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A green synthetic route for zinc oxide nanoarchitectures using L-lysine

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ABSTRACT

Zinc oxide (ZnO) flowers comprising nanorods of average size ~160 nm were rapidly synthesized using L-lysine as a precipitating and capping agent in aqueous medium in the absence of hydrothermal conditions. When NaOH substituted lysine, formation of only ZnO stars was observed, proving the crucial role of lysine in forming nanorods. XRD analysis of nanorods proved the formation of hexagonal ZnO and the preferential growth of (001) planes in complementary to SEM analysis. Effect of reaction temperature on resulting ZnO samples has been studied. Increase in the reaction temperature has increased the crystallite and the particle sizes of nanorods. A plausible mechanism of formation of ZnO architectures has been proposed.

1. Introduction

Zinc oxide, a wide band gap (3.37 eV) semiconductor, is an important functional material because of its optoelectronic, piezoelectric, sensor, electrical and catalytic properties [1,2]. Nano-sized ZnO are given much attention due to the size- and morphology-dependent properties [3]. Among the various morphologies, 1D morphology is preferred for different applications due to their favorable electron transport properties [4]. Nanowires of ZnO have been known to be synthesized by various routes, which are broadly classified as physical and chemical methods [5]. In general, solution-based synthetic methods are preferred due to their scalability, cost-effectiveness and morphology-tuning possibilities. Although different solution-based synthetic methods are known for ZnO with desirable shapes, efficient methods are still sought by researchers. Solution-based synthetic methods mainly employ a base such as NaOH, NH_4OH, or organic amines etc. to precipitate metal ions (here, Zn^{2+}) in solution as hydroxide, which further decomposes to yield ZnO [6]. Herein, synthesis of ZnO architectures including flowers comprising nanorods, and ellipsoids using aqueous solutions of L-lysine, an amino acid, and zinc nitrate is reported. To the best of the authors' knowledge, synthesis of ZnO using L-lysine as the precipitating and capping agent has never been reported.

2. Experimental

All the chemicals were obtained from Sigma-Aldrich with the purity of ≥98%. Deionized water was used for the synthesis and the purification. In a typical synthesis, aqueous solutions of $Zn(NO_3)_2$ (15 mM) and of L-lysine (45 mM) were heated separately to 50, 60 or 70 °C and mixed. The mixture was stirred magnetically, maintaining the temperature, for 10 min to form a white precipitate that settled down slowly while ageing for 2 h. Then, it was washed with deionized water thrice before drying at 150 °C for 2 h in air followed by calcination at 400 °C for 2 h in air atmosphere. At room temperature, no precipitate was observed. To understand the role of lysine, ZnO synthesis was performed using NaOH or both lysine and NaOH (equimolar) under similar conditions, but at room temperature (27 °C) and without calcination, to obtain stars or elongated-ellipsoids respectively. Since sodium hydroxide is a strong base, it yields precipitate with Zn^{2+} ions at room temperatures [7].

SEM images were recorded using FEG quanta 250 field emission scanning electron microscope. Powder X-ray diffraction patterns were recorded using PANalytical EMPREAN X-ray diffractometer with CuK_α (λ=1.5418 Å) and Ni filter at the scan rate of 0.05° s^{-1}. During the measurement, samples were rotated constantly at the speed of 0.25 s^{-1} to minimize the effect of orientation of the particles in XRD patterns.

3. Results and discussion

SEM analysis: SEM images of the ZnO samples are given in Fig. 1. The average sizes of the ZnO samples are provided in Table 1. The ZnO synthesized at 70 °C given in Fig. 1(a) and (b) shows flower-shaped particles made of nanorods. Average size of flowers and nanorods is 2168 and 160 nm, respectively, and aspect ratio of the nanorods is ~5. Some individual nanorods are also seen, which might have detached from flowers during synthesis due to

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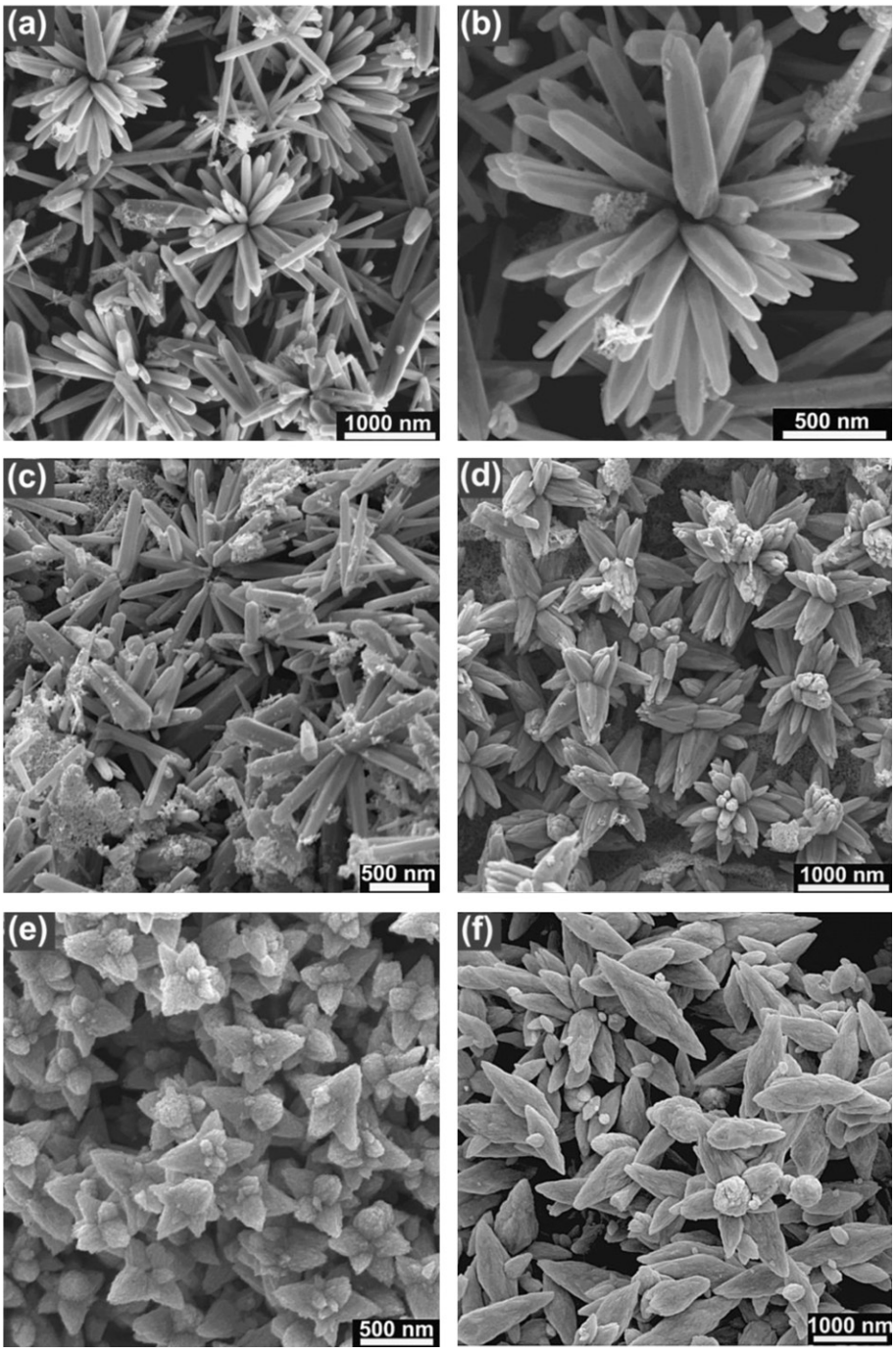

Fig. 1. SEM images of ZnO samples. (a) and (b) ZnO (T=70 °C), (c) ZnO (T=60 °C) and (d) ZnO (T=50 °C) synthesized using lysine, (e) ZnO stars (using NaOH) and (f) ZnO ellipsoids (using equimolar NaOH and lysine).

Table 1
Morphology, reaction detail, dimension and XRD peaks intensity ratio of ZnO samples.

Morphology-bulk (Unit)	Precipitating agent/capping agent	Temperature (°C)	Average crystallite size (L) (nm) (by XRD)	Average size (nm) (by FESEM)		$I_{(002)}/I_{(100)}$
				Thickness-bulk structure (Unit)	Length (Unit)	
Flowers (rods)	Lysine	70	30.0	2168 (160)	840	0.52
Flowers (rods)	Lysine	60	28.3	1896 (138)	734	0.52
Flowers (petals)	Lysine	50	20.0	1333 (333)	697	0.82
Stars (arms)	NaOH	27	20.0	605 (184)	347	1.11
Elongated ellipsoids	NaOH + lysine	27	25.7	441	1323	0.92