# **Inorganic Chemistry**



## Why Does Bi<sub>2</sub>WO<sub>6</sub> Visible-Light Photocatalyst Always Form as Nanoplatelets?

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**ABSTRACT:** Bi<sub>2</sub>WO<sub>6</sub> nanocrystals exhibit excellent photocatalytic properties in the visible range of the solar spectrum, and intense efforts are directed at designing effective synthesis processes with control of size, morphology, and hierarchical structure. All known hydrothermal syntheses produce either nanoplatelet morphology or hierarchical structures based on such primary entities. Here we investigate the nucleation and growth of Bi<sub>2</sub>WO<sub>6</sub> nanocrystals under hydrothermal conditions using *in situ* X-ray total scattering (TS) and powder X-ray diffraction (PXRD) measurements. It is shown that the preferential growth of Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> molecular complexes in the precursor solution with an approximate length of 13 Å. These layers interact with tetrahedral WO<sub>4</sub><sup>2-</sup> molecular units and eventually form the disordered cubic



 $(Bi_{0.933}W_{0.067})O_{1.6})$  crystalline phase. When enough tungsten units are intertwined between  $Bi_2O_2^{2+}$  layers formation of  $Bi_2WO_6$  pristine nanoplates takes place by necessary sideways addition of units in the *ac* plane. The experimentally observed formation mechanism suggests that the Bi/W atomic ratio must play a central role in the nucleation (assembly of initial crystal layers). Indeed, it is observed in separate continuous flow supercritical synthesis that for a stoichiometric (Bi/W = 2:1) precursor, a ( $Bi_{0.933}W_{0.067}O_{1.6}$ ) impurity phase is always observed together with the main  $Bi_2WO_6$  product. Excess tungsten is required in the precursor to form phase-pure  $Bi_2WO_6$  material. Thus, the present study also reports a fast, scalable, and green method for production of this highly attractive photocatalyst.

he discovery of excellent visible light photocatalytic properties of Bi<sub>2</sub>WO<sub>6</sub> nanoplatelets in 2004 has spurred tremendous research activity.<sup>1</sup> Numerous synthesis procedures have been developed to synthesize samples exhibiting optimal photocatalytic activity. Indeed, there is a plethora of references discussing various synthesis approaches and their effect on the performance of the products, and several excellent reviews summarize these trends.<sup>2,3</sup> Curiously, most synthesis pathways produce either nanoplatelets of Bi2WO6 or hierarchical structures based on such nanoplatelets. For example, square nanoplates and hierarchical complex morphologies, namely, flower-, tire-, and helixlike Bi2WO6, were successfully synthesized by hydrothermal processes and the morphology of these nanoparticles were controlled by varying hydrothermal temperature and reaction time.<sup>4–10</sup> Zhang et al. reports that nanoparticles of Bi2WO6 could be obtained by calcining amorphous complex precursor at a relatively low temperature of above 450 °C.11 While low-temperature combustion produced nanoflake Bi<sub>2</sub>WO<sub>6</sub>, nanosheets were obtained by the microwave-assisted hydrothermal method.<sup>12,13</sup> It has been shown that the pH of the solution plays a role in controlling whether the nanoplatelets remain suspended in the solution or arrange into hierarchical structures.<sup>14,15</sup> The morphology, size, and any possible hierarchical assembly of these nanoplatelets are crucial for the photocatalytic activity. It has been observed that ultrathin nanoplatelets and porous microstructures of nanoplatelets could improve the surface area and adsorption capability resulting in higher photocatalytic activity.<sup>16</sup> Therefore, exact control over the parameters governing the precise nanostructure of the  $Bi_2WO_6$  products is essential if the optimal photocatalytic activity is to be achieved.

Bismuth tungstate (Bi<sub>2</sub>WO<sub>6</sub>) is not only an excellent photocatalyst under visible light irradiation, but also like many semiconductors holds a range of interesting physical properties such ferroelectricity piezoelectricity, pyroelectricity, and a nonlinear dielectric susceptibility.<sup>17–22</sup> Composites of bismuth tungstate have also been found with photocatalytic activity.<sup>23–27</sup> Bi<sub>2</sub>WO<sub>6</sub> is an Aurivillius phase. The structure consists of layers having the formula (Bi<sub>*n*-1</sub>M<sub>*n*</sub>X<sub>3*n*+1</sub>)<sup>2–</sup> (for *n* = 1, M = W), intercalated between Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> layers. The WO<sub>6</sub>



Received: April 27, 2020

octahedra share corners along the crystallographic *a*- and *c*-axes, forming infinite WO<sub>6</sub> layers with alternate  $\text{Bi}_2\text{O}_2^{2+}$  layers along the *b*-axis (Figure 1).<sup>28</sup> The tungsten polyhedra are connected to  $\text{Bi}_2\text{O}_2^{2+}$  layers through oxygen atoms shared between polyhedra and layers.



Figure 1. Crystal structure of  $Bi_2WO_6$  showing the arrangement of  $WO_6$  layers with alternate  $Bi_2O_2^{2+}$  layers.

Hydrothermal synthesis is one of the preferred methods for obtaining Bi<sub>2</sub>WO<sub>6</sub> nanocatalysts since it is robust, green, and scalable, and it provides a high degree of control over the size of the nanoplates. Previous efforts have been made to understand the mechanism governing Bi<sub>2</sub>WO<sub>6</sub> formation and growth under hydrothermal conditions via both in situ and ex *situ* powder X-ray diffraction (PXRD) studies.<sup>4,29,30</sup> One major result from these studies is the anisotropic growth of the nanoplate crystallites which was attributed to a "crystalripening" process.<sup>4</sup> A particularly effective hydrothermal synthesis method is to use one-step continuous flow supercritical reactors,<sup>31,32</sup> which can produce large amounts of the product very quickly (reaction time in seconds). Supercritical flow methods allow tuning of unique properties of supercritical fluids, e.g., solvent strength, viscosity, diffusivity, dielectric constant, ionic product, and surface tension.<sup>33,34</sup> In continuous flow reactors, the supercritical fluids provide very rapid heating at the mixing point with the precursor solution leading to high supersaturation conditions resulting in rapid nucleation of nanoparticles.<sup>35–37</sup> The particle size, size distribution, crystallinity, and phase composition may be controlled through simple variation of reaction parameters such as temperature, pressure, precursor concentration, reactor residence time, and choice of solvent.31,38,39

One of the major aims of the *in situ* studies is to use the obtained information to develop effective methods for mass production of nanomaterials for industrial applications. Even though reactor configurations are different, the knowledge gained from the *in situ* hydrothermal experiments possibly can be applied to the continuous flow supercritical reactors as in both cases the reaction involves rapid heating and supercritical conditions.<sup>31</sup> However, sometimes it has been found that the

reaction parameters obtained from in situ PXRD measurements do not lead to high-quality products.<sup>40</sup> This is because the information on the crystallization is obtained after nucleation has occurred since PXRD only provides access to the growth mechanisms and kinetics of the crystalline parts of the synthesis mixture by analysis of the Bragg diffraction signal. However, the crucial nucleation step, which often determines the fate of a given crystalline product, remains unexplored due to the lack of techniques able to probe the solvated molecular structure in solution under hydrothermal conditions. An ensemble-averaged atomistic insight into the pristine crystal nuclei can be obtained by measuring in situ X-ray total scattering data on the reaction mixture and subsequently calculating and modeling the atomic pair distribution function (PDF).<sup>41,42</sup> Total scattering (TS) studies enable extraction of atomic-scale structural information from gases, liquids, amorphous materials, nanocrystalline, and disordered materials as well as crystalline structures. In several recent studies, it has been shown that cluster structures in the precursor solution play a crucial role not only in determining the crystal polymorph of a particular material but also in directing the microstructural evolution during nanoparticle formation and growth.43-52 Here we probe the hydrothermal synthesis of Bi<sub>2</sub>WO<sub>6</sub> by in situ X-ray total scattering and PXRD measurements to answer the basic questions of nucleation and to understand the peculiar preference for nanoplatelet formation in this important system. Furthermore, we use the in situ information to develop an effective synthesis method to obtain phase-pure Bi<sub>2</sub>WO<sub>6</sub> in a continuous flow supercritical reactor.

## EXPERIMENTAL SECTION

All chemicals were purchased from commercial sources (Sigma-Aldrich) and used as received. Bismuth citrate  $[O_2CCH_2C(OH)-(CO_2)CH_2CO_2]$ Bi (99.99%, CAS: 813–93–4) and sodium tungstate dihydrate Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (99%, CAS: 10213–10–2) were used as precursors for the bismuth tungstate Bi<sub>2</sub>WO<sub>6</sub> nanoparticle synthesis. Bismuth citrate was dissolved in water and few drops of dilute NH<sub>4</sub>OH were added to make a clear solution. Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O was dissolved in water. The concentrations of bismuth citrate solution and sodium tungstate solution were ~2 and ~1 M, respectively. Both solutions were mixed to prepare the final precursor solution used, and the pH of each was ~13. An additional precursor mixture was made, where the pH of the solution was adjusted to approximately 7 (measured by pH paper) by adding HNO<sub>3</sub> for studying the effect of pH on the reaction mechanism. The molar ratio of the final mixture was Bi/W = 2:1 (denoted as F2 precursor solution).

These clear precursor solutions were used for the in situ experiments, which were conducted in a custom-made capillary reactor (fused silica capillary) pressurized to 250 bar and heated to temperatures of 250 and 350 °C.53 The in situ total X-ray scattering experiments were carried out at beamline ID11 at the European Synchrotron Radiation Facility, Grenoble, France. The 14-bit dynamic Frelon4M CCD detector (50  $\times$  50 um<sup>2</sup> pixel size) was placed offcenter, which provided a useful  $Q_{max}$  of 21.7 Å<sup>-1</sup>. The sample-todetector distance was ~103 mm, and the monochromatic X-ray beam had a wavelength of 0.18896 Å. Exposure time was set to 1 s, and with a detector readout time of few milliseconds, this gives a time resolution of  $\sim$ 2.2 s. The flat-field and distortion-corrected data were integrated using Fit2D.54 The integrated total scattering data were converted into pair distribution function by the use of the PDFgetX3 program.<sup>55</sup> Prior to the Fourier transformation, the data were corrected for background scattering using measurements on the deionized water in the same capillary at appropriate temperatures. A  $Q_{\rm min}$  and  $Q_{\rm max}$  of 0.6 and 21.7 Å^{-1} were used for the Fourier



**Figure 2.** (a) Selected PDFs illustrating the reaction progress at 250 °C. (b) Fitted PDF for the precursor solution with both a  $Bi_2O_2$  layer phase and  $WO_4$  tetrahedra ( $R_w = 14.4\%$ ). Inset shows the low *r*-region. (c) Fitted PDF for the precursor solution with only the  $Bi_2O_2$  layer phase ( $R_w = 20.1\%$ ). (d) Molecular clusters present in the precursor solution.

transformation. Structural models were refined against resulting PDFs using PDFgui.  $^{56}$ 

In situ PXRD experiments were performed at beamline I711, MAXII, MAX-lab, Sweden. The wavelength used was 0.9941 Å. A MAR165 CCD 2D detector was placed ~90 mm behind the reactor. The exposure time was 4 s, and with a detector readout time of 1 s, this gave a time resolution of 5 s. The in situ PXRD data were integrated using Fit2D.54 Structural information as a function of reaction time was extracted from the as-integrated PXRD data by sequential Rietveld refinement<sup>57</sup> using FullProf.<sup>58</sup> The sequentially refined instrumental parameters were zero point displacement and Chebychev polynomials (9) to fit the background. The sequentially refined structural parameters for both phases  $[(Bi_{0.933}W_{0.067})O_{1.6}$  and Bi<sub>2</sub>WO<sub>6</sub>] were scale factor, unit cell parameters, and peak profile using Thompson-Cox-Hastings-pseudo-Voigt (TCHpV) profile parameters.<sup>58</sup> Instrumental resolution was taken into account by refining TCHpV profile parameters for the LaB<sub>6</sub> standard and including them in an instrumental resolution file (\*.irf) implemented in the sequential refinements.

In the continuous flow synthesis, the flow rate of the precursor solution was 6 mL/min, while the flow rate of the preheated solvent (water) was 12 mL/min. The temperature was 250, 300, 350, and 390 °C, and the pressure was 250 bar. Details of the flow reactor can be found elsewhere.<sup>59</sup> The collected product slurries were spun down by centrifugation (6500 rpm), and the product was washed four times with deionized water and once with ethanol. Subsequently, the washed powders were dried overnight in a vacuum furnace set to 40 °C. The samples prepared by the flow method are named according to the Bi/W molar ratio of the precursor solution with "F1" for Bi/W = 1:1 and "F2" for Bi/W = 2:1. *Ex situ* PXRD data were measured for the flow synthesis samples on a Rigaku SmartLab powder diffractometer with Bragg–Brentano geometry. A Ge(111) single-crystal monochromator was used to produce Cu K $\alpha_1$  radiation.

TEM images were recorded on a TALOS F200A with a TWIN lens system, X-FEG electron source, and a Ceta 16 M Camera operated at 200 keV using a Ceta 16M CMOS camera.

## RESULT AND DISCUSSION

In Situ X-ray Total Scattering. Figure 2a shows the evolution of the PDF with respect to time, where the bottom curve represents the PDF obtained from the aqueous precursor solution of bismuth citrate and sodium tungstate dihydrate. This solution was heated in the capillary reactor and in situ PDF data were collected while the reaction progressed. The PDF obtained from the precursor solution represents solvated molecular complexes, which have an average size of 13 Å as there is no PDF signal observed beyond 13 Å in real space, Figure 2b. The peak at 1.77 Å can be attributed to W–O bond distances typically found for tungsten tetrahedrally coordinated to oxygen, while the peak at 2.20 Å arises due to Bi-O bond distances. Detailed modeling of the data revealed that the PDF could best be described by a combined model ( $R_w = 14.4\%$ ) containing layers of Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> and additional WO<sub>4</sub><sup>2-</sup> tetrahedra (Figure 2b,c, phase fractions of Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> 74.5% and WO<sub>4</sub><sup>2-</sup> 25.5%). The most intense peak at ca. 4 Å can be attributed to the Bi–Bi distances present in the  $Bi_2O_2^{2+}$  layers (Figure 2b). The average size of the Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> layers was determined to be 13.2(1) Å by the PDF refinement (Figure 2d). The existence of  $Bi_2O_2^{2+}$  and  $WO_4^{2-}$  units in the precursor solution has previously been proposed, and moreover, it was hypothesized that these molecular entities interact with each other to initiate the nucleation event.<sup>14</sup> Here we for the first time provide experimental evidence to support this hypothesis. The  $Bi_2O_2^{2+}$ layer presumably is positively charged, while the tungstate tetrahedra are negatively charged. Therefore, it is a reasonable expectation that they interact electrostatically with each other and form the initial nuclei for eventual crystallization of Bi<sub>2</sub>WO<sub>6</sub>. However, as demonstrated below, the formation mechanism involves several steps.

PDF data were collected separately for a bismuth citrate solution and a sodium tungstate solution. The two separate

PDFs were added manually and compared with the PDF obtained after mixing and injection of the solution into the reactor tube (the cold precursor solution). Significant differences (marked by arrows) were observed between them (Figure 3). The W–O distance changes slightly from 1.76 to



**Figure 3.** Comparison of PDFs between manually added data measured separately on bismuth citrate and sodium tungstate solutions and the PDF collected after mixing to form the precursor solution.

1.78 Å after mixing the solutions. Although there is no significant change in the Bi–O distances, peaks corresponding to Bi–Bi nearest neighbors at 3.76 Å get broader and next nearest neighbor Bi–Bi peak position shifts toward higher r values. This corroborates the fact that when bismuth citrate and sodium tungstate solutions are mixed, the molecular entities interact and form specific clusters. Probing these changes in the PDF while mixing cold solution is a challenging future project since it requires a new reactor setup.

Figure 4 shows the PDFs from the first 3 min of the reaction after heating is commenced. The reaction can be divided into two distinct steps. In the first step immediately after the initiation of heating, the PDF signal is only observed up to distances of  $\sim 20$  Å in the real space. During step 1, there are no significant changes in the PDF signal until after 1 min of the reaction. This indicates two distinct feature of the nucleation process. First, it is clear that the  $Bi_2O_2^{2+}$  layers do not disintegrate upon heating. Second, these layers do not initially interconnect at the edge of the layer, but instead, they stack on top of each other with  $WO_4^{2-}$  in between the layers. While this structural arrangement is occurring, no increase in the average particle size is observed, i.e., no new peaks appear in the PDF, indicating that rearrangement is limited to occur within the layers themselves. In other words, new bond formation only occurs to connect the  $WO_4^{2-}$  tetrahedra within each layer resulting in corner-shared  $WO_6$  octahedra formation. At this stage of the reaction presumably the clusters are very disordered due to the continuously ongoing bond formation. As a consequence of the lack of particle growth, these prenucleation structures presumably act as nuclei for the formation of the nanocrystal. Once the initial local bond formation between layers of  $Bi_2O_2^{2+}$  and  $WO_4^{2-}$  tetrahedra is complete, the reaction progresses into step 2, where the growth of the nanocrystals occurs. Since the molecular complexes exist in layered form, it is easier to interconnect edgewise than growing layers on top of each other. These platelet nuclei play a crucial role in the intrinsic anisotropic growth since the number of dangling bonds is much higher on the surface than on the edge of the nuclei. According to Gibbs-Thomson theory, the number of dangling bonds per atom over the entire crystal determines the chemical potential of a surface. $^{60-62}$ Therefore, it is safe to say that the platelet nuclei surface has a higher chemical potential than the edge, and two-dimensional growth is therefore preferred. Once a platelet has nucleated, it uses other small platelets to form larger ones.<sup>60</sup> Hence, this process is more energy efficient since less bond formation is required to join the layers. If the disordered nuclei formed in step 1 were to stack on top of each other, then they would need  $WO_4^{2-}$  tetrahedra as connectors between them. However, this already occurred in step 2, and  $WO_4^{2-}$ 



Figure 4. Evolution of the PDF with respect to time at a synthesis temperature of 250 °C. The structures present at the different reaction stages are sketched.

tetrahedra have been exhausted in the process. Furthermore, if the stacking of the layers were to happen in step 2 instead of sideways growth, then a steady appearance of new PDF peaks would have been observed. Thus, the bond formation in between layers of  $\text{Bi}_2\text{O}_2^{2+}$  of  $\text{WO}_4^{2-}$  constitutes the initial nuclei that subsequently interconnect along the edges of the layers, resulting in the sudden appearance of additional peaks in the PDF (Figure 4). We conclude that the crystallization in the second step does not occur by stacking of nanoplates but by connectivity in the *ac* planes.

The PDF of the heated reaction mixture after 20 min of reaction time was fitted with the reported structure of crystalline  $Bi_2WO_6$  (Figure 5a). Interestingly, by applying a



**Figure 5.** (a) PDF fitted with  $Bi_2WO_6$  structure including unreacted precursor complexes ( $R_w = 21.1\%$ ). (b) PDF fitted with  $Bi_2WO_6$  structure without unreacted precursor complexes ( $R_w = 29.8\%$ ) showing a poorer fit.

solely  $Bi_2WO_6$  structural model, no satisfactory fit of the data could be obtained (Figure 5b). Only by including unreacted precursor molecules, it was possible to obtain a good fit to the total PDF data. This indicates that under the applied reaction conditions some amount of unreacted precursor complexes remains present even after 20 min. Furthermore, it is observed that the intensities of the PDF peaks at higher *r*-values (20–40 Å) do not match the calculated model (Figure 5). This is attributed to the anisotropic size of the crystallites (nanoplatelets) not accounted for in the model. Therefore, the average size of the nanoparticles obtained by fitting PDF is expected to be smaller than observed by PXRD.

Separate *in situ* PXRD measurements were carried out under the same reaction conditions as used for the *in situ* total scattering experiment. Pristine  $Bi_2WO_6$  nanocrystals were obtained after 20 min of reaction using the F2 precursor

(Bi/W = 2:1). The crystalline phase could be indexed in space group  $Pca2_1$  with cell parameters of a = 5.4687(14) Å, b =16.503(3) Å, c = 5.4823(16) Å (see Figure S1). Figure 6 shows the time-resolved PXRD patterns of Bi<sub>2</sub>WO<sub>6</sub>. From the time evolution of the PXRD it is obvious that the reaction progresses in two steps in agreement with the TS data. Immediately after heating is initiated, the formation of the disordered crystalline phase of cubic  $(Bi_{0.933}W_{0.067})O_{1.6}$  is observed. The (Bi<sub>0.933</sub>W<sub>0.067</sub>)O<sub>1.6</sub> structure consists of interconnected Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> layers with W partially occupying the Bi positions. In step 2, peaks corresponding to the Bi<sub>2</sub>WO<sub>6</sub> phase start to appear. At increased temperature, the transformation of  $(Bi_{0.933}W_{0.067})O_{1.6}$  to  $Bi_2WO_6$  is significantly faster. It has been previously reported that the disordered cubic (Bi<sub>0.933</sub>W<sub>0.067</sub>)- $O_{1.6}$  phase only is observed at higher pH (~11) when bismuth nitrate is used as the Bi source. The formation of the disordered phase is due to the increased solubility of WO<sub>4</sub><sup>2-</sup> tetrahedra in basic solution.<sup>29,63</sup> In the present synthesis, we use bismuth citrate and sodium tungstate dehydrate precursors, which gives a high pH of about 13. However, as seen in Figure 6b,d, the reaction is unchanged even when the pH is adjusted to 7. In both cases, the disordered cubic phase  $(Bi_{0.933}W_{0.067})O_{1.6}$  is observed initially in the reaction steps. The origin of the formation of this disordered phase is directly seen in in situ TS data. At the beginning of the reaction, there are  $\text{Bi}_2\text{O}_2^{2+}$  layers with  $\text{WO}_4^{2-}$  tetrahedra in between, and the amount of available  $\text{WO}_4^{2-}$  is not sufficient to produce the fully ordered Bi<sub>2</sub>WO<sub>6</sub> phase with a corner-shared WO<sub>6</sub> unit. Therefore, the average structure, which is probed by PXRD, is the disordered phase (Bi<sub>0.933</sub>W<sub>0.067</sub>)O<sub>1.6</sub>. As the reaction progresses, more WO<sub>4</sub><sup>2–</sup> fills the layers, and once there is a sufficient number of WO<sub>4</sub><sup>2–</sup> tetrahedra to hold the layers together, the formation Bi<sub>2</sub>WO<sub>6</sub> begins.

The PXRD data in Figure 7a represent the reaction progress with respect to time. They demonstrate that preferential growth of the nanoparticles occurs along the *ac* plane since the profile widths of the (200) and (002) reflections get significantly sharper compared with the remaining reflections. Figure 7b,c shows the variation of cell parameters and particle size, respectively, extracted from sequential Rietveld refinement. Initially, only the disordered cubic phase was observed and the cell parameter is represented in Figure 7b with open diamonds. After 1.5 min of reaction, this phase starts to transform to Bi<sub>2</sub>WO<sub>6</sub>. The cell parameters are larger when the nanoparticles are small, and they reach a smaller stable value during the growth of the nanoparticles. The growth kinetics were monitored for Bi2WO6 nanoparticle with Avrami-Erofe'ev equation, which is a model to simulate nucleationgrowth crystallization.<sup>64-66</sup>

$$\alpha = 1 - e^{(-[k(t-t_{ind})]^n)}$$

The extent of the reaction,  $\alpha$ , can be evaluated from the normalized particle size with respect to time. Here *k* denotes the rate constant, and the exponent *n* is often used to distinguish between different reaction mechanisms.  $t_{ind}$  is the induction time defined as the time interval until the first detectable particle size is observed. Growth kinetics of both the platelet diameter and the thickness were evaluated by fitting the above equation to the nanoplatelet growth (Figure 8).

The analysis reveals that the growth rate of the platelet diameter  $(k = 0.86(1) \text{ min}^{-1})$  is more than three time faster than the thickness growth  $((k = 0.25(1) \text{ min}^{-1}))$ . This is in accordance with the finding from the TS studies. The exponent

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**Figure 6.** In situ PXRD data using precursor (Bi/W = 2:1) at different temperatures and pH: (a) pH 13 and T = 250 °C, (b) pH 7 and T = 250 °C, (c) pH 13 and T = 300 °C, and (d) pH 7 and T = 300 °C. For clarity, only 5 min of the reaction is shown in this figure.



Figure 7. (a) Selected PXRD patterns illustrating the reaction progress at 250 °C. Variation of cell parameters (b) and particle size (c) with respect to time of *in situ* PXRD at temperature 250 °C.

(*n*) of the diameter and thickness of nanoplate growth were found to be 1.36 and 1.63, respectively, indicating nucleation controlled growth kinetics of  $Bi_2WO_6$ .<sup>29,67</sup> Earlier growth kinetics analysis of  $Bi_2WO_6$  reported *n* values in the range between 0.54 and 0.77 using the same kinetic model as the present study. It was suggested that the growth is diffusion-controlled.<sup>27</sup> However, in the report of Zhou et al. the intensity of the Bragg diffraction was used to evaluate the extent of the reaction; furthermore, no preferential particle growth was considered. The present study not only shows the preferential growth of nanoplatelets but also establishes the anisotropic growth rates of the nanoparticle.

### Continuous Flow Hydrothermal Synthesis of Bi<sub>2</sub>WO<sub>6</sub>.

The knowledge gained from the *in situ* experiments was used to develop conditions for synthesis of phase-pure  $Bi_2WO_6$  in a continuous flow supercritical reactor.<sup>39</sup> Flow syntheses were carried out with a stoichiometric mixture of Bi and W precursor (2:1, sample F2) at different temperatures 250, 300, 350, and 390 °C. The product obtained was always found to consist of mixed phases of  $Bi_2WO_6$  and disordered ( $Bi_{0.933}W_{0.067}$ )O<sub>1.6</sub> with phase fractions of 48.5:51.5%, 53.39:46.61%, 63.68:36.32%, and 68.79:31.21% at 250, 300, 350, and 390 °C, respectively (see the Supporting Information sections S2 and S3). This is in contrast to the *in situ* TS and PXRD results where pure phase  $Bi_2WO_6$  was obtained at the



Figure 8. Fitted curve with growth of  ${\rm Bi}_2{\rm WO}_6$  nanoplate diameter and thickness.

end of the reaction when using stoichiometric precursor. Although the amount of impurity decreased with increasing synthesis temperature, completely phase-pure Bi<sub>2</sub>WO<sub>6</sub> could not be obtained with the F2 precursor. TEM images clearly illustrate the presence of two different types of particles in all the F2 samples (Figure 9). Note that the TEM image of the F2@250 °C sample only has few platelets indicating a lower percentage of Bi2WO6 than that obtained from Rietveld refinement on representative samples. The explanation of the formation of the impurity phase may be gathered from the in situ PXRD and TS analysis. The in situ PXRD data shows that at 250 °C the transformation from  $(Bi_{0.933}W_{0.067})O_{1.6}$  to Bi<sub>2</sub>WO<sub>6</sub> is very slow. Therefore, it might be concluded that  $(Bi_{0.933}W_{0.067})O_{1.6}$  did not have enough time to completely transform to Bi<sub>2</sub>WO<sub>6</sub> as the flow synthesis is very fast. At high temperature, the transformation is faster, but phase-pure Bi<sub>2</sub>WO<sub>6</sub> still could not be obtained in flow synthesis with the F2 precursor. The *in situ* TS analysis shows that the bond formation between  $Bi_2O_2^{2+}$  and  $WO_4^{2-}$  requires significant incubation time as more and more  $WO_4^{2-}$  molecules have to arrange themselves in between the  $Bi_2O_2^{2+}$  layers to initiate bond formation between the layers. This step is crucial for the formation of a completely pure phase  $Bi_2WO_6$  sample. If more  $WO_4^{2-}$  tetrahedra are present in the solution, then the interaction between  $Bi_2O_2^{2+}$  layers and  $WO_4^{2-}$  tetrahedra should be better facilitated. This can be achieved by increasing the molar ratio of Bi to W to 1:1 (precursor F1).

Indeed, when the molar ratio was changed to 1:1 (F1), the impurity phase fraction of disordered  $(Bi_{0.933}W_{0.067})O_{1.6}$  at 250 °C decreases to 3–4% (see Figure S4). This change is also clear in the corresponding TEM images (Figure 9), where the  $Bi_2WO_6$  platelets now are present along with a minor  $(Bi_{0.933}W_{0.067})O_{1.6}$  phase. Completely phase-pure  $Bi_2WO_6$  is obtained at higher temperatures of 300, 350, and 390 °C with the F1 precursor (see Figure S5). The TEM images also confirm the formation of phase pure samples as no other particles are seen except the  $Bi_2WO_6$  platelets.

## CONCLUSIONS

The present *in situ* PXRD and PDF study demonstrates that the initial presence of layers of  $Bi_2O_2^{2+}$  is responsible for the preferential growth of nanoplatelets of  $Bi_2WO_6$  in hydrothermal synthesis. The crystallization occurs in two steps. In



**Figure 9.** TEM images for all flow synthesized samples. F2 denotes the molar ratio of Bi and W was 2:1, while F1 represents a molar ratio of 1:1.

the first step, precursor molecular complexes of disordered  $Bi_2O_2^{2+}$  (length ~ 13 Å) layer interact with  $WO_4^{2-}$  tetrahedra leading to the stacking of  $WO_4^{2-}$  tetrahedra in between the  $Bi_2O_2^{2+}$  layers. This interaction leads to the formation of the disordered, but crystalline, phase of (Bi<sub>0.933</sub>W<sub>0.067</sub>)O<sub>1.6</sub>, as confirmed by in situ PXRD. As the reaction progresses, the disordered phase stacks more WO42- tetrahedra between the layers of  $Bi_2O_2^{2+}$ . In the second step, the disordered phase gets converted to Bi<sub>2</sub>WO<sub>6</sub> nanoplatelets by "sideways" attachment/ growth along the ac plane. Kinetic analysis of the growth reveals that the "sideways" ac plane growth is three times faster than that along the "stacking" b direction explaining the universal observation of nanoplatelet morphology. The atomistic information obtained from in situ measurement was used to obtain phase-pure Bi<sub>2</sub>WO<sub>6</sub> in continuous flow hydrothermal synthesis. Since the in situ data reveal that the crucial step in formation of  $Bi_2WO_6$  is the presence of  $WO_4^{2-}$  tetrahedra, the molar ratio of tungsten must be increased relative to the stoichiometric ratio of Bi/W = 2:1. The *in situ* data also clearly show that the two-step reaction progresses much faster at high

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temperatures. Indeed, by using the surplus of W in the precursor and perform synthesis at high reaction temperatures, it is possible to obtain phase-pure  $Bi_2WO_6$  nanoplatelets in a scalable and sustainable continuous-flow supercritical process. The present study provides a rationale for the observed  $Bi_2WO_6$  nanoplatelet morphology reported in the large body of papers on the subject, and it reiterates the importance of having atomic-scale information about the prenucleation clusters if we are to properly understand and control nucleation and growth phenomena.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01249.

Total scattering data treatment and fitting protocol for precusrsor complexes; Rietveld and PDF refinement parametrs; Rietvel refined profile and phase fractions (PDF)

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#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The work was supported by the Villum Foundation, and the Danish National Research Foundation (DNRF93). We thank ESRF, France, and MAXLabII, Sweden, for beamtime, and we gratefully acknowledge beamline scientist Dr. Andrea Bernasconi for help during data collection at beamline ID11 at ESRF.

### REFERENCES

(1) Tang, J.; Zou, Z.; Ye, J. Photocatalytic decomposition of organic contaminants by  $Bi_2WO_6$  under visible light irradiation. *Catal. Lett.* **2004**, 92 (1–2), 53–56.

(2) Zhang, L.; Zhu, Y. A review of controllable synthesis and enhancement of performances of bismuth tungstate visible-lightdriven photocatalysts. *Catal. Sci. Technol.* **2012**, *2* (4), 694–706.

(3) Zhang, N.; Ciriminna, R.; Pagliaro, M.; Xu, Y.-J. Nanochemistryderived  $Bi_2WO_6$  nanostructures: towards production of sustainable chemicals and fuels induced by visible light. *Chem. Soc. Rev.* **2014**, *43* (15), 5276–5287. (4) Zhang, C.; Zhu, Y. Synthesis of square  $Bi_2WO_6$  nanoplates as high-activity visible-light-driven photocatalysts. *Chem. Mater.* **2005**, 17 (13), 3537–3545.

(5) Zhang, L.; Wang, W.; Zhou, L.; Xu, H.  $Bi_2WO_6$  Nano- and microstructures: Shape control and associated visible-light-driven photocatalytic activities. *Small* **2007**, *3* (9), 1618–1625.

(6) Fu, H.; Pan, C.; Yao, W.; Zhu, Y. Visible-light-induced degradation of rhodamine B by nanosized Bi<sub>2</sub>WO<sub>6</sub>. J. Phys. Chem. B **2005**, 109 (47), 22432–22439.

(7) Zhang, L.; Wang, W.; Chen, Z.; Zhou, L.; Xu, H.; Zhu, W. Fabrication of flower-like  $Bi_2WO_6$  superstructures as high performance visible-light driven photocatalysts. *J. Mater. Chem.* **2007**, *17* (24), 2526–2532.

(8) Wu, J.; Duan, F.; Zheng, Y.; Xie, Y. Synthesis of  $Bi_2WO_6$  nanoplate-built hierarchical nest-like structures with visible-light-induced photocatalytic activity. *J. Phys. Chem. C* **2007**, *111* (34), 12866–12871.

(9) Kim, N.; Vannier, R.-N.; Grey, C. P. Detecting different oxygenion jump pathways in  $Bi_2WO_6$  with 1-and 2-dimensional <sup>17</sup>O MAS NMR spectroscopy. *Chem. Mater.* **2005**, *17* (8), 1952–1958.

(10) Yang, A.-M.; Han, Y.; Li, S.-S.; Xing, H.-W.; Pan, Y.-H.; Liu, W.-X. Synthesis and comparison of photocatalytic properties for Bi<sub>2</sub>WO<sub>6</sub> nanofibers and hierarchical microspheres. *J. Alloys Compd.* **2017**, *695*, 915–921.

(11) Zhang, S.; Zhang, C.; Man, Y.; Zhu, Y. Visible-light-driven photocatalyst of  $Bi_2WO_6$  nanoparticles prepared via amorphous complex precursor and photocatalytic properties. *J. Solid State Chem.* **2006**, *179* (1), 62–69.

(12) Zhang, Z.; Wang, W.; Shang, M.; Yin, W. Low-temperature combustion synthesis of  $Bi_2WO_6$  nanoparticles as a visible-light-driven photocatalyst. *J. Hazard. Mater.* **2010**, *177* (1), 1013–1018.

(13) Wu, L.; Bi, J.; Li, Z.; Wang, X.; Fu, X. Rapid preparation of  $Bi_2WO_6$  photocatalyst with nanosheet morphology via microwaveassisted solvothermal synthesis. *Catal. Today* **2008**, 131 (1–4), 15–20.

(14) Tian, Y.; Hua, G.; Xu, W.; Li, N.; Fang, M.; Zhang, L. Bismuth tungstate nano/microstructures: Controllable morphologies, growth mechanism and photocatalytic properties. *J. Alloys Compd.* **2011**, *509* (3), 724–730.

(15) Zhou, Y.; Vuille, K.; Heel, A.; Patzke, G. R. Studies on Nanostructured Bi2WO6: Convenient Hydrothermal and TiO2-Coating Pathways. Z. Anorg. Allg. Chem. 2009, 635 (12), 1848–1855. (16) Li, W.; Zhu, Y.; Yu, J.; Jaroniec, M.; Jiang, C. Chapter 12 -

Synthesis and performance enhancement for  $Bi_2WO_6$  photocatalysts. *Interface Sci. Technol.* **2020**, *31*, 379–413.

(17) Jiménez, R.; Castro, A.; Jiménez, B. Evidence of ferroelastic– ferroelastic phase transition in BiMoxW1-xO6 compounds. *Appl. Phys. Lett.* 2003, 83 (16), 3350–3352.

(18) Castro, A.; Bégué, P.; Jiménez, B.; Ricote, J.; Jiménez, R.; Galy, J. New Bi2Mo1-xWxO6 Solid Solution: Mechanosynthesis, Structural Study, and Ferroelectric Properties of the x = 0.75 Member. *Chem. Mater.* **2003**, *15* (17), 3395–3401.

(19) Noguchi, Y.; Satoh, R.; Miyayama, M.; Kudo, T. New Intergrowth Bi<sub>2</sub>WO<sub>6</sub>.Bi<sub>3</sub>TaTiO<sub>9</sub> Ferroelectrics. *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi* **2001**, *109* (1265), 29–32.

(20) Senthil Murugan, G.; Varma, K. B. R. Dielectric, linear and nonlinear optical properties of lithium borate–bismuth tungstate glasses and glass-ceramics. J. Non-Cryst. Solids **2001**, 279 (1), 1–13.

(21) Murugan, G. S.; Subbanna, G. N.; Varma, K. B. R. Nanocrystallization of ferroelectric bismuth tungstate in lithium borate glass matrix. *J. Mater. Sci. Lett.* **1999**, *18* (20), 1687–1690.

(22) Mahanty, S.; Ghose, J. Preparation and optical studies of polycrystalline Bi2WO6. *Mater. Lett.* **1991**, *11* (8–9), 254–256.

(23) Ge, L.; Han, C.; Liu, J. Novel visible light-induced g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> composite photocatalysts for efficient degradation of methyl orange. *Appl. Catal., B* **2011**, *108–109*, 100–107.

(24) Gao, E.; Wang, W.; Shang, M.; Xu, J. Synthesis and enhanced photocatalytic performance of graphene-Bi<sub>2</sub>WO<sub>6</sub> composite. *Phys. Chem. Chem. Phys.* **2011**, *13* (7), 2887–2893.

(25) Yang, J.; Chen, D.; Zhu, Y.; Zhang, Y.; Zhu, Y. 3D-3D porous  $Bi_2WO_6/graphene$  hydrogel composite with excellent synergistic effect of adsorption-enrichment and photocatalytic degradation. *Appl. Catal., B* **2017**, 205, 228–237.

(26) Meng, X.; Li, Z.; Zeng, H.; Chen, J.; Zhang, Z. MoS<sub>2</sub> quantum dots-interspersed Bi<sub>2</sub>WO<sub>6</sub> heterostructures for visible light-induced detoxification and disinfection. *Appl. Catal., B* **2017**, *210*, 160–172.

(27) Zhang, X.; Yu, S.; Liu, Y.; Zhang, Q.; Zhou, Y. Photoreduction of non-noble metal Bi on the surface of  $Bi_2WO_6$  for enhanced visible light photocatalysis. *Appl. Surf. Sci.* **2017**, *396*, 652–658.

(28) Knight, K. S. The crystal-structure of russellite - a redetermination using neutron powder diffraction of synthetic  $Bi_2WO_6$ . Mineral. Mag. **1992**, 56 (384), 399-409.

(29) Zhou, Y.; Antonova, E.; Bensch, W.; Patzke, G. R. In situ X-ray diffraction study of the hydrothermal crystallization of hierarchical Bi<sub>2</sub>WO<sub>6</sub> nanostructures. *Nanoscale* **2010**, *2* (11), 2412–2417.

(30) Zhou, Y.; Zhang, Q.; Lin, Y.; Antonova, E.; Bensch, W.; Patzke, G. One-step hydrothermal synthesis of hierarchical Ag/Bi2WO6 composites: In situ growth monitoring and photocatalytic activity studies. *Sci. China: Chem.* **2013**, *56* (4), 435–442.

(31) Hald, P.; Becker, J.; Bremholm, M.; Pedersen, J. S.; Chevallier, J.; Iversen, S. B.; Iversen, B. B. Supercritical Propanol–Water Synthesis and Comprehensive Size Characterisation of Highly Crystalline anatase TiO2 Nanoparticles. *J. Solid State Chem.* **2006**, *179* (8), 2674–2680.

(32) Hellstern, H. L.; Becker, J.; Hald, P.; Bremholm, M.; Mamakhel, A.; Iversen, B. B. Development of a Dual-Stage Continuous Flow Reactor for Hydrothermal Synthesis of Hybrid Nanoparticles. *Ind. Eng. Chem. Res.* **2015**, *54* (34), 8500–8508.

(33) Reverchon, E.; Adami, R. Nanomaterials and supercritical fluids. J. Supercrit. Fluids **2006**, 37 (1), 1–22.

(34) Adschiri, T.; Kanazawa, K.; Arai, K. Rapid and Continuous Hydrothermal Crystallization of Metal Oxide Particles in Supercritical Water. J. Am. Ceram. Soc. **1992**, 75 (4), 1019–1022.

(35) Aymonier, C.; Loppinet-Serani, A.; Reverón, H.; Garrabos, Y.; Cansell, F. Review of supercritical fluids in inorganic materials science. *J. Supercrit. Fluids* **2006**, 38 (2), 242–251.

(36) Lester, E.; Blood, P.; Denyer, J.; Giddings, D.; Azzopardi, B.; Poliakoff, M. Reaction engineering: The supercritical water hydro-thermal synthesis of nano-particles. *J. Supercrit. Fluids* **2006**, *37* (2), 209–214.

(37) Adschiri, T.; Hakuta, Y.; Sue, K.; Arai, K. Hydrothermal Synthesis of Metal Oxide Nanoparticles at Supercritical Conditions. *J. Nanopart. Res.* **2001**, 3 (2), 227–235.

(38) Toft, L. L.; Aarup, D. F.; Bremholm, M.; Hald, P.; Iversen, B. B. Comparison of T-piece and concentric mixing systems for continuous flow synthesis of anatase nanoparticles in supercritical isopropanol/ water. *J. Solid State Chem.* **2009**, *182* (3), 491–495.

(39) Becker, J.; Hald, P.; Bremholm, M.; Pedersen, J. S.; Chevallier, J.; Iversen, S. B.; Iversen, B. B. Critical Size of Crystalline ZrO2 Nanoparticles Synthesized in Near- and Supercritical Water and Supercritical Isopropyl Alcohol. *ACS Nano* **2008**, *2* (5), 1058–1068.

(40) Birgisson, S.; Saha, D.; Iversen, B. B. Formation mechanisms of MnO<sub>2</sub> polymorphs under hydrothermal conditions. *Cryst. Growth Des.* **2018**, *18*, 827–838.

(41) Egami, T.; Billinge, S. J. Underneath the Bragg Peaks: Structural Analysis of Complex Materials; Pergamon, 2012; Vol. 16.

(42) Billinge, S. J. L.; Kanatzidis, M. G. Beyond Crystallography: The Study of Disorder, Nanocrystallinity and Crystallographically Challenged Materials with Pair Distribution Functions. *Chem. Commun.* (*Cambridge*, U. K.) **2004**, No. 7, 749–760.

(43) Jensen, K. M. Ø.; Christensen, M.; Juhas, P.; Tyrsted, C.; Bøjesen, E. D.; Lock, N.; Billinge, S. J. L.; Iversen, B. B. Revealing the Mechanisms Behind  $SnO_2$  Nanoparticle Formation and Growth During Hydrothermal Synthesis: An In Situ Total Scattering Study. J. Am. Chem. Soc. **2012**, 134 (15), 6785–6792.

(44) Tyrsted, C.; Ørnsbjerg Jensen, K. M.; Bøjesen, E. D.; Lock, N.; Christensen, M.; Billinge, S. J. L.; Brummerstedt Iversen, B. Understanding the Formation and Evolution of Ceria Nanoparticles Under Hydrothermal Conditions. Angew. Chem., Int. Ed. 2012, 51 (36), 9030-9033.

(45) Saha, D.; Jensen, K. M. Ø.; Tyrsted, C.; Bøjesen, E. D.; Mamakhel, A. H.; Dippel, A.-C.; Christensen, M.; Iversen, B. B. In Situ Total X-Ray Scattering Study of WO<sub>3</sub> Nanoparticle Formation under Hydrothermal Conditions. *Angew. Chem., Int. Ed.* **2014**, 53 (14), 3667–3670.

(46) Jensen, K. M. Ø.; Andersen, H. L.; Tyrsted, C.; Bøjesen, E. D.; Dippel, A.-C.; Lock, N.; Billinge, S. J. L.; Iversen, B. B.; Christensen, M. Mechanisms for Iron Oxide Formation under Hydrothermal Conditions: An In Situ Total Scattering Study. *ACS Nano* **2014**, *8* (10), 10704–10714.

(47) Bremholm, M.; Felicissimo, M.; Iversen, B. B. Time-Resolved In Situ Synchrotron X-ray Study and Large-Scale Production of Magnetite Nanoparticles in Supercritical Water. *Angew. Chem., Int. Ed.* **2009**, 48 (26), 4788–4791.

(48) Tyrsted, C.; Becker, J.; Hald, P.; Bremholm, M.; Pedersen, J. S.; Chevallier, J.; Cerenius, Y.; Iversen, S. B.; Iversen, B. B. In-Situ synchrotron radiation study of formation and growth of crystalline  $Ce_xZr_{1-x}O_2$  nanoparticles synthesized in supercritical water. *Chem. Mater.* **2010**, 22 (5), 1814–1820.

(49) Bremholm, M.; Becker-Christensen, J.; Iversen, B. B. High-Pressure, high-Temperature formation of phase-pure monoclinic zirconia nanocrystals studied by time-resolved in situ synchrotron X-Ray diffraction. *Adv. Mater. (Weinheim, Ger.)* **2009**, *21* (35), 3572–3575.

(50) Saha, D.; Bøjesen, E. D.; Mamakhel, A. H.; Bremholm, M.; Iversen, B. B. In Situ PDF Study of the Nucleation and Growth of Intermetallic PtPb Nanocrystals. *ChemNanoMat* **2017**, 3 (7), 472– 478.

(51) Saha, D.; Bøjesen, E. D.; Jensen, K. M. Ø.; Dippel, A.-C.; Iversen, B. B. Formation mechanisms of Pt and  $Pt_3Gd$  nanoparticles under solvothermal Conditions: An in situ total X-ray scattering study. *J. Phys. Chem. C* **2015**, *119* (23), 13357–13362.

(52) Birgisson, S.; Saha, D.; Iversen, B. B. Formation mechanisms of nanocrystalline  $MnO_2$  polymorphs under hydrothermal conditions. *Cryst. Growth Des.* **2018**, *18* (2), 827–838.

(53) Becker, J.; Bremholm, M.; Tyrsted, C.; Pauw, B.; Jensen, K. M. O.; Eltzholt, J.; Christensen, M.; Iversen, B. B. Experimental Setup for In Situ X-Ray Saxs/Waxs/Pdf Studies of the Formation and Growth of Nanoparticles in Near-and Supercritical Fluids. *J. Appl. Crystallogr.* **2010**, 43 (4), 729–736.

(54) Hammersley, A.; Svensson, S.; Hanfland, M.; Fitch, A.; Hausermann, D. Two-Dimensional Detector Software: From Real Detector To Idealised Image or Two-Theta Scan. *High Pressure Res.* **1996**, *14* (4–6), 235–248.

(55) Juhas, P.; Davis, T.; Farrow, C. L.; Billinge, S. J. L. Pdfgetx3: A Rapid and Highly Automatable Program for Processing Powder Diffraction Data into Total Scattering Pair Distribution Functions. *J. Appl. Crystallogr.* **2013**, *46* (2), 560–566.

(56) Farrow, C. L.; Juhas, P.; Liu, J. W.; Bryndin, D.; Božin, E. S.; Bloch, J.; Proffen, T.; Billinge, S. J. L. Pdffit2 and Pdfgui: Computer Programs for Studying Nanostructure in Crystals. *J. Phys.: Condens. Matter* 2007, 19 (33), 335219–335226.

(57) Rietveld, H. A profile refinement method for nuclear and magnetic structures. J. Appl. Crystallogr. 1969, 2 (2), 65–71.

(58) Rodríguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. *Phys. B* **1993**, *192* (1–2), 55–69.

(59) Lock, N.; Christensen, M.; Jensen, K. M. Ø.; Iversen, B. B. Rapid one-step low-temperature synthesis of nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Angew. Chem., Int. Ed. **2011**, 50 (31), 7045–7047.

(60) Peng, Z. A.; Peng, X. Nearly monodisperse and shapecontrolled CdSe nanocrystals via alternative routes: Nucleation and growth. J. Am. Chem. Soc. **2002**, 124 (13), 3343–3353.

(61) Mullin, J. W. Crystallization; Elsevier, 2001.

(62) Yu, S.-H.; Liu, B.; Mo, M.-S.; Huang, J.-H.; Liu, X.-M.; Qian, Y.-T. General synthesis of single-crystal tungstate nanorods/nano-

wires: A facile, low-temperature solution approach. Adv. Funct. Mater. 2003, 13 (8), 639–647.

(63) Yao, S.; Wei, J.; Huang, B.; Feng, S.; Zhang, X.; Qin, X.; Wang, P.; Wang, Z.; Zhang, Q.; Jing, X.; Zhan, J. Morphology modulated growth of bismuth tungsten oxide nanocrystals. *J. Solid State Chem.* **2009**, *182* (2), 236–239.

(64) Avrami, M. Granulation, Phase Change, and Microstructure Kinetics of Phase Change. III. J. Chem. Phys. **1941**, 9 (2), 177–184. (65) Avrami, M. Kinetics of Phase Change. I General Theory. J.

(65) Aviani, M. Kineles of Flase Charge. F General Theory, J Chem. Phys. **1939**, 7 (12), 1103–1112.

(66) Avrami, M. Kinetics of Phase Change. II Transformation-Time Relations for Random Distribution of Nuclei. *J. Chem. Phys.* **1940**, 8 (2), 212–224.

(67) Zhou, Y.; Pienack, N.; Bensch, W.; Patzke, G. R. The Interplay of Crystallization Kinetics and Morphology in Nanostructured W/Mo Oxide Formation: An in situ Diffraction Study. *Small* **2009**, *5* (17), 1978–1983.