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# Preparation of biomorphic porous zinc oxide by wood template method

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ABSTRACT

This paper presents an effective method to fabricate highly porous zinc oxide (ZnO) derived from different wood templates, where the microstructure features of wood template were well reproduced in the final product. Biomorphic ZnO was fabricated via the sol–gel method by the infiltration of the precursor sol into the wood template and the sintering of wood template at high temperature under air atmosphere. Many characterization methods such as x-ray diffraction (XRD), scanning electron microscopy (SEM) and pore size analyzer detection were used to investigate the crystalline phase and microstructure of the product as well as the pore size of biomorphic ZnO. In our work, highly porous ZnO derived from different wood templates had been prepared. The relevant results revealed that the specie of wood template and sintering temperature played vital roles in the pore size, specific surface area and pore volume of the product.



## 1. Introduction

It is well known that biomass is all biologically-produced matter based in carbon, hydrogen and oxygen. Biomass materials are structured in a hierarchical way over many length scales [1] such as wood, bamboo, crop residues, hemp and more. As one of the most important biomass materials resource, wood is a sort of natural organic composite materials with fine hierarchical porous structure and is structured on several levels of hierarchy, ranging from millimeter (growth ring patterns) via micrometer (tracheid cell patterns, macro- and micro-fibril cell wall textures) through to nanometer scale (molecular cellulose fibers and membrane structures of cell walls) [2]. At the same time, the resource of wood is abundant and different species of wood exhibits a large variety of available pore structures. Softwood is mainly made up of parenchyma cells and tracheid cell which account for around 90% of the volume of softwood. The vessels shape of hardwood is diversity including circular, elliptical polygonal and others.

In recent years, biomass material has been employed as a natural template for the manufacture of porous ceramics which has attracted increasing interest. In general, two different approaches have been applied to convert the biological preforms into non-oxide (transformation) as well as oxide (substitution) ceramics. In the transformation process, biological preforms were pyrolysed to yield porous carbon templates which subsequently reacted with metal containing infiltrants, thus forming carbide phases by melting, or vapor infiltration. In the substitution process, native or pyrolysed biological preforms were internally coated with salts or metal organic precursors and subjected to oxidation to remove the carbon afterwards [3–6]. Many researchers reported the fabrication of porous ceramics via the conversion of biomorphic material [7–13]. For example, Wood tissue was converted into SiC [14] ceramics using liquid Si infiltration. Sun et al. [15,16] produced TiC ceramic by infiltrating tetrabutyl titanate sol into wood template. Biomorphic oxide ceramics like $Fe_2O_3$ [17,18], $Al_2O_3$ [19,20], and $TiO_2$ [21,22] also have been prepared. The ceramic materials with biological morphology structure have potential applications in photo-catalytic [23,24], adsorption [25] and medical fields [26,27].

ZnO is an important functional material and possesses excellent performances including gas sensors [28], solar cell [29], and photo-catalytic performance [30], which has received widespread attention. The porous ZnO ceramics have been successfully fabricated [31–33]. The characteristic of ZnO with hierarchical porous structure can be significantly improved. For example, the wood-template ZnO [33] displayed high sensitivity and selectivity to $H_2S$ than that of non-template ZnO.

In this paper, the wood template was infiltrated with the sol through high heat sintering to fabricate biomorphic ZnO. The aim was to replicate wood morphology in a metal oxide material that would retain the structure of the cellulose framework. The challenge of this work was to maintain the morphological structure of the wood template after removing the carbon anatomy from the template during sintering. The research focused on the infiltration

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and annealing behavior during the fabrication of porous ZnO. Besides, the relationship between calcination temperatures and pore size of the product was reported.

## 2. Experimental

### 2.1. Materials

The CAS number, purity (%) and provenance of the chemicals used were given in Table 1. All chemicals were used as received without further purification. The wood templates (Larch and Lauan) were supplied by timber trading market, digital photo images of wood pieces used from low mag (general view) with scale bar was shown in Fig. 1a.

### 2.2. Fabrication method

In this work, two kinds of woods (Larch and Lauan) were cut in dimension of 20 mm × 10 mm × 10 mm. The wood was cooked with extractive liquid (the volume ratio of benzene to absolute ethanol was 2:1) for 6 h. The purpose of this step was to get rid of the wood extractive compounds including fatty acids, fats and wax. Then woods were washed by deionized water and dried at 60 °C for 24 h.

For preparation of the precursor sol, zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was dissolved in the mixture of absolute ethanol and monoethanolamine (MEA, $C_2H_7NO$) at room temperature. The concentration of the sol was adjusted to 0.6 M and the molar ratio of MEA to zinc acetate was kept at 1.0. The solution was continuously stirred at 70 °C for 2 h until the sol became clear and homogeneous (Fig. 1b). The hydrolysis, condensation reactions and the formation of precursor sols were presumed as follows [34–36]:

After pretreatment the wood templates were vacuum-infiltrated with the sol at RT in a vacuum apparatus (the vacuum degree was −0.06 MPa) and dried in air at 130 °C for 2 h. This procedure was repeated for several times to increase the precursor sol content in the wood samples (first infiltration process). The samples were pyrolysed in $N_2$-atmosphere. Then, further infiltration steps were performed into the porous carbon templates. The steps were the same as the first infiltration process. Finally, the samples were sintered at 600 °C, 800 °C, 1000 °C for 3 h under air atmosphere and air-cooled to RT. Fig. 2 showed the process of the synthesis of porous ZnO with wood templates.

### 2.3. Characterization

The thermal decomposition and weight changes of samples during sintering in air were detected by Thermo gravimetric analyses (TGA/DTA, TGAQ50, TA Instruments). The microstructure of biomorphic ZnO was investigated by a scanning electron microscopy (SEM, TM3030, Hitachi). The phase formation during the

**Table 1**
The CAS number, purity (%) and provenance of the chemicals used.

| Chemical | CAS no. | Purity (%) | Provenance |
|---|---|---|---|
| Zinc acetate dehydrate | 5970-45-6 | 99.0 | Tianjin Zhiyuan Chemical Reagent Co., Ltd. |
| Monoethanolamine | 141-43-5 | 99.0 | |
| Benzene | 71-43-2 | 99.5 | Tianjin Tianli Chemical Reagent Co., Ltd. |
| Absolute ethanol | 64-17-5 | 99.7 | |

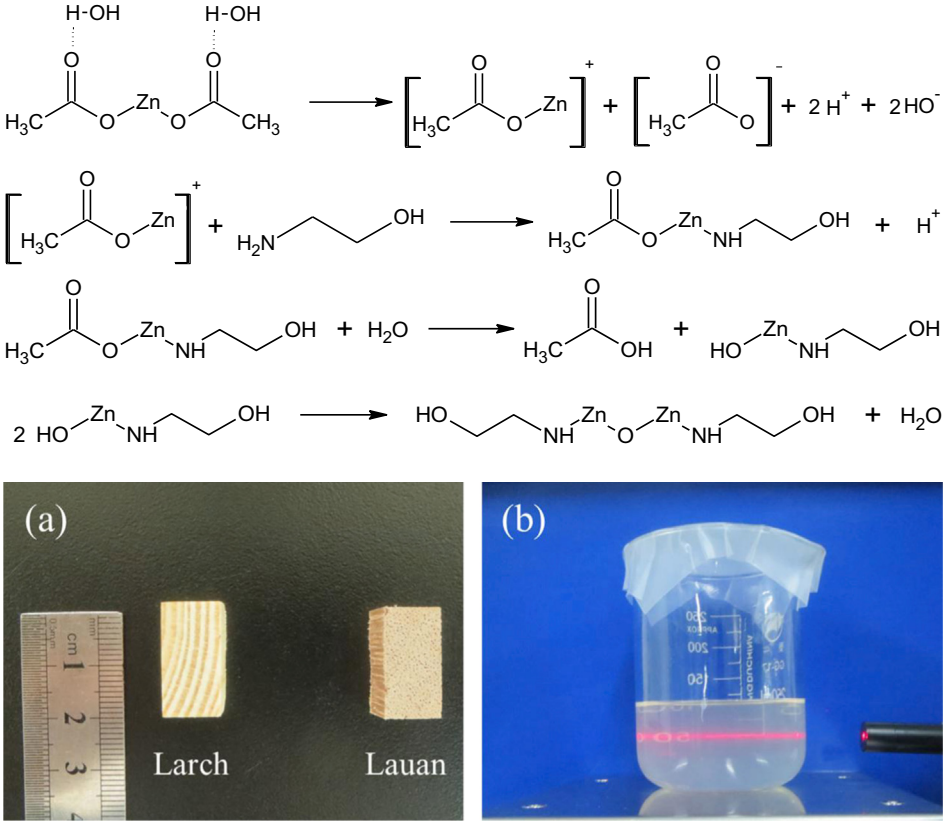


**Fig. 1.** Digital photo images of (a) wood pieces used from low mag (general view) with scale bar, (b) sol after homogenization.