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Cobalt(II)heteroarylalkenolate precursor for homogeneous Co₃O₄ coatings by atomic layer depositionReceived 00th January 20xx,
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We present a new and efficient cobalt precursor, Co^{II}(DMOCHCOF₃)₂, to prepare Co₃O₄ thin films and conformal coatings. In the synthesis of this Co complex, heteroaryl moieties and CF₃-groups were combined leading to high thermal stability and volatility precursor. The suitability of this precursor for ALD deposition was tested on flat silicon substrates and TiO₂/C nanofibers upon process optimization. Deposition at 200°C results in homogeneous and smooth Co₃O₄ thin films with a growth per cycle of 0.02 nm/cycle. Conformal coatings have been successfully obtained on TiO₂/C nanofibers being thus an attractive platform for surface chemistry studies on high aspect ratio structures for future photocatalysts, sensors, supercapacitors and batteries.

Introduction

Cobalt oxide thin films are attracting huge interest for a wide variety of applications including energy storage¹, conversion^{2,3}, catalysis⁴⁻⁷, magnetism⁸ and also sensor applications⁹. When the surface and interface related effects start to become dominant over the bulk counterpart it is important to use adequate fabrication tools to have precise control at the nanometer scale. Atomic layer deposition (ALD), afforded by the self-limiting reaction mechanism, represents one of the most promising techniques to prepare nanostructures and coatings on high aspect ratio structures with strict control of film thickness and composition.¹⁰ The chemical precursor plays a key role on the deposition parameters and final film properties. Stability, volatility, reactivity, safe handling, cheap and no self-decomposition are some of the general requirements for a suitable ALD precursor where substrate limitations can make this choice even more challenging. Although the number of ALD precursors available increased significantly in the last ten years, there are still many ALD processes frustrated by the lack of suitable precursors. Therefore, it is important to design new and improved

precursor molecules that can broaden the material and process variety in this emerging ALD field.

The preparation of cobalt oxide by ALD has been previously demonstrated using a wide variety of precursors including oxygen-coordinated compounds: Co(thd)₂ (Hthd=2,2,6,6-tetramethylheptan-3,5-dione)^{11,12} and Co(acac)₃¹³ (acac= acetylacetonate), halides as CoI₂¹⁴ and organometallics Co(Cp)₂ (Cp= cyclopentadienyl)¹⁵⁻¹⁹. Another interesting and evolving family of ALD precursors is the nitrogen-coordinated precursors (alkylamides, silylamides and amidinates, aromatic heterocycles) which have been studied for the deposition of several metals and metal oxides²⁰⁻²⁷ but it has been barely explored for the case of Co.²⁸⁻³⁰ In addition, the air instability of many Co compounds led to increased focus on research of precursors using new ligand systems.^{23-27,31}

In this work we report on the synthesis and characterization of a novel cobalt precursor Co^{II}(DMOCHCOF₃)₂ (DMOCHCOHCF₃=1-(Dimethyl-1,3-oxazol-2-yl)-3,3,3-trifluorprop-1-en-2-ol). The high thermal stability and volatility of this synthesized metal-β-heteroarylalkenolate, owing to the positive inductive effect of the heteroaryl moieties and negative effect of the CF₃-groups, make it very suitable precursor for the preparation of nanostructured ceramic materials by different fabrication methods ranging from solvothermal and microwave synthesis to vapor deposition for thin films (metal-organic chemical vapor deposition (MOCVD), plasma-enhanced chemical vapor deposition (PECVD), atomic layer deposition (ALD)). Here, we demonstrate the successful use of this new Co precursor to prepare uniform ALD thin film on silicon (100) substrates as well as conformal coatings on nanofibers TiO₂/C. TiO₂/C nanofibers are low-cost, structurally stable and environmentally friendly 1D structures that hold great potential to be used for energy and catalytic applications including anode for ion batteries^{32,33} and support for noble metal catalysts³⁴. In particular, conformal coatings of dense

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Co₃O₄ are envisaged as next generation candidates for high capacity anodes in lithium ion batteries for its high theoretical capacity (890 mAh/g) based on the conversion reaction, compared to commercial graphite (372 mAh/g).³⁵

Results and discussion

Synthesis and Characterization of Co^{II}(DMOCHOCF₃)₂

The cobalt complex Co^{II}(DMOCHOCF₃)₂ was prepared by the reaction of cobalt(II) acetate tetrahydrate with two equivalents of deprotonated ligand 1-(Dimethyl-1,3-oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ol (DMOCHOCF₃) in a mixture of tetrahydrofuran (THF) and water, according to the reported procedure.³⁶ The mixture was stirred for 15 minutes at room temperature and was added dropwise to the solution of Co^{II}(OOCCH₃)₂·4H₂O in water. The reaction mixture was stirred overnight at 50 °C. After filtration and drying at room temperature a solid was obtained, which was purified by sublimation (120 °C, 10⁻³ mbar) to obtain the precursor as crystalline red product. The chemical synthesis route is presented in Scheme S1.

Scheme 1. Synthesis of complex Co^{II}(DMOCHOCF₃)₂.

The yield of the reaction is 0.76 g (81 %). The obtained red product crystallized in the monoclinic space group *P*₂₁/*c* with four molecules per unit cell, see Table 1.

Table 1. Crystallographic data for Co^{II}(DMOCHOCF₃)₂.

Compound	Co ^{II} (DMOCHOCF ₃) ₂
Chemical formula	C ₁₆ H ₁₄ Co F ₆ N ₂ O ₄
Molecular weight (g/mol)	471.23
Crystal system	monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> (Å)	8.500(6)
<i>b</i> (Å)	11.800(5)
<i>c</i> (Å)	19.500(1)
α (deg)	90.00
β (deg)	97.20
γ (deg)	90.00
<i>V</i> , Å ³	1940.4
<i>Z</i>	4
<i>R</i> _{int}	0.0738
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ₀ > 2σ(<i>I</i>)]	0.0421 / 0.1033
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0801 / 0.1222
Goodness of fit	1.026

The molecular structure and the coordination polyhedra of Co^{II}(DMOCHOCF₃)₂ are shown in Figure 1. The distorted tetrahedral complex is composed of the central atom Co(II) that is surrounded by two chelate ligands. The reason for the distorted structure is the steric hindrance of these ligands that are coordinated with their O- and N-donor sites in a bidentate fashion. In general, the metal-ligand interactions are similar to other reported Co(II) precursor in the literature with corresponding chelating N, O ligands. The Co-O and Co-N bond lengths were found

to be between 1.928(2) - 1.944(2) Å and 1.982(3) - 1.985(3) Å, respectively, which are comparable with Co^{II}L₂ (H-L = Z-4-((2,5-dimethylphenylamino)(phenylmethylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one) (Co-O = 1.931 Å, Co-N = 1.994 Å) and Co^{II}L₂ (H-L = (Diethylaminosalicylaldiminato)nitrobenzene) (Co-O = 1.859(5) Å, Co-N = 1.983(6) Å).^{37,38} Furthermore, the angles (O1-Co1-N1 = 93.87(10)°, O1-Co1-N2 = 110.40(11)°, O3-Co1-N1 = 115.75(11)°, O3-Co1-N2 = 94.25(10)°) varied slightly from the ideal value (109.47°) of a typical tetrahedral molecular geometry caused by the steric hindrance of the ligands in the compound. In addition, intermolecular interactions were observed for this compound. It is particularly noticeable that the molecules are antiparallel aligned owing to the Co-O interactions with distances of 3.898 Å, as displayed in the supporting information, Figure S1. Magnetic moment measurement (M(T)) of Co^{II}(DMOCHOCF₃)₂ at 1 kOe shows paramagnetic behavior, see Figure S2.

Figure 1. (a) Molecular structure and (b) coordination polyhedra of Co^{II}(DMOCHOCF₃)₂. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): Co1-O1 = 1.944(2), Co1-O3 = 1.928(2), Co1-N1 = 1.982(3), Co1-N2 = 1.985(3), O3-Co1-O1 = 128.06(10), O3-Co1-N1 = 115.75(11), O1-Co1-N1 = 93.87(10), O3-Co1-N2 = 94.25(10), O1-Co1-N2 = 110.40(11), N1-Co1-N2 = 116.05(10).

The thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analysis of Co^{II}(DMOCHOCF₃)₂ were carried out under air atmosphere and ambient pressure between 30 and 600 °C using a heating rate of 10 °C/min (Figure 2). The TG curve indicates rapid single-step mass loss between 100 and 320 °C. The mass loss identified for Co^{II}(DMOCHOCF₃)₂ was 97%, higher than the theoretical value for the formation of Co₃O₄ (83%), which is attributed to the sublimation and high volatility of the precursor. This behavior was confirmed by the DSC curve showing one sharp endothermic signal at 160 °C. Importantly this precursor can be stored and handled under ambient conditions having long-term stability >9 months.

Figure 2. TG (black line) and DSC (blue line) curves of Co^{II}(DMOCHOCF₃)₂.

Film deposition

For the cobalt oxide deposition, $\text{Co}^{\text{II}}(\text{DMOCHCOF}_3)_2$ precursor was heated at 145°C and sequentially pulsed with ozone (O_3) on Si(100) substrate and carbon/ TiO_2 nanofibers. The ALD optimization process and growth characteristics were performed on Si (100) substrates. Saturation conditions were evaluated varying the Co dose time from 0.5 to 3 s and constant ozone pulse length of 1 s. It was observed that at high Co dose time (3s) the growth rate decreases suggesting the presence of etching reactions, figure S3. Therefore, for subsequent studies, a Co pulse time of 2 s was chosen. A well-defined range with constant growth per cycle (GPC) of 0.02 nm/cycle was identified between 150°C and 200°C, see Figure 3. This deposition rate is similar to that obtained when depositing $\text{Co}(\text{thd})_2$ with O_3 on silicon.³⁹ Metalorganic precursors such as cobaltocene or cyclopentadienyl isopropyl acetaminato-cobalt lead to higher deposition rates, i.e. 0.045-0.05 nm/cycle.¹¹ Halogen based Co precursors, CoI_2 and liquid cobalt precursors are those that give the highest deposition rates when combined with O_2 or O_3 (0.1-0.2 nm/cycle)^{14,17,40,41}. A linear dependence of film thickness with the number of ALD cycles was also obtained. Optimized deposition conditions provide continuous thin films with smooth surface morphology (rms ~0.5 nm), as shown in the AFM topographic image in Figure S4. Preliminary studies on the reactivity of $\text{Co}^{\text{II}}(\text{DMOCHCOF}_3)_2$ with water T(150-250°C) did not lead to the formation of Co_3O_4 .

Figure 3. (a) Cobalt oxide GPC as a function of substrate temperature. (b) Dependence of cobalt oxide film thickness with the number of ALD cycles at 200°C.

Figure 4 shows GIXRD 2θ scans from as-deposited (200°C) and post-annealed films. While from the as-deposited film the cobalt oxide peaks can be barely identified, typical reflections of spinel Co_3O_4 are clearly observed in the post annealed one (800°C for 3 h under static air). Therefore, polycrystalline Co_3O_4 film was obtained after processing the sample. The mass density of the as-deposited films, important parameter for high capacity anode materials in lithium-ion batteries, was obtained from x-ray reflectometry analysis ($5.84 \pm 0.04 \text{ g/cm}^3$) and is in agreement with previously reported mass densities of ALD prepared Co_3O_4 films (5.8 g/cm^3)⁴².

Further analysis on the surface chemical composition was performed by XPS on as-deposited cobalt oxide/silicon samples after being exposed to air, see Figure 5. From the survey spectrum, the presence of Co, Si, O and C was identified, consistent with the expected cobalt oxide deposition on silicon substrate. Also, the absence of N confirmed no impurities from the organic precursor remained in the film. High resolution $\text{Co}2\text{p}$ and $\text{O}1\text{s}$ spectra

confirmed the formation of Co_3O_4 , in agreement with the literature^{43,44}.

Figure 4. GIXRD of Co_3O_4 films deposited on Si (100) substrate by ALD (a) as-deposited, (b) post annealed.

Figure 5. XPS study of Co_3O_4 film on Si (a) survey spectrum (b) $\text{Co}2\text{p}$ and (c) $\text{O}1\text{s}$.

High resolution $\text{Co}2\text{p}$ spectrum, figure 5 (b), shows two main peaks at 779.9 eV and 795.2 eV attributed to the spin-orbit doublet $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$, with a splitting of 15.3 eV. Also, it was identified a broad satellite peak at 803.6 eV. These values and spectrum shape are in agreement with the literature values for Co_3O_4 films. Nonetheless, it is reported that at the initial stages of the film growth of cobalt

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oxide by ALD, CoO and Co₃O₄ species may coexist changing to pure Co₃O₄ as film thickness increases.⁴⁵ O1s spectrum is shown in figure 5(c). The main contribution is centered at 529.5 eV attributed to metal-oxide bond. The shoulder that appears at 531.8 eV is due to chemisorbed hydroxyl or carbonyl species formed for the reaction of the oxide surface with moisture in the air.

Figure 6. SEM image of bare TiO₂/C fibers (a) ALD-Co₃O₄ coated TiO₂/C fibers and the (b), EDX spectrum of the bare fibers (c) EDX spectrum of ALD-Co₃O₄ coated fibers (d).

Co^{II}(DMOCHCOF₃)₂ was simultaneously deposited on TiO₂/C nanofibers to investigate the ability to coat 3D structures. SEM images collected from backscattered electrons were acquired from

bare TiO₂/C nanofibers and cobalt oxide-coated TiO₂/C nanofibers, figure 6(a) and (b), respectively. In both cases well defined nanofibers are observed indicating that the ALD conditions do not degrade the nanofibers. EDX analysis performed at different points of the bare and coated fibers also demonstrates the cobalt deposition in the sample exposed to ALD, figure 6(c) and (d), respectively.

Representative STEM image of 18 nm ALD-Co₃O₄ coated TiO₂/C fiber is shown in figure 7 (a). Qualitative information on cobalt and titanium elemental distribution was obtained by line-scanning across this nanofiber in several regions. Figure 7(b),(c) and (d) show the image profile, Ti and Co distribution along the scan identified in yellow in figure 7(a). Importantly, Co was identified throughout the scan line with lower intensity than Ti which indicates the formation of an ultrathin coating. Also, at the edges of the fiber the intensity of the Co is higher confirming that the titanium is the core of the fiber and Co forms a conformal shell. Therefore, these coated nanofibers could be an attractive support to perform thorough studies on surface reaction mechanisms for future sensors, batteries, supercapacitors and (photo)catalysis-related applications.

Figure 7. (a) STEM-EDX analysis of ALD-Co₃O₄ coated TiO₂/C fibers. The yellow line indicates the region where the elemental analysis was acquired (b) image profile (c) Ti profile and (d) Co profile.

Experimental

All chemicals were purchased from Acros Organics and used without further purification. Data collection for X-ray precursor structure elucidation was performed on a STOE IPDS I diffractometer using graphite-monochromated Mo K α radiation (0.71073). The programs used in this work are STOE's X-Area,⁴⁶ and the WINGX suite programs,⁴⁷ including SIR-92⁴⁸ and SHELXL-97 for structure solution refinement. Fourier transform infrared (FT-IR) measurements were recorded on a PerkinElmer Spectrum 400 and the UV-vis spectrum was carried out with a Lambda 950 device between 250 and 800 nm on 1,2-dichloroethane solutions by using quartz cuvettes. Microanalysis for C, H, and N contents was carried out using a HEKAtech CHNS EuroEA 3000 analyzer. Thermal analyses were performed on a TGA/DSC 1 (Mettler-Toledo-GmbH, Germany) in an air atmosphere (25 mL/min) at a rate of 10 °C/min from 30 to 600 °C. EI-MS spectra were obtained on a Finnigan MAT 95 (20 eV) in *m/z* (relative percentage), operating in positive ion modes.

CHN Anal. Calc.: C, 40.76; N, 5.94; H, 2.97. Found: C, 40.80; N, 5.96; H, 3.78. EI-MS: 471 (100, M^+), 402 (8, $M^+ - CF_3$), 265 (5, $M^+ - DMOCHCOCF_3$). IR (cm^{-1}): $\nu(C=O)$ 1666, $\nu(C=C)$ 1589, 1536, $\nu(CF)$ 1184, $\nu(=CH)$ 772. UV-vis (1,2-dichloroethane, λ_{max}/nm): 304, 382, 598 – 729.

Cobalt oxide thin films (from 12 to 50 nm) were deposited on reference Si (100) substrates and TiO_2/C nanofibers by atomic layer deposition, using a thermal Ultratech/Cambridge NanoTech S100 reactor, under long exposure time. $Co^{II}(DMOCHCOCF_3)_2$ was loaded in the ALD cylinder under ambient conditions and sublimed at 145°C upon optimization (130-160°C). Before deposition, the substrates were exposed to 150 cycles of ozone. In order to form the cobalt oxide, $Co^{II}(DMOCHCOCF_3)_2$ was sequentially pulsed with ozone (O_3) provided by a Del Ozone LG-7 ozone generator. A fixed N_2 flow rate of 20 sccm was used. Pulse doses of 2s and exposure times of 20 s were used for the cobalt precursor to ensure full surface saturation of the 3D fibers. The substrate temperature deposition to identify the ALD window was optimized in this work. 200°C was chosen as standard substrate temperature where most of the studies were performed. Post annealing processes were performed in a tubular furnace at 600°C-800°C for 3h under static air to improve film crystallinity.

Phase identification and purity was investigated by grazing incident X-ray diffraction (GIXRD) using a Bruker D8 Discover A25. X-ray reflectometry (XRR) was performed using a SIEMENS D5000 diffractometer to study the cobalt oxide film thickness on Si(100) substrates, both operating with Cu $K\alpha$ radiation. Surface morphology and chemical composition was evaluated by mean of scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) FEI Nova 600 Nanolab Dual-Beam FIB. X-ray photoelectron spectroscopy (XPS) was performed on ESCA M-Probe (Al $K\alpha$) with an energy resolution of 0.8 eV. Binding Energies were normalized using the C1s binding energy (284.8 eV) as a reference. Scanning HAADF STEM images, EDX spectra and STEM-EDX profiles were acquired on an FEI Tecnai G2 F20 microscope operated at 200 kV and equipped with an EDAX super ultra-thin window (SUTW) X-ray detector at ICN2, Barcelona.

Conclusions

We have presented an effective synthetic approach to prepare the novel $Co^{II}(DMOCHCOCF_3)_2$ complex providing their structural and chemical characterization. This precursor, containing heteroaryl moieties and CF_3 -groups, compared to many existing β -diketonate and cyclopentadienyl-based Co precursors, can be stored and handled under ambient conditions and shows long-term stability. We have also demonstrated the viability of $Co^{II}(DMOCHCOCF_3)_2$ for low temperature ALD deposition (200°C) of spinel Co_3O_4 with a growth per cycle of 0.02 nm/cycle. EDX and XPS analysis confirmed the effectiveness of this precursor to generate films free of impurities with smooth surface (0.5 nm). Homogeneous coatings have been successfully obtained on TiO_2/C nanofibers as demonstrated by SEM-EDX and STEM characterization. Therefore, the $Co^{II}(DMOCHCOCF_3)_2$ precursor and ALD process here reported offer a valuable and reproducible approach to prepare low temperature high-quality cobalt oxide

homogeneous films starting from a stable and easy to handle precursor. Co_3O_4 conformal coatings on TiO_2/C nanofibers could be an attractive architecture to investigate their feasibility for supercapacitors, batteries and even photocatalysts.

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We present a robust approach to **prepare** conformal Co_3O_4 **nanocoatings** on **high aspect ratio structures** from **a new cobalt metalorganic complex**.