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Peanut shaped ZnO microstructures: Controlled synthesis and nucleation growth toward low-cost dye sensitized solar cells

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Abstract

This paper describes a simple, low-temperature and cost effective chemical precipitation method in aqueous media to synthesis uniformly distributed zinc oxide (ZnO) microstructures for the fabrication of dye-sensitized solar cells (DSSCs). The size and morphology of the ZnO microstructures are systematically controlled by adjusting the concentration of the precursors, zinc acetate dihydrate and ammonium hydroxide. X-ray diffraction (XRD) and scanning electron microscopy (SEM) are used for the structural characterizations and photoluminescence and Fourier transform infrared spectroscopy are used to characterize the optical properties of the ZnO, respectively. The results reveal that ZnO crystallites exhibit hexagonal wurtzite structure with preferential orientation along *c*-axis. The effect of ammonia concentration on the crystallinity, morphology and optical properties of ZnO microstructures and the concomitant effect on the efficiency of dye-sensitized solar cells is also quantified. The peanut-shaped ZnO microstructure, which was found to increase DSSCs performance over other microstructure, is studied in detail in order to develop a formation mechanism. A sandwich type eosin yellow sensitized solar cell is prepared using peanut-shaped ZnO microstructures, which showed an efficiency of 0.37%. Ammonia was found to play a crucial role in the evolution of ZnO morphologies. These results are promising and provide a path towards low-cost high-performance DSSCs based on peanut-shaped ZnO microstructures and produced with only relatively simple wet chemistry synthesis.

Keywords: Chemical precipitation; morphology; peanut-shaped microstructures; optical properties; dye-sensitized solar cell.

1. Introduction

The development of nanomaterials of specific shapes, size and morphologies for emerging energy applications such as low cost dye sensitized solar cells is a current challenge in materials engineering. Recently, growing interest is observed in metal oxide nano/micro structures due to their easy, safe, environmental friendly and low-cost synthesis procedure.¹⁻⁵ Methods for highly controllable structures with uniformity in morphology, novel physical and chemical properties are being developed that could positively impact energy harvesting applications such as dye sensitized solar cells.^{6,7} Several challenges are encountered in the preparation of nano materials that include control of their size, shape, and distribution, in addition to their environmental friendly handling.⁸⁻¹⁰ Among various inorganic semiconductor

materials, zinc oxide (ZnO) has attracted the attention of researchers since its morphology can be easily tailored. Apart from this, it is environmental friendly, chemically flexible, multifunctional and abundantly available on Earth.^{11,12} These attributes make it a particularly attractive candidate for PV applications, which must be sustainable¹³, able to produce low level costs of electricity¹⁴ and as the scale of the PV industry has grown substantially the core materials must be earth abundant.¹⁵

ZnO is n-type II-VI compound semiconductor with a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, which enable ZnO to exhibit near-UV emissions that are suitable for short-wavelength optoelectronic applications.¹⁶⁻²⁰ In addition to this, it has wide applications in piezoelectric devices, spintronic devices, laser diodes, solar cell displays as highly transparent conducting windows, and gas sensors.²¹⁻²³ However, better control of specific properties (i.e. crystal size, orientation, morphology, aspect ratio, and crystalline density) still need to be enhanced so that the full potential of ZnO can be realized. The strategic design and precise morphology for a given application of ZnO with high specific surface area can be developed by a variety of physical, chemical and electrochemical methods.²⁴⁻²⁸ Among the various growth methods, solution based chemical synthesis is a simple, easy to handle, and low-cost technique to prepare nano/micro structures in a controllable manner.^{29,30}

Recently, aqueous chemical systems have been found appropriate for the synthesis of ZnO with different morphologies. Using this method, a variety of ZnO structures such as nanowires,^{31,32} nanorods,^{33,34} nanoflowers,³⁵ dumbbell shapes,³⁶ nanoprisms³⁷ and nanopillars³⁸ have been successfully synthesized and characterized. For example, Pan et al.³⁹ reported, the synthesis of controllable dumbbell-shaped ZnO rod crystals at 90 °C using hexamethylenetetramine (HMT) as the structural-directing agent. Sharifzadeh et al.⁴⁰ reported the controllable synthesis of various morphologies such as hollow spheres, rod and coral-like structures. They also demonstrated that the choice of solvent and reaction conditions could affect the shape of the nano-scale products. Achieving control over the size and morphology of the ZnO nanostructures and their further self-organization into 2D or 3D superstructures is still a challenging task. In a pioneering work, Sun et al.,⁴¹ reported the synthesis of peanut and spindle-like ZnO mesocrystals with controllable size and shape by tailoring the concentration of OH⁻ and Zn²⁺ ions, which might affect the balance between thermodynamics and kinetics during the nucleation growth. In addition, Song et al.,⁴² investigated the influence of growth parameters on hexagonal bullet-like ZnO morphology and found that the reaction time, precursor concentration, temperature and the concentration of O²⁻ and Zn²⁺ ions have a strong effect on morphology. These ZnO morphologies exhibit excellent performance in DSSCs and offer the potential for expanding the market for this 3rd generation PV device. Generally, special structures of ZnO not only offer sufficient internal surface area for dye-adsorption, but also provide effective light-scattering centers, which enhance absorption.^{5,43,44} However, most of the investigations have focused on the synthesis of ZnO nano/microstructures in powder form through homogeneous precipitation in aqueous medium and thus the study of the fundamental nucleation growth mechanism of ZnO nano/microstructures is still limited.

In order to overcome this knowledge gap the present work investigates the controlled synthesis of ZnO microstructures via a low temperature chemical precipitation method in

aqueous media. The size and morphology of the particles are systematically controlled by adjusting the concentration of the precursors, zinc acetate dihydrate and ammonium hydroxide. Here, ammonia plays a crucial role in the evolution of ZnO morphologies. The peanut-shaped ZnO microstructure is studied in detail in order to develop a formation mechanism. In addition the effect of ammonia concentration on the crystallinity, morphology and optical properties of peanut-shaped ZnO microstructures and the concomitant effect on the efficiency of dye-sensitized solar cells is quantified. The results are presented and discussed in order to further develop low-cost fabrication of ZnO for DSSCs.

2. Experimental section

2.1. Materials

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 98\%$), ammonia solution (NH_3 , $\geq 30\%$), acetone ($\geq 99\%$), and ethanol ($\geq 99.9\%$) were purchased from Merck Specialities Pvt Ltd. All the chemicals are analytical reagents and used directly without further purification. Double distilled water was used in all experiments.

2.2. Synthesis of ZnO microstructures

ZnO microstructures were synthesized by a simple chemical precipitation method.^{45,46} In a typical synthesis procedure, 15 mM of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 200 ml of distilled water and kept at 60 °C under vigorous stirring. To this solution, 45 mM of ammonia solution was added drop wise and the mixture was subjected to strong magnetic stirring for 2 h. After cooling to room temperature naturally, homogeneous white precipitates in the colloidal form were collected by centrifugation and rinsed with distilled water, absolute ethanol and acetone in order to remove the unreacted ions. Then, the product was filtered and dried in air atmosphere at 50 °C. This procedure was repeated for different concentrations of ammonia (60, 65, and 70 mM) at constant concentration (15 mM) of $\text{Zn}(\text{CH}_3\text{COO})_2$ solution. As a result, four ZnO samples were obtained with ammonia to zinc ratios of 3, 4, 4.3, and 4.6 and they are identified here as Z1, Z2, Z3, and Z4, respectively. All samples were finally annealed in air at 200 °C for 2 h.

2.3. Solar cell fabrication and testing

For DSSCs fabrication, uniform ZnO pastes were prepared by gradually adding 20 μl of glycerol anhydrous with 0.2 g of ZnO powder with continuous mixing. The resultant paste was deposited on tin doped indium oxide (ITO) coated glass substrates using the doctor blade technique. After evaporation of the solvent at room temperature, the film was dried at 60 °C for 30 min and annealed at 400 °C for 1 h to remove the organic materials, which resulted in photoanode ZnO layer. The ZnO photoanode was sensitized by immersing in an absolute ethanol solution of 0.5 mM eosin yellowish dye for 15 h. Then, the sensitized ZnO film was rinsed in absolute ethanol to remove excessive dye molecules. Carbon coated glass was used as the counter electrode. The dye-sensitized ZnO photoanode (active area: 0.25 cm^2) and the carbon counter electrode were assembled into a sandwich type cell. A drop of electrolyte solution containing 0.5 M potassium iodide and 0.05 M iodine in acetonitrile was injected into the cell before the solar cell measurements. Solar cells fabricated using ZnO microstructures were

characterized by measuring their current-voltage characteristics, where the cells were irradiated with a solar simulator with AM 1.5 40 mW/cm² illumination.

2.4. Characterization

The crystal structure of the samples were examined by X-ray diffraction (XRD) at room temperature using an X-ray diffractometer (PANalytical X'Pert Pro) with Cu-K α as the radiation source (wavelength: 1.54056 Å) at a step size of 0.02° over the 2 θ range of 10°-90°. The morphology and size of the samples were characterized by scanning electron microscope (SEM) (FEI Quanta 200 FEG-ESEM). UV-Vis absorption measurements were carried out at room temperature with a UV-Vis absorption spectrometer (Shimadzu-2450). The photoluminescence (PL) properties were investigated at room temperature by employing a 372 nm wavelength laser source (PicoQuant, 50 ps-pulsed, average power 2 mW @ 40 MHz) and a fiberoptic spectrometer (Ocean Optics, Inc., USB4000, 2 nm spectral resolution). Fourier transform infrared (FTIR) spectra were measured using the KBr method on a FTIR spectrometer (Shiraz) at room temperature in the range of 4000-400 cm⁻¹ with a resolution of 1 cm⁻¹. Current-voltage (I-V) characteristics of DSSCs under simulated AM 1.5 G sunlight illumination (Oriel Class-A solar simulator (91195A, Newport) containing ozone-free 450 W xenon lamp) were measured using computer-controlled Autolab PGSTAT302N electrochemical workstation.

3. Results and Discussion

3.1. Structural analyses

The XRD patterns of the synthesized samples are shown in Figure 1. All the diffraction peaks can be indexed to hexagonal ZnO with wurtzite structure (space group P6₃mc; $a = 3.249$ Å, $c = 5.206$ Å; JCPDS card, No. 65-3411). For the four samples, no peaks from any other phase of ZnO and impurities were observed, indicating that all samples were of high purity.⁴⁷ However, the intensities of all diffraction peaks decrease to various degrees with increasing ammonia concentration. The crystallinity also gradually reduces with the formation of large crystallites. The average crystallite size, relative intensity and lattice parameters are listed in Table 1. Furthermore, three main strong characteristic (100), (002), and (101) peaks are observed in the XRD patterns. The peaks corresponding to these planes of Z2, Z3, and Z4 were slightly shifted when compared to Z1 and this small shift is attributed to minor tensile stress caused by appropriate ammonia concentration.^{48,49} In addition to this, the relative intensity of the peaks corresponding to the $I_{(100)}/I_{(002)}$ and $I_{(101)}/I_{(002)}$ planes varied significantly as shown in Table 1. These results also reveal two more aspects about the samples. First, the relative intensity $I_{(100)}/I_{(002)}$ with small value of 1.1 to 1.2 for the samples Z1 and Z2 indicates the formation along the c -axis orientation with (0001) or (000 $\bar{1}$) end faces. Second, the high $I_{(100)}/I_{(002)}$ ratio of 1.5 revealed shortening along the c -axis. From these results, it is inferred that Z2 has perfect crystallinity with well-ordered orientation, which is clearly shown in Figure 1. However the relative intensities do not change systematically. This may indicate random growth along the length and diameter of ZnO structures, which will be confirmed by SEM studies discussed below.

3.2. Morphological evolution of ZnO microstructures

Figure 2 shows the low magnification images of Z1, Z2, Z3, and Z4 samples, each of which shows a variation in its appearance. The SEM images of Z1 (Figure 3(a,b)) show the formation of peanut-shaped structures, which are uniform in size. From the image, along with these structures, one can also see the formation of a cluster of particles.

Z1 was synthesized at the $[\text{NH}_3/\text{Zn}^{2+}]$ molar ratio of 3. This concentration of ammonia is insufficient for the complete growth of ZnO into peanut-shaped microstructures and thus forms clusters of particles or proto-peanuts. However, ZnO of other morphologies are not found in this sample. The average diameter and the length of Z1 sample are found to be 420 nm and 950 nm, respectively, indicating an aspect ratio of about 2.26 ± 0.02 . Since the particle formation is due to the insufficient ammonia concentration, its concentration is increased to achieve uniform distribution of peanut-shaped ZnO microstructures without particle clusters and this is achieved with the $[\text{NH}_3/\text{Zn}^{2+}]$ molar ratio of 4. Figure 3(c,d) shows the SEM images of Z2, where microstructures have an average diameter of about 420 nm and length of about 1500 nm and their aspect ratio was estimated to be about 3.57 ± 0.02 . When the concentration of ammonia is increased further, i.e., when the molar ratio of $[\text{NH}_3/\text{Zn}^{2+}]$ is 4.3 for Z3, the peanut-shaped ZnO microstructures have an average diameter, length, and aspect ratio of about 320 nm, 950 nm, and 2.97 ± 0.02 , respectively. Along with this peanut structure, some hexagonal, spherical, and ellipsoidal shaped ZnO (shown by dotted ellipses and circles) can also be seen in Figure 4(a,b), which are randomly distributed among peanut-shaped structures. With a further increase in the ammonia concentration ($[\text{NH}_3/\text{Zn}^{2+}] = 4.6$), even though peanut-shaped ZnO microstructures are observed, their growth is affected, as shown in Figure 4(c,d). The diameter and length of the structures are about 420 nm and 1150 nm with an aspect ratio of 2.74 ± 0.02 . From the SEM images of Z4 (inset of Figure 4(c)), it can be seen that many semi-elliptical shaped structures are aligned to form an array of microstructures and flower-like structures. The high concentration of ammonia also results in hollow structures, which is indicated by a dotted circle in Figure 4(d). Apart from this, in Z4, a cluster of semi elliptical shaped structures is also present and indicated with an arrow.

The SEM results show that high ammonia content affects the growth of the peanut-shaped microstructures. It is also inferred that the ammonia concentration affects the aspect ratio of the microstructures. This is quantified in Figure 5(a), which shows a detailed particle size and aspect ratio distribution obtained from the SEM images in the form of a histogram. From the histogram, it is seen that compared to other conditions, Z2 shows a more uniform distribution with aspect ratio in the range of 3 to 3.5 ± 0.02 . The high aspect ratio of peanut-shaped microstructures have been successfully achieved by controlling the super saturation degree of solutions, that is, simply by controlling the molar concentration (60 mM; Z2 sample) of ammonia as shown in Figure 5(a,b). The aspect ratio decreased with higher ammonia concentrations (65, 70 mM), which affected the super-saturation point and also create new nucleation sites, which results in the formation of new microstructures. Thus under these conditions the optimum concentration of ammonia that gives the uniform distribution of peanut-shaped ZnO microstructures is 60 mM.

3.3. Chemistry of ZnO growth in aqueous solutions

To synthesis ZnO microstructures, an appropriate molar ratio between $\text{Zn}(\text{CH}_3\text{COO})_2$ and NH_3 in aqueous solution was used at a relatively low reaction temperature. ZnO crystals were obtained according to the following reactions.^{45,50} Initially, when zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2$) was dissolved in water, it dissociated into zinc ion (Zn^{2+}) and acetate ion (CH_3COO^-) as shown in Eq.1. Then, the acetate ions were hydrolyzed to give OH^- ions as shown in Eq.2.

In the case of ammonia, when it reacts with water molecules, it forms ammonium (NH_4^+) ions and hydroxide ions (OH^-).

The Zn^{2+} ions have the chance to combine with both NH_4^+ and OH^- ions. They can readily react with hydroxide ions to generate large amount of stable zinc hydroxide ($\text{Zn}(\text{OH})_2$) and tetrahydroxozincate ions ($\text{Zn}(\text{OH})_4^{2-}$), as given in Eq. 4 & 5. With NH_4^+ ions, they form tetraamine zincate ions ($\text{Zn}(\text{NH}_3)_4^{2+}$), as shown in Eq. 6.

ZnO nuclei were formed as a result of dehydration of both $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{NH}_3)_4^{2+}$ complex ions, as shown in Eq. 7 & 8.

In addition, $\text{Zn}(\text{OH})_2$ also yields ZnO nuclei with $\text{Zn}(\text{OH})_4^{2-}$ as an intermediate product, as shown in Eq. 9.

The growth of peanut-shaped microstructures is achieved through the adsorption of $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{NH}_3)_4^{2+}$ on the preformed ZnO nuclei. Both $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{NH}_3)_4^{2+}$ act as growth units.^{51,18}

3.4. Formation mechanism of peanut-shaped ZnO microstructures

The reactions that occur between the precursors during the synthesis process are discussed in section 3.3. From the results above, the ammonia solution is obviously the key factor in deciding the growth of anisotropic structure and in controlling the morphology. It is already discussed that at low ammonia concentration (Z1), the formation of peanut-shaped ZnO microstructures is accompanied by particles. Hence the ammonia concentration is increased further to get uniform distribution of peanut-shaped ZnO microstructures. The formation of which occur by the following proposed mechanism: At the early stage of the reaction, both zinc acetate and ammonia provides a large number of OH^- ions, which is essential for the formation of one of the growth units, namely $\text{Zn}(\text{OH})_4^{2-}$ and also for the crystallization of ZnO from $\text{Zn}(\text{NH}_3)_4^{2+}$ (Eq. (1-9)). It is expected that when the concentration of $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{NH}_3)_4^{2+}$ exceeds the critical value, the precipitation of ZnO nuclei starts. This is the initial nucleation

process for the formation of ZnO microstructures. ZnO is a polar wurtzite crystal with alternating planes of tetrahedral coordinated zinc and oxygen atoms along the c -axis, which consists of positively charged polar Zn^{2+} -terminated (0001) plane and negatively charged polar O^{2-} -terminated (000 $\bar{1}$) plane.⁵²⁻⁵⁴ These two polar planes are thermodynamically unstable and hence growth of ZnO along these planes is energetically favourable, which reduces their surface energy, making the system stable. The growth rate of ZnO is different along different planes with high growth rate along the (0001) plane followed by (01 $\bar{1}$ 0), (2 $\bar{1}$ $\bar{1}$ 0), (10 $\bar{1}$ 0), and (000 $\bar{1}$) planes, respectively.^{47,55} After the formation of ZnO nuclei, the growth units in the solution get adsorbed on the different planes of ZnO nuclei. The adsorbed growth units further crystallized into ZnO. The microstructure forming into a peanut-shaped microstructure undergoes a series of steps before reaching the final shape. Figure 6 illustrates an innovative schematic representation of the whole growth process of peanut-shaped ZnO microstructure. Here the peanut-shaped ZnO microstructure is formed from two types of semi-elliptical shaped ZnO. In the first case, since $\text{Zn}(\text{OH})_4^{2-}$ exists in the form of negatively charged ion, it can easily coordinate with the positively charged Zn^{2+} -terminated (0001) plane (having high surface energy) of ZnO nuclei by electrostatic interaction.^{10,55} The Zn^{2+} coordinated $\text{Zn}(\text{OH})_4^{2-}$ ion further undergoes dehydration resulting in the formation of ZnO. With this positively charged Zn^{2+} -terminated plane, once again $\text{Zn}(\text{OH})_4^{2-}$ ion coordinates and the whole process is repeated until the supply of growth units stop. Since the growth rate along the side facets i.e., along (01 $\bar{1}$ 0) plane is low compared to (0001) plane, the attachment of $\text{Zn}(\text{OH})_4^{2-}$ ions results in the formation of hexagonal semi elliptical shaped ZnO with alternating planes of O and Zn atoms along the c -axis. Thus the formed semi elliptical shaped ZnO has Zn atoms at its tip and O atoms at its base as shown in Figure 6 (Case I). In the second case, $\text{Zn}(\text{NH}_3)_4^{2+}$ ions, which are positively charged, get coordinated with the negatively charged O^{2-} ions of the remaining ZnO nuclei. The OH^- ions released by the addition of ammonia reacts with $\text{Zn}(\text{NH}_3)_4^{2+}$ to form ZnO. Further, with the O^{2-} ion of the formed ZnO, $\text{Zn}(\text{NH}_3)_4^{2+}$ ion gets adsorbed and this process continues, which also results in the formation of hexagonal semi elliptical shaped ZnO with Zn atoms at its base and O atoms at its tip as represented in Figure 6 (Case II). Thus, the semi elliptical shaped ZnO formed from $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{NH}_3)_4^{2+}$ ions have polar fields in opposite directions. Finally, in order to counterbalance the polar field, the two semi elliptical shaped ZnO with opposite polar field directions were strongly twinned due to the polar field interaction to form peanut-shaped ZnO microstructures as shown in Figure 6&3(c,d). Even though the peanut-shaped ZnO microstructure is formed due to the oriented attachment of ZnO, the surface of the final product is smooth, which is evident from the SEM images. This is achieved by the well-known Ostwald ripening mechanism by which the irregularities on the surface have been removed.

3.5. Effect of ammonia on morphology

Wang et al., reported that the peanut-like structures were formed as a result of the competition between ammonia erosion and ZnO growth.⁵⁶ Thus the ammonia concentration has a great impact on the morphology of ZnO. In this work also, from the SEM results, it is observed that the chemical action between the amount of ammonia solution and ZnO growth plays an important role in the formation of peanut-shaped ZnO microstructures. At constant reaction temperature, such as 60 °C and at low ammonia concentration (45 mM, Z1), the availability of

NH_3 in the solution is low and hence the number of growth units formed is low. Thus only a few ZnO nuclei can access the growth units in order to form the peanut-shaped microstructures and the structure is incomplete. Due to insufficient ammonia concentration, the growth along the (0001) direction is controlled and hence some of the ZnO nuclei remained as particles. One can also see the aggregation of nanoparticles in the SEM image, which occurs in order to reduce the surface energy. At 60 mM of ammonia concentration (Z2), the concentration of ions (Zn^{2+} and OH^-) and hence the number of growth units increased. In this case, the concentration of Zn^{2+} and OH^- ions is favourable for the complete growth of peanut-shaped ZnO microstructures with high uniformity and good monodispersity (Figure 3(c,d)).

Further increasing the ammonia concentration to 65 mM (Z3), along with the peanut-shaped microstructures, few spherical, hexagonal and elliptical shaped structures were also observed. This is because, when the concentration of ammonia increases, its solubility decreases and hence the release of OH^- ions is reduced after a certain time. Thus the growth of ZnO along the c -axis was suppressed, which resulted in the formation of hexagonal structures. The spherical and ellipsoidal structures were obtained as a result of Ostwald ripening of the hexagonal structures (Figure 4 (a,b)). At very high concentration (70 mM) of ammonia (Z4), the growth of ZnO is uncontrollable and random. The crystalline nature was decreased and inhomogeneous peanut-shaped ZnO microstructures were formed. One can also see a number of different in this sample and the discussion for the formation of spherical, hexagonal, and elliptical shaped structures is the same as that for Z3 reaction conditions. The high concentration of ammonia also initiated the secondary nucleation from the six planes of preformed hexagonal ZnO crystals, thus leading to the multidimensional growth of ZnO along the $\langle 0001 \rangle$ direction, which results in the formation of flower-like microstructures. Apart from this, at this concentration of ammonia, most of the $\text{Zn}(\text{NH}_3)_4^{2+}$ ions were decomposed into free Zn^{2+} ions, which by interacting with the OH^- ions transformed into $\text{Zn}(\text{OH})_4^{2-}$ (Eq.7). This resulted in the decreased concentration of $\text{Zn}(\text{NH}_3)_4^{2+}$ ions and hence the formation of semi elliptical shaped ZnO with Zn atoms at its base and oxygen atoms at its tip is decreased. Thus, the concentration of semi elliptical shaped ZnO with the same polar field increases and in order to reduce the surface energy, these ZnO microstructures were attached side by side to form an array, as shown in Figure 4(c,d). Finally, this sample also hosted hollow ZnO microstructures. It should be noted that only the upper part of the semi ellipse is observed to be hollow, while the lower part may possibly be dense. Interestingly, the hollow nature is owing to the erosion by ammonia at the center of the structure.⁵⁶ If the concentration of ammonia is increased further, it may be possible that all the peanut-shaped ZnO microstructures are hollow at both edges. These results demonstrate that various nano and micro structures were obtained depending upon the rate of nucleation and crystal growth, which are sensitive to ammonia concentration in the precursor solution. From the present work, it is inferred that the optimum concentration of ammonia for the formation of highly uniform peanut-shaped ZnO microstructures is 60 mM (Z2).

3.6. Optical analysis

UV-Vis absorption spectrum of as synthesized peanut-shaped ZnO microstructures is shown in Figure 7. The absorption spectrum of all the samples shows a well-defined exciton band at about 391 nm corresponding to the intrinsic band gap of ZnO. In addition, the direct

band gap values of 3.18 eV for Z1, 3.17 eV for Z2, Z3 and 3.16 eV for Z4 were obtained from the α - absorption plot, which is given in the inset of Figure 7. The band gap values showed a red-shift compared to the bulk band gap value (3.37 eV).⁵⁷ The shift towards the higher wavelength region is due to the larger dimensions of the ZnO microstructures. UV-Vis spectra clearly show that the synthesized samples are highly transparent in the visible region.

Figure 8 shows the photoluminescence (PL) spectra of the synthesized peanut-shaped ZnO microstructures. The measurement was performed at room temperature of 300 K by using a laser source with an excitation wavelength of 372 nm. The spectra shows sharp and strong ultraviolet (UV) emission peaks with the central wavelength at around 400 nm for all samples. It is reported that the UV emission originates from the recombination of the free excitons through an exciton-exciton collision process in the near-band-edge of the wide band gap ZnO.^{58,59} The broad visible emission (450 to 900 nm) indicates that several deep-level defects may co-exist in the synthesized peanut-shaped ZnO microstructures. Generally, a visible emission peak at higher wavelength was mainly due to the radiative recombination of the photo generated holes with the electrons associated with the structural defects such as ionized oxygen vacancies and zinc interstitials.^{9,60,61} It is seen that the UV and visible emission peak intensities vary with ammonia concentration. The peak intensities increase with the increase in the ammonia concentration initially, but at high ammonia concentration the PL intensities decrease. The variation in the PL intensity results from the different amount of strain accumulated in the microstructures due to their various size and morphology. Z2 and Z3 show a high intense excitonic peak compared to Z1 and Z4. This is because in Z2 and Z3 the structures are more uniformly distributed than in Z1 and Z4. The aspect ratio is also high for Z2 and Z3, which is confirmed from SEM analysis. Since Z2 shows slightly decreased visible emission compared to Z3, this sample is of high optical quality compared to others. Thus, the sample Z2 may serve as an efficient photoanode in the fabrication of solar cells. In addition, these results make it clear that the luminescence properties of ZnO can be controlled by changing its morphology.

Figure 9 shows the compositional analysis carried out by FTIR spectroscopy. The band in the region of 3430 cm⁻¹ corresponds to O-H mode of vibration. From the spectra, it is seen that the peak form of O-H changes from sharp to broad peaks, which indicated the change in size and shape of peanut-shaped ZnO microstructures due to change in the NH₃ concentration. The absorption peaks at 2924 and 2854 cm⁻¹ are due to the characteristic vibrations of C-H bond.⁶² The bands observed at about 2362 and 2336 cm⁻¹ are related to CO₂ molecule in air. The strong asymmetric stretching modes of C=O and C=C were observed between 1744 and 1651cm⁻¹.⁶³ The peak positions centered at 1463 and 1021cm⁻¹ were related to O₂²⁻ ions, which may arise from the O-O bands. The bands observed in the wavelength range of 400-500 cm⁻¹ correspond to the Zn-O vibration modes.^{62,64,65}

3.7. Morphology based performance of DSSCs

The photocurrent density-voltage characteristics of the DSSCs are shown in Figure 10 and the corresponding photovoltaic parameters are summarized in Table 2. The energy conversion efficiency (η) and fill factor (FF) were calculated by using the following equations:

$$\eta (\%) = \frac{I_{\max} \times V_{\max}}{P_{in}} \times 100 \quad (1)$$

$$FF = \frac{I_{\max} \times V_{\max}}{I_{sc} \times V_{oc}} \quad (2)$$

Where, I_{sc} is the short-circuit photocurrent, V_{oc} is the open circuit photovoltage, P_{in} is the incident light power (40 mW/cm^2). $I_{\max}$ and $V_{\max}$ represent the current and voltage delivered at maximum power point, respectively. It should be pointed out that these solar cells were fabricated with a yellow dye that was thus poor absorber over the entire solar spectrum, but is useful for probing the properties of the thin films. The maximum short-circuit current density (J_{sc}) of 0.797 mA/cm^2 was obtained for Z2, which was far superior to the other ZnO sample preparation conditions. The better solar cell parameters (J_{sc} and FF), as observed for Z2 conditions, can be attributed to the uniform distribution of peanut-shaped ZnO microstructures as shown in Figure 3(c,d). These microstructures have near-perfect aggregation, which help in more dye adsorption and hence capture a larger number of photons. From these results it can be concluded that the presence of crystalline peanut-shaped ZnO microstructures without any other structures enhance the direct conduction paths for electron transport, which suppresses the charge recombination thereby enhancing the short-circuit current.

It should be pointed out here that the power conversion efficiency (η) values should be compared primarily to one another. In order to reduce experimental uncertainty of the effects of geometrically complex substrates on growth, non-optimized ITO was used for all cases. This reduced the optical enhancement as compared to record efficiency DSSCs using ZnO.⁶⁶ Considerable future work is needed on the optimization of the use of these peanut-shaped ZnO microstructures for DSSCs. First, a thickness series is needed to determine the optimal ZnO thickness. The other deposition parameters of the peanut-shaped ZnO microstructures should be further refined to reduce charge recombination. Next, optimal ITO should be used to maximize the optical path length and light trapping for all wavelengths of light. Ideally, the ITO would also be fabricated with a low-cost means such as the sol-gel process.⁶⁷ The combination of highly textured ITO and optimal peanut-shaped ZnO microstructure deposition should be tested for optimal dye loading to ensure the structures have maximum dye available surface area. In addition, the lower illumination power should be noted, which was used here to screen these cells for possible use indoors and for low light conditions. In the future, tests should be performed with one sun illumination.

To date, most of the ZnO based DSSCs were fabricated using ruthenium (N719) based photosensitizers, which are an expensive dye. In this work, DSSCs were fabricated using a low-cost dye, namely, eosin yellowish (EY) dye and an efficiency of 0.37 % is achieved. The efficiency of ruthenium dye based DSSCs for various ZnO nanostructures reported in recent literatures is summarized in Table 3. Similar efficiencies were noted in our device as previous reports mentioned in Table 3 that shows there is room for improvement in future generation devices. Obviously higher efficiencies could be obtained with higher performance ruthenium photosensitizers. Additional future work is needed to find tolerably-efficient replacement low-cost photosensitizers and tune their energy levels for high performance,⁷² while also enabling geographically optimization based on atmospheric conditions.⁷³

4. Conclusions

To conclude, various ZnO microstructures, such as peanut-shaped, spherical, hexagonal, elliptical and flower have been synthesized successfully via a simple chemical precipitation method. The highest performance microstructure for use in DSSCs applications was found to be a peanut-shaped ZnO microstructure with an efficiency of 0.37 % using a yellow dye. The XRD and SEM analyses of the peanut-shaped ZnO microstructure indicated that they have good crystallinity. The results of this study showed that ammonia decomposition in the reaction solution plays a very important role in controlling the nucleation and growth of peanut-shaped ZnO microstructures. A growth mechanism was proposed and with the experimental results it is clear that the concentration of intermediates can be optimized by varying the ammonia concentration in order to get uniform distribution of peanut-shaped ZnO microstructures. Both the optical and electrical properties and the concomitant DSSCs properties were also significantly modified by controlling the ammonia content. The enhancement in the PV device performance is due to the uniform distribution of peanut-shaped ZnO microstructures, which offer a direct carrier transport pathway for the electrons. These results are promising and provide a path towards low-cost high-performance dye sensitized solar cells produced with only relatively simple wet chemistry synthesis and based on peanut-shaped ZnO microstructures.

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References

1. Y. Yin and D. Talapin, *Chem. Soc. Rev.* 2013, **42**, 2484-2487.
2. Q. Zhang, E. Uchaker, S. L. Candelaria and G. Cao, *Chem. Soc. Rev.* 2013, **42**, 3127-3171.
3. D. Wu, W. Wang, F. Tan, F. Sun, H. Lu and X. Qiao, *RSC Adv.* 2013, **3**, 20054-20059.
4. A. P. Bhirud, S. D. Sathaye, R. P. Waichal, L. K. Nikam and B. B. Kale, *Green Chem.* 2012, **14**, 2790-2798.
5. S. H. Ko, D. Lee, H.W. Kang, K. H. Nam, J.Y. Yeo, S.J. Hong, C. P. Grigoropoulos and H. J. Sung, *Nano Lett.* 2011, **11**, 666-671.
6. T. Kundu, S. C. Sahoo and R. Banerjee, *Cryst. Growth Des.* 2012, **12**, 2572-2578.
7. P. Jiang, J.-J. Zhou, H.-F. Fang, C.-Y. Wang, Z. L. Wang and S.-S. Xie, *Adv. Funct. Mater.* 2007, **17**, 1303-1310.
8. R. Bardhan, H. Wang, F. Tam and N.J. Halas, *Langmuir* 2007, **23**, 5843-5847.
9. P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He and H.-J. Choi, *Adv. Funct. Mater.* 2002, **12**, 323-331.
10. S. Cho, S.-H. Jung and K.-H. Lee, *J. Phys. Chem. C* 2008, **112**, 12769-12776.
11. Y. Liu, K. Tai and S. Dillon, *J. Chem. Mater.* 2013, **25**, 2927-2933.
12. Y. Zhang and C.-T. Lee, *J. Phys. Chem. C* 2009, **113**, 5920-5923.

13. J. M. Pearce, *Futures*, 2002, **34**(7), 663-674.
14. K. Branker, M. J. M. Pathak, and J. M. Pearce, *Renewable and Sustainable Energy Reviews*, 2011, **15**, 4470-4482.
15. L.M. Peter, *Phil. Trans. R. Soc. A* 2011, **369**, 1840-1856.
16. C.V. Manzano, O. Caballero-Calero, S. Hormeño, M. Penedo, M. Luna and M. S. Martín-González, *J. Phys. Chem. C* 2013, **117**, 1502-1508.
17. X. Hu, Y. Masuda, T. Ohji and K. Kato, *J. Am. Ceram. Soc.* 2009, **92**, 922-926.
18. S. Baruah and J. Dutta, *Sci. Technol. Adv. Mater.* 2009, **10**, 013001-1-013001-18.
19. O. Lupan, T. Pauporte, B. Viana, I. M. Tiginyanu, V. V Ursaki and R. Cortes, *ACS Appl. Mater. Interfaces* 2010, **2**, 2083-2090.
20. S. Chu, D. Li, P.-C. Chang and J.G. Lu, *Nanoscale Res. Lett.* 2011, **6**, 1-4.
21. Y. Masuda, N. Kinoshita, F. Sato and K. Koumoto, *Cryst. Growth Des.* 2006, **6**, 75-78.
22. X.-Y. Xue, Z.-H. Chen, L.-L. Xing, C.-H. Ma, Y.-J. Chen and T.-H. Wang, *J. Phys. Chem. C* 2010, **114**, 18607-18611.
23. M. Ahmad and J. Zhu, *J. Mater. Chem.* 2011, **21**, 599-614.
24. L. Carbone and P. D. Cozzoli, *Nano Today*. 2010, **5**, 449-493.
25. L. Feng, A. Liu, M. Liu, Y. Ma, J. Wei and B. Man, *J. Alloys Compd.* 2010, **492**, 427-432.
26. J. Das, and D. Khushalani, *J. Phys. Chem. C* 2010, **114**, 2544-2550.
27. P. Chithaiah, S. Ashoka, K.V. Thipperudraiah and G. T. Chandrappa, *Cryst. Res Technol.* 2012, **47**, 1075-1082.
28. P. K. Giri, S. Bhattacharyya, D. K. Singh, R. Kesavamoorthy, B. K. Panigrahi and K. G. M. Nair, *J. Appl. Phys.* 2007, **102**, 093515-1- 093515-8.
29. C. Liu, Y. Masuda, Z. Li, Q. Zhang and T. Li, *Cryst. Growth Des.* 2009, **9**, 2169-2172.
30. C. -H. Ku, H.-H. Yang, G.-R. Chen and J.-J. Wu, *Cryst. Growth Des.* 2008, **8**, 283-290.
31. B. Panigrahy, M. Aslam, D. S. Misra and D. Bahadur, *CrystEngComm*. 2009, **11**, 1920-1925.
32. H. Li, M. Xia, G. Dai, H. Yu, Q. Zhang, A. Pan, T. Wang, Y. Wang and B. Zou, *J. Phys. Chem. C* 2008, **112**, 17546-17553.
33. C-Y. Kuo, R.-M. Ko, Y. -C. Tu, Y -R. Lin, T -H. Lin and S.-J. Wang, *Cryst. Growth Des.* 2012, **12**, 3849-3855.
34. M. Raja, N. Muthukumarasamy, D. Velauthapillai, R. Balasundaraprabhu, S. Agilan, and T.S. Senthil, *Solar Energy*, 2014, **106**, 129-135.
35. N. Rajkumar, R. N. Mariammal and K. Ramachandran. *Int. J. Mod. Phys. B.* 2010, **24**, 1289-1298.
36. Q. Yu, C. Yu, H. Yang, W. Fu, L. Chang, J. Xu, R. Wei, H. Li, H. Zhu, M. Li and G. Zou, *Inorg. Chem.* 2007, **46**, 6204-6210.
37. S.D.G. Ram, G. Ravi, A. Athimoolam, T. Mahalingam and M.A. Kulandainathan, *Appl. Phys. A*. 2011, **105**, 881-890.
38. C. Li, G. Hong, P. Wang, D. Yu and L. Qi, *Chem. Mater.* 2009, **21**, 891-897.
39. X. Pan, M.-Q. Yang and Y.-J. Xu, *Phys. Chem. Chem. Phys.* 2014, **16**, 5589-5599.
40. Z. Sharifzadeh, S. Abedi and A. Morsali, *J. Mater. Chem. A*. 2014, **2**, 4803-4810.

41. S. Sun, X. Zhang, J. Zhang, X. Song and Z. Yang, *Cryst. Growth Des.* 2012, **12**, 2411-2418.
42. L. Song, S. Zhang, X. Wu and Q. Wei, *Ind. Eng. Chem. Res.* 2012, **51**, 4922-4926.
43. L. Liu, Y. Chen, T. Guo, Y. Zhu, Y. Su, C. Jia, M. Wei, and Y. Cheng, *ACS Appl. Mater. Interfaces*, **2012**, 4, 17-23.
44. C. Cheng, Y. Shi, C. Zhu, W. Li, L. Wang, K. K. Fung and N. Wang, *Phys. Chem. Chem. Phys.* 2011, **13**, 10631-10634.
45. Y. Masuda, N. Kinoshita and K. Koumoto, *Electrochim. Acta.* 2007, **53**, 171-174.
46. N. Rajkumar, M. Prabhu and K. Ramachandran, *Int. J. Nanosci.* 2011, **10**, 87-92.
47. Q. Hu, G. Tong, W. Wu, F. Liu, H. Qian and D. Hong, *CrystEngComm* 2013, **15**, 1314-1323.
48. A. McLaren, T.V. Solis, G. Li and S. C. Tsang, *J. Am. Chem. Soc.* 2009, **131**, 12540-12541.
49. T. Ghoshal, S. Kar and S. Chaudhuri, *Cryst. Growth Des.* 2007, **7**, 136-141.
50. J.-M. Jang, S.-D. Kim, H.-M. Choi, J.-Y. Kim and W.-G. Jung, *Mater. Chem. Phys.* 2009, **113**, 389-394.
51. J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, *Chem. Mater.* 2002, **14**, 4172-4177.
52. Y. Sun, D. J. Riley and M. N. R. Ashfold, *J. Phys. Chem. B* 2006, **110**, 15186-15192.
53. M. Palumbo, T. Lutz, C.E. Giusca, H. Shiozawa, V. Stolojan, D. C. Cox, R. M. Wilson, S. J. Henley and S. R. P. Silva, *Cryst. Growth Des.* 2009, **9**, 3432-3437.
54. R. H. Zhang, E. B. Slamovich and C. A. Handwerker, *Nanotechnology* 2013, **24**, 195603-1-195603-11.
55. J. Liu, S. Lee, K. Lee, Y. H. Ahn, J.-Y. Park and K. H. Koh, *Nanotechnology* 2008, **19**, 185607-1-185607-7.
56. A.-J. Wang, Q.-C. Liao, J.-J. Feng, P.-P. Zhang, A.-Q. Li and J.-J. Wang, *CrystEngComm* 2012, **14**, 256-263.
57. N.P. Herring, L.S. Panchakarla and M.S. El-Shall, *Langmuir* 2014, **30**, 2230-2240.
58. T. Mahalingam, K. M. Lee, K. H. Park, S. Lee, Y. Ahn, J.-Y. Park and K. H. Koh, *Nanotechnology* 2007, **18**, 035606-1-035606-5.
59. M.R. Alenezi, S.J. Henley, N. G. Emerson and S.R.P. Silva, *Nanoscale* 2014, **6**, 235-247.
60. Q. Xie, J. Li, Q. Tian and R. Shi, *J. Mater. Chem.* 2012, **22**, 13541-13547.
61. Z. Chen and L. Gao, *Cryst. Growth Des.* 2008, **8**, 460-464.
62. S. Cheng, D. Yan, J. T. Chen, R. F. Zhuo, J. J. Feng, H. J. Li, H. T. Feng and P. X. Yan, *J. Phys. Chem. C* 2009, **113**, 13630-13635.
63. H.-T. Liu, X.-F. Zeng, H. Zhao and J.-F. Chen, *Ind. Eng. Chem. Res.* 2012, **51**, 6753-6759.
64. Y. -M. Hao, S. -Y. Lou, S.-M. Zhou, R.-J. Yuan, G.-Y. Zhu and N. Li, *Nanoscale Res. Lett.* 2012, **7**, 1-9.
65. P.R. Potti and V.C. Srivastava, *Ind. Eng. Chem. Res.* 2012, **51**, 7948-7956.
66. J. Han, F. Fan, C. Xu, S. Lin, M. Wei, X. Duan and Z. L. Wang, *Nanotechnology*, 2010, **21**, 405203-1-405203-7.
67. M. Marikkannan, V. Vishnukanthan, A. Vijayshankar, J. Mayandi, and J. M. Pearce, *AIP Advances*, 2015. **5**, 027122-1-027122-8.

68. R. Marczak, F. Werner, R. Ahmad, V. Lobaz, D.M. Guldi, W. Peukert, *Langmuir* 2011, **27**, 3920–3929.
69. B. Weintraub, Y. Wei and Z.L. Wang, *Angew. Chem. Int. Ed.* 2009, **48**, 1- 6.
70. F. Yan, L. Huang, J. Zheng, J. Huang, Z. Lin, F. Huang and M. Wei, *Langmuir* 2010, **26**, 7153-7156.
71. N.K. Huu, D-Y. Son, I-H. Jang, C-R. Lee and N-G. Park, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1038-1043.
72. M. Xu, S. Wenger, H. Bala, D. Shi, R. Li, Y. Zhou, S.M. Zakeeruddin, M. Gratzel, and P. Wang, 2009, *J. Phys. Chem. C*, **113**, 2966-2973.
73. C. Zhang, J. Gwamuri, R. Andrews and J. M. Pearce, 2014, *International Journal of Photoenergy*, **2014**, 1-7.

Figure Captions:

Figure 1. X- ray diffraction patterns of ZnO (a) Z1, (b) Z2, (c) Z3, and (d) Z4.

Figure 2. Low magnification SEM images of Z1, Z2, Z3, & Z4.

Figure 3. SEM images of peanut-shaped ZnO microstructures (a, b) Z1 and (c, d) Z2.

Figure 4. SEM images of peanut-shaped ZnO microstructures (a, b) Z3 and (c, d) Z4.

Figure 5. (a) Histograms derived from the SEM images showing particle size distribution (b) Normalized NH₃ concentration Vs Aspect ratio.

Figure 6. Schematic illustration of the stepwise growth mechanism of peanut-shaped ZnO microstructures.

Figure 7. UV-Vis absorption spectrum and α -absorption plot of peanut-shaped ZnO microstructures.

Figure 8. PL spectrum of peanut-shaped ZnO microstructures.

Figure 9. FTIR spectrum of peanut-shaped ZnO microstructures.

Figure 10. Current density-voltage (I–V) curves of preliminary peanut-shaped ZnO-based DSSCs.

Samples	NH ₃ Conc. (mM)	[NH ₃ /Zn ²⁺] Ratio	Average crystallite size (nm)	Relative Intensity		Lattice Parameters (Å)
				I ₍₁₀₀₎ /I ₍₀₀₂₎	I ₍₁₀₁₎ /I ₍₀₀₂₎	
Z1	45	3	27	1.2968	1.8614	a: 3.253(1) c: 5.215(2)
Z2	60	4	32	1.1159	1.7484	a: 3.251(1) c: 5.209(2)
Z3	65	4.3	30	1.4916	2.0712	a: 3.250(1) c: 5.209(3)
Z4	70	4.6	33	1.5608	1.9050	a: 3.251(1) c: 5.213(6)

Table 1. Average crystallite size, relative intensity and lattice parameters of ZnO samples formed with various [NH₃/Zn²⁺] ratios.

Samples	J _{sc} (mA/cm ²)	V _{oc} (V)	J _{max} (mA/cm ²)	V _{max} (V)	FF	η (%)
Z1	0.352	0.414	0.279	0.282	0.542	0.20
Z2	0.797	0.351	0.602	0.243	0.524	0.37
Z3	0.296	0.302	0.187	0.192	0.402	0.09
Z4	0.184	0.417	0.107	0.253	0.351	0.07

Table 2. Photovoltaic Performance of peanut shaped ZnO-based DSSCs

Morphology	Synthesis technique	Photosensitizer	Efficiency %	Reference
Nanowire arrays	Hydrothermal method	N719	0.12	40
Nanoparticles	Simple collide method	N719	0.37	68
Nanowire arrays	Wet-chemical method	N719	0.44	69
Nanowires forest	Hydrothermal method	N719	0.45	5
Nanoflower	Hydrothermal method	N719	0.51	70
Nanorod	Sol-gel method	N719	0.54	71
Groundnut microstrucutres	Chemical precipitation method	Eosin yellowish	0.37	This work

Table 3. Comparison of efficiency of DSSCs sensitized with N719 dye based on different ZnO nanostructures.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig.5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10