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Preparation of nano-ZnO/regenerated cellulose composite particles via co-gelation and low-temperature hydrothermal synthesis

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ABSTRACT

The nano-ZnO/regenerated cellulose composite particles were prepared via a novel co-gelation and low temperature hydrothermal synthesis by using $ZnCl_2$ aqueous solution as both solvent of cellulose and zinc source of ZnO nanoflakes. The reaction system was systematically studied and the optimal reaction conditions for growing the nano-ZnO/regenerated cellulose particles were determined to be liquid: solid ratio of 30:1, solution pH=7, and hydrothermal temperature of 120 °C. The composite particles consisted of regenerated cellulose in the center and hexagonal structured ZnO nanoflakes with thickness of 100 nm, on the surface. The nano-ZnO/regenerated cellulose composite particles were decomposed at 300 °C, and the total weight loss was 67%. This novel synthesis strategy can be very useful for preparing eco-friendly nano-ZnO/regenerated cellulose composite structure in photocatalytic industry.

1. Introduction

ZnO is a typical wide band gap semiconducting material with excellent performance [1]. Due to the quantum size effect, ZnO nano-materials exhibit special properties and have been widely used in various fields such as photocatalysis, gas sensors, and solar cell [2,3]. ZnO nano-materials are mainly prepared by vapor deposition method, template method, sol-gel method, and hydrothermal method. The morphology of obtained products include nano-particles, nano-rods, nano-wire arrays, and nano-film. However, ZnO nano-materials possess small particle size and high surface energy, so that they are easy to aggregate, difficult to separate and recycle, and less stable than TiO_2. These shortcomings greatly limit the application of ZnO nano-materials in photocatalytic industry. Therefore, assembling ZnO nano-materials by a specific carrier to form a composite material is one of the effective ways to achieve their excellent photocatalytic performance in industrial applications [4,5].

Cellulose is a linear polymer of β(1→4) linked d-glucose units and contain many reactive hydroxyl groups. It has attracted much attention from materials scientists because it is environmentally friendly, renewable, biodegradable, and the most abundant organic polymer on Earth [6]. Currently, nano-ZnO/cellulose composite materials have been prepared in two types of methods: the first method is to disperse ZnO nano-materials in aqueous solution of cellulose (or its derivative) and then precipitate to get ZnO/regenerated cellulose composite materials [7–11]. In this way, it is very difficult to dissolve cellulose, and the ZnO nano-materials are usually dispersed inside cellulose, which is unfavorable for the light absorption and thus exhibits poor photocatalytic activity. The second method is to immerse cellulose in a Zn^{2+}containing solution, and then heat-treat to obtain a ZnO-loaded cellulose composite [12–17]. In this way, although cellulose has many hydroxyl groups which can promote the formation of nano-ZnO [17], its high degree of crystallinity prevents Zn^{2+} from penetrating into the crystalline regions and thus hydroxyl groups cannot be fully utilized and it is very difficult to assemble ZnO on the surface of the cellulose. In present work, we developed a novel method of preparing nano-ZnO/regenerated cellulose composite particles by using $ZnCl_2$ aqueous solution as both the solvent of cellulose [18] and the zinc source of ZnO nanoflakes. $ZnCl_2$ aqueous solution effectively dissolved cellulose so that Zn^{2+}could readily access to reactive hydroxyl groups and then nano-ZnO/regenerated cellulose were successfully prepared via co-gelation and low-temperature hydrothermal method. The optimal reaction conditions including the liquid/solid ratio, solution pH value, and hydrothermal temperature, were studied systematically.

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2. Experimental

Wood pulp cellulose was provided by Nantong Cellulose Acetate Co., Ltd. Zinc chloride and sodium hydroxide (analytical grade) were provided by the Nanjing Chemical Co., Ltd. In a general procedure, 1 g of wood pulp cellulose and certain amount of 65% $ZnCl_2$ (wt%) aqueous solution were mixed in a three-head flask, stirring at room temperature for 1 h. The three-head flask was then placed in a magnetic stirrer, set at 80 °C, stirring till the mixture turned into a uniform clear liquid. The clear solution was moved into a 100 mL beaker, and its pH was adjusted to 7–10 by adding 20% NaOH solution, with stirring. After settled for 24 h, the solution was moved into a Teflon-lined stainless steel autoclave with a volume of 100 mL, and heated at 100–160 °C for 8 h under autogenous pressure, followed by filtration and washing. The hydrothermal reaction product was frozen at −80 °C for 10 h, and then freeze-dried at −40 °C for 12 h before sealed for storage.

The sample phase analysis was conducted on a SmartLab X-ray diffractometer (Rigaku, Japan) with Cu Ka radiation, 100 mA current, 40 kV voltage, scan rage of 5–60°, and step scan of 0.02°/sec. The sample morphology was observed with a field emission scanning electron microscope (JEOL JSM-7600F). The thermal stability was analyzed by Netzsch STA 449C (Germany, Netzsch) with heating rate of 20 °C/min, heating range of ~600 °C, and N_2 flow rate of 20 mL/min.

3. Results and discussion

The crystal phase of nano-ZnO/regenerated cellulose composite was characterized by X-ray diffraction. Fig. 1a shows the X-ray diffraction patterns of composite samples prepared with different liquid/solid ratio, namely the ratio of $ZnCl_2$ aqueous solution to cellulose. All four samples contain strong diffraction peaks at 31.8°, 34.4°, 36.3°, 47.6°, and 56.6° that are well indexed to the (100), (002), (101), (102), and (110) planes of hexagonal ZnO (JSPDS card No.01-089-0150), and impurity peaks belonging to $Zn_5(OH)_8Cl_2 \cdot H_2O$ (JSPDS card No.00-007-0155). When the liquid/solid ratio was adjusted to 50:1 and 60:1, the intensity of impurity peaks was comparable to that of ZnO diffraction peaks. When the liquid/solid ratio was lowered to 30:1 and 40:1, the impurity peak intensity significantly decreased. The X-ray analysis indicates that the increase of solid cellulose content suppressed the formation of impurity phase of $Zn_5(OH)_8Cl_2 \cdot H_2O$. $Zn_5(OH)_8Cl_2 \cdot H_2O$ is a common impurity phase that can be generated in the synthesis of ZnO crystals by using $ZnCl_2$ as starting material [19]. In order to obtain relatively pure phase ZnO crystals, the concentration of Zn^{2+}should be controlled less than 0.01 M [20] or a heat treatment is needed to convert $Zn_5(OH)_8Cl_2 \cdot H_2O$ to ZnO at higher temperatures. However in this work, we obtained ZnO/regenerated cellulose products by using relatively high concentrated (65%) $ZnCl_2$ aqueous solution at a low temperature, which are controversy to these general strategies. It has been reported that the combination between hydroxyl groups on mono- or polysaccharide molecules and Zn^{2+}accelerates the formation of ZnO nano-structures [17]. We thus speculate that the reactive hydroxyl groups on dissolved cellulose play a very important role in our synthesis procedure. Intact cellulose has high degree of crystallinity and strong hydrogen bonds are formed both among cellulose molecules and within the molecules, which cause the hydroxyl groups on cellulose molecules unaccessible and useless. In this work, wood pulp cellulose was first dissolved by $ZnCl_2$ aqueous solution and thus many reactive hydroxyl groups got exposed to reaction system. These hydroxyl groups further reacted with Zn^{2+} to form $Zn(OH)_4{}^{2-}$/cellulose complex through co-gelation process. The combination between hydroxyl groups and Zn^{2+}greatly

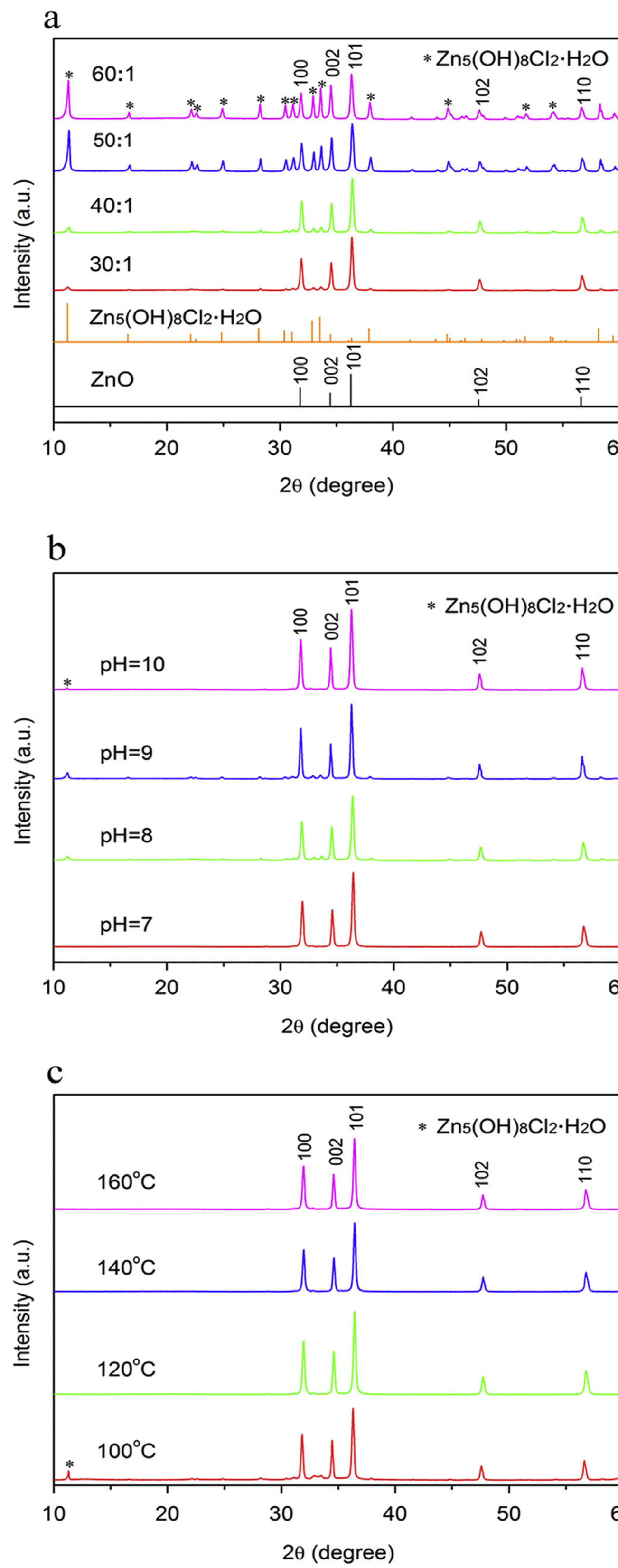

Fig. 1. Study of different preparation conditions of ZnO/regenerated cellulose composite particles: (a) different liquid/solid ratio, with system pH=8 and hydrothermal temperature was 160 °C; (b) different system pH, with liquid/solid ratio was 30:1 and hydrothermal temperature was 160 °C; (c) different hydrothermal temperature, with liquid/solid ratio was 30:1 and system pH=7.