Temperature-controlled Deposition of Copper(i) Oxide and Metallic Copper Nanostructures from Single-source Molecular Precursor

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A simple method of depositing morphology- and phase-tailored thin films of copper(i) oxide and metallic copper from \([\text{Cu(dmae)}(\text{TFA})]_4\cdot\text{CH}_2\text{Cl}_2\) (1), where dmae is N,N-dimethylaminoethanolato and TFA is trifluoroacetato, on glass substrates by aerosol-assisted chemical vapour deposition is demonstrated. The tetrameric precursor 1 was synthesized and its structure was determined by single-crystal X-ray crystallography. Precursor 1 was applied for the deposition of nanostructured thin films of copper(i) oxide and copper nanowires at 250 and 375°C respectively. The deposited thin films were characterized by powder X-ray diffraction, field emission scanning electron microscopy, energy-dispersive X-ray diffraction, and ultraviolet-visible spectroscopy. The results indicate that the phase and morphology of the deposited material are strongly dependent on deposition temperature. UV-vis studies reveal that copper(i) oxide films with a band gap of 2.48 eV may find possible applications in tandem photoelectrochemical devices as light-absorbing material.

Introduction

Copper has a wide range of diverse applications in the electronic industry, communications, and electrical power lines, and many more due to its high thermal and electrical conductivity and considerable resistance to atmospheric corrosion.\(^1\) Copper is a preferred choice for use in plumbing and transport of potable water not only because of its exceptional corrosion resistance, but also owing to its biocidal effects on some bacterial species.\(^2\) Less resistive copper metal has replaced aluminium in Al thin-film wiring in order to decrease resistive-capacitive (RC) delay.\(^3\)

Copper-based materials (Cu, CuO, CuO) having dimensions of the order of a few nanometers have received considerable interest in the last few decades.\(^4\) They have potential applications in sensors, superconductors and semiconducting devices.\(^6,7\) CuO, CuO, and Cu2O/CuO (mixed phase) nano-composite thin films have been proved to be an ideal material as the anode for Li ion batteries,\(^8\) while Cu2O is a p-type semiconductor and is a potential candidate for photovoltaic devices.\(^9\) Similarly, copper nanostructures possess excellent catalytic and optical properties.\(^7\)

Recent efforts\(^9\) to synthesize nanostructures with well-defined geometries have opened up new possibilities for developing copper-based nanomaterials and thin films by sono-chemical, hydrothermal, electrodeposition,\(^1\) and solution methods.\(^11,12\) Arrays of copper nanorods have been synthesized by these preparative routes; however, they do not control the size, shape and structure of the as-prepared copper-based nanostructures. Moreover, all these methods rely on a dual source, which often results in mixed phases of Cu2O–CuO in deposited materials. The properties of nanostructured materials vary with composition, size and shape,\(^10\) therefore for technological applications, a strict control of these properties is always desirable.

Single-source molecular precursors (SSPs) have been of considerable interest for the deposition of thin films by chemical vapour deposition (CVD). Air and moisture stability, ease of handling, comparatively low toxicity, and lower decomposition temperatures are unique features that make them versatile for coating and depositing thin films. Further, the use of only a single-source molecular precursor in the CVD supply stream minimizes the probability and extent of pre-phase reaction and contamination in deposited films. Moreover, intrinsic control of the film stoichiometry can also be realized by employing SSPs.\(^13\) Numerous aminoalkoxide and aminoalkoxide carboxylate complexes of transition metals have been synthesized and used for CVD applications.\(^14,15\)

Here, we report the synthesis and characterization of a new tetranuclear complex, namely \([\text{Cu(dmae)}(\text{TFA})]_4\cdot\text{CH}_2\text{Cl}_2\) (1), where dmae is N,N-dimethylaminoethanolato and TFA is trifluoroacetato, which was used to fabricate thin films by aerosol-assisted chemical vapour deposition (AACVD) on glass...
is believed that this cubane-like caged complex breaks down in the spectrum are due to the corresponding to TFA ligands. The low-frequency absorptions caused by TFA. The difference \( \Delta \) which is consistent with reported values. [16] The spectrum of and the absorption band at \( \nu \) due to the presence C–F and C–O bonds, 1 due to the stability under MS conditions.

**Results and Discussion**

**Synthesis and Characterization**

Cu(OCH\(_3\))\(_2\) reacts with \( \text{N,N\text{-dimethylaminoethanol (dmaeH)}} \) and trifluoroacetic acid (TFAH) in a 1 : 1 : 1 molar ratio to give complex 1 in THF at room temperature as shown in Eqn 1.

\[
\text{4CuCl}_2 \xrightarrow{\text{8LCH}_3\text{OH}_2} \text{4Cu(OCH}_3)_2 \xrightarrow{\text{4CF}_3\text{COOH/CH}_2\text{Cl}_2} \text{[Cu(dmae)(TFA)]_4 CH}_2\text{Cl}_2 + \text{8CH}_3\text{OH}
\]

The progression of the reaction was indicated by the dissolution of Cu(OCH\(_3\))\(_2\) in the reaction mixture to give a greenish-blue solution. The complex was successfully isolated from the greenish-blue solution and characterized by melting point, elemental analysis, Fourier-transformation infrared (FT-IR) spectroscopy, mass spectrometry, and single-crystal X-ray diffraction. In the FT-IR spectrum of 1, characteristic bands at 1414 and 1593 cm\(^{-1}\) are asymmetric and symmetric CO\(_2\) vibrations caused by TFA. The difference \( \Delta \nu \) between \( \nu_{\text{as}}\text{CO}_2 \) and \( \nu_{\text{s}}\text{CO}_2 \) vibrations suggests the carboxylate unit of the TFA ligand to be bridging. The absorption bands attributed to the \( \mu\text{-dmae} \) (\( \nu(C\text{-H}) \)) are clearly observed in the range 2800–3000 cm\(^{-1}\) and the absorption band at \( \approx 530 \text{ cm}^{-1} \) is assigned to Cu–O, which is consistent with reported values. [16] The spectrum of 1 was also characterized by two strong absorptions in the range 1120–1210 cm\(^{-1}\) due to the presence C–F and C–O bonds, corresponding to TFA ligands. The low-frequency absorptions in the spectrum are due to the \( \nu(C\text{-N}) \) vibrations. [17] In the atmospheric pressure chemical ionization–mass spectra (APCI-MS), complex 1 does not show a molecular ion peak; however, it is believed that this cubane-like caged complex breaks down into various ions of different \( m/z \) ratios with the base peak at \( m/z \) 860.7 corresponding to \([\text{Cu}_4(\text{dmae})_2(\text{TFA})_3] \text{^+}\). This disintegration of 1 indicates its low stability under MS conditions.

**Single-crystal Structure Analysis**

The molecular structure of 1 is shown in Fig. 1a and the selected geometrical data are listed in Table 1. The single-crystal X-ray structure shows that the asymmetric unit of complex 1 is tetranuclear. In the solid-state structure, four Cu atoms are bridged by dmae oxygen atoms and all four dmae ligands are bonded to Cu atoms in a chelating or bridging fashion. The oxygen atoms of all four dmae ligands bridge three Cu atoms (Fig. 1b) in a similar fashion to that found in \([\text{Cu}_4(\text{dmae})\text{Cl}]_4 \text{^+}\). [16] i.e. \( O(7) \) bridges Cu(1), Cu(2), Cu(3) via Cu(1)–O(7), Cu(2)–O(7), Cu(3)–O(7); \( O(8) \) bridges Cu(2), Cu(3), Cu(4) via Cu(2)–O(8), Cu(3)–O(8), Cu(4)–O(8), while \( O(11) \) bridges Cu(1), Cu(3), Cu(4) via Cu(1)–O(11), Cu(3)–O(11), Cu(4)–O(11); and \( O(12) \) acts as a bridge between Cu(1), Cu(2), Cu(4) via Cu(1)–O(12), Cu(2)–O(12), Cu(4)–O(12). Cu–O distances are in the range of 1.923 (16)–2.720(18) Å and this long-distance interaction (2.720 (18) Å) is again due to steric crowding of methyl groups of one dmae and the second dmae plane. Nitrogen coordinates to copper through bonds Cu(1)–N(1), Cu(2)–N(2), Cu(3)–N(3), and Cu(4)–N(4), and these bond lengths agree with the reported range. [18] All four TFAs coordinate to Cu atoms in \( \mu\text{-bridging}

![Fig. 1.](image)

**Table 1. Selected bond distances (Å) and bond angles (°) of complex 1**

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)–O(7)</td>
<td>1.923(16)</td>
</tr>
<tr>
<td>Cu(1)–O(12)</td>
<td>1.939(19)</td>
</tr>
<tr>
<td>Cu(1)–O(11)</td>
<td>2.720(18)</td>
</tr>
<tr>
<td>Cu(1)–N(1)</td>
<td>2.056(2)</td>
</tr>
<tr>
<td>Cu(2)–O(8)</td>
<td>1.930(18)</td>
</tr>
<tr>
<td>Cu(2)–O(12)</td>
<td>2.681(19)</td>
</tr>
<tr>
<td>Cu(2)–O(7)</td>
<td>1.951(19)</td>
</tr>
<tr>
<td>Cu(2)–N(2)</td>
<td>2.041(2)</td>
</tr>
<tr>
<td>O(7)–Cu(1)–N(1)</td>
<td>85.73(8)</td>
</tr>
<tr>
<td>O(11)–Cu(3)–O(8)</td>
<td>90.24(7)</td>
</tr>
<tr>
<td>O(12)–Cu(1)–N(1)</td>
<td>173.49(9)</td>
</tr>
<tr>
<td>O(8)–Cu(2)–O(2)</td>
<td>173.26(9)</td>
</tr>
<tr>
<td>O(8)–Cu(2)–N(2)</td>
<td>172.77(9)</td>
</tr>
<tr>
<td>O(7)–Cu(2)–N(2)</td>
<td>89.01(9)</td>
</tr>
<tr>
<td>O(7)–Cu(2)–N(2)</td>
<td>173.39(8)</td>
</tr>
</tbody>
</table>

860.7 corresponding to \([\text{Cu}_4(\text{dmae})_2(\text{TFA})_3] \text{^+}\). This disintegration of 1 indicates its low stability under MS conditions.
fashion and each TFA coordinates to two different Cu atoms. The dmae O–Cu–N ‘bite’ angles (85.73(8)–86.20(9)) are less than 90°. The geometric environment around all four Cu atoms is similar, i.e. each Cu atom forms a six-coordinated CuO$_2$N sphere with tetragonally elongated octahedral geometry.

**Thermogravimetric Studies**

The thermal decomposition behaviour of complex 1 was examined by thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) measurements in the temperature range 25–550°C under an inert atmosphere of argon gas (130 mL min$^{-1}$) at a heating rate of 10°C min$^{-1}$ (Fig. 2). The TG curve of 1 shows a two-step weight loss beginning at 195°C and completed at 480°C, resulting in a residue of 23.46% of the initial mass, which is slightly less but comparable with 24.01% calculated for copper metal. It is believed that the slow decrease in residual mass between 259 and 480°C indicates first the formation of copper(II) oxide and then conversion to copper metal as the residual mass (27.59%) at 259°C is comparable with that of 27.03% calculated for copper(I) oxide. The DTG curve also shows two major stages of weight loss, i.e. 230 and 415°C. The formation of both copper(I) oxide and copper phases was ascertained by powder X-ray diffraction (PXRD) of films deposited separately on glass substrates at 250 and 375°C respectively from complex 1. The TG analysis of the complex recorded under an inert atmosphere clearly indicates that complex 1 is a potential precursor for the deposition of copper nanowires. Thus, the new, robust precursor 1 is suitable for obtaining copper metal wires at the relatively low temperature of 375°C.

**Thin-film Studies**

By utilizing the thermal decomposition information obtained from the TGA data, thin films of copper(i) oxide and metallic copper were deposited by the AACVD method at 250 and 375°C using precursor 1. The thin films of copper(i) oxide and metallic copper prepared from precursor 1 were characterized by XRD, scanning electron microscopy (SEM), and energy-dispersive X-ray diffraction (EDX). The deposited thin films exhibit good adhesion to the glass substrates as verified by the ‘Scotch-tape test’.$^{188}$ Moreover, the films deposited at 250°C reflect light in multi-shaded colours depending on thickness, and the denser parts of the films deposited at 375°C shine in the red metallic lustre characteristic for copper.

Powder X-ray diffraction analysis was used to ascertain the crystallinity and phase of thin films deposited from complex 1 at 250 and 375°C. The fingerprints of the powder X-ray diffractograms of the materials obtained from the decomposition of the precursor indicate the formation of impurity-free single-phase copper(i) oxide$^{19}$ (Fig. 3a) and pure copper metal (Fig. 3b). The 2θ peak pattern shows the decomposition of the complex at 250°C yielding copper(I) oxide as the cuprite syn with the cubic space group $Pn$ 3 $m$, and cell parameters $a = b = c = 4.2696$ Å, $\alpha = \beta = \gamma = 90.00°$, and at 375°C confirms crystalline-phase Cu [01–085–1326] metal that exhibits space group $Fm$ 3 $m$ with lattice parameters of $a = b = c = 3.6150$ Å, $\alpha = \beta = \gamma = 90.00°$. All the peaks were indexed with their respective Miller indices and the maximum intensity of the (111) peak indicates that the particles are oriented in the (111) direction in both cases. The volume-average mean crystallite sizes of copper(i) oxide and copper determined from broadening of the (111) diffraction peak by the Scherrer equation$^{20}$ are 76 and 39 nm respectively. The identified copper(i) oxide and copper phases are highly crystalline and this observation suggests that the decomposition of complex 1 proceeds with the removal of volatiles.

The surface morphology of deposited thin films was characterized by SEM. The film deposited from precursor 1 (Fig. 4) at 250°C shows a compact morphology consisting of irregular-shaped nanoparticles emerging from the substrate surface with random orientation, whereas the SEM image of the films obtained at 375°C shows the formation of wire-like structures of copper, randomly oriented and having lengths of 0.1–4.5 µm and diameters of 0.09–0.22 µm. The calculated aspect ratio of these wires lies in the nanometer range (1.1–20.4). The EDX analysis (Fig. 5) of the films deposited at 375°C from complex 1 proves the presence of only metallic copper. Furthermore, the EDX analysis proves the clean decomposition of the complex without incorporation of impurities either from organic groups of the complex or the carrier gas and confirms the formation of single-phase thin films.

**Optical Studies of Thin Films**

The optical properties of nanomaterials, such as refraction, reflection, absorption, and transmission, depend on their interaction with electromagnetic radiation. The energy band gap of a

![Image](332x603 to 548x761)

**Fig. 3.** Powder X-ray diffractograms of the films obtained from precursor 1 at (a) 250°C; and (b) 375°C.

![Image](94x613 to 269x739)

**Fig. 2.** Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves for complex 1 under an inert atmosphere of argon gas (130 mL min$^{-1}$) at a heating rate of 10°C min$^{-1}$. The dmae O–Cu–N ‘bite’ angles (85.73(8)–86.20(9)) are less than 90°. The geometric environment around all four Cu atoms is similar, i.e. each Cu atom forms a six-coordinated CuO$_2$N sphere with tetragonally elongated octahedral geometry.
semiconductor is affected by residual strain, defects, charged impurities, disorder at the grain boundaries, and also particle size restrictions. In order to study the optical properties of the deposited thin films, UV-vis analysis was carried out. The optical band gap ($E_g$) of the as-deposited films was estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$, where $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy. Extrapolation of the linear portion of the curve to $(\alpha h\nu)^2 = 0$ gives the value of the optical band gap. The optical band gap of the copper(I) oxide thin film obtained from precursor 1 at 250°C is estimated as 2.48 eV (Fig. 6a inset). This value is higher than the bulk value (copper(I) oxide, 2.1 eV), showing a significant blue shift (0.38 eV). This marked value of blue shift can be attributed to the formation of nanosized structures in films deposited at 250°C from precursor 1. Similarly, film deposited at 375°C was characterized by UV-vis spectroscopy. The absorption spectrum (Fig. 6b) of the film deposited at 375°C showed a shoulder at 610 nm, which is caused by plasmonic resonance absorption (PRA) of nanostructures of copper and this recorded value is in good agreement with literature values.

**Conclusions**

We have successfully shown that single-phase copper(I) oxide and metallic copper thin films can be deposited from the
single-source polynuclear complex \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4 \cdot \text{CH}_2\text{Cl}_2\) 1 by controlling the deposition temperature of the AACVD system. Complex 1 was synthesized and characterized by various physicochemical methods. The thin films of copper(i) oxide and metallic copper deposited on soda glass substrates at 250 and 375°C display spherical and wire-like morphologies respectively. Thus, the morphology and particle size of the deposit can be tuned by employing a suitable deposition temperature. The band gap of copper(i) oxide thin films obtained from I was determined to be 2.48 eV, showing a significant blue shift in comparison with the bulk value (2.1 eV). Hence, it is hoped that such thin films will prove to be suitable light-absorbing materials for tandem photoelectrochemical devices.

**Experimental**

**General Considerations**

All reagents were purchased from Sigma–Aldrich and synthetic work was carried out under an inert atmosphere of dry argon gas using Schlenk and glovebox techniques. Solvents were rigorously dried over sodium diphenyl ketyl. Absorbing materials for tandem photoelectrochemical devices.

**Thin-film Deposition**

The copper(i) oxide and copper thin films were grown on soda–glass substrates in a hot-walled reactor containing a quartz tube (1.5-cm diameter) by gas-phase reaction of the precursor in an argon environment using a self-designed AACVD assembly described elsewhere.[22] In a typical experiment, 0.1 g of precursor I dissolved in 15 mL THF in a two-neck round-bottomed flask was connected via rubber tubing to a quartz reactor into which 2.5 × 1-cm substrate slides were placed inside a Carbolite graphite monochromated Mo Kα source. A flow of argon gas was regulated using a piezoelectric modulator of an ultrasonic humidifier for atomization of the precursor solution to tiny droplets of aerosol that were ultimately transferred by the carrier gas into the reactor chamber. Glass substrates were treated with concentrated nitric acid, followed by several washings with deionized water, and then oven-dried at 100°C before placing into the deposition chamber. Deposition was carried out at 250 and 375°C at a constant argon flow rate of 130 mL min⁻¹.

**Synthesis of \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4 \cdot \text{CH}_2\text{Cl}_2\) 1**

\(N,N\)-Dimethylaminoethanol (0.71 g, 7.96 mmol) and trifluoroacetic acid (1.07 g, 7.96 mmol) were added to a suspension of \(\text{Cu(OCH}_3\text{)}_2\) (1.00 g, 7.96 mmol) in tetrahydrofuran (THF, 20 mL). The reaction mixture was stirred for 2 h at room temperature and then evaporated to dryness under vacuum. A small quantity of the solid obtained was re-dissolved in dichloromethane (30 mL) and kept for crystallization at 15°C to give blue crystals of I after 5 days, yield 70%, mp 210°C. Anal. Calc. for \(\text{C}_{29}\text{H}_{40}\text{N}_4\text{O}_{12}\text{F}_{12}\text{Cu}_4\): C 27.23, H 3.80, N 5.29. Found: C 27.93, H 3.88, N 5.42%. v_max (KBr/cm⁻¹) 2982 m, 2923 w, 2884 m, 1692 s, 1593 m, 1466 w, 1420 m, 1276 w, 1210 m, 1202 s, 1135 s, 1120 m, 1065 s, 1016 m, 952 s, 901 m, 839 m, 795 m, 726 s, 637 m, 525 m, 432 w. m/z (APCI-MS positive scan) 947.9 \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4\) 1, 859.7 \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4\) 1, 745.8 \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4\) 1, 682.6 \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4\) 1, 615.9 \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4\) 1, 531.2 \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4\) 1, 351 \([\text{Cu}(\text{dmae})(\text{TFA})_4]_4\) 1, 202.1 \([\text{M-Cu}(\text{dmae})(\text{TFA})_4]_4\) 2. TGA 195–259°C (72.41 wt-% loss), 259–480°C (residue 23.46%).

**X-Ray Crystallography**

Single-crystal X-ray data measurements were made using graphite monochromated Mo Kα radiation on a Bruker Apex diffractometer. The structure was solved by direct methods[25] and refined by full-matrix least-squares on \(F^2\).[26] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms bonded to C were placed in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. Those bonded to the C atom of \(\text{CH}_2\text{Cl}_2\) in I were found by difference Fourier methods and refined isotropically. Crystallographic and structure refinement data for complex 1: empirical formula: \(\text{C}_{29}\text{H}_{40}\text{N}_4\text{O}_{12}\text{F}_{12}\text{Cu}_4\), formula weight 1134.69, \(T = 100\) (2 K), \(λ = 0.71073\) Å, monoclinic, space group \(P2(1)/c\), \(a = 14.0200(10), \ b = 21.1890(16), \ c = 0.6997(10)\) Å, \(α = 90, \ β = 104.8640(10), \ γ = 90°\), \(V = 4047.7(5)\) \(Å^3\), \(Z = 4\), \(ρ_{calc} = 1.877 \) \(mg \) \(cm^{-3}\), \(μ = 2.320 \) \(mm^{-1}\), 25195 reflections collected, 9441 unique (\(R_{int} = 0.0725\)). Refinement was by full-matrix least-squares on \(F^2\); goodness-of-fit on \(F^2\) was 0.981. Final \(R\) indices where \(I > 2σ(I)\) are \(R_I = 0.0655\) and \(wR_I = 0.1886\). The \(R\) indices (all data) are \(R_I = 0.0986\) and \(wR_I = 0.2029\). The largest differences between peaks and holes are 1.849 and –2.362 e Å⁻³, respectively.

**Supplementary Material**

CCDC no. 649744 contains the supplementary crystallographic data for compound I. These data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (accessed 20 September 2013) or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or email: deposit@ccdc.cam.ac.uk.

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(b) Bruker Advanced X-Solutions SHELXTL (Version 6.10) 2000 (Bruker AXS Inc.: Madison, WI).