Formation of aluminum-doped zinc oxide nanocrystals via the benzylamine route at low reaction kinetics

Julian Ungerer1*, Ann-Kathrin Thurm2, Georg Garnweitner2, Hermann Nirschl1
1Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany
2Institute for Particle Technology and Laboratory for Emerging Nanometrology, Technische Universität Braunschweig, Volkmaroder Str. 5, 38104 Braunschweig, Germany
*Correspondence: Julian Ungerer (E-mail: julian.ungerer@kit.edu), Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany

Abstract
This work demonstrates the influence of essential process parameters on the adjustability of specific process- and particulate properties of aluminum-doped zinc oxide (AZO) nanocrystals during synthesis via the benzylamine route at low reaction kinetics by enabling time-resolved access of selected measurement technique. Here, it will be shown that the validity of the pseudo-first order process kinetics could be extended to the minimum operable reaction kinetics, on the one hand. On the other hand, the impacts of process temperature and initial precursor concentration on both process kinetics and particle morphology will be discussed. The obtained data provide a versatile tool for precise process control adjusting defined application-specific particle properties of AZO during synthesis.
Keywords: Aluminum-doped zinc oxide, kinetics pseudo-first order, low reaction kinetics, particle morphology, time-resolved analysis

1 Introduction

The n-type semiconductor aluminum-doped zinc oxide (AZO) offers versatile applications due to its special properties, e.g. low electrical resistance, good mechanical stability and high degree of transparency in the visible range. Due to these properties AZO is considered to be a significantly cheaper and non-toxic alternative in order to replace existing and finite indium based oxides in the future for diverse scopes e.g. thin-film solar modules, touch-panels, light-emitting diodes or printable electronics. Especially the application of AZO as transparent conducting oxide (TCO) in thin-film solar modules has a high potential with regard to the sustainable energy generation from renewable sources[1-5]. Therefore, the availability of high quality nanocrystals with fitted sizes and shapes of crystals is required[2, 4]. In contrast to gas-phase-, solids-processes[6] or co-precipitation[7], solvent-based liquid-phase syntheses result in better process control with moderate reaction rates[8, 9]. This synthesis route provides time-resolved access to measurement technologies in terms of particle
formation analysis, as we will show in this work. For synthesizing highly-crystalline metal oxide nanostructures the non-aqueous sol-gel-synthesis is used, wherein crystalline precursors are dissolved in aromatic solvents and converted to nanoscale crystals with defined sizes, narrow particle size distributions and adjustable morphologies at moderate temperatures[10-14]. The work by Zellmer et al.[14] has shown time-resolved studies of crystal growth of AZO nanocrystals via the benzylamine route preferably at high temperatures(≥200°C), high precursor concentrations(~50 gL⁻¹) and relatively short reaction times(~30 min). However, in order to be able to resolve the crystal growth more accurately using measurement technique, longer reaction rates at lower process temperatures are desirable. In our previous paper, the growth behavior of AZO nanocrystals via the benzylamine route at low process temperatures(~110°C) was already successfully investigated by using small-angle X-ray scattering(SAXS)[15]. Following on from this, in our current work the process parameters are to be extended to lower process temperatures(TRY ≤ 120) and initial precursor concentrations(CP ≤ 25 gL⁻¹) and their influences on crystal growth kinetics and particle morphology are to be investigated. In detail, we will clarify in a first step weather the already proven pseudo-first order reaction kinetics of AZO nanocrystal synthesis via the benzylamine route at constant TTRY = 110°C from our previous work will be also valid by extending to lower process temperatures in the range 80°C ≤ TRY ≤ 120°C. Quantitative phase analysis(QPA) by X-ray scattering and gravimetric analysis will be used to describe the ongoing consumption and growth processes, independent of particle morphology and aggregation state. Furthermore, the impact of significant process parameters(TRY, CP) on the growth kinetics of AZO nanocrystals will be investigated in more detail using the Arrhenius model. Finally, transmission electron microscopy(TEM) and dynamic light scattering(DLS) will explore the question of how much particle properties(e.g. size, shape, crystallinity etc.) can be influenced by process parameters discussed above.

2 Material and Methods

2.1 Synthesis of AZO via the benzylamine route

For the non-aqueous sol-gel synthesis of AZO nanocrystals via the benzylamine route, the crystalline precursors zinc acetylacetonate hydrate (Zn(acac)₂ powder, ≥ 99%, Aldrich) and aluminum isopropoxide (Al(OiPr)₃, ≥ 98%, Aldrich) in the initial concentration range 6.25 g L⁻¹ ≤ CP ≤ 25 g L⁻¹ were used, wherein the molar fraction of aluminum precursor was set to 2.5 mol%. The aromatic solvent benzylamine (BnNH₂, benzylamine for synthesis, ≥ 99%, Merck) served as reaction medium. For a detailed description of the synthesis- and sampling procedure at low process temperatures in the range 80°C ≤ TRY ≤ 120°C using a closed and ideally stirred batch reactor, we refer to our previous work[15]. Due to the physical limitation with regard to Zn(acac)₂ solubility at TRY ≤ 50°C, the minimum solution-limited process temperature for the reaction system used was set at TRY = 80°C.

2.2 Sample purification and characterization methods

For the time-resolved access of measurement techniques to the synthesis for analyzing the AZO nanocrystal growth behavior, we developed a new sample purification procedure considering both the solubility limit of Zn(acac)₂ and the high corrosivity of BnNH₂ with regard to the measurement techniques used. The sequence of the individual sample preparation steps including their associated analysis methods is shown in Figure 1.
During the synthesis at $T_r \geq 80^\circ C$, only AZO is present as crystalline phase in the solvent BnNH$_2$. After sampling and rapid cooling at different reaction times $t < t_{END}$, the unreacted precursor Zn(acac)$_2$ precipitated completely at $T_r \approx 25^\circ C$ due to its poor solubility in BnNH$_2$, thus the two crystalline phases AZO/Zn(acac)$_2$ were present in BnNH$_2$. Applying QPA analysis using our self-developed SAXS laboratory camera, referring to our previous works for more details on the analytical procedure[15-17], we were able to quantify the time-resolved consumption concentration $C_{Zn(acac)_2}$ of crystalline Zn(acac)$_2$ based on scattering intensity $I_{2\theta=16^\circ}^{Zn(acac)_2}$ at constant scattering angle $2\theta = 16^\circ$, as shown in Eq.(1).

$$C_{Zn(acac)_2} = (259 \pm 7\%) \cdot I_{2\theta=16^\circ}^{Zn(acac)_2} \text{[gL}^{-1}]$$  \hspace{1cm} (1)

In the subsequent washing process, two purification steps were carried out: In a first step, BnNH$_2$ was removed by centrifugation for 15 min with a g-force of 7200 at 20$^\circ$C (Centrifuge 5430R, Eppendorf). In a second step, the ethanol-soluble Zn(acac)$_2$ crystals were completely separated from AZO by washing twice with ethanol excess of the factor four by re-centrifugation. To characterize particle properties of AZO after finishing growth, the AZO present in pure ethanol were then analyzed by DLS using Zetasizer(Nano ZS, Malvern) and TEM(Osiris ChemiStem, FEI). For TEM, the samples had to be diluted with ethanol and air-dried on a TEM grid at 25$^\circ$C. Finally, for recording of AZO concentration $C_{AZO}$ by gravimetric analysis, the nanocrystals were completely dried at 80$^\circ$C for 24 h under ambient pressure in a drying oven("UN260", Memmert) and afterwards quantified with an analytical scale(Secura 224-1S, Sartorius) by using Eq.(2), dependent on sampling volume $V_s$ and dry matter $m_{AZO}$.

$$C_{AZO} = \frac{m_{AZO}}{V_s} \text{[gL}^{-1}]$$  \hspace{1cm} (2)

### 2.3 Kinetic model describing the AZO nanocrystal synthesis

For quantitative description of consumption and growth processes during the AZO synthesis via the benzylamine route, the pseudo-first-order kinetics model was used. For the purposes of applying this model to the AZO synthesis several assumptions, which were described in more detail in our previous work[15], have been made for simplicity in order to get the final expression of the product formation rate $r_{AZO}$ in Eq.(3), depending on the unreacted zinc precursor concentration $C_{Zn(acac)_2}(t)$ and the rate constant $k [s^{-1}]$.

$$r_{AZO}(t) = -\frac{dC_{Zn(acac)_2}}{dt} = kC_{Zn(acac)_2}(t)$$  \hspace{1cm} (3)

After separation of variables, integration and exponentiation, a pseudo-first-order model resulted in Eq.(4), describing a time-dependent exponential consumption of $C_{Zn(acac)_2}(t)$ as a function of initial zinc precursor concentration $C_{Zn(acac)_2}(0)$.

$$C_{Zn(acac)_2}(t) = C_{Zn(acac)_2}(0)e^{-kt}$$  \hspace{1cm} (4)

In case of full conversion, the pseudo-first-order model of restricted exponential growth of AZO concentration $C_{AZO}(t)$ resulted in Eq. (5) with equal rate constant.

$$C_{AZO}(t) = C_{AZO}(\infty)(1 - e^{-kt})$$  \hspace{1cm} (5)
3 Results and Discussions

3.1 Validity of pseudo-first order kinetics at low process temperature range

In this section the validity of the kinetics pseudo-first order, which was already successfully demonstrated in our previous work for \( T_R = 110^\circ C \), is to be demonstrated at minimum operable process temperature \( T_R = 80^\circ C \) and thus for the low temperature range \( 80^\circ C \leq T_R \leq 120^\circ C \) investigated in this work[15]. For better comparability of both kinetics, the normalized pseudo-first-order growth model function of AZO from Eq.(5), based on gravimetric data, and the normalized pseudo-first-order consumption model function of Zn(acac)\(_2\) from Eq.(4), based on QPA by SAXS data using Eq.(1), from our previous work at \( T_R = 110^\circ C \) (dashed lines, \( R^2 \geq 99 \% \)) are plotted next to the here observed equivalent growth- and consumption kinetics at \( T_R = 80^\circ C \) (solid lines, \( R^2 \geq 98 \% \)) in Figure 2.

**Figure 2.** Normalized pseudo-first-order Zn(acac)\(_2\) consumption model functions based on QPA data by SAXS and associated normalized pseudo-first-order AZO growth model functions from gravimetric data at two different process conditions: \( T_R = 80^\circ C; C_E = 12.5 g L^{-1} \) (synthesis 1, solid lines) and \( T_R = 110^\circ C; C_E = 25 g L^{-1} \) (synthesis 2 from previous work[15], dashed lines).

In Figure 2, the qualitative trajectories of the respective growth and consumption functions formed an intersection at a concentration ratio of approx. 50%. This fact suggests a similar kinetics of the consumption and growth process at both process temperatures, indicating the validity of the pseudo-first order kinetics even at \( T_R = 80^\circ C \). The final proof can be provided by the comparison of each consumption(\( k_{Zn(acac)2} \)) and growth(\( k_{AZO} \)) rate constant, calculating their relative deviation \( \Delta k_{AZO/Zn(acac)2} \) as listed in Table 1.

| Process parameters | Synthesis 1 \( T_R = 80^\circ C; C_E = 12.5 g L^{-1} \) | Synthesis 2 \( T_R = 110^\circ C; C_E = 25 g L^{-1} \) |
|--------------------|---------------------------------|---------------------------------|
| \( k_{Zn(acac)2} \) \( [s^{-1}] \) | \( 2.1 \cdot 10^{-4} \pm 15\% \) | \( 11.3 \cdot 10^{-4} \pm 15\% \) |
| \( k_{AZO} \) \( [s^{-1}] \) | \( 1.9 \cdot 10^{-4} \pm 11\% \) | \( 9.80 \cdot 10^{-4} \pm 8\% \) |
| \( \Delta k_{AZO/Zn(acac)2} \) \( [%] \) | 10 | 13 |
| \( \overline{R^2} \) \( [%] \) | 98 | 99 |

Taking into account the respective errors in Table 1, the equality of both the consumption kinetics of Zn(acac)\(_2\) and the growth kinetics of AZO is proven at the two investigated process conditions. This fact provides the decisive indication that the synthesis of AZO via the benzylamine route not only...
follows pseudo-first-order kinetics at $T_R = 110^\circ C$, as shown in our previous work, but also at minimum $T_R = 80^\circ C$. Thus, the validity of the reaction order can be extended to the entire low process temperature range $80^\circ C \leq T_R \leq 120^\circ C$ investigated in this work.

### 3.2 Behavior of reaction kinetics at low process temperature range

In addition to the successful validation of the reaction kinetics following pseudo-first order, even at minimum solution-limited process temperature, Figure 2 shows a clear shift of the intersection point along the X-axis indicating an extension in overall process time($t_{END}$) by reducing process temperature. Since a temperature reduction of only 27% resulted in a significant extension of $t_{END}$ by factor of about five, from originally $t_{END} = 56 \text{ min}$ to $285 \text{ min}$, this section will focus in more detail on the influence of temperature on reaction kinetics of AZO synthesis. Due to the validity of the pseudo-first-order kinetics, further kinetics studies were continued only with gravimetric analysis of AZO by investigating further process conditions in the ranges $80^\circ C \leq T_R \leq 120^\circ C$ and $6.25 \text{ g L}^{-1} \leq C_E \leq 25 \text{ g L}^{-1}$ in more detail. In Figure 3, the normalized pseudo-first-order growth kinetic functions of AZO in the range of $80^\circ C \leq T_R \leq 120^\circ C$ based on gravimetric data($R^2 > 98\%$) were averaged over the entire initial precursor concentration range $6.25 \text{ g L}^{-1} \leq C_E \leq 25 \text{ g L}^{-1}$ and finally plotted over the logarithmic reaction time.

**Figure 3.** Temperature dependence of normalized pseudo-first-order growth kinetic functions of AZO in the range of $80^\circ C \leq T_R \leq 120^\circ C$ based on gravimetric data($R^2 > 98\%$), averaged over the entire initial precursor concentration range $6.25 \text{ g L}^{-1} \leq C_E \leq 25 \text{ g L}^{-1}$.

A good reproducibility of the gravimetric analysis method could be emphasized by a high agreement of multiply determined data in Figure 3 (dotted lines). An increase in process temperature obviously led to a shift of the growth functions towards smaller reaction times and thus to higher mean rate constants, which are averaged over $6.25 \text{ g L}^{-1} \leq C_E \leq 25 \text{ g L}^{-1}$ and listed in detail in Table 2.

**Table 2.** Mean rate constants, averaged over the initial precursor concentration range of $6.25 \text{ g L}^{-1} \leq C_E \leq 25 \text{ g L}^{-1}$, dependent on process temperature of the investigated synthesis processes.

| Process temperature $T_R$ [°C] | 80   | 100  | 110  | 120  |
|-------------------------------|------|------|------|------|
| Mean rate constant $\bar{k}$ $[10^{-4} \text{ s}^{-1}]$ | 1.51 ± 20% | 4.50 ± 5% | 10.2 ± 5% | 19.5 ± 9% |

Analogous to $t_{END}$, a high sensitivity of $\bar{k}$ to small changes in $T_R$ can be underpinned again in Table 2, since even a change in $\Delta T_R = 40 K$, $\bar{k}$ already changed significantly by a factor of about eighteen. To quantify the temperature dependency towards the kinetics of the AZO synthesis in detail, the Arrhenius model in Eq.(6) was used.

$$k(T_R)=Ae^\frac{-E_A}{RT}$$

(6)

The Arrhenius model generally describes the temperature dependence of the rate constant $k(T_R)$ of a chemical reaction process as a function of a constant pre-exponential factor $A$, the activation energy $E_A$, the universal gas constant $R$, and the absolute temperature $T$. To check on the one hand,
if the temperature dependency of the AZO synthesis process corresponds to the Arrhenius model and to determine on the other hand all process-relevant parameters from Eq. (6), the mean rate constants from Table 2 were plotted in an Arrhenius plot in Figure 4 (black squares).

**Figure 4.** Logarithmic rate constants of the AZO growth model functions from Table 2 (black squares), averaged in terms of the initial precursor concentration range \(6.25 g L^{-1} \leq C_E \leq 25 g L^{-1}\) (error bars), plotted versus the reciprocal absolute process temperature in the range \(80°C \leq T_R \leq 120°C\) and approximated by means of linear regression of Eq. (6) with \(R^2 \approx 98\%\).

By linear regression of Eq. (6) to the data in Figure 4, the validity of Arrhenius’ law could be investigated with a very high coefficient of determination \((R^2 \approx 98\%)\) within the investigated process temperature range \(80°C \leq T_R \leq 120°C\). The parameters obtained from linear regression, such as \(A = 1.16 \cdot 10^7 s^{-1} ± < 1\%\) and \(E_A = 73.8 kJ mol^{-1} ± 8\%\), are within an expected range for generally activation-controlled reactions\[18, 19\]. The negligible systematic errors in Figure 4 and Table 2 underpinned the independence of the process kinetics in terms of initial precursor concentrations within the investigated process conditions. Similar findings of strong dependence of temperature but low influence of precursor concentration on the reaction kinetics have also been observed for the non-aqueous formation of ZrO\(_2\) nanoparticles in benzyl alcohol\[20\]. The successful description of the AZO synthesis using the Arrhenius model showed on the one hand, the reproducibility and applicability of the measuring methods used over an extended process control range. On the other hand, the determined Arrhenius parameters represent a general tool predicting process kinetics of the investigated AZO synthesis via the benzylamine route, especially for higher kinetics at \(T_R > 120°C\), which are difficult to access for measurement techniques.

### 3.3 Impact on particle morphology and size

In this section, the main influencing parameters on the final particle morphology of AZO nanocrystals after finished growth are to be investigated more closely using TEM and DLS in order to elucidate important questions about the specific influence on particle properties, such as size, shape and crystallinity. Considering a single AZO particle in Figure 5 using TEM, synthesized at \(T_R = 120°C\) and \(C_E = 25 g L^{-1}\), a very high similarity to the mesocrystalline structure of AZO from our previous work can be observed based on the typical hexagonal form and remaining internal grain boundaries\[15\]. Compared to TEM images of our earlier work, crystalline structure parameters are more recognizable at the atomic level due to the higher resolution of the TEM used here.

**Figure 5.** TEM image of a single hexagonal AZO-mesocrystal after completion of growth with monocristalline\((inlet a)\) and polycristalline\((inlet b)\) regions at \(T_R = 120°C\) and \(C_E = 25 g L^{-1}\).

With a crystal size of ca. 85 nm, various crystalline regions with different mutual orientations could be seen on the particle surface finally forming a hexagonal-shaped polycrystalline particle with uniform outer edge lengths. On the one hand, monocristalline regions with uniform lattice plane orientation could be observed on the basis of visible atomic lattice distances\((inlet a in Figure 5)\) and polycristalline regions could be seen, on the other hand, in which an overlapping of several monocristalline lattice planes occurred\((inlet b in Figure 5)\). Especially, the polycristalline areas are recognizable on the so-called Moiré stripes, which arose due to the double diffraction of electrons at superimposed crystal lattice planes with similar periodicity\[21\]. Both the typical hexagonal particle shape and the remaining internal grain boundaries could be attributed to a prior oriented aggregation with incomplete intergrowth during the growth process and thus fits very well with the findings about the non-classical growth behavior from our prior work\[15\].

In order to investigate the influence of \(T_R\) and \(C_E\) on the particle morphology, the above described AZO mesocrystal is contrasted to final growth states at three further boundary process conditions of
the ranges $80°C \leq T_R \leq 120°C$ and $6.25gL^{-1} \leq C_R \leq 25gL^{-1}$ in Figures 6a–d. At all of these process conditions studied here, mesostructured particles of AZO with crystalline phases have been formed by a non-classical growth, as shown by the Moiré stripes in Figures 6a–d (white arrows). By comparing Figures 6a, c at $C_R = 25gL^{-1} = \text{const.}$ and Figures 6b, d at $C_R = 6.25gL^{-1} = \text{const.}$, it could be shown that the crystallinity of the observed AZO-mesocrystals is more pronounced with rising $T_R$, as evidenced by the more regular shape and the smoother outer surfaces of the single mesocrystals from Figures 6a, b (white dashed lines). Diffuse areas at the particle surfaces at minimum reaction kinetics in Figures 6c, d (black arrows) indicated either amorphous structures, thus partial crystallinity of the final AZO particles, or non-removable organic solvent residues. The increasing crystallinity at increasing $T_R$ could be explained by the higher energy supply for applying the required lattice energy in the formation of the crystalline lattice, on the one hand, and an annealing of the agglomeration-induced crystal defects by increased diffusion during synthesis, on the other hand[22].

**Figure 6.** Comparison the final growth states of mesocrystalline AZO-nanocrystals (white dashed lines) with TEM at the four boundary process conditions (a–d) of the ranges $80°C \leq T_R \leq 120°C$ and $6.25gL^{-1} \leq C_R \leq 25gL^{-1}$.

At $T_R = 120°C = \text{const.}$, magnification of the AZO-mesocrystals in Figures 6a, b was observed after increasing $C_R$, which could be more accurately quantified by the increase of the mean equivalent diameter of mesocrystals from $d_{50,0} = 61.36nm \pm 4%$ at $C_R = 6.25gL^{-1}$ to $d_{50,0} = 90.43nm \pm 3%$ at $C_R = 25gL^{-1}$ using DLS. In addition, the DLS results at $T_R = 80°C = \text{const.}$ have shown a similar tendency due to the increase from $d_{50,0} = 60.87nm \pm 2%$ to $d_{50,0} = 86.16nm \pm 5\%$, which obviously could not be noticed by comparing Figures 6c, d due to the amorphous matrix. Both the mesocrystal sizes from DLS at $C_R = 6.25gL^{-1} = \text{const.}$ and at $C_R = 25gL^{-1} = \text{const.}$ have shown respectively similar values independently of the process temperature resulting in no significant influence of process temperature on the final mesocrystal size of AZO, as also shown in the work of Zellmer et al.[14].

4 Conclusions

The major finding of this work is showing the impact of essential process parameters on particle- and process properties during non-classical growth of AZO mesocrystals via the benzylamine route in the low temperature range $80°C \leq T_R \leq 120°C$ and initial precursor concentration range $6.25gL^{-1} \leq C_R \leq 25gL^{-1}$ by getting time-resolved access with selected measurement techniques. It could generally be observed that, on the one hand, both the growth kinetics and crystalline properties of AZO were significantly influenced by the process temperature setting, while on the other hand, the final mesocrystal size was predominantly controlled by the initial precursor concentration. In detail, the validity of the already proven pseudo-first-order kinetics for the overall AZO nanocrystal synthesis via the benzylamine route at $T_R = 110°C$ could also be successfully demonstrated for the solution-limited minimum process temperature of $T_R = 80°C$ by QPA and gravimetric analysis and thus expanding the validity of process kinetics throughout the low temperature range $80°C \leq T_R \leq 120°C$ examined in this work. Furthermore, a very strong process temperature influence of the process kinetics was observed using gravimetric analysis, which could be successfully approximated to the Arrhenius model agreeing with kinetics parameters of similar works and expectations of an activation-controlled synthesis. Finally, in accordance to our previous work, a non-classical mesocrystal growth of AZO could be observed in the studied parameter range by TEM and DLS demonstrating both a visible increasing crystallinity by raising process temperature and an enlargement of the final AZO mesocrystals by increasing initial precursor concentration. The detailed knowledge gained in this work on the two important process influencing parameters, the process
temperature, on the one hand, and the initial precursor concentration, on the other hand, is generally a versatile tool for precise process control adjusting defined application-specific particle properties of $AZO$ nanocrystals during synthesis.

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Symbols used

Symbols

\( A \) \([s^{-1}]\) pre-exponential factor
\( C \) \([gL^{-1}]\) mass concentration
\( C_E \) \([gL^{-1}]\) initial precursor concentration
\( d_{50,0} \) \([nm]\) number-weighted mean diameter
\( E_A \) \([kJ mol^{-1}]\) activation energy
\( I \) \([a.u.]\) scattering intensity
\( k \) \([s^{-1}]\) first-order rate constant
\( m \) \([g]\) dry matter
\( r \) \([kg(Ls)^{-1}]\) formation rate
\( R \) \([kg m^2(s mol K)^{-1}]\) universal gas constant
\( R^2 \) [-] mean coefficient of determination
\( t \) \([s]\) reaction time
\( t_{END} \) \([s]\) time after 97% of reaction conversion
\( T \) \([°C]\) process temperature
\( T \) \([K]\) absolute temperature
\( V_S \) \([L]\) sampling volume

Greek Letters

\( \Delta \) [-] mean deviation
\( 2\theta \) \([°]\) scattering angle

Abbreviations

\( AZO \) aluminum-doped zinc oxide
\( Al(OiPr)_3 \) aluminum isopropoxide
\( BnNH_2 \) benzylamine
\( DLS \) dynamic light scattering
\( EtOH \) ethanol
\( QPA \) quantitative phase analysis
\( SAXS \) small-angle X-ray scattering
\( TCO \) transparent conducting oxide
\( TEM \) transmission electron microscopy
\( Zn(acac)_2 \) zinc acetylacetonate hydrate
\( ZrO_2 \) zirconium dioxide
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Table captions

Table 1. Consumption- and growth rate constants $k_{Zn\text{(acac)}_2}$, $k_{AZO}$, the relative mean deviation of both rate constants $\Delta k_{AZO/Zn\text{(acac)}_2}$ and the mean coefficients of determination at two different process conditions $T_R = 80^\circ C; C_E = 12.5 \, g \, L^{-1}$ (synthesis 1) and $T_R = 110^\circ C; C_E = 25 \, g \, L^{-1}$ (synthesis 2 from previous work[15]).

Table 2. Mean rate constants, averaged over the initial precursor concentration range of $6.25 \, g \, L^{-1} \leq C_E \leq 25 \, g \, L^{-1}$, dependent on process temperature of the investigated synthesis processes.
Figure captions

**Figure 1.** Sequence of the newly developed sample purification steps after sampling and the associated analysis methods for time-resolved characterization of the AZO-nanocrystal synthesis via the benzylamine route.

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**Figure 3.** Temperature dependence of normalized pseudo-first-order growth kinetic functions of AZO in the range of \( 80°C \leq T_R \leq 120°C \) based on gravimetric data\( (\bar{R^2} > 98%) \), averaged over the entire initial precursor concentration range \( 6.25 \text{g L}^{-1} \leq C_E \leq 25 \text{g L}^{-1} \).

**Figure 4.** Logarithmic rate constants of the AZO growth model functions from Table 2 (black squares), averaged in terms of the initial precursor concentration range \( 6.25 \text{g L}^{-1} \leq C_E \leq 25 \text{g L}^{-1} \) (error bars), plotted versus the reciprocal absolute process temperature in the range \( 80°C \leq T_R \leq 120°C \) and approximated by means of linear regression of Eq.(6) with \( R^2 \approx 98% \).

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Figures

Figure 1. Sequence of the newly developed sample purification steps after sampling and the associated analysis methods for time-resolved characterization of the AZO-nanocrystal synthesis via the benzylamine route.

Figure 2. Normalized pseudo-first-order Zn(acac)$_2$ consumption model functions based on QPA data by SAXS and associated normalized pseudo-first-order AZO growth model functions from gravimetric data at two different process conditions: $T_R = 80^\circ C; C_E = 12.5\, g\, L^{-1}$ (synthesis 1, solid lines) and $T_R = 110^\circ C; C_E = 25\, g\, L^{-1}$ (synthesis 2 from previous work[15], dashed lines).
Figure 3. Temperature dependence of normalized pseudo-first-order growth kinetic functions of AZO in the range of $80^\circ C \leq T_R \leq 120^\circ C$ based on gravimetric data($R^2 > 98\%$), averaged over the entire initial precursor concentration range $6.25\,g\,L^{-1} \leq C_E \leq 25\,g\,L^{-1}$.
Figure 4. Logarithmic rate constants of the AZO growth model functions from Table 2 (black squares), averaged in terms of the initial precursor concentration range $6.25 \text{g L}^{-1} \leq C_E \leq 25 \text{g L}^{-1}$ (error bars), plotted versus the reciprocal absolute process temperature in the range $80^\circ C \leq T_R \leq 120^\circ C$ and approximated by means of linear regression of Eq.(6) with $R^2 \approx 98\%$.

Figure 5. TEM-image of a single hexagonal AZO-mesocrystal after completion of growth with monocrystalline (inlet a) and polycrystalline (inlet b) regions at $T_R = 120^\circ C$ and $C_E = 25 \text{g L}^{-1}$. 

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Figure 6. Comparison the final growth states of mesocrystalline AZO-nanocrystals (white dashed lines) with TEM at the four boundary process conditions (a–d) of the ranges $80^\circ C \leq T_R \leq 120^\circ C$ and $6.25 g L^{-1} \leq C_E \leq 25 g L^{-1}$. 
Research Article: The performance of cost-effective functional thin films using aluminum-doped zinc oxide (AZO) nanocrystals essentially depends on the adjustability of particle properties during synthesis. A time-resolved access for measuring nanoscale particle properties was developed at low process speeds. Thus, effects of essential process parameters on process- and particle properties of AZO are investigated.