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Continuous Growth Synthesis of Zinc Oxide Nanocrystals with Tunable Size and Doping

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ABSTRACT

Chemical syntheses of nanocrystals using colloidal techniques enable the production of a large variety of nanomaterials of a desired size, shape and composition. Therefore, these syntheses hold tremendous promise for the production of nanoparticles for next-generation technologies. However, they suffer from scalability issues, which can limit, or prevent, their translation into commercial technologies. Here we show the synthesis of zinc oxide nanocrystals with controlled size and doping using a continuous growth method, which is easily scalable. We demonstrate the tunable growth of pure ZnO nanocrystals from ~ 5 nm up to ~ 30 nm, and the synthesis of plasmonic ZnO nanocrystals by incorporating substitutional trivalent dopants such as aluminium, gallium and indium. We investigated the growth kinetics of these nanocrystals and used a variety of characterization techniques to fully elucidate the relationship between synthetic conditions and nanocrystal properties. We validate our reaction method by synthesizing Al-doped ZnO nanocrystals on a gram-scale, and with a reaction yield of 100%. These nanocrystals are used to deposit thin coating with excellent transparency and enhanced electrical conductivity compared to native ZnO.

INTRODUCTION

The synthesis of nanocrystals (NCs) using colloidal techniques is one of the more versatile and powerful methods for the preparation of high-quality, stable suspensions of NCs. Obtaining a colloidally stable dispersion of NCs, rather than having clusters of aggregated particles is vital for many applications, including depositing coatings of optical quality, and embedding NCs within matrices.^{1,2,3} Therefore, colloidal reactions for NCs have been constantly refined and improved since the seminal works conducted decades ago.^{4,5} A clear understanding of the nucleation and growth events in colloidal NC syntheses has made possible to create a large library of synthetic methods for the preparation of colloidal NCs, including metals, semiconductors, quantum dots (QDs), oxides, and dielectrics.^{6,7,8,9,10} Among these, doped metal oxides have attracted increasing interest, due to the thermal and chemical stability of metal oxides, as well as the enhanced optical, electrical and magnetic properties that may be imparted to the NCs when appropriately doped.^{11,12,13,14,15} One of the main area of research for doped metal oxides is the synthesis of degenerately (aliovalently) doped wide band gap oxides, for use as transparent electrodes in optoelectronic devices including photovoltaics, light emitting diodes (LEDs) and electrochromics, but also as IR active materials for catalysis and sensing.^{16,17,18,19}

The colloidal synthesis of doped metal oxide NCs has been traditionally achieved using hot injection methods, which rely on the swift injection of one or more precursors into a solution containing hot solvents and/or surface ligands to trigger the nucleation of NCs. Despite the high quality of NCs produced, the inherent non-scalable nature of this hot injection event has motivated the search for other types of colloidal synthesis approaches such as heat-up and flow reactions.^{8,20} One of the main methods that has been developed for the synthesis of metal oxide colloidal NCs is the reaction of a metal precursor with water that is formed *in-situ* from

an esterification reaction between metal carboxylates and alcohols, at temperatures below those required for the thermal decomposition of the metal carboxylates themselves. This reaction can be used in both hot-injection and heat up protocols, and has been explored for a variety of pure and doped metal oxides including ZnO, TiO₂, MnO, etc.^{21,22,23,24} However, despite the robustness and versatility of this synthetic protocol, and its proven application within heat-up (potentially scalable) reactions, there is an intrinsic issue with this type of synthesis routes, that hinders their scalability: the amount of water that is generated by the esterification reaction is directly related to the amount of precursors used. If the reaction is scaled up, the excess water generated causes well-known problems such as inhomogeneous nucleation of particles, sudden growth, and precipitation of large aggregates.

A potential solution to this issue has been recently reported by the Hutchison group, which proposed a slow injection approach coupled to a continuous flow of nitrogen gas.²⁵ In this system, metal oleates are slowly injected into a hot solution of oleyl alcohol, causing the resultant esterification reaction to trigger the formation of metal oxide NCs. The excess water that is formed is removed as water vapor thanks to a constant stream of nitrogen flushed through the headspace of the reaction vessel. In conjunction with metal precursors with the right reactivity, this technique enables the highly controlled growth of NCs in a layer-by-layer fashion, similarly of what happens in the production of polymers through living polymerization.²⁶

Based on these encouraging results, more work was done on refining this synthetic method to achieve unprecedented control of NC size, dopant concentration and even dopant location in the case of indium oxide.^{27,28} Recently, iron oxide NCs have also been prepared with good control on their size and size distribution using a continuous growth method.²⁹ However, adapting this reaction method to other metal oxides has proven highly challenging

especially in the case of zinc oxide. The synthesis of ZnO NCs using this method has shown poor reproducibility and low reaction yields.²⁵ Moreover, zinc oleate is a solid at room temperature, and therefore the reaction must be done by slowly injecting a hot precursor (above ~80 °C) over the course of several minutes, which is problematic and itself becomes a source of irreproducibility. It is worth highlighting at this stage that ZnO colloidal NCs have been widely investigated for decades, starting from the seminal works of Bahnemann and Spanhel involving the precipitation of ZnO clusters in alcohols using bases such as NaOH and LiOH.^{30,31} Several reaction methods for ZnO have been developed since, including forced hydrolysis, solvothermal reactions, and high temperature colloidal reactions.^{32,33,34,35,36,37} Of all the available methods, high temperature reactions (either through heat up or hot injection) provided the best results in terms of NC quality, colloidal stability, and tunability of size, shape and composition (especially aliovalent doping). However, the issues associated with scalability (such as the *in-situ* water generation mentioned earlier) still plague these reactions, and therefore a synthesis that enables control of NC properties using a scalable protocol is highly desirable.

In this study we overcome all these issues by developing a synthesis for ZnO NC based on a slow injection approach, through the use of a zinc precursor that is not only liquid at room temperature, but is also more reactive. This drastically increases the reproducibility of our slow injection process, and also results in a reaction yield close to 100%. We successfully developed a robust reaction protocol that enables the synthesis of ZnO NCs with fine control over their size and doping levels. Our reaction protocol is also readily scalable and enables the isolation of grams of materials without any of the aforementioned issues.

RESULTS AND DISCUSSION

We firstly formed zinc oleate by reacting zinc acetate with oleic acid at $\sim 100\text{ }^{\circ}\text{C}$ under vacuum, in order to remove the acetic acid formed in the process. Preliminary reactions were carried out through either the injection of hot ($\sim 80\text{ }^{\circ}\text{C}$) zinc oleate, or through the injection of commercially available zinc neodecanoate (a zinc carboxylate which is liquid, albeit very viscous, at room temperature) into hot oleyl alcohol. However, these reactions did not produce any appreciable recoverable material, suggesting a low reactivity of zinc carboxylates alone. We therefore decided to modify the zinc oleate to achieve the dual goal of increasing its reactivity towards the formation of ZnO *via* the esterification with oleyl alcohol, and of increasing its stability at low temperatures, enabling a simpler and more reproducible synthetic protocol. Once the metal oleate complex was formed as mentioned earlier, oleylamine was added. Amines are commonly used to form complexes with zinc,³⁸ and in fact this is one of the main strategies used to solubilize zinc acetate in alcohols for use as sol-gel precursors for ZnO.³⁹ Through this strategy, we prepared a zinc precursor which can be cooled down to room temperature obtaining a viscous liquid, suitable for a continuous slow injection over the course of several minutes. In addition, the prepared precursor enabled the nucleation and growth of ZnO NCs very reproducibly within a range of reaction temperatures, with $\sim 100\%$ reaction yield, indicating that the role of oleylamine is to increase the reactivity of the zinc carboxylates.

Figure 1 shows an overview ZnO NCs prepared with our slow injection protocol. The detailed description of the experimental conditions is presented in the Methods section. Briefly, the zinc oleate/oleylamine precursor is slowly dripped (0.3 mL/min) into preheated oleyl alcohol ($240\text{--}280\text{ }^{\circ}\text{C}$) under a constant stream of nitrogen flushed through the headspace of the reaction flask. We conducted our reactions using a large excess of oleyl alcohol (16 mL , 50 mmol) compared to the amount of zinc precursor injected (usually less than 2 mmol in total). The synthesized NCs are generally isotropic, either spheroidal or pyramidal in shape (Figure 1a), with size ranging between ~ 5 and 30 nm . The size can be readily controlled through the

reaction temperature and the amount of precursor used, as it will be thoroughly discussed later in the manuscript. Our ZnO NCs are highly crystalline, displaying the commonly observed wurtzite crystal structure (ICDD No. 36-1451, Figure 1b). Moreover, as expected from ZnO, the NCs are highly transparent in the visible range and show a pronounced absorption onset in the near UV region (Figure 1c), associated with the direct band gap of ZnO at around 3.3 eV (Figure 1d).

Figure 1. Characterization of typical ZnO NCs synthesized with the slow growth approach. a) TEM image (the scale bar is 100 nm). b) XRD pattern (the ZnO wurtzite reference ICDD No. 36-1451 is highlighted as vertical lines). c) Optical absorption spectra and d) respective Tauc plot for a ZnO colloidal solution.

After demonstrating the ability to synthesize ZnO NCs with a slow injection protocol, we explored the parameter space of this colloidal synthesis starting from the investigation of the effect of the reaction temperature and of the amount of precursor added on the properties of ZnO NCs. Adding slowly the amine/oleate precursor into hot oleyl alcohol triggers the formation of ZnO NCs quite reproducibly. However, if we inject just a couple of drops of zinc

precursor into the alcohol, ZnO NCs do not nucleate. We confirmed this through UV-Vis spectroscopy, which shows no presence of the ZnO absorption edge. By performing a series of slow addition reactions at various temperatures we consistently found that ZnO NCs form after injecting 0.2 - 0.3 mmol of precursor, corresponding to a monomer concentration of at least 0.012 M. The formed NCs could then be easily recovered from the mother liquor with common antisolvent precipitation protocols (see Methods). Therefore, a critical amount of precursor is required to trigger the nucleation of the ZnO NCs. This is consistent with the conventional nucleation and growth theory of nanocrystals (first outlined by LaMer), which demonstrated that a threshold concentration of monomer is required for the solution to become supersaturated and to promote nucleation.⁴⁰ Notably, once this threshold is reached, ZnO NCs nucleate and stop growing almost instantly. In fact, by monitoring optically the absorption edge of ZnO we found no change over time (see Figure S1 in the Supporting Information). This suggests that once the critical concentration is reached and the NCs nucleate, the reactivity of our precursor is high, and this enables fast growth of NCs. This is a desirable scenario for our synthesis because it will prevent build-up of unreacted precursor during the slow injection process.

Considering the role played by this critical amount of precursor, we decided to isolate the nucleation phase from the growth by rapidly injecting a small aliquot of precursor (1 mL, corresponding to 0.33 mmol of zinc giving a monomer concentration of ~0.02 M) into hot oleyl alcohol and let it react for a few minutes before adding the remainder of the precursor through the slow injection protocol. In this way we could undertake a detailed study of the parameter space of the growth of ZnO NCs independent of the nucleation event. All reactions conducted at 240 °C and above yielded NCs, while reactions carried out below this temperature failed to nucleate ZnO reproducibly. All materials synthesized above 240 °C are crystalline and show phase pure wurtzite ZnO (Figure 2a). The NCs synthesized at higher temperatures are on average bigger than those synthesized at lower temperatures, as commonly observed in

colloidal syntheses. This is obvious from the TEM images presented in Figure 2b-e and from the crystallite size evaluated using the Scherrer formula from the XRD patterns (Figure S2). Unexpectedly, ZnO NCs synthesized at the highest temperature (300 °C) show a slightly smaller crystallite size. TEM analysis of these NCs revealed some evidence of etching (Figure 2e), with many particles showing a concave cone shape, not observed in the other samples. We believe that the excess oleic acid is responsible for the slow dissolution of ZnO through the formation of zinc oleate at such high temperatures. To prove that, we synthesized a sample in the same exact conditions, but with half the amount of oleic acid. This amount is still enough to form pure oleate precursor, but the “free” oleic acid in the reaction mixture is drastically reduced. We observed a substantial reduction in the degree of etching, and a slightly larger crystallite size, therefore confirming the role played by oleic acid in the slow dissolution of ZnO (Figure S2 and Figure S3). It is worth noting that similar effects have been observed previously for various metal oxide NCs, including ZnO.^{41,42,43,44}

Figure 2. Effect of reaction temperature. a) XRD patterns for ZnO NCs synthesized at different temperatures. The reference pattern for bulk ZnO (ICDD No. 36-1451) is reported at the bottom. b-e) TEM images of ZnO NCs synthesized at 240 °C (b), 260 °C (c), 280 °C (d) and 300 °C (e). The scale bar is 50 nm. f) High resolution TEM of a single ZnO NC (scale bar 2 nm) and (g) respective FFT image.

As mentioned earlier, all synthesized particles are crystalline, as confirmed by XRD data as well as by high resolution TEM and the associated Fast Fourier Transform (FFT) presented in Figure 2f,g. Importantly, while we studied the growth of ZnO by isolating the nucleation event through the swift injection of the first 0.33 mmol of precursor, we demonstrated that this modification has little or no effect on the final product compared to a conventional continuous addition method, as shown in Figure S2 and Figure S4. Interestingly, the photoluminescence properties of ZnO NCs are dependent on the reaction temperature. It is well known that besides the band edge emission, ZnO NCs show a distinctive emission band in the visible region associated with a variety of defects, mostly located at the surface, including oxygen vacancies, zinc vacancies and zinc interstitials.^{45,46,47,48} In this study we noted that the defect band is well defined for ZnO synthesized at high temperatures, while is suppressed in NCs synthesized at lower temperatures (Figure S5). This points to either less defective NCs and/or better defect passivation in NCs synthesized at lower temperatures, which is somewhat unexpected, as higher reaction temperatures are known to reduce the amount of surface defects and the related emission properties in semiconductor NCs, including ZnO.^{49,50,51}

The other parameter other than reaction temperature that is responsible for particle size is the amount of precursor used. It has been reported that for indium oxide the size of the nanocrystals can be accurately controlled through the progressive addition of metal precursors, which preferentially decompose on the surface of pre-formed NCs rather than nucleating

homogeneously in solution.^{26,52} We performed a series of reactions and analyzed the growth of the NCs at different temperatures by collecting aliquots at different addition times (volumes), and analyzing the optical properties (band gaps) and the size of the NCs by TEM. Representative results are reported in Figure 3. A reduction of band gap is observed by either increasing the reaction temperature or increasing the amount of precursor added, confirming progressive growth of particles (Figure 3a). The band gap values tend to converge to ~ 3.3 eV, the value for bulk ZnO, regardless of the reaction temperature. When a small amount of precursor added (less than ~ 1 mmol) the NCs are in the quantum confined regime, while if more precursor is added, the NCs grow beyond quantum confinement and behave optically as bulk ZnO. For reference, all the Tauc plots used to obtain the graph presented in Figure 3a are in the Supporting Information as Figure S6.

The growth of ZnO NCs according to reaction temperature and amount of precursor used is further confirmed by TEM images and the respective size histograms (Figure 3b and Figure S7), which show progressive particle growth with the amount of precursor added and on average larger particles at higher reaction temperatures. The size of the NCs can be easily tuned between ~ 5 nm to above 25 nm with our reaction protocol. The size distribution for these ZnO particles is around 15% for small particles (< 10 nm) and increases to $\sim 25\%$ for larger particles (see Table S1 for complete statistics). This broadening of the size distribution could be due to the fact that a small fraction of zinc precursor homogeneously nucleates in solution, rather than contributing to the growth of existing particles. This is a major difference compared to previously reported In_2O_3 syntheses where after the nucleation event, the growth happens almost exclusively on existing surfaces, ensuring a narrow particle size distribution ($\sim 10\%$) even for large particles.⁵² Moreover, looking at the emission properties, we did not find any substantial difference in photoluminescence of ZnO NCs as a function of their size if the synthesis temperature remains the same, except for the expected slight shift of the band edge

emission towards lower energies (Figure S8). We tried to improve the dispersity in our ZnO NCs by reducing the growth temperature (210-225 °C) after the nucleation event (achieved at 240-260 °C). We noted that even if the size distribution was slightly narrowed, reaching ~15% at the end of the reaction, both the NC size and the yield of the reaction were lower than expected (Figure S9). This shows that at low growth temperature (<225 °C) the zinc precursor is not reactive enough to contribute substantially to NC growth. We therefore decided not to pursue further these two-temperature reactions and focus on the synthesis at constant temperature, which ensure higher reaction yields even if the distribution of the size of the NCs is slightly broadened.

Figure 3. Effect of reaction time and temperature. a) Optical band gap for ZnO NCs synthesized at different temperatures and using different amounts of precursor. The dashed horizontal line identifies the bulk band gap of ZnO. b) Size distribution histograms obtained from TEM of NCs synthesized at 240 °C and 280 °C with different amounts of zinc precursor.

As mentioned earlier, in the temperature range we investigated we observed that the nucleation of ZnO is very fast, and once the precursor is injected into the hot oleyl alcohol it reacts almost immediately. This enables the reaction to be stopped and kept at a set temperature without the further growth of particles. This is shown in Figure S1 for small NCs synthesized with 0.33 mmol (0.02 M) zinc precursor and in Figure S10 where particle synthesized using 1.66 mmol precursor (0.079 M) are kept at the reaction temperature (280 °C) for one hour without adding any more precursor. This stability of ZnO NCs towards prolonged annealing in solution allows for the reliable tracking of the NC sizes (for example with a simple UV-Vis measurement) and if larger particles were required, to re-start the addition. We further confirm this by adding even more precursor, maintaining all the other reaction parameters constant. This is shown in Figure S11 for ZnO NCs synthesized with up to 6.64 mmol precursor (zinc concentration 0.185 M): the diffraction patterns show sharper peaks with increasing amount of precursor added, indicating larger NC size.

Having described in detail the effect of temperature and amount of precursor on the growth of ZnO NCs using a slow injection method, and showing full tunability in the size of ZnO NCs, we now focus on the synthesis of doped ZnO. Plasmonic semiconducting NCs, and especially doped metal oxides have recently attracted a lot of interest for a variety of applications in optoelectronics, catalysis and sensing. Most of the literature focuses on ITO due to its sharp LSPR in the near infrared and the ability to synthesize NCs of a specific size, doping level and dopant location within the NCs.^{27,53,54} In this work we focus on doped ZnO, as a cheaper, earth-abundant alternative, which is also still relatively unexplored in the form of colloidal NCs. When ZnO is doped with aliovalent cations such as Al, Ga or In, it can become a degenerate semiconductor showing enhanced electrical conductivity and the rise of a LSPR,

typically in the mid-IR range.^{55,56,57,58} Here we chose aluminium as the dopant because of its earth abundance, and also because (due to the large difference in ionic radius between divalent zinc and trivalent aluminium) it is the hardest of the trivalent cations mentioned earlier to be incorporated within the ZnO lattice.^{59,60} We synthesized a series of Al-doped ZnO (AZO) NCs with different dopant amounts by substituting a fraction of zinc precursor with Al precursor, and performing the reaction in the same way as for the undoped ZnO (see Methods for details).

A distinctive change in color of the synthesized NCs from colorless to green-blue is observed when Al is present, with the color being more intense at higher doping levels. This color has been observed previously in doped ZnO,^{60,61} and is common in other plasmonic metal oxides such as ITO, WO_{3-x}, and Sb-doped SnO₂.^{62,63,64} Figure 4a shows the optical absorption spectra in the visible and near infrared for AZO NCs synthesized with different Al doping level (5, 10 and 20 atomic % nominal). A strong absorption in the infrared is observed, corresponding to the rise of the LSPR peak. In addition, a progressive widening of the optical band gap is observed, which is ascribed to the Burstein-Moss effect, given that the NCs are well outside the quantum confinement regime.⁴⁹ The nature of the NIR absorption has been confirmed with FTIR (Figure S12) which shows the LSPR peak centered between ~5 and 8 μm depending on the doping level. From the position of the plasmon we may roughly estimate the free carrier concentration using simple Mie-Drude formalism, assuming spherical particles and homogeneous doping. A detailed description of the equation used is reported elsewhere.⁶⁰ Despite the assumptions made, this model gives a metric to estimate the carrier concentrations and therefore the amount of active dopants within ZnO. In addition, through compositional analysis we evaluated the amount of Al incorporated into the NCs. Figure 4b shows a plot of Al doping amount vs. carrier concentration. The carrier concentration is as high as 10^{20} cm^{-3} for the NCs synthesized with the highest doping, which is consistent with previous results on doped ZnO.^{65,60} Moreover, the doping efficiency (dopant effectively incorporated within ZnO

with respect to the amount of precursor used) is ~40%, regardless of the actual doping level (see also Table S2). This is a remarkable result, considering the reported low reactivity of Al precursors combined with the stresses induced in the ZnO lattice by the small Al^{3+} ions. Therefore, with this synthetic method we were able to achieve tunable doping levels up to 10%, without the segregation of any impurity phases, as confirmed by XRD analyses (Figure S13). However, we did notice a progressive broadening of the LSPR peak with increasing dopant concentration. The measured full width at half maximum (FWHM) values are $\sim 1200\text{ cm}^{-1}$, $\sim 1450\text{ cm}^{-1}$ and $\sim 1900\text{ cm}^{-1}$ for AZO5, AZO10 and AZO20, respectively. This broadening can be indicative of increased ionized impurity scattering, which is common in plasmonic metal oxides, especially at high doping levels.¹⁴ In addition, doping variations between individual NCs, and shape effects in faceted NCs can also be held accountable for such broadened LSPR when measured for an ensemble of particles.⁶⁶

We analyzed the synthesized AZO NCs using TEM (see Figure S14) and we noted that the presence of small amounts of Al does not affect significantly the NC size or shape. This is in contrast with what was observed previously.^{65,60} However, for large Al doping levels, the NCs become highly polydisperse and irregular, possibly due to the stresses caused by excess Al to the ZnO crystals, which heavily affect their growth.

Figure 4. Synthesis of Al-doped ZnO NCs. a) UV-Vis-NIR spectra of ZnO NCs doped with different amounts of Al. The inset shows the respective Tauc plots. b) Charge carrier concentration evaluated from the LSPR frequency and nominal vs. real (from EDX) Al concentration for ZnO NC doped with different amounts of aluminum.

After establishing the reaction protocol for highly doped ZnO NCs, we decided to investigate the kinetics of doping using this continuous growth method. As discussed earlier, undoped NCs do not change over time when the addition of the precursor is stopped, *i.e.* the precursor reacts almost instantly and completely. However, in the case of doped NCs, the kinetics are slightly different. Figure 5 shows the results of a kinetic study conducted on an Al-doped ZnO sample (AZO10, 4% actual doping), in which aliquots are collected over time, even up to 4 hours after the addition of the precursor has stopped, while the NCs are kept at the reaction temperature (280 °C). A progressive increase in the IR absorption (plasmon) is seen

up to 2 hours after stopping the addition of the precursor (Figure 5a). This is likely due to both the Al precursor being less reactive than the zinc precursor and the thermodynamic barrier to dopant incorporation within the host lattice. A similar behavior has been observed previously.⁶⁵ This is exemplified in Figure 5b, which shows the amount of precursor added over time (blue line, left vertical axis) and the recorded absorbance value in the near IR for the corresponding AZO NCs (open circles with colors matching those of the spectra in Figure 5a, right vertical axis). We can clearly see how the IR absorption rapidly increases during the injection stage (see also Figure S15 for a zoomed view of the early stages of growth), and keeps increasing during the annealing stage, albeit at a slower rate, until eventually it plateaus. Such a behavior can be explained with the low reactivity and corresponding slow incorporation rate of aluminum. In fact, a very weak IR absorption is observed for small ZnO NCs at the beginning of the reaction. However, the IR absorption increases substantially during the course of the injection, and after the injection is concluded. This may point towards a higher dopant concentration at the surface of the NCs, which is also another factor that could be responsible for the increased broadening of the LSPR at high doping levels. Interestingly, looking at the TEM of NCs at different stages of the reaction (Figure 5d-g) we can see how doped particles show a slight “delay” in growth, with smaller particles being present even at the latest stages of the reaction. This is clear from the size distribution histograms which does not show much change up to 0.66 mmol (0.037 M), and also shows a largely polydisperse, almost bimodal distribution at the end of the slow addition of the precursor. Interestingly, this size distribution sharpens when annealing the NCs in the mother liquor at the reaction temperature for longer times. This suggests a slower growth rate for doped NCs compared to undoped ZnO, possibly due to the Al-induced stresses in the host wurtzite lattice. Therefore, this prolonged heating after finishing the addition of the precursor has the dual effect of promoting additional dopant incorporation and of properly growing the NCs to their final size.

Figure 5. Growth kinetics of AZO NCs. a) UV-vis-NIR spectra of AZO10 NCs synthesized with different precursor amounts and different reaction times. b) Absorbance value monitored at 2200 nm as a function of the reaction time and the amount of precursor added. c) Size distribution histograms for AZO10 NCs at different stages of the reaction. d-g) TEM images for AZO10 NCs synthesized with 0.33 mmol (0.02 M, d), 0.66 mmol (0.037 M, e), 1.66 mmol (0.079 M, f,g) of precursor. Sample (g) has been let react for 2 hours from the end of the injection. Scale bar is 50 nm and is common to all TEM images.

To prove the versatility of our reaction system, we synthesized ZnO NCs doped with other trivalent cations, namely Ga and In. In all cases we were successful in synthesizing phase pure, plasmonic ZnO NCs. XRD results show pure phase wurtzite ZnO for both Ga-doped and In-doped ZnO (Figure S16), similar to what we observed for both Al-doped ZnO and undoped ZnO. Interestingly, the (002) diffraction peak of Ga-doped ZnO is much sharper, indicating a larger crystallite size along the (002) direction, corresponding to the *c*-axis of the hexagonal wurtzite lattice. This indicates the presence of elongated, rod-like particles, which was confirmed with TEM analyses (Figure S17). This is not the case for IZO NCs, which are

spheroidal and isotropic. Elemental analysis confirms the presence of trivalent dopants within ZnO, and shows that the doping efficiency for Ga and In is larger than that for Al, as expected from their ionic radius.⁵⁹ Specifically, for a nominal 5% doping, Al-doped ZnO NCs show a 2% doping level (efficiency of 40%), while Ga-ZnO have a 2.8% doping level (efficiency of 56%) and In-ZnO has a 3.9% doping level (efficiency of 78%). These details are summarized in Table S2 in the supporting information. Analyzing the optical properties of these doped NCs in colloidal solutions (Figure S18), we can see a clear plasmonic absorption for all doped NCs, with In-doped ZnO having the most intense absorption, as expected. It is worth noting that Ga-ZnO NCs have a lower absorption in the near IR compared to Al-ZnO, despite having a larger dopant fraction. This is not surprising considering the shape of the NCs: while AZO NCs are reasonably isotropic, GZO NCs are elongated, with a large aspect ratio. This will cause a prominent red shift of the longitudinal plasmon, as predicted by Mie-Gans theory, resulting in lower absorption intensity in the near infrared.⁶⁷

To demonstrate the full potential of this reaction system, we performed a gram-scale synthesis, as proof that our optimized method is readily scalable. We scaled up both the amount of precursor (15 mmol) and the amount of oleyl alcohol (160 mL) achieve a final metal concentration of 0.073 M. We also adjusted the injection rate in order to keep it consistent with the standard “small scale” syntheses (see Methods for details), and we used Al-doped ZnO as a model system. As shown in Figure 6, after continuously dripping the 15 mmol (45 mL) of metal precursor into oleyl alcohol at 280 °C we achieved deep-blue colored powders, which are highly crystalline and possess an intense infrared absorption. Compared to a small batch reaction, the NCs are slightly more polydisperse, however the particle size is identical, confirming the robustness of our reaction for gram-scale syntheses. Importantly, we analyzed the reaction yield by weighing the dried product (Figure 6a), and quantifying the amount of organic material using TGA (Figure S19): our reaction produced ~1.37 g of dry powders, which

correspond to ~ 1.21 g of purely inorganic material, considering a weight loss of $\sim 11.5\%$ associated with the decomposition of the organic surface ligands. Since the reaction was conducted using 15 mmol of metal precursor, we would have expected ~ 1.22 g of inorganic product. Therefore, we can conclude that the reaction yield is remarkably close to 100%.

Figure 6. Large scale reaction of AZO10 NCs. a) Picture of the dried product recovered from the large scale reaction. b) TEM image (scale bar 100 nm) of the NCs. c) XRD pattern. d) UV-Vis-NIR spectrum. e) Transmittance spectra and f) SEM cross-sectional images of two AZO10 nanocrystalline films of different thickness (scale bar 200 nm).

The ability to assemble colloidal NCs into high quality thin films is one of the main features sought after for the use of NCs within various devices, including optoelectronics. Owing to their hydrophobic surface ligands, these ZnO and doped ZnO NCs can be readily

dispersed in several organic solvents such as toluene, hexane, and octane, at high concentration (>100 mg/mL). These NC “inks” can then be used for thin film deposition with conventional solution-based methods. Figures 6e and 6f show the optical transmission spectra and the cross-sectional SEM of two AZO10 films (nominal Al concentration 4%) deposited by layer-by-layer spin coating and annealing cycles, to achieve a thickness of ~ 220 nm (2 layers) and 450 nm (4 layers). The AZO coatings are highly transparent in the visible range, and show a prominent NIR absorption, confirming that the colloidal NCs properties are readily transferred to the thin-film NC assemblies. After correction for the substrate (glass) absorption, the AZO films show exceptional transparency in the visible range, achieving 98.5% and 97% average transmittance in the 400-1200 nm range for the 220 and 450 nm thick film, respectively. The quality of the thin film is indicated by the clear interference fringes and is confirmed by cross sectional SEM images (Figure 6f), which show uniform and homogeneous assembly of AZO NCs (see also Figure S20 for additional SEM images). Preliminary electrical measurements demonstrate that these NC assemblies are indeed conductive, showing resistivity values of the order of $10^3 \Omega \cdot \text{cm}$ after annealing in air, and a drop of three orders of magnitude down to few $\Omega \cdot \text{cm}$ after annealing in forming gas. These results, even if obtained for non-optimized conditions, are on par with the current literature values for NC-based, Al-doped ZnO films, highlighting the promise of our AZO NCs. The ability to use these colloidal NCs to fabricate coatings of optical quality with enhanced conductivity makes our reaction method very appealing for the scalable production of ZnO-based materials for use in devices including (photo)catalysts, solar cells, LEDs, electrochromics and sensors.

CONCLUSION

In conclusion, we have presented a continuous growth reaction for zinc oxide colloidal nanocrystals which enables the production of ZnO with highly controllable size and doping. The slow addition of a solution of zinc oleate, excess oleic acid and additional oleylamine into hot oleyl alcohol triggers the formation of zinc oxide through an esterification reaction between the zinc precursor and the alcohol. The method developed here entails the slow but continuous addition of precursor, favoring a heterogeneous layer-by-layer growth rather than homogeneous nucleation in solution. Through this strategy, simply controlling the reaction temperature and the amount of precursor used permits access to ZnO nanocrystals with size tunable from ~5 nm to ~25 nm and above. Moreover, doped nanocrystals could be readily synthesized by substituting some of the zinc precursor with appropriate dopant oleates. This was demonstrated through the synthesis of plasmonic ZnO nanocrystals doped with either aluminium, gallium or indium. In addition, gram-scale syntheses with 100% reaction yield are presented, validating the scalability of our reaction protocols. Finally, thin films with outstanding quality (visible transmittance >95%) and enhanced electrical conductivity could be easily fabricated from our Al-doped ZnO nanocrystal inks. These results constitute a marked advancement in the synthesis of pure and doped ZnO nanocrystals with controllable properties, and will help translating laboratory-scale achievements into commercial technologies.

METHODS

Materials

Zinc acetate dihydrate (99%), oleic acid (OA, 90%), oleylamine (OLA, 70%), and tetrachloroethylene (TCE, 99.5%) were supplied by Sigma-Aldrich. Aluminum acetylacetonate ($\text{Al}(\text{Acac})_3$, 99%) gallium acetylacetonate ($\text{Ga}(\text{Acac})_3$, 99.99%) indium acetylacetonate ($\text{In}(\text{Acac})_3$, 99.99%) were supplied by Strem Chemicals. Oleyl alcohol (80-85%) was supplied by Alfa Aesar. Toluene (99.5%), ethanol (99.5%), methanol (99.8%) and

acetone (99.5%) were purchased from Univar. All chemicals were used without further purification.

Nanocrystal synthesis

In a typical reaction, 16 mL oleyl alcohol is loaded in a 100 mL three-neck round bottom flask (RBF) and connected to a heating mantle. One of the side necks of the RBF is sealed with a rubber septum and a thermocouple and a 19-gauge needle are pierced through it. The needle is connected to a nitrogen line and the RBF is constantly purged with 8-10 L/h of nitrogen flow. The central neck is sealed with a rubber septum and used for precursor injection (see below). The other side neck is connected to an elbow joint and a short piece of tubing that act as a drain to remove excess water formed during the reaction. This setup avoids the build-up of excess condensation around the necks of the RBF. The oleyl alcohol is then heated to the desired reaction temperature under a constant flow of nitrogen. In the meantime, a 50 mL RBF is loaded with 2.4 mmol of the metal precursor and 4.8 mL of oleic acid. In the case of doped NCs, the precursor is composed of a mixture of zinc acetate and dopant acetylacetonate, and the dopant (*D*) nominal concentration is defined as

$$D(\%) = \frac{n_D}{(n_{Zn} + n_D)} \times 100$$

where *n* is the number of moles. Doped NCs are labelled AZOX, GZOX and IZOX (for Al-, Ga- and In- doped ZnO, respectively), where *X* is the dopant nominal concentration. The RBF is connected to a Schlenk line and heated under vacuum ($3\text{-}5 \cdot 10^{-3}$ mbar) to 110 °C and kept at temperature for 20 minutes. The RBF is then backfilled with nitrogen, and OLA (2.4 mL) is added. The precursor is further degassed for 5 minutes at 100 °C, and then kept at temperature under a nitrogen blanket for further use. Once the oleyl alcohol reached the desired temperature, the precursor solution was loaded into a glass syringe equipped with a long 16-

gauge needle and slowly injected into the hot alcohol through the center neck using a syringe pump at a rate of 0.3 mL/min. A photo of the reaction setup is shown in Figure S21. For consistency across different reactions, the slow injection was stopped after a total of 5 mL (1.66 mmol) precursor was added. One hour after the addition of the precursor is finished, the heater is turned off and the NC suspension is let cool to room temperature naturally under the nitrogen flow. Excess ethanol is then added to precipitate the NCs, which are then centrifuged (4400 rpm, 5 minutes) and resuspended in toluene or TCE. This process is repeated 2-3 times to further purify the NCs. During the reactions, aliquots are taken at different stages and precipitated with excess ethanol. At the very early stages of the NC growth, methanol had also to be used to cause flocculation of small NCs. As discussed in the manuscript, to isolate growth from nucleation a series of reactions was performed with the rapid injection of 1 mL (0.33 mmol) of the metal precursor the hot oleyl alcohol under strong stirring and let react for 15 minutes. After this step, the slow injection protocol was carried out as described earlier. Deviations from the typical reaction conditions including the use of less oleic acid (2.4 mmol instead of 4.8 mmol, Figure S3), the use of more precursor in the slow injection process (up to 6.6 mmol, Figure S11) and the use of two growth temperatures in a single reaction (Figure S9).

To synthesize AZO10 NCs in large scale, the synthesis was adapted as follows. The metal precursor was prepared by dissolving zinc acetate (14.4 mmol) and $\text{Al}(\text{Acac})_3$ (1.6 mmol) in 32 mL oleic acid, degassed at 110 °C for one hour, followed by addition of 16 mL OLA and further degassed at temperature for 15 minutes. Excess oleyl alcohol (160 mL) was heated in a 250 mL RBF under strong stirring and after the desired temperature was reached, 45 mL (15 mmol) precursor was slowly added using a syringe pump. In order to maintain the same NC growth rate, the injection rate was increased to 3 mL/min. Moreover, the nitrogen flowrate was increased to ~20 L/h, to facilitate the removal of the excess water vapor formed. A parallel reaction conducted with the swift injection of 5 mL (1.66 mmol) metal precursor to isolate the

nucleation event, followed by the slow addition of 40 mL (13.33 mmol) precursor resulted in almost identical NCs.

AZO thin films were deposited from concentrated (~50 mg/mL) AZO NC suspensions in toluene using spin coating with a spinning speed of 3000 rpm for 5 seconds, followed by 5000 rpm for 30 seconds. The deposited films were stabilized at 150 °C in air on a hot plate for 5 minutes, and additional layers were deposited with the same procedure if required. Post annealing was conducted at 300 °C in air for 1 hour. Additional annealing in forming gas at 500 °C for 1 hour was conducted to increase the conductivity of the AZO coatings.

Characterization techniques

Transmission electron microscopy (TEM) images of NCs deposited on carbon-coated copper grids were acquired on a JEOL 2100F microscope operated at 200 kV. The images were analyzed using the ImageJ software. X-ray diffraction (XRD) patterns of dried NCs powders were collected using a Bruker D4 Endeavor diffractometer equipped with a Cu-K α radiation source and operated at 40 kV and 35 mA. The crystallite size was evaluated with the Scherrer relationship using the full width at half-maximum of the diffraction peaks fitted using Pseudo-Voigt functions. For each sample the extracted size values from each of the 11 diffraction peaks detected between 20 and 80 degrees were averaged and the error was calculated as one standard deviation. Optical absorption spectra of NCs dispersed in tetrachloroethylene (TCE) were obtained on Agilent Cary60 UV-Vis and Cary7000 UV-Vis-NIR spectrophotometers. Photoluminescence (PL) spectra were acquired with a Horiba Jobin Yvon Fluoromax-4 fluorometer with an excitation wavelength of 330 nm. Fourier transform infrared (FTIR) spectroscopy of NCs was carried out using a Perkin-Elmer Frontier spectrometer equipped with a Pike GladiATR attenuated total reflectance (ATR) stage. A drop of NCs dispersed in TCE was deposited on the ATR crystal and the measurement was taken upon TCE evaporation.

Thermogravimetric analysis (TGA) was conducted on a Perkin Elmer Pyris 1 instrument at a heating rate of 5 °C/min in air. Energy dispersive X-ray (EDX) spectra were acquired on a Nova 200 NanoSEM with a voltage of 15 kV. Scanning electron microscopy (SEM) images were acquired on a FEI Verios 460L SEM operated at 2 kV and 25 pA.

ASSOCIATED CONTENT

Supporting Information. Additional characterizations and data (Figure S1-S21 and Table S1-S2): UV-Vis-NIR, FTIR and PL spectra; XRD patterns; TEM and SEM images; size distribution histograms; crystallite size values; TGA scan; photo of the reaction setup; and additional tables. This material is available free of charge via the Internet at <http://pubs.acs.org>

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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