ZnO superstructures *via* oriented aggregation initiated in a block copolymer melt

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Martin Klaumünzer,^a Monica Distaso,^a Jakob Hübner,^b Mirza Mačković,^c Erdmann Spiecker,^c Carola Krysch^b and Wolfgang Peukert^{*a}

A fast and simple one pot synthesis of ZnO nano- and microparticles initiated and driven by an amino block copolymer *O,O'*-bis(2-aminopropyl)polypropylene glycol-*block*-polyethylene glycol-*block*-polypropylene glycol (Jeffamine®) is reported. The specific building mechanism of ZnO mesocrystals is investigated in detail using electron microscopy and diffraction methods. Mesocrystals with a complex superstructure are formed as a result of a consecutive and oriented multiple stage aggregation process: first a 0D → 1D aggregation process is observed, then a 1D → 3D aggregation process occurs in which secondary particles form cones and multiple cone symmetries. Dots, rods, cones, and multiple cones have been isolated within a time resolved study which clearly supports the growth model. To control the morphology of the product particles, the influence of relevant synthesis parameters including stirring and sonication of the intermediate were investigated. Extensive surface characterization of the resulting mesocrystals is presented using infrared and photoluminescence spectroscopies as well as thermogravimetric analysis. Even after multiple washing steps, the particles exhibit a Jeffamine® coated surface that allows for easy dispersion in both polar and nonpolar solvents. The obtained mesocrystals efficiently scatter in the whole range of visible light.

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Introduction

With a wide band gap of 3.37 eV^{1,2} and a high exciton binding energy of 60 meV,² ZnO is a very popular and highly favored material suited for different electronic, optoelectronic and photonic applications like field effect transistors, solar cells and laser diodes.² Since ZnO is nontoxic,³ it is also used as a broadband UV-absorber in pharmaceutical and cosmetic applications^{4–7} or as a diagnostic tool for cancers.³ Therefore, the high-tech industry is interested in adopting facile and fast synthesis routes for diverse ZnO particles.

ZnO is well known for its strictly anisotropic growth and its high affinity to aggregate in a well-oriented manner.^{8–11} Due to its non-centrosymmetric wurtzite hexagonal crystal structure, preferred orientation and growth occur along (0002) or rather [000+/-1]. Polar and high energy facets at the base and tip of ZnO rods follow the “ABAB” chemical structure with alternating planes of Zn²⁺ and O²⁻-ions.^{12,13} Also

perpendicular to these (1010) facets, oriented attachment of primary ZnO particles to secondary particles or hierarchical superstructures is observed.^{11,14} The latter superstructures are often denoted as mesocrystals. There are three principal pathways to explain the 3D self-organization of nanoparticles into a mesocrystal in compliance with the literature: i) nanoparticle alignment by electrical or magnetic (or both) fields, ii) epitaxial growth employing a mineral bridge and iii) spatial constraints (entropy driven).¹⁵

The use of polymers as templating agents during synthesis offers a unique possibility to control the size, morphology and composition of inorganic systems. Besides the achievement of different particle morphologies, the residual polymer on the surface of nanostructures provides colloidal stability and additional anchor groups for further surface functionalization of the particles. Recently, it was shown that solvothermal conditions can influence the final morphology and sizes of hierarchical ZnO structures *via* the precursor salt counterion and the relative concentration of *N*-poly-vinylpyrrolidone (PVP) used as a polymeric additive.¹⁰ Moreover, the sizes and optical properties of the resulting ZnO/PVP hybrid mesocrystals were found to crucially depend on the process parameters during synthesis, allowing excellent control of the size and optical properties of the resulting material. These particle systems are formed by oriented attachment and the polymer plays an important role during synthesis, providing the matrix inside which the reaction

^a Institute of Particle Technology, Friedrich-Alexander-University Erlangen-Nuremberg, Cauerstr. 4, 91058 Erlangen, Germany.

E-mail: wolfgang.peukert@fau.de; Tel: +49 (0)913185 29401

^b Institute of Physical Chemistry I, Friedrich-Alexander-University Erlangen-Nuremberg, Egerlandstraße 3, 91058 Erlangen, Germany.

E-mail: krysch@chemie.uni-erlangen.de; Tel: +49 (0)913185 27307

^c Center for Nanoanalysis and Electron Microscopy (CENEM), Friedrich-Alexander-University Erlangen-Nuremberg, Cauerstr. 6, 91058 Erlangen, Germany.

E-mail: erdmann.spiecker@www.uni-erlangen.de; Tel: +49 (0)913185 28603

takes place.¹⁶ Also, Taubert *et al.* reported that the use of copolymers favors the formation of twin structures of ZnO with various morphologies.¹⁷

In the present paper, a novel synthesis route for hierarchical ZnO structures is reported using the three block copolymer *O,O'*-bis(2-aminopropyl)polypropylene glycol-*block*-polyethylene glycol-*block*-polypropylene glycol (Jeffamine[®]) with ether moieties and amino- and methyl-terminating functional groups as a specific template for ZnO. This particular block copolymer enables also the synthesis of noble metal nanoparticles¹⁸ where the polymer acts as the reducing and stabilizing agent.^{19,20} Here, we focus on the optimization of synthesis boundary conditions leading to specific ZnO mesocrystal structures and the understanding of their formation mechanism, since the control of shape, size, and interface organization in a mesocrystal is of great fundamental interest.

The surface chemistry of the resulting ZnO mesocrystals is characterized using infrared (FTIR) and photoluminescence (PL) spectroscopy as well as thermogravimetric analysis (TGA). Furthermore, we discuss how the mesocrystals are formed using a combination of time resolved scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction methods (XRD). The self-assembly of primary nanoparticulate building blocks for the formation of mesocrystals is further examined precisely using time resolved UV/VIS absorption spectroscopy. The as-obtained structures present remarkably high scattering properties in the visible region as a result of multiple aggregation processes and may be used as a high efficiency scattering material for solar cell electrodes. Finally, a growth model is proposed to shed light on the initial nucleation and subsequent building process of the superstructure within the mesocrystals.

Experimental section

Synthesis

All chemicals were purchased from Sigma Aldrich and used without further purification. *O,O'*-bis(2-aminopropyl)polypropylene glycol-*block*-polyethylene glycol-*block*-polypropylene glycol (Jeffamine[®] ED-2001) with a specific molecular weight of 1900 g mol⁻¹ was used for synthesis. Ultra-pure water from a Millipore system (ELGA Purelab, flex, $R > 18.3$ MΩ) was used for aqueous processing steps. In a typical synthesis, the polymer (Jeffamine[®]) (10.82 g, 5.70 mmol) was heated up to 150 °C (flash point 113 °C) and stirred thoroughly in a conventional one neck flask. Once the polymer was molten, Zn(CH₃COO)₂·2H₂O (50 mg, 0.23 mmol) was added and allowed to dissolve in the polymer melt. After a reaction time of 1 min, the flask was cooled down to room temperature with stirring using a water bath. The solid mixture was then solubilized in 30 ml of water in an ultrasonic bath (Branson, 1510) for a time period of 20 min. Hereafter, the particles were isolated by centrifugation and washed three times with water through centrifugation and redispersion cycles.

For mechanistic studies, the sonication time was controlled in the presence of water. The solid mixture was

divided into four equal parts and 5 ml of water was added to each of these parts using a pipette. The different samples were sonicated for 5, 10, 15 and 20 minutes, respectively. The obtained suspensions were then centrifuged and a gel residue was isolated. In order to extract the particles from the gel matrix and to prevent them from further growing, the particles were washed using isopropanol. In fact, preliminary tests demonstrated that isopropanol was able to dissolve the polymer but did not promote any growth of ZnO structures during sonication.

In order to determine the effect of sonication on the reaction mechanism, the solution was kept under stirring for 20 minutes and the isolated mesocrystals were compared with the sonicated samples using scanning electron microscopy. The role of the hot polymer melt in the reaction mechanism was studied by performing the following experiment. A solid mixture of the polymer (10.82 g, 5.70 mmol) and Zn(CH₃COO)₂·2H₂O (50 mg, 0.23 mmol) was prepared; water was added to the solid mixture and the solution was sonicated for 20 minutes. The particles were then isolated as described above.

Characterization

Spectroscopy. *UV/VIS absorption* spectra were recorded on a Varian Inc. Cary 100 UV/VIS spectrophotometer. *In situ UV-VIS* study was carried out using a transmission probe (Avantes) with an optical path of 10 mm and a portable spectrophotometer (Ocean Optics). *Photoluminescence* (PL) spectra were measured using a FluoroLog 3 spectrofluorometer (Horiba Jobin Yvon GmbH) equipped with a double grating on the excitation and emission sides. The samples were measured using 1 cm cuvettes containing an aqueous suspension of ZnO particles for PL spectroscopy and an isopropanol suspension for UV/VIS absorption spectroscopy, respectively.

Fourier transform infrared (FTIR) absorption spectra of ZnO powder were obtained using an IR Prestige-21 (Shimadzu) in attenuated total reflectance mode.

Photon correlation spectroscopy (Dynamic Light Scattering, DLS) was performed on a Zetasizer Nano-ZS (Malvern).

Thermogravimetric analysis. Thermogravimetric analysis (TGA) was performed using a platinum pot on a TGA Q50 (TA Instruments) based on the following ramp parameters: 10 °C min⁻¹ until $T = 150$ °C, 30 min isotherm at 150 °C followed by 10 °C min⁻¹ until 800 °C, and 30 min isotherm at 800 °C.

Electron microscopy. *Scanning electron microscopy* (SEM) images were recorded with a field emission scanning electron microscope (ULTRA 55, Carl Zeiss NTS GmbH, Oberkochen, Germany) at an operating voltage of 20 kV, using an in-lens secondary electron detector. The SEM samples were prepared by dropping the dispersions onto the surface of Si/SiO₂ wafer slides pretreated by air plasma. *Transmission electron microscopy* (TEM) was performed using a Philips CM300 UltraTWIN (Netherlands) with a nominal point resolution of 1.7 Å at Scherzer defocus. The microscope was operated at 300 kV acceleration voltage using a LaB₆

filament. TEM images were recorded with a fast scan charged coupled device camera (from TVIPS, Germany) with an image size of 2048×2048 pixels. Electron diffraction patterns (DP) were evaluated using JEMS software (version 3.5505U2010), incorporating crystal data from the inorganic crystal structure database (ICSD). For TEM investigations the samples were prepared by drop-casting the particles suspension on commonly used copper TEM grids coated with an amorphous holey carbon film layer.

X-Ray diffraction analysis. X-Ray diffraction analysis (XRD) scans in Bragg–Brentano geometry were performed with a Bruker AXS Advance D8 (Karlsruhe, Germany) X-ray diffractometer using Cu K α radiation ($\lambda_{K\alpha}$) of $1.54 \text{ \AA}$ (ref. 21) at an acceleration voltage of 30 kV. The coherence lengths L_{hkl} along the different crystal directions were calculated from the full width at half-maximum (FWHM) of diffraction peaks by using the Scherrer equation assuming Gaussian shaped peaks.²¹

Photography. Photography was done using a Nikon D3200 with an AF-S Nikkor 18–105 mm, 1:3.5–5.6 object lens.

Results and discussion

Synthesis and characterization of ZnO mesocrystals

The scanning electron microscopy (SEM) image in Fig. 1(a) illustrates the morphologies and size distribution of the as-synthesized ZnO mesocrystals. The particle morphologies comprise mono- to x -fold symmetries ($x = 2$ –8) with cone-like substructures. The surface of the particles exhibits aligned ZnO nanorods. Typical shapes are bi-cones ($x = 2$) coupled through the flat facet (end) generating an interface (coupled base area). It appears that these interfaces act as high energy docking stations for further growth of smaller cones leading to multiple structures ($x > 2$). Fig. 1(a) #1 shows a significant mismatch at the base area of two cones that is rather untypical. The particle size distribution (PSD) of the aggregated particles and

secondary particles is shown in Fig. 1(c). No further aggregation of superstructures (secondary particles) took place after 20 min as observed from the DLS analysis. The PSD ranges from 200 nm to 650 nm and exhibits a modal maximum of 308 nm. This is consistent with the particle sizes found in the SEM image depicted in Fig. 1(a). Fig. 1(b) shows the chemical structure of the polymer which was simultaneously used as solvent, stabilizing agent and dispersing agent during the synthesis of the ZnO superstructures. This approach leads to comparatively fast kinetics of the formation of secondary mesostructures.^{22,23} The Jeffamine® polymer is a commercially available amphiphilic block copolymer with amino group terminations and functional ether bridges. To the best of our knowledge, no metal oxide particle synthesis using this polymer has been published so far. In Fig. 1(b), the polyethylene glycol block indicated by b is about 9 units, whereas the size of the polypropylene block ($a + c$) is about 3.6. Since the Jeffamine® polymer used is of amphiphilic nature, the ZnO mesocrystals are easily dispersible in both highly polar and completely nonpolar solvents. The following solvents were used: water (permittivity $\epsilon = 80.10$), isopropyl alcohol ($\epsilon = 20.18$) and hexane ($\epsilon = 1.89$).²⁴ Exemplarily stable mesocrystal dispersions in water, alcohol and hexane are depicted in Fig. 2.

All samples resulted in a slightly milky suspension after sonication for 1 min (Fig. 2, photograph taken 10 min after sonication). No differences are observable between the different solvents. Even after several washing steps, the ZnO mesocrystals were still coated with Jeffamine®, which was clearly detected by FTIR transmission spectroscopy and TG analysis as presented in the following sections.

Particle surface characterization

The functional groups of the polymer interact with the particle surface and thus modify the particle surface *in situ*.

Fig. 1 (a) SEM image of ZnO mesocrystals. The mesocrystals are nanostructured and exhibit diverse x -fold ($x = 2$ –8) symmetries with cone-shaped subunits. (b) Chemical formula of the block copolymer with intrinsic amino termination and ether moieties. (c) Particle size distribution obtained from DLS analysis.

Fig. 2 Photograph of Jeffamine® coated ZnO mesocrystal suspensions taken 10 min after being simultaneously dispersed in a sonication bath for 1 min. (a) ZnO suspension in water, (b) in isopropyl alcohol, and (c) in hexane.

Further chemical surface functionalization, for instance by covalent coupling reactions to form amides, is readily possible.²⁵ For a detailed surface characterization of

superstructures, FTIR, PL, and TGA investigations are combined which finally suggest that the Jeffamine® polymer remains at the ZnO surface even after multiple washing steps. In Fig. 3(a), the FTIR transmission spectrum of Jeffamine® coated ZnO mesocrystals is displayed. Fig. 3(b) shows the PL spectrum of this sample. Fig. 3(c) illustrates possible interactions between the nonpolar side plane (1010) at the ZnO surface and the block copolymer.

The dominant vibrational bands in the FTIR transmission spectrum of Jeffamine®-capped ZnO mesocrystals (Fig. 3(a)) are assigned to $\nu(\text{O-H})$ stretching (3300 cm^{-1}), $\nu(\text{N-H})$ stretching (3300 cm^{-1}), $\nu(\text{C-H})$ stretching (2975 cm^{-1}), $\delta(\text{N-H})$ bending (1635 cm^{-1}), $\delta(\text{C-H})$ bending (1461 cm^{-1} and 1385 cm^{-1}) and $\nu(\text{C-N})$ stretching (1278 cm^{-1}) vibrations which unambiguously characterize the ZnO surface structures as predominantly arising from the Jeffamine® coating. Bands at 500 cm^{-1} are attributed to $\nu(\text{Zn-O})$ stretching. The photoluminescence (PL) spectrum of Jeffamine®-coated ZnO mesocrystals in aqueous solution reported in Fig. 3(b) was recorded upon photoexcitation at 330 nm. The PL spectrum is

Fig. 3 (a) FTIR transmission spectrum of Jeffamine®-capped ZnO mesocrystals. (b) Photoluminescence spectrum of an aqueous dispersion of ZnO mesocrystals which were excited at 330 nm. (c) Proposed interactions between Jeffamine® at the (10-10) ZnO interface and (d) TG analysis of the ZnO particles. Three basic sections (i)–(iii) are detected.

composed of a prominent peak at 393 nm, a smaller one at 466 nm and a broad maximum at 560 nm that exhibits a shoulder around 660 nm. While the peak at 393 nm is assigned to radiative recombination of electron-hole pairs initially photo-generated in the ZnO bulk, the broad emission band in the visible region arises from the radiative decay of excited defect states.²⁶ Optically active defect structures are mostly located at the surface of ZnO particles and built on neutral, single or double oxygen and zinc vacancies or interstitials.²⁶ The green PL emission around 560 nm is attributed to radiative recombination of a shallowly trapped electron and a deeply trapped hole.^{27,28} The latter is ascribed to a doubly positively charged oxygen vacancy formed by hole trapping through a monovalent, positively charged oxygen vacancy at the surface of ZnO.^{26–28} The orange emission (660 nm) of ZnO nanostructures may involve bulk defects associated with excess oxygen occupying interstitial lattice sites.²⁹ In any case, the bulk emission (393 nm, 660 nm) to surface emission (560 nm) intensity ratio is expected to crucially depend on both the size and morphology (surface to bulk ratio) and the surface coating of the ZnO mesocrystals. In case of the latter, the Jeffamine® surfactant should strongly interact *via* its amino groups with negatively charged surface states of ZnO and thereupon partially quench the green PL emission based on the polymer chemical structure and the nature of the nonpolar facet of ZnO in the wurtzite phase.

A scheme for the polymer-ZnO interaction is proposed in Fig. 3(c). The polymer is able to interact *via* free electron pairs of the amino groups with Zn^{2+} -ions from the bulk. Moreover, hydrogen bonds between the ether bridges and protons of the amino groups are likely to be formed besides interactions of the free electron pairs at O^{2-} and the Zn^{2+} -ions.

Additionally, thermogravimetric analysis (TGA) was performed to show the mass evolution of a ZnO mesocrystal sample over temperature. Three basic sections (i)–(iii) are shown in Fig. 3(d). The total sample mass loss reaches 5% (i–iii). Since the removal of physically adsorbed water should be completed after a 30 min isothermal treatment at 150 °C,³⁰ 50% of that mass loss is supposed to be primarily bound water (detected in FTIR transmission spectroscopy due to a significant intensity loss of the $\nu(\text{O-H})$ stretching band) and other physically adsorbed chemicals (ambient nature or synthesis residues). In the range between ~180 °C and 450 °C (ii), the partially physisorbed and covalently bound Jeffamine® surfactant is released from the ZnO surface. Hydrogen bonds may be formed between the ether bridges and protons of the amino groups besides electrostatic interactions between O^{2-} and Zn^{2+} -ions. In section (iii), a temperature above 450 °C ushers a terrace followed by a continued but significantly reduced mass loss indicating desorption of a few residual organic compounds.

Formation of mesocrystals

In the following section, the time resolved formation of the ZnO superstructures and mesocrystals is highlighted. Therefore, detailed TEM analysis was performed. Consistent with

the SEM images and XRD data, the formation of mesocrystals *via* oriented aggregation of single ZnO nanoparticles is clearly rationalized. Furthermore, the main steps of the synthesis are taken into consideration namely: a) the melting step, *i.e.* heating of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ inside the Jeffamine® melt at 150 °C for 1 minute and b) the sonication of the intermediate complex in water. The influence of each parameter on the formation of the final particles, in terms of size, morphology and degree of aggregation, is reported in the following sections.

Influence of the polymer melting step on the formation of ZnO mesocrystals

In order to better understand the process of dissolving $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in a polymer melt at 150 °C, the reaction was carried out by preparing a solid mixture of Jeffamine® and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ at room temperature at the same molar ratio used for preparing the particles shown in Fig. 1. Thus the fundamental difference from the previous procedure is the missing 150 °C hot polymer melting step. SEM imaging of the product shows that ZnO particles exhibit a different size and a completely different morphology when compared to ZnO mesocrystals which were obtained by heating at 150 °C. The microcrystal shown in Fig. 4(a) is representative and exhibits a flower-like structure with needle-like substructures of *ca.* 500 nm in length. According to XRD data analysis, the ZnO microcrystals possess a wurtzite crystal structure (B4 type, ICSD 34477).

This result suggests that the heating procedure at 150 °C is fundamental: it is required for controlling both chemical reaction and crystal growth. Complementary information on the crystallization process in the polymer melt was obtained from *in situ* UV/VIS absorption spectroscopy. Thereupon it was found that the absorption spectrum of the Jeffamine®– $\text{Zn}(\text{CH}_3\text{COO})_2$ mixture overlaps with that of the molten Jeffamine® (Fig. 4(b)) with an onset at about 475 nm. The Jeffamine® melt was kept under stirring at 150 °C for longer than 1 minute, which was usually used to carry out the reaction, revealing that no detectable ZnO species was formed at high temperature even after 30 min. However, ZnO absorbs light within the detected region with an onset below 368 nm (3.37 eV).³¹ But then, the exact fit of the extinction spectra of the melting mixture with the extinction spectra of the molten Jeffamine® demonstrates that the formation of superstructures does not take place during the melting step of the reaction and suggests that the formation of ZnO quantum dots or ZnO clusters during the melting of the polymer is implausible. Still, the melting step (Jeffamine®– $\text{Zn}(\text{CH}_3\text{COO})_2$ mixture) ensures a close contact between the polymer layer and the Zn^{2+} precursors through the formation of coordination complexes with dehydrated $\text{Zn}(\text{CH}_3\text{COO})_2$ according to Scheme 1.

In this scheme, the dehydrated $\text{Zn}(\text{CH}_3\text{COO})_2$ coordinates *via* the ether functional group of the polymer by dipole interactions and electrostatic interactions between Zn^{2+} and the free electron pairs from oxygen.

Fig. 4 (a) SEM image of a ZnO microcrystal obtained without heating up $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and Jeffamine® to 150 °C. (b) *In situ* UV-VIS absorption spectra recorded during heating up, evidencing no evolution of the optical fingerprint over time.

Scheme 1 Suggested dehydration step and complexation of $\text{Zn}(\text{CH}_3\text{COO})_2$ within the Jeffamine® matrix at 150 °C during the polymer melting step.

Influence of the sonication step on the formation of ZnO mesocrystals

To shed light on the role of sonication in the formation of ZnO mesocrystals, the reaction has also been carried out

under magnetic stirring. Accordingly, after the melting step, water was added to the solid mixture and the as-obtained suspension was kept under conventional stirring. Samples were analyzed by SEM. It was found that the particles formed as bi-cones and multiple structures with x -fold symmetries ($x > 2$) were observed. In the sample prepared also under magnetic stirring, small and rather spherical ZnO nanoparticles (*ca.* 10 nm in diameter) that were highly interconnected were isolated, indicating an incomplete reaction with respect to superstructured particles. These particles cluster into a percolation network depicted in Fig. 5(a).

To obtain quantitative information, a statistical evaluation was carried out upon examining of a total of 250 particles (100%). It was found that the reaction under sonication produced a larger number of multiple structures (Fig. 5(b)) and was accomplished on a time scale much shorter than that under stirring. Obviously, sonication of the reaction is associated with higher energy and power input and is more efficient than conventional stirring. The power input in conventional stirring is negligible,³² whereas the ultrasonic Branson 1510 device applies a power of 70 watts at 42 kHz to the water bath. In conclusion, sonication leads to faster building kinetics of complex ZnO particle symmetries. Besides the relevance of this result to the understanding of the reaction mechanism, it can be inferred that the choice of conventional stirring or sonication upon water addition allows for control of the degree of aggregation of single nanoparticles, bi-cones or even multiple x -fold ($x > 2$) superstructures, respectively. This is relevant, considering that the ZnO multiple superstructures show good light scattering properties with increasing reaction time according to the degree of aggregation of ZnO nanoparticles presented in this paper (optical characterization section).

TEM analysis

After the melting step, water was added to the solid mixture and the as-obtained suspension was kept under sonication for different time periods in accordance with the Experimental section. Fig. 6 shows the TEM results of the 5 min sample.

The bright-field TEM image in (a) reveals that the sample consists of nanoparticles which are organized into a percolated hollow network. Selected area electron diffraction (SAED) confirms that these nanoparticles are ZnO with a hexagonal crystal structure, consistent with ICSD 34477. The first peak in the intensity profile is related to the direct electron beam with the strongest intensity. The first diffraction ring in the diffraction pattern appears broad and can be indexed with (10-10), (0002) and (10-11) reflections of wurtzite-type ZnO. High-resolution TEM (HRTEM) imaging in (b) clearly reveals crystalline ZnO quantum dots showing their characteristic (0002) lattice planes with a spacing of 0.26 nm. Interestingly, it was found that these building blocks undergo oriented attachment forming elongated nanorods. This “*in statu nascendi*” of a ZnO nanorod is depicted in Fig. 6(b): two ZnO quantum dots attach to each other forming an elongated ZnO nanorod (marked by a white line).

Fig. 5 Influence of the sonication step on the size and morphology of ZnO particles synthesized in a melt at 150 °C for 1 minute. (a) SEM micrograph showing that in the absence of sonication the sample comprises ZnO nanoparticle building blocks clustering into a percolation network. (b) Quantitative comparison of the degree of aggregation between samples prepared by sonication and samples prepared by stirring. Insets to Fig. 5(b) show relevant symmetry samples.

Fig. 6 TEM analysis of the 5 min sample: (a) overview bright-field TEM showing an agglomerate consisting of ZnO quantum dots and an inverted electron diffraction pattern (inset), confirming ZnO with a hexagonal crystal structure (ICSD 34477). The red intensity profile was obtained by radial averaging of the diffraction pattern. (b) HRTEM image of two ZnO quantum dots, forming a rodlike particle by oriented attachment.

The weaker atomic contrast between these two particles indicates the interface where oriented attachment takes place in the [0002] direction. Within the region of weaker contrast, lattice planes which connect the two quantum dots are clearly

visible. This indicates that the interface between the ZnO quantum dots has not yet been fully developed and supports that oriented attachment is in progress. Fig. 7 shows the TEM analysis of a sample synthesized by 15 min of sonication.

The bright-field TEM image in (a) reveals that the sample consists of a mixture of both, nano building blocks and ZnO mesocrystals: the latter superstructures comprise a x -fold symmetry ranging from bi-cones ($x = 2$) to multiple structures ($x > 2$). This result follows from the SEM analysis reported above (Fig. 1a). Besides the well-formed ZnO mesocrystals, also a fraction of ZnO nano building blocks is visible, similar to our observation of the 5 min sample (Fig. 6). The co-presence of building blocks and mature mesocrystals in the sample isolated after 15 min of sonication indicates that the growth of multiple structures with x -fold symmetry occurs by the attachment of building blocks and has not yet been completed after 15 min of ultrasonication. In fact, Fig. 7(b) depicts the attachment of ZnO nano building blocks onto a ZnO mesocrystal with a 2-fold symmetry. The building blocks are concentrated in the region close to the coupled base area between two cones (see black arrow in (b)). The SAED patterns shown in (c) and (d) are observed for the regions marked with black and white dotted circles in (b), respectively. Both diffraction patterns are valid for ZnO (consistent with ICSD 34477). The first intense diffraction ring in (c) appears broad, containing (10–10), (0002) and (10–11) reflections of ZnO. The diffraction pattern reported in Fig. 7(d) stems from the coupled base area (white dotted circle) and shows strong main reflections, which after indexing fit well to the [0001] zone axis of ZnO, even though the ZnO mesocrystal is illuminated from the side with the electron beam. This suggests that in this region a superstructured cone (composed of single ZnO building blocks) is attached perpendicularly to the long axis of the ZnO mesocrystal. Moreover, it can be concluded that in the area marked by the white dotted circle the ZnO building blocks preferentially orient along the [0001] direction. The distinct streaking of reflections suggests a slight misalignment between the ZnO building blocks. Also, the diffraction patterns in (c) and (d) support the phase transition from an isotropic organization to an almost anisotropic organization of the nano building blocks. The latter result is expressed by the transition from diffraction rings to streaked dots. The HRTEM image in Fig. 7(e) depicts the tip region of a ZnO mesocrystal (see black arrow) shown in (a). (0002) lattice planes are clearly visible, exhibiting the characteristic spacing of 0.26 nm and marking the growth of the mesocrystal along the crystallographic c -axis. Moreover, this HRTEM image reveals the presence of stacking faults (exemplarily shown by white arrows in (e)) in the ZnO mesocrystal, revealing misalignment between formerly single ZnO building blocks. In fact, stacking faults are often detected as a consequence of an imperfectly oriented aggregation.³³

XRD and SEM studies

Fig. 8 presents a more detailed SEM image of the as-synthesized ZnO superstructures with higher magnification compared to Fig. 1(b). The substructure of the mesocrystals is clearly visible at the particle surface, where in most cases ZnO rods can be identified. Arrows in this SEM pattern point out former aggregation sites of single cones.

Fig. 7 TEM analysis of the 15 min sample: (a) overview bright-field TEM image of ZnO mesocrystals flanked by a fraction of unconsolidated nanoparticles; (b) higher magnification bright-field TEM image of a ZnO mesocrystal with ZnO nanoparticles attached to the coupled base area (black arrow); (c and d) corresponding inverted SAED patterns which were observed for the regions marked with black and white dotted circles in (b), respectively. The intensity profile (inset in (c)) was obtained by radial averaging of the electron diffraction pattern shown in (c); (e) HRTEM image showing the tip region of a ZnO mesocrystal, marked with the black arrow in (a).

Measuring the rod-like substructure at the particle surface, anisotropic primary particles of about 70 nm in length and ~20 nm in diameter (aspect ratio of 3.5) were derived. From XRD and TEM measurements, it is also obvious that the particles grow along the [0001] and [000–1] directions as displayed in Fig. 8(a) and as expected for ZnO. In fact, from

the well-known Scherrer equation [11] the coherence length of the (101) reflection or rather [10-10] is 25.0 nm, whereas that of (002) or rather [0001] is 79.7 nm and that of (101) or rather [10-11] is 28.2 nm. [0002] belongs to the crystallographic *c*-axis, therefore this reflection can be seen as the “length” of the primary rods. [10-10] belongs to the *a*-axis, standing perpendicularly on (002) and therefore can be assumed as the diameter of the ZnO rods. Clearly, the anisotropic primary structure is derived from XRD with an aspect ratio of ~ 3 , which is in good agreement with the results obtained from the SEM analysis (Fig. 8(a)). XRD analysis clearly shows the substructure of the ZnO particles with mostly ZnO nanorods as primary particles. A loss of coherence is a basic hint for defects within the ZnO lattice of the mesocrystals. The presence of polymers inside the mesocrystals, being within the inorganic network bound to former interfaces

of ZnO building blocks, is also plausible and would account for the smaller coherence lengths observed by XRD when compared to the absolute total sizes of superstructured particles when measured by SEM and DLS. Moreover, the loss of coherence in XRD suggests that fast growth takes place by oriented aggregation. In fact, a slow growth, even ion per ion (layer per layer), may not lead to high defect-formation rates in comparison with nonclassical crystallization and interruption of the coherence of Cu K α through imperfect orientation leading to 2D defects (e.g. stacking faults, see Fig. 7(e)). So, the defect formation rate may be associated with the growth rate.

Optical characterization

The spectra in Fig. 9 show the time evolution of the light extinction and light scattering behavior of the ZnO particle dispersions in isopropanol.

With the reaction time rising from 5 min to 20 min, the extinction maximum due to band gap absorption is red-shifted from 348 nm for the 5 min sample to 363 nm for the 15 min sample (a). The extinction maximum of the 20 min sample at wavelengths larger than 370 nm is superimposed by a broad extinction band presumably arising from the formation of large ZnO mesocrystal superstructures that efficiently scatter light. Noteworthy is the surprisingly high extinction level within the whole visible range for the 20 min sample. ZnO nanorods, nanosheet-assembled flowers, and nanotetrapods in the micrometer range, for instance, exhibit smaller extinction intensities when compared to the sample observed here.^{34–36} This makes the material highly interesting as white pigment and for high efficiency dye-sensitized solar cells: Gao *et al.* reported on a ZnO nanorod layer on top of a ZnO nanoparticle electrode that effectively improves light harvesting and enhances the photocurrent by a superior light-scattering effect.³⁷ Since ZnO nanocrystals do not exhibit any light absorption in the visible spectra range, the broad

Fig. 8 (a) SEM image: higher magnification of the sample from Fig. 1(a). The particles are clearly nanostructured at their surface and offer diverse *x*-fold (*x* = 1–8) symmetries with cone-shaped subunits. The nanorods in the substructure of the cones can be seen. (b) XRD pattern in the range from 27° to $40^\circ = 2\theta$ of ZnO mesocrystal synthesis after 20 min reaction time. The pattern shows the prominent (100), (002) and (101) reflections from left to right indicating the well-known wurtzite (B4 type) structure (ICSD 34477).

Fig. 9 Time evolution of the UV/VIS spectra of ZnO mesocrystals: with increasing reaction time from 5 to 20 minutes (5 min: red dots, 10 min: blue stars, 15 min: magenta circles, 20 min: green squares), the extinction maximum experiences a red-shift (a) and an increase in extinction within the whole visible spectra range (b).

extinction band between 400 and 800 nm can unambiguously be ascribed to light scattering due to the formation of superstructured mesocrystals with sizes between 200 and 650 nm according to our DLS data. The red-shift of the extinction maximum (5–15 min) with rising reaction time is explained with the growth of ZnO nanostructures which is accompanied by a decrease in the electronic band gap due to the quantum confinement effect.³⁸ According to the particle size dependence of the optical band gap, the 5 min sample reveals ZnO nanoparticle sizes in the range of 3.5 nm^{38,39} which is in excellent agreement with HRTEM data (Fig. 6). The optical band gap at a wavelength of 363 nm is already outside the quantum confinement regime.³⁹ An extinction maximum at 368 nm (3.37 eV) corresponds to the band edge absorption from bulk ZnO at room temperature.^{1,2} The increase in the broad extinction band between 350 and 700 nm (b) with rising reaction time is ascribed to light scattering due to growing ZnO mesocrystal superstructures that consecutively emerge from agglomeration of the initially formed primary crystals.

Growth model by means of oriented aggregation

As described in previous sections, the growth of ZnO multiple cone superstructures occurs *via* the oriented attachment of primary anisotropic building units embedded in the Jeffamine® polymer matrix. The first step of the reaction is the formation of a coordination complex of the polymer ether functional groups and Zn²⁺ ions (Scheme 1). ZnO nuclei are formed very fast at room temperature (25 °C) upon addition of water and under the influence of sonication treatment (Fig. 5(b)). A time resolved study reveals that after 5 minutes of sonication only quantum dots with diameters between 3 and 5 nm can be isolated. These building blocks are highly interconnected with each other inside the polymer matrix, forming fiber-like superstructures that are initially unconsolidated (Fig. 6(a)). With longer reaction time, the building blocks self-organize into cone and bi-cone structures. Bi-cones are found to be mismatched in a few cases (Fig. 1(a) #1), suggesting that the bi-cones also arise from a coupling process of single cones. Finally, the building blocks grow at the coupled base area forming smaller secondary cones that decorate this interface. The growth of secondary cones around the coupled base area indicates that this topological location is a preferential point on the surface of the bi-cones. Obviously, the coupled base area is a high energy region and the further growth of smaller cones reduces the total energy of the system: the formation of cone-like particle morphologies is attributed to the lower surface energy of the (10–11) family of habit planes as compared to that of the (0001) facets.⁴⁰ One Zn²⁺ terminated ending (0001) and one O²⁻ terminated ending (000–1)¹⁰ are involved as introduced. These aggregation processes are surprisingly fast compared to similar approaches reported in the literature. Masuda *et al.* and Zhang *et al.* described comparable ZnO flowerlike particles after a reaction time of 13 h at 180 °C in heptane.^{22,41} Also, Gan *et al.* described related “peanut like” 3D ZnO architectures from biomimetic synthesis with gelatin as matrix and with a reaction time of up to 24 h.

Gan *et al.* supposed an intermediate state within their model specified by flowerlike ZnO structures.²³ In our case, we recommend the occurrence of oriented agglomeration and subsequent aggregation because of reduced overall energy in reference to Gibbs free energy.⁴² Thus, the single nanoparticle alignment is driven by spatial constraints and leads to an entropy-driven mechanism.¹⁵ High energy faces are saturated and entropy increases due to free excess volume from a modified theory of Onsager.^{43,44} According to Onsager, the phase transition from an isotropic phase to an exclusively nematic crystalline phase is valid for rod aspect ratios that approach infinity. Modifying Onsager's theory, Bolhuis *et al.* showed that the smectic phase first becomes stable at an aspect ratio of 3.1, whereas the nematic phase becomes stable at an aspect ratio of 3.7. Below this ratio, an orientationally ordered crystal phase occurs. Mixed phases are possible within the complete range of aspect ratios for spherocylinders.⁴⁴ In these theoretical approaches, the transition from isotropic phase to smectic/nematic phase is hypothesized to occur above a critical rod volume fraction c_i . The latter critical rod volume fraction can be easily achieved (although the initial Zn to polymer molar ratio is 1 to 25) due to the polymer matrix that provides cavities with a high ZnO particle concentration within the reaction mixture. Also, the nucleation of the ZnO nanoparticles probably takes place randomly within these cavities allocating solubilized water clusters and Zn²⁺ ions at sufficiently high concentration. This implies that the formation of ZnO mesocrystals may be rationalized in terms of a modified theory of Onsager, since the primary ZnO nanoparticles are mostly rod-like and may be therefore assumed to behave like molecules in the smectic/nematic liquid crystalline phase.^{43,44} Therefore, we claim a preferred transition to the nematic phase by consulting our experimental results from XRD and SEM (Fig. 8) regarding the aspect ratio of the ZnO nanorods (about 3–3.5) and the substructure detected in SEM. Aside from these factors, due to the already mentioned crystallographic and energetic anisotropy of ZnO, the mechanism is also brought forward by physical fields (electric, magnetic, or dipole fields since ZnO exhibits a dipole structure) and mutual alignment of identical crystal faces:¹⁵ as obtained from TEM analysis, the growth axis of the ZnO mesocrystals is parallel to the [0001] direction. This indicates a self-assembly of primary ZnO nanorods through oriented attachment of their nonpolar surfaces because of protection of the polar surfaces, with Jeffamine® providing polar amino groups. The elimination of the high-energy surfaces by self-oriented attachment of ZnO nanorods is assumed to be the driving force of crystal growth.

Fig. 10 depicts a typical single mesocrystal displayed from TEM analysis in sub-figure (a) and in sub-figure (b) an explicit growth and formation model for the ZnO mesocrystals presented in this paper.

In this model, the nucleation process takes place inside the polymer matrix (i), followed by subsequent growth and oriented 0D → 1D aggregation of spherical ZnO particles along the crystallographic *c*-axis as described within the TEM section (ii). Then, a first 1D → 3D arrangement of ZnO nanorods into superstructured cones (iii) occurs. Step (iv) is affected

Fig. 10 (a) Bright-field TEM image of a single ZnO superstructured particle. (b) Formation model of the as-synthesized particles driven by consecutive attachment of nano ZnO building blocks and coupling of superstructured cones. The high energy coupled base area is labeled with red arrows.

by the coupling of single cones into larger mesocrystals (bicones) with generation of an interface (coupled base area, red arrows in Fig. 10(b), white arrows in Fig. 10(a)). The last step (v) is the attachment of single nano building blocks to saturate reactive interfaces.

Conclusions

Electron microscopy (SEM, TEM) images and spectroscopy experiments (UV/VIS, FTIR, PL) prove the formation and synthesis of hierarchical ZnO superstructures by consecutive oriented aggregation (OA) of quantum dots to rods, rods to cones and finally to ZnO mesocrystals. A consistent mechanistic scheme based on the oriented attachment of ZnO nano building blocks for secondary particle formation is presented and discussed in detail based on a modified theory of Onsager. Relevant synthesis route steps and influencing parameters like sonication or the influence of the hot Jeffamine® melt were investigated. These reaction conditions allow for an exact control of the product particles regarding their specific morphology. The surface of the mesocrystals exhibits a strongly bound polymer monolayer which offers a potential and alternative

anchorage area for further modification of the surface and is characterized in detail. Time resolved UV/VIS extinction measurements track the aggregation process and exhibit comparably high extinction properties due to light scattering in the entire visible range. The latter feature is highly interesting for potential applications as white pigments and in solar cell electrodes.

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Notes and references

- 1 M. Voigt, M. Klaumünzer, A. Ebel, F. Werner, G. Yang, R. Marczak, E. Spiecker, D. M. Guldi, A. Hirsch and W. Peukert, *J. Phys. Chem. C*, 2011, **115**, 5561–5565.
- 2 A. Janotti and C. G. van de Walle, *Rep. Prog. Phys.*, 2009, **72**, 126501.
- 3 P. Kumar, P. Kumar, A. Deep and L. M. Bharadwaj, *Appl. Nanosci.*, 2013, **3**, 141.
- 4 C. Klingshirn, *ChemPhysChem*, 2007, **8**, 782–803.
- 5 N. Erathodiyil and J. Y. Ying, *Acc. Chem. Res.*, 2011, **44**, 925.
- 6 S. Baldwin, M. R. Odio, S. L. Haines, R. J. O'Connor, J. S. Englehart and A. T. Lane, *J. Eur. Acad. Dermatol. Venereol.*, 2001, **15**, 5.
- 7 N. Serpone, D. Dondi and A. Albini, *Inorg. Chim. Acta*, 2007, **360**, 794.
- 8 Y. S. Fu, Y. F. Song, S. A. Kulinich, J. Sun, J. Liu and X. W. Du, *J. Phys. Chem. Solids*, 2008, **69**, 880.
- 9 Z. R. Tian, J. A. Voigt, J. Liu, B. McKenzie, M. J. Mcdermott, M. A. Rodriguez, H. Konishi and H. Xu, *Nat. Mater.*, 2003, **2**, 821.
- 10 (a) M. Distaso, M. Mačković, E. Spiecker and W. Peukert, *Chem.–Eur. J.*, 2012, **18**, 13265; (b) M. Distaso, R. N. Klupp Taylor, N. Taccardi, P. Wasserscheid and W. Peukert, *Chem.–Eur. J.*, 2011, **17**, 2923.
- 11 M. Voigt, M. Klaumünzer, H. Thiem and W. Peukert, *J. Phys. Chem. C*, 2010, **114**, 6243.
- 12 R. A. Laudise and A. A. Ballman, *J. Phys. Chem.*, 1960, **64**, 688.
- 13 S. Xu and Z. L. Wang, *Nano Res.*, 2011, **4**(11), 1013.
- 14 S. Schäfer, R. Srikantharajah, M. Klaumünzer, V. Lobaz, M. Voigt and W. Peukert, 2013, submitted.
- 15 H. Cölfen and Markus Antonietti, *Mesocrystals and Nonclassical Crystallization*, Wiley, 2008.
- 16 M. Distaso, D. Segets, R. Wernet, R. Klupp Taylor and W. Peukert, *Nanoscale*, 2012, **4**, 864.
- 17 (a) A. Taubert, D. Palms, Ö. Weiss, M. T. Piccinni and D. N. Batchelder, *Chem. Mater.*, 2002, **14**, 2594; (b) A. Taubert, C. Kabel and D. C. Martin, *J. Phys. Chem. B*, 2003, **107**, 2660.
- 18 M. Klaumünzer, M. Distaso, J. Hübner, C. Wolfrum, C. Krysch and W. Peukert, *Technical Proceedings of the 2013*

- NSTI Nanotechnology Conference and Expo, NSTI-Nanotech*, 2013, 1, p. 341.
- 19 T. Sakai and P. Alexandridis, *Langmuir*, 2004, **20**, 8426.
 - 20 M. Iwamoto, K. Kuroda, V. Zaporozhchenko, S. Hayashi and F. Faupel, *Eur. Phys. J. D*, 2003, **24**, 365.
 - 21 H. Krischner and B. Koppelhuber-Bitschnau, *Röntgenstrukturanalyse und Rietveldmethode*, 5., neubearbeitete Auflage edn, Vieweg, Braunschweig/Wiesbaden, Germany, 1994.
 - 22 J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, *Chem. Mater.*, 2002, **14**, 4172.
 - 23 Y. Gan, F. Gu, D. Han, Z. Wang and G. Guo, *J. Nanomater.*, 2010, 289173.
 - 24 D. R. Lide, *Handbook of Chemistry and Physics*, 2003, vol. 84, CRC Press.
 - 25 R. A. Sperling and W. J. Parak, *Philos. Trans. R. Soc., A*, 2010, 368.
 - 26 A. B. Djurišić and Y. Hang Leung, *Small*, 2006, **2**, 944.
 - 27 M. Klaumünzer, U. Weichsel, M. Mačković, E. Spiecker, W. Peukert and C. Kryschi, *J. Phys. Chem. B*, 2013, **117**(33), 9683.
 - 28 C. Bauer, G. Boschloo, E. Mukhtar and A. Hagfeldt, *Chem. Phys. Lett.*, 2004, **387**, 176.
 - 29 J. W. Hsu, D. R. Tallant, R. L. Simpson, N. A. Missert and R. G. Copeland, *Appl. Phys. Lett.*, 2006, **88**, 252103.
 - 30 L. T. Zhuravlev, *Colloids Surf., A*, 2000, **1731**, 1.
 - 31 L. Spanhel, *J. Sol-Gel Sci. Technol.*, 2006, **39**, 7.
 - 32 J. Mejia, V. Valembois, J.-P. Piret, F. Tichelaar, M. V. Huis, B. Masereel, O. Toussaint, J. Delhalle, Z. Mekhalif and S. Lucas, *J. Nanopart. Res.*, 2012, **14**, 815.
 - 33 N. D. Burrows, V. M. Yuwono and R. L. Penn, *MRS Bull.*, 2010, **35**, 133–137.
 - 34 P. K. Samanta, S. K. Patra, A. Ghosh and P. R. Chaudhuri, *Int. J. Biomed. Nanosci. Nanotechnol.*, 2009, **1**, 81.
 - 35 S. Liu, C. Li, J. Yu and Q. Xiang, *CrystEngComm*, 2011, **13**, 2533.
 - 36 D. Liu, W. Wu, Y. Qiu, S. Yang, S. Xiao, Q.-Q. Wang, L. Ding and J. Wang, *Langmuir*, 2008, **24**, 5052.
 - 37 R. Gao, Z. Liang, J. Tian, Q. Zhang, L. Wang and G. Cao, *RSC Adv.*, 2013, **3**, 18537.
 - 38 D. Segets, J. Gradl, R. N. Klupp Taylor, V. Vassilev and W. Peukert, *ACS Nano*, 2009, **3**(7), 1703.
 - 39 E. A. Meulenkamp, *J. Phys. Chem. B*, 1998, **102**, 5566.
 - 40 M. Kim, Y. J. Hong, J. Yoo, G.-C. Yi, G.-S. Park, K.-J. Kong and H. Chang, *Phys. Status Solidi RRL*, 2008, **2**, 197.
 - 41 Y. Masuda, N. Kinoshita and K. Koumoto, *Electrochim. Acta*, 2007, **53**, 171.
 - 42 J. W. Gibbs, *Trans. Conn. Acad. Arts Sci.*, 1873, **2**, 382.
 - 43 L. Onsager, *Ann. N. Y. Acad. Sci.*, 1949, **51**, 627.
 - 44 P. Bolhuis and D. Frenkel, *J. Chem. Phys.*, 1997, **106**, 666.