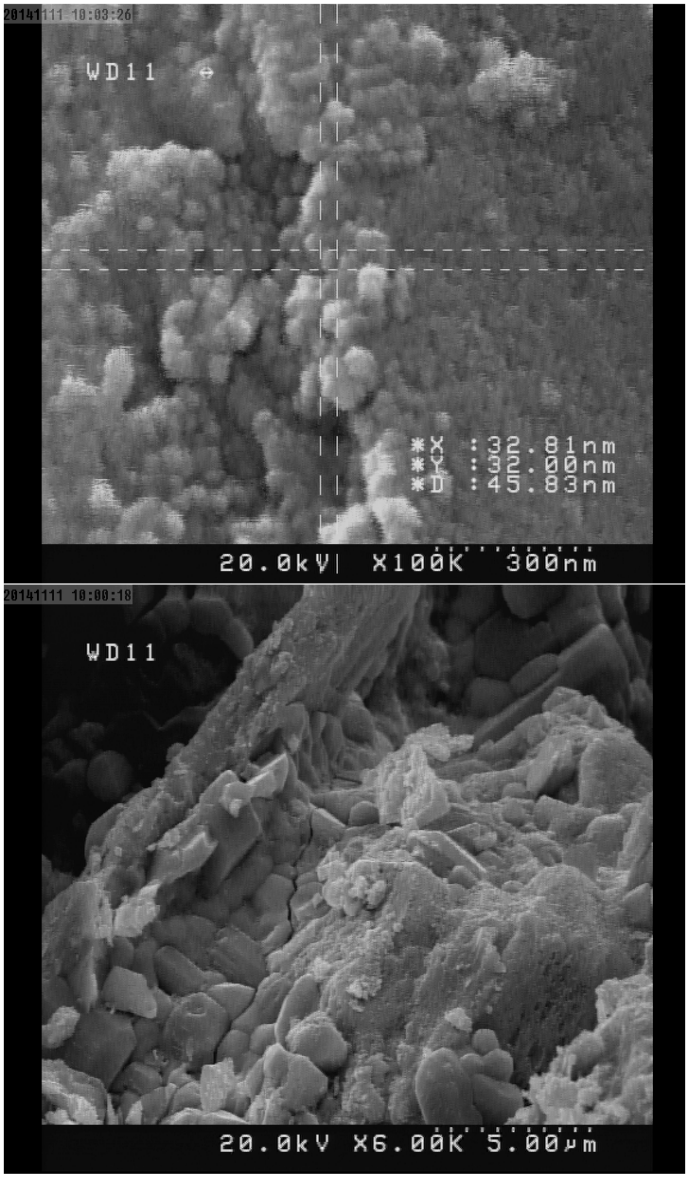


Figure 2: FE-SEM micrographs of Bi_2O_3 nano-particles.

Figure 3 shows the size distribution of nanopowder. Focusing on the results, the intensity-average diameter determined by DLS is about 63 nm.

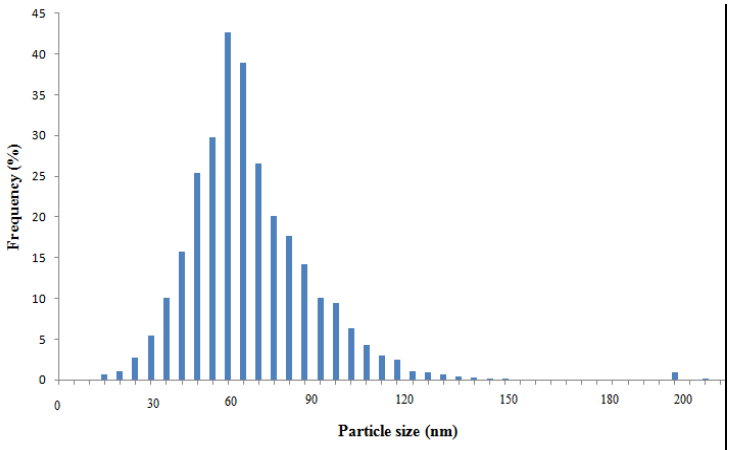


Figure 3: Particle size distribution of Bi_2O_3 nanopowder**.**

The catalytic activity of Bi_2O_3 nanopowder was examined on the condensation reaction of 4-hydroxy-2H-benzo[h]chromen-2-one (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) as a tentative experiment in different condition including solvent, temperature and catalyst dosage (Table 3). The progress of the reaction was monitored by TLC. After completion of the reaction a work-up afforded the pure product in low yields, in common organic solvents and also water at the reflux condition and did not afford the product in non-polar solvents and also in different solvents at room temperature (Table 3, Entries 1-9). Investigation of the procedure at higher temperatures showed that a significant change was observed in the relative yields, and reaction times decrease under these conditions (Table 3). It is noteworthy to mention that the best result was obtained in aqueous medium. In another experiment, the effect of different catalyst dosages was examined and it was found that the yield of the reaction increases with increasing of the quantity of the catalyst (Table 3, Entries 12-15).

The optimal catalyst amount was found to be 0.25 mmol. The use of lesser amounts of the catalyst afforded lower product yield. On the other hand, the use of higher quantities of the catalyst did not provide any significant advantage in the increasing of the reaction yield.

To study the scope and limitations of this procedure, a series of experiments were carried out using a variety of aromatic aldehydes. The results have been shown in Table 1. The reactions worked well with almost all the aldehydes. However, aromatic aldehydes bearing electron withdrawing groups showed better reactivity and the reactions were completed in shorter time.

In continuing the one-pot three-component reaction of 5,7-dihydroxy-4-methyl-2H-chromen-2-one/7-hydroxy-5-methoxy-4-methyl-2H-chromen-2-one, aromatic aldehydes and malononitrile for the synthesis of pyrano[3,2-g]chromene-7-carbonitriles was investigated. To our delight, under the above optimized conditions, the reactions proceeded smoothly and a variety of the desired products were obtained in good yields (Table 1).

Table 2: Specific surface area, total pore volume and average pore diameter of Bi_2O_3 nanopowder

Specific surface area (m^2/g)	Pore diameter (nm)	Pore volume (cc/g)
49.14	64.12	0.041

Table 3: Optimization of the reaction conditions in the synthesis of 3-Amino-12-oxo-1-(phenyl)-1,12-dihydrobenzo[h]pyrano[3,2-c]chromene-2-carbonitrile.

Entry	Catalyst (mmol)	T (°C)	Solvent (10 mL)	Time (h)	Yield (%)[a]
1	0.1	r.t.	H_2O	24	-
2	0.1	r.t.	EtOH	24	-
3	0.1	r.t.	CH_3CN	24	-
4	0.1	reflux	H_2O	24	35
5	0.1	reflux	EtOH	24	55
6	0.1	reflux	*n*-Hexane	24	-
7	0.1	reflux	CH_2Cl_2	24	-
8	0.1	reflux	CH_3CN	24	40
9	0.1	reflux	EtOAc	24	15
10	0.1	reflux	H_2O/EtOH (50% v/v)	24	80
11	0.1	50 °C	H_2O/EtOH (50% v/v)	24	40
12	0.1	80 °C	H_2O/EtOH (50% v/v)	20	76

Entry	Catalyst (mmol)	T (°C)	Solvent (10 mL)	Time (h)	Yield (%)[a]
13	0.25	80 °C	H_2O/EtOH (50% v/v)	20	85
14	0.5	80 °C	H_2O/EtOH (50% v/v)	20	80
15	1	80 °C	H_2O/EtOH (50% v/v)	20	78

[a] Isolated Yields

4. CONCLUSIONS

In summary, a high yielding one-pot condensation reaction of 4-hydroxy-2*H*-benzo[h]chromen-2-one /5,7-dihydroxy-4-methyl-2*H*-chromen-2-one/7-hydroxy-5-methoxy-4-methyl-2*H*-chromen-2-one, aromatic aldehydes and malononitrile for the synthesis of benzo[h]pyrano[3,2-c]chromene-2-carbonitriles and pyrano[3,2-g]chromene-7-carbonitriles using Bi_2O_3 nano-particles was developed. Bi_2O_3 nanopowder prepared via a simple precipitation method has been used in catalytic quantities. Various aromatic aldehydes afforded the corresponding products is high yields.

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