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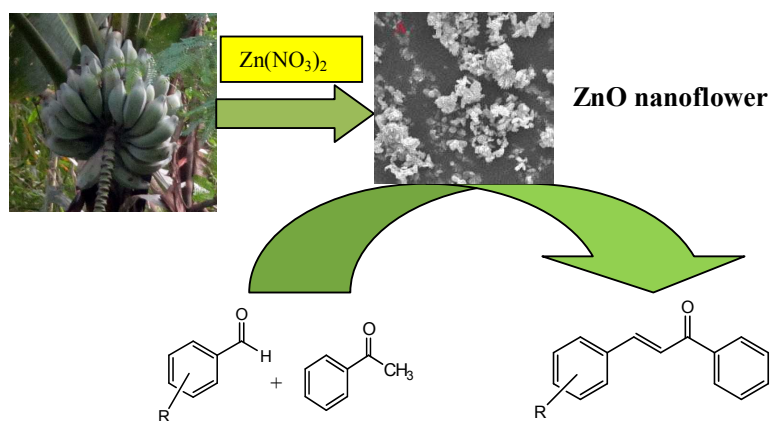
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Graphical Abstract

Green, eco-friendly synthesis of ZnO nanoparticles using peel of *Musa balbisiana* and its utility as nanocatalyst in synthesis of chalcone derivatives is reported



Cite this: DOI: 10.1039/c0xx00000x

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Paper

Bio-derived ZnO nanoflower: A highly efficient catalyst for synthesis of chalcones derivatives

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Green, eco-friendly synthesis of ZnO nanoparticles using peel of *Musa balbisiana* and its utility as nanocatalyst in synthesis of chalcones derivatives is reported here. Bio-derived ZnO nanoparticles were characterized by XRD, XPS, FTIR, SEM, BET and TEM techniques. The single step condensation of substituted aryl carbonyls is an attractive feature to obtain substituted chalcones with 88-98% yield in less than 2 min under microwave irradiation in solvent free condition. Short time period with excellent yield of chalcones is the main privilege in our study.

1. Introduction

Among various metal oxides, ZnO nanoparticles have come to the limelight for its semiconducting properties, unique antibacterial, antifungal, wound healing and UV filtering properties, high catalytic and photochemical activity¹. Over the past several years, plants and different natural sources have come up as a low cost, energy-efficient, eco-friendly and non-toxic approach for synthesis of nanomaterials.²⁻³ These synthesized nanoparticles have the advantage of good polydispersity, dimensions and stability with a negligible synthesizing cost. Moreover, using plants extract for nanoparticles synthesis can be advantageous over other biological processes because it eliminates the elaborate process of maintaining cell cultures and can also be suitably scaled up for large-scale nanoparticles synthesis⁴. Many examples are found in literature for eco-friendly synthesis of ZnO nanoparticles using leaf extract such as *Corriandrum Sativum* with $Zn(CH_3CO)_2 \cdot 2H_2O$ as precursor⁵, *Calotropis procera*⁶, seaweeds such as green *Caulerpa peltata*, red *Hypnea Valencia* and brown *Sargassum myriocystum*,⁷ orange juice⁸, *Calotropis procera* latex⁹, aqueous leaf extract of *Acalypha indica*¹⁰, and leaf extract of *Calotropis Gigantea*¹¹.

The *Musa balbisiana* is a medicinal and economic plant in North East India. The peel of the plant is a food additive and helps in normalizing digestive disorder of stomach. It is widely used as soaps and detergents for washing clothes and shampooing hairs¹²⁻¹³.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:xxxxxxx

In this present investigation we synthesized ZnO nanoparticles, a green and low cost method using peel of *Musa balbisiana*. This procedure is environmentally benign for production of well characterized nanoparticles without use of harsh, toxic and expensive chemicals.

Furthermore, this procedure is more valuable due to its cost effectiveness. Besides the green synthesis, the catalytic activity of ZnO in the microwave synthesis of chalcones in solvent free condition is reported.

2. Experimental Section

2.1. Materials

Materials used for the synthesis of ZnO nanoparticles are Zinc nitrate [$Zn(NO_3)_2 \cdot 2H_2O$] (Merck, India) and *Musa balbisiana* peel extract which was prepared by burning the peel of the plant.

2.2. Synthesis of ZnO nanoparticles

In this method, the peel of *Musa balbisiana* was dried and then burnt. To the 1 gm of ash of the peel, 10 ml of distilled water was added and filtered. 4ml 1M $Zn(NO_3)_2 \cdot 2H_2O$ solution was added to the filtrate and stirred for 20 min. White precipitate was obtained. The precipitate was then filtered and washed three/four times with distilled water. The precipitate was heated for 2 h at 120°C temperature for the formation of powder ZnO nanoparticles. It is the first report of eco-friendly green synthesis of ZnO nanoparticles by using peel of *Musa balbisiana*.

2.3. Characterization:

Scanning electron microscopy (SEM) characterization was performed on JEOL JSM - 6360 at 15 kV. X-ray diffraction (XRD) measurement were carried out by Rigaku X-ray diffractometer (Model: ULTIMA IV, Rigaku, Japan) with Cu-K α X-ray source ($\lambda = 1.54056 \text{ \AA}$) at voltage 40 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 300 (Thermo-VG Scientific). The high resolution transmission electron microscopy (HR-TEM) images were

recorded by a JEOL Model 2100 EX, Japan operated at voltage of 200 kV. Specific surface area, pore volume, average pore diameter were measured with the Autosorb-1 (Quantachrome, USA). Specific surface area of the samples was measured by adsorption of nitrogen gas at 77 K and applying the Brunauer–Emmett–Teller (BET) calculation. Pore size distributions were derived from desorption isotherms using the Barrett–Joyner–Halenda (BJH) method. The ^1H & ^{13}C NMR spectra were recorded at room temperature in CDCl_3 solution on a Bruker DPX-300 spectrometer and chemical shifts were reported relative to SiMe_4 .

2.4. Claisen Schmidt condensation

Acetophenone (10 mmol), benzaldehyde (10 mmol) mixed with ZnO nanoparticles (5mol %). Then the mixture was irradiated in a microwave reactor for 1 min after setting reaction power at 40% (maximum output 400 W) at 100°C . After cooling to room temperature ethyl acetate (15 ml) was added to the reaction mixture and filtered the mixture through filter paper to separate the solid catalyst. The ZnO catalyst could be used consecutively for five times for the condensation of acetophenone and benzaldehyde. After washing the filtrate the separated organic layer was concentrated under reduced pressure and the product was purified by column chromatography using hexane/ethyl acetate as solvent system in different concentration to obtain the pure compound.

Results and Discussion

3.1. Characterization of ZnO nanoparticles

In the present investigation, ZnO nanoparticles are synthesized using the peel of *Musa balbisiana*. It contained 233.60 gm of K^+ , 2.00 gm of Na^+ , 161.40 gm of CO_3^{2-} and 6.62 gm of Cl^- when prepared from 1 kg of the ash¹²⁻¹³. So, these ions may be responsible for synthesis of ZnO nanoparticles [Scheme 1S, supporting information (SI)].

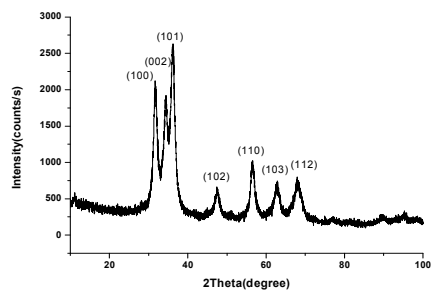


Figure 1: XRD pattern of ZnO nanoparticles

The formation of ZnO nanoparticles was confirmed using XRD, XPS, FTIR, SEM and TEM analysis. In XRD analysis, the 2θ values 31.7° , 34.4° , 36.3° , 47.4° , 56.6° , 62.8° and 67.9° assigned (100), (002), (101), (102), (110), (103) and (112) plane indicate the wurtzite structure of ZnO nanoparticles (JCPDS card No. 36–1451). The corresponding ‘d’ spacing value of ZnO nanoparticles are 2.87, 2.71, 2.49, 1.91, 1.54 and 1.35 respectively (Figure 1). All diffraction peaks of sample correspond to the characteristic hexagonal wurtzite structure of ZnO nanoparticles ($a = 0.315$ nm and $c = 0.529$ nm). It is similar

as reported data¹⁴.

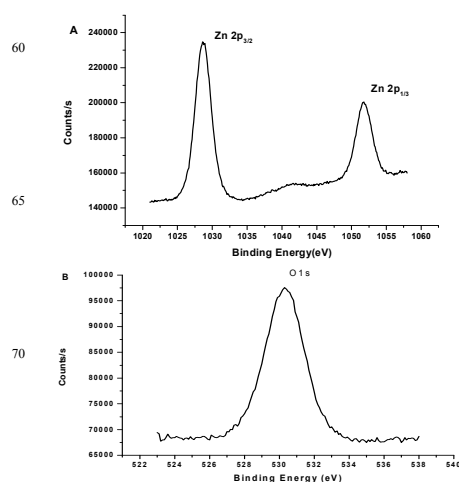


Figure 2: XPS spectra of (A) Zn 2p and (B) O 1s of ZnO nanoparticles

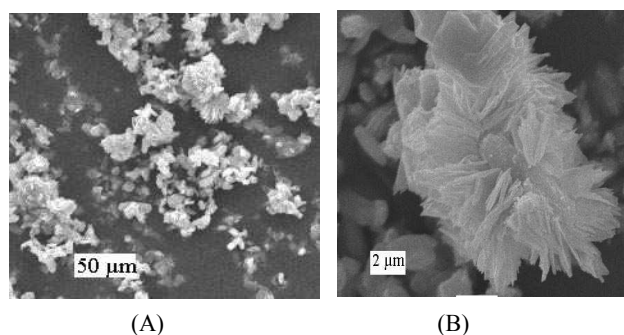


Figure 3: SEM images (A-B) of ZnO synthesized using *Musa balbisiana*

In XPS analysis, the instrument was standardized against the $\text{Cl}1\text{s}$ spectral line at 284.6 eV. The binding energy of the Zn $2\text{p}_{3/2}$ and Zn $2\text{p}_{1/2}$ component is recorded to be 1028.6 eV and 1051.8 eV respectively (Figure 2A). The binding energy of O 1s is found at 530.16 eV (Figure 2B). Such results suggested that there is no impurity existing within the sample. The result is supported by reported data¹⁵⁻¹⁶. In FTIR analysis, the peak observed at 3452.30 and 1119.15 cm^{-1} may be due to O-H stretching and deformation respectively of atmospheric vapours. The peaks at 1634.00 and 620.93 cm^{-1} are corresponds to Zn-O stretching and deformation vibration, respectively (Figure 1S, SI). The metal-oxygen frequencies observed for the respective metal oxide are in accordance with literature values¹⁷⁻¹⁸.

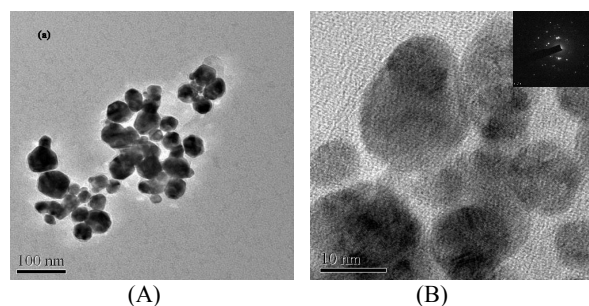


Figure 4: TEM image (A-B) of ZnO synthesized using *Musa*

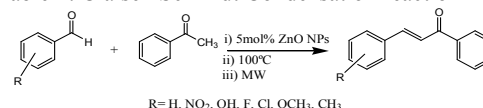
balbisiana

The SEM images indicate the formation of flower like morphology of ZnO. The size of petal of ZnO nano flower is in the range of 100-400 nm (Figure 3A-B). The flower like morphology consists of petal like small nanosheets. However, it is difficult to examine the surface structure of the nanosheets by SEM images and therefore it was examined by HR-TEM analysis. The results showed the formation of flower like cluster of ZnO nanostructure. The nanoparticles overlap each other which strongly support the formation of flower like nanostructure along with oval shape nanoparticles (Figure 4A-B). The size of ZnO nanoparticles was found in the range of 5.0±0.2 – 22.0±1.2 nm. The average size of the particles is 10.5±0.8 nm. The distance between the two atomic layers is 0.26 nm. The formation of flower like structure of nanoparticles may be due to synergic effect of ions like K⁺, CO₃²⁻, Na⁺, Cl⁻ etc which are available in the extract during synthesis of nanoparticles. Similar result was observed in other metal oxide with same precursors¹²⁻¹³.

formation of pentagonal, hexagonal ZnO nanoparticless. The size of the nanoparticles ranged 8.0±0.2–30.0±1.1 nm [Figure 3S, SI]. The average size of particles was 18.2±0.2 nm. In FTIR analysis the peak at 3378 cm⁻¹, 1620 cm⁻¹, and 1122 cm⁻¹ accountable for H₂O and CO₂ which usually take up from the environment [Figure 4S, SI]. The results supported by reported data¹⁸. The size and shape of the nanoparticless similar as synthesized using peel extract of *Musa balbisiana*. So, from the observation it revealed that the ions like K⁺, CO₃²⁻, Na⁺, Cl⁻ etc may responsible for synthesis of ZnO nanoparticles.

3.2. Claisen Schmidt Condensation reaction

Table 1: Claisen Schmidt Condensation reaction



Entry	Substrate	Product	Temp (°C)	Time ^a (min)	Yield ^b (%)	TON	TOF(h ⁻¹)
1			100	0.8	98	1.96	147.3
2			100	1.2	92	1.84	92.6
3			100	1.0	94	1.88	117.4
4			100	0.9	92	1.86	124.0
5			100	1.2	90	1.8	90.0
6			100	1.1	91	1.82	99.4
7			100	1.3	88	1.76	81.4

^a Reactions performed at 80°C & 100°C and monitored using TLC until all the aldehyde and acetophenone were found to be consumed. ^b Isolated yield after column chromatography with 2% standard deviation.

In order to understand the role of ions like K⁺, CO₃²⁻ etc we have performed an experiment using commercially available reagent. In this experiment ZnO nanoparticles was synthesized using 1mM K₂CO₃ with 1 mM Zn(NO₃)₂·2H₂O then heated the synthesized product at about 120°C for 1 h. The synthesized nanoparticles were characterized using XRD, TEM and FTIR analysis.

In XRD analysis, the 2θ values 31.6°, 34.4°, 36.4°, 47.4°, 56.6°, 62.8° and 67.9° assigned (100), (002), (101), (102), (110), (103) and (112) plane strongly indicated formation of ZnO nanoparticless [Figure 2S, SI] The TEM image indicated the

As we were emphasizing solvent less single step synthesis of chalcones without using any protecting group, the reaction between benzaldehyde (A) and acetophenone (B) was studied in detail taking equimolar mixtures of A and B under microwave irradiation in different conditions to optimize the reaction

We studied the reaction using ZnSO₄, Zn(NO₃)₂, ZnCl₂, commercial ZnO nanopowder (characterized by XRD and TEM analysis, supporting information Figure 5S& 6S), ZnO nanocatalyst and without any catalyst. The results are presented in Table 1S, SI. The reaction was carried out under solvent free condition by mixing benzaldehyde and acetophenone in microwave run at 100°C and power at 40% (maximum output 400 W). No product was formed when catalyst was not used at 80°C

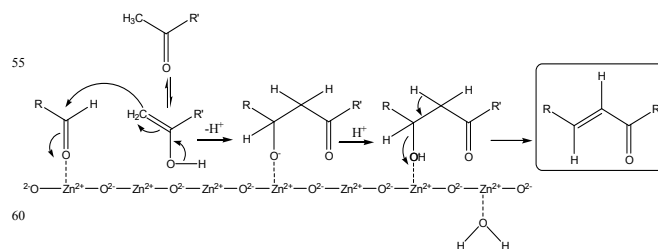
and 100°C keeping the other reaction conditions unchanged as a control reaction (Table 1S, entries 1-2). From the table 1S, it was observed that use of 5 mol% ZnO produce the best result (98%) with in 0.8 min microwave irradiation at 100°C. Thereafter reactions were carried out with different substituted aldehydes and ketones [Table 1]. The electron donating and withdrawing substituent in the aryl ring were well tolerated to give moderate high yield of the desired chalcones. The result was found significant and yield ranged 88-98 %. The isolated compounds were characterised by ¹H NMR, ¹³C NMR analysis. These data of all products were comparable with the commercialized compounds (Scheme 2S, SI).

Table 2: Recycling potential of ZnO nanocatalyst

No of cycle	Run 1	Run 2	Run 3	Run 4	Run 5
Yield (%)	98	97	96	95	94
Time(min)	0.8	0.8	0.8	0.8	0.8
TON	1.96	1.94	1.92	1.90	1.88
TOF(h ⁻¹)	147.3	145.8	144.3	142.8	141.3

Reaction condition, 10 mmol benzaldehyde, 10 mmol acetophenone, 5mol% ZnO nanocatalyst

We have tested the reusability of ZnO catalyst in condensation reaction of benzaldehyde and acetophenone. The ZnO catalyst was recovered by filtration and was washed with hot water/ethanol to remove any absorbed products. The catalyst was reused without obvious loss of their catalytic activity, up to five cycles and efficiency remain almost same (1st recycle 98%, 2nd recycle 97% and 3rd recycle 96%, 4th recycle 95% and 5th recycle 94% chalcones was obtained) (Table 2). It was further confirmed by using XRD and TEM analysis after 5th recycle [Figure 7S & 8S]. TEM and XRD investigation also showed that the activity, morphology and size distribution of the ZnO nanocatalyst remain unchanged after use of 5 times. Further investigation was done for precise evidence through adsorption-desorption of nitrogen molecule. The BET surface area and total pore volume of ZnO was found to be 11.402 m²/g and 0.1859 m³/g respectively for the fresh catalyst. The specific surface area of the recovered catalysts decrease marginally to 140 (5th run) compared to 237 m² g⁻¹ of freshly prepared catalyst [Figure 9S, SI]. The decrease of the surface area of the catalyst after reaction may be due to the partial destruction of the support by the small amount of base used in the reaction. It was observed that the adsorption-desorption hysteresis loop of the catalyst used in the 5th run ranging between P/P₀ = 0.3 and 0.9 shifted to P/P₀ = 0.6 and 0.9, respectively. This may be due to the change in the structure of pores. The BJH pore size distribution curve of the recovered catalyst shows a slight broadening of the distribution pattern compared to fresh catalyst [Figure 10S, SI] indicating breakdown of the pore walls forming larger pores. However, it is strongly supported that there is no loss of efficiency of the catalyst after 5th recycle.



Scheme 1: Plausible mechanism for condensation reaction

In the plausible mechanism, it has been observed that nano-ZnO activates the aldehyde and react with the enol form of ketone to form the condensed product. One H₂O molecule was eliminated from the condensed product to form 1,3-Diphenyl-1-phenylpropenone (chalcones) and its derivatives (Scheme 1)¹⁹.

Table 3: Comparison of Nano-ZnO catalyst for chalcone formation from benzaldehyde and acetophenone with earlier report

Sl No	Catalyst	Time (min)	Temperature	Yield(%)	Reference
1	BF ₃ -Et ₂ O/ Dioxane	15	Room tempture	90	[20]
2	I ₂ -Al ₂ O ₃ (neutral)	1.5	M.W.(300W) 60°C	95	[19]
3	NH ₄ Cl/ Solvent free MW	3	M.W. (480 W)	95	[21]
4	BiCl ₃ /Solvent free	20	140 °C	85	[22]
5	Phosphonium Ionic Liquid	150	145°C	80	[23]
6	Nano-ZnO	0.8	100 °C	98	Present work

The catalytic performance of the chalcones is compared with earlier supported catalyst and was observed the use of nano-ZnO as catalyst in the reaction between benzaldehyde and acetophenone under microwave irradiation at 100°C, showed highest yield of chalcones (Table 3). So, this is one of suitable, simple, efficient method for synthesis of chalcones and its derivatives.

4. Conclusion

It is a first report of green, efficient and eco-friendly synthesis of ZnO nanoparticles using peel of *Musa balbisiana*. The ions like K⁺, Na⁺, CO₃²⁻ etc may be responsible for the synthesis of ZnO micro-flower like nanostructure. We have developed a novel, quick, environmentally safe and clean process for synthesis of chalcone and its derivatives. The mild reaction conditions, easy work-up, clean reaction profiles render this approach as an interesting alternative to the existing methods.

Acknowledgement

The authors thank Director CSIR-North East Institute of Science & Technology, Jorhat, Assam for providing facilities and valuable advice. The authors also thankful to SAIF, Shillong for TEM analysis. The authors thankful to SEED, Division, DST,

and CSIR, New Delhi for financial support. IS thanks to CSIR New Delhi for fellowship.

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