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Controlled hydrothermal growth of ZnO nanostructures by sequestering the Zn metal ions with the chelating agent EDTA

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ABSTRACT

In the present work, a controlled growth of ZnO nanostructures by manipulating Zn metal ion concentration by the chelating action of ethylene diaminetetra acetic acid in hydrothermal method is studied. EDTA produces metal–chelate complex by the formation of bidentate ligand with Zn^{2+} in the solution and diminishes the reactivity of Zn metal cations. Concentration of EDTA in the mother solution was varied in different ranges like 3, 5 and 10 mM while retaining the zinc metal salt and the NaOH concentration the same. Three different morphologies of wurtzite structured ZnO nanostructures such as nanorods-bunch, separate/discrete uniformly sized hexagonal nanorods and tapered flower petals like shapes are achieved by 3, 5 and 10 mM strengths of EDTA, respectively. The medium concentration 5 mM of EDTA is found to have moderate control over producing ZnO nanostructures of uniform diameter and a high aspect (length to diameter) ratio. An array of vertically aligned free standing ZnO nanorods with uniform spacing is successfully achieved by the addition of 5 mM of EDTA in the mother solution and the same is studied for its fluorescence property at an excitation of 325 nm and it has exhibited a characteristic UV emission of ZnO around 383 nm.

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1. Introduction

Nanostructured zinc oxide is one of the versatile semiconductors and many investigations are in progress to achieve size controllability, shape uniformity and repeatability in the process [1]. Moreover, engineering the size and shape do have direct impact in the fabrication of nanodevices [2]. The feasibility of achieving control over various aspects in the hydrothermal growth of nanostructures poses a challenge and is of immense interest [3]. Many attempts are being made to adjust the chemical ambience of the precursors to obtain shape engineered ZnO nanostructures [4–7]. In the present work, we have investigated the feasibility of using EDTA as a reagent and exploit its chelating property for the preparation of ZnO nanostructures.

2. Experimental details

Various molarities of EDTA are added to a mixture of 0.2 M zinc acetate dihydrate, 2 M NaOH solution to study the role of chelating agent EDTA, and hydrothermal reaction is carried out to obtain ZnO nanostructures. Various molarities of EDTA such as 3, 5 and 10 mM are carefully selected from various trial runs carried out previously. As prepared aqueous solutions are transferred into Schott Duran autoclavable glass bottles and were hydrothermally treated for 4 h at a temperature of 115 ± 5 °C. As soon as the hydrothermal reaction is completed, the containers are naturally cooled to ambient. Next, the particles were centrifuged, separated, washed in water and ethanol for several times, dried and finally kept ready for further analysis.

3. Results and discussion

X-ray diffraction patterns and SEM pictures of the as prepared powders from the solutions at three different chelant concentrations such as 0.003, 0.005 and 0.01 M is shown in Figs. 1 and 2, respectively.

3.1. Structural analysis

X-ray diffraction patterns shown in Fig. 1 for all the three cases of EDTA concentrations reveal that, the medium concentration of EDTA (5 mM) exhibits an improved crystallinity along the preferred

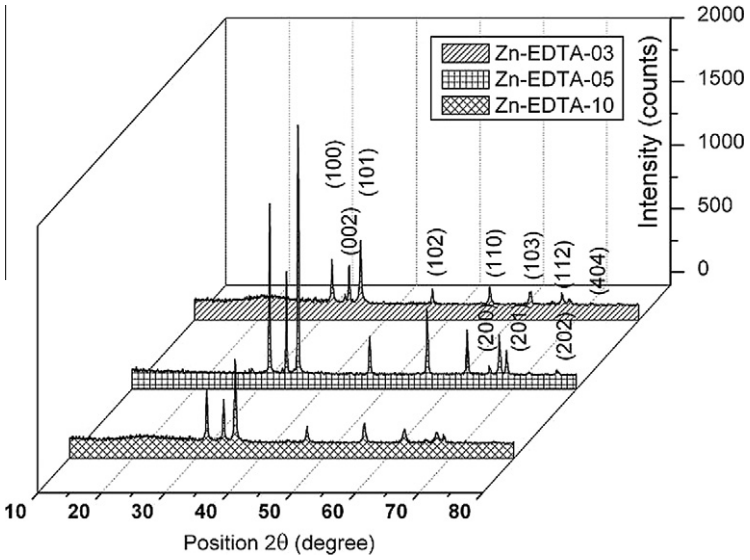

Fig. 1. P-XRD patterns of ZnO prepared from Zn–EDTA complex.

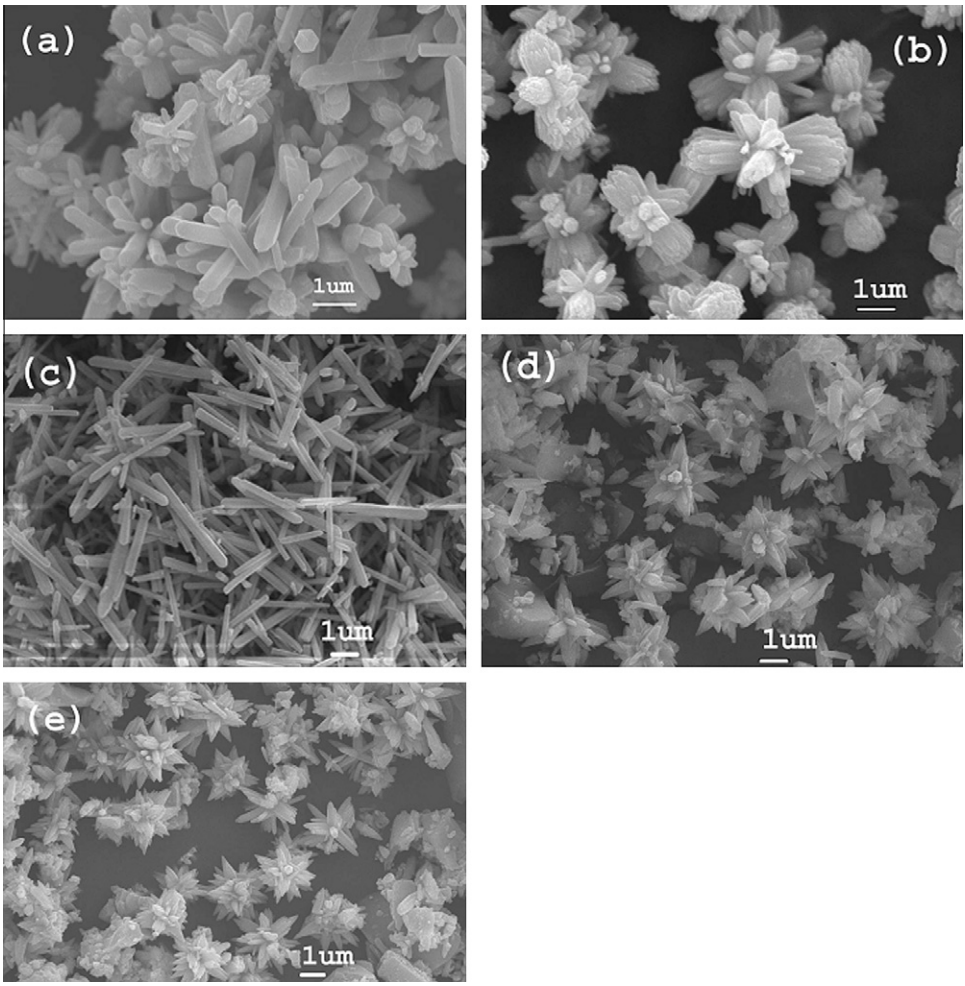

Fig. 2. SEM pictures showing morphologies of ZnO nanostructures prepared from (a and b) 3 mM, (c) 5 mM and (d and e) 10 mM EDTA solutions.

orientation of (1 0 1) which is a characteristic of hexagonal wurtzite structure (JCPDS – 36-1451). The pattern shown in the middle has a lowest full width half maximum (FWHM) of 0.1472, with a larger peak intensity of nearly 2000 counts. Comparatively, the other concentrations of EDTA are having a FWHM in the range of 0.2943 and peak heights of less than 600 counts. Hence, it is observed that the medium concentration of the chelant influences a moderate, controlled extended growth which has resulted in an improved well defined crystallinity.

3.2. Effect of EDTA on the morphology of ZnO nanostructures

The lowest chosen concentration of EDTA (3 mM) has yielded nanorods in bunch formation (Fig. 2a and b). The medium range concentration 5 mM of EDTA could produce discrete, uniformly sized solid hexagonal nanorods, with smooth edges (Fig. 2c). However, for the higher concentration of EDTA (0.01 M), a peculiar flower shaped structure with tapered leaf-like petals is formed (Fig. 2d and e). A schematic diagram depicting the reaction and growth phenomenon is given in Fig. 3.

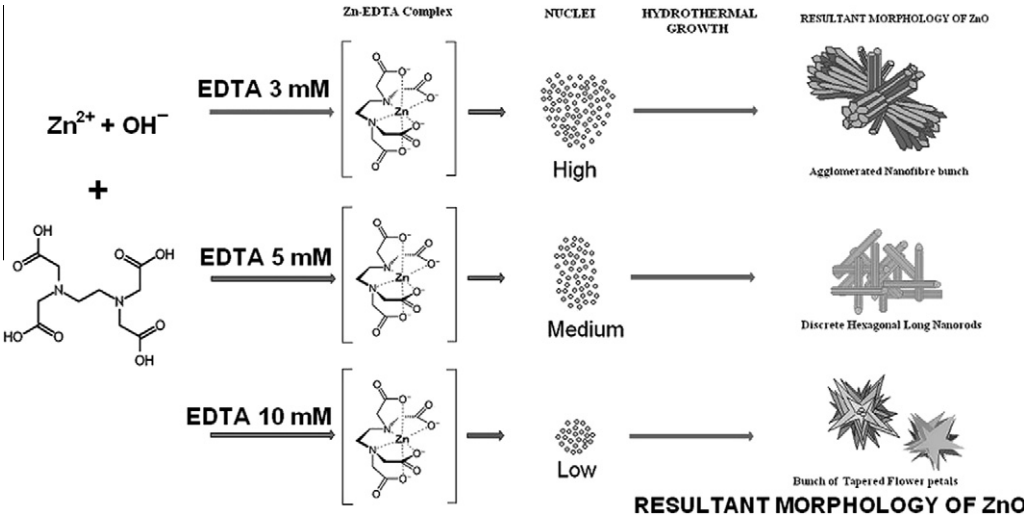

Fig. 3. Schematic representing the nucleation and growth of ZnO from different strengths of Zn–EDTA complex.

The possible sequestering reaction may be given as follows. The $EDTA^{4-}$ present in the solution usually binds to Zn^{2+} ions through its two amines (R–N–H_2) and four carboxylate anions $(R–COO)^-$.

$$[Zn(H_2O)_6]^{3+} + H_4EDTA \leftrightarrow [Zn(EDTA)]^- + 6H_2O + 4H^+ \quad (1)$$

In the above reaction, the four hydrogen atoms present in the EDTA are sacrificed to form a carboxylate ion which further acts as a bidentate ligand to form $[Zn(EDTA)]^-$ Zn–EDTA complex. Zinc cations compete with protons for binding to EDTA. Because, the metal ions are extensively enveloped by EDTA, their catalytic protons are mostly inhibited. The population of $[Zn(EDTA)]^-$ is comparable to that of the strength of the EDTA present in the solution. Therefore, the Zn^{2+} ions, spared without being bound by the ligand formation can only take part in the hydrothermal process to further form, $Zn(OH)_2$ intermediate complex which as a consequence form ZnO as in the following reaction:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (2)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (3)$$

The bunch-like petal formation for sample prepared with 10 mM EDTA, shows more number of different structures originating from the same nucleus. But, in the case of low EDTA concentration, the production of more number of dense nucleations $[Zn(OH)_2]$, than the number of growth units $[Zn(OH)_4]^{2-}$ are possible. As the reaction progresses, the dense nucleation, in due course tries to form nanofibres along *c*-axis ((0 0 0 1) direction). Then these fine nanofibres might have agglomerated to form a bunch of ZnO nanofibres. This is clearly seen in the SEM picture showing tiny pointed tips attached to each other to form a bunch. When the number of nucleations is controlled by the addition of EDTA in medium concentration (5 mM), nearly uniform sized nanorods are obtained. These nanorods reveal smooth edges instead of sharp, tapered or hollow features. Usually, in hydrothermal growth the emergence of sharp or hollow features may be an indication of faster growth rates. [8]. On the contrary, from the smoothly finished rods, it is inferred that, a moderate and controlled growth has occurred to form hexagonal nanorods. This is due to the selective sequestering of Zn^{2+} metal ions by the EDTA and formation of metal–chelant complex in the solution. Eventhough these metal–chelant complexes remain in the solution, they do not react in the solution, thereby reducing the number of active growth units and hence, the growth proceeds at the moderate growth velocity by the min-

imum supply of growth units $\{[Zn(OH)_4]^{2-}\}$ from the available low population. When the sequestering effect is further increased by increasing the concentration to 10 mM, the freely available number of metal ions is very less to feed the electrostatically attracting growth faces to form solid with uniform shape. With the diameter of a rod-shape is bigger at the base and it gets on reducing to the tip give rise to tapering effect. This tapering feature is again due to the difference in the growth velocities of different planes [9,10]. In this case, especially because of the limited availability of the Zn^{2+} ions which also constitute the growth units, the tapering feature is obtained. Thus, due to the sequestering action of the chelating agent the nucleation and growth of nanocrystalline ZnO are controlled.

The scanning electron micrographs illustrate that there are more number of size difference from a few nanometer to sub-micrometer, when the EDTA concentration is low. This supports us to ascertain that, the size variation is due to the difference in the large time span of first and the latest nucleation formed and their subsequent growth. The nucleations produced in the beginning of the reaction would have grown bigger, whence some other nucleations which are being produced will eventually take time to grow up. The time lag in between the formation of nucleations can eventually result in the size differences of the nanostructures grown from the corresponding nuclei. At a point of time when the reaction comes to the termination having exhausted in producing the intermediate growth complex, the nucleation produced earlier would have grown to an arbitrary size, and lately produced nuclei

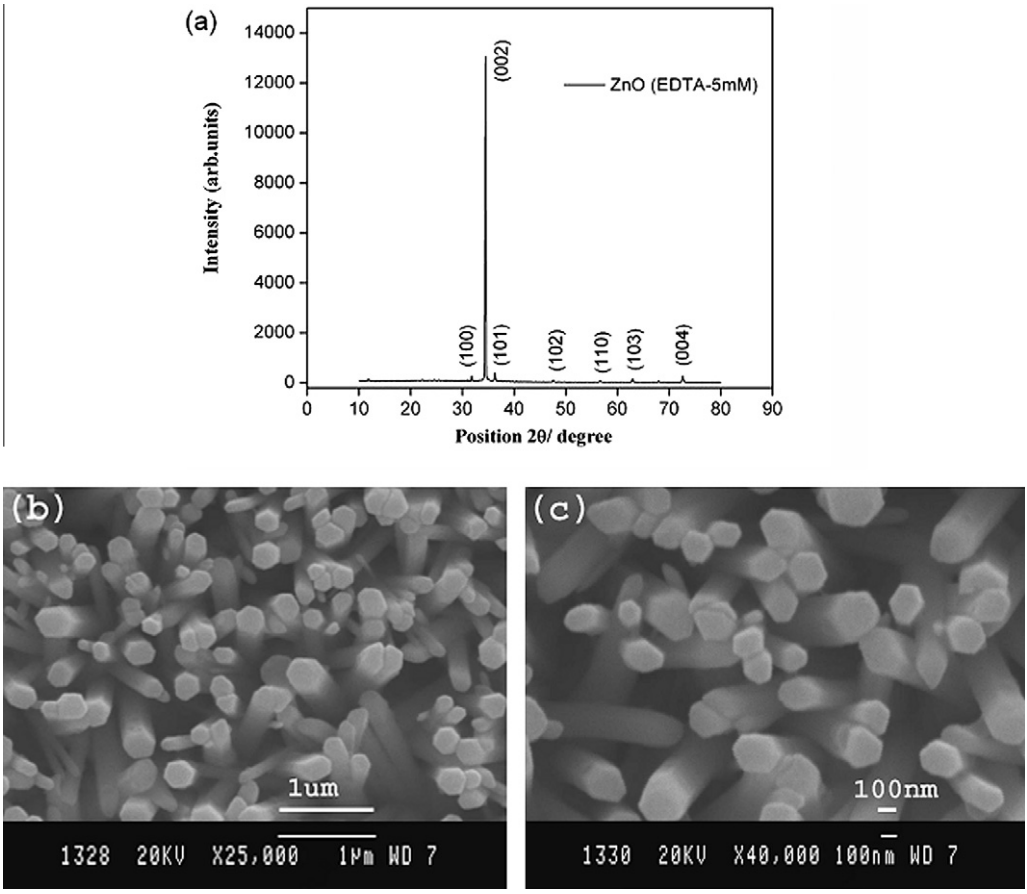

Fig. 4. (a) X-ray diffraction pattern showing preferred oriented unidirectional growth of ZnO nanostructure. (b and c) The SEM images showing the 1-D uniformly sized vertical ZnO nanostructures grown using EDTA-5 mM solution in two different magnifications.

would not have grown up to that size and they result in or remain in lesser in diameter and shorter in length and totally smaller in size. This could be the probable reason for the more number of size variations among the ZnO nanocrystals.

3.3. Preparation of vertically aligned ZnO nanostructure array

To prepare vertically aligned ZnO nanostructures with a high texture, a precoated ZnO seed layer formed by chemical bath deposition is introduced into the solution containing Zn–EDTA chelant complex and the same hydrothermal procedure as detailed earlier for ZnO particles was carried out. The EDTA concentration of 5 mM is chosen from the prepared nanopowders to yield nanorods of higher aspect ratio, uniform diameter throughout the length, and uniformly spaced texture. From the XRD pattern of the as prepared nanostructures a well defined highly crystalline unidirectional preferred orientation is obtained as shown in Fig. 4a. The SEM image of the nanorods array is shown in the Fig. 4b and c.

From the SEM image, it is evident that size variation is well controlled. In the growth process there is already a seed layer provided for the ready growth. Therefore, the growth nutrients are readily available as soon as the reaction starts and the Zn–EDTA complexes prevent further nucleations since, a portion of metal ions are sequestered by the chelant. Here, the population of Zn cations is moderate, which is not too excessive to induce many nucleations and not below the level of the demand to produce hollow or tapered growth. Due to this moderate supply of zinc metal ions, a controlled growth is achievable. So, they result in uniformly sized vertically aligned hexagonal nanorods.

The photoluminescence emission spectrum of the as prepared hexagonal nanorods array taken at an excitation of 325 nm is displayed in Fig. 5. The emission observed at 383 nm may be attributed to the recombination of free excitons [11,12]. A broad peak in the visible region may be due to surface defects present in the examples [13]. The broad and weak green emission 520–590 nm may be the result of recombination of photogenerated hole with an electron which belongs to a singly ionized oxygen vacancy [14]. It has been previously reputed that point defects in ZnO films could easily generate recombination centers [15]. Further it is seen that due to the addition of chelating agent, the optical property too was not altered.

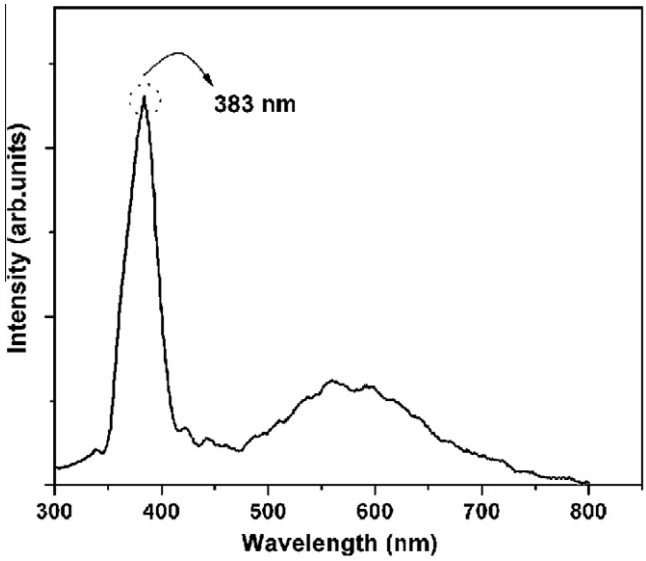

Fig. 5. The photoluminescence spectrum of the as grown vertically aligned ZnO nanorods array showing a characteristic emission around 383 nm.

4. Conclusions

In this work, a novel way of sequestering the metal cations in solution is introduced for the controlled growth of ZnO nanostructures by hydrothermal method for the first time. The sequestering action of the ligands formed by EDTA is evident from the unidirectional growth of uniformly sized ZnO nanorods array for the medium concentration level. The conceived idea of using EDTA for size control in the growth of ZnO nanostructures is confirmed and successfully demonstrated in this work.

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