ZnO nanoflowers-based photoanodes: Aqueous chemical synthesis, microstructure and optical properties

DOI 10.1515/chem-2016-0016
received June 30, 2016; accepted July 29, 2016.

Abstract: We have developed an efficient, low temperature, synthetic route for ZnO nanoflowers (NFs) as photoanode material. This alternative route yields small flower-like nanostructures, built from densely self-assembled tip-ended rod structures. The obtained ZnO NFs possess a large bandgap of 3.27 – 3.39 eV, enabling the generation of an average open current voltage of 0.56 V. Additionally, they show a high internal light harvesting of $14.6 \cdot 10^{-7} \text{A} \cdot \text{mol}^{-1}$. The growth mechanism and self-assembly of ZnO NFs were studied in detail by joint spectroscopic-TEM investigations. It is shown that the ZnO crystallite size increases with increasing annealing temperatures and that the stress and the improved crystallinity are induced by annealing and reduce the lattice strain and the dislocation density. The bandgaps of ZnO are affected by the lattice strain revealing an optimal region of lattice strain to gain high bandgap energies. The properties of the synthesized ZnO NFs are compared with other morphologies, i.e. ZnO spherical aggregates (SPs) and ZnO nanorods (NRs), and are tested as electrode materials in dye-sensitized solar cells.

Keywords: ZnO nanoflowers, Microstructures, Bandgap, Light harvesting, Dye-sensitized solar cell

1 Introduction

Zinc oxide (ZnO), an n-type metal oxide semiconductor with a band-gap of 3.37 eV and a large exciton binding energy of ~ 60 meV at room temperature [1,2], has recently attracted attention owing to its versatile properties and rich possibilities to form various nanostructures [3]. The properties of ZnO including its piezoelectricity [4], electrical conductivity [5], biocompatibility [6], and UV-visible luminescence [7], have led to numerous applications in various fields including piezoelectric devices [4], biolabelling [8], light emitting diodes [9], and short-wavelength nanolasers [10]. In the last decade, ZnO has also been considered in the context of photoelectrochemical cells [11–13], such as dye-sensitized solar cells (DSSCs). In principle, DSSC generate photocurrent by electron injection from a sensitizer into the excited state into the conduction band of ZnO and the photovoltage is determined by the difference between redox potential and the fermi level of ZnO. Also, ZnO has a similar optical bandgap and similar conduction and valence band energies as TiO$_2$, the widely used photoanode material for DSSCs. Moreover, due to its high electrochemical stability, slightly higher conduction band edge, and an electron mobility of ~150 cm$^2$ V$^{-1}$ s$^{-1}$ [2], the use of ZnO could allow for the generation of a higher photovoltage and a rapid charge collection. ZnO is considered to be an attractive photoanode material, despite the yet lower efficiency e.g. in ZnO-based DSSCs with respect to TiO$_2$-based devices as a consequence of a higher charge recombination rate [13–15]. However, ZnO-based photoanodes are available via low-temperature synthetic methods.

Considerable efforts have been undertaken to develop new ZnO structures for efficient photoanode materials [11–
It is known that different ZnO morphologies critically influence the properties of ZnO including microstructural properties, optical bandgap and surface defect characteristics [2,16], which are substantial parameters for optimizing the performance of the material for applications in photoanodes [13]. Various ZnO morphologies have been investigated such as 3D morphologies based on spherical aggregates with increased surface area and pore structure for optimal dye sensitization and regeneration [15,17]. Aggregate sizes comparable to the light wavelength extend the optical path length of scattered light within the photoanode and improve the light harvesting efficiency [17]. On the other hand, the use of 1D ZnO morphologies, such as ZnO nanowires and ZnO nanorods, was shown to be advantageous for rapid electron collection because of the accessibility of the direct conduction paths for electrons and the increase of the electron transport within the photoanodes [18]. Efforts to combine the virtues of both 3D and 1D ZnO nanostructures have been undertaken by developing either randomly branched nanorods or nanoflower structures which show an enhanced light-dye interaction without sacrificing the electron transport properties [18–20]. However, further efforts are required to optimize the photoanode parameters, including the surface properties, such as surface correlated bandgap energies, dislocation and defect properties as well as electron transport. For the synthesis of ZnO nanoflowers a couple of routes were developed, such as chemical vapor deposition [21], pulsed laser deposition [22], and hydrothermal methods [19,23]. Despite the success of these methods to prepare ZnO nanoflowers with controllable morphology, these methods require processing at high pressure or temperature and have limitations with regard to the yield of ZnO nanoflowers. Low-temperature processing of ZnO nanoflowers is possible through aqueous chemical approaches and was shown to gain high-quality crystalline ZnO [24–26]. The simplicity and flexibility of an aqueous chemical process allows for facile scale up of the synthesis. Nonetheless, the architectural order and control of the resulting morphologies and hence the properties, remain the ultimate challenge in the development of ZnO nanoflower-based photoanodes.

We report an alternative low-temperature aqueous-chemical synthetic route (90 °C in ambient atmosphere) to ZnO nanoflowers with shorter reaction times and milder conditions, as compared to the procedures reported in literature [24–30]. The developed synthesis yields small sized nanoflowers, basing the synthesis on a zinc nitrate/hexa-methylenetetramine (HMTA) system and using a low concentrated weak base growing solution. The formation and the growth mechanism of the reported ZnO nanoflowers are discussed on the basis of joint spectroscopic and TEM investigations. The thermodynamics and kinetic parameters during thermal degradation and crystallization as well as the purity of ZnO nanostructures were analyzed using differential scanning calorimetry/ thermogravimetric analysis (DSC/TGA) and FTIR spectroscopy, respectively. Thermal treatment up to the crystallization temperature was applied in order to modify the microstructural properties. In order to elucidate the structural origin of the affected optical properties, a detailed microstructural analysis on X-ray diffraction data supported by the HRTEM measurement was carried out. UV–vis absorption and photoluminescence studies were conducted to elucidate the features of the optical bandgap and the visible emissions that are correlated with the microstructural properties. Additionally, the microstructural and optical properties are compared with wet-chemically synthesized ZnO spherical aggregates and ZnO nanorods. The different ZnO morphologies, namely nanoflowers, spherical aggregates and nanorods, are compared in a benchmark DSSC. ZnO nanoflowers prepared in this work revealed an enhanced internal light scattering and comparable efficiency with respect to the benchmark ZnO spherical aggregate photoanodes.

2 Experimental

2.1 Synthesis of ZnO Nanostructures

All chemicals were of analytical grade and were used without further purification. ZnO nanoflowers (NFs) were synthesized using a seeding procedure prior to the growth. The seed solution, containing 0.15 M of Zn(CH₃COO)₂·2H₂O in 20 ml of an ethanol-water mixture (70:30 %v/v), was stirred for 1 h at 60 °C. The obtained suspension was filtered and then spin coated onto transparent conductive oxide (TCO) glass slides. The coated glass was then annealed at 350 °C for 30 min before being placed into the flask containing the growth solution and being heated at 90 °C for 5 h. The growth solution of ZnO nanoflowers was prepared based on zinc nitrate and hexa-methylenetetramine (HMTA) system, which is, together with strong base reactants (KOH, NaOH, LiOH), known to prepare either ZnO nanorods or ZnO nanoflowers [27–30]. In contrast to the synthetic approaches published to date [19,24–30], which required high pressure in an autoclave, elevated temperatures (100 – 200 °C) and long reaction times (10 – 24 h), the here-reported synthetic route
employed temperature treatment of only 90 °C for 5 h and was undertaken in ambient atmosphere. Specifically, the growth solution contained 10 ml of 30% ammonia solution, 340 mL of distilled water, 5.205 g of Zn(NO$_3$)$_2$·6H$_2$O and 1.227 g of HMTA. Thereafter, the TCO glass was taken out of the solution and subsequently cleaned with distilled water. For the sake of reproducibility, the synthesis was undertaken in triplicate.

Other morphologies including ZnO spherical aggregates (SPs) and ZnO nanorods (NRs) were synthesized according to our previous studies [31,32]. ZnO SPs were synthesized in a two-step procedure [31]. In the first step, 0.1M Zn(CH$_3$COO)$_2$·2H$_2$O in 100 ml of diethylene glycol (DEG) was heated under reflux at 180 °C and stirred for 1h. The mixture was cooled to room temperature and the precipitate was removed by centrifugation. The supernatant (composed of remaining DEG, unreacted Zn(CH$_3$COO)$_2$·2H$_2$O, water and other dissolved reaction products) was kept for the second step: a solution of 0.1M Zn(CH$_3$COO)$_2$·2H$_2$O in 100 ml of DEG was heated without stirring. Upon reaching 140 °C, 5 ml of the supernatant solution from step one was added, followed by a temperature drop and the precipitation of ZnO. The resulting reaction solution was further heated to 160 °C and stirred at this temperature for 1h. Cooling to room temperature and subsequent centrifugation engendered monodisperse ZnO SPs. ZnO NRs were synthesized using ethylene glycol (EG) as solvent [32]. An amount of 0.033 M Zn(CH$_3$COO)$_2$·2H$_2$O in 80 mL of EG was stirred and heated in Si-oil bath at 200 °C for 5 h. When the solution temperature reached 100 °C, 40 mL of water was injected into the solution which was then continuously stirred and heated. The resulting white precipitation was cooled down and the white suspension was filtered from the remaining solution.

### 2.2 ZnO Characterizations

The morphologies of the ZnO nanostructures were investigated with field emission scanning electron microscopy (FESEM, JEOL JSM6300F) operating at 5 kV accelerating voltage. In order to avoid charging, the samples were coated with few nm of Pt. For more detailed structural insights into the ZnO nanostructures as well as the formation of intermediate states in nucleation, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out by using a JEOL JEM-3010HT equipped with a LaB$_6$ cathode operating at 300 kV. Specific surface areas were determined through multipoint BET (Brunauer-Emmett-Teller) test under N$_2$ atmosphere (Autosorb-1, Quantachrome) at 77 K. The ZnO powder was heated at 350 °C for evaporating the remaining water from the surface prior to the physisorption test. For TGA/DSC measurements (Mettler Toledo Star-e), 11.5 – 13.5 mg of ZnO samples were placed in a crucible under N$_2$ atmosphere and heated from 36 to 1000 °C with a heating rate of 10K/min. FT-IR transmission spectra of ZnO nanostructures were measured on a Thermo Scientific Nicolet iS10 over the range of 400 – 4000 cm$^{-1}$. The crystal structures of the powders were determined through powder X-ray diffraction (XRD) with a PANalytical X’pert diffractometer (40 kV, 40 mA). Diffraction patterns were obtained for 15° – 70° (2θ) by step scanning with a step size of 0.02°. The X-ray radiation used consists of both Cu K$_\alpha$ (transition K$_{cu}$; $\lambda$=1.54056 Å) and Cu K$_\beta$ (transition K$_{cb}$; $\lambda$=1.54439 Å). In cases having sufficiently narrow peaks, Cu K$_\alpha$ appears as a small shoulder with approximately 10% intensity on the high angle side of a given peak. All the diffraction data was Rietveld-refined for further analysis. The phase analysis was undertaken by comparison with a JCPD Standard (No. 75 – 576). UV-vis absorption spectra were measured on a UV-Vis-NIR spectrophotometer (Varian Cary 5000) in the wavelength range between 200 and 800 nm. The room temperature emission spectra were recorded with a Perkin Elmer LS-50 instrument upon excitation at 320 nm as provided by a Xenon lamp.

### 2.3 DSSC Fabrication and Characterization

To fabricate DSSCs, ZnO pastes consisting of ZnO powders, ethyl cellulose and terpineol (weight ratio of 1:5:10) were deposited on FTO substrates using doctor-blading and subsequently annealed at 300 °C. The ZnO photoanodes were dye-sensitized by soaking them in a 0.5 mM ethanolic solution of either N719 ([([C$_{6}$H$_{5}$])$_{3}$N]$_{2}$RuL$_2$(NCS)$_2$) L:2,2’-bipyridine-4-carboxylic acid-4’-carboxylate) or N749 ([([C$_{6}$H$_{5}$])$_{3}$N]$_{2}$[Ru-{(Hcterpypy)(NCS)$_2$}] terpy: 4,4’,4”-tricarboxy-2,2’,2’’-terpyridine; black dye). The redox couple $I_{1}/I_{2}$, containing 0.5 M tert-butylammonium iodide, 0.1 M Lithium iodide, 0.1 M iodine and 0.5 M 4-tert-butylpyrididine, was used. Platinized FTO was utilized as the counter electrode. The photoelectrochemical properties of DSSCs were characterized by current-voltage (I-V) measurements under 100 mWcm$^{-2}$ irradiation intensity using a solar simulator (SS-80 PET) equipped with an AM1.5 filter.
3 Results and discussion

3.1 Growth Mechanism and Micromorphology of ZnO Nanoflowers

In the following, first the growth mechanism as well as the self-assembly on the ZnO nanoflowers will be discussed based on a joint spectroscopic-TEM investigation (see Fig. 1). While there have been several reports on mechanistic investigations for the formation of ZnO nanostructures synthesized from Zn(NO$_3$)$_2$$\cdot$6H$_2$O and HMTA (CH$_2$$_6$N$_4$) [33], no explicit model regarding the self-assembly of ZnO NFs has yet emerged [34,35]. Elucidations the synthetic state of the nucleation and the early growth of ZnO NFs are essential for further control of self-assembly ZnO nanostructures. While the number of nucleation sites critically affects the self-assembly during NF growth, the length of the ZnO-NF petals can be controlled in the stage of early growth.

To investigate the different conditions within the synthesis of ZnO and to elucidate the growth mechanism of each ZnO micromorphology, a total of six solutions were sampled at different times and solution temperatures during the synthesis reaction and were subsequently characterized by UV-Vis absorption spectroscopy (see Fig. 2A). In the synthesis of ZnO NFs, HMTA is hydrolyzed in water forming ammonia, which acts as a weak base and as a buffer [36,37]. In addition, the low concentration of OH$^-$ facilitates relatively high nucleation rates [38]. In the resulting solution the Zn$^{2+}$ ions react with ammonia to form $[\text{Zn(NH}_3]_4]^{2+}$. The clear reaction solution, obtained from zinc nitrate and HMTA turns white upon addition of NH$_4$OH and minimal precipitation occurs (see state 2 in Fig. 2B). Supersaturated conditions are achieved in this stage [39]. The hydrolysis and decomposition reaction to $[\text{Zn(OH)}_4]^{2-}$ can be followed in the absorption spectra indicated by the absorption peak of $[\text{Zn(OH)}_4]^{2-}$ at 301 nm (Fig. 2A) [40]. This absorption peak increases at higher temperature and longer synthesis time since more $[\text{Zn(OH)}_4]^{2-}$ is formed. A dehydration reaction of $[\text{Zn(OH)}_4]^{2-}$ at higher temperatures eventually forms ZnO nuclei with excess OH$^-$ (the reaction mechanism can be found in Fig. 1). Absorption and baseline shift in the visible region (Fig. 2A) are ascribed to the formation of larger nuclei and the presence of defect states as can be seen in the emission spectra (Fig. 2B). These defect states increase during the growth of ZnO nuclei resulting in higher visible emission. The visible emissions observed at 425, 486, 530, and 575 nm could stem from the electronic transition between either zinc interstitial or oxygen vacancies and valence band [1,2]. A weak absorption peak at 375 nm was found when the temperature reached approximately 90 °C (cf. state (5) and state (6) in Fig. 2A), which is attributed to the early growth of ZnO.

At a low temperature, the reaction will form ZnO with small aspect ratios (length/diameter), low densities and hexagonal-ended nanorods. Upon increasing the temperature, the hexagonal-ended nanorod-morphology transforms into prism-ended nanorods on the account of...
electrostatic interactions between ions within the reaction solution and the polar surface of ZnO [41]. According to the TEM image in Fig. 2C–2D, an intermediate structure is observed reminiscent of individual screw driver structures, which subsequently assemble into flower-like structures in active sites provided by the seeding layer. Fig. 2G–2I shows a micrograph of ZnO NFs. This hierarchically structured nanoflower with an average size around 2 to 2.5 µm is formed by radial arrangement of tens of prism-ended rod-like nanostructures. Each petal is approximately 0.5 – 1.0 µm long, 200 nm in diameter and has a tip width of 20 nm. To the best of our knowledge, these nanoflowers are significantly smaller than other reported ZnO nanoflower structures (average diameters of 4 – 8 µm) [27–31]. These features may be beneficial for generating high internal light harvesting, i.e. potentially improving the light-scattering within the anode material, and relatively high surface areas for photoanodes application – an effect that is further discussed below. For a comparative study, the growth mechanism of ZnO SPs and ZnO NRs and more SEM/TEM images of the early growth ZnO nanostructures can be found in Supporting Information.

3.2 FTIR Study and Thermal Analysis

In order to assess the purity of the ZnO structures under different thermal treatments, infrared absorption studies were performed. Fig. 3A – 3C depicts the infrared absorption spectra of ZnO samples at different annealing temperatures. At 100 °C a series of IR absorption bands between 3500 and 1000 cm$^{-1}$ is observed, which corresponds to carboxylate and hydroxyl impurities: A broad peak between 3500 and 3200 cm$^{-1}$ is attributed to the O–H stretching of the hydroxyl group from water molecules [42]. For ZnO NFs, which are synthesized from Zn(NO$_3$)$_2$·6H$_2$O as precursor, the band at 1363 cm$^{-1}$ reflects the symmetric stretching vibration of NO$_3$$^{-}$ [43]. The peaks observed at 1550 and 1665 cm$^{-1}$ for ZnO SPs and ZnO NRs can be ascribed to the C=O vibration modes of the carboxylate group [44]. All C=O and O–H bands eventually disappear at 300 °C as shown in Fig. 3B and 3C. The infrared absorption data show that all ZnO samples with their impurities existing at low temperatures are transformed into a more pristine ZnO upon elevating the annealing temperatures. The characteristics of the metal oxide itself are represented by the Zn–O deformation mode at 621 cm$^{-1}$. Furthermore, the band at 508 cm$^{-1}$ may be associated with oxygen vacancies which are inherent defects in ZnO [45].

The influence of the thermal treatment on ZnO decomposition as well as the crystallization offset was investigated. The DSC thermograms, i.e. the heat flow curves in Fig. 3D – 3F, reveal weak endothermal peaks below 250 °C and weak exothermal peaks at 356, 285, and 345 °C for ZnO NFs, ZnO SPs and ZnO NRs, respectively. These exothermal peaks can be assigned to the minimum energy required to form native ZnO. Correspondingly, as depicted in Fig. 3, the least amount of energy that is explicitly related to the temperature at which the exothermic peak occurs is required to form ZnO SPs with high crystallinity. According to the TG(T), it is clear that all ZnO structures undergo several stages of decomposition followed by weight loss. The differences in their thermal decomposition can be seen more clearly in the derivative thermogravimetric (DTG) curves depicted in the inset of Fig. 4. As observed in the infrared spectra presented before, the weight loss in the first thermal decomposition region, i.e. within temperatures up to 250 °C concomitant with weak endothermal peaks in DSC thermogram, is due to the evaporation of water and volatilization of small molecules from the ZnO surface. The weight loss at higher temperatures, which is accompanied by the presence of an exothermal peak on the DSC thermogram, is generally believed to be due to crystallization.

The kinetic analysis of thermal decomposition of ZnO was carried out by reviewing the dynamic weight
loss data. The thermodynamical activation parameters of the decomposition process were graphically evaluated by employing the Coats–Redfern relation for first order kinetics [46]:

\[
\log_{10} \left( \frac{1 - \alpha}{T^2} \right) = \log_{10} \left( \frac{AR}{hE} \right) \frac{2RT}{E} - \frac{E}{2.3RT} \quad (1)
\]

where \( \alpha \) is the fraction of mass decomposed at temperature \( T \), \( A \) is the pre-exponential factor associated with Arrhenius constant, \( R \) is the universal gas constant, \( h \) is the linear heating rate, \( E \) is the activation energy measured in J mol\(^{-1}\). As shown in Fig. 6, the plot of left hand side of Eq. (1) against 1/T results in a nearly linear curve, the slope of which is proportional to the activation energy of \( -E/2.3R \). The magnitude of activation energy (\( \Delta E^* \)), activation entropy (\( \Delta S^* \)), activation enthalpy (\( \Delta H^* \)) and Gibbs-free energy change of decomposition (\( \Delta G^* \)) for the high temperature decomposition region of ZnO NFs, ZnO SPs, and ZnO NRs are summarized in Table S1 (SI†). Apparently, the activation energy of ZnO SPs (401 kJ ∙ mol\(^{-1}\)) is smaller than that of ZnO NFs (493 kJ ∙ mol\(^{-1}\)) and ZnO NRs (547 kJ ∙ mol\(^{-1}\)). These results are consistent with the DSC analysis. In addition, the values of \( \Delta E^* \), \( \Delta S^* \) and \( \Delta H^* \) increase with increasing temperature. This indicates that elevated temperatures cause an increased thermal mobility (\( \Delta G^* \)), an increased stability (\( \Delta H^* \)) and a decreased order (\( \Delta S^* \)) of the ZnO. Combined thermodynamic and FTIR analysis show that the crystallization onset of various ZnO nanostructures is approximately 300 – 350 °C, but the impurities and defects are still present in ZnO. This suggest that annealing at temperature equal to or higher than 300 °C is required to prepare ZnO-based photoanode.

3.3 Microstructural Analysis

The evolution of the ZnO bandgap, is commonly considered to be related to morphological changes [47,48]. Nonetheless, combined theoretical and experimental studies point to the possibility of tuning the bandgap of nanocrystalline metal oxides by using microstructural parameters, such as the lattice mismatch and lattice strain [48]. Microstructural variations in this investigation are caused by thermal treatment in the regime of low annealing temperatures up to the crystallization onset of native ZnO as previously discussed in the context of the thermal analysis. This thermally-induced lattice strain modifies the intrinsic interatomic spacing and thus changes the energy levels of the bonding electrons [48]. This significantly alters the electronic and optical properties, including the absorption and emission band edges as the most prominent parameters [47,48]. The resulting microstructural properties, such as crystallite size, microstrain, dislocation density and lattice stress, were evaluated using XRD and HRTEM measurements: Fig. 5 depicts the XRD pattern of the ZnO NFs annealed at different temperatures and Fig. 6 displays both TEM and HRTEM of the ZnO nanostructures before and after annealing. All diffraction peaks can be indexed as hexagonal wurtzite ZnO [49]. Sharper (narrower peaks with lower FWHM) and more intense peaks, observed at 400 °C, are an indicator of increased crystallinity. The position of the (1 0 0), (0 0 2), (1 0 1) peaks is shifted to a larger 2θ upon increasing the annealing temperature.

It is known that thermal treatment of ZnO nanoparticles can enlarge the crystallite size during the grain and crystal growth. Hence, the mean crystallite size D for each annealing temperature was estimated from the line broadening of the XRD patterns according to the Debye-Scherrer equation. The respective analysis reveals that the average crystallite size of ZnO increases as the annealing temperature increases (see Fig. 5B). However, the ZnO crystallite sizes obtained by annealing at 300 °C are slightly lower compared to those samples annealed at 200 °C, which may correspond to higher lattice stress upon the onset of crystallization (see Fig. 5C). The crystallite size of ZnO NFs, ZnO SPs, and ZnO NRs varies from 27 ± 1.1 to 32 ± 1.0, 15 ± 1.3 to 19 ± 0.5, and 57 ± 2.3 to 72 ± 2.4 nm, respectively, depending on the annealing temperature. As described above, the lattice strain
contributes to the FWHM of the XRD peaks as it causes densification and localization of charge, energy, and mass within the surface of the nanostructures. As the annealing temperature increases from 100 to 400 °C, the average lattice strain of ZnO NFs decreases from $2.2 \times 10^{-3}$ to $1.8 \times 10^{-3}$, whereas the average lattice strain of ZnO SPs and ZnO NRs is reduced from $4.1 \times 10^{-3}$ to $3.2 \times 10^{-3} and $1.2 \times 10^{-3}$ to $9.9 \times 10^{-4}$, respectively. The deviant of (1 0 0), (0 0 2) and (1 0 1) peaks could be the result of the defect concentration and the reduced deviation from the reference peak after annealing indicates the relaxation of defects [50].

In general, the unit cell volumes as well as the microstrains decrease with increasing crystallite sizes upon annealing. This is corroborated by HRTEM measurements shown in Fig. 6. The lattice fringes show the $d$ spacing of (1 0 0), (0 0 2) and (1 0 1) crystallite plane for the unannealed and the annealed ZnO NFs and ZnO SPs. The $d$ spacing was determined from the HRTEM images by applying a fast Fourier transformation (FFT). The maxima in the resulting FFT diffractograms enable a precise quantification of the average $d$ spacing sampled over the entire image. ZnO NFs exhibit $d_{(1 0 0)}$ and $d_{(0 0 2)}$ values of 2.86 and 2.65 Å prior to annealing, respectively. Upon annealing lattice spacings decrease to 2.84 and 2.63 Å for $d_{(1 0 0)}$ and $d_{(0 0 2)}$, respectively, which is consistent with a shrinking of the unit cell volumes after thermal treatment. Correspondingly, the annealed ZnO SPs and ZnO NRs exhibit shorter $d_{hkl}$ than that of the unannealed ZnO SPs and ZnO NRs.

As previously mentioned, microstrain can be promoted by dislocation, which constitutes a crystallographic defect affecting the electronic properties of ZnO, such as the conduction band edge and the defect level. When the annealing temperature increases, the dislocation density of ZnO NFs decreases from $2.7 \times 10^{15}$ to $1.9 \times 10^{15}$ lines/m$^2$. The dislocation density of ZnO NFs and ZnO NRs also decreases upon increasing annealing temperatures. The dislocation density declines due to the formation of higher crystallinity of ZnO and the decreasing of defect concentrations that originate from oxygen vacancies [51].

The enhanced crystallinity and the decreasing oxygen vacancies of ZnO can be investigated by evaluating the electron density distribution. The three-dimensional Fourier map of electron density reveals bonding electrons around the center of the Zn–O bonds in the $c$-direction for ZnO NFs annealed at 300 °C (see Fig. 5E–5F). Additionally, the 2D electron density maps at annealing temperatures of 200 °C show the localization of positive electron density near the O atom and negative contributions are observed around Zn atom. The negative distribution could be related to the atomic structural disorder around the Zn atom baring higher dislocations and defects at low annealing temperatures. The progressive changes observed at higher annealing temperatures of 300 °C could be attributed to self-displacement of electron density to the center of the Zn-O bond during crystallization. This reveals that crystallization starts at an annealing temperature of 300 °C which is in a good agreement with previously discussed in thermal analysis. A further increase of the annealing temperature leads to increased oxygen diffusion which occupies oxygen vacancies and hence reduces the dislocation density [52].
UV-Vis absorption spectra of ZnO nanostructures at different annealing temperatures are depicted in Fig. 7. At room temperature, a typical exciton absorption in the range of 373 – 385 nm is observed. This band is red-shifted (ca. 0.08 eV) upon increasing the annealing temperature and thus upon formation of larger particles. The pronounced red-shift results from debilitated quantum confinement effect altering the ZnO energy band. Fig. 7A shows that the absorption band is broadened at higher annealing temperature and its intensity decreases, implying that a distribution of large particle dominates the electronic transition [2,35,48,53]. In addition, the absorption onset in the visible absorption spectra indicates that the formation of ZnO nanostructures is followed by the presence of a high concentration of defects, which is typically observed for ZnO synthesized through a wet chemical synthetic route [35].

For further analysis, the ZnO crystal radius can be determined by exploring the effective mass approximation [54]:

\[
E_g \approx E_{g}^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2ea^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon a}
\]  

where \(E_g\) is the bandgap energy in eV, \(E_{g}^{\text{bulk}}\) is the bulk bandgap energy of ZnO (3.20 eV) [54], \(\hbar\) is reduced Planck’s constant, \(a\) is the particle radius, \(m_e^*\) is the effective mass of electrons, \(m_h^*\) is the effective mass of holes, \(e\) is the elementary charge, \(\varepsilon\) and \(\varepsilon_0\) are the relative permittivity and the permittivity of free space, respectively. Depending on the ratio of the crystal radius to the bulk exciton Bohr radius (\(a_B \approx 2.34\) nm) [54], the quantum confinement effect of ZnO crystals with the radius, \(a\), are categorized into a weak confinement regime \((a \gg a_B)\), an intermediate confinement regime \((a > a_B)\) and a strong confinement regime \((a < a_B)\). The quantum confinement effects can be associated with the tunability of optical properties of the obtained ZnO upon microstructural alteration [1,47,48]. According to the fitted result, the smallest crystalline radii for ZnO NFs, ZnO SPs, and ZnO NRs are 3.2, 2.9, and 3.5 nm, respectively. These results report a stronger quantum confinement effect in ZnO SPs followed by ZnO NFs with a moderate confinement effect. Hence, the optical bandgap of ZnO NFs are moderately tunable.
compared to the other morphologies as indicated by the shifted-absorption peak in the absorption spectra upon changing the thermal treatments.

The absorption coefficient ($\alpha$) is strongly dependent on the photon energy at the onset of the near UV absorption (Fig. 7). Therefore, the optical bandgap ($E_g$) of ZnO can be estimated by assuming that a direct transition of electrons between the valence band and the conduction band can be explained by the following relation [55]:

$$\alpha (\nu) = \frac{A (h\nu - E_g)^{3/2}}{h\nu}$$

where $\alpha$ is the absorption coefficient defined by Lambert-Beer’s law, $A$ is a proportionality constant, $h\nu$ is the photon energy, and $E_g$ represents the optical bandgap. The functional dependences of $(\alpha h\nu)^2$ vs. $h\nu$ are exhibited in Tauc plots (see inset Fig. 7A–7C). The extrapolation of the linear portion of the curves to zero absorption has been used to estimate the direct bandgap: $E_g$ values of 3.27 – 3.39, 3.04 – 3.21, and 3.07 – 3.36 eV are obtained for ZnO NFs, ZnO SPs, and ZnO NRs, respectively. Fig. 7D shows the bandgap as a function of annealing temperature and lattice strain. In a pictorial view, higher energy gaps of ZnO are obtained by using annealing temperatures of $100^\circ C$, i.e. keeping the metal oxide close to the equilibrium.

Interestingly, ZnO lattice strain ranging between 0.002 and 0.003 is found to be the optimal region of strain to obtain a higher bandgap. In addition, the absorbance in the near band-edge reveals an exponential dependence on the photon energy (see Tauc plots), which corresponds to the Urbach energy. The Urbach energy correlates with the tail width of the localized states in the bandgap due to microstructural disorder [55]. The tail width of ZnO NFs, ZnO SPs, and ZnO NRs tends to increase with increasing annealing temperature (see the detailed value in SI†). A longer tail width is indicative for deep trapping states, which in turn affect the transport properties of ZnO.

### 3.5 Photoelectrochemical Performance of ZnO-based DSSCs

In order to compare the performance of photoanodes made from the different ZnO nanostructures, dye-sensitized solar cells were fabricated using wet-chemically prepared ZnO NFs, ZnO SPs, and ZnO NRs. In this benchmark experiment, all tested ZnO photoanodes were annealed at $300^\circ C$, in order to remove all impurities (vide supra). The photocurrent density-voltage ($J-V$) curves of the ZnO based-DSSCs recorded under 100 mW·cm$^{-2}$ AM1.5 irradiation are presented in Figure 8. When using the N719 dye as sensitizer the $J-V$ curves reveal that the power conversion efficiencies of ZnO SPs-based DSSC ($\eta=3.3\%$, $V_{oc}=0.50$ V, $J_{sc}=17$ mA·cm$^{-2}$, fill factor ($FF$) = 0.39) is superior to those of ZnO NF- and ZnO NR-based DSSCs. The utilization of the black dye N749 enables ZnO NFs-based DSSC to perform high efficiency ($\eta=4.7\%$, $V_{oc}=0.57$ V, $J_{sc}=19.6$ mA·cm$^{-2}$, $FF = 0.42$) comparable to ZnO SPs-based DSSC (see the detail values in table S5) and two fold higher compared to ZnO nanoflowers-based DSSCs reported in literature.
Efficiencies of N749-sensitized ZnO solar cells in general are higher than that of N719-sensitized ZnO solar cells since N749 has broad visible absorption with higher extinction coefficient at wavelength longer than 600 nm (see Fig. S9) and hence enable light harvesting higher than N719. The overall performance of ZnO-based DSSCs can be correlated with the optical bandgap and the different morphologies. On one hand, the open circuit voltage $V_{OC}$ value, which is theoretically higher from the difference between the quasi Fermi-level of ZnO and the electrolyte redox potential, is slightly higher in ZnO NF and ZnO NR-based DSSC (see Fig. 8B). This result is in a good agreement with the previous analysis that revealed a higher bandgap (0.2 eV) in ZnO NFs and ZnO NRs than in ZnO SPs. On the other hand, the short circuit current density, $J_{SC}$, which depends on the surface area of the ZnO nanostructures, is higher in ZnO SPs-based DSSC since more dye can be adsorbed onto ZnO SPs (3.3 x 10^{-17} mmol cm^{-2}) than that onto ZnO NFs and ZnO NRs (1.2 x 10^{-17} mmol cm^{-2}). This result is corroborated with the surface characteristics of the ZnO nanostructures: the specific surface area of ZnO NFs, ZnO SPs, and ZnO NRs is 10.0, 30.7, and 12.9 m^{2}/g, respectively, and the pore volumes for ZnO NFs, ZnO SPs, and ZnO NRs are 0.033, 0.134, and 0.035 cm^{3}/g, respectively. However, the light harvesting of ZnO NFs and ZnO NRs, which is related to the photocurrent per mol sensitizer adsorbed on ZnO surface (Fig. 8C), is greater than that of SPs irrespective to the dye used in this study. The ZnO NFs and the ZnO NRs studied here show an increased internal light scattering compared to the ZnO SPs. This increased light scattering increases the light harvesting efficiency and might be used to construct an internal scattering layer of ZnO-based DSSC.

4 Conclusions

A facile aqueous chemical synthetic route towards synthesizing wurtzite-ZnO nanoflowers (NFs) is demonstrated. Insights into the growth mechanism for ZnO nanoflowers are derived. The optical bandgap of the synthesized ZnO nanostructures after annealing is comparable to the optical bandgap of bulk ZnO, while ZnO NFs possess a notably higher optical bandgap. Annealing affects the lattice strain which in turn affects the optical bandgap. Interestingly, the tunability of the bandgap shows a region of intermediate lattice strain optimal for obtaining high bandgap energies and affects the voltage generation in the DSSC performance. The hierarchically ZnO NFs studied here also show a suitable internal light harvesting, which is higher than that of the widely-used ZnO spherical aggregates. An extended bandgap tail, which reveals the presence of localized, defect associated states was observed, in dependence on the annealing temperatures. Further spectroscopic and electrochemical investigations will focus on this observation, since this points towards altered transport properties and the evolution of the defect concentration.

Acknowledgements: We thank the Deutscher Akademischer Austauschdienst (DAAD) for PhD Scholarship for RAW. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Information: Supplementary information associated with this article can be found in the online version.

Conflict of Interest: Authors declare no conflict of interest.

References

[1] Meyer B.K., Alves H., Hofmann D.M., Kriegseis W., Forster D., Bertram F., et al., Bound exciton and donor-acceptor pair recombinations in ZnO, Phys. Status Solidi Basic Res, 2004, 241, 231–260.
[2] Özgür Ü., Alivov Y.I., Liu C., Teke A., Reschiikv M.A., Doğan S., et al., A comprehensive review of ZnO materials and devices, J. Appl. Phys, 2005, 3, 98–103.
[3] Gao P.X., Ding Y., Wang Z.L., Crystallographic orientation-aligned ZnO nanorods grown by a tin catalyst, Nano Lett., 2003, 3, 1315–1320.
[4] Yin B., Qiu Y., Zhang H., Lei J., Chang Y., et al., Piezoelectric performance enhancement of ZnO flexible nanogenerator by a NiO-ZnO p-n junction formation, Nano Energy, 2014, 14, 95–101.
[5] Baxter J.B., Schmuttenmaer C.A., Conductivity of ZnO nanowires, nanoparticles, and thin films using time-resolved terahertz spectroscopy, J. Phys. Chem. B., 2006, 110, 25229–25239.
[6] Zhou J., Xu N., Wang Z.L., Dissolving behavior and stability of ZnO wires in biofluids: A study on biodegradability and biocompatibility of ZnO nanostructures, Adv. Mater., 2006, 18, 2432–2435.
[7] Wang H.Q., Wang G.Z., Jia L.C., Tang C.J., Li G.H., Polychromatic visible photoluminescence in porous ZnO nanotubes, J. Phys. D. Appl. Phys., 2007, 40, 6549 - 6553.
[8] Barui A.K., Veeriah V., Mukherjee S., Manna J., Patel A.K., Patra S., et al., Zinc oxide nanoflowers make new blood vessels, Nanoscale, 2012, 4, 7861–7819.
[9] Zhu L., Li C., Li Y., Feng C., Li F., Zhang D., et al., Visible-light photodetector with enhanced performance based on a ZnO@CdS heterostructure, J. Mater. Chem. C, 2015, 3, 2231–2236.
[10] Van Vugt L.K., Ruhle S., Vannmaekelbergh D., Phase-correlated nondirectional laser emission from the end facets of a ZnO nanowire, Nano Lett., 2006, 6, 2707–2711.

[11] Hassan N.K., Hashim M.R., Alam N.K., ZnO nano-tetrapod photoanodes for enhanced solar-driven water splitting, Chem. Phys. Lett., 2012, 549, 62–66.

[12] Wei Y., Ke L., Kong J., Liu H., Jiao Z., Lu X., et al., Enhanced photoelectrochemical water-splitting effect with a bent ZnO nanorod photoanode decorated with Ag nanoparticles, Nanotechnology, 2012, 23, 235401.

[13] Chen H.M., Chen C.K., Liu R.-S., Zhang L., Zhang J., Wilkinson D.P., Nano-architecture and material designs for water splitting photoelectrodes, Chem. Soc. Rev., 2012, 41, 5654–5671.

[14] Anta J.A.J., Guilién E., Tenaza-Raer R., Gilile E., ZnO-Based Dye-Sensitized Solar Cells, J. Phys. Chem. C, 2012, 116, 11413–11425.

[15] Zhang Q., Dandeneau C.S., Zhou X., Cao G., ZnO Nanostructures for Dye-Sensitized Solar Cells, Adv. Mater., 2009, 21, 4087–4108.

[16] Schmidt-Mende L., MacManus-Driscoll J.L., ZnO - nanostructures, defects, and devices, Mater. Today, 2007, 10, 40–48.

[17] Zhang Q., Chou T.P., Russo B., Jenekhe S.A., Cao G., Aggregation of ZnO nanocrystallites for high conversion efficiency in dye-sensitized solar cells, Angew. Chemie - Int. Ed., 2008, 47, 2402–2406.

[18] Jiang CY, Sun XW, Lo GQ, Kwong DL, Wang JX. Improved dye-sensitized solar cells with a ZnO-nanoflower photoanode. Appl. Phys. Lett. 2007;90:263501.

[19] Wang JX, Wu CML, Cheung WS, Luo LB, He ZB, Yuan GD, et al. Synthesis of hierarchical porous ZnO disklike nanostructures for improved photovoltaic properties of Dye-Sensitized solar cells. J. Phys. Chem. C. 2010;114:13157–61.

[20] Mir N., Salavati-Niasari M., Davar F., Preparation of ZnO nanoflowers and Zn glycerolate nanoplates using inorganic precursors via a convenient route and application in dye sensitized solar cells, Chem. Eng. J., 2012, 181-182, 779–789.

[21] Zhang N., Yi R., Shi R., Gao G., Chen G., Liu X., Novel rose-like ZnO nanoflowers synthesized by chemical vapor deposition, Mater. Lett., 2009, 63, 496–499.

[22] Yang B., Kumar A., Zhang H., Feng P., Katiyar R.S., Wang Z., Growth of ZnO nanostructures on metallic and semiconducting substrates by pulsed laser deposition technique, J. Phys. D. Appl. Phys., 2009, 42, 045415.

[23] Jung H.I., Lee S., Yu Y., Hong S.M., Choi H.C., Choi M.Y., Low-temperature hydrothermal growth of ZnO nanorods on sol–gel prepared ZnO seed layers: Optimal growth conditions, Thin Solid Films, 2012;524:144–50.

[24] Fang B., Zhang C., Zhang W., Wang G., A novel hydrazine electrochemical sensor based on a carbon nanotube-wire ZnO nanoflower-modified electrode, Electrochim. Acta., 2009, 55, 178–182.

[25] Wahab R., Ansari S.G., Kim Y.S., Seo H.K., Kim G.S., Kang G., et al. Low temperature solution synthesis and characterization of ZnO nano-flowers, Mater. Res. Bull., 2007, 42, 1640–1648.

[26] Wahab R., Kim Y., Shin H.-S., Synthesis, Characterization and Effect of pH Variation on Zinc Oxide Nanostructures, Mater. Trans., 2009, 50, 2092–2097.

[27] Kilic B., Gunes T., Besirli I., Sezginer M., Tuzemen S., Construction of 3-dimensional ZnO-nanoflower structures for high quantum and photocurrent efficiency in dye sensitized solar cell, Appl. Surf. Sci., 2014, 318, 32–36.

[28] Pawar R.C., Shaikh J.S., Suryavanshi S.S., Patil P.S., Growth of ZnO nanodisk, nanospindles and nanoflowers for gas sensor: PH dependency, Curr. Appl. Phys., 2012, 12, 778–783.

[29] Iqbal M., Mahendra R., Wahyuono R.A., Sawitri D., Risanti D.D., Evolution of ZnO Nanoflower-Like Structure Formation and Growth during Synthesis and Paste Preparation, Adv. Mater. Res., 2015, 1123, 219–222.

[30] Dhas V., Moduli S., Lee W., Han S.-H., Ogale S., Enhanced conversion efficiency in dye-sensitized solar cells based on ZnO bifunctional nanoflowers loaded with gold nanoparticles, Appl. Phys. Lett., 2008, 93, 243108.

[31] Wahyuono R.A., Risanti D.D., Shirouaki T., Nagaoka S., Takafuji M., Ibara H., Photoelectrochemical performance of DSSC with monodisperse and polydisperse ZnO SPs, AIP Conf. Proc., 2014, 1586, 78–81.

[32] Wahyuono R.A., Risanti D.D., Modeling and experiment of dye-sensitized solar cell with vertically aligned ZnO nanorods through chemical bath deposition, Proc. SPIE, 2015, 9444, 94440Q.

[33] Umar A., Rahman M.M., Al-Hajry A., Hahn Y.B., Highly-sensitive cholesterol biosensor based on well-crystallized flower-shaped ZnO nanostructures, Talanta, 2009, 78, 284–289.

[34] Tseng Y.-K., Chuang M.-H., Chen Y.-C., Wu C.-H., Synthesis of 1D, 2D, and 3D ZnO Polycrystalline Nanostructures Using the Sol-Gel Method, J. Nanotechnol, 2006, 5, 1–8.

[35] Samanta P.K., Patra S.K., Ghosh A., Chaudhuri P.R., Visible Emission from ZnO Nanorods Synthesized by a Simple Wet Chemical Method, Int. J. Nanosci. Nanotechnol., 2009, 1, 81–90.

[36] Wang H., Xie J., Yan K., Duan M., Growth Mechanism of Different Morphologies of ZnO Crystals Prepared by Hydrothermal Method, J. Mater. Sci. Technol., 2011, 27, 153–158.

[37] Xu S., Lao C., Weintraub B., Wang Z.L., Density-controlled growth of aligned ZnO nanowire arrays by seedless chemical approach on smooth surfaces, Mater. Res. Soc., 2008, 23, 2072–2077.

[38] Govender K., Boyle D.S., Kenway P.B., O’Brien P., Understanding the factors that govern the deposition and morphology of thin films of ZnO from aqueous solution, J. Mater. Chem., 2004, 14, 2575–2591.

[39] Ashfold M.N.R., Doherty R.P., Ndfor-Angwafo N.G., Riley D.J., Sun Y., The kinetics of the hydrothermal growth of ZnO nanostructures, Thin Solid Films, 2007, 515, 8679–8683.

[40] John T.T., Priolkar K., Bessiere A.B., Sarode P. R., Viana D.P., Nano-architecture and material designs for water splitting solar cell, Appl. Surf. Sci., 2014, 318, 32–36.

[41] Al-lami S., Jaber H., Controlling ZnO Nanostructure Morphology on Seedless Substrate by Tuning Process Parameters and Additives, Chem. Mater. Res., 2014, 6, 101–109.

[42] Khan Z.R., Khan M. S., Zulfequar M., Khan M. S., Optical and Structural Properties of ZnO Thin Films Fabricated by Sol-Gel Method, Int. J. Nanosci. Nanotechnol., 2012, 1, 94440Q.
[44] Ivanova T., Harizanova A., Koutzarova T., Vertruyen B., Study of ZnO sol−gel films: effect of annealing, Mater. Lett., 2010, 64, 1147–1149.
[45] Kaschner A., Haboeck U., Strassburg M., Strassburg M., Kaczmarczyk G., Hoffmann A., et al., Nitrogen-related local vibrational modes in ZnO:N, Appl. Phys. Lett., 2002, 80, 1909–1911.
[46] Coats A.W., Redfern J.P., Kinetic Parameters from Thermogravimetric Data, Nature, 1964, 201, 68–69.
[47] Burda C., Chen X., Narayanan R., El-Sayed M.A., Chemistry and properties of nanocrystals of different shapes, Chem. Rev., 2005, 105, 1025-1102.
[48] Smith A.M., Mohs A.M., Nie S., Tuning the optical and electronic properties of colloidal nanocrystals by lattice strain, Nat. Nanotechnol., 2009, 4, 56–63.
[49] Caglar M., Caglar Y., Ilican S., The determination of the thickness and optical constants of the ZnO crystalline thin film by using envelope method, J. Optoelectron. Adv. Mater., 2006, 8, 1410–1413.
[50] Laurent K., Yu D.P., Tusseau-Nenez S., Leprince-Wang Y., Thermal annealing effect on optical properties of electrodeposited ZnO thin films, J. Phys. D Appl. Phys., 2008, 41, 195410.
[51] Wu X.L., Siu G.G., Fu C.L., Ong H.C., Photoluminescence and cathodoluminescence studies of stoichiometric and oxygen-deficient ZnO films, Appl. Phys. Lett., 2001, 78, 2285–2287.
[52] Kumar R., Khare N., Kumar V., Bhalla G.L., Effect of intrinsic stress on the optical properties of nanostructured ZnO thin films grown by rf magnetron sputtering, Appl. Surf. Sci., 2008, 254, 6509–6513.
[53] Pesika N.S., Stebe K.J., Searson P.C., Relationship between Absorbance Spectra and Particle Size Distributions for Quantum-Sized Nanocrystals, J. Phys. Chem. B., 2003, 107, 10412–10415.
[54] Senger R., Bajaj K., Optical properties of confined polaronic excitons in spherical ionic quantum dots, Phys. Rev. B., 2003, 68, 1–8.
[55] Rai R.C., Analysis of the Urbach tails in absorption spectra of undoped ZnO thin films, J. Appl. Phys., 2013, 113, 153508.