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ORIGINAL PAPER

ZnO nanorods as an efficient catalyst for the synthesis of imidazo[1,2-*a*]azines and diazines

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Abstract ZnO nanorods were synthesized using a novel and solvent-free procedure and their catalytic activity in the preparation of imidazo[1,2-*a*]azines and diazines was studied. The effects of the amount of catalyst and its reusability were investigated to optimize the reaction conditions. The ZnO nanorods exhibited higher catalytic activity than that of bulk ZnO.

Keywords ZnO · Nanorods · Imidazo[1,2-*a*]azine

Introduction

The synthesis of nanostructure metal oxides attracts much attention owing to their enhanced sinterability, mechanical [1], electrical [2], and chemical properties [3]. Zinc oxide (ZnO), a versatile semiconductor material, has been attracting attention because of its wide range of applications in optoelectronic devices, solar cells, gas sensors, optical waveguides, light emitting diodes, and laser diodes [4, 5]. Developments in material science will doubtless reveal further applications for ZnO.

Recently various approaches, e.g., microwave-assisted solution-phase synthesis [6], wet chemical bath deposition (CBD) [7], galvanostatic electrodeposition [8], and hydrothermal methods [9] have been reported for the preparation of ZnO nanostructures. Considering the importance of ZnO nanostructures, development of new procedures for their synthesis is of great importance.

Several biological and pharmaceutical properties have been discovered for imidazo[1,2-*a*]azine and diazine derivatives [10]. Classically these compounds can be obtained from the two-component reaction of α-haloketones and 2-aminoazines [11]. Although this procedure gave the desired products in good to excellent yields, the application of excessive amounts of sodium bicarbonate and ionic liquid is one of the disadvantages of this procedure [12]. In recent years many procedures for the synthesis of imidazo[1,2-*a*]azines and diazines have been developed [13]. Various catalysts have been used for the synthesis of imidazo[1,2-*a*]azines such as *p*-toluenesulfonic acid [14] and ammonium chloride [15]. Imidazo[1,2-*a*]azine and diazine derivatives can be synthesized by the three-component reaction of a 2-aminoazine, aldehydes, and trimethylsilylcyanide (TMSCN) under microwave irradiation using $Sc(OTf)_3$ as a catalyst [16]. Recently ionic liquids have been used in the synthesis of imidazo[1,2-*a*]azines and diazines [17].

Herein, we report the synthesis of ZnO nanorods through a solvent-free procedure and their catalytic activities in the preparation of imidazo[1,2-*a*]azines and diazines are investigated (Scheme 1).

Results and discussion

The ZnO nanorods were synthesized through a simple and solvent-free procedure. As is known, the distinctive ZnO crystal habit exhibits polar basal [0001]/top [0001] planes and six nonpolar [1010] planes parallel to the *c* axis. This polarity not only directly induces the characteristic

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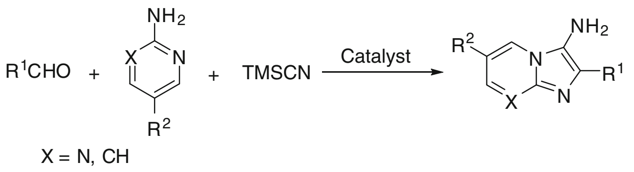

Scheme 1

piezoelectricity and spontaneous polarization, but also plays a key role in the crystal growth. The growth velocities of the ZnO crystals in different directions are as follow: [0001] > [0111] > [0110] > [0111] > [0001]. Normally, ZnO is apt to grow along the [0001] direction owing to its faster growth rate. Therefore, the ZnO crystals were grown along the [0001] direction and nanorods were synthesized by heat treatment in a furnace.

Scanning electron microscopy (SEM) images of the synthesized ZnO nanorods grown at 500 °C are shown in Fig. 1. The average diameter and length of the nanorods are about 50 nm and 2 µm, respectively.

Figure 2 shows the X-ray diffraction (XRD) pattern of the ZnO nanorods. All the diffraction peaks were indexed as a ZnO wurtzite structure (JCPDS36-1451, $a = 3.24982$ Å, $c = 5.20661$ Å). The crystal size of the ZnO nanorods was measured using the Debye–Scherrer relation ($D = 0.94\lambda/B\cos\theta$). The average crystal size is 42 nm.

The synthesis of imidazo[1,2-*a*]azines and diazines by the reaction of benzaldehydes, 2-aminoazine, and TMSCN was then performed at reflux in the presence of a catalytic amount of ZnO nanorods. As shown in Table 1, benzaldehydes containing electron-withdrawing groups led to products with slightly higher yields than those obtained with benzaldehydes containing electron-donating groups.

To optimize the reaction conditions, the synthesis of 2-(4-nitrophenyl)imidazo[1,2-*a*]pyrimidine-3-amine was selected as a model reaction. To study the effect of the amount of catalyst on the reaction yield, the model reaction was carried out in the presence of various amounts of catalyst (0.1, 0.3, 0.5, 0.7, 1 mg) under refluxing conditions. As shown in Table 2, the optimum amount of catalyst was 0.5 mg.

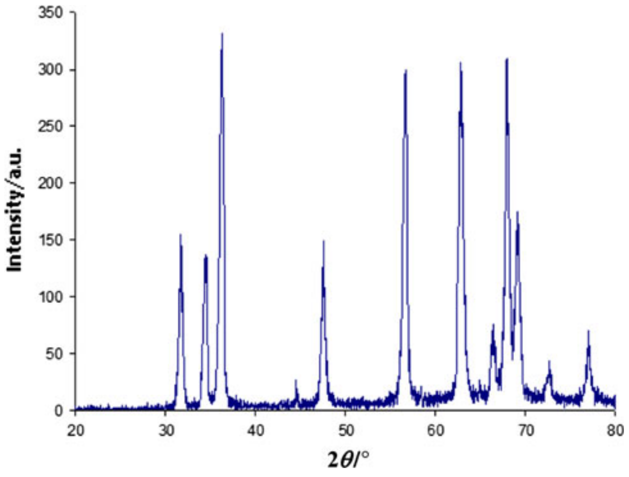

Fig. 2 XRD pattern of ZnO nanorods

It is presumed that the ZnO nanorods can catalyze the reaction through coordination to the carbonyl group of benzaldehyde. The catalytic activity of these nanorods for the synthesis of imidazo[1,2-*a*]azines and diazines was compared with that of bulk ZnO. As shown in Table 3, the catalytic activity of the ZnO nanorods is much better than that of bulk ZnO. The higher activity of the ZnO nanorods is due to their higher surface area.

In conclusion, ZnO nanorods were synthesized using a solvent-free procedure and were successfully used in the synthesis of imidazo[1,2-*a*]azines and diazines. The reasonable reaction times, very good yields, simple workup procedure, and reusability of the catalyst are the main merits of this method. The ZnO nanorods exhibit much better catalytic activity than that of bulk ZnO.

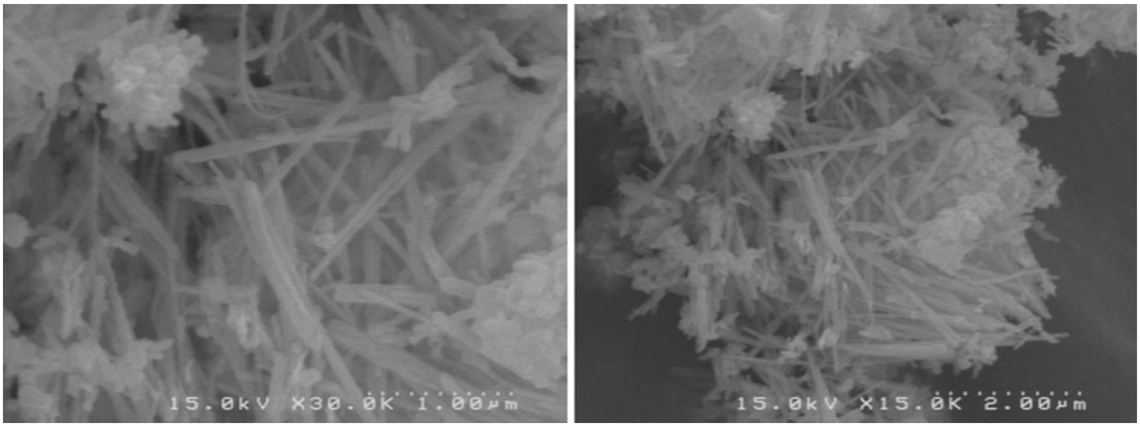

Fig. 1 SEM image of ZnO nanorods

Table 1 Synthesis of imidazo[1,2-*a*]azines and diazines using 0.5 mg ZnO nanorods under reflux

Entry	R^1	R^2	X	Time/min	Yield /%[a]	M.p./°C	Lit. m.p./°C [10]
1	4-NO_2-C_6H_4	H	N	30	81	213–215	215–218
2	4-MeO-C_6H_4	H	N	40	70	211–215	212–214
3	C_6H_5	Br	CH	30	82	231	230
4	3-NO_2-C_6H_4	Me	CH	30	85	221–224	220–223
5	4-Cl-C_6H_4	Me	CH	20	85	250	248–250
6	4-Me-C_6H_4	Me	CH	40	85	230–232	230

[a] Yields refer to isolated products

Table 2 Results of using various amounts of ZnO nanorods on the yields of 2-(4-nitrophenyl)imidazo[1,2-*a*]pyrimidine-3-amine under reflux

Entry	Catalyst amount/mg	Yield/%[a]
1	0.1	69
2	0.3	75
3	0.5	81
4	0.7	80
5	1	80

[a] Yields refer to isolated products

Table 3 Comparison of efficiency of ZnO nanorods and bulk ZnO in the synthesis of 2-(4-nitrophenyl)imidazo[1,2-*a*]pyrimidine-3-amine under reflux

Entry	Catalyst (0.5 mg)	Yield/%[a]
1	ZnO nanorods	81
2	Bulk ZnO	66

[a] Yields refer to isolated products

Experimental

Synthesis of ZnO nanorods

Zinc acetate dihydrate [$Zn(CH_3COO)_2\cdot 2H_2O$] was used as the precursor for the synthesis of the ZnO nanorods. $Zn(CH_3COO)_2\cdot 2H_2O$ was heated in a furnace at 500 °C for 3 h. Samples were characterized using SEM (Philips) and XRD with Cu Kα radiation, $\lambda = 1.54178$ Å (XPERT model 95).

General procedure for the synthesis of imidazo [1,2-a]azines and diazines

A catalytic amount of ZnO nanorods (0.5 mg) was added to a mixture of benzaldehyde (1 mmol), 2-aminoazine (1 mmol), and TMSCN (1 mmol) and the mixture was refluxed in 10 cm^3 EtOH. The progress of the reaction was monitored by TLC. At the end of the reaction (Table 1) the catalyst was separated by centrifugation. To obtain pure product the solid residue was recrystallized from ethyl acetate. All products were synthesized and characterized by comparing their physical and spectral data with those of authentic samples [10].

Table 4 Reusability of ZnO nanorods in the synthesis of imidazo[1,2-*a*]azines and diazines derivatives under reflux after three runs

Entry	R^1	R^2	X	Yield/%[a]/run		
				First	Second	Third
1	4-NO_2-C_6H_4	H	N	81	80	78
2	4-MeO-C_6H_4	H	N	71	69	68
3	C_6H_5	Br	CH	85	82	80
4	3-NO_2-C_6H_4	Me	CH	88	88	85
5	4-Cl-C_6H_4	Me	CH	86	86	85
6	4-Me-C_6H_4	Me	CH	85	85	83

[a] Yields refer to isolated products

Reuse of the catalyst

At the end of the reaction, the catalyst could be recovered by centrifugation. The recycled catalyst was washed with diethyl ether and subjected to further reaction runs. The efficiency of this catalyst in the synthesis of imidazo[1,2-*a*] azine and diazine derivatives after three runs is shown in Table 4, which indicates that the reduction in the yields using reused catalyst is slight.

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