Nanorod to quantum dot conversion in ZnO dispersions with co-surfactants

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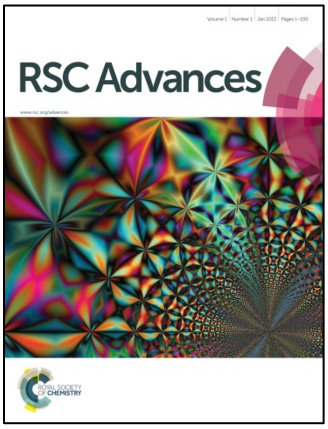

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Response to reviewer comments

Journal: RSC Advances
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Dear Dr. Monica Carreira-Mendez

Thank you for your email dated August 8th (2014) enclosing the reviews of the manuscript. We are very glad to note that our manuscript has been favorably recommended for publication.

The suggestions provided by reviewer 2 mostly involve language corrections. We have taken all three of her/his comments seriously, and have corrected the text suitably. The response to the referees is enclosed herewith. The modifications to the original manuscript are shown in italics.

Dr. Monica, finally we would like to place a request here:
Would you be able to withhold the publication of this article until Jan 2015, please? For strictly professional reasons, we prefer this article to be there in the *January or February 2015 edition of RSC Advances*. Kindly get back to us regarding this.

We are very grateful to you and your editorial team for providing us with an opportunity to publish in *RSC Advances.* Let me express my thanks to our reviewers for setting aside their valuable time for reviewing our work.

Thanking you,
Sincerely,
Tiju Thomas

Response to referee comments has been given below:

Reviewer #2:
Recommendation: The author replied all the comments thoroughly and considered all the useful suggestions in the manuscript. The only concern that I have with manuscript is its language. Language and word choice at times is too colloquial.

Response: We are very glad to note that our manuscript has been favorably recommended. We also thank our reviewer for pointing us to sentences that need to be rewritten, so that we conform to accepted standards in formal writing. The manuscript has been modified in accordance with the suggestions provided by the reviewer. We request our reviewer to refer to the revised paper.

***Comment 1:* Page 22, Last paragraph: If what we see is an outcome of Rayleigh instability, the d should have been ~190 nm (since r of the nanorod is ~50 nm).**

Reply: We thank our reviewer for pointing out the language issue.

Modifications: The sentence has been modified in the revised manuscript.

Cut-and-Paste:

"According to the Rayleigh equation, the fragmented particle diameter (d) can be determined by the radius (r) of the starting wire/rod; d = 3.78r.[20] *If the observed nanorod to quantum dot transition is an outcome of Rayleigh instability, the d is expected to be ~190 nm (since r of nanorod is ~ 50 nm). However the particle diameter of the nanodots obtained is 8.7±2.3 nm."*

……

***Comment 2:* Page 23: Note that this means, at room temperature, the nanorod must be purely a kinetic product, and not a thermodynamically favorable phase.**

Reply: We thank our reviewer for the suggestion.

Modifications: The sentence has been suitably modified.

Cut-and-Paste:

"This directly implies that at room temperature the nanorod is a purely kinetic product, and not a thermodynamically favored phase."

……

***Comment 3:* I will take out the word "speculate" from conclusion**

Reply: We would thank our reviewer for the suggestion.

<u>Modifications:</u> The word ‘speculate’ has been replaced by ‘hypothesize’, which is more acceptable in a scientific text.

Cut-and-Paste:

“We hypothesize that the observed phenomenon is driven by micellar dynamics.”

....

In addition, the following sentences have also been rewritten, to ensure accuracy in grammar, and usage of formal structure.

i. **Old sentence**
“However a purely chemical method for top-down nanosizing of a 1-D system is hitherto unknown in any inorganic system.”

New sentence
“However a purely chemical method for top-down nanosizing of a 1-D system is hitherto unreported for any inorganic system.”

ii. **Old sentence**
“It may be noted that a physical approach to 1-D to 0-D transition, which is driven by Rayleigh instability, have been reported in case of metal nanoparticles and polymers,[9-13] *but never in chalcogenides.”*

New sentence
“It may be noted that a physical approach to 1-D to 0-D transition, which is driven by Rayleigh instability, have been reported in case of metal nanoparticles and polymers.[9-13] *However this phenomenon has never been reported in chalcogenides.”*

iii. **Old sentence**
“We observe that ZnO_{NR} *shows a nanorod to quantum dots transition when it kept at room temperature for 24 h.”*

New sentence
“We observe that ZnO_{NR} *shows a nanorod to quantum dot transition when it kept at room temperature for 24 h.”*

……………………………………………………………………………………………..

On behalf of all my co-authors, I wish to thank Reviewer 2 for the relevant and helpful suggestions provided. I believe that the quality of our manuscript has significantly improved due to the feedback provided to us by our reviewers.

With regards,
Tiju Thomas

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COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Nanorod to quantum dot conversion in ZnO dispersions with co-surfactants

Niya Mary Jacob[a] and Tiju Thomas[a,b*]

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A chemically-induced nanorod to quantum dot transition is reported in ZnO. This transition is achieved using co-surfactants in a marginally polar solvent in chimie douce (soft chemical) conditions. This is different from the physical instability driven transitions reported so far in metal nanowires and polymers. We propose a suitable mechanism for the observed phenomenon.

In the nano regime, a wide range of nanostructures have been reported; (i) 0-D (e.g. quantum dots),[1] (ii) 1-D (e.g. nanorods, nanotube, nanowires etc.),[2, 3] (iii) 2-D (e.g. planar triangles, plates, discs etc.)[4] and (iv) 3-D (e.g. cubes, prism, tetrahedral, octahedral etc.).[5, 6] Materials that are studied most extensively include noble metals,[7] and chalcogenides[8] . In reports so far, morphology transition from one shape to another is often explained using orientation attachment, Ostwald ripening, digestive ripening, or some combination of these. However a purely chemical method for top-down nanosizing of a 1-D system is hitherto unreported for any inorganic system. In fact this transition is not expected since this morphology transition is completely counter to the one dictated by grain growth mechanisms reported so far. It is in this context that this study becomes significant. It may be noted that a physical approach to 1-D to 0-D transition, which is driven by Rayleigh instability, have been reported in case of metal nanoparticles and polymers.[9-13] However this phenomenon has never been reported in chalcogenides. These reported transitions have always been thermally activated, and occur due to perturbations in the system. A purely chemical approach to transition remains hitherto unreported. Also a 1-D to 0-D transition has never been observed in an oxide.

In this work, we show a novel transition of ZnO nanorod to monodisperse quantum dots (i.e. 1-D to 0-D morphology transition). ZnO is chosen since it is an applied material with several applications.[14, 15] To achieve this transition in ZnO, we use carefully chosen co-surfactants (Hexadecylamine (HDA) and Triethanolamine (TEA)) in a marginally polar solvent DCE (1, 2-Dichloroethane). The morphological transition occurs over a period of 24 hours at room temperature. The method to obtain this morphology transition is green, soft (i.e. chimie douce, which means employing low temperature), and facile. Furthermore we would like to point to the fact that here ZnO is obtained via decomposition of $Zn(NO_3)_2$ precursor in DCE at ~ 80 ^oC. To the best of our knowledge this is the first report on ZnO formation via decomposition of $Zn(NO_3)_2$ in an amine mediated reaction. This is achieved without any use of external oxygen sources.

ZnO reported here is synthesized using $Zn(NO_3)_2.6H_2O$ (98.0 %), Hexadecylamine (HDA) (98.0 %), 1,2- Dichloroethane (DCE) (99.0-99.5 %) and Triethanolamine (TEA) (99.0%). These chemicals are used without further purification. Synthesis of ZnO is carried out at 80 ^oC by use of a reflux setup. Silicone oil bath is used to maintain the reaction temperature. We always start with freshly prepared 3 mM $Zn(NO_3)_2.6H_2O$ in DCE. To do this, solid $Zn(NO_3)_2.6H_2O$ is added to DCE, which is maintained at 80 ^oC. Magnetic stirring (at 900-1000 rpm) of the mixture is continued throughout the reflux process. Once the $Zn(NO_3)_2.6H_2O$ dissolves completely, HDA is added to the reaction mixture in solid form. To this, TEA is added in drop wise manner to get monodisperse ZnO QD. In order to study the impact of precursor concentration on the stability of QDs, we vary the concentration of HDA and TEA with respect to the concentration of $Zn(NO_3)_2.6H_2O$. In doing so, we find that the molar ratio, $Zn(NO_3)_2.6H_2O$:HDA:TEA = 1:3:15, yields stable dispersions. Here the $Zn(NO_3)_2.6H_2O$ concentration in DCE is 3 mM. We would like to emphasize that TEA plays an important role in stabilizing the dispersions.[1]

Crystal structure of ZnO is examined by X-ray diffraction (XRD) (PAN analytical X'pert PRO) using Cu K_α (wavelength=1.54 Å) source. Material obtained using $Zn(NO_3)_2.6H_2O$ and HDA (but without TEA stabilization) is aged for 2-3 days at room temperature. This allows precipitation of the ZnO product, which is then drop cast on a glass slide for performing XRD. The diffraction pattern (Fig. 1a) obtained is consistent with JCPDS card no. 80-0075.

Formation of ZnO is also confirmed using UV-Vis spectroscopy (using Shimadzu UV-1700 Pharmaspec Spectrometer) (Fig. 1b). Absorption edge of ZnO sample without TEA corresponds to the bulk. Presence of TEA and HDA in the ZnO dispersion does not interfere with the observed absorption edge of ZnO. This is so since the absorption edges of TEA and HDA occur at much lower wavelength regimes (~ 220-230 nm). The data presented (both fig. 1b and the inset) shows that TEA and HDA are not absorbing in the region wherein ZnO absorbs. From Fig. 1b it is clear that the use of

TEA diminishes the size of the ZnO formed, since a blue shift of ~ 50 nm is observed in the corresponding UV-Vis spectrum.

To analyze the diminution of ZnO nanoparticles in presence of TEA, we study the TEM images of respective samples (Fig. 1c and d). TEM and High Resolution TEM (HRTEM) images are obtained from JEM 2100F microscope. We note that these TEM images are relatively grainy. This is due to the high concentration of surfactants in these samples. Fig. 1c shows the ZnO sample obtained from the reaction between $Zn(NO_3)_2.6H_2O$ and HDA without TEA. Image shows that the ZnO particles formed tend to be quasi-spherical, and have a high tendency to agglomerate. Fig. 1d shows the ZnO sample with TEA refluxed for 5 min. It is clear that TEA helps in reduction of particle size from ~ 50-100 nm to ≤ 20 nm, which is consistent with the blue shift observed in the UV-Vis spectrum. Hence we conclude that HDA helps in ZnO formation and TEA is responsible for stabilization of the QD dispersion formed. Due to the high concentration of surfactants present in this sample, it is hard to get clearer TEM images on this sample. Graininess in these images is an outcome of the same. But from HRTEM analysis we know that ZnO is in the range 10-20 nm; anything smaller is an artifact in the TEM image.

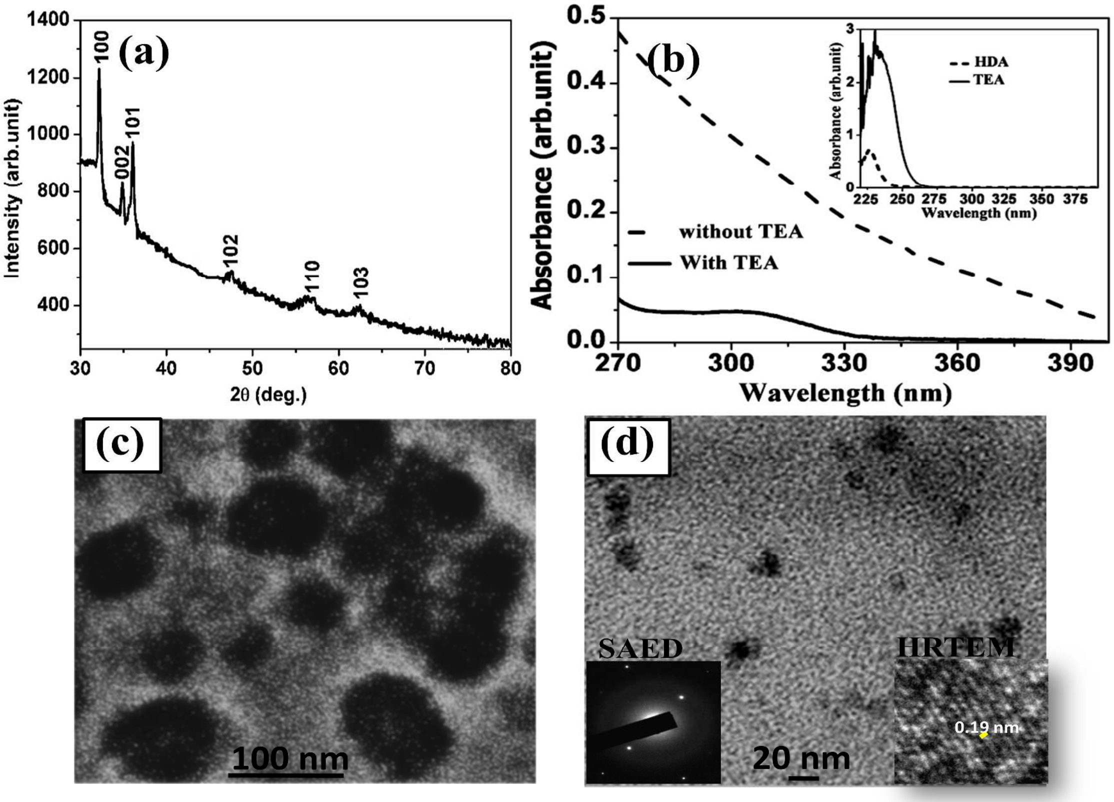

Fig. 1 (a) XRD of ZnO synthesized by the reaction between $Zn(NO_3)_2.6H_2O$ and HDA at 80 °C in DCE. (b) UV-Vis spectra of ZnO dispersion with and without TEA. Inset shows absorption spectra of 15 mM TEA and 3 mM HDA in DCE. (c) TEM image of as-synthesized ZnO without TEA shows agglomeration. (d) TEM image of ZnO QD after 5 min. refluxing in presence of TEA. Its addition results in stable spherical ZnO. Inset shows HRTEM and SAED of respective sample. The lattice fringe with 0.19 nm spacing corresponds to [102] plane of wurtzite ZnO and is crystalline.

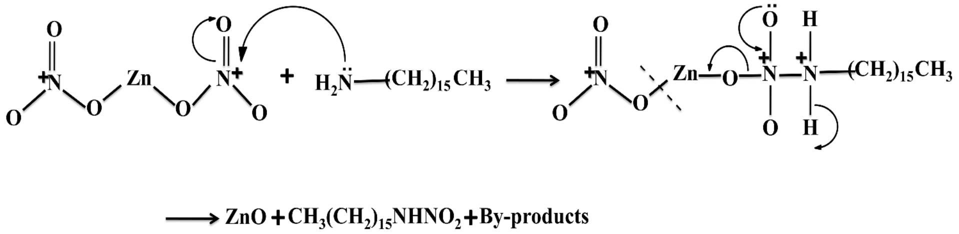

Fig. 2 Proposed amine (HDA)-mediated formation of ZnO using $Zn(NO_3)_2$ as starting precursor.

To our knowledge this is the first report on the synthesis of ZnO nanoparticle, using $Zn(NO_3)_2$ precursor in an amine mediated reaction. In analogy with the addition-elimination mechanism proposed by Zhang et. al,[16] we suggest that ZnO formation from $Zn(NO_3)_2$ is aided by HDA through the electron transfer process (Fig. 2). We propose that in this reaction, the N-atom in $Zn(NO_3)_2$, which has a positive formal charge, accepts a lone pair of electrons from the sp^3 hybridised N-atom of HDA. This leads to an intermediate formation (shown in Fig. 2), followed by an addition-elimination process. This results in ZnO. Since this is the first report on the synthesis of ZnO by use of $Zn(NO_3)_2$ and HDA, the precise mechanism, kinetics and thermodynamics involved deserve further investigation. However HDA addition alone results in a cloudy dispersion, which is due to ZnO's tendency for agglomeration and precipitation. This issue can be overcome through use of adequate amount of TEA ($Zn(NO_3)_2.6H_2O$: TEA= 1:15).

We study the effect of reflux time on the ZnO stability. Aliquots are collected at different time intervals from the dispersion in which the $Zn(NO_3)_2.6H_2O$ is 3 mM, $Zn(NO_3)_2.6H_2O$:HDA:TEA =1:3:15. Fig. 1d shows that 5 min. refluxed sample has particles of quasi-spherical nature. We observe nanorod formation in this sample when it is refluxed for 2 h; hence this sample is called ZnO_{NR} (Fig. 3a). Beyond 6 h of reflux, precipitation is observed. Therefore we choose ZnO nanorods obtained using a 2 h reflux.

We observe that ZnO_{NR} shows a nanorod to quantum dot transition when it kept at room temperature for 24 h. This sample is called $ZnO_{NR\rightarrow QD}$. Fig. 3b shows nanorod fragmentation stage and finally quantum dot formation (Fig. 3c). Both Fig. 3b and c are grainy; in fact we could not get clearer TEM images of these samples due to the high concentration of co-surfactants. It may be noted that, at these magnifications, it is relatively straightforward to get clear images of the nanorod samples, as opposed to that of quantum dots (Fig. 1c and d, 3b and c). This is possibly because in the nanorods, most of the surfactants added adhere to the ZnO surfaces, and do not phase separate.

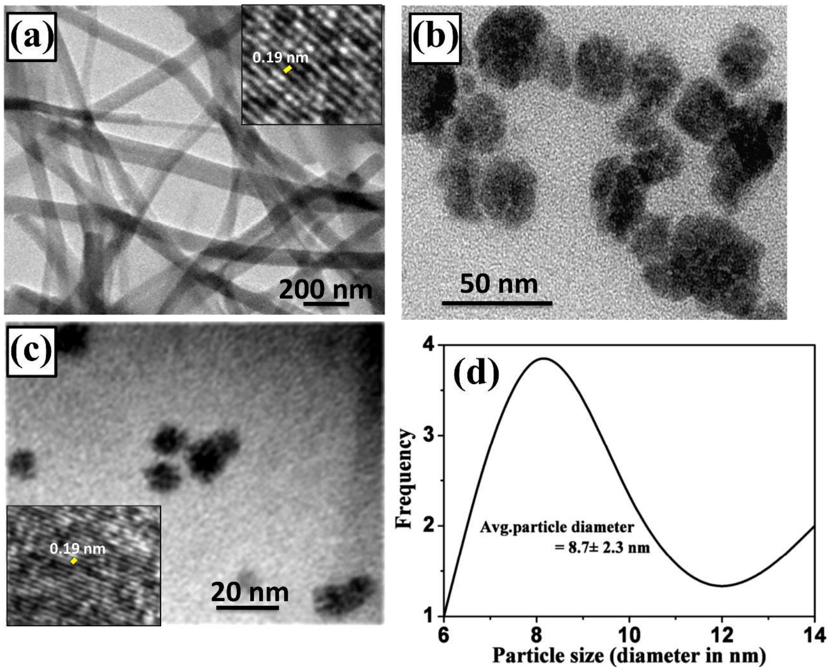

Fig. 3 TEM images of (a) ZnO_{NR} obtained after 2 h reflux of the precursors using optimized concentration, (b) the nanorod fragmentation stage, and (c) ZnO $_{NR\rightarrow QD}$, i.e. quasi-spherical quantum dots obtained from ZnO_{NR}. (d) Shows the particle size distribution of ZnO $_{NR\rightarrow QD}$. Inset of (a) and (c) shows the HRTEM of respective samples. The lattice fringes with 0.19 nm spacing corresponds to [102] plane of wurtzite ZnO.

The particle size distribution (Fig. 3d) of these ZnO quantum dots is obtained using 'ImageJ' analysis of respective TEM images. The average particle diameter is found to be 8.7± 2.3 nm. HRTEM (inset of Fig. 3a and c) confirms that both nanorod and the quantum dots formed are ZnO. The lattice fringe with 0.19 nm spacing corresponds to [102] plane of wurtzite ZnO and is consistent with JCPDS card no. 80-0075. It is well known that ZnO yields nanorods when growth occurs along the c-axis.[17] Furthermore, we would like to recall that the QDs are polycrystalline; so are the nanorods. This is entirely expected since the nanostructures (QDs, and nanorods) studied here are soft-chemically assembled.[18]

Fragmentation of nanorods which eventually yield quantum dots is analogous to Burke's observation, where a similar morphology transition is observed in polystyrene-b-poly(acrylic acid).[19] Given the fragmentation of the nanowires, it is reasonable to ask if the morphological transition we notice is due to a 'Rayleigh instability' driven fragmentation of the nanorods. It may be noted that similar morphological transitions have been observed in polymer systems,[9, 10] and metal nanorods (e.g. Cu, Au) etc.[11-13] However in each of these cases, the instability is introduced via annealing at fairly high temperatures (100-600 °C). This is because Rayleigh instability requires surface diffusion, which is favoured by high temperatures.

In the present work, given that the fragmentation of the nanorods is observed at room temperature, we believe that the phenomenon is more likely to be chemical in origin. That is to say that the fragmentation of nanorods is likely due to the eventual micelle formation of co-surfactants, since they are used in fairly high concentrations here. Co-surfactants that are initially chemisorbed on ZnO nanorods undergo thermodynamically driven re-assembly, which results in the observed morphology transition. According to the Rayleigh equation, the fragmented particle diameter (d) can be determined by the radius (r) of the starting wire/rod; $d = 3.78r$.[20] If the observed nanorod to quantum dot transition is an outcome of

Rayleigh instability, the *d* is expected to be ~190 nm (since *r* of nanorod is ~ 50 nm). However the particle diameter of the nanodots obtained is 8.7±2.3 nm. Therefore the statistics of the fragmented particles cannot be explained based on expressions derived for Rayleigh instability. Hence we conclude that the observed phenomenon is not an outcome of a physical instability. The nanorod to quantum dot transition is most likely of chemical origin. To the best of our knowledge this is the first report on chemically-induced, nanorod to quantum dots transition observed in an inorganic material. Due to the novelty of the observation, the fundamental mechanisms underlying this transition is not fully understood or known. However based on the chemistries involved, a mechanism has been proposed.

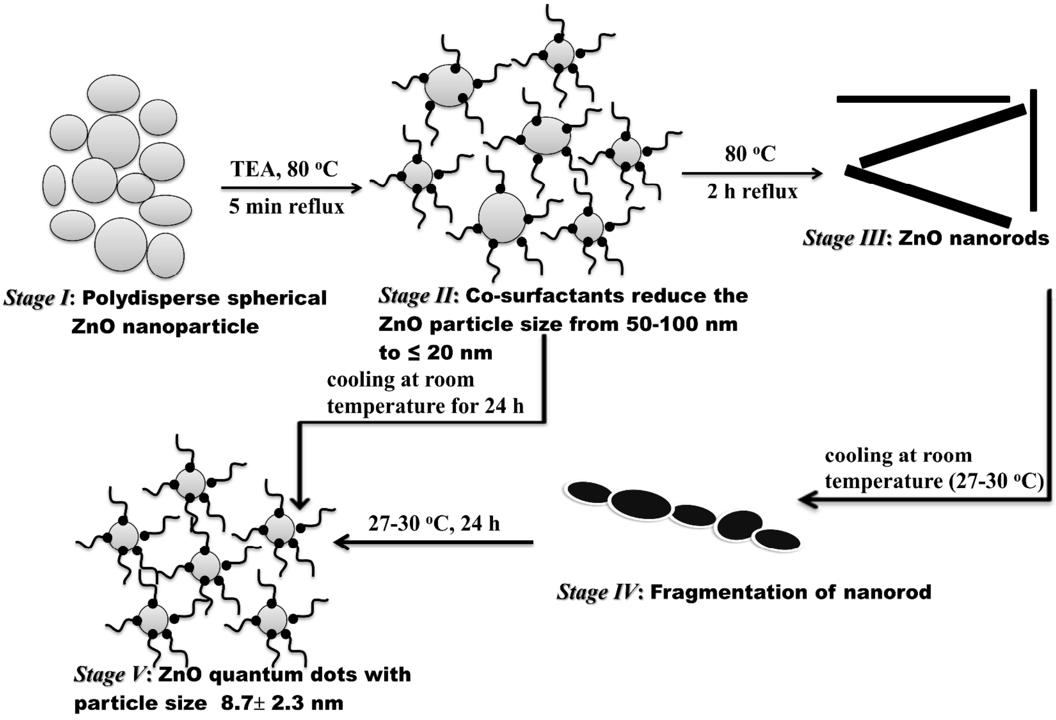

Fig. 4 Schematic representation of morphological transitions reported. Polydisperse ZnO QDs (Stage II) can form nanorods (Stage III) under 80 °C reflux condition. These nanorods in turn undergo a chemically-induced transition at room temperature (Stage IV), which can eventually result in monodisperse QDs (Stage V). Stage II to Stage V indicates the direct transition of polydisperse ZnO QDs to a monodisperse QDs over a period of 24 h, when stored at room temperature

Fig. 4 shows the reported stages of the nanorod to quantum dots morphological transformation. Stage I and II show that co-surfactants (TEA and excess HDA) help in reduction of the: (i) particle size of ZnO formed, and (ii) agglomeration tendency. The introduction of co-surfactants results in a particle size reduction of ~ 30 nm (from 50-100 nm to ≤ 20 nm). This is confirmed using respective TEM images (Fig. 1 c and d). These quasi-spherical particles form nanorods under 2 h reflux condition at 80 °C (Fig. 3 a; Fig. 4 S*tage III*). This is consistent with Li et. al's observations that at elevated temperatures, the tendency of surfactants to detach from the surface of nanoparticle increases significantly. This leads to agglomeration, ripening and orientation attachment, which in turn causes nanorod growth.[21] S*tage IV* represents the room temperature instability of nanorod (coated with co-surfactants). This directly implies that at room temperature the nanorod is purely a kinetic product, and not a thermodynamically favored phase. That is, at room temperature, with the co-surfactants reported, ZnO nanorods are merely metastable phases. The final stage (*Stage V*) shows monodisperse ZnO quantum dots, due to digestive ripening of ZnO nanoparticles that are formed from the nanorods.

Conclusions

The current work deals with a purely chemical method for top-down nanosizing of a 1-D system. We show a novel morphology transition of ZnO nanorod to quantum dots (with particle diameter = 8.7±2.3 nm). This is the opposite of the crystal growth pattern which is normally expected. The morphology transition is achieved in soft chemical condition (at reaction temperature of 80 °C) using a combination of co-surfactants in a marginally polar solvent. We hypothesize that the observed phenomenon is driven by micellar dynamics. To the best of our knowledge this is the first report on chemically-induced, nanorod to quantum dots transition observed in an inorganic material. Incidentally this is also the first report of ZnO synthesis using an amine-mediated process.

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Niya Mary thanks Mr. Vadivel (Inorganic and Physical chemistry Department, IISc) and Ms. Shravani (AFMM, IISc) for help with material characterization. Tiju Thomas thanks Department of Science and Technology for support in the form of research grant (DST 01117). He also thanks Prof. T. A.

Abinandanan (Materials Engineering, IISc), Prof. Sandeep Kumar (Raman Research Institute) and Prof. Abhik Choudhuary (Materials Engineering, IISc) for useful discussions.

Notes and references

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Graphical Abstract

A chemically-induced nanorod to quantum dot transition is reported in ZnO. This transition is achieved using co-surfactants in a marginally polar solvent in chimie douce conditions. This is different from the physical instability driven transitions reported so far in metal nanowires and polymers. We propose a suitable mechanism for the observed phenomenon.