

ZnO Nanobelts: An Efficient Catalyst for Synthesis of 5-Arylidine-2,4-Thiazolidinediones and 5-Arylidine-Rhodanines

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ABSTRACT

A facile preparation of ZnO nanobelts by chemical precipitation technique and its utility as catalyst in Knoevenagel condensation of 2,4-thiazolidinedione/rhodanine has been described. X-ray diffraction and transmission electron microscopy techniques revealed the formation ZnO nanobelts. Scanning electron microscopic observations indicate that the lengths of nanobelts are ranging from a few hundreds of micrometers to a few millimeters. Its use for the condensation of aldehydes and active methylene compounds under solvent free reaction condition at 90°C afforded the corresponding products in excellent yields in minute time.

Keywords: ZnO Nanobelts; Knoevenagel Condensation; 2,4-Thiazolidinedione; Rhodanine; Solvent-Free

1. Introduction

In present decade, metal nanoparticles have attracted much attention because of their many significant applications in various areas such as catalysis [1-4], optoelectronics [5], spintronics [6], piezoelectric transducers [7], ultraviolet optoelectronics [8]. Therefore for the production of metal nanoparticles several methods have been developed like solvothermal, hydrothermal, self-assembly, and template assisted sol-gel [9-14]. However, in this protocol a very simple and low temperature fabrication method is employed for production of long nanobelts of ZnO. Further, Zinc oxide nanoparticles are inexpensive, effective, recyclable and require only mild reaction conditions to produce high yields of products in shorter reaction times in comparison to traditional used catalysts [15].

2,4-thiazolidinedione and rhodanine derivatives have been attracted significant attention of pharmacologists as well as chemists because of extensive applications of these in building clinically used molecules (**Figure 1**) [16,17]. Furthermore, Knoevenagel products viz. 5-arylidene derivatives of 2,4-thiazolidinedione and rhodanine have been evaluated for pharmacological activities and in results it is found that they exhibit several potential activities such as antidiarrheal [18], anticonvulsant [19], antimicrobial [20], antihistaminic [21], anticancer [22], anti-HIV [23], 15-hydroxyprostaglandin dehydrogenase inhibitors [24], antischismic activities [25] etc.

Therefore, synthetic development of commercially important derivatives of these molecules was necessary and in this direction many attempt have been carried out by changing catalysts/reaction conditions such as piperidine [26], piperidinium benzoate [27], tetrabutylammonium bromide [28], baker's yeast [29], sodium acetate [30,31] and ionic liquids [32-35] etc. But these are not suitable to the point of green synthetic chemistry because formation of toxic by-products on usual work-up, long reaction time, sometime low efficacy with non-recyclability of catalysts and use of polluting organic solvents. Therefore, this condensation reaction required further improved, efficient, facile and rapid protocol.

Metal nanoparticles particularly, based on ZnO are inexpensive, easy to synthesize and effectively used to accelerate important organic reactions [15]. Because of these features and its successful applications in synthetic transformation prompted us to explore the catalytic activities of ZnO based nanoparticles in the synthesis of 5-arylidine-2,4-thiazolidinediones and 5-arylidine-rhodanines.

2. Results and Discussion

Zinc oxide nanobelts were synthesized by chemical precipitation technique using zinc acetate and absolute ethanol as starting materials. Nanobelts of ZnO were characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis. SEM images obtained from JSM microscope and XRD patterns obtained from

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PW1710 type diffractometer as shown in **Figures 2-4**. SEM images (**Figure 2**) reveal long length nanobelts ranging to a few micrometers in length and XRD patterns (**Figure 3**) reveals their high crystallinity. Wurtzite geometry of ZnO was confirmed as lattice constants $a = b = 0.32$ nm, $c = 0.52$ nm and diffraction peaks corresponding to the planes $\langle 100 \rangle$, $\langle 002 \rangle$ and $\langle 101 \rangle$ were obtained. These long nanobelts of ZnO were obtained by refluxing a solution of precursor containing zinc acetate and ethanol for long time. Addition of a catalyst stops isotropic agglomeration of particles instead anisotropic agglomeration occurs resulting in nanowires or nanobelts [36]. 0.1M LiOH give positively charged nanobelts (pH = 6.5) whereas 0.14M LiOH gives nearly neutral nanobelts (pH = 8.0) [37]. It is very much clear from the SEM images obtained from two methods that positively charged clusters results in deformation of nanobelts (**Figure 4**) and nearly neutral charged clusters results in long length nanobelts (**Figure 2**).

Role of ZnO Nanoparticles as Catalyst

Initially, ZnO nanoparticles were used to catalyse the Knoevenagel reaction of 4-methoxybenzaldehyde **1a** (1 mmol) with 2,4-thiazolidinedione **2a** (1 mmol) under

different reaction conditions. The best results obtained, when reaction was catalyzed by 5 mol% of zinc oxide nanobelts at 90°C using oil bath for 10 min under solvent-free condition and corresponding Knoevenagel adduct **3a** was isolated with 99% yield (**Table 1**). For the optimization of catalyst amount reaction of **1a** with **2a** was carried out using different amount of catalyst (2, 5, 10, 15 and 20 mol%). In observation, large amount of catalyst (>5 mol%) did not affect the yields and reaction rate but amount less than 5 mol% considerably decreased the yields of product.

Keeping optimized reaction condition, a variety of carbonyl compounds such as aromatic aldehydes **1a-b**, heterocyclic aldehydes **1c-e** (furan-2-carbaldehyde **1c**, thiophene-2-carbaldehyde **1d** and 3-formylchromone **1e**) were condensed with 5-membered active hydrogen compounds 2,4-thiazolidinedione **2a**, and rhodanine **2b** in presence of ZnO nanoparticles at 90°C under solvent-free conditions to provide Knoevenagel products **3-4** in excellent yields (**Scheme 1**). Aromatic aldehydes **1a-b** afforded excellent yields in shorter reaction time, whereas heterocyclic **1c-e** afforded high yields in slightly long reaction time (**Table 1**).

Active methylene compounds **2a-b** afforded the Kno-

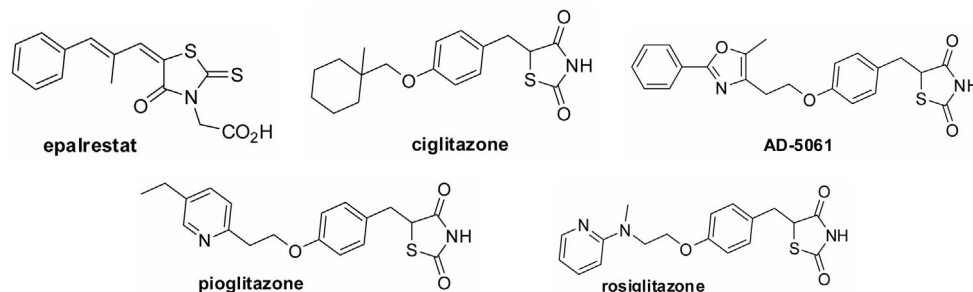


Figure 1. 2,4-thiazolidinedione and rhodanine derivatives.

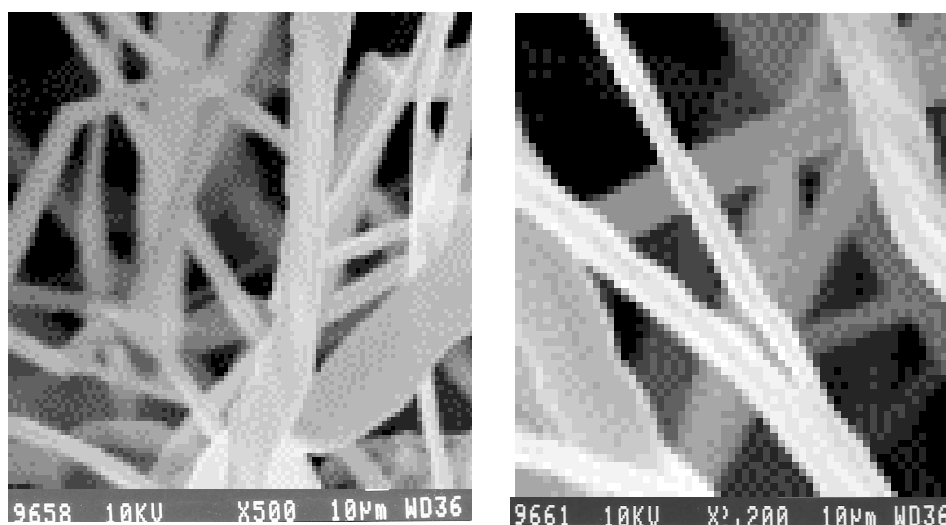


Figure 2. SEM image of the sample employing 0.14M LiOH.

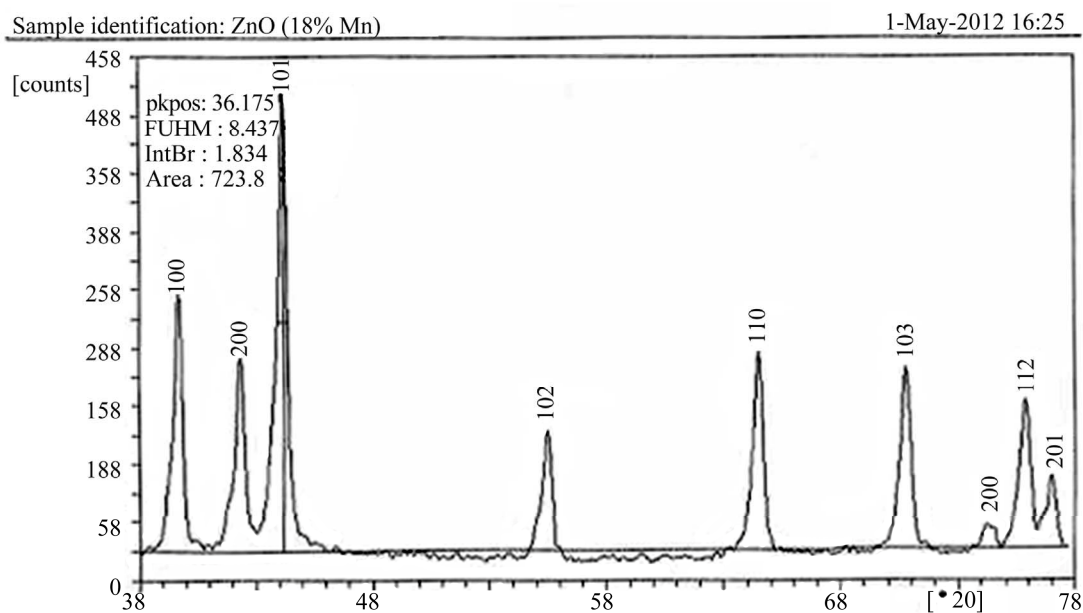


Figure 3. X-ray diffraction pattern (XRD) pattern of ZnO nanobelts.

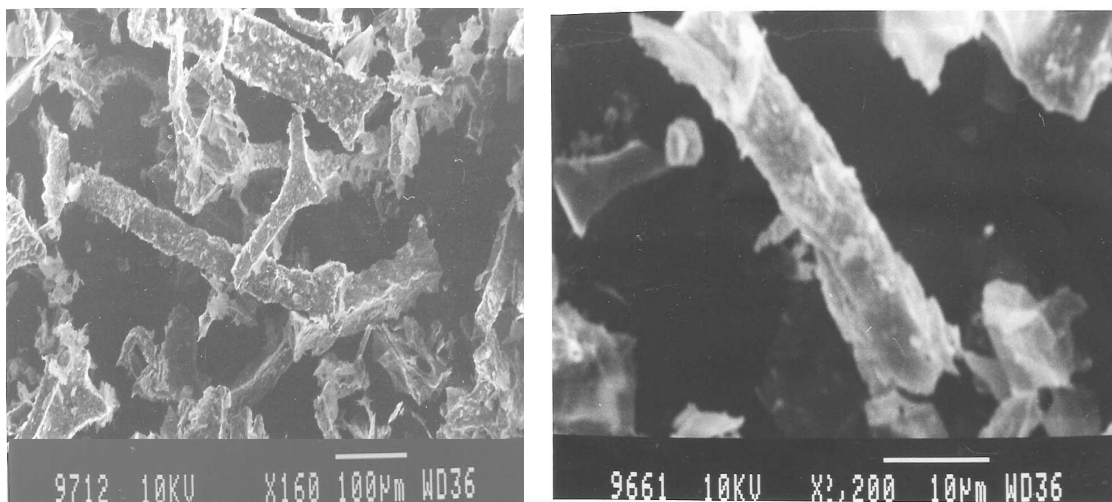


Figure 4. SEM images of the samples employing 0.1M LiOH.

evenagel products selectively with *exo* double bond without the formation of any other side-products/bis-products as shown in **Scheme 1**. Electron withdrawing and donating groups on aromatic aldehyde, were shown slightly diversion in rate of reaction and yields *i.e.* electron withdrawing group containing aromatic aldehydes afforded arylidene compounds **3-4** with better yields in shorter reaction time.

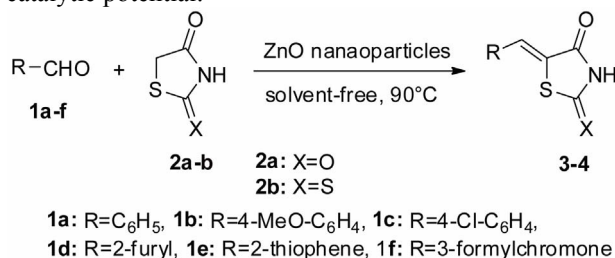
Next, the recyclability of the catalyst was studied by using **1a** and **2a** as the model substrate. We observed that catalyst could be recovered and reused for a new set of reaction. The reaction mixture with minimum quantity of solvent was centrifuged for 10 min at 5000 rpm. The supernatant was collected and the centrifuged pellet,

which is ZnO nanoparticles. Finally, ZnO nanoparticles were dried in oven at 100°C. The recovered catalyst was successfully recycled and reused for five runs without further purifications.

3. Conclusions

In summary, we have developed a simple, rapid, and environmentally benign protocol for the synthesis of 5-arylidene-2,4-thiazolidinediones and 5-arylidene-Rhodanines via ZnO nanoparticles catalysed Knoevenagel reaction. The present protocol has following synthetic features: 1) in contrast to known methods, this procedure does not need volatile organic solvents, 2) a variety

of aldehydes can be employed, 3) catalyst ZnO nanoparticles shows an excellent catalytic activity by activating both reactants without the formation of any complexes/by-products, 4) this method produces excellent yields in shorter reaction time, 5) used catalyst can be recycled and reused many times without the reduction in catalytic potential.



Scheme 1. Knoevenagel reaction of **1** and **2** catalyzed by nanoparticles.

4. Experimental Section

4.1. General

All starting materials were commercial products, and were used without further purification except liquid aldehydes, which were distilled before use. Yields refer to yield of the isolated products. Melting points were determined in open capillaries in paraffin bath and are uncorrected. Nuclear magnetic resonance spectra (¹H, ¹³C) were obtained on a 400 MHz Bruker AVANCE II instrument in DMSO-d₆ using TMS as a standard. Infrared spectra were recorded using Shimadzu FT-IR-8400s spectrophotometer as KBr pellets. X-ray diffraction (XRD) data for structural characterization of the various prepared samples of ZnO were collected on an X-ray diffractometer (PW1710) using Cu-Kα radiation (1.541 Å). Scanning electron microscope (SEM) images of the samples were obtained from JSM-6100 type microscope.

4.2. General Preparation of ZnO Nanobelts

0.1 M solution having Zn²⁺ was prepared from zinc acetate in absolute ethanol and it was refluxed for 3 hours with stirring at 80°C. After this, two routes were opted to obtain nanobelts from precursor. In the first method, the precursor obtained was mixed with 0.1M LiOH prepared in 100 mL triply deionized water. Precipitates were formed immediately and separated out using centrifugal machine at room temperature. Finally, precipitates were dried in oven at 100°C. In the second method, the precursor was mixed with 0.14M LiOH prepared in 100 mL triply deionized water. Immediately precipitation starts forming, which were kept at 4°C for few hours and then the precipitates, were separated out using centrifugal machine at -10°C. Precipitates were then dried in the oven at 100°C.

4.3. General Procedure for the Synthesis of Arylidene-Thiazolidenediones

A mixture of aldehyde (**1** mmol), 2,4-thiazolidinedione/rhodanine (**1** mmol) and ZnO nanoparticles (5 mol%) was heated under oil bath at 90°C for minutes time (see **Table 1**). The progress of reaction was monitored via thin layer chromatography. After the reaction completion, reaction mass was cooled (15°C - 20°C) and stirred with ethanol (50 mL) for 30 min. Then, reaction mass was centrifuged for 10 min at 5000 rpm. The supernatant was collected and reduced under pressure. The obtained products were recrystallize in EtOH:DMF (3:2). During centrifugation obtained pellet was ZnO nanoparticles, which was dried in the oven at 100°C to recover and reuse of catalyst.

The products **3-4** were confirmed by their spectral data after comparison with authentic samples, IR, ¹H NMR, mass spectra and melting points.

4.4. Spectral Data of Representative Compounds

(**3a**): Mp. 249°C - 250°C, IR (KBr, cm⁻¹): 3393, 1671, 1605, 1434, 1201; ¹H NMR (300 MHz, DMSO-d₆) δ 3.09 (s, 3H), 7.08 (d, 2H, J = 8.2 Hz), 7.52 (d, 2H, J = 8.2 Hz), 7.61 (s, 1H), 13.71 (s, 1H); Anal. Calcd. for C₁₁H₉NO₂S₂: C, 52.57; H, 3.61; N, 5.57; S, 25.52%; found: C, 52.78; H, 3.95; N, 5.48; S, 25.79%.

(**3e**): Mp. 259°C - 260°C. IR (KBr, cm⁻¹): 1647 (γ pyrone CO); ¹H NMR δ 7.54 (ddd, 1H, 6-H), 7.62 (s, 1H, C=C-H), 7.71 (d, 1H, J_{8,7} = 8.41 Hz, 8-H), 7.98 (ddd, 1H, 7-H), 8.17 (dd, 1H, J_{5,6} = 8.41 Hz, J_{5,7} = 1.68 Hz, 5-H), 8.83 (s, 1H, 2-H), 12.41 (s, 1H, NH); Anal. Calcd. for

Table 1. ZnO nanoparticles catalysed solvent-free Knoevenagel reaction.

Entry	Aldehydes	Thiazolidines	Product ^a	Time (min)	Yield (%) ^b
1	1a	2a	3a	10	99
2	1b	2a	3b	18	94
3	1c	2a	3c	15	97
4	1d	2a	3d	20	90
5	1e	2a	3e	26	92
6	1f	2a	3f	20	95
7	1b	2b	4a	15	96
8	1c	2b	4b	10	99
9	1d	2b	4c	15	93
10	1e	2b	4d	18	91
11	1f	2b	4e	12	97

^aReaction conditions: **1a-f** (1 mmol), **2a-b** (1 mmol), ZnO nanoparticles (5 mol%), were heated under oil bath at 90°C. The products were characterized by spectral techniques like IR, ¹H NMR, ¹³C NMR. ^bIsolated yields after recrystallization.

C₁₃H₇NO₃S₂: C, 53.98; H, 2.42; N, 4.84; S, 22.15%; found: C, 53.84; H, 2.74; N, 4.95; S, 21.96%.

(3b): Mp. 268°C - 269°C. IR (KBr, cm⁻¹): 3148, 1719, 1610; ¹H NMR (300 MHz, DMSO-d₆) δ_H: 7.53 (2H, m), 7.72 (2H, m), 7.76 (1H, s), 12.65 (1H, bs); Anal. Calcd. for C₁₀H₆ClNO₂S: C, 50.11; H, 2.52; N, 5.84; S, 13.38%; found: C, 49.87; H, 2.63; N, 5.92; S, 13.78%.

(4e): Mp. 290°C. IR (KBr, cm⁻¹): 1637 (γ pyrone CO); ¹H NMR : δ 7.58 (ddd, 1H, 6-H), 7.61 (s, 1H, C=C-H), 7.74 (d, 1H, J_{8,7} = 8.40 Hz, 8-H), 7.88 (ddd, 1H, 7-H), 8.13 (dd, 1H, J_{5,6} = 8.40 Hz, J_{5,7} = 1.60 Hz, 5-H), 8.85 (s, 1H, 2-H), 12.48 (s, 1H, NH). Anal. Calcd. for C₁₃H₇NO₄S: C 57.14, H 2.58, N 5.13, S 11.73%; found: C 56.84, H 2.74, N 5.25, S 11.46%.

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