Direct visualization of Li dendrites effect on LiCoO₂ cathodes by
\textit{in situ} TEM

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Abstract

Li dendrites are known to cause deleterious and, in many cases, catastrophic effects on the performance of Li rechargeable batteries. However, the mechanisms of cathodes failure upon contact with Li metal is far from clear. In this study, using \textit{in situ} transmission electron microscopy, we directly visualize at an atomic scale the interaction of Li metal with well-defined, epitaxial thin films of LiCoO₂, the most widely used cathode material. We show that a spontaneous and prompt chemical reaction is trigged once Li contact is made, leading to expansion and pulverization of LiCoO₂ and ending with the final reaction products of Li₂O and Co metal. A topotactic phase transition is identified close to the reaction front, resulting in the formation of CoO as a metastable intermediate. Dynamic structural and chemical imaging, in combination with \textit{ab initio} simulations, reveal that a high density of grain and antiphase boundaries are formed at the reaction front, which are critical for enabling the short-range topotactic reactions and long-range Li propagation. The fundamental insights are of general importance in mitigating Li dendrites related issues and guiding the design principle for more robust energy materials.

Keywords: \textit{In situ} transmission electron microscopy (TEM), LiCoO₂, STEM, Lithium dendrite, Phase transition, Epitaxy

Introduction

Lithium (Li)-ion batteries (LIBs) have been considered to be one of the most promising energy storage solutions since the first commercialization by Sony in 1991¹³. To meet increasing demands in traditional and emerging markets, such as portable electronics, electric vehicles, and large scale energy storage devices, an urgent need is to develop rechargeable batteries with increased energy output⁴⁻⁷. Li metal has been regarded as an ideal anode material because of its ultrahigh theoretical specific capacity (3,860 mAhg⁻¹) and low electrochemical redox potential (-3.040 V vs. standard hydrogen electrode)⁸⁻¹¹. However, the practical utilization of Li metal anodes is greatly hampered by the formation of Li dendrites during repeated charge/discharge
cycles and the low Coulombic efficiency. The most serious concern is the direct contact of Li metal with the cathode material after Li penetrates the battery separator layer, which causes short circuiting and can lead to serious safety hazards\cite{12-14}. Therefore, significant efforts have been devoted to detect, understand, and prevent the Li dendrite formation processes within liquid electrolytes\cite{15-24}.

The use of solid state electrolytes (SSEs) in Li metal batteries (LMBs) is considered attractive as most SSEs are not volatile or flammable\cite{25}. SSEs are also thought to be less susceptible to the growth of Li dendrites. However, recent studies have shown that Li dendrites can form in the voids and grain boundaries of Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) based SSEs \cite{26-30}. Once the dendrites penetrate through the SSEs, the interactions between Li metal and cathode materials set off a chain of highly energetic reactions. Mechanistic pathways of such far-from-equilibrium processes are not understood and approaches to their control and/or mitigation are missing.

Over-lithiation can also occur when the LIBs are over-discharged or during synthesizing Li-rich cathodes. For example, even though some Li-rich cathode materials (e.g., Li[LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ (Li-rich NMC)) have shown greatly increased reversible capacity\cite{31}, Li$_x$CoO$_2$ (LCO), the most widely used cathode material, does not have a stable Li-rich (x>1) form\cite{32}. Over-lithiation in LCO causes degradation in structural integrity and device performance. It has been reported that LCO will eventually be converted to Co metal during the over-discharge process, and various reaction intermediates, including Li$_{1+x}$CoO$_{2-y}$, Co$_3$O$_4$, and CoO have also been proposed through \textit{ex situ} studies\cite{33}. Recent in operando X-ray absorption spectroscopy (XAS) and spectroscopic transmission X-ray microscopy (TXM) studies reveal a core-shell conversion pathway from LCO to Li$_2$O and Co metal during over-lithiation of the cathode\cite{34}. However, the atomic-scale structural and chemical evolution during the over-lithiation reaction is still unclear.

In this work, using \textit{in situ} transmission electron microscopy (TEM) \cite{35-40}, we investigate the atomic-scale reaction processes upon Li dendrites placed in direct contact with well-defined epitaxial LCO thin film cathodes. Epitaxial LCO films with controlled orientations allow the direct comparison of crystallographically-dependent reactivity. In addition, the steady support from an inert SrTiO$_3$ substrate is ideal for \textit{in situ} TEM studies as reliable mechanical contact can be readily achieved. Through the combination of high-resolution TEM, nano-beam diffraction (NBD), electron-energy loss spectroscopy (EELS) and density functional theory (DFT) calculations, we elucidate the reaction intermediates and detailed reaction steps. We find that Co metal and Li$_2$O are the final products of the full conversion reaction while CoO is an intermediate phase at the reaction front. Moreover, we reveal that an unexpected Li propagate direction along [001], which generates large amount of grain boundaries (GBs) and antiphase boundaries (APBs). A topotactic phase transformation from LCO to nanocrystalline CoO is observed in the nanocrystals generated. Our detailed investigation of the reaction steps, intermediates, and microstructural evolution can be critical for a better understanding of the failure mechanisms, and may provide detection and design principles to overcome the aforementioned challenges.
Results

**Experimental set-up for in situ TEM.** LCO is an intercalation type compound with a layered rhombohedral structure (space group R-3m) as shown in Fig. 1a. Reversible and facile extraction/intercalation of Li along the layers occur during the charge/discharge (Li_xCoO_2, 0.5<x<1) cycles. In this study, LCO thin films with thicknesses in the range of ~100-200 nm were grown on top of a 10-20 nm thick SrRuO_3 (SRO) buffer layer on either (001) or (111) oriented SrTiO_3 (STO) substrates by pulsed laser deposition (PLD). Fig. 1b shows the high-angle annular-dark-field (HAADF)-scanning transmission electron microscopy (STEM) image for the sandwich structure grown on a STO(111) substrate. High resolution STEM images (Figs. 1c and 1d) reveal that the Li containing planes LCO(001) are parallel to the STO(111), and the most commonly observed defects are APBs resulting from interfacial strain or surface steps, as indicated by the red arrow in Fig. 1d. Considering that LCO exhibits a very low Li ion diffusion rate along [001] axis, the disarrangement of atoms along the APBs may offer a faster, alternative path along c axis. In contrast, Li containing layers in LCO are intersecting to the SRO buffer layer when grown on SRO/STO(001) (Fig. 2a), where the APBs are largely eliminated and the dominant defects are twin boundaries due to the four-fold symmetry of the substrate. For LCO thin film grown on SRO/STO(001), LCO (104) planes are parallel to the surface.

![Figure 1. Crystal model and HAADF-STEM images of LCO grown on SRO/STO(111). (a) Crystal structure of LCO viewed along [010] zone axis. (b) A HAADF-STEM image of an epitaxial LCO/SrRuO_3/SrTiO_3(111) heterostructure viewed along STO[110]. (c-d) Enlarged images corresponding to the two boxed areas in b showing an antiphase boundary. The yellow arrow marked in c shows that the Co layers can merge together along the APB. (e) Schematic diagram of the experimental setup for in situ TEM.](image)

An in situ TEM setup, as illustrated in Fig. 1e, was used to investigate the microstructural evolutions in an LCO cathode upon Li contact. A cross-sectional TEM sample, prepared by focused ion beam (FIB) milling, is held fixed while fresh Li metal on a tungsten tip is used to mimic a Li dendrite. The mechanical contact of Li is driven by a commercial Nanofactory holder. It has been shown that combining advanced microscopy and spectroscopy techniques, such as STEM, NBD, and EELS, is powerful in elucidating atomic-scale Li-induced redox chemistry occurring in transition metal oxides, such as WO_3 and Fe_3O_4.
As shown in Movie S1 in the Supporting Information (SI), the LCO structure is stable under high energy electron beam prior to contact with the Li metal. Note however, that a conversion reaction occurs immediately upon contact between the LCO and tip without applying a voltage. This reaction is due to chemical potential of LCO is far beyond the stability range of Li. In order to ascertain whether the chemical reaction is driven by the electron beam, we performed controlled studies. As shown in Fig. S1, the reaction front traveled a comparable distance upon Li tip contact whether the electron beam was on or off. Furthermore, we show in Movie S2 (in Supporting information, where the frame rate is accelerated 20 times) that the reaction front did not progress further when the beam was turned back on after the Li tip was removed. These results, taken together, reveal that the electron beam from the TEM does not play a significant effect in the observed chemical reaction.

Figure 2. The reaction between Li tip and LCO/SRO/STO(001). (a) HAADF-STEM image of a pristine LCO thin film sample on SRO/STO(001) viewed along [110] zone axis. The LCO
(001) planes intersect with SRO and exhibit a twin-boundary-like structure between two LCO grains. (b) Low magnification TEM image of LCO thin film after reaction with Li. (c-f) NBD patterns for different spots labeled in b. (g-i) Li K-edge, O K-edge, and Co L-edge EELS spectra taken at pristine LCO (grey) and fully reacted (red) regions, respectively.

The reaction between Li tip and LCO/SRO/STO(001). The reaction products upon over-lithiation in an LCO/SRO/STO(001) heterostructure are revealed by NBD and EELS in Fig. 2. The HAADF-STEM image of the LCO/SRO interface (Fig. 2a) shows that the LCO(001) plane intersects with SRO(001) by an angle of 55°, consistent with the angle between (001) and (104)45. The dominating defects observed are twin boundaries that appear nearly atomically-sharp. Fig. 2b shows a partially reacted LCO/SRO/STO(001) structure right after Movie S2. A 19% expansion (from 105 to 125 nm) is observed in the thickness of the film. Assuming the same magnitude of expansion along the other two directions, the volume expansion is estimated to be 68.5%. A pristine LCO region (labeled as spot 1 in Fig. 2b) can be characterized mainly by diffraction contrast, while a lithiated region displaying a reduced mass-thickness contrast with notable expansion is labeled as spot 4 to the right. Shown in Fig. 2c-f, a set of nano-beam diffraction patterns are collected at different locations marked in Fig. 2b. The sharp, spotty NBD pattern displayed in Fig. 2c is an overlay result of two LCO grains shown in Fig. 2a, which is consistent with its Fast Fourier Transform (FFT) pattern shown in Fig. S2. At the fully lithiated region (spot 4, Fig. 2f), the NBD pattern confirms that the reaction products are Co metal and $\text{Li}_2\text{O}$33,34. Owing to the high spatial resolution of NBD, it is possible to search for intermediate reaction products close to the reaction front. Near the reaction front (spot 3, Fig. 2e), the NBD pattern reveals that in addition to Co metal, diffraction spots corresponding to CoO are observed, according to the simulated diffraction patterns shown in Fig. S2. Moreover, at the reaction front (spot 2, Fig. 2d), the intensities of the diffraction spots associated with CoO are found to increase while those associated with Co metal disappear, indicating an irreversible two-step conversion reaction:

$$\text{Li + LiCoO}_2 \rightarrow \text{CoO + Li}_2\text{O} \quad (1)$$

$$\text{CoO + 2Li \rightarrow Co + Li}_2\text{O} \quad (2)$$

This is consistent with enthalpy change of $\Delta H = -0.41$ and $-0.46$ eV, as predicted by our DFT calculations for the reactions (1) and (2), respectively. The EELS spectra taken through the Li K-edge, O K-edge as well as the Co L-edge (Fig. 2g-i, respectively) show appreciable changes between the pristine region (spot 1) and the fully-lithiated region (spot 4). Compared to the LCO reference, the plasmon loss peaks at ~18 eV observed in the fully-lithiated region (Fig. 2g) are consistent with $\text{Li}_2\text{O}$49. A characteristic O K-edge EELS feature of $\text{LiCoO}_2$ is the presence of an O peak (feature A in Fig. 2h) ~12 eV from the main O peak (feature C)50. After reaction, this peak is located ~6 eV from the main O peak (feature B), corresponding to $\text{Li}_2\text{O}$51 and consistent with our previous NBD analysis. After full-lithiation, the Co L-edge spectra (Fig. 2i), aligned by the pre-peaks of O-K, show a ~4.2 eV energy shift to the lower energy direction relative to the pristine state, supporting that Co cations are reduced to Co metal during the reactions. These results are consistent with what were observed in electrochemically over-discharged $\text{LiCoO}_2$34.
Figure 3. The reaction front of LCO/SRO/STO(001). (a) HRTEM image of the lithiation front of an LCO thin film on SRO/STO(001). FFT patterns corresponding to dash red box areas are shown in the inset of a. The interface between pristine and reacted area is indicated by the white dash line. (b) Fourier-filtered image corresponding to yellow box area in a. (c-e) Magnified images corresponding to the box areas marked in b. The crystal structure of LiCoO$_2$ and CoO are overlaid on c and e, respectively.

Atomic structure at the reaction front in LCO/SRO/STO(001). Fig. 3a shows a typical HRTEM micrograph illustrating the structure of the LCO thin film on SRO/STO(001) at the reaction front captured after Movie S2. For the area 1 (reaction front), the FFT pattern shown at the bottom right corner is dominated by a periodicity consistent with CoO. While for the area 2 (slightly away from the reaction front), the FFT pattern shows a mixture of CoO, Li$_2$O and Co metal, consistent with the former NBD results (Fig. 2e). Fig. 3b is a Fourier filtered image corresponding to the yellow box area shown in Fig. 3a. Magnified views shown in Figs. 3c-e reveal a clear transition from layered LCO structure to an FCC CoO structure along [110] zone axis, as illustrated in the corresponding ball models. Because the surface atomic densities of Co in CoO(111) (0.127/Å$^2$) and LCO (001) (0.126/Å$^2$) planes are nearly identical, and the distance between adjacent Co-containing (001) planes along LiCoO$_2$ (4.6827 Å) is close to twice that of CoO(111) (2.4612 Å), a low barrier topotactic phase transformation may allow such structural transition, which will be discussed later.

The dynamic reaction between Li tip and LCO/SRO/STO(111). To check whether there is a crystallographic dependence, we have also tested the same reaction on films grown on SRO/STO(111). As mentioned earlier, negligible Li diffusion is expected along [001] during electrochemical cycling owing to the facile nature of diffusion within the Li planes. However, for the Li metal induced conversion reactions, no significant difference in reaction rate between the two film orientations was detected. As shown in Fig. S3, a comparable linear expansion of ~18% (from 170 to 200 nm) occurred in the film thickness is observed after the full lithiation reaction. The overall intensity of the reacted area becomes brighter, similar to Fig. 2b, resulting from the
weakening diffraction contrast and decrease of atomic density due to volume expansion. The pristine LCO retains its layered structure (Fig. S3c), while after reaction with Li, the LCO thin film transformed into a polycrystalline structure (Fig. S3d). The final reaction products, Co metal and Li$_2$O, and reaction processes for the LCO films on STO(111) are the same with what we observed in LCO/SRO/STO(001). Analyzing a time-elapsed TEM video (Movie S3 with 10x frame rate in Supporting Information) of Li metal reaction with LCO/SRO/STO(111) provides further insights into the overall reaction pathways and the dynamic topotactic transformation from LiCoO$_2$ to CoO.

Figure 4. The dynamic reaction between Li and LCO/SRO/STO(111). (a-f) Time series images captured in the recorded video. (g-i) Enlarged images corresponding to the red box area in e, d and c, respectively. Yellow and red triangles mark the reaction front and an antiphase boundary (APB).

A set of TEM images (Fig. 4) extracted from Movie S3 in time sequence show the Li reaction propagation within the LCO/SRO/STO(111) sample. The progress of the reaction front is marked by yellow triangles. A clear fast diffusion channel is observed along the APB from the captured Movie S3: Li related reaction was first observed at the APB of the LCO thin film at 84 s (Fig. 4g), and the reaction along APB is visibly faster than that in other directions (100 s, Fig. 4h). We associate this effect with the defects and displacement of atoms along the APB, which provide a lower activation energy path for Li to react and diffuse$^{52}$. While the reaction slow down when the reaction forefront meet the merged Co layers (Fig. 4i) similar to the structure shown in Fig. 1c.

Figure 5a is a TEM micrograph captured at the reaction front following Movie S3. This snapshot of the reaction front reveals several key features. From the inverse FFT (IFFT) shown in Fig. 5b, several antiphase boundaries (marked with yellow arrows) and grain boundaries (marked by white arrows) with grain size of ~3 nm are created at the reaction front, most likely to accommodate the large volume expansion upon reaction. In turn, knowing that the APBs allow the fast transport of Li across Li containing planes, the creation of high density APBs will catalyze the conversion reaction over a long-range. In Fig. 5a, an area corresponding to LiCoO$_2$ is highlighted, and its IFFT and schematic ball model are shown in Fig. 5e. In contrast, a
crystallite along the APBs appear to have partial visible contrast in the Li-containing layers. Because of the low atomic mass of Li and O, the contrast is most likely due to the insertion of Co into the Li planes, and we refer to this regions as “Co/Li exchange” with its IFFT shown in Fig. 5f. The excess Co atoms along the APBs may exchange positions with the Li ions in the LCO lattice, facilitating the formation of Li$_2$O.

To further understand the reaction between Li metal and LCO, we perform DFT calculations on LCO models with extra Li atoms embedded. The embedded Li metal atoms are converted into Li$^+$ which are coordinated by oxygen tetrahedra. Energy gain calculated with respect to that of an isolated Li atom is found to increase rapidly with increasing number of extra Li atoms. For the case of 5 extra Li atoms, an energy gain of 7.59 eV is obtained. The cluster causes breaking of Co-O and Li-O bonds in the surrounding and induces a crack along [001] in the LCO lattice instead of transport within the Li containing planes (Fig. 5c). Such defects can serve as precursors of grain boundaries, which may evolve into APBs due to a small motion driven by the volume expansion. Furthermore, Bader charge analysis indicates that electrons are transferred from the embedded Li cluster to surrounding Co ions and lower their ionic charges. This makes the Co-O bond become weaker. Hence, one may expect that defects associated with extraction of Co from its site would have lower formation energies in the presence of extra Li ions. Indeed, we found that formation energy of a pair of anti-site defects of Li$_{Co}$ near the cluster and Co$_{Li}$ at a distance (i.e., swapping sites of the Co and Li ions) is strongly decreased with increasing number of extra Li atoms in the cluster. In particular, for the cluster of 5 Li atoms, formation energy is only 0.20 eV, compared with 3.28 eV for swapping of Li and Co atoms in a pristine crystal (Fig. 5c). Therefore, the presence of a Li cluster promotes the exchange of Co with Li, acting as the initial path for a topotactic phase transformation from LCO to CoO.

From previous discussions about Figs. 3b and 3c, a schematic ball model (Fig. 5f) for the partially converted area preceding the formation of CoO is proposed. It still appears as a layered structure rather than FCC structure of CoO (Fig. 3e) as the intercalated Co planes may not be fully occupied or developed, and the overall reaction can be described as:

$$xLi + yLiCoO_2 \rightarrow xLi_2O + Li_{y-x}Co_yO_{2y-x}$$  \hspace{1cm} (3)

where $y \geq x$. The CoO intermediate is formed when $y = x$ (equation (1)). For comparison, the IFFT image (Fig. 5g) for a monocrystalline labeled as CoO shows a lattice plane distance half of the LCO (003). According to this model, the intercalation of Co atoms into the LCO lattice further creates voids along the APBs, through which the long range Li diffusion can proceed.
Figure 5. The reaction forefront of LCO/SRO/STO(111). (a) Colored TEM image of the dynamic reaction interface in LCO thin film. (b) IFFT image of the dotted area in a) obtained by using (003) and (006) diffraction spots shows the APBs at the reaction front. The blue (white) arrows in a and b show the high density APBs (GBs) formed during the reaction. (c) DFT results showing energy required for swapping Co and Li sites as a function of number of extra Li atoms and (d) a model of an APB like defect formed in an LCO, as obtained using DFT simulations, by inserting 5 extra Li metal atoms into the LCO (10×1×1) cell. IFFT images and ball models of (e) pristine LiCoO$_2$, (f) Co/Li exchange, and (g) CoO-like areas, which are also indicated in a).

Discussion

It had been anticipated that the LCO/SRO/STO(111) structures would show a higher resistivity towards Li metal as the Li conducting planes are encapsulated parallel to the substrates. However, because of the creation of antiphase and grain boundaries upon lithiation, the reaction proceeds independent of crystallographic orientation.

As discussed earlier, the CoO would be eventually reduced to Co metal when fully lithiated. However, the crystallographic transformation from CoO to Co is not as well-defined as the evolution from LCO to CoO, which is also reflected by the diffused diffraction pattern of Co shown in Figs. 2e-f and Fig. 3a. It is most likely due to the lack of consistent structure in the mixed amorphous/polycrystalline environment upon initial lithiation. The transform from LCO to heavier Co metal and much lighter Li$_2$O in fully reacted region should result in periodic
In conclusion, the atomic level structural and chemical evolutions of LCO upon Li dendrite contact were directly imaged using in situ TEM. It shows that the reaction will result in an irreversible conversion of the LCO cathodes to form Co metal and Li$_2$O, with CoO as a metastable reaction intermediate. This irreversible chemical reaction proceeds regardless of LCO crystallographic orientation suggesting that epitaxy cannot offer enhanced stability against Li dendrites. The conversion reaction leads to a ~18-19% expansion along the film growth direction, which facilitates the microstructural destruction of LCO at the reaction front. Both our experimental results and theoretical simulations show that Li metal clusters tend to create cracks along [001] direction of LCO lattice, instead of along the Li-containing planes, leading to a large number of antiphase and grain boundaries at the reaction front. A topotactic phase transformation from LCO to CoO is observed in the nanocrystalline structures separated by APBs and/or GBs at the reaction front, involving the swapping of Li and Co. These APBs and GBs generated during lithiation, together with those APBs intrinsic to LCO thin films grown on SRO/STO(111), offer viable pathways for the long range transport of Li perpendicular to the Li layers. These pathways essentially expedite the failure process, but might be exploit to assist Li ion transport in designed devices. The reaction steps and intermediates revealed at the reaction front provide a clear failure mechanism for the LCO cathodes caused by Li dendrites, and may also offer insights into the over-discharge processes in cathodes.

**Experimental section**

**Thin film growth.** LCO thin films with thickness in the range of 100-300 nm were deposited on STO(111) or STO(001) substrates with a ~10-20 nm SRO buffer layer using pulsed laser deposition (PLD). The system setup has been described elsewhere$^{54}$. The SRO and LCO were deposited at 650 °C and 600 °C, respectively, under oxygen pressure of 10 mTorr. Laser ablation was performed at a repetition rate of 5 Hz and an energy density of of ~2 J/cm$^2$ with a 248 nm KrF excimer. After growth, the samples were cooled down to room temperature under the same oxygen ambient.

**In situ S/TEM sample preparation.** The S/TEM samples used for in situ TEM were prepared using a focus ion beam (Helios). Pt and C were coated on the sample surfaces to protect them from Ga ion damage. Then the grid samples were glued to a Cu wire to perform the in situ TEM experiment using the commercial scanning tunneling microscope-transmission electron microscope (Titan, STM-TEM, Nanofactory Instruments) holder$^{48}$. The Li tip is scraped from a fresh Li foil using a W tip in the glove box to minimize the oxidation of Li. High-angle annular-dark- field scanning transmission electron microscopy (HAADF-STEM), TEM and electron...
energy loss spectroscopy (EELS) were performed using a probe-corrected FEI Titan 80-300 microscope operating at 300 kV.

**Density functional theory calculations.** The calculations were performed using the Vienna Ab Initio Simulation Package (VASP)\(^5\)\(^5\)\(^6\). The projected augmented wave method was used to approximate the electron-ion potential\(^5\)\(^7\). Exchange-correlation effects were treated within the Perdew-Burke-Ernzerhof functional form of the generalized gradient approximation, modified for solids (PBEsol)\(^5\)\(^8\). Periodic supercell models have initial lattice parameters of \(10a, b,\) and \(c\), where \(a=b=2.815\) Å and \(c=14.05\) Å are lattice constants of the LCO unit cell. A plane-wave basis with a 500 eV cutoff and \(1\times9\times3\) Monkhorst-Pack \(k\)-point meshes were used. Supercell parameters, atomic positions, spin, and electronic degrees of freedom are relaxed until the forces acting on the ions become less than \(10^{-2}\) eV/Å.

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**Contributions**

Z.Y. and Y.D. designed and initiated the research; Z.Y. and Y.D. wrote the manuscript with input from all authors; TEM experiments were performed and analyzed by Z.Y. with the help from Y.H. and C.W.; Growth of LiCoO\(_2\) thin film samples were performed by Z.Y. and L.W. under the guidance of T.C.D and Y.D.; Ex-situ characterization of thin film samples were performed by M.E.B. and W.X.; The first principle simulations were performed by P.V.O. under the guidance of P.V.S.; All authors participated in the discussion and interpretation of results.

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