Supplementary Information

Direct *in situ* observation of ZnO nucleation and growth via transmission x-ray microscopy

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1. ZnO electrodeposition

Zinc oxide (ZnO) is an attractive material widely studied for various applications such as transistors,¹ solar cells,² and light emitting diodes.³ Many methods have been developed to synthesize ZnO. These methods broadly fall into two categories: vacuum and solution methods. Vacuum methods such as sputtering⁴ and vapour deposition⁵ produce high crystallinity films at the cost of high temperature and high vacuum requirements. On the other hand, solution methods such as hydrothermal growth⁶ and electrodeposition,⁷ produce ZnO films of respectable crystallinity at lower temperatures without the need for vacuum. In terms of operational costs, solution methods would be attractive due to the obviation of high thermal and vacuum requirements.

Among solution techniques, electrodeposition provides several advantages. Parameters such as electrolyte composition, deposition potential, temperature, deposition time and pH could be used to control morphology and thickness of the ZnO film.⁸ In addition, the versatility of electrodeposition as a deposition technique has been demonstrated on various organic substrates such as polypyrrole,⁹ reduced graphene oxide,¹⁰ polyethylene naphthalate,¹¹ copper phthalocyanine and pentacene.¹² Furthermore, electrodeposition is a long-established process used in industry, which makes scaling of ZnO electrodeposition feasible.

The first instance of ZnO electrodeposition was demonstrated by Peulon and Lincot.¹³ Hydroxide ions are produced when dissolved oxygen or nitrate ions are reduced as shown in (1) and (2). The reduction of dissolved oxygen results in an increase in the local pH of the electrode, which precipitates Zn²⁺ as Zn(OH)₂ as shown in (3). At elevated temperatures, Zn(OH)₂ is converted to ZnO (4). In the same paper, Peulon and Lincot detected the ZnO phase when deposition was performed at 50 °C and 80 °C but not at 25 °C. In our experiments, deposition was conducted at 65 °C, within the range for ZnO formation.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	(1)
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 $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$ (2)

$$\operatorname{Zn}^{2+} + 2\operatorname{OH}^{-} \to \operatorname{Zn}(\operatorname{OH})_2$$
 (3)

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$
 (4)

The supersaturation of the solution could be adjusted to produce ZnO of various morphologies such as nanorods, dense films, and nanoplates.¹⁴ At low Zn²⁺ precursor concentrations (< 2 mM), supersaturation is low and ZnO nanorods with pointed tops are formed as a result of screw dislocations. When the concentration is increased to between 2 mM to 20 mM, medium supersaturation occurs and ZnO nanorods experience growth on the sides with distinct hexagonal flat (002) planes. At high supersaturation (> 20 mM), nanoplates are formed from nucleation of low-index planes. Peulon and Lincot proposed the following reaction¹³ of zinc hydroxychloride nanoplates:¹⁵

$$5Zn^{2+} + 2O_2 + 5H_2O + 2Cl^- + 8e^- \rightarrow Zn_5(OH)_8Cl_2H_2O$$
 (5)

These zinc hydroxychloride nanoplates have the potential to form ZnO nanoplates when annealed at elevated temperatures.¹⁶ Long *et al.* reported porous ZnO nanoplates when zinc hydroxychloride nanoplates were annealed. With results from thermogravimetric analysis, they proposed that zinc

hydroxychloride decomposes into ZnO with the release of water and hydrogen chloride in the following reaction:¹⁷

$$Zn_5(OH)_8Cl_2H_2O \rightarrow 5ZnO + 4H_2O + 2HCl$$
(6)

2. Methods

2.1 In situ cell

An electrochemical cell was designed to meet the requirements of the TXM at SSRL beamline 6-2. The cell was 3D printed with the high temperature material Objet RGD525, and consists of a reservoir holding ~30 mL of electrolyte. The cross section is 2 cm at the top of the cell to accommodate the counter and reference electrodes as well as a resistive heater, temperature sensor, and pipette for bubbling oxygen. The cell's reservoir thins to 2 mm at the bottom to reduce the path length of x-rays through the electrolyte.

Data were acquired in transmission mode, with X-rays passing at 90° through two Kapton windows separated by 2 mm of electrolyte. The front window of electrochemical cell is also the working electrode, and consists of 6 μ m Kapton with 10 nm of Au sputtered on top to ensure good electrochemical contact. The metallized side of the window is in contact with the electrolyte and under electrochemical control. With this geometry, *in situ* data of ZnO nanoparticles growing on the Au electrode can be collected, without the problems associated with transport-limiting thin electrolyte layers. The cell also incorporates an additional through-hole, not occluded by the sample or electrolyte, which allows reference images to be taken for removal of imaging artefacts and to convert the raw intensity images to absorption images.

2.2. Electrodeposition

A three-electrode setup was used with Pt as the counter electrode and Ag/AgCl as the reference electrode. The working electrode was a film of sputtered gold (10 nm thick) on Kapton. The films were cleaned in the order of acetone, isopropanol, and DI water for 10 min at each step. After cleaning, the film was attached to a 3D-printed cell using Araldite[®] glue and left to harden for a minimum of two hours. The electrolyte solution contained $Zn(NO_3)_2$ (Riedel DeHaën, 98%) and KCl (BDH, 99%). To investigate the effect of $[Zn^{2+}]$, two different concentrations of $Zn(NO_3)_2$ at 5 mM and 50 mM were used while the concentration of KCl was fixed at 0.1 M. The solution was bubbled with oxygen for 30 min and the temperature adjusted to about 65 °C with a heating element. The temperature of the solution potential of -0.97 V using a Gamry Reference 600 potentiostat for 30 min. After electrodeposition, the cell was gently rinsed with DI water with the deposited film still attached. Next, the Kapton film was carefully detached from the cell and remounted for *ex situ* XANES characterization as well as SEM analysis.

2.3. Characterization

TXM was performed using a Carl Zeiss (formerly Xradia) full-field X-ray microscope at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline 6-2. Micrographs were taken at 9700 eV directly above the Zn K-edge, which has an onset at 9661 eV (see Figure 2l) and provided good absorption contrast of both Zn nanoparticles and Au fiducial markers. For the *in situ* microscopy of ZnO nanoparticle growth, samples were imaged at 2.2 s intervals during ~30 min of ZnO nanoparticle (NP) growth. The field of view was ~40 × 40 μ m² with a 19 nm pixel size, and the spatial resolution provided by the instrument was ~ 30 nm. Reference images acquired through an additional hole in the *in situ* cell were taken before each growth experiment and were used to remove imaging artefacts due to imperfections in the X-ray beam and detector system. Additional details about the microscope are found in papers by Andrews *et al.* ¹⁸, Liu *et al.* ¹⁹, and Meirer *et al.* ²⁰.

After ~30 minutes of NP growth, the *in situ* cells were immediately emptied and gently rinsed with DI water. The Kapton film was carefully detached from the cell and remounted for XANES characterisation. 2D XANES images were collected at the Zn K-edge. However, as 2D XANES datasets did not reveal any chemical variation across the field of view, only the spatially averaged XANES spectra are reported in this paper. Energy intervals of down to 0.25 eV were used in the near edge region, and energy steps of 1-10 eV were used away from the edge to optimize collection time. The scans covered an energy range from about 50 eV below to about 140 eV above the Zn K-edge. The transmission images were normalized by the reference images collected at corresponding energies to account for small changes in illumination between energies.

For TXM imaging during *in situ* growth, data analysis included reference correction, averaging and alignment of sequential images using TXM Wizard.^{21, 22} Additional alignments and Fourier filtering for removal of bright single-pixel artefacts were performed using ImageJ. For XANES analysis, reference correction, magnification correction, image alignment and background subtraction were performed using TXM Wizard, and per pixel spectra were obtained from image stacks using TXM-XANES Wizard. Single pixel spectra with an edge jump ratio of >5 were summed to form the displayed bulk XANES spectra.

After XANES analysis, substrates were remounted for SEM analysis. Secondary electron SEM micrographs were acquired on a Carl Zeiss Auriga FIB-SEM operated at 5 kV.



Figure S1. False colour absorption images that have not been processed by Fourier-filtering, showing the evolution of nanoparticle morphology (thickest regions in green/yellow) *in situ*. Experimental

parameters are: 5 mM $Zn(NO_3)_2$ for nanorods and 50 mM $Zn(NO_3)_2$ for nanoplates, deposition potential -0.97 V.



Figure S2. (a-c) Fourier filtered absorption images of nanorod samples 300 s, 500 s, and 700 s into electrodeposition, and (d) normalised intensity profiles across one feature (arrow) showing increasing diameter with time. Experimental parameters: 5 mM Zn(NO₃)₂ and deposition potential of -0.97 V.

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