



Process of in situ forming well-aligned Zinc Oxide nanorod arrays on wood substrate using a two-step bottom-up method

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ABSTRACT

A good nanocrystal covering layer on wood can serve as a protective coating and present some new surface properties. In this study, well-aligned ZnO nanorods (NRs) arrays were successfully grown on wood surface through a two-step bottom-up growth process. The process involved pre-sow seeds and subsequently their growing into NRs under hydrothermal environment. The interface incorporation between wood and ZnO colloid particles in the precursor solution during the seeding process was analyzed and demonstrated through a schematic. The growth process of forming well-aligned ZnO NRs was analyzed by field-emission scanning electron microscopy and X-ray diffraction, which showed that the NRs elongated with increased reaction time. The effects of ZnO crystal form and capping agent on the growth process were studied through different viewpoints.

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1. Introduction

As is widely reported, ZnO nanostructures are attracting remarkable attention because of their excellent properties, such as a large direct band gap of 3.37 eV, large exciton binding energy (60 meV) at room temperature, as well as excellent chemical and thermal stability [1]. ZnO nanorods (NRs) are one-dimensional ZnO nanostructures that demonstrate potential in certain applications, e.g., transistors [2,3], UV light-emitting diodes [4], piezoelectric field [5], solar cells [6,7], and gas sensors [8]. Many methods including top-down and bottom-up ones have been used to fabricate ZnO NRs. However, the top-down method has the disadvantages of remarkable crystallography defects, imperfection of the surface structure compared with the bottom-up method involving atmospheric metalorganic chemical vapor deposition [9–11], catalyst-free pulsed laser deposition [12,13], aqueous solution growth [14–16], etc. Among them, the hydrothermal method appears the most promising way for the growth of ZnO NRs because of its large-scale, low-temperature, low-pressure, and environmentally benign advantages [17,18]. Through this method, well-aligned ZnO NRs arrays are grown on different substrates to achieve properties such as UV photodetection, photoresponse behaviors, superhydrophobicity, and biological sensing [19–23]. The main substrates such as Si, ITO, FTO, and glass usually have a smooth

surface [24–28], but there are some with a rough surface such as organic flexible substrate, paper, cellulose fiber, and wood [29–33].

Wood is abundant in hydroxyls and has the beneficial properties of reproducibility, degradability, environmental friendliness, and high strength-to-weight ratio. These features make wood superior to some architectural materials [34]. However, a number of factors limit the applications of wood, including crazing caused by hygroexpansion, degradability under lighting, and proneness to damage by worms. Thus, in recent years, with the combination of wood materials, colloid chemistry [35], and hydrothermal technique [36], composites of ZnO NRs with wood have been successfully prepared through soft aqueous hydrothermal method, endowing wood with increased functionality [37,38]. Generally, a two-step growing system under a hydrothermal environment is widely used in the formation of ZnO NRs. The first step is the thermal decomposition of the colloid precursor solution to form seeds and subsequently growing them on substrates. Many studies have demonstrated that the seed layer plays an important role in the growth of ZnO NRs [39,40]. The Dyndall effect is used to ensure the successful fabrication of the ZnO seed precursor. Although some studies have reported on the mechanism of growth of ZnO NRs, most of them use silica, ITO, and glass as substrates [41,42]. There were some studies of growing ZnO nanorods on woods, but the in situ forming ZnO colloids on wood substrate, their bottom-up growth process and the influence mechanism are still not very clear.

In the previous work, our group successfully fabricated superhydrophobic wood by growing ZnO NRs arrays in situ on wood surface to improve its self-cleaning properties. Moreover, the wettability of solvents with different polarities as well as other

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liquids such as oil and coke were tested [33]. In this study, well-aligned ZnO NRs have been successfully grown on wood surface through a two-step hydrothermal method. Except for achieving superhydrophobic wood, we focus on learning the forming process of ZnO nanorods and finally reach a goal of controllable growth on wood surface. Higher aspect ratio and dense of ZnO nanorods on wood surface will create a rougher and thicker protective layer, which is important in protecting wood from water and UV light, and endowing some superior properties for low-grade wood. Field-emission scanning electron microscopy (FESEM) was used to characterize their morphology, and X-ray diffraction (XRD) was used to examine the crystal structure. The process of growing well-aligned ZnO NRs was investigated from the viewpoints of the nature of the ZnO crystal interface and the effect of the nonionic surfactant hexamethylenetetramine (HMTA).

2. Experimental

2.1. Materials

Poplar wood (*Populus tomentosa*) was cut into 20 mm (tang.) \times 20 mm (rad.) \times 5 mm (long.) pieces and used as test specimens. All pieces were washed twice with acetone and once with water, and then dried in an oven at 60 °C for 6 h. All chemicals used were analytically pure, including zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], NaOH, ethyl alcohol, zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], and hexamethylenetetramine [$(\text{CH}_2)_6\text{N}_4$]. Distilled water was also prepared.

2.2. Preparation of precursor solution and solution-immersion process

$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.3 M) was dissolved in 500 mL of ethyl alcohol. Then, an alcoholic solution with 0.1 M NaOH was added dropwise to the above solution under continuous stirring at 60 °C for 2 h. A transparent colloid solution was obtained and labeled as solution A. The prepared pieces were immersed in solution A for 6 h, and then placed in an oven at 60 °C for 3 h. This process was repeated several times, and a seeded wood surface was finally obtained. Blank wood was also prepared for comparison.

2.3. Hydrothermal growing of ZnO NRs

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{CH}_2)_6\text{N}_4$ were dissolved in distilled water with a molar ratio of 1:1 and used for the hydrothermal growth of ZnO NRs. The mixture solution was placed in an ultrasonic cleaner for 30 min to form a clear solution and labeled as solution B. The seeded samples together with solution B were placed into a Teflon-lined stainless steel autoclave with 80% capacity. The reaction temperature was 105 °C and the reaction time was variable. The reaction time was varied from 1, 3, 6 and 10 h, respectively. After the hydrothermal treatment, the autoclave was naturally cooled to room temperature. The wood samples were dried in an oven at 60 °C for 6 h. A control sample and an unseeded one were also subjected to hydrothermal treatment to discuss the formation process.

2.4. Characterization

The crystal structure of the seeds and ZnO NRs on wood surface was characterized using an X-ray diffractometer (D/MAX 2200, Rigaku, Tokyo, Japan) under the following conditions: Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) from 5° to 70° at a scan rate of 3° min⁻¹, accelerating voltage of 40 kV, and current of 30 mA. The morphology of the ZnO seeds and NRs on the wood surface was characterized by FESEM. A Sirion 200 microscope (FEI Inc., Eindhoven, the Nether-

lands) operated at 20 kV was used. The elemental compositions of the wood substrates and obtained samples were examined by an energy-dispersive X-ray spectroscopy (EDS) system (Genesis, EDAX Inc., Mahwah, USA).

3. Results and discussion

3.1. Morphology and crystal phase analysis

Fig. 1A shows the elemental composition of the coating materials obtained by EDS analysis. The main constituents detected on the coated wood surface were Zn and O. This finding illustrated that the inorganic layer on the wood surface could be ZnO, which was thick that it covered nearly the entire surface, leaving the elemental C in wood at a low intensity peak. Compared with the control group, except for the patterns at $2\theta = 15^\circ$ and 22° (the typical cellulose peaks in wood), the seeded wood only had weak intense peaks of ZnO crystal (Fig. 1B). This result can be attributed to seeds that did not grow and had poor crystallinity at low temperatures. However, after the growth process, a crystallographic phase was clearly detected, which demonstrated a typical crystalline wurtzite structure. The obvious hexagon shape of ZnO nanorods is presented. Three pronounced diffraction peaks, namely, (100), (002), and (101), appeared at $2\theta = 31.89^\circ$, 34.65° , and 36.45° , which well agreed with the ZnO power standard (JCPDS 036-1451). The strong peak (002) of ZnO showed preferential growth orientation along the c-axis perpendicular to the wood substrate. Thus, ZnO NRs were successfully grown on wood. Although the ZnO NRs had a well-aligned orientation, (101) and (100) patterns were detected due to the rough surface and grooves of wood.

Compared with the FESEM images of the blank wood (Fig. 1C), a well-distributed and uniform ZnO seed layer was found to grow on the wood surface after the growth of seeds in a precursor solution (Fig. 1D). The seeds were particle-like and nanosized. At high magnification, the average diameter about 102 nm of the seeds was measured. At a low magnification, the wood surface wore a thick “coat,” leaving the pits, cell walls, and other wood structures nearly invisible (Fig. 1E). The “coat” was composed of large numbers of single NRs with high density and uniform distribution. At a high magnification, the ZnO NRs were completely well aligned with an orientation perpendicular to the wood surface (Fig. 1F). The average length of rods was about 900 nm. The growth started at the edge of the seed layers at the bottom of the NRs, which illustrated that the seed layers played an important role in the growth of well-aligned ZnO NRs, similar to the growth of crops with seeds. The anisotropy of the ZnO NRs observed in the low-magnification FESEM image can be explained by the rough surface and grooves of wood.

3.2. Growth process ZnO NRs on wood surface

The growth of ZnO NRs on wood substrate comprised two steps. First was nucleation of the ZnO seeds on wood substrates. Second was the in situ growth of ZnO NRs based on the seeded surface.

3.2.1. Fabrication of ZnO seeds

The formation of ZnO nanoseeds was as follows. ZnO seeds were obtained through the formation of ZnO colloid precursor. First, $[\text{Zn}(\text{OH})_4]^{2-}$ was obtained through the mixture of $\text{Zn}(\text{CH}_3\text{COO})_2^{2-}$ and NaOH in an alcoholic solution with continuous stirring under 60 °C for 2 h, and then dehydrated to ZnO colloid particles as seeds, as shown in Formulas (1) and (2). The Dyndall effect occurred after the formation of the colloid solution (Fig. 2A). The low-polarity ethanol environment promoted the formation of ZnO nanoseeds.

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