Acetobacter xylenium as a shape-directing agent for the formation of nano-, micro-sized zinc oxide

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Zinc oxide (ZnO) is an *n*-type, II–IV compound semiconductor with a wide band gap of 3.37 eV and is currently attracting considerable interest due to its various applications: as chemical sensors [1, 2], non-contact atomic force microscopy sensors [3, 4], pigments, and medical materials [5], to name a few.

Various methods were adopted to modify physicochemical properties of ZnO for various purposes. For example, combining ZnO nanoparticles with a polymer such as polyamic acid was found to affect the fluorescence properties of the resulting materials [6]. On the other hand, doping ZnO with Al and combining it with TiO_2 for the formation of nanostructured film resulted in the production of humidity sensitive property, which is important in humidity sensors applications [7]. Similarly, doping with rare earth ions such as erbium is useful for optoelectronic devices [8].

Apart from doping, nanostructured ZnO material with high surface area and quantum confinement effect is also currently attracting considerable interest. ZnO with various nanostructures namely combs, rings, helixes/springs, bows, belts, wires, and cages has been fabricated by various methods under specific growth conditions. These nanostructures can have novel applications in optoelectronics, sensors, transducers, and biomedical science, as they are bio-safe [9].

Thermal decomposition of $Zn(CH_3COO)_2$ is among popular routes to obtain ZnO nanostructured materials, due to its high solubility and low decomposition temperature [10]. It has been reported that from the precursor of zinc acetate, ZnO nanomaterials with a specific shape or dimension can be obtained by using organic additives as the modifying and protecting agent. For example, spherical and uniform-sized ZnO nanoparticles can be obtained by thermal decomposition of zinc acetate coated on organic additives [11]. Previous work also shows that solvent [12] and templating agent [13] play a role in controlling the morphology of the resulting ZnO particles.

The objective of this work is to prepare ZnO with a specific shape, using a simple method, hydrolysis of zinc acetate in the presence of a shape-directing agent or templating agent, *Acetobacter xylenium*, a type of cellulose-producing bacterium used for the formation of *nata de coco*. The physicochemical properties of the resulting materials were characterized and will be reported and discussed here.

All solutions were prepared using decarbonated distilled water. Sample of ZnO was directly synthesized by hydrolysis of zinc acetate and ammonia solution. Ammonia solution (0.025 M) was added to a teflon-lined autoclave of 40 ml capacity filled with 1.0 M zinc acetate and stirred vigorously. The autoclave was maintained at 200 °C for 2 hr in a temperature-controlled oven and then air-cooled to room temperature. The precipitates were filtered off, washed with deionized water, and dried overnight in an electrical oven at 90 °C. The as-synthesized powder was then stored in a sample bottle for further use and characterizations.

Nata de coco heavy syrup, purchased from a local supplier was washed and soaked overnight in distilled water for many times to remove the color and taste of the syrup. The *nata de coco* was then soaked again in deionized water for few times, and gently blot dried with a filter paper. About 40 g of *nata de coco* was blended with deionized water and various concentrations of *nata de coco* shown in Table I were prepared. This solution containing 0.67 gl^{-1} *nata de coco* was then added into a teflon-lined stainless steel vessel containing zinc acetate and ammonia solution. The solution and the resulting ZnO formed were treated as stated earlier. Similar experiments were repeated for 1.67 and 2.67 gl^{-1} *nata de coco*. The samples were labeled as in Table I.

Powder X-ray diffraction (PXRD) patterns of the resulting materials were recorded on a Shimadzu XRD-6000 powder diffractometer using CuKα ($\lambda = 1.54$ Å) at 40 kV and 20 mA. The surface properties of the resulting materials were determined by a Micromeritics surface area and pore size analyzer, Model ASAP 2000 using nitrogen gas adsorption–desorption technique at 77 K. Scanning electron microscope, JEOL JSM-6400 was used to study the surface morphology of the samples. Each sample was placed on a stub by using a

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TABLE I Surface properties for the as-synthesized ZnO particles without NDC and in the presence of NDC

Sample's label	Amount of NDC (gl^{-1})	BET surface area (m^2 g^{-1})	BJH desorption pore volume (cm^3 g^{-1})	BET average pore diameter (Å)	BJH average pore diameter (Å)
ZnO	0.00	1.0	0.006	215.5	176.9
ZnO-a	0.67	7.1	0.031	150.3	114.1
ZnO-b	1.67	12.8	0.050	136.5	90.8
ZnO-c	2.67	13.6	0.059	153.5	106.1

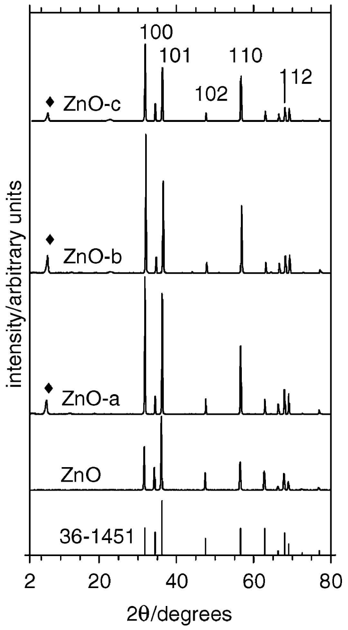

Figure 1 PXRD patterns for ZnO synthesized without *nata de coco* (ZnO) and in the presence of *nata de coco* at various amounts; 0.67 gl^{-1} (ZnO-a), 1.67 gl^{-1} (ZnO-b), and 2.67 gl^{-1} (ZnO-c). JCPDS Card No. 36-1451 is also given for comparison, (♦) unknown phase.

piece of double-sided tape and coated with gold using a Bio-Ras sputter coater. The SEM micrographs were recorded at various magnifications.

PXRD pattern of the as-synthesized ZnO is shown in Fig. 1. The diffraction peaks can be indexed to zincite structure (JCPDS No. 36-1451) in which all the samples show similar diffraction profiles. This indicates that all the precursors have been completely decomposed for the formation of ZnO phase and no other products have been retained after the decomposition process. However, when *nata de coco* is introduced, a diffraction peak at about $2\theta=6.5^\circ$ can also be detected, which belongs to unknown phase as indicated by a diamond shown in Fig. 1.

Fig. 2 shows SEM images for the ZnO synthesized at different amounts of *nata de coco*, 0.00–2.67 gl^{-1}. As shown in the figure, ZnO synthesized in the absence of *nata de coco* resulted in a mixture of vari-

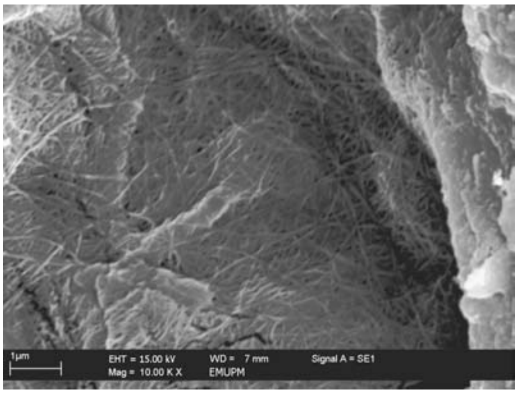

Figure 2 SEM micrographs of dried *nata de coco* and (a) ZnO synthesized without *nata de coco* and (b) in the presence of *nata de coco* at various amounts: 0.67 gl^{-1} (c), 1.67 gl^{-1} (d), and 2.67 gl^{-1} (e).

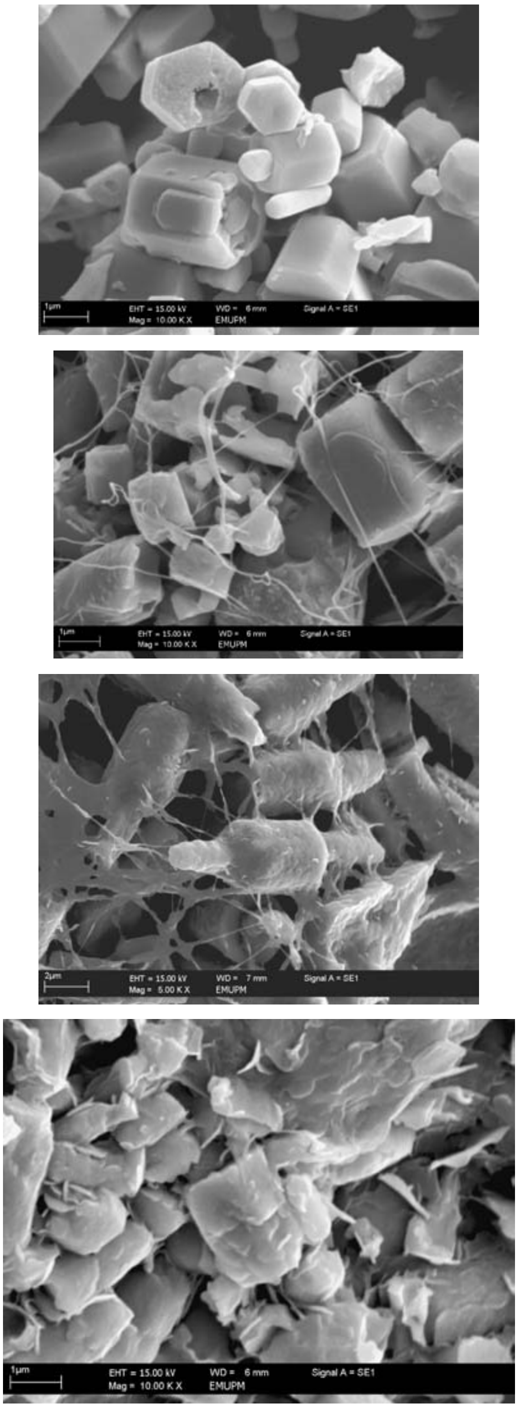

Figure 2 Continued

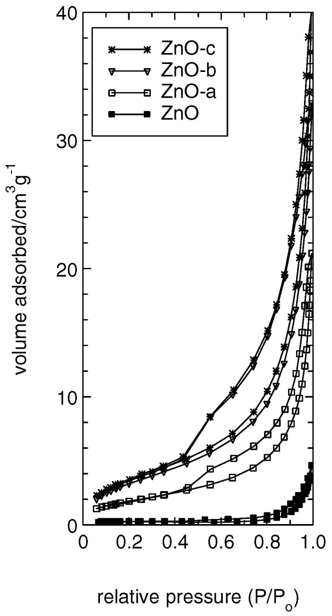

Figure 3 Adsorption–desorption isotherms of nitrogen gas on ZnO synthesized without *nata de coco* (ZnO) and in the presence of *nata de coco* at various amounts: 0.67 gl^{-1} (ZnO-a), 1.67 gl^{-1} (ZnO-b), and 2.67 gl^{-1} (ZnO-c).

ous shapes, but dominated by hexagonal shape. On the other hand, the presence of *nata de coco* resulted in the presence of thread-like structure together with various shapes of ZnO. In addition, a bottle-like shape can be clearly observed. The thread-like and the bottle-like shape (Fig. 2d) can be correlated to the known structure of *nata de coco* itself in which it is due to the cellulose (Fig. 2a) and the bacteria, respectively.

The adsorption–desorption isotherms of the materials are shown in Fig. 3, showing a typical Type IV isotherm of a nonporous material for all of them. However, the BJH pore size distributions shown in Fig. 4 show a slightly different trend. ZnO synthesised without any *nata de coco* show no peak at around 40 Å, while a peak can be observed at this value when *nata de coco* is introduced. In addition, two-mode of pore size distribution can be clearly observed for the latter, with the second broad distribution starting at around 50 Å and extending to around 700 Å.

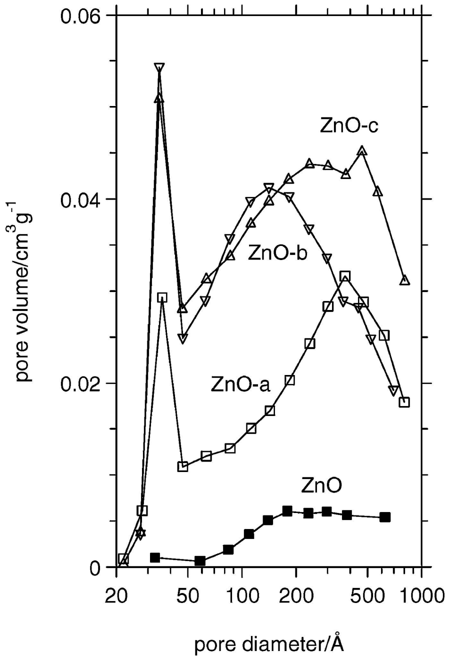

Figure 4 BJH pore size distribution for ZnO synthesized without *nata de coco* (ZnO) and in the presence of *nata de coco* at various amounts: 0.67 gl^{-1} (ZnO-a), 1.67 gl^{-1} (ZnO-b), and 2.67 gl^{-1} (ZnO-c).

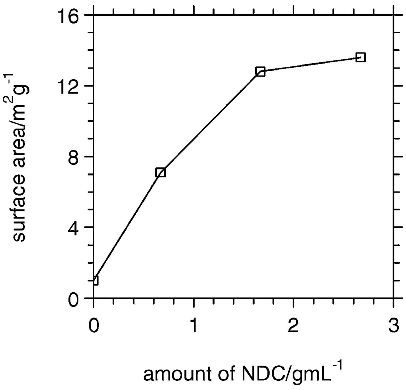

Figure 5 Plot of BET surface area against amount of *nata de coco* used in the synthesis.

The effect of the Breuner–Emmet–Teller (BET) surface area to the amount of *nata de coco* present during the hydrothermal synthesis of ZnO is shown in Fig. 5. The BET surface area increased with the amount of *nata de coco* used, presumably due to the shape-contributing factor of the *nata de coco* of the resulting ZnO.

In conclusion, this study shows that ZnO can be prepared through hydrolysis of zinc acetate in the presence of bacteria as a shape-directing agent or templating agent, *Acetobacter xylenium*, a type of cellulose-producing bacterium used for the formation of *nata de coco* to mimic the resulting shape desired. The XRD pattern of the as-synthesized ZnO shows a relatively pure phase can be obtained. The amount of the templating agent added plays a role in determining the physicochemical properties of the resulting synthesized material.

Acknowledgments

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