

Template-free self-assembly of hierarchical ZnO structures from nanoscale building blocks

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ABSTRACT

We study chemical bath deposition method for synthesizing large variety constructions of ZnO nanostructures. By varying reaction kinetics we control the shape, size and morphology to yield flower-like, rolling-pin-like, viscous-fingers-like and antenna-like structures. In solution-based methods, factors responsible for crystal growth are largely affected by slight changes in the reaction processes/conditions and cause different hierarchical architectures when very low concentrations of precursor material used. The ability to grow different morphologies just by controlling solution growth parameters may open up new avenues to solution growth and provide systems to study natural growth behavior of materials as well as their novel applications.

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1. Introduction

Nanomaterials based on semiconducting oxides are emerging as an important class of compounds for a variety of applications. Among them, ZnO nanostructures enjoy a special status due to the possibility of synthesis via simple chemical routes in solution at low temperatures [1,2]. ZnO is an important wide band-gap semiconducting material with many useful properties [3] such as piezoelectricity, conductivity, optical absorption and emission, high voltage–current nonlinearity, sensitivity to gases and chemical agents, and catalytic activity. It has been extensively investigated [4–7] for a variety of applications such as electrode material for solar cells [8], phosphors [9], piezoelectric transducers and actuators [10], surface acoustic coatings [11], varistors [12], microsensors [13], photocatalysts [14], transparent field-effect transistors (FETs) [15], (bio) chemical sensors [16], piezoelectric generators [17] and so on. These promising applications provide an impetus for the investigation of simple growth routes for ZnO structures. In addition to elementary micro- and nanostructures, sophisticated hierarchical superstructures are more attractive due to their significance in self-assembly and other appealing applications [18]. Most importantly hierarchical structures provide new functionality through diverse morphologies [19], which are interesting for applications in catalysis. Furthermore, the surface area of such structures increases rapidly as

the complexity is increased. This makes them promising candidates for a variety of sensing applications [20,21].

Hierarchical superstructures are generally composed of a basic building block that repeats itself in a defined manner. In order to generate the hierarchy a growth-directing agent is usually used which controls the direction in which the growth is repeated. A major proportion of the hierarchical ZnO structures reported until now use capping agents, surfactant molecules or growth promoters/inhibitors [22,23] to tune the morphology. Another common strategy involves the use of templates [7] such as biological motifs [24,25] to grow the superstructure. In all these cases, the hierarchical organization is defined by the underlying template or the growth-directing agent and cannot be altered arbitrarily without affecting the reaction equilibrium. Hierarchical superstructures have also been demonstrated using other methods such as vapor phase growth [26] or electrodeposition [27]. However, such procedures require either high temperatures or a suitable substrate and hence show very little versatility or flexibility for tuning the underlying architecture.

Here we demonstrate the formation of hierarchical structures without the use of templates or growth-directing agents, which otherwise tend to increase the complexity of the system and in some cases affect the purity of the products. Furthermore, we use a simple low-temperature chemical bath based growth procedure that shows high potential for large-scale fabrication of hierarchical nanostructures in a very versatile manner [16]. Simple nanostructures such as nanoplatelets and nanowires serve as building blocks and the hierarchical morphology is dictated by a judicious variation of the reaction conditions. At very low reactant

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Table 1
Reaction conditions for obtaining the various hierarchical superstructures.

Precursors (ratio)	Concentration	Substrate (Si/SiO ₂)	Parameters	Hierarchical superstructures
Zn(NO ₃) ₂ ·6H ₂ O + (CH ₂) ₆ N ₄ (1:1)	0.5 mM each	Not seeded	85 °C for 36 h	Flower-like (3D)
Zn(NO ₃) ₂ ·6H ₂ O + CH ₃ ·NH ₂ (1:1)	0.5 mM each	Not seeded	85 °C for 36 h	Viscous-fingers-like (2D)
Zn(NO ₃) ₂ ·6H ₂ O + (CH ₂) ₆ N ₄ (1:1)	0.5 mM each	Not seeded	100 °C for 4 h + 85 °C for 36 h	Rolling-pin-like (1D)
Zn(NO ₃) ₂ ·6H ₂ O + (CH ₂) ₆ N ₄ (1:1)	0.25 mM each	Seeded	85 °C for 15 h + 85 °C for 15 h + 85 °C for 15 h	Yagi-Uda-antenna-like (1D)

concentrations, the pH of the growth medium, the temperature and other conditions have a decisive effect on the growth leading to 1D, 2D or 3D hierarchies with multiple levels. We demonstrate the self-assembly of flower-like (3D, multi-level), viscous-fingers-like (2D, 3-level) and rolling-pin-like (1D, 2-level) using nanoplatelets as basic building blocks. Furthermore, deploying nanowires as building blocks, we show the growth of Yagi-Uda-antenna-like (1D, 3-level) structures.

2. Experimental

2.1. Materials for growth

Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] was purchased from Fluka (>99% pure) and used as a precursor. Hexamethylene

tetramine [(CH₂)₆N₄] (HMT) was purchased from Aldrich (>99% pure). Methyl amine [CH₃NH₂] (MA, 40% w/w aqueous solution) was purchased from Alfa Aesar. Gold nanoparticles were synthesized in the colloid preparation method of Turkevich [28,29]. Silicon substrates were used for the growth of all hierarchical ZnO nanostructures in order to facilitate later characterization by Scanning electron microscopy (SEM). Substrates were cleaned with piranha solution to avoid any contamination on the surface. Subsequently the samples were rinsed with water and dried in oven for 2 h at 110 °C.

2.2. Reaction conditions for hierarchical self-assembly

An aqueous solution composed of zinc nitrate and either methyl amine (MA) or hexamethylenetetramine (HMT) was used for the

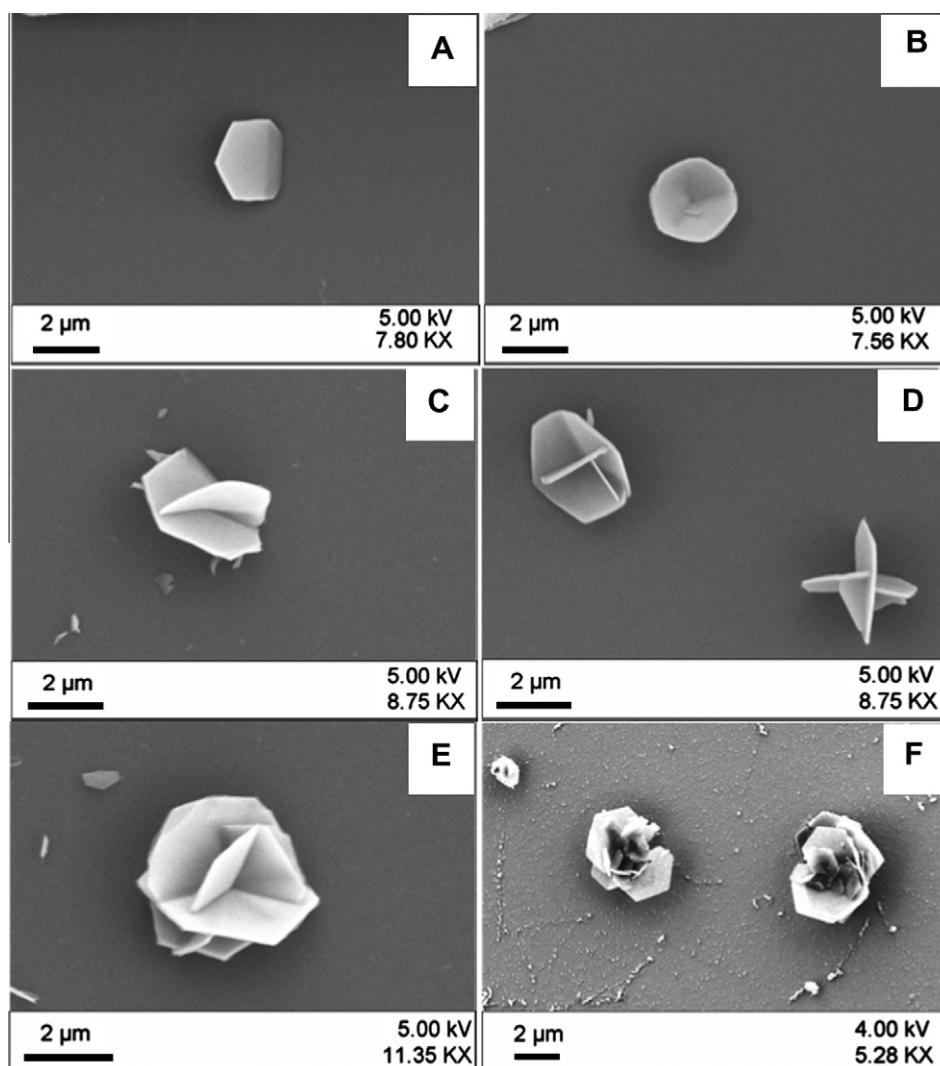


Figure 1. Temporal evolution of hierarchical flower-like ZnO superstructures formed in a growth solution of HMT and zinc nitrate at 85 °C. The SEM images show representative structures after (A and B) 6 h, (C and D) 15 h (E) 24 h and (F) 36 h of growth. The basic building block here is a nanoplatelet that self-organizes in three dimensions to form multiple levels of hierarchy: (A and B) 1-level (C and D) 2-level (E) 3-level and (F) multi-level.

synthesis of the various hierarchical structures. The precursor solution (200 ml) was filled into 400 ml glass beakers and Si substrates (seeded/unseeded) were dipped in the growth solution before/after putting the beakers in a hot air oven depending on the growth procedure (see Table 1). Samples were removed at different time intervals, cleaned in deionized water, dried and taken for SEM characterization. In order to grow Yagi-Uda-antenna-like structures, the samples were seeded with gold nanoparticles before putting the samples in the growth solution. The experiments were repeated a couple of times to assure the reproducibility of grown superstructures.

3. Results and discussion

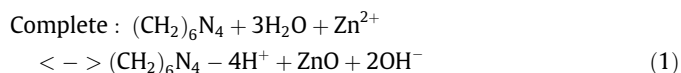
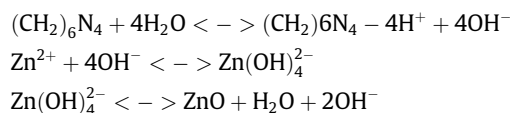
We start first with a description of hierarchical structures obtained with nanoplatelets as building blocks. Figure 1 shows SEM images of the products obtained with HMT in a chemical bath at 85 °C for 44 h. These conditions deliver flower-like ZnO structures as can be seen in Figure 1E and F. These flowers comprise of individual hexagonal ZnO platelets that are assembled in a hierarchical manner. This is apparent in the Figure 1A–E, which show a typical temporal evolution of the growth. The platelets are not always complete hexagons, 50–100 nm in thickness and typically 2–4 μm in diameter. The structures in Figure 1C and D exhibit a 2-level hierarchy, where a main hexagonal plate can be seen in the

centre of the structure on which secondary platelets are attached. In Figure 1E, tertiary growth can be seen originating from the secondary platelets, while the final structures in Figure 1F show higher level of hierarchical self-assembly. Since the platelets from the secondary level onwards are oriented in all possible directions, the repeat direction can be considered to be an arbitrary vector in 3D and hence we refer to these structures as 3D multi-level structures [27].

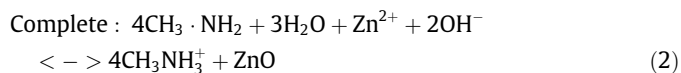
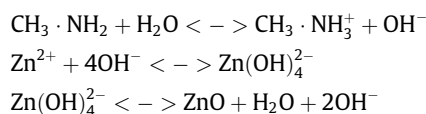
In a second series of experiments, we replaced hexamethylenetetramine with methylamine keeping all the other reaction conditions the same as before. Figure 2 shows SEM images of typical products observed at the end of the reaction. It is evident that dendritic structures are obtained with up to three levels of hierarchical self-organization. The repeat direction in this case is a 2D vector lying in the plane of the substrate. We refer to these viscous-fingers-like structures as 2D, 3-level hierarchical structures. The basic building block is again nanoplatelets similar to the previous case. However, as is apparent in the zoomed-in image in Figure 2B, the basic block is not an individual platelet but is composed of stacks of a large number of platelets.

In general, the growth of ZnO nanostructures starts with the formation of ZnO nuclei generated by the dissolution of zinc salt in the appropriate medium [30–32]. Under the reaction conditions used here (mainly the concentration of the precursor and the absence of growth promoters); the coagulation of ZnO nuclei in preferred orientations promotes the formation of nanoplatelets which acts as a building block to the grown nanostructures. After a certain growth period, the nanoplatelets may start assembling together in different configurations most likely to minimize the surface energy and give the final morphology of the product or may represent a primitive level of hierarchy which might serve as nucleation sites for further growth at subsequent levels of hierarchy (Scheme 1) [33].

In order to shed light on the mechanism behind the growth of the different types of hierarchical structures (2D or 3D), we take a closer look at the chemistry of the formation of ZnO nuclei in solution. The reactions involved here for the case of HMT are as follows:



The growth of ZnO nanoclusters with MA follows the following pathway:



Both the chemical processes involved in the growth of nanostructures are similar yet yield different morphologies of the product. This is attributed to different crystal growth behavior of ZnO nanostructures depending on the varied coagulation patterns of ZnO nuclei in preferred axes, affecting the shape, size and assembling pattern of the building blocks (hexagonal nanoplatelets in our case). The preferred axes of coagulation are due to the capping

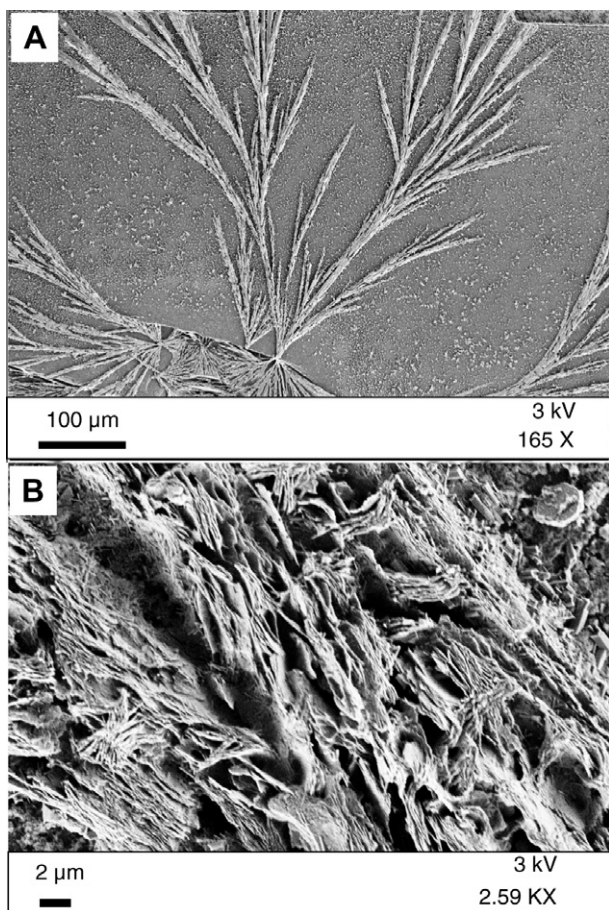
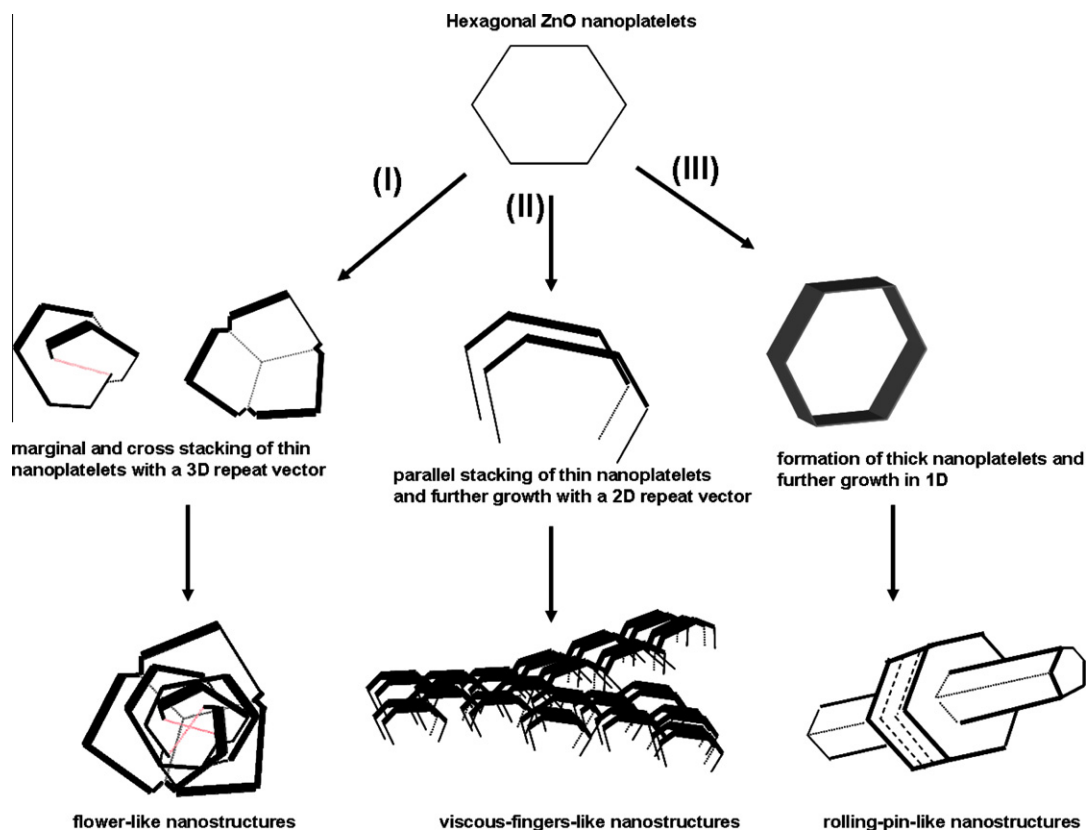


Figure 2. Dendritic viscous-fingers-like ZnO superstructures obtained at the end of growth in methyl amine and zinc nitrate at 85 °C. The SEM images show an overview (A) and a zoomed-in region (B) of the grown structures. The nanoplatelets tend to stack together and such stacks form the basic building block of the hierarchical structure. At least three levels of hierarchy can be identified in A.



Scheme 1. A possible route towards the formation of different ZnO hierarchical superstructures from *nanoplatelets* as building blocks. (I) Flower-like superstructures where the nanoplatelets self-assemble in arbitrary orientations. (II) The nanoplatelets stack together to form the basic unit that repeats itself in two dimensions resulting in dendritic viscous-fingers-like superstructures. (III) Thick nanoplatelets act as a building block to self-assemble into rolling-pin-like structures along one dimension.

of cation-complexes and anions onto the differently charged crystal planes of ZnO nuclei. The resultant morphology is largely dependent on the amount of capping which in turn is a function of the stability of the cation-complexes and the anion's in the solution and also the amount of ZnO nuclei (concentration and temperature dependent) in the solution [34–36]. HMT is a weaker base than MA and dissolves at a slower rate. Further closed-chain hexamethylenetetrammonium cation complex is more stable than methylammonium cationic complex which dissociates readily in water. This is consistent with the reactions shown in Eqs. (1) and (2). The reaction equilibrium is shifted to the right when MA used for the growth accelerating the formation of ZnO nuclei. Figure 3 shows the evolution of solution pH for both these reactions and reflects higher pH values in the start of reaction for MA than HMT as their difference in basicity and solubility in the solution. Furthermore, the solution pH reduces as the growth proceeds in the case of MA, while for the HMT-based growth the solution pH increases slowly as the growth proceeds consistent with the fact that HMT-cation complex is more stable and dissolves rather slow than the MA-cation-complexes. Imaginable that slow dissolution of more stable HMT-cation-complexes and anions make capping too effective to stack ZnO hexagonal nanoplatelets together unlike less stable MA-cation-complexes and anions where capping might not be as effective as the previous case to prevent ZnO nanoplatelets to stack together. This aspect coupled with the pH decrease induces the stacking of the sheets. On the other hand, the slow formation of ZnO in the HMT case leads to the possibility of secondary and tertiary growth on existing nanoplatelets. In addition to these kinetic effects, electrostatic effects induced by the surface charge of the platelets (or nanostructures),

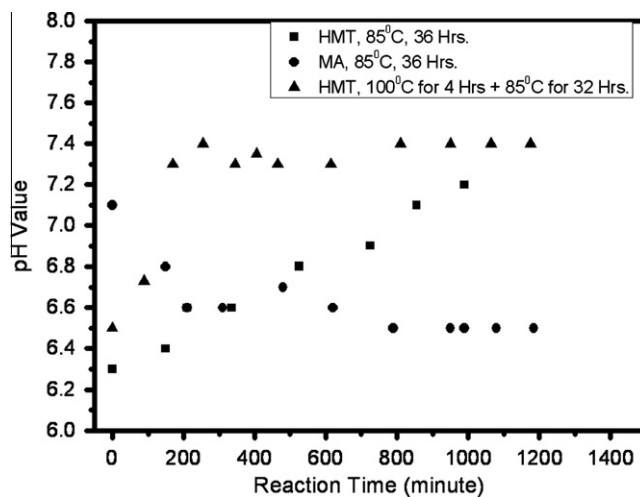


Figure 3. Evolution of solution pH during the growth of different hierarchical structures: (A) rolling-pin-like structures, (B) flower-like structures, and (C) viscous-fingers-like structures.

crystal's polarization [37] might also play a role in self-assembling process in solution-based growth processes.

In order to gather support that the reaction kinetics has a strong effect on hierarchical organization, we conducted a third series of experiments now using HMT but at an increased temperature during the initial growth phase. As expected, the pH increases much more rapidly in this case as shown in Figure 3.

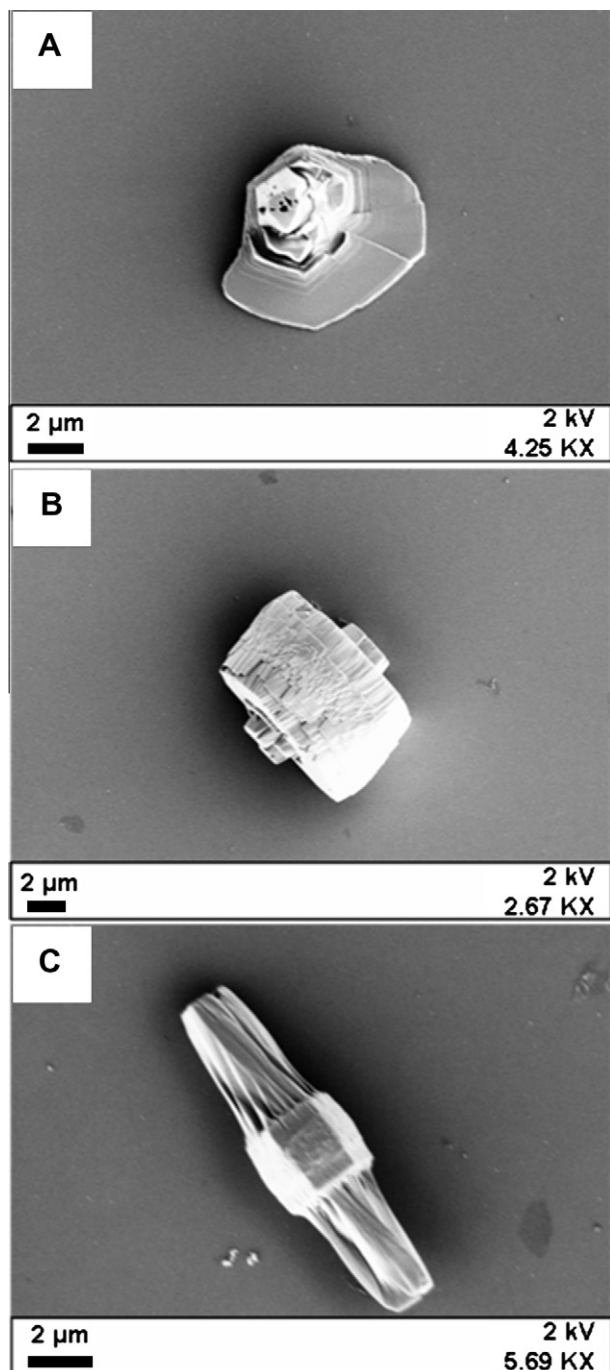


Figure 4. SEM images of rolling-pin-like structures at different growth stages: (A) after 7 h (B) after 15 h and (C) final structure after 36 h. The basic building block here is a thick platelet. In (A) the platelet in the first level is still growing. In (B) the first level is complete and the second level starts to grow. The diameter at the second level is lower due to the depleted amount of zinc ions in solution. In (C) the final structure with two levels of hierarchy can be clearly identified.

Typical examples of the resulting structures are shown in Figure 4. The only difference in the reaction conditions between this case and that of Figure 1 (flower-like structures) is the higher temperature for the initial 4 h. It is apparent from Figure 4 that just this increased reaction rate is sufficient to change the morphology of self-assembly. At an increased temperature, hexamethylenetetramine will have more rapid dissolution and hence pushing the reaction towards producing larger amount of ZnO

nanoclusters, cation-complexes and anions in the growth solution (reaction 1). It has been proven that relative higher OH^- concentrations can accelerate the dehydration rate of hydroxides ($\text{Zn}(\text{OH})_2$) and promotes the burst of the homogeneous nucleation. With the burst of ZnO nanoclusters the coagulation rate would be much higher in the solution and here it leads to the formation of thicker hexagonal nanoplatelets [38,39]. Taking the thick platelets as the basic building block here, the repeat direction is a vector in 1D (along the axis of the structure). Hence, we refer to these structures as 1D, 2-level hierarchical superstructures. The smaller diameter at the second level is probably due to a reduction in Zn species and/or a different capping behavior.

From the foregoing discussions, it is clear that by just varying the reaction conditions without the use of templates or growth-directing agents, we have demonstrated 3D, 2D and 1D hierarchical structures with varying levels of complexity. The underlying structure can be understood by assuming that nanoplatelets or stacks of nanoplatelets are the basic building blocks and that the repeat direction can be a vector in 3D, 2D or 1D. A schematic of the three kinds of structures and the underlying organization is summarized in a Scheme 1. These examples clearly demonstrate that the kinetics of the reaction and the choice of reducing agent can be varied to dictate the kind of hierarchical structures obtained in the investigated regime of low concentrations.

We explore the possibility of hierarchical self-assembly further by deploying an alternative building block namely nanowires. For this purpose, we have reduced the concentration of the precursor and HMT to 0.25 mM [16]. In addition, Au nanoparticles are used as seeds for the growth of nanowires in the first stage. A representative image of such a sample with nanowires after the first growth stage is shown in Figure 5A. In order to obtain hierarchical structures, we just replace the solution and start the growth afresh. Figure 5B shows a typical image of samples a few hours (3 h) into the second growth stage. It is apparent that new nanowires start to grow from positions along the nanowire grown in the first stage. At the end of the second stage, secondary nanowires of comparable lengths have grown from the first level nanowire as shown in Figure 5C. Upon repeating the same procedure by replacing the solution a second time, tertiary nanowires are found to grow from the secondary nanowires, as shown in Figure 5D. Since the repeat direction is in 1D (the growth of nanowires at any level happens predominantly perpendicular to the sub-level nanowire) and the structures show three levels of growth, we refer to these Yagi-Uda-antenna-like structures as 1D, 3-level hierarchical superstructures.

The choice of the reaction conditions (the lower concentration and the use of growth seeds) determines the kind of building block that one can have in solution. The repeat direction for the hierarchical self-assembly is then a consequence of the solution pH, concentration ratio of precursors, their dissolution rate, and reaction kinetics, etc. in low-temperature solution growth processes, as also suggested in some recent reports [40]. It is worth mentioning here, that the substrate on which the superstructures grow have an effect on the morphology. With nanowires as building blocks we mainly obtain mainly 1D superstructures. However, structures with a 2D-repeat vector and 2-, 4- and 6-fold symmetry have also been reported [27]. The absence of these kinds of structures here supports the argument that the substrate has a considerable effect on the formation of these superstructures. Future experiments may be devoted to changes in morphology observable by tuning surface charge of the substrate with varying solution pH.

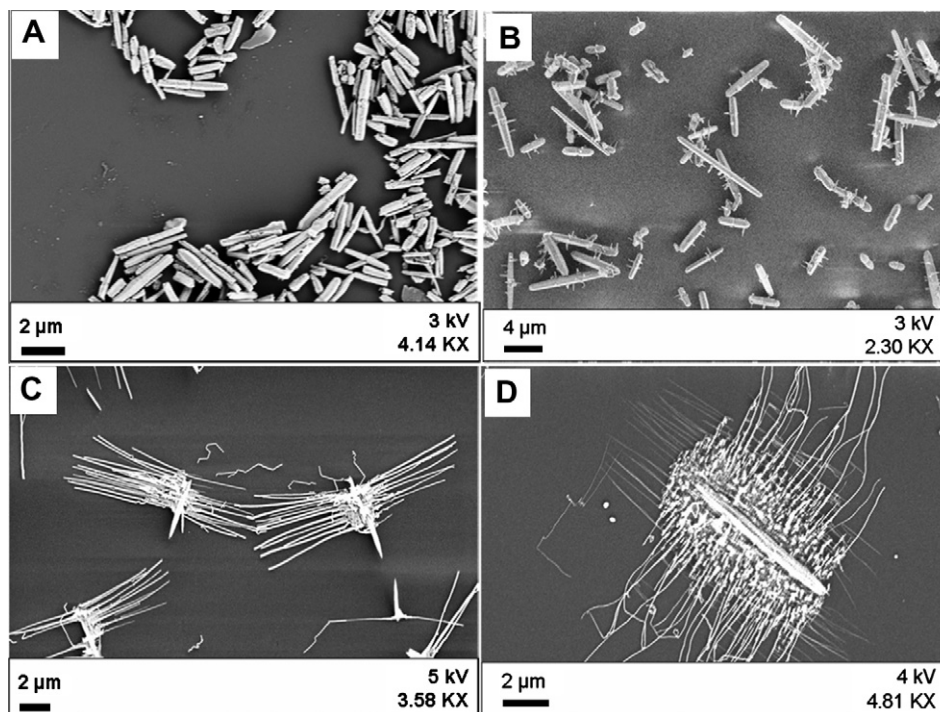


Figure 5. Yagi-Uda-antenna-like ZnO superstructures obtained with nanowires as building blocks. The SEM images show different stages of growth: (A) after one cycle of growth in 0.25 mM HMT at 85 °C for 2 h; after a (B and C) second and (D) a third repeated cycle in a fresh growth solution with same composition. Au nanoparticles were used as seeds only in the first cycle.

4. Conclusions

In conclusion, we have demonstrated the self-assembly of hierarchical ZnO superstructures in a low-temperature aqueous chemical bath deposition method. The structures comprise of building blocks such as nanoplatelets or nanowires, which repeat themselves in a certain pattern. We show that the concentration of the precursor controls the type of building block and other growth conditions such as reaction kinetics and choice of precursor determine the architecture of the obtained hierarchy. This kind of an additive-free bottom-up approach takes advantage of innate physicochemical interactions favoring the self-assembly of the nanoscale building blocks. The possibility to engineer materials using such simple synthesis conditions may present a tremendous leap for fundamental studies and industrial applications of sophisticated nanostructured materials. Future work may address the use of such structures for applications in catalysis and sensors.

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