Kinetically controlled vapor-diffusion synthesis of novel nanostructured metal hydroxide and phosphate films using no organic reagents

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Nanostructured Co$_3$(OH)$_8$Cl$_2$·3H$_2$O, Co$_3$(OH)$_6$(NO$_3$)$_2$·2H$_2$O, Co$_2$(OH)$_3$SO$_4$·2H$_2$O, Zn$_2$(OH)$_6$(NO$_3$)$_2$·2H$_2$O, Cu$_2$(OH)$_3$(NO$_3$) and Mn$_2$(PO$_4$)$_2$·7H$_2$O thin films have been prepared using a kinetically controlled vapor-diffusion method. Vectorial control by diffusion of ammonia as a base catalyst into an aqueous metal salt solution yields large area (2 cm$^2$) metal hydroxide and metal phosphate films with unique structures. No supporting substrate for growth of the films is necessary in this approach. The films were characterized using X-ray powder diffraction and scanning electron microscopy. The cobalt containing films were studied in more detail using transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray absorption near edge structure and various chemical analysis techniques. For the first time the electronic properties and crystal structure of these materials could be studied in thin films not influenced by the presence of an underlying substrate. For Co$_3$(OH)$_6$(NO$_3$)$_2$·2H$_2$O films, which crystallize in a layered hydrotalcite-like structure that is homogeneous from the nanoscale to the macroscale, unprecedented photoconductivity properties were observed. Resistivity measurements show that this material is a p-type semiconductor with an unusually long minority carrier lifetime and high carrier density.

Introduction

Synthesis of nanostructured thin films has attracted increasing attention in recent years due to their potentially superior electronic and optical properties compared to those of the corresponding bulk materials. The application of semiconducting thin films in electro-optical devices, solar cell technology or gas sensors requires high purity, defect-free material. Most thin films are prepared by epitaxially growing the material on a substrate. Crystal lattice mismatch between the substrate and the epitaxially grown material generates defects that degrade the electronic properties of the film. Incorporation of carbon impurities, originating from the use of organometallic precursor molecules or organic solvents, can also degrade the performance.

Alternative routes to high purity semiconductor materials to replace techniques such as cost-intensive metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and liquid phase epitaxy (LPE) are being explored in response to demands for more flexible and lower energy synthesis strategies.

Techniques that mimic biomineralization have received much attention because of the inherently benign conditions of biological syntheses. In addition, these biomineralization processes often produce highly ordered structures on the nanoscopic as well as the macroscopic scale. Examples of inorganic nanostructures prepared include the formation of nanocrystalline TiO$_2$ and Ga$_2$O$_3$. In these studies, silicatein (a catalytically active, structure-directing enzyme) was used as a catalyst and template for the hydrolysis and subsequent polycondensation of water stable molecular complexes of titanium and gallium to form nanocrystalline TiO$_2$ and Ga$_2$O$_3$, respectively. However, the resulting nanoparticles remain in intimate contact with the macroscopic (2 μm × 1 mm) protein filaments that catalyzed and templated their synthesis; they are therefore largely unsuitable for device applications that require high purity material.

We report here a kinetically controlled vapor-diffusion synthesis of inorganic thin films. This method uses the following principles borrowed from biomimetic synthesis routes:

a) slow catalysis of synthesis from molecular precursors provides the opportunity for kinetic control; and  
b) crystal growth is vectorially regulated by a template, operating in concert with kinetic control to provide spatial and temporal control of crystal polymorph, orientation and morphology.

To capture the advantage of the slow catalysis and anisotropic, vectorial control of biocatalytic crystal growth, we developed a low-temperature, solution-based method employing the slow diffusion of ammonia vapor as a catalyst for hydrolysis of metal-containing molecular precursors. This diffusion through a solution of molecular precursor establishes a spatially and temporally regulated gradient of the catalyst, while the vapor–liquid interface serves as a nucleation template. The resulting vectorially controlled combination of the molecular precursor and hydrolysis catalyst at room temperature yields a nanostructured thin film at the vapor–liquid interface, formed as the gaseous catalyst dissolves in an
aqueous metal salt solution to initiate hydrolysis. The diffusion of the basic catalyst (ammonia) into the aqueous solution creates a pH gradient that determines the morphology of the growing film, resulting in a unique structure of the film. This morphology was previously reported for similar cobalt hydroxide materials by Hosono et al. However, the methodology described here proves widely applicable for the growth of relatively large area (2 cm$^2$) thin films suitable for structural and electronic characterization of a number of different materials, and offers the potential of growing even larger films for device applications.

We here demonstrate the feasibility of characterizing the electronic properties of these self-supporting films and illustrate the high quality of the prepared material by describing the properties of the three different cobalt hydroxide nanostructured films, materials that have received increasing scientific interest in recent years. Co(OH)$_2$ is used as an additive in numerous industrial processes and has potential for applications as an oil additive and in alkaline batteries. 9–16 Co(OH)$_2$ exists in two phases: $\alpha$-Co(OH)$_2$ and the much more common $\beta$-Co(OH)$_2$. The cobalt hydroxide thin films prepared in this study are $\alpha$-Co(OH)$_2$ materials. We also describe use of the vapor diffusion method for the preparation of zinc hydroxide, copper hydroxide and manganese phosphate thin films.

**Experimental**

All starting materials used in this study were commercially available and used without further purification. Two beakers, one containing a dilute solution of NH$_4$OH (0.7%–1.2%, depending on the experimental conditions) and one containing a separate solution of either aqueous 0.1 M CoCl$_2$, 0.1 M Co(NO$_3$)$_2$, 0.1 M CoSO$_4$, 0.1 M Zn(NO$_3$)$_2$ or 0.1 M Cu(NO$_3$)$_2$ were placed in the same enclosed chamber. The synthesis of metal hydroxide thin films occurred at room temperature and ambient pressure over the course of 18 h.

For the preparation of Mn$_3$(PO$_4$)$_2$$\cdot$7H$_2$O, 0.058 g of (NH$_4$)$_2$HPO$_4$ (0.5 equiv.) was added to 4 ml of 0.1 M MnCl$_2$ solution. The beaker containing this mixture was then exposed to ammonia vapor from a dilute solution of NH$_4$OH (0.7%) in a separate beaker, enclosed within the reaction chamber. The metal phosphate thin film formed at room temperature and ambient pressure over the course of 18 h. After formation, the metal hydroxide or phosphate films were transferred onto a doubly distilled water surface and allowed to dry approximately 0.05 g of flakes of the metal hydroxide film were placed in an alumina crucible and this was loaded into a 2 cm$^2$ diameter tube furnace. The material was then heated under air at 400°C and 300°C, respectively, for 4 h.

Continuous sheets of product were transferred to a platinum interdigitated array of electrodes (IDE) with a width and spacing of 5 μm. The material on the electrode was dried at room temperature under vacuum (762 mmHg) for 12 hours. The IDE was connected to a Keithley 4200 SCS testing system for IV and photoconductance analyses. For IV analysis the voltage was ramped from $-$0.75 to 0.75 V while monitoring the current passing through the device. Photoconductivity was observed by applying 2.5 V of bias while continuously monitoring the current through the device in the dark. The device was then exposed to visible light pulses of 2 s duration using a fiber optic light source (Ehrenreich Ind. Garden City, NY) to minimize the amount of sample heating. The light source provided an average intensity of $80 \times 10^3$ lux with a spectral range of 400–1400 nm.

**Results and discussion**

We have used the described kinetically controlled vapor-diffusion synthesis route to prepare metal hydroxide films from aqueous CoCl$_2$, Co(NO$_3$)$_2$, and CoSO$_4$, Zn(NO$_3$)$_2$ and Cu(NO$_3$)$_2$ solutions, as well as metal phosphate thin films (e.g. Mn$_3$(PO$_4$)$_2$$\cdot$7H$_2$O) from the appropriate precursors. The area of continuous films grown by this method depends on the diameter of the reaction vessel used. In this study the largest area of continuous film grown was ~50 cm$^2$. The largest inorganic films, however, broke when transferred onto glass slides using the Langmuir–Blodgett technique and cracked further during the subsequent drying process. The overall mechanical stability of the films varies with the composition of the films, e.g. Zn$_3$(OH)$_6$(NO$_3$)$_2$$\cdot$2H$_2$O and Mn$_3$(PO$_4$)$_2$$\cdot$7H$_2$O are more robust and less prone to cracking during the drying process than the cobalt- and copper-containing films. The largest continuous film we used for electronic characterization thus far was ~2 cm$^2$ (Co$_5$(NO$_3$)$_2$(OH)$_8$$\cdot$2H$_2$O).
Surface tension at the air–water interface and the induced pH-gradient provide a template that directs the growing materials to adopt a continuous sheet morphology. Scanning electron microscopy (SEM) images of the resulting hydroxide and phosphate films are shown in Fig. 1.

All of these materials show similar morphologies: a continuous backplane parallel to the air–water interface with plates that grow orthogonally from the backplane into the aqueous solution. Kinetic studies revealed that the crystalline plates, orthogonally oriented into the aqueous solution with respect to the common backplane, form after initial island nucleation and during consolidation of the crystalline film at the gas–liquid interface. The density, size and shape of these orthogonal plates, as well as the size of the crystalline domains, depend on the choice of the metal salt precursor and the reaction time.

This unique morphology of macroscopic and microscopic organization of the material was previously reported only by Hosono et al. in their study of Co(OH)₂ films. But their method, involving growth on glass substrates with urea and methanol as reagents, yielded material with a composition of Co(OH)₀.₉₉(NO₃)₀.₀₃(CO₃)₀.₅₂°.₇H₂O, revealing the stoichiometric incorporation of carbon, which is in marked contrast to the results reported here. No organic reagents or solvents were used to prepare the inorganic thin films displayed in Fig. 1.

The cobalt hydroxide and zinc hydroxide films, shown in Fig. 1a and c, respectively, were dehydrated and converted to the corresponding metal oxide films by heating in air. Complete conversion to the metal oxide was confirmed by XRD. No change in morphology could be detected by SEM (pictures not shown).

In the following section we will describe in detail the characterization of three cobalt hydroxide films prepared from different metal salt precursors. These self-supporting films—prepared by the kinetically controlled vapor-diffusion process—also proved suitable for the characterization of electronic properties, as described below.

The cobalt hydroxide films were prepared from three different precursor solutions: CoCl₂, Co(NO₃)₂ and CoSO₄; the respective products are designated (I), (II) and (III). Films prepared from these three precursor solutions show similar morphologies. In all cases the plates on the roughened side of the thin film (plates growing into the aqueous solution, Fig. 1a) are approximately 50 nm thick, 3–5 μm tall, depending on the reaction time, and randomly oriented perpendicular to a 1 μm thick backplane.

Powder XRD patterns of the ground films (Fig. 2) indicate a monoclinic crystal structure (*C*₂/m) of *α*-Co(OH)₂ for all three products (I, II, III). The literature suggests that *α*-Co(OH)₂ is a molecular composite of cobalt-containing crystalline layers, rather than a single defined compound. These layers

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**Fig. 1** Morphological and crystallographic characterization of metal hydroxide and phosphate thin films. Scanning electron microscopy (SEM; side- and bottom-view) images and XRD patterns of (a) Co₅(OH)₈(NO₃)₂·2H₂O (hydrotalcite-like structure), (b) Cu₂(OH)₃(NO₃) (rouaite structure), (c) Zn₅(OH)₈(NO₃)₂·2H₂O (hydrotalcite-like structure) and (d) Mn₅(PO₄)₂·7H₂O (switzerite structure). Peaks at 39.7° and 46.2° in the XRD spectra of (a) and (d) result from the Pt holder of the instrument.
have a net positive charge and are held together by incorporated counter ions. The net positive charge of the individual layers has been attributed to a hydroxyl deficiency within the cobalt-containing sheets of Co(OH)$_2$ which in some cases is explained by the presence of mixed valent octahedrally coordinated cobalt ions (2+ and 3+) in those layers.\textsuperscript{9,14} The mineral hydroaluminate (Mg$_6$Al$_2$(CO$_3$)(OH)$_{16}$·2H$_2$O) crystallizes in a hydrotalcite-like structure in which the positively charged sheets held together by counter anions (CO$_3^{3-}$). Therefore the α-Co(OH)$_2$ structure is often referred to as a hydroaluminate-like structure.

Kurmoo, however, showed in a study involving X-ray absorption near edge structure (XANES) that for Co$_2$(OH)$_3$(NO$_3$), Co$_2$(OH)$_3$(C$_2$H$_4$CO$_2$)$_2$·4H$_2$O and Co$_2$(OH)$_3$(C$_2$Ni)$_2$·6H$_2$O the positive charge of the Co(OH)$_2$ sheets results from the incorporation of tetrahedrally coordinated Co$^{2+}$ ions into the crystal structure.\textsuperscript{10} In a related system, Zn$_5$(NO$_3$)$_2$(OH)$_8$·2H$_2$O crystallizes in a hydroaluminate-like structure in which the net positive charge of the Zn$^{2+}$ containing sheets results from the incorporation of tetrahedrally coordinated ions into the crystal structure of otherwise octahedrally coordinated ions.\textsuperscript{21}

Our findings by powder XRD are in agreement with Stählin and Oswald’s reports for Zn$_5$(OH)$_2$(NO$_3$)$_2$·2H$_2$O\textsuperscript{21} and also with the works by Kurmoo on layered α-Co(OH)$_2$ compounds.\textsuperscript{10,16}

Well resolved (001) and (002) reflections in the XRD patterns (Fig. 2) demonstrate an increased interlayer spacing along the c-axis of the crystal structure in comparison to β-Co(OH)$_2$ (c = 4.6 Å\textsuperscript{15}). The lattice parameter value in the c-direction for Co$_2$(NO$_3$)$_2$(OH)$_8$·2H$_2$O (II, c$_{\text{II}}$ = 9.19 Å) is in good agreement with previous reports (c = 8.4 Å\textsuperscript{2}) of α-Co(OH)$_2$ thin films prepared with nitrate incorporation between the Co$^{2+}$ containing layers. We observe a progressive increase of the interlayer spacings with increasing anion size in the order Cl$^-$ (c$_{\text{I}}$ = 8.12 Å < NO$_3$$^-$ (c$_{\text{II}}$ = 9.19 Å < SO$_4^{2-}$ (c$_{\text{III}}$ = 11.26 Å). While this trend had been reported before by Rajamathi et al.\textsuperscript{19} for anion incorporation into α-Co(OH)$_2$ powder, the c-axis lattice spacings they report are up to ~13% smaller. However, not too much should be interpreted from this difference, since Rajamathi\textsuperscript{19} et al. analyzed less crystalline materials with a different water content than reported here.

As expected, 2-D reflections [(100) and (110)] in the XRD pattern (Fig. 2) agree with the lattice parameters of β-Co(OH)$_2$ (a layered brucite structure, without any anion incorporation between the cobalt-containing layers\textsuperscript{15,20}) and do not shift with changes in interplanar lattice spacings as they contain no c-axis component. Reflections corresponding to (111) and (011) show small shifts in d-spacing with respect to β-Co(OH)$_2$ again consistent with the larger c-axis dimension. The crystalline correlation lengths of the three α-Co(OH)$_2$ materials were calculated using the Scherrer\textsuperscript{22} formula. The crystalline correlation length was largest for II (441 Å) followed by compounds I (350 Å) and III (185 Å).

The electron diffraction (ED) patterns in Fig. 2 mirror the respective crystalline correlation lengths calculated from the XRD data, showing large single crystals for II and decreasing crystallite size in I and III. Slight imperfections and possible double diffraction are observed for I and higher polycrystallinity is observed for III (Fig. 2). Narrow line widths in the XRD and single crystal ED patterns of II suggest that each layer is in alignment with neighboring layers and not randomly oriented around the c-axis.\textsuperscript{15,23} The polycrystallinity of I may be due to the stacking order of the cobalt-containing sheets being parallel and equidistant but rotationally translated with respect to one another.\textsuperscript{24} The sulfate-containing material is the most defective of the three, resulting in the observation of polycrystalline rings in the ED. Single crystal diffraction patterns were observed for II down the (01−1) zone axis, with d-spacings corresponding to the lattice planes (110), (112), and (123) (α = 3.13 Å; c = 9.19 Å). The calculated unit cell parameters for I, II, and III are a$_{\text{I,II,III}}$ = 3.14 Å; c$_{\text{I}}$ = 8.12 Å; c$_{\text{II}}$ = 9.19 Å; and c$_{\text{III}}$ = 11.26 Å, which are in perfect agreement with the XRD data. Unit cell dimensions obtained by the two techniques are thus identical, indicating that the material is homogeneous on the crystalline and bulk length scales.

XRD and electron diffraction data agree with one another, and indicate that the material is structurally similar to Zn$_5$(OH)$_2$(NO$_3$)$_2$·2H$_2$O.\textsuperscript{21} This latter material is known to consist of layered sheets with octahedrally coordinated Zn ions in the brucite layer, one quarter of which are replaced by two tetrahedrally coordinated Zn ions located above and below the plane of the octahedrally coordinated Zn ions. This structure thus exhibits an overall ratio of 3 : 2 octahedral to tetrahedral sites and a charged cation layer. The same crystal structure has been previously proposed by Kurmoo for Co$_2$(OH)$_3$(NO$_3$)$_2$·(CO$_3$)$_2$·(OH)$_8$·2H$_2$O.\textsuperscript{21} More recently, Forster et al. synthesized another α-cobalt hydroxide, Co$_2$(OH)$_3$(C$_2$H$_4$S$_2$O$_2$)(H$_2$O)$_2$, in which one sixth of the octahedrally coordinated Co$^{2+}$ are replaced by two tetrahedral sites.\textsuperscript{25}
The compositions of the α-Co(OH)₂ films I, II and III were analyzed using ICP-AES and C, H, N analysis. Based on these results, compound I is proposed to be Co₅(OH)₈Cl₂·3H₂O (anal. found: H, 2.70%; Co, 52.9%; calc.: H, 2.54%; Co, 53.0%). Compound II was found to have the composition known from the literature as Co₅(OH)₈(NO₃)₂·2H₂O¹⁵ (anal. found: H, 2.51%; N, 4.73%; Co, 52.7%; calc.: H, 2.05%; N, 4.74%; Co 49.9%) and is a direct analog of Zn₅(OH)₈(NO₃)₂·2H₂O.¹¹ ICP-AES analysis of III gave a Co : S ratio of 5 : 1 and analyses are consistent with a formula of Co₅(OH)₈SO₄·2H₂O (anal. found: H, 2.29%; S, 5.91%; Co 51.8%; calc.: H, 2.15%; S, 5.70%; Co 52.4%).

X-Ray photoelectron spectroscopy (XPS) data indicate the presence of Co²⁺ with the 2p peak centred at 780.6 eV (Fig. 3a) in all three materials. The peak position and shape are consistent with literature values reported for Co(OH)₂.²⁶,²⁷ Also these data restrict the potential presence of Co³⁺ centers to a few mol%. The O 1s peaks for all materials have a maximum intensity component centered at 530.8 eV (data not shown). This is in good agreement with previously reported data for β-Co(OH)₂.²⁶,²⁷ The XPS data of the respective counterions for compounds I (Cl⁻), II (NO₃⁻) and III (SO₄²⁻) are shown in Fig. 3b. All observed binding energy values are in good agreement with corresponding reference spectra (Cl 2p Cl = 198–200;²⁸ N 1sNO₃ = 407–408 eV;²⁸ S 2pSO₄ = 168–171 eV²⁸).

Fig. 3 High resolution XPS spectra of (A) Co 2p region for I, II, and III and (B) Cl 2p, N 1s and S 2p regions for I, II, and III respectively.

The Co₅(OH)₈Cl₂·3H₂O (I), Co₅(OH)₈(NO₃)₂·2H₂O (II) and Co₅(OH)₈SO₄·2H₂O (III) films are dark green in color, with visible absorption (UV/Vis) spectra showing strong peaks near 660 and 600 nm (Fig. 4) for all materials. Compound I absorbs at slightly higher wavelengths compared to II, while the spectrum of III is marginally blueshifted. Absorption above ~600 nm in the visible spectrum is indicative of tetrahedral Co²⁺ centers.²⁹ Possible features indicating octahedral Co²⁺ centers are obscured by the diffuse reflectance of the samples below 600 nm.¹⁰,²⁹ In contrast, β-Co(OH)₂ with symmetric octahedral bonding geometry around the cobalt center is pink in color (λmax = 470 nm).¹⁵

These UV/Vis observations provide strong confirmation that our materials indeed contain tetrahedrally coordinated Co²⁺ ions. No bands indicating the presence of Co³⁺ ions could be seen. In combination with our XPS data, this supports the suggestion that the positive net charge in these α-Co(OH)₂ materials indeed originates from differently coordinated metal ions (as described above) instead of mixed valence ions.

X-Ray absorption near edge structure (XANES) was recorded for Co₅(NO₃)₂(OH)₈·2H₂O (II). The K-edge energy is 7719 eV, which is in agreement with reported values for Co(II) reference compounds.¹⁰ A weak pre-edge feature is observed at 7709 eV. This pre-edge feature results from a lack of inversion symmetry in crystal sites due to the presence of tetrahedral coordination of some of the cobalt ions present in the material, supporting the above conclusions.

Methods used previously to make α-Co(OH)₂ materials involved electrochemical,¹⁵ chemical,¹⁹,²⁶ and sonication assisted synthesis routes,¹³,¹⁴ but direct electronic measurements previously could not be carried out on the resulting materials because of the low quality powder morphology, low crystallinity and the absence of suitable thin films. Few publications report the growth of Co(OH)₂ thin films on substrates. In most cases the material described was either β-Co(OH)₂,³⁰ or it is extremely amorphous,³¹ with the
exception of the thin film study by Hosono et al.\textsuperscript{9} \(\alpha\)-Co(OH)\(_2\) has been investigated primarily in nanocrystalline morphology. In contrast, the continuous morphology of the films reported here makes such direct electronic measurements possible for the first time.

The continuous morphology and high degree of crystallinity of Co\(_2\)(NO\(_3\))\(_3\)(OH)\(_6\)\(\cdot\)2H\(_2\)O (II) made this material the best choice for further electronic characterization. Ohmic contact with a metallic conductor is readily achieved with physical contact between II and a platinum interdigitated micro-electrode without the need for annealing or alloying, as evident in the observed linear response to voltage in the IV curve (data not shown). The IV characteristics were measured parallel to the plane of the material and the dark sheet resistance was observed to be \(\sim 100\ \Omega\ \text{cm}\). A high anion density within the material, resulting from the interlayer incorporation of anions into the crystal structure, is consistent with the observed resistivity assuming that the contact resistance is small with respect to the bulk material resistance.\textsuperscript{32}

We measured the photoconductive properties of II in view of the unique electronic environment around the cobalt centers created by the mixture of octahedrally and tetrahedrally coordinated ions in close proximity. The material is expected to behave as a p-type semiconductor because of the additional positive charge induced in the cobalt-containing layers by the replacement of one octahedral Co\(^{2+}\) site with two tetrahedral Co\(^{2+}\) sites in the crystal lattice. p-Type semiconductors exhibit an increase in conductivity when irradiated with light of sufficient energy to excite charge carriers in the material.\textsuperscript{33} Light of energy greater than the material’s band gap (\(E_g\)) generates an equal number of electrons and holes. In a p-type material this results in a large increase in concentration of minority carriers (i.e., electrons), thereby changing the conductivity of the material.\textsuperscript{34} The absorption spectrum indicates that the material absorbs strongly in the visible, and therefore should be photoactive in this range of the spectrum.

We see that conductivity of the material increases sharply when exposed to visible light as a result of the increase in minority carriers (Fig. 5). After the light is turned off the minority carrier concentration decreases as \(\exp(-t/\tau)\), where \(\tau\) is the minority carrier lifetime. The observed decay curve is fit to a single exponential (Fig. 5 dark grey line) with \(\tau = 4.8\ \text{s}\) and \(R^2 = 0.991\). This high quality fit to a single exponential is an indication that one process dominates the decay of the conductivity response; it is in good agreement with the above physical characterization indicating relatively defect-free crystallinity. These results suggest that the material behaves as a highly doped p-type semiconductor with a long minority carrier lifetime and a degree of crystallinity sufficient for low resistance conduction. The apparent high doping concentration is most likely a result of the counter anions between the crystalline sheets of Co(OH)\(_2\). The unusually long minority carrier lifetime is consistent with the large single crystal domains observed by XRD and ED.

Diffraction and analytical methods similar to those described above were used to confirm the structures of the Cu\(_2\)(OH)\(_2\)(NO\(_3\))\(_3\), Zn\(_2\)(OH)\(_3\)(NO\(_3\))\(_2\)\(\cdot\)2H\(_2\)O and Mn\(_3\)(PO\(_4\))\(_2\)\(\cdot\)7H\(_2\)O thin films. Properties of these materials will be reported elsewhere.

![Figure 5](https://example.com/figure5.png)

**Fig. 5** Observation of photoconductive behavior of II on a platinum interdigitated micro-electrode with 2 s light pulses (grey box represents duration of time light is on) from a fiber optic visible light source (spectral range of 400–1400 nm with an intensity of 80 \(\times\) 10\(^3\) lux) and 2.5 V applied bias. Dark grey line represents an exponential curve fit to the data \(\tau = 4.8\ \text{s}\) \((R^2 = 0.991)\). Inset shows reproducibility of the photoconductive response over an extended time course (200 s).

**Conclusions**

Using a kinetically and spatially controlled vapor-diffusion process, we have synthesized a variety of nanostructured metal hydroxide and metal phosphate thin films at ambient temperature and pressure. Most of these materials have not been reported in thin film morphology before.

Our template-free large area films allow for the first time characterization of films in which the electronic properties and crystal structure are not influenced by the presence of a substrate. The layered Co\(_2\)(NO\(_3\))\(_3\)(OH)\(_6\)\(\cdot\)2H\(_2\)O material produced by this method exhibits a high degree of crystallinity and unique electronic properties. Characterization of photoconductive properties shows a weak photoconductive response and indications of a long minority carrier lifetime (4.8 s) and high doping density within the material. The observed photoconductive response is not very intense, but considering that this behavior has not been observed before for \(\alpha\)-Co(OH)\(_2\), our observations support the suggestion that this low-temperature solution-based synthesis of inorganic thin films described here may provide an important new route to materials synthesis to facilitate the characterisation of electrochemical properties of both known and new materials.

Although it is not yet known whether the materials described here may be useful for large-scale applications, the methodology for synthesis that we report is versatile and the materials described here are simply first examples of thin films grown by this vapor-diffusion mechanism. As we have shown, the process is generic and not limited to metal hydroxide synthesis. We have observed that the as-synthesized thin films can be dehydrated and converted to the respective metal oxide films with no change in morphology by heating in air. It may therefore be widely useful for room temperature fabrication of semiconducting films based on a variety of other materials.
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