Hexanuclear copper–nickel and copper–cobalt complexes for thin film deposition of ceramic oxide composites†

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Heterobimetallic molecular Cu–Ni and Cu–Co complexes \([\text{Cu}_2\text{Ni}_4\text{acac}_2(\text{dmae})_2(\text{dmaeh})_2(\text{OH})(\text{TFA})_6] \) (1) and \([\text{Cu}_2\text{Co}_4(\text{acac})_2(\text{dmae})_2(\text{dmaeh})_2(\text{OH})(\text{TFA})_6] \) (2) \([\text{dmae}=N,N\text{-dimethylaminoethanol},\text{TFA}=\text{trifluoroacetic acid and acac}=2\text{-pentanedionato}] \) were prepared and tested as precursors for the deposition of mixed metal oxide composite thin films. The complexes were synthesized by reaction of the tetrameric copper(II) complex \([\text{Cu}(\text{dmae})(\text{TFA})_4]\) with \(\text{M(acac)}_2\cdot x\text{H}_2\text{O} \) \((\text{M}=\text{Ni}, x=2; \text{Co}, x=1) \) in THF and were characterized by melting point, elemental analysis, FT-IR spectroscopy, TG/DTG and single-crystal X-ray diffraction. The complexes are isomorphous and crystallize in the triclinic centrosymmetric space group \(\text{P}1\). Aerosol assisted chemical vapour deposition (AACVD) studies carried out on (1) and (2) showed that they are promising precursors for the deposition of thin films of crystalline CuO–NiO and CuO–CoO composites, respectively. The size, shape, surface morphology, microstructure, chemical composition and crystallinity of the resulting mixed-metal oxide composite thin films were analysed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The analysis proved that the thin films are crystalline, uniform, smooth and tightly adherent to the substrates.

Introduction

Besides numerous materials science related applications,1 mixed metal oxides have found their way into the production of ceramic semiconductor devices, microelectronics including photoluminescent devices, catalysts and ceramic membranes for solid oxide fuel cells. The key factors that determine the potential applications of mixed metal oxide ceramics include stoichiometry and homogeneity of composition, crystal morphology, surface area, and their particle size and shape.2,3 Various methods have been adopted for the synthesis of nano-structured mixed metal oxides, such as mechanochemical processing,4 sol–gel reaction processes,4,6 solvothermal,7 hydrothermal8 and sonochemical methods, and chemical vapor deposition, to name just a few. Chemical vapour deposition that involves single-source precursors (SSP) provides relatively low deposition temperatures compared to the solid state or multi-source precursor approaches9,10 which allows a greater control of the stoichiometry in the final oxide. In addition, the use of SSPs makes it possible to access new phases that are not available at higher reaction temperatures and thus provides more flexibility in the preparation of heterometallic oxide materials than with other more conventional methods.11 However, one of the most significant challenges in developing single-source precursor methods for the preparation of mixed-metal oxide materials is the availability of suitable precursors and accessibility of synthetic approaches towards their synthesis that allow gaining control over the stoichiometry of the individual metal species in relation to one another in the SSP and thus the final product. So far, only a few heterometallic late-transition complexes have been explored as SSPs towards mixed-metal oxides.

Metal oxides find applications in heterogeneous catalysis, sensors, photocatalysis,12 photoelectrochemical cells,13 electrochromic windows and electrical and optoelectronic devices.14 This has ignited the interest in mixed metal oxides such as copper–cobalt and copper–nickel composites. Because of their good response and recovery time, devices made from mixed metal CuO–NiO composites have been used in humidity sensing devices and in multi-layered capacitors.15,16 CuO–CoO based mixed metal oxides are promising catalysts for the synthesis of methanol and higher alcohols because of their high selectivity for.
formation of alcohols rather than hydrocarbons. They not only possess high catalytic activity but also high stability at relatively low pressure.\textsuperscript{17} Also they are active in CO oxidation\textsuperscript{18} and in the synthesis of precursors for polycarbonates which are used as a substitute for metals and glasses with high strength, transparency and heat resistance.\textsuperscript{19} The activity of such mixed metal oxide catalysts is heavily influenced by the method of their preparation and other factors that affect the electronic structure.

Among the alternative thin film deposition techniques, aerosol-assisted chemical vapour deposition (AACVD) is a relatively simple and easy route to deposit metal oxides. The advantages of AACVD are that a single solution source can be used to fabricate multicomponent layers while ensuring both reproducibility and the presence of all necessary components stoichiometrically in the final product (typically in the form of a thin film). High quality thin films can readily be produced by controlling the size of the aerosol droplets \textit{via} variation of the frequency of the ultrasonic modulator. The composition and architecture of the films can be easily controlled \textit{via} tailoring of experimental parameters, such as solution concentration, solvent, nature of the carrier gas, carrier gas flow, deposition time, and substrate temperature, to name just a few. It is the multiplicity of these adjustable parameters that indicates the advantages of the AACVD techniques.

Recently work was undertaken to develop heterobimetallic precursors of copper with main group and transition metals for multiplicity of these adjustable parameters that indicates the solvent, nature of the carrier gas, carrier gas flow, deposition architecture of the films can be easily controlled via an atmosphere of flowing nitrogen gas at a heating rate of thermal analyzer. The measurements were carried out under TGA of the complexes were performed using a Seiko SSC/S200

**Synthesis of [Cu$_2$Ni$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)(TFA)$_6$](2)**

Complex (2) was prepared by the same procedure as that adopted for the preparation of complex (1). The quantities used are as follows: 0.75 g (7.3 mmol) [Cu(dmae)(TFA)$_4$], 1.5 g (3.25 mmol) Co(acac)$_2$:H$_2$O and 25 ml THF. Yield 75%, mp 190 °C. Analysis: calc. for C$_{38}$H$_{58}$N$_4$O$_{22}$F$_{18}$Co$_4$Cu$_2$: C, 28.03; H, 3.59; N, 3.44%; found: C, 28.06; H, 3.47; N, 3.36%. FT-IR/cm$^{-1}$: 3425(b), 2903(m), 2876(m), 1591(s), 1513(s), 1460(m), 1390(m), 1331(w), 1277(m), 1205(w), 1106(m), 1019(m), 536(m), 453(w). TGA: 180–240 °C (14.10% wt. loss); 240–280 °C (45.1% wt. loss); 280–425 °C (40.80% wt. loss); (residue left 27.10%).

**Experimental section**

**Materials and methods**

All manipulations were carried out under an oxygen free nitrogen atmosphere by employing standard Schlenk line and a glove box technique. Solvents were rigorously predried and distilled over calcium oxide, and redistilled from sodium metal/benzophenone, while N,N-dimethylaminoethanol (dmaeH) was dried by refluxing over K$_2$CO$_3$ for 10 h and distilled immediately before use. Ni(acac)$_2$:2H$_2$O, Co(acac)$_2$:H$_2$O and lithium were purchased from Aldrich. [Cu(dmae)(TFA)$_4$]$_2$ was prepared according to literature procedures. Melting points were located in capillary tubes using an electrothermal melting point apparatus, model MP.D Mitamura Riken Kogyo (Japan), and are uncorrected. FT-IR spectra were recorded on a single reflectance ATR instrument (4000–400 cm$^{-1}$, resolution 4 cm$^{-1}$). Controlled thermal analyses (TGA) of the complexes were performed using a Seiko SSC/S200 thermal analyzer. The measurements were carried out under an atmosphere of flowing nitrogen gas at a heating rate of 10 °C min$^{-1}$.

**Synthesis of [Cu$_2$Ni$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)(TFA)$_6$](1)**

0.75 g (7.3 mmol) of [Cu(dmae)(TFA)$_4$]$_2$ was added to a solution of 1.5 g (3.25 mmol) Ni(acac)$_2$:2H$_2$O in 25 ml of THF at room temperature. After stirring for three hours, the solution was filtered through a cannula to eliminate traces of solid residue and the reaction mixture was evaporated to dryness under reduced pressure. The solid was washed with hexane and redissolved in 10 ml of THF to give a crystalline product after one week. The complex crystallized in 68% yield, mp 184 °C. Analysis: calc. for C$_{38}$H$_{58}$N$_4$O$_{22}$F$_{18}$Ni$_4$Cu$_2$: M$_w$ 1626.74, C, 28.05; H, 3.59; N, 3.44%; found: C, 27.94; H, 3.43; N, 3.26%. FT-IR/cm$^{-1}$: 3435(b), 2953(w), 2867(m), 1591(s), 1513(s), 1460(m), 1390(m), 1331(w), 1277(m), 1205(w), 1106(m), 1019(m), 536(m), 453(w). TGA: 180–240 °C (14.10% wt. loss); 240–280 °C (45.1% wt. loss); 280–425 °C (40.80% wt. loss); (residue left 27.10%).

**Deposition of thin films by AACVD**

Composite metal oxide thin films were grown by AACVD from 0.1M solution of (1) and (2) prepared in THF on...
commercially available glass substrates (1 × 2 cm), which were
cleaned prior to use using distilled water, acetone and finally
ethyl alcohol. Detail of the AACVD assembly is described
elsewhere.28 The precursors were dissolved in the solvent and
transformed into an aerosol mist by using an ultrasonic
humidifier at room temperature. The aerosol was carried into
the reactor via a stream of nitrogen gas through a regulator to
obtain a laminar flow. Depositions were conducted for a
period of 30 min. The exhaust from the reactor was vented
directly into the extraction system of the fume cupboard. Once
the deposition was complete the aerosol line was closed, and
nitrogen was continued to flow over the substrate and cool the
films to about 40 °C before they were removed from the reaction
chamber for studies. The morphology and nano-
structure of the thin films were controlled by altering the
deposition parameters. Thin films with well-defined compact
structures were deposited at four different temperatures, 350,
400, 450 and 500 °C, using THF as the solvent.

The films prepared by AACVD were highly adhesive to the
FTO substrate and passed the Scotch tape test. Visual observations
showed that the films had a good surface coverage, uniformity and
reproducibility.

Characterization of thin films

Scanning electron microscopic (SEM) studies were carried out
using a FEG-SEM Philips XL30 electron microscope to study
the structure and morphology of thin films. EDX was used to
calculate the composition (metal ratio) of the films. XRD peak
patterns of the thin films were collected with a Bruker AXS D8
diffractometer using monochromatic Cu-Kα radiation.

Results and discussion

Single crystal X-ray studies

The two isomorphous complexes [Cu2Ni2(acac)2(dmae)2
(dmaeH)2(OH)2(TFA)6] (1) and [Cu2Co4(acac)4(dmae)2
(dmaeH)2(OH)2(TFA)6] (2) were prepared in 68% and 75%
yields, respectively, by reacting appropriate amounts of tetra-
meric N,N-dimethylaminoethantotrifluoroacetato copper (ii)
with bis-2,4-pentanedione nickel (ii) and bis-2,4-pentanedione
cobalt (ii) as shown in the chemical equation below. The
complexes are soluble in common organic solvents such as
toluene, tetrahydrofuran and alcohols and are stable in air.

\[
\begin{align*}
6/4 [\text{Cu(dmae)}(\text{TFA})_4 + 4 \text{M(acac)}_2 & \times \text{H}_2\text{O} \\
M &= \text{Ni, Co, } x = 1, 2 \\
\text{THF} & \\
[\text{Cu}_2\text{M}_4(\text{acac})_2(\text{dmae})_2(\text{dmaeH})_2(\text{OH})_2(\text{TFA})_6] & + 2 \text{Cu(acac)}_2 + 2 \text{Cu(dmae)}_2 + x \text{H}_2\text{O}
\end{align*}
\]

Complexes (1) and (2) were characterized by elemental
analysis, FTIR spectroscopy, thermogravimetric analysis and
their structures were established by single crystal X-ray
diffraction analysis. Both complexes crystallize in the triclinic
space group \(P\overline{1}\) with one molecule per unit cell. Each of
the \([\text{M}_2\text{Cu}_2(\text{acac})_2(\text{dmae})_2(\text{dmaeH})_2(\text{OH})_2(\text{TFA})_6]_n\) molecules
\((M = \text{Ni, Co})\) is centrosymmetric and is located at a crystallo-
graphic inversion center. Crystal data and structure refinement
parameters for complexes (1) and (2) are given in Table 1 and
an ORTEP-style diagram of the molecular structure of (1) is
displayed in Fig. 1. The isomorphous molecular diagram for
complex (2) is given in (Fig. S1, ESI†). Selected bond distances
and bond angles for complexes (1) and (2) are also given in
Table S1 and Table S2 (ESI†), respectively.

As the two compounds crystallize in an isomorphous setting,
only one of them (cobalt complex) will be discussed in detail.
The two copper and four cobalt ions are linked together by oxygen
and nitrogen atoms from the chelating and bridging acac anions,
briding and non-bridging TFA anions, from chelating/bridging
dmae ligands, and by the \(\mu_2\)-OH bridging hydroxyl anions. All
copper ions have a non-metal coordination number of five with a
CuO4N ligand set which comprises a chelating/bridging dmae
group \([\text{Ni}, \text{O}]\) (the oxygen of which as a bridge towards
cobalt ions Co2 and Co2i generated by the inversion center;
symmetry operator \((i): -x + 1, -y + 1, -z + 1)\), an oxygen
atom of a triply coordinated hydroxyl group \([\text{O11}]\) connecting
Cu1 with Co1 and Co2, a \(\mu_2\)-oxygen atom O4 of a bridging acac
ligand (which chelates Co2 and O7 of a bridging TFA anion
connecting to Co1). A structural chemdraw diagram of the M–O
core of (2) is shown in Fig. 2. The M–O core for complex (1)
is given in Fig. S2, ESI†. The CuO4N coordination environment of
the copper ion is distorted square pyramidal with an
[O11–Cu1–N1] bite angle of 85.89(8)° (less than 90°) and an
[O1–Cu1–O4] angle of 78.40(7)° (smaller than 90°). Also the
[Cu–O] bond distance of Cu1 to the apical oxygen atom O4 is
much longer (2.394(2) Å) than all other [Cu–O] bond lengths in
complex (1), which ranges between 1.946(2) Å for [Cu1–O11] and
1.955(1) Å for [Cu1–O1].

The cobalt(ii) centres have a coordination environment
close to octahedral. There are two crystallographically distinct
cobalt ions in each of the molecules. The central cobalt atom,
Co2, is bonded to one chelating/bridging terminal acetyl-
acetate anion in an \(\eta^1\)-manner \([\text{O3, O4}]\), to the oxygen
atoms of two triply bridging dmae molecules \([\text{O1, O1i}]\) and
to one triply bridging hydroxyl anion \([\text{O11}]\). One TFA molecule
(O5 and O6) bridges Co2 with Co2i generated by the inversion center;
[Co2–O9] and [Co2–O1], respectively, and are in general
agreement with those found in similar complexes such as
[Co4Ta2(OMe)12]31 or [Co4(acac)4(OMe)4(MeOH)4]30.

The coordination sphere of the second cobalt ion, Co1, consists
of two oxygen atoms \([\text{O6, O8}]\) of a bridging TFA
anion, one oxygen O11 of triply bridging hydroxyl group, one
oxygen atom O9 of a non-bridging TFA and the oxygen and
nitrogen atoms \([\text{O2, N2}]\) of a chelating dmae ligand forming a
distorted octahedron with bond lengths in the range of
2.047(2) Å to 2.113(2) Å which is in coherence with the
Table 1 Crystal data and refinement parameters for the complexes [Cu$_2$Ni$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)$_2$(TFA)$_6$] (1) and [Cu$_2$Co$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)$_2$(TFA)$_6$] (2)

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C$<em>{38}$H$</em>{58}$Ni$<em>4$O$</em>{22}$</th>
<th>C$<em>{38}$H$</em>{58}$Cu$_2$Ni$<em>4$O$</em>{22}$</th>
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</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>1626.80</td>
<td>1627.68</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100 (2)</td>
<td>100 (2)</td>
</tr>
<tr>
<td>Wavelength/Å</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>P1</td>
<td>P1</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>9.7276 (18) Å</td>
<td>9.7417 (11) Å</td>
</tr>
<tr>
<td>b</td>
<td>106.364 (3) Å</td>
<td>106.594 (2) Å</td>
</tr>
<tr>
<td>c</td>
<td>10.3244 (19) Å</td>
<td>10.3399 (12) Å</td>
</tr>
<tr>
<td>α</td>
<td>16.045 (3) Å</td>
<td>100.096 (2) Å</td>
</tr>
<tr>
<td>β</td>
<td>99.83 (3) Å</td>
<td>16.1733 (18) Å</td>
</tr>
<tr>
<td>γ</td>
<td>100.640 (3) Å</td>
<td>99.876 (2) Å</td>
</tr>
<tr>
<td>Volume/Å$^3$</td>
<td>1475.5 (5)</td>
<td>1494.1 (3)</td>
</tr>
<tr>
<td>Density (calc.)/mg m$^{-3}$</td>
<td>1.831</td>
<td>1.809</td>
</tr>
<tr>
<td>Absorption coefficient/mm$^{-1}$</td>
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<td>1.914</td>
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<tr>
<td>F(000)</td>
<td>822</td>
<td>818</td>
</tr>
<tr>
<td>Formula weight</td>
<td>0.55 × 0.40 × 0.08</td>
<td>0.44 × 0.19 × 0.06</td>
</tr>
<tr>
<td>α Range for data collection (°)</td>
<td>1.37 to 28.28</td>
<td>1.35 to 28.28</td>
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<tr>
<td>Index ranges</td>
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<td>−12 ≤ h ≤ 12, −13 ≤ k ≤ 13, −21 ≤ l ≤ 21</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>15203</td>
<td>15308</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>7296 (R(int) = 0.0273)</td>
<td>7379 (R(int) = 0.0231)</td>
</tr>
<tr>
<td>Max. and Min. transmission</td>
<td>0.846 and 0.531</td>
<td>0.892 and 0.603</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Goodness of fit on F$^2$</td>
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<td>1.166</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>$R_1$ = 0.0363, w$R_2$ = 0.0985</td>
<td>$R_1$ = 0.0391, w$R_2$ = 0.1033</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1$ = 0.0445, w$R_2$ = 0.1087</td>
<td>$R_1$ = 0.0464, w$R_2$ = 0.1078</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>1.153 and −0.662 e × Å$^{-1}$</td>
<td>0.914 and −0.648 e × Å$^{-1}$</td>
</tr>
</tbody>
</table>

Fig. 1 ORTEP-style drawing showing the molecular structure of [Cu$_2$Ni$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)$_2$(TFA)$_6$] (1). Thermal ellipsoids are at the 50% probability level. Dotted lines indicate hydrogen bonding interactions. Symmetry operator (i): −x + 1, −y + 1, −z + 1.

The [Ni–O] distances observed in complex (1) are 2.033(2) Å to 2.088(2) Å, which are in agreement with those found in the literature but slightly shorter than the Co–O bonds of the cobalt complex (2).

Fig. 2 Chemdraw sketch of the M–O central core of [Cu$_2$Co$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)$_2$(TFA)$_6$] (2).

Thermal decomposition study and deposition of thin films

Heterobimetallic complexes (1) and (2) were tested as sources of copper oxide–metal oxide composite materials. The thermal decomposition of (1) and (2) was investigated by TGA analysis under a flow of nitrogen gas (25 ml min$^{-1}$), and the results are presented in Fig. 3. The thermograms show that the complexes go through three different decomposition steps when heated in the temperature range of 50 to 500 °C. The initial weight loss of complex (2) in the temperature range of 50–100 °C might be due to loss of solvent. However inception of major decomposition steps at 180 °C of complexes (1) and (2) is common as shown by DTG (Fig. 3). At this stage complexes (1) and (2) experience a weight loss of 14.10% and 10.10%, respectively. Complex (1) undergoes two more decomposition steps at 280 °C and 345 °C and the last thermolysis stage of complex (2) commences around 325 °C and is complete at 490 °C. All pyrolysis stages appear to be complex in nature and (1) and (2) seem to have separate decomposition pathways but arrive at the same plateau, representing a residual mass of 27.10% and 27.82%, respectively. The final weight agrees well with residues of CuO–NiO and Cu$_2$O–CoO, respectively. In these complexes each metal centre
Considering the basic concept of homogeneous and heterogeneous deposition reactions to control the morphology of thin films and taking the decomposition data from TGA, the deposition parameters were controlled. The AACVD reactor temperature was initially adjusted to 350 °C and then increased systematically to study the influence of temperature on film morphology and structure. Thin films were deposited by following the procedure as described in the experimental section. The films deposited exhibited excellent adhesion properties to the substrate as verified by the “scotch tape test” and are stable in air and moisture. The films reflected light in multi-shaded colours and the reflection varied as the particle size and thickness of the films were changed. The films show a black appearance after 30 min deposition and have uniform coverage over the 1 × 2 cm substrate.

**Structural characterization of thin films**

XRD patterns of thin films deposited from precursor (1) at 350 °C, 400 °C, 450 °C and 500 °C are shown in Fig. 4. The crystallinity and structural changes that occur in the film when the deposition temperature is gradually increased from 350 °C to 500 °C are reflected in the diffractogram. The crystallinity of the film increases with the increase of the deposition temperature to 500 °C. All the peaks correspond to only CuO–NiO phases and were indexed successfully on the basis of monoclinic CuO and cubic NiO phases, respectively (ICCD.01-089-5895 and ICCD.00-004-0835). The XRD phase crystalline analysis shows that the CuO and NiO phases are in the ratio of 1:1.95 for all the deposition temperatures, indicating that complex (1) decomposes quantitatively under AACVD deposition conditions according to the above thermal decomposition equation. The NiO diffraction lines are in good agreement with reported values of intensity and d-spacing of NiO in the bunsenite form in the cubic space group $I\bar{m}3m$ and in the lattice dimensions of $a = b = c = 4.1771$ Å. The CuO found in the films deposited from complex (1) is tenorite with a monoclinic $C2/c$ space group, with cell parameters $a = 4.68$, $b = 3.42$, $c = 5.12$, and $\beta = 99.30°$. The crystallite size

![Figure 3](image-url)  
**Fig. 3** Thermogravimetric curve showing loss in weight with increase in temperature for complexes (1) and (2).

![Figure 4](image-url)  
**Fig. 4** X-Ray diffractogram of the thin films obtained from precursor (1) X = CuO [tenorite, 01-089-5895] and Y = NiO [bunsenite, 00-004-0835]. (a) = 350 °C, (b) = 400 °C, (c) = 450 °C and (d) = 500 °C.

The CVD process is largely governed by the homogenous and heterogeneous chemical reactions and nucleation which in turn depend on the deposition temperature which hence affect the morphology and structure of the films. In AACVD, the first step consists of the aerosol delivery to the heated zone in which solvent evaporation and precursor vaporization starts. The film is deposited as a result of decomposition of vaporized precursor either in the gas phase (homogeneous) or on the heated substrate (heterogeneous). Hence the thin film formation in the AACVD process is either due to individual homogeneous or heterogeneous reactions or a combination of both. It is the decomposition type and the ratio between homogeneous and heterogeneous processes that governs the morphology, structure, and composition of the thin films. The ratio between these two reactions can be adjusted by appropriately controlling the deposition parameters (e.g. preheating temperature, the substrate temperature, the carrier gas flow rate, the type of solvent, and the concentration of precursor solution) which in turn determine the type of chemical reaction by controlling the chemical kinetics and thermodynamics of the deposition process which directly control the structure, morphology, and composition of the resulting thin films.
Calculated using the Scherrer equation was 38.7 and 26.4 nm for CuO and NiO, respectively, at 500 °C.

Fig. 5 shows the XRD patterns of the thin films deposited in the temperature range of 350–500 °C from complex (2). The diffractograms show the formation of a Cu$_2$O–CoO composite with relative peak intensities and positions of the diffraction peaks at 2θ values of 36.44°, 42.33°, 61.40° and 73.55° corresponding to Cu$_2$O and CoO (in ICCD.01-078-2076 and ICCD.03-065-2902 respectively). The XRD phase crystalline analysis shows that the Cu$_2$O and CoO phases are in the ratio of 0.93 : 3.07 for all the films deposited at 450 and 500 °C, indicating that complex (2) decomposes quantitatively under AACVD conditions according to the above thermal decomposition equation. The phase ratio varies slightly for the lower decomposition temperatures which may be due to the very low crystalline nature of the deposited material. The Cu$_2$O found in the films deposited from complex (2) is in its cubic cuprite form with the primitive space group $Pn\bar{3}m$, with cell parameters $a = b = c = 4.2690$ and $\alpha = \beta = \gamma = 90°$. The crystallite size calculated using the Scherrer equation was 45.9 nm for both Cu$_2$O and CoO phases as all the high intensity peaks in the XRD pattern correspond to both Cu$_2$O and CoO at 500 °C.

**Thin film surface characterization**

Typical SEM images of the thin films prepared using THF as a deposition solvent at four different deposition temperatures (350, 400, 450 and 500 °C) for the complexes (1) and (2) are presented in Fig. 6 and 7. The effect of the nature of the precursor on the deposited films can be seen from the SEM micrographs of the films of CuO–NiO and Cu$_2$O–CoO composites. Although the elemental composition of all the deposited films remains the same, the morphologies of the films are different in each case and seem to depend on the nature of the complex and the temperature of deposition. SEM micrographs of the films deposited at different temperatures of 350 °C, 400 °C, 450 °C and 500 °C from precursor (1) are shown in Fig. 6(a–d). The micrograph of the film deposited at 350 °C indicates formation of dense nanocrystalline particles without any distinguishable features. At 400 °C the morphology of the film completely changes from dense particles to a well developed inter-grown urchin like structure. When the deposition temperature was increased to 450 °C (Fig. 6c) the film morphology showed the growth of fine wire-like features with short edges. A further increase of the deposition temperature to 500 °C resulted in a fine network of thin wires of varying lengths.

**Fig. 5** X-Ray diffractogram of the thin films obtained from precursor (2); X = Cu$_2$O [cuprite, 01-078-2076] and Y = CoO [03-065-2902]. (a) = 350 °C, (b) = 400 °C, (c) = 450 °C and (d) = 500 °C.

**Fig. 6** SEM micrographs of films deposited from precursor (1) at (a) 350 °C, (b) 400 °C, (c) 450 °C and (d) 500 °C.

**Fig. 7** SEM micrographs of films deposited from precursor (2) at (a) 350 °C, (b) 400 °C, (c) 450 °C and (d) 500 °C.
the atomic% of Cu/M for the films deposited at different temperatures using complexes (I) and (2) by AACVD. The EDX analyses also confirm clean decomposition of the complexes without incorporation of any impurities, which is in agreement with the hypothesis that the bridging oxygen atoms with metal ensure the formation of impurity-free ceramic oxides during the decomposition process.

Conclusions

This work presents syntheses of hexanuclear complexes [Cu$_2$Ni$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)(TFA)$_6$]$_2$ (1) and [Cu$_2$Co$_4$(acac)$_2$(dmae)$_2$(dmaeH)$_2$(OH)(TFA)$_6$]$_2$ (2) by reaction between M(acac)$_2$-H$_2$O, [M = Ni, x = 2; Co, x = 1] and the tetrameric copper(ii) complex [Cu(dmae)(TFA)$_4$]$_4$ in a molar ratio of 1:4, and their clean decomposition to crystalline CuO-NiO and Cu$_2$O-CoO thin films under mild AACVD conditions. The complexes possess a structure in which two copper and four Ni/Co atoms are bridged by oxygen atoms of dmae, acac and TFA groups and thermally decompose to mixed-metal oxide residues. FT-IR studies of the residues from TG and EDX studies indicate the absence of any carbonate impurities. The XRD and SEM of the thin films show formation of CuO–NiO and Cu$_2$O–CoO with cubic and monoclinic crystal system and texture, morphology and orientation of composite thin films are strongly dependent on the AACVD parameters. The characterization of the films provides useful information for their possible applications in the field of catalysis, electrocatalysis and solid oxide fuel cells.

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Notes and references