Controlled vapor-phase synthesis of cobalt oxide nanomaterials with tuned composition and spatial organization

Davide Barreca, *a Alberto Gasparotto, b Oleg I. Lebedev, c,d Chiara Maccato, b Andrea Pozza, b Eugenio Tondello, b Stuart Turner and Gustaaf Van Tendeloo c

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Cobalt oxide nanostructures are deposited by Chemical Vapor Deposition (CVD) on Si(100) substrates at temperatures between 300 and 550 °C, using for the first time a novel Co(ii) adduct as molecular precursor [Co(hfa)₂·TMEDA; hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato, TMEDA = N,N',N'-tetramethylethylenediamine]. The preparation is conducted either under dry (O₂) or wet (O₂ + H₂O) oxygen atmospheres, at total pressures of 3.0 or 10.0 mbar. The obtained results evidence that, upon dry O₂ at 10.0 mbar, the initial nucleation of CoO occurs, followed by its progressive oxidation to Co₃O₄ during the subsequent growth stages. In a different way, cobalt monoxide can be selectively obtained at 3.0 mbar. In all cases, water vapor acts as an oxidant towards cobalt, favoring the formation of Co₃O₄ phases with a more pronounced {111} and {110}-type faceting. Structural, compositional and morphological characterization evidences the possibility of obtaining high purity Co/O/Co₃O₄ systems with tailored morphological features, from films to columnar nanostructures, thus highlighting the potential and versatility of the proposed synthetic strategy.

Introduction

In the last decade, cobalt oxides (CoO and Co₃O₄) have received a widespread attention due to their appealing multi-functional properties of technological interest. To this regard, actual challenging issues concern the devising and optimization of synthetic strategies towards high purity nanomaterials with specific features, opening new frontiers not only for understanding their fundamental properties, but also for developing new generation nanodevices with improved performances.¹–⁶ Nanostructured Co₃O₄, the most stable cobalt oxide with a spinel-type structure [(Co(ii)Co(III))₃O₄], is an important p-type semiconductor (direct optical bandgaps at 1.5 and 2.0 eV)⁷–¹³ for applications in secondary Li/O₂ cells, negative electrodes for Li-ion batteries and supercapacitors,¹¹,¹²,¹⁴–²⁰ as well as in field emitters,⁶,¹⁶,²¹ heterogeneous catalysts, electrochromic devices, solar absorbers, solid-state sensors,²,²,³,⁵,⁸,⁹,¹³,¹⁷–¹⁹,²²–⁴⁰ and, recently, superhydrophobic surfaces.⁴¹ On the other hand, less studies have been focused on cobalt monoxygen (CoO) nanostructures,²¹,²² which are hard to synthesize because of the special requirements necessary to force cobalt in a low oxidation state under common ambient conditions.⁴²–⁴⁵ Yet, CoO nanosystems, with the rocksalt structure, representing p-type semiconductors due to O excess,¹⁵,⁴⁶ are also significant for applications as pigments for glasses and ceramics, in electrochemistry, as well as in magnetic, catalytic and gas sensing fields.⁵,⁹,¹¹,²¹,⁴²,⁴³,⁴⁶–⁵³

In view of these profitable utilizations, a large variety of synthetic techniques has been applied to grow cobalt oxide nanosystems with controlled properties, from nanosheets/nanoparticles to thin films, mesoporous systems and, ultimately to nanorods/wires, nanocolumns, nanoplates and nanobelts. Among physical routes, it is worth remembering evaporation,⁴⁵,⁵² sputtering⁴⁰ and pulsed laser deposition.⁵³ On the other hand, chemical processes include combustion synthesis,⁵ controlled oxidation of cobalt nanoparticles/foils/films,⁴,⁶,¹⁶,²³ molten salt synthesis,²⁴ precursor decomposition/calcination,⁹,¹¹,¹²,¹⁴–²⁸,⁵¹ electrospinning,² liquid phase processes,¹³,⁷,¹⁵,¹⁷–²⁰,²⁵–²⁸,⁴⁰,⁴²,⁴⁷,⁵⁴,⁵⁵ and virus-enabled assembly.⁵⁶ Among the various procedures, soft chemical techniques enable a bottom-up approach to properly tune the system properties, with a better control of the nano-objects size, shape and distribution.⁷,²⁹,³⁰,³²,³⁸,⁴⁹,⁵⁰ In this context, Chemical Vapor Deposition (CVD) and related routes offer several advantages, including the production of high-quality coatings or supported nano-assemblies, such as nanorods/nanotubes/nanowalls, by a judicious choice of the processing conditions. In the literature, reports on the CVD of cobalt oxide films have concerned the use of various precursors, ranging from conventional Co(ii) and (iii) acetylacetonates¹¹,¹²,¹³,¹⁵,³⁸,⁵⁷ and Co(dpm)₂ (dpm = 2,2,6,6-tetramethyl-3,5-heptanediionate)³⁴,³⁹,₅₈,₅₉ to second-generation systems like Co(hfa)₂·monoglyme (hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato; monoglyme = dimethoxyethane),⁴⁶ Co(hfa)₂·2H₂O,¹³ Co(acac)₂·TMEDA and Co(dpm)₂·TMEDA (acac = 2,4-pentanediionate; TMEDA = N,N',N'-tetramethylethylenediamine).³⁶,⁵⁷

Recently, we have proposed Co(hfa)₂·TMEDA as an innovative molecular source for CVD of cobalt oxides,⁶⁰,⁶¹ showing
that it possesses superior properties in terms of vapor pressure and mass transport with respect to the previously proposed β-diketone compounds. Preliminary experiments displayed the possibility of obtaining pure Co₃O₄ layers on Si(100). Starting from these results, in the present work our attention is directly devoted to an innovative CVD synthesis of Co–O systems for advanced technological applications. Specifically, depositions were initially carried out under dry O₂ atmospheres on Si(100) substrates at different temperatures, with particular attention to the nucleation and growth processes of CoO/Co₃O₄ as a function of the adopted experimental conditions. Following our recent papers on zinc and copper oxide nanosystems obtained by homologous precursors, the role of water vapor as a reactive agent was also examined, since it is expected to result in the activation of different precursor reaction pathways, determining, in turn, the properties of the final systems. The microstructure, composition, and morphology of the samples and their interplay with the synthesis conditions were investigated by a plethora of advanced characterization techniques. To the best of our knowledge, no such reports on the vapor phase synthesis of CoO/Co₃O₄ nanostructures from Co(hfa)₂·TMEDA and on the thorough characterization of their nucleation/growth processes have ever appeared in the literature.

Experimental

Nanomaterial synthesis

The synthesis and characterization of the Co(hfa)₂·TMEDA complex used as precursor for the obtained cobalt oxide nanomaterials were recently described elsewhere. Cobalt oxide nanomaterials were grown in a reduced pressure, horizontal, cold-wall CVD reactor equipped with a quartz chamber, a resistively heated susceptor and an external precursor reservoir kept at 60 °C. Growth processes were carried out for a total duration of 120 min on p-type Si(100) (MEMC®, Merano, Italy) substrates, previously subjected to a cleaning pre-treatment. Deposition temperatures were varied between 300 and 550 °C. As concerns experiments carried out at 3.0 (10.0) mbar total pressure, precursor vapors were transported to the deposition zone by a 20 (100) sccm oxygen flow (purity = 6.0), whereas an independent O₂ flow of 20 (100) sccm was introduced directly in the reaction chamber. For growth processes carried out in the presence of water vapor, a water reservoir maintained at 50 °C was introduced in the gas line of the auxiliary oxygen flow. Under these conditions, water partial pressure was estimated to be of the order of 0.3 (1.5) mbar for a total operating pressure of 3.0 (10.0) mbar.

Analytical methods

Glancing Incidence X-Ray Diffraction (GIXRD) measurements were carried at a fixed incidence angle of 1.0° by means of a Bruker D8 Advance diffractometer equipped with a Göbel mirror and a Cu-Kα source powered at 40 kV, 40 mA.

Fourier Transform-InfraRed (FT-IR) spectra were recorded on a Nicolet Nexus 870 instrument operating in transmittance mode at normal incidence, using a spectral resolution of 4 cm⁻¹. In each spectrum, the substrate contribution was subtracted.

X-Ray Photoelectron and X-ray Excited Auger Electron Spectroscopies (XPS and XE-AES) analyses were performed on a Perkin-Elmer Φ 5600ci spectrometer using a non-monochromatized Al Kα radiation (1486.6 eV). The reported Binding Energies (BEs, standard deviation = ±0.2 eV) were corrected for charging effects assigning to the adventitious C1s line a BE of 284.8 eV. The analysis involved Shirley-type background subtraction, and, whenever necessary, spectral deconvolution, carried out by nonlinear least-squares curve fitting, adopting Gaussian-Lorentzian sum functions. The atomic composition was evaluated by means of sensitivity factors provided by Φ V5.4A software (Perkin-Elmer). In-depth analyses were performed by Ar⁺ sputtering at 3.0 kV, with an argon partial pressure of 5 × 10⁻⁸ mbar. For a more detailed distinction between CoO and Co₃O₄, the Auger α parameter was evaluated as the sum of the BE value of the Co2p₃/₂ XPS peak and the Kinetic Energy (KE) of the CoLMM Auger peak.

The morphological features of the samples were investigated by Field Emission-Scanning Electron Microscopy (FE-SEM) using a Zeiss SUPRA 40 VP instrument, operated with a constant primary beam acceleration voltage of 10 kV. The mean nanoaggregate sizes were evaluated through the SmartSEM® software.

Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM) and Electron Diffraction (ED) experiments were performed on a JEOL 4000EX microscope operated at 400 kV, with a point resolution of 0.17 nm. Scanning Transmission Electron Microscopy-Electron Energy Loss Spectroscopy (STEM-EELS) and High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) experiments were performed on a JEOL 3000F TEM/STEM apparatus, equipped with a GIF-2000 spectrometer. STEM-EELS spectra were acquired using a convergence semi-angle α of 22.15 mrad, a collection semi-angle β of 29 mrad, a nominal spot size of 0.5 nm, an energy dispersion of 0.3 eV per pixel and an energy resolution of 1.2 eV. Core-loss spectra background subtraction was performed using a power-law background model. To obtain the cobalt L₃/L₂ lines ratio, the second derivative of the EELS spectra was computed to remove the slowly varying background, and the ratio of the integrated intensity under the remaining L₃ and L₂ peaks was calculated. The HAADF detector inner semi-angle used was 40 mrad.

Results and discussion

Microstructural characterization

Based on our previous results, in the present study our attention was devoted to investigating the influence of the total pressure on the system morphology, structure, phase composition, with particular regard to the selective obtainment of CoO and Co₃O₄. To this aim, CVD experiments were preliminarily performed at different deposition temperatures and total pressures of 3.0 and 10.0 mbar under a dry O₂ atmosphere, as described in the Experimental section.

Fig. 1a displays the GIXRD patterns of specimens obtained at total pressure of 3.0 mbar. Whereas no appreciable diffraction peaks could be detected up to 350 °C, the sample deposited at 400 °C was characterized by the presence of two reflections centred at 2θ = 36.6 and 42.5°, attributable to the (111) and (200)
planes of cubic CoO. The $I_{200}/I_{111}$ intensity ratio of the two peaks was only slightly lower than that expected for the powder reference sample, thus suggesting no significant texturing. An increase in the growth temperature up to 550 °C produced an intensity decrease of the lower angle (111) reflection with respect to the (200) one. In addition, a slight peak shift towards higher 2\(\theta\) values could be observed on going from 400 to 550 °C ($\Delta(2\theta) = +0.2\)°$. This phenomenon, along with the fact that the signals were always located at higher angular values with respect to bulk CoO (Fig. 1a), could be tentatively ascribed to a corresponding increase of the structural defect content in CoO systems, due to the occurrence of non-equilibrium growth conditions.

An increase in the total operating pressure up to 10.0 mbar resulted in a different system microstructure (Fig. 1b). In fact, for $T \geq 350$ °C, four diffraction peaks located at $2\theta = 19.0, 31.2, 36.7$ and 44.6° were observed and assigned to the (111), (220), (311) and (400) reflections of the Co$_3$O$_4$ phase with the spinel-type cubic structure.

Regarding the specimen deposited at 450 °C, beside the above-mentioned signals, a further reflection located at $2\theta = 42.4°$, related to the CoO (200) planes, appeared. The absence of further diffraction peaks related to cobalt monoxide agreed with the fact that the (200) peak is the most intense even in the powder spectrum. An analogous situation was observed for the specimen grown at 500 °C, apart from a systematic increase of the diffracted intensity. At 550 °C, the disappearance of the CoO reflections and the concomitant rise of the Co$_3$O$_4$ peaks, in particular the (222) one at $2\theta = 38.6°$, took place. A comparison of the present relative intensities with those of bulk Co$_3$O$_4$ enabled us to rule out the occurrence of significant preferred orientations.

Taken together, the above results indicate that, at 3.0 mbar, the selective obtainment of CoO deposits was possible, in agreement with the necessity of milder oxidative conditions in order to stabilize this phase. In fact, Co$_3$O$_4$ formation is known to require the use of more oxidizing atmospheres, thus explaining its obtainment at 10.0 mbar total pressure. Nevertheless, the presence of crystalline CoO under the latter conditions at 450 and 500 °C might be an unexpected result, considering that the adopted Co(hfa)$_2$-TMEDA precursor enabled the obtainment of Co$_3$O$_4$ already at lower deposition temperatures under the same atmosphere (Fig. 1b).

Similarly to the case of CVD of copper oxides from Cu(hfa)$_2$-TMEDA, these observations prompted us to hypothesize that, at 10.0 mbar, the lower-valence oxide (CoO) formation took place in the first deposition stages, followed by its subsequent oxidation to Co$_3$O$_4$, the most thermodynamically stable phase, upon increasing the growth temperature. As a consequence, it was reasonable to suppose that, for $T < 450$ °C, the main CoO (200) signal at $2\theta = 42.4°$ could not be revealed for the overall lower diffracted intensity, depending, in turn, on the low amount of the deposited material (compare the FE-SEM micrographs in Fig. 6 and the growth rate values in Fig. 7). In a different way, at 550 °C Co$_3$O$_4$ was the only crystalline phase and no cobalt monoxide peaks could be detected.

These hypotheses could be further confirmed by a more careful inspection of Fig. 1b, indicating that, for $T < 550$ °C, all the peaks attributed to Co$_3$O$_4$ were indeed located at lower angular values with respect to the reference bulk ones, marked by continuous lines. Such a trend is exemplified by the inset of Fig. 1b, referring to the most intense reflection, revealing intermediate 2\(\theta\) locations between those expected for CoO and Co$_3$O$_4$, except for the sample grown at 550 °C. As a whole, these observations suggested that,
under dry \( \text{O}_2 \) (total pressure = 10 mbar), the formation of \( \text{Co}_3\text{O}_4 \) as the only crystalline phase was progressively favored by an increase of the substrate temperature.

Subsequently, the influence of the reaction atmosphere on the system structure was investigated for two selected growth temperatures, i.e. 400 and 500 °C. At a total pressure of 3.0 mbar (Fig. 2a), the introduction of water vapor during CVD deposition resulted in the partial oxidation of \( \text{CoO} \) to \( \text{Co}_3\text{O}_4 \). At 400 °C, the occurrence of this phenomenon was testified by the appearance of the \( \text{Co}_3\text{O}_4 \) (220) and (400) signals at 2\( \theta \) = 31.4 and 44.9°, respectively. In addition, the (111) \( \text{CoO} \) diffraction peak located at 2\( \theta \) = 36.6° underwent an intensity increase and an upward shift of \( \Delta(2\theta) = +0.2° \), in line with the \( \text{CoO} \rightarrow \text{Co}_3\text{O}_4 \) transformation. At 500 °C, the latter phenomenon was even more marked, since a very intense (311) \( \text{Co}_3\text{O}_4 \) peak at 2\( \theta \) = 36.9° was developed.

Even for the specimens deposited at 10.0 mbar (Fig. 2b) the introduction of water vapor induced an increase of the overall diffracted intensity, suggesting a higher crystallinity of the systems with respect to the homologous ones obtained under dry \( \text{O}_2 \). In particular, regarding the growth at 400 °C, this increase could also be related to a higher deposit thickness, as shown by the corresponding growth rates in Fig. 7. This phenomenon could be explained taking into account that water vapor enhanced the precursor decomposition by favoring the ligand removal thanks to the presence of more nucleation sites (–OH groups) per unit area, as already observed in the CVD of \( \text{Zn} \) and \( \text{Cu} \) oxides from \( \text{M(hfa)}_2\cdot\text{TMEDA} \) (\( \text{M} = \text{Zn}, \text{Cu} \)). In addition, note that a systematic shift of all the signals towards higher 2\( \theta \) values occurred under \( \text{O}_2 + \text{H}_2\text{O} \) atmospheres, leading exactly to the peak positions expected for bulk \( \text{Co}_3\text{O}_4 \). Such a phenomenon was also observed at 500 °C. Furthermore, at this temperature, the introduction of water vapor also led to the disappearance of the (200) \( \text{CoO} \) peak at 2\( \theta \) = 42.4°. These results, along with those obtained for samples of Fig. 2a, suggest that, beside favoring the precursor decomposition, water vapor acts as an oxidizing agent towards \( \text{Co(II)} \) centers, with an effect even stronger than that exerted by the sole \( \text{O}_2 \). As a result, under a wet oxygen atmosphere the obtainment of pure \( \text{Co}_3\text{O}_4 \) was possible also at growth temperatures lower than 550 °C.

### Chemical composition

A preliminary investigation of the system chemical composition and purity was attained by FT-IR analyses. As a general rule, it is worth highlighting that no appreciable absorptions from precursor residuals were ever detected. This result anticipated a clean \( \text{Co(hfa)}_2\cdot\text{TMEDA} \) conversion into cobalt oxides under the adopted reaction conditions, as also confirmed by photoluminescent spectroscopies (see below). As an example, representative spectra for cobalt oxide specimens deposited under dry \( \text{O}_2 \) are displayed in Fig. 3. Whereas at 300 °C no appreciable signal could be detected, at higher growth temperatures all the spectra were dominated by two absorption bands centred at 557 and 657 cm\(^{-1} \), both relating to \( \text{Co-O} \) modes of \( \text{Co}_3\text{O}_4 \). More precisely, whereas the former was associated to \( \text{B-O} \) vibrations in the spinel lattice, with \( \text{B} \) indicating \( \text{Co(II)} \) centers in octahedral sites, the latter could be attributed to \( \text{ABO}_3 \) vibration modes, where \( \text{A} \) is a \( \text{Co(II)} \) center in a tetrahedral environment. These observations, in line with GIXRD analyses, confirmed the presence of \( \text{Co}_3\text{O}_4 \) as the main phase.

Nevertheless, since \( \text{CoO} \) presents an absorption band at 550 cm\(^{-1} \) strongly overlapped with \( \text{Co}_3\text{O}_4 \) signals, FT-IR analyses did not enable more detailed and unambiguous conclusions regarding the mutual \( \text{CoO}/\text{Co}_3\text{O}_4 \) content. Accordingly, XPS/XE-AES analyses were also performed. Besides providing a further valuable insight into the system chemical composition, such techniques yielded information complementary to FT-IR thanks to their intrinsic surface sensitivity.

A common feature to all the deposit XP spectra was the reduction of the carbon signal to a noise level after 5 min Ar\(^+\) sputtering, confirming the clean conversion of the \( \text{Co(hfa)}_2\cdot\text{TMEDA} \) precursor into cobalt oxides. The presence of fluorine in negligible amounts further proved the above observation, in agreement with FT-IR results.
A first discrimination between CoO and Co₃O₄ in the obtained samples was accomplished by analyzing the Co₂p band shape. To this regard, representative surface Co₂p photoelectron peaks are displayed in Fig. 4, top. In general, it is worth observing that the absence of signals centred at 778.0 eV indicated the non-existence of Co metal impurities. As a matter of fact, all the samples obtained under dry O₂ at 3.0 mbar total pressure presented spectra very similar to that of Fig. 4a, characterized by intense shake-up satellites located at BE = 5.6 eV higher than the corresponding spin–orbit split components. Such an indication was a fingerprint for the presence of paramagnetic and high-spin Co(II) centers in CoO.

The main Co₂p₃/₂ spin–orbit component was located at a mean BE of 780.9 eV, in agreement with previous reports on CoO. Such findings were further corroborated by computing the Auger a parameter, defined as reported in the Experimental section, whose mean value was 1554.1 eV, as expected for cobalt monoxide. In a different way, all the samples deposited at 10.0 mbar and the ones prepared in the presence of water vapor at 3.0 mbar had the typical band profile of Co₃O₄, with relatively weak satellites on the high BE side of the main 2p components (≈9.5 eV higher) and a slightly lower BE than the previous case [BE(Co₂p₃/₂) = 780.7 eV]. This attribution was unequivocally supported by the Auger parameter (mean α value = 1552.3 eV) and by the Co₂p₁/₂–Co₂p₃/₂ energy separation, always close to 15.5 eV.

Overall, the phase identification performed by compositional analyses was in good agreement with the indications provided by GIXRD, except for the samples deposited under dry O₂, 10.0 mbar for T < 500 °C. In this case, whereas structural analyses pointed out to the coexistence of CoO and Co₃O₄, XPS and XE-AES investigation showed only the presence of the latter in the outermost system layers. Similar results were also recently reported in the CVD of copper oxides from the homologous Cu(hfa)₂·TMEDA, where the presence of Cu₂O was detected in the inner system layers and the outer regions were composed of CuO. Such a discrepancy seemed to indicate that the initial nucleation led to the formation of the lower-valence cobalt monoxide, and its subsequent oxidation to Co₃O₄ took place in the outermost deposit regions. Indeed, it is known that Co₃O₄ may form at the CoO surface under oxidizing conditions.

In all samples, the surface O1s lineshape was appreciably broadened on the high BE side and, indeed, spectral deconvolution enabled to identify the presence of different contributing species. As an example, the fitting results for a specimen deposited at 10.0 mbar are reported in Fig. 4, bottom. Beside the component of O1s lattice (I) centred at BE = 530.0 eV, two
further bands at 531.6 eV (II) and 532.6 eV (III) were detected and attributed to the presence of coordinatively unsaturated oxygen species (surface defects). Nevertheless, since the component (II) intensity depended on the duration of air exposure, contributions from hydroxyl/carbonate species arising from contact with the outer atmosphere to this band could not be excluded. This hypothesis was in line with the presence of a shoulder in the surface C1s photopeaks located at BE close to 288.0 eV. As a result, the surface O/Co atomic ratios were higher than the expected stoichiometric values (typically 1.1–1.5 and 1.8–3.0 for CoO- and Co3O4-containing samples, respectively). The presence of excess surface oxygen was in agreement with previous AES results on cobalt oxide specimens.

Electron microscopy characterization

Preliminary important information on the system morphology as a function of the growth temperature under dry oxygen atmospheres were obtained by plane-view (pv) and cross-sectional (cs) FE-SEM analyses. Representative micrographs for specimens deposited at 3.0 mbar are proposed in Fig. 5. For \( T = 400 \, ^\circ\text{C} \), samples were characterized by an anisotropic growth habit comprising a sort of nanotowers assembly, with mean lateral dimensions of 90 nm and an average deposit thickness of 110 nm. Upon increasing the growth temperature to 450 \( ^\circ\text{C} \), the sample morphology presented apparently more spaced aggregates (mean size \( \approx 150 \, \text{nm} \)) protruding from a relatively compact seed layer \( \approx 40 \, \text{nm} \) thick and formed by the three-dimensional agglomeration of small nanoparticles (\( \Theta = 6 \, \text{nm} \)). In a different
way, an increase of the thermal energy supply ($T \geq 500 \, ^\circ\text{C}$) produced the formation of compact layers, characterized by uniformly interconnected globular particles ($\Omega \approx 20$ and $50 \, \text{nm}$ at $500$ and $550 \, ^\circ\text{C}$, respectively), with overall mean thicknesses of $170$ and $210 \, \text{nm}$. Interestingly, in both cases $\text{cs}$ images enabled us to discern a thin outermost layer on the top of both films, whose composition corresponded to $\text{Co}_3\text{O}_4$, as shown by ED analyses (see below and Fig. 8a).

As a general trend, the use of a total pressure of $10.0 \, \text{mbar}$ resulted in significantly different growth habits and spatial organization (Fig. 6). In fact, at $400 \, ^\circ\text{C}$ the sample was characterized by the presence of pseudo-columnar nanostructures, with average lateral dimensions up to $\approx 100 \, \text{nm}$ and mean lengths of $260 \, \text{nm}$. A careful inspection enabled us to discern the presence of a spiral-type growth, similar to the one obtained in the CVD of $\text{CeO}_2$ nanostructures. A further increase of the deposition temperature to $450 \, ^\circ\text{C}$ led to the obtainment of peculiar anisotropic structures with a more marked faceting, comprising agglomerated pyramidal grains (typical sizes $= 400 \, \text{nm}$) formed by smaller triangular particles. The vanishing of the previously observed columnar growth was associated with the presence of secondary nucleation processes on the grain facets. The corresponding $\text{cs}$ structure was characterized by an uniform distribution of aggregates with heights up to $1 \, \mu\text{m}$, protruding from an homogeneous underlayer $\approx 90 \, \text{nm}$ thick. The increase in the grain size with respect to the sample obtained at $400 \, ^\circ\text{C}$ was in agreement with the occurrence of a kinetically controlled regime in the adopted temperature range (compare Fig. 7 and related comments). The growth of similar trigonal pyramids is a typical feature of $\text{Co}_3\text{O}_4$ nanomaterials, and has been associated with

**Fig. 6** $\text{Pr}$ and $\text{cs}$ FE-SEM images for cobalt oxide nanomaterials deposited under dry $\text{O}_2$, at a total operating pressure of $10.0 \, \text{mbar}$. 
the exposure of the low surface energy {111} planes, as often observed in face-centered cubic systems.\cite{34,35} Similar morphologies have already been reported in the CVD of Co$_3$O$_4$ systems.\cite{11,12,33,35,51}

At 500 °C, more compact pseudo-pyramidal aggregates with a higher interconnection were observed. The Cs pictures enabled us to identify a double-layer structure, with an underlying film ≈200 nm thick. Based on GIXRD analyses, that evidenced the co-existence of both CoO and Co$_3$O$_4$ under these conditions (Fig. 1b), and XPS analyses, that revealed the presence of the sole Co$_3$O$_4$ in the outermost regions, the underlayer composition was assigned to CoO (see above). Indeed, the validity of this hypothesis was confirmed by Cs TEM and EELS analyses (see Fig. 10 and 12).

In line with the above observations, this double-layer structure was not detected for the 550 °C-grown sample, which, according to GIXRD, was composed by the sole Co$_3$O$_4$ (see above). In this case, the morphology was characterized by a uniform compact structure, with an overall average thickness of 750 nm and faceted aggregates (θ = 600 nm) displaying 30 nm globular particles randomly distributed over their surface. The increase in the aggregate sizes agreed with the general enhancement of lateral growth expected at higher deposition temperatures.\cite{34,51}

Fig. 7 reports the Arrhenius plot of the growth rate values,\cite{32} that were calculated as the ratios between the overall specimen thickness, determined by FE-SEM Cs analyses, and the deposition duration (120 min in each case, see Experimental section). At a total pressure of 10.0 mbar under a dry O$_2$ atmosphere, a maximum growth rate close to 9.0 nm min$^{-1}$ could be obtained at 450 °C. In this case, a surface-reaction limited regime occurred for $T \leq 450$ °C, whereas for higher temperatures the growth rate remained almost constant. A similar saturation of the growth rates in an analogous temperature range has already been reported in the CVD of Co–O from an acetylacetonate Co(II) adduct.\cite{37} A linear fit of the experimental points (Fig. 7, continuous line) enabled us to evaluate the apparent activation energy related to the precursor decomposition under these conditions, as $E_a = 90.0$ kJ mol$^{-1}$. This value agreed to a good extent with previous literature reports on the CVD of polycrystalline cobalt oxides.\cite{11,12,33,35,51} In a different way, for $T \approx 450$ °C, the overall process was likely diffusion-limited. This transition in the deposition kinetics regime might contribute to the system microstructural and morphological evolution, as observed in Fig. 1b and Fig. 6.

A comparison with the experimental data pertaining to samples deposited at 3.0 mbar indicated systematically lower growth rate values in the latter case, a phenomenon which could be likely ascribed to a less efficient precursor conversion into cobalt oxides under these milder oxidative conditions.

For comparison, the values related to 10.0 mbar samples obtained under O$_2$ + H$_2$O atmospheres are also reported in Fig. 7. As can be noticed, at 400 °C water vapor presence enhanced the growth rate, whereas at 500 °C no appreciable variations were observed. This difference could be associated to a diffusion-controlled growth at 500 °C and/or to a less efficient water chemisorption with respect to 400 °C.

A valuable insight into the system nanostructure and morphology was gained by the combined use of advanced TEM, HRTEM, ED, HAADF-STEM and STEM-EELS techniques. Attention was preliminarily devoted to specimens deposited at a total operating pressure of 3.0 mbar. In this regard, Fig. 8 shows a detailed investigation of a sample deposited at 500 °C onto Si(100) under a dry O$_2$ atmosphere. The Cs TEM image in Fig. 8a evidenced the presence of a compact layer resulting from the 3D-agglomeration of relatively small grains, in agreement with the indications provided by the corresponding FE-SEM micrograph in Fig. 5. The ED pattern recorded in Cs (Fig. 8a) was consistent with the presence of CoO as the main phase, and the occurrence of blurred rings confirmed the obtainment of a nanocrystalline system.\cite{44} As indicated by the white arrows, it is worth highlighting the presence of an outermost layer = 12 nm thick of an apparently different composition. Indeed, the ED pattern taken in py (Fig. 8b) corresponded to that of Co$_3$O$_4$, whose formation might have occurred upon air exposure.\cite{45,46}

The HRTEM image for the same specimen, shown in Fig. 8c, indicated that the main layer consisted of randomly oriented CoO crystals, in agreement with the absence of preferred orientations in the XRD patterns (compare Fig. 1a). Between CoO grains and the Si substrate, a thin layer of amorphous SiO$_2$ ≈10 nm thick could be clearly discerned, whose formation likely took place during the growth process, as already observed in the CVD of copper oxides from Cu(hfa)$_2$·TMEDA.\cite{65}

Subsequently, the influence of water vapor introduction on the system morphology was investigated. To this regard, Fig. 9 compares representative bright-field py TEM images and corresponding ED patterns for samples grown at 10.0 mbar total pressure at 400 and 500 °C, under dry O$_2$ [(a), (b)] and under O$_2$ + H$_2$O [(c), (d)].Irrespective of the synthesis parameters, all the diffraction spots could be indexed with the normal spinel cubic-structured polycrystalline Co$_3$O$_4$ phase.\cite{47,48} Upon increasing the deposition temperature from 400 to 500 °C under dry O$_2$, an
increase of the average grain size from 25 ± 5 to 50 ± 5 nm took place. The introduction of water vapor in the reaction atmosphere resulted in a further grain coarsening (average size = 110 ± 5 and 200 ± 5 nm at 400 and 500 °C), along with the formation of more faceted aggregates (compare Fig. 9a–c, and Fig. 9b–d). This observation, in line with the more intense spots in the ED patterns, suggested a parallel enhancement of the nanodeposit crystallinity upon water vapor introduction, in line with the GIXRD results (see Fig. 2b and related comments).

Fig. 10 displays bright-field TEM images for the same samples of Fig. 9. For depositions performed under dry O₂ (Fig. 9a–b), a layer-like and relatively compact morphology was observed. Differently oriented CoO grains close to the substrate, along with an amorphous SiO₂ layer on Si(100), can be clearly discerned. For the sake of clarity, representative dₜₐₜ for the CoO crystal structure are marked in the cs ED pattern.
characterized by the growth of pyramidal-like structures, in agreement with the more faceted surface texture evidenced in Fig. 9c–d.

In order to further investigate this phenomenon, HRTEM measurements were undertaken and representative micrographs are shown in Fig. 11. As can be observed, both samples display a typical triangular faceting and are made up of nanoprisms, with a <100> growth direction and mainly {111} (Fig. 11, top) and {110}-type (Fig. 11, bottom) exposed surface planes. As already stated, similar trigonal pyramids are typically observed for Co3O4 nanomaterials and the {111} faceting corresponds to the exposure of high density, low surface energy planes, as recently reported for Co3O4 materials synthesized by a redox-precipitation route.31,42 Despite most of the nanoprisms appeared as single crystals (Fig. 11, top), others showed an extensive Moiré contrast in the high-resolution images, possibly indicating an overlap of differently oriented crystals. All these phenomena concurred in highlighting that H2O introduction in the reaction atmosphere promoted the formation of more structured crystalline Co3O4.

Further important information related to the role of water vapor arose from a more careful comparison of Fig. 10b and d, i.e. of the specimens grown at 500 °C, 10 mbar under O2 and O2 + H2O atmospheres, respectively. In particular, Fig. 10b evidenced a clear contrast change approximately 100 nm below the outermost surface (marked by arrows), possibly indicating the occurrence of a phase change at this position, whereas no such phenomena could be observed for the homologous specimen deposited at 500 °C under O2 + H2O (Fig. 10d). This observation was in line with GIXRD results, indicating that, for samples grown at 10.0 mbar in dry O2 at 450 and 500 °C, the CoO reflection at 2θ = 42.4° could be observed along with Co3O4 diffraction peaks (Fig. 1b).

The combined analyses of XPS/XE-AES results and of PV ED patterns, pointing out to the presence of the sole Co3O4 in the outermost region, suggested that CoO was confined in the inner system layers, as already anticipated. In order to attain a deeper insight into this phenomenon, a combined HAADF-STEM and EELS analysis on these samples was undertaken. As an example, data for the deposit grown at 450 °C, 10 mbar under dry O2 are proposed in Fig. 12. In particular, Fig. 12a displays an enlarged bright-field TEM image, showing the occurrence of pyramidal aggregates protruding from an underlying layer with an average thickness of ≈90 nm.

As a matter of fact, ED patterns recorded in cS (not reported) indicated that the phase composition of the bottom layer corresponded to CoO. To confirm this indication, EELS line-scans were used. Fig. 12c evidences the boundary between the two layers with different composition, whereas the white arrow marks the line-scan performed across the two layers. Fig. 12d reports the O-K and Co-L2,3 edges taken from the EELS spectra collected above and below the boundary evidenced in Fig. 12c. The fine structure of these edges, with onsets at 532 (O) and 779

Fig. 10 Cs TEM micrographs of cobalt oxide nanostructures grown at a total pressure of 10 mbar, at: (a) 400 and (b) 500 °C, under a dry O2 atmosphere; (c) 400 and (d) 500 °C, under an O2 + H2O atmosphere.

Fig. 11 HRTEM images of cobalt oxide samples grown under an O2 + H2O atmosphere at a total pressure of 10.0 mbar, at 400 (top) and 500 °C (bottom). In both cases, HR images of the regions marked by white squares and the corresponding ED patterns are reported as insets.
(Co) eV in the EELS spectra, are sensitive to the chemical environment of the probed area, thus representing a valuable mean for selective identification of cobalt oxide phases.\textsuperscript{73} In order to perform a reliable discrimination between CoO and Co\textsubscript{3}O\textsubscript{4}, two different indicators in the EELS fine structure were used in the present work. The first was the L\textsubscript{3}/L\textsubscript{2} lines ratio for Co-L edge, which has been reported to be a fingerprint for the Co valence state, thus enabling us to distinguish the occurrence of the sole CoO vs. Co\textsubscript{3}O\textsubscript{4}.\textsuperscript{74} The second marker was the shape of the O-K edge and its splitting into separate peaks, which are directly related to the sampled cobalt oxide phase.\textsuperscript{73} As can be observed in Fig. 12d, below the boundary (point B in Fig. 12c) the average L\textsubscript{3}/L\textsubscript{2} lines ratio for the Co peak was 4.9 ± 0.2, in good agreement with values reported for CoO.\textsuperscript{74} This finding was further corroborated by the analysis of the oxygen K-edge fine structure. In fact, the edge starting at 532 eV consisted of 3 closely spaced sub-peaks a, b and c, approximately 3–4 eV apart. This spectral shape, in combination with the intensity increase of the component located at 565 eV (\(*\)), is typical for the CoO structure, thus indicating that the inner layer was composed of CoO. Above the boundary, in the outermost system region (point A in Fig. 12c), the L\textsubscript{3}/L\textsubscript{2} lines ratio for the Co peak dropped to 2.9 ± 0.2, close to the value expected for Co\textsubscript{3}O\textsubscript{4}.\textsuperscript{74} In addition, the O-K edge starting at 532 eV was split into two main components, a and c, with a mutual energy separation of ≈ 12 eV. Furthermore, the intensity of both the b peak and of the signal centred at 565 eV (\(*\)) underwent a significant decrease. Overall, such features were typical for cobalt centers arranged in the Co\textsubscript{3}O\textsubscript{4} crystal structure.

Taken together, the present data confirmed the validity of the hypothesis presented in the discussion of XPS and XE-AES data (see above), i.e., that CoO formation took place in the first deposition stages, followed by its subsequent oxidation to Co\textsubscript{3}O\textsubscript{4} (the most thermodynamically stable phase) in the outermost deposit regions.\textsuperscript{58,59} A similar behavior has also been recently reported in the growth of Co\textsubscript{3}O\textsubscript{4} nanowires by oxidation of cobalt foils.\textsuperscript{23}

Conclusions

Cobalt oxide nanostructures were grown on Si(100) substrates by an innovative CVD route at temperatures between 300 and 550 °C, using Co(hfa)\textsubscript{2}·TMEDA as the molecular source in O\textsubscript{2}/O\textsubscript{2} + H\textsubscript{2}O reaction atmospheres. Experimental results evidenced the effectivenss of the proposed precursor for the production of high purity cobalt oxide nanostructures. In addition, the important role of the growth temperature and reaction
atmosphere in determining the system phase composition and morphological organization was evidenced.

As a general rule, the selective formation of Co$_2$O$_4$ was favoured by an increased growth temperature and total pressure (from 3.0 to 10.0 mbar). In the latter case, mixed CoO + Co$_2$O$_4$ nanosystems could be obtained at substrate temperatures of 300–500 °C, whereas single-phase Co$_3$O$_4$ nanostructures were synthesized at 550 °C and in the presence of H$_2$O in the reaction atmosphere. Beside exerting an oxidizing action towards Co(II) centers, water vapor had a peculiar influence on the system morphology, producing highly crystalline Co$_3$O$_4$ pyramidal nanoaggregates with a pronounced triangular faceting. Conversely, less oxidative conditions (3.0 mbar) enabled the obtainment of CoO nanosystems, displaying a morphological evolution from anisotropic nanoaggregate assemblies to homogeneous compact coatings on increasing the deposition temperature.

In conclusion, the proposed route is an amenable and versatile strategy for the simultaneous control of both the phase composition (CoO vs. Co$_2$O$_4$, mixed oxide systems) and the morphological organization of the resulting nanostructures, providing important guidance for the obtainment of cobalt oxides with prescribed features. The present results disclose interesting perspectives concerning their eventual functional applications in solid state gas sensing devices, as well as in innovative electrodes for Li-ion batteries, an unprecedented use of CVD cobalt oxide materials.

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