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CTAB assisted hydrothermal synthesis of ZnO/Co(OH)₂ nano-composites: Mechanisms of synthesis and growth of composite

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In this paper, nano-composites of $ZnO/Co(OH)_2$ were synthesized via Hydrothermal processing. $Co(NO_3)_2.6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$ (0.5 M, 200 ml) and KOH (2 M, 200 ml) were used as precursors. N_Cetyl_N,N,N,_tri methyl ammonium bromide (CTAB) was used as surfactant and its effects on the morphologie was investigated. The crystal growth mechanism was studied via Growth Unit Model and thermodynamics of cobalt oxide formation from its hydroxide under hydrothermal condition. Nano-rods and nano-hexagonals were prepared via hydrothermal synthesis with and without using CTAB, respectively. Also, the effects of hydrothermal periods on morphologies and particle growth were investigated in this paper. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the products obtained.

Key words: Nanostructures, Growth models, Hydrothermal crystal growth, ZnO/Co(OH)2 nanocomposites, Nanocomposites.

Introduction

Mixed oxide systems can be classified in three categories: first category includes those that form distinct chemical compounds, such as $ZnSn_2O_4$, into second category fall those mixed oxides that form solid solutions, such as TiO_2 -SnO₂. Finally, there are systems that form neither compounds nor solid solutions such as TiO_2/WO_3 [1]. Due to their ability for improving and modifying the properties of their components, synthesis of Mixed oxides for various applications have been extended recently [2-3].

Nano structured materials have for example been produced by reverse micells [1], Sol-gel [2-3], chemical bath deposition (CBD) [4], hydrothermal processing [5-6], sonochemical processing [7], etc.

Zinc oxide is a polar crystal whose polar axis is the caxis; its space group is $P6_3mc$ and a well known wide band gap semiconductors II-VI compound. ZnO has a wide variety of applications such as chemical sensors, varistors, UV emitters, catalysts, transparent high power electronics, surface acoustic wave devices, piezo-electric transducers, etc [8].

Recently, lamellar materials have been widely researched; layered hydroxide materials have attracted much interest in the production of catalyst, sorbent, ionic exchangers, ionic conductors, and electrochemical materials [9]. β -Cobalt hydroxide, has recently received increasing attention due to its application in the electric, magnetic and catalytic materials [10]. The

atomic arrangement of $Co(OH)_2$ represents a member of the brucite type structure family (space group: P3 ml, point symmetry $\overline{32}/m$). The cobalt hydroxide has hexagonal layered structure in which a divalent metal cation is located in an octahedral site generated by six hydroxyl oxygen atoms [11].

Three different theories were reported for studying the growth behaviour of materials. The BFDH law starting from planar mesh density, and considering the effects of screw axis and glide plane on crystal growth habit, provides a predicted theoretical growth habit of the crystal [12]. The PBC theory provides an ideal growth habit of crystals in terms of bond chain types between molecules and attachment energy [13]. But the above mentioned models have some shortages in explaining or predicting the crystal growth habit. The Growth Unit Model is based on the individual units which they contribute in the growth procedure. This theory hypothesizes that in the crystallization stage of oxides, cations exist in the form of complexes with OH- ligands which their coordination numbers are equal to those of the crystal formed. These complexes are called growth units. W. Zhong was the first to put forward the Growth Unit Model [14] and nowadays many investigations were carried out by considering this theory for describing the growth behavior of the different materials [15].

The effects of surfactants on the morphologies produced in hydrothermal synthesis of different compounds were studied extremely [16-17-18]. The surfactants can be divided into two major categories including ionic and non-ionic surfactants. These surfactants affect the morphologies of the synthesized nanoparticles. In fact for the reaction system in the presence of surfactants, the surface tension of solution is reduced due to the

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Fig. 1. The structure of (a) CTAB and (b).

existence of surfactant, which reduces the energy needed for the formation of a new solid phase [19]. CTAB is a well known cationic surfactant which can be ionized completely in water. The structure of this surfactant is shown in Fig. 1(a) [20].

In this paper, ZnO/ Co(OH)₂ nano-composites were synthesized by hydrothermal method at 160 °C for different synthesis periods. CTAB was used as ionic surfactant. X-Ray diffraction (XRD) was used for characterization of obtained nano-composites. Scanning electron microscopy (SEM) was also used to study their morphologies.

Experimental

Raw Materials

The starting materials including cobalt nitrate-6hydrate, $Co(NO_3)_2 \cdot 6H_2O$, potassium hydroxide, KOH and zinc nitrate-4-hydrate, $Zn(NO_3)_2 \cdot 4H_2O$ were purchased from Merck and used without further purification. N-Cetyl-N,N,N,_tri methyl ammonium bromide (CTAB) was used as a surfactant and purchased from Merck and were used as received.

Devices

Scanning electron microscopy studies were performed by using a Philips XL30. The images were analyzed with image processing program programmed with MATLAB 7.0.1 at Material Simulation Center of Materials and Energy Research Center laboratory. Powder X-ray diffraction studies were carried out by a Siemens (D-500) diffractometer with Cu-K α radiation source ($\lambda = 0.154051$ nm).

Synthesis

Three separate aqueous solutions of $Zn(NO_3)_2 \cdot 4H_2O$ (0.5 M, 200 ml), KOH (2 M, 200 ml) and Co (NO₃)₂ · 6H₂O (0.5 M, 200 ml) were prepared. Zn (NO₃)₂ · 4H₂O and Co(NO₃)₂ · 6H₂O solutions were added dropwise to KOH aqueous solution simultaneously ([Zn²⁺]/[OH⁻] = 1/2[Co²⁺]/[OH⁻] = 1/2) under high stirring conditions. This procedure lasts for 15 minutes. After mixing, the obtained solution was divided into 4 portions and poured to separate beakers. Then the surfactants were added to beakers while the solutions were being stirred with high intensity. After 5 minutes, the solutions were poured into a 35 mL Teflon-lined autoclave with a filling capacity of about 80%, then sealed and maintained at

Table 1. Synthesis conditions of samples.

Sample –	Surfactant		Tomporatura (°C)	Time (hrs)
	Туре	Amount (g)		Time (ms)
Ι			160	5
Π	CTAB	0.1	160	5
III			160	24
IV	CTAB	0.1	160	24

160 °C for different periods. The conditions of synthesis are shown in Table 1.

The prepared samples were filtered and washed with distilled water and absolute methanol several times. Then samples were dried at 60 $^{\circ}$ C for 24 hrs.

Results and Discussion

XRD patterns of samples I, II and III are shown in Fig. 2. From these patterns, $Co(OH)_2$ and ZnO were detected. From XRD patterns and SEM images (Fig. 3), the effect of surfactant on XRD patterns and the obtained morphologies can be understood. In sample I, the absence of surfactant causes producing sharper XRD peaks, but the surfactant in other samples affects the growth conditions and thereby particle sizes and morphologies, so the sharpness of the peaks in sample II is different to sample I.

From SEM images and XRD patterns, the intensity of the peaks can be contributed to the type of morphologies obtained. For example, by comparing sample I to sample II, the morphologies were converted from semi spherical to needle like morphologies, due to presence of CTAB as a surfactant, and the intensities of XRD peaks were differed too. The obtained size distributions of samples I and II and also their ranges



Fig. 2. (a) XRD patterns of samples I and II.



(a)Sample I (b)Sample II Fig. 3. SEM images of samples synthesized for 5 hrs at 160.



Fig. 4. The Size distributions of Samples I and II.



Fig. 5. XRD patterns of samples III and IV.



(a)Sample III



(b)Sample IV

Fig. 6. SEM images of samples synthesized for 24 hrs at 160.



difference are illustrated in Fig. 4.

For other samples synthesized for 24 hrs, the XRD patterns are shown in Fig. 5. Same as samples I and II the XRD patterns with and without CTAB are different. Also, the intensity of peaks is different like the previous samples and this can be related to size distribution and type of morphology. SEM images of samples III and IV are shown in Fig. 6.

Fig. 7 shows the size distributions of samples obtained in 24 hrs. By comparing Fig. 4 to Fig. 7, the effect of periods of hydrothermal synthesis on the morphology and growth rates can be detected. As it can be seen, in presence of CTAB, the growth rate of samples II and IV is reduced in comparison with samples I and III.

The average crystallite size of the particles was determined utilizing Debye-Sherrer formula:

$$\mathbf{D} = \mathbf{K}\lambda/\mathbf{B}\,\cos\,\theta\tag{1}$$

where d is the mean crystallite size of the powder, λ is the wavelength of Cu-K α ($\lambda = 0.154051$ nm), B is the





Fig. 7. The Size distributions of Samples III and IV.

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In range particles numbers

Sample	ZnO plane	Mean Crystallite Size (nm)	Co(OH) ₂ plane	Mean Crystallite Size (nm)
Ι	(101)	24	(101)	29
Π	(101)	23	(101)	21
III	(101)	33	(101)	32
IV	(101)	27	(101)	23

Table 2. The mean crystallite sizes of the samples.

full width at half maximum (FWHM) intensity of the peak in radian, θ is Bragg's diffraction angle and k is a constant usually equal to ~0.89 [21]. The results of median sizes and crystallite size of samples are listed in Table 2.

Synthesis of ZnO without surfactants

The main efforts have been carried out on hydrothermal synthesis of ZnO nanoparticles by Wen-Jun Li *et al.* [22]. They synthesized ZnO from $Zn(AC)_2$ and Na(OH) precursors at 200-300 °C by hydrothermal method and conclude from the IR and Raman analyses that the growth units of ZnO are Zn complexes with OH⁻ ligands in the form of $Zn(OH)_4^{2-}$. The main reactions in forming ZnO can be divided into four stages, including:

Stage I) Ionization of zinc salts and sodium hydroxide in water:

$$Zn(M)_2 \xrightarrow{\text{ionization}} Zn^{2+} + 2(OH)^{-}$$
 (1)

$$Na(OH) \xrightarrow{\text{ionization}} Na^+ + (OH)^-$$
(2)

Where M represents negatively charged groups of Zinc salts.

Stage II) Precipitation of Zinc hydroxide:

$$\operatorname{Zn}^{2+} + 2(\operatorname{OH})^{-} \xrightarrow{\text{solved in water}} \operatorname{Zn}(\operatorname{OH})_2 \downarrow$$
 (3)

Stage III) Formation of in hydrothermal conditions:

$$\operatorname{Zn}(\operatorname{OH})_2 + 3(\operatorname{OH})^{2-} \xrightarrow{\text{hydrothermal}} \operatorname{Zn}(\operatorname{OH})^{2-}_4$$
(4)

Stage IV) dehydration of complexes:

$$\begin{array}{l} x(Zn(OH)_{4}^{2-}) \xrightarrow{dehydration durring hydrohermal} \\ (Zn_{x}O_{y}(OH)_{z}^{(x+2y-2x)-}) + (x-1)H_{2}O \end{array}$$

$$(5)$$

Where, the x, y and z represent the numbers of Zn^{2+} , O^{2-} and OH^{-} respectively.

Therefore, the oxide particles can be produced by stacking of these complex polyhedrons by sharing their elements. In the interior parts, the oxygen ions are the connection centers where the exterior and the surface of the particles are (OH⁻) ligands, which have been proved by IR [23-24] and Raman [25-26] spectra in



Fig. 8. Idealized interface structure image of ZnO crystal in [0001] direction and the Growth Unit Mechanism of crystallization of ZnO.



Fig. 9. Phase diagram for Co(OH)2/CoO system.

other investigations. So in the complex of $(Zn_xO_y(OH)_z^{(x+2y-2x)-})$, OH^- ligands exist in the interface of the crystal while the interior parts consist of ZnO units as shown in Fig. 8. So stacking of these crystallites in hydrothermal condition can produce nanostructures [22]. Existence of Cobalt ions during this process can affect the morphologies and can be doped in the ZnO structures too [27].

Synthesis of Co(OH)₂ in hydrothermal processing

The formation mechanism of Co(OH)₂ is different to that of ZnO. When Cobalt salt is dissolved in water, it is ionized to Co^{2+} and M^- (where M represents negatively charged groups of Cobalt salts) and the first and second stages are same as ZnO, as is shown in equations (6) to (8).

Stage I) Ionization of Cobalt salts and Sodium hydroxide in water:

$$\operatorname{Co}(M)_2 \xleftarrow{\operatorname{ionization}} \operatorname{Co}^{2+} + 2 \operatorname{M}^-$$
 (6)

$$N\alpha(OH) \xrightarrow{\text{ionization}} Na^+ + (OH)^-$$
 (7)

Stage II) Production of Cobaltous hydroxide:

$$\operatorname{Co}^{2^+} + 2(\operatorname{OH})^{-} \xrightarrow{\operatorname{solved in water}} \operatorname{Co}(\operatorname{OH})_2 \checkmark$$
 (8)

B. Basavalingu et al. investigated the transformation of

Co(OH)₂ to Cobalt oxides by hydrothermal synthesis. They calculated the minimum pressure and temperature for formation of CoO from Co(OH)₂. Fig. 9 illustrates the calculated values which are in good agreement with experimental data [28].

The saturated pressure of water in 160°C can be calculated from Antoine equation [29]:

$$log P = A - \frac{B}{C+T} \tag{9}$$

Where A, B and C are 8.07131, 1730.63 and 233.426, respectively.

At 160 °C, the pressure calculated from equation (9) is about 2.98144 bars, while for formation of CoO in this temperature higher pressure is necessary. The pressure for this transformation is higher than 500 bars. So by considering growth unit model and thermodynamics of formation of cobalt oxide from Co(OH)₂, the growth units of cobalt oxide do not form at 160 °C and 3 bar pressure. So the nanoparticles of Co(OH)₂ grow by gathering the crystallites of Co(OH)₂.

Growth in the presence of CTAB

The effects of CTAB on the final morphology in the hydrothermal synthesis have been investigated extremely [30-16]. After ionization in water, CTAB produces a cationic structure with a positively charged tetrahedron and a long hydrophobic tail. This tetrahedron is positively charged and can act as a cationic surfactant and affect the final structure of synthesized particles due to its electrostatic forces and stereochemical effects. The complimentary between CTA^+ and $Zn(OH)_4^{2-}$ (Fig. 1) endows the surfactant the capability to act as an ionic carrier [23]. As it is shown in Fig. 8, due to presence of OH⁻ ligands on (Zn_x $O_v(OH)_z^{(x+2y-2x)-})$ surface in the hydrothermal processing, a negatively charged film forms on its surface when CTA⁺ which has a good complimentary with $Zn(OH)_4^{2-}$ attract on its surface and a networks of CTA⁺ forms on $(Zn_xO_v(OH)_z^{(x+2y-2x)-})$ surface. When the surfactant molecules leave, zincate will be carried away in the form of ion-pairs, so that the barrier layer becomes thinner (as shown in Fig. 10), and forms a rod-like morphology [16]. These phenomena can become more effective after CMC point of CTAB [20].

In the crystallization process, surfactant molecules may serve as a growth controller, as well as an agglomeration inhibitor, by forming a covering film on the newly formed ZnO crystals. This can be resulted not only from absorption of CTA^+ on the surface of zinc complexes but also the stereochemical effect of its hydrophobic tail.

Due to thermodynamics limits for formation of growth units of cobalt oxide, as cited before, CTAB absorption on cobalt ions is restricted. The main effect of CTAB on the morphologies of $Co(OH)_2$ can be deduce from the stereochemical effects of surfactants



Fig. 10. Schematic illustration of the erosion process in the presence of CTAB. Black color, Zn(OH)2, gray color, . The wave -like patterns indicates the CTA+ ions. A CTA+ ion carrying a zincate ion is shown.

which gathered on adjacent Zinc complex surfaces and also the repulsion of CTA^+ and Co^+ which restrict the in-situ ion concentrations of Co^+ and Zn^+ .

Thus as shown in Fig. 3 and 6 the morphology of nano-composite consists of ZnO nano-rods and $Co(OH)_2$ nano-hexagonals.

Conclusions

In this paper, we synthesized $ZnO/Co(OH)_2$ nanocomposites via hydrothermal processing. The effects of CTAB in synthesis were investigated. When the time for synthesis is 5 hrs, the effect of surfactant on changing morphology is negligible and the microstructure is less uniform. With increasing time to 24 hrs we can detect more different morphology and more uniform nanostructure. By comparing mean crystallite sizes and SEM images of samples obtained at different periods of times, the growth rates of nano-composites in absence of surfactant are higher and the uniformity of grown particles is lower than that in presence of surfactant. Also the thermodynamic aspects of growth were considered besides using Growth Unit Model for explaining the growth conditions of obtained composites.

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