

## Synthesis and properties of nano ZnO using polysaccharides as chelating agents: Effects of various parameters on surface modification of polysaccharides

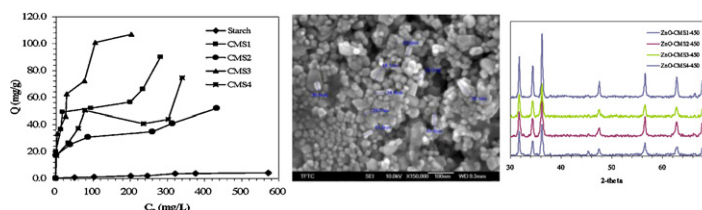
Munusamy Thirumavalavan, Kai-Lin Huang, Jiunn-Fwu Lee\*

Graduate Institute of Environmental Engineering, National Central University, Chung-Li, Taoyuan County, 320, Taiwan

### HIGHLIGHTS

- ▶ Polysaccharides (sodium alginate and corn starch) as chelating and structure directing agents.
- ▶ Elaborate studies on effect of different parameters on surface modification.
- ▶ Freundlich isotherms of  $Zn^{2+}$  and ZnO from Zn-polysaccharides organic polymers.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 14 September 2012

Received in revised form 18 October 2012

Accepted 1 November 2012

Available online 10 November 2012

#### Keywords:

Starch  
Sodium alginate  
Nano ZnO  
SEM  
BET

### ABSTRACT

Using polysaccharides (corn starch and sodium alginate) as both chelating and structure directing agents nano zinc oxides (ZnO) with moderate surface area and high pore volume were prepared. FT-IR and TGA analyses revealed that modified polysaccharides are more stable than that of unmodified one. Surface modification of starch was controlled by sodium chloracetate concentration and reaction temperature. Freundlich adsorption isotherms as preliminary studies confirmed that modified starch showed enhanced interaction with zinc ions. The interaction of zinc salt with polysaccharides produced zinc-polysaccharides polymers, which finally cleaved upon calcination to produce nano ZnO. Preparation of nano ZnO using native (unmodified) starch was unsuccessful. Experimental results indicated that 450 °C is the optimum calcination temperature to produce effective nano ZnO. Surface and optical properties of ZnO were carried out. SEM and TEM of ZnO indicated that uniform particle and shape distributions were obtained at low calcination temperature (450 °C).

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Zinc oxide ZnO is a promising optoelectronic and electronic functional material and has been recognized as one of the most interesting materials due to wide direct band gap energy and large exciton binding energy [1]. ZnO is also a green material that is bio-safe, biocompatible and biodegradable, and as a versatile material it has been widely used in various fields such as medical and environmental science [2,3], catalysts [4,5], microsensors [6], photoelectrochemical cells [7], piezoelectric transducers and actuators [8]. These properties are generally governed by structure, orientation and morphology of ZnO. Therefore, controlling of these

features is one of the most challenging tasks in ZnO preparation [9]. So far, a variety of methods [10] has been developed to synthesize nano ZnO including vapor phase growth, vapor-liquid-solid processes, soft chemical methods, electrophoretic deposition, sol-gel process and homogeneous precipitation. In these preparation techniques, by-products being formed via different reaction pathways can presumably control the formation and morphology of the resulting inorganic material in various ways. Since the electrical and optical properties of nanomaterials, depend on both the particle shape and the particle size, the preparation method must also ensure the control over the morphology and the growth [11]. However, the use of metal-organic supramolecular compounds [12] as precursors for the preparation of nano ZnO has not yet been thoroughly investigated [13–15] and also the use of a simple, cost-effective method, starting from commercially available, low-price chemicals, is important for the facile production of ZnO.

\* Corresponding author. Tel.: +886 3 4227151x34658; fax: +886 3 4226742.  
E-mail address: [jflee@ncuen.ncu.edu.tw](mailto:jflee@ncuen.ncu.edu.tw) (J.-F. Lee).

Inspiring by these, we have endeavored to attain controlled synthesis of nano ZnO using polysaccharides (corn starch and sodium alginate) as both chelating and structural directing agents. Even though, ZnO nanoparticles have already been synthesized using unmodified sodium alginate as chelating agent [16], the detailed characterization of zinc–polysaccharides organic polymer, product and effect of preparation conditions are yet to be explored. This study attempts to take advantage of interaction of both unmodified and modified polysaccharides such as sodium alginate (acidic) and starch (neutral) with zinc metal salts to form zinc–organic polymers. Finally nano ZnO was obtained by the cleavage of zinc–organic polymer chelates. These polysaccharides are comprised of hydroxyl and carboxyl functional groups which can form complex with Zn metal salts by chemical adsorption and finally calcination resulted into the cleavage of Zn–polysaccharides chelate to form nano ZnO. Starch and alginate, a natural low-cost polymer, has been a subject of academic as well as of industrial interest because of their renewability and biodegradability. However, new approaches must be made to utilize them introducing the functional groups of chelating activity for enhanced interaction with Zn ions. The effects of reaction temperature, concentration of reactants, and calcination temperatures on surface modification were also discussed. The adsorption efficiency of these polysaccharides towards zinc metal was also explained using Freundlich adsorption isotherms.

In this paper, we report on the preparation and characterization of ZnO nanostructures obtained with various morphologies and crystalline sizes using polysaccharides. The study mainly focused on the effects of various parameters on surface modification process. The formation of ZnO nanostructures with different morphologies has been discussed in detail. The cheap, high stability, low toxicity and environmentally friendly features of these polysaccharides along with simple and convenient technology have enabled to obtain nano ZnO in this present investigation. The objective of this investigation was to elucidate the formation of coordinate linkages and the surface microstructure when  $Zn^{2+}$  ion complexes with polysaccharides under specific conditions.

## 2. Experimental

### 2.1. Chemicals

Deionized distilled water was used to prepare all solutions. Standard metal ion solutions were commercially obtained. Corn starch was obtained commercially from Aldrich. Sodium alginate (viscosity about 250 cP) was obtained commercially from Sigma. All the chemicals and reagents used in this study were of analar grade (AR grade) obtained from Sigma–Aldrich and used without any further purification.

### 2.2. Chemical modification of corn starch

Corn starch was modified in order to increase the carboxyl contents according to the modified method [17]. The effect of concentration of sodium chloroacetate and reaction temperature was studied in order to explore the impact of these parameters on carboxyl modification process. Carboxymethylation of corn starch was carried out in aqueous–organic liquid media. Organic solvent used in this experiment was ethanol. Ten gram of corn starch was dispersed in 100 ml of ethanol (99.9%) and stirred at 28 °C for 30 min. A solution of 30 ml 10 M sodium hydroxide was added gradually over 20 min under stirring and continued to stir for additional 30 min. Then different concentration [(1.0 and 1.5)M] of sodium chloroacetate dissolved in 30 ml deionized water was added to the mixture and the reaction mixture was stirred for 30 min at 40 °C. The

resultant solution was filtered, washed with ethanol for three times, and then dried in an oven at 50 °C for one day to get modified corn starch. The similar reaction was carried out at 60 °C also by varying the reaction temperature. Native (unmodified) corn starch was referred to S. Chemically modified starch prepared at 60 °C using 1.0 and 1.5 M sodium chloroacetate were referred to CMS1, CMS2 respectively. Chemically modified starch prepared at 40 °C using 1.0 and 1.5 M sodium chloroacetate were referred to CMS3, CMS4, respectively.

### 2.3. Modification of sodium alginate

Modification of sodium alginate was obtained by varying the composition of both sodium alginate beads and zinc nitrate solution. Sodium alginate powder was added into 500 ml of distilled water heated at 60 °C and configured as 1%, 3% and 5% solutions. To this, zinc nitrate hexahydrate (5, 15, 25 g) [ $Zn(NO_3)_2 \cdot 6H_2O$ ] dissolved in 500 ml distilled water was added under vigorous stirring to form immobilized beads (zinc–sodium alginate beads, w/v%). ZnAl1 was obtained mixing 1% sodium alginate solution and 1% zinc nitrate solution. ZnAl3 was obtained mixing 3% sodium alginate solution and 3% zinc nitrate solution. ZnAl5 was obtained mixing 5% sodium alginate solution and 5% zinc nitrate solution. ZnAl36 was obtained mixing 3% sodium alginate solution and 6% zinc nitrate solution.

### 2.4. Adsorption studies

In order to understand the affinity of native and modified starch for zinc metal ions, adsorption experiment was carried out as a primary study and fitted with Freundlich isotherm model.

The adsorption of  $Zn^{2+}$  was investigated in batch equilibrium experiments using zinc nitrate solution. The experiments were performed in 25 ml centrifuge bottle by stirring 25 ml zinc ion solution and 0.1 g of the adsorbents (native and surface modified starch) at 130 rpm in a Lab-line orbit environ shaker for 24 h. The temperature was maintained at 28 °C. The adsorption of metal ions from the aqueous solutions was studied. After the desired reaction period, the aqueous phases were separated from the materials by centrifugation at 4500 rpm for 5 min and the concentration of metal ions was measured using a Varian AA-400 atomic absorption spectrophotometer (AAS).

### 2.5. Synthesis of ZnO using native and surface modified starch

Three gram (3 g) zinc nitrate hexahydrate [ $Zn(NO_3)_2 \cdot 6H_2O$ ] was dissolved in 100 ml water in a standard flask. To this zinc nitrate aqueous solution three gram (3 g) of native and surface modified starch was added respectively and the reaction mixture was stirred constantly at 28 °C for 6 h. Then the reaction mixture was filtered and the solid collected was dried in an oven at 40 °C to obtain zinc–starch organic polymers. Finally, this zinc–starch organic polymer was calcined at three different temperatures namely (450, 650 and 850) °C to obtain ZnO nanostructures such as ZnO–CMS1 (from CMS1), ZnO–CMS2 (from CMS2), ZnO–CMS3 (from CMS3), ZnO–CMS4 (from CMS4).

### 2.6. Synthesis of ZnO using zinc–sodium alginate beads

Various ZnAl (ZnAl1, ZnAl3, ZnAl5 and ZnAl36) was stirred constantly at 28 °C for 6 h. Finally, this zinc–sodium alginate organic polymer was calcined at three different temperatures namely (450, 650 and 860) °C to obtain ZnO nanostructures such as ZnO–ZnAl1 (from ZnAl1), ZnO–ZnAl3 (from ZnAl3), ZnO–ZnAl5 (from ZnAl5),

Download English Version:

<https://daneshyari.com/en/article/593814>

Download Persian Version:

<https://daneshyari.com/article/593814>

[Daneshyari.com](https://daneshyari.com)