Nanostructured copper oxide semiconductors: a perspective on materials, synthesis methods and applications

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The oxides of copper (CuO) are fascinating materials due to their remarkable optical, electrical, thermal and magnetic properties. Nanostructuring of CuO can further enhance the performance of this important functional material and provide it with unique properties that do not exist in its bulk form. Three distinctly different phases of CuO, mainly CuO, Cu2O and Cu4O3, can be prepared by numerous synthesis techniques including, vapour deposition and liquid phase chemical methods. In this article, we present a review of nanostructured CuO focusing on their material properties, methods of synthesis and an overview of various applications that have been associated with nanostructured CuO.

1. Introduction

Lately, there has been a great deal of interest in nanostructured copper oxide (CuO) semiconductors. This interest in nanostructured CuO is fuelled due to their remarkable physical and chemical properties as well as exciting prospects for a variety of applications.1,2 Nanostructured copper oxides are relatively abundant in nature, and a wide range of information is now available for their synthesis. Nanostructured CuO can be grown using different synthesis techniques, including vapour and liquid phase deposition processes, in which a variety of nanostructures can be obtained.

Nanostructured copper oxides are exceptionally versatile and offer unique characteristics in many applications. CuO nanomaterials have been used as colouring agents for the production of Roman mosaic glasses and antique ceramics for thousands of years.3,4 Nanosized CuO has been widely utilized as a fungicide5,6 and in anti-fouling paints7,8 due to its biocidal capability. With the advent of nanotechnology, CuO has shown a great impact in numerous research fields including optics,
sensors, tribology, superconductors, electrochemistry and electronics. 

The most common crystal phases of Cu$_2$O are: (a) CuO also known as copper(II) oxide or cupric oxide where the mineral is known as tenorite, (b) Cu$_2$O also known as copper(I) oxide or cuprous oxide with the mineral name of cuprite, and (c) Cu$_4$O$_3$ with the mineral name of paramelaconite.$^{1,2,15,16}$

In this feature article, we present a general, yet complete, review of nanostructured Cu$_2$O. The present review is distinguishable from other reviews,$^{3,17}$ which have a focus on one type of Cu$_2$O (generally CuO or Cu$_2$O), while this review endeavors to thoroughly discuss three types of Cu$_2$O, including CuO, Cu$_2$O and Cu$_4$O$_3$. The organization of this review is as follows: firstly, we discuss the fundamental chemical and physical properties of nanostructured Cu$_2$O and then we summarize the different methods of synthesis that have been reported. Finally we present a selection of interesting applications that exploit Cu$_2$O and illustrate the enhancements made possible by using the nanostructured form of this material.

2. Fundamental properties

In this section, the fundamental properties such as crystal structures, electronic band structures, optical and electrical as well as transport properties of nanostructured Cu$_2$O are discussed. This section also describes the effect of doping or the presence of impurities on the properties of nanostructured Cu$_2$O.

2.1 Crystal structure

CuO has a black colour and crystallizes in the monoclinic centered Bravais lattice in the space group of $C2/c$. The crystallographic properties of CuO are tabulated in Table 1.$^{1,2,15,16,18}$ The copper atom is coordinated to four coplanar oxygen atoms situated at the corners of a rectangular parallelogram, which forms chains by sharing edges. The oxygen atom is coordinated to four copper atoms situated at the corners of a distorted tetrahedron. The chains traverse the structure in the [110] and [110] directions. The two types of chains alternate in the [001] direction and each type is stacked in the [010] direction with a separation between the chains of about 2.7 Å.$^{16,18,19}$ Fig. 1a demonstrates the crystal structure of CuO.

Cu$_2$O is the second stable phase of copper-oxide compounds which is reddish in colour. Cu$_2$O has a cubic structure (space group, $O_h^4$ or $Pn\bar{3}m$) with a lattice constant of 4.2696 Å. Each Cu atom in the unit cell is coordinated by two oxygen atoms.$^{19}$ The crystallographic properties of Cu$_2$O are tabulated in Table 1.$^{2,15,16,18}$ Fig. 1b demonstrates the crystal structure of Cu$_2$O.
Table 1 Crystallographic properties of CuO, Cu2O and Cu4O3

<table>
<thead>
<tr>
<th></th>
<th>CuO</th>
<th>Cu2O</th>
<th>Cu4O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice</td>
<td>Monoclinic</td>
<td>Cubic</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>a</td>
<td>4.6837 Å</td>
<td>4.2696 Å</td>
<td>5.837 Å</td>
</tr>
<tr>
<td>b</td>
<td>3.4226 Å</td>
<td></td>
<td>9.932 Å</td>
</tr>
<tr>
<td>c</td>
<td>5.1288 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>99.54°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>γ = 90°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shortest distance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interatomic distances Cu–O</td>
<td>1.95 Å</td>
<td>1.84 Å</td>
<td>1.87 Å</td>
</tr>
<tr>
<td>Interatomic distances O–O</td>
<td>2.62 Å</td>
<td>3.68 Å</td>
<td>2.56 Å</td>
</tr>
<tr>
<td>Interatomic distances Cu–Cu</td>
<td>2.90 Å</td>
<td>3.01 Å</td>
<td>2.92 Å</td>
</tr>
<tr>
<td>Formula weight</td>
<td>79.57</td>
<td>143.14</td>
<td>302.18</td>
</tr>
<tr>
<td>Density</td>
<td>6.52 g cm⁻³</td>
<td>5.75 g cm⁻³</td>
<td>5.93 g cm⁻³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1201 °C</td>
<td>1235 °C</td>
<td>400 °C</td>
</tr>
<tr>
<td>Cell volume</td>
<td>81.08 Å³</td>
<td>77.833 × 10⁻²⁴ cm⁻³</td>
<td>338 Å³</td>
</tr>
</tbody>
</table>

This wide range is attributed to several factors, including interpretation of the nature of the gap (i.e. direct or indirect), annealing treatment, grain dimensions, morphology and doping.²,²⁵,²⁶,²⁸,²⁹ According to the Tauc relationship, for photon energies (E) greater than the band gap energy, the light absorption can be approximated using:

$$\alpha E = \alpha_o (E - E_g)^n$$  \hspace{1cm} (1)

where α is the absorption coefficient, α₀ is a constant, E₉ is the band gap energy and n is an exponent that depends on the type of transition involved. The value of n is \(\frac{1}{2}\) or 2 for direct or indirect transitions, respectively. Rakhshani et al. have reported detailed studies of band gap determination of RF sputtered CuO films.³³ They found that their CuO films exhibited an indirect transition with a band gap of 1.21 eV. In contrast, Pierson et al., while reporting the same deposition technique (RF sputtering), determined that their CuO films exhibited a direct band gap with a value of 1.71 eV.³² The different values of E₉ were due to different models ([(αE)² or (αE)¹²]) being used to determine the band gap value. The other significant factor that contributes to the variation of band gap values of CuO films is related to the heat treatment.³⁸,³⁹ Iziki et al. demonstrated that annealing electrodeposited CuO films altered the E₉ value.³⁹ They reported a reduction of 7.5% in E₉ after annealing the as-deposited CuO at 773 K. They suggested that the changes in the composition, grain size and lattice constant were induced by the annealing process, altering the CuO band gap.²⁹

In nanostructured CuO, the band gap generally increases with reducing crystallite dimensions.¹,³⁴,³⁵ Experimentally, this is often observed as a blue shift of the optical absorption band-edge when the nanostructure dimensions are reduced. The blue shift can be attributed to the quantum confinement (QC) effect.¹,³⁴,³⁵ The strong QC effect occurs when the size of the crystal is reduced much smaller than the Bohr radius for the electron wavefunctions and hence significantly alters the E₉. A weak QC effect occurs when the crystal size is larger than the Bohr radius. This causes indirect perturbation of the electron wavefunction due to Coulomb effects and results in more subtle changes in the band gap energy.³⁴,³⁵ In a recent study conducted by Rehman et al., different scales of CuO nanoparticles were reported, where the crystallite dimension is controlled by annealing.³³ The crystallite dimensions obtained ranged from 11 nm (T = 250 °C) to 20 nm (T = 600 °C). They reported a reduction of 7% in direct E₉ with an increase of crystallite dimensions.³³ In addition, it has been reported that the band gap values of nanostructured CuO can be tuned via engineering the morphology,¹⁶,¹⁸,²⁹ as well as doping.²⁹,⁴²

CuO is also a p-type semiconductor material due to the presence of copper vacancies.²,²¹ It is a direct band gap material with E₉ > 2.1 eV. However the band gap can be tuned via engineering the grain dimensions.²⁴,²⁸,²⁹,³⁳,³⁴,³⁶ In a recent study conducted by Poulopoulos et al.,⁴⁶ on Cu₂O thin films with thicknesses...
2.3 Optical properties

The optical behaviour of CuO films have been experimentally studied, in particular the complex dielectric function \( \varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E) \) was determined via spectroscopic ellipsometry.\(^{24-30}\) For comparison, the imaginary part \( \varepsilon_2 \) of the dielectric function for CuO, Cu\(_2\)O and Cu\(_4\)O\(_3\) is shown in Fig. 3(a) and (b) with Gaussian fitting marked with numbers 1 to 7. For Cu\(_2\)O the peaks originate from the various band gaps corresponding to 2.59 eV (1), 2.71 eV (2),... 5.24 eV (7).\(^2\) The difference in energy between these two first peaks is attributed to the spin–orbit splitting energy of \(~0.12\) eV for Cu\(_2\)O.\(^{49}\) The absence of any sharp peaks for the CuO \( \varepsilon_2 \) spectrum is due to low symmetry of this crystal. Similarly no sharp peak is seen for Cu\(_4\)O\(_3\) for energies of less than 3.7 eV.

There are many reports regarding the absorption coefficient \( \alpha \) and normal-incidence reflectivity \( R(E) \) of CuO films in optical ranges.\(^{24-32}\) CuO is expected to have an essentially full Cu 3d shell with a direct forbidden band gap of 2.17 eV in the bulk, which can only absorb light up to the visible region. In contrast, CuO has an open 3d shell with a direct band gap (1.2 eV in bulk) of charge-transfer type, which can absorb light up to the near infrared (IR) region.\(^{1,15,27}\) A detailed analysis of the absorption coefficient obtained on bulk and thin film CuO can be found in the report by Malerba et al.\(^{31}\) Additionally, Rehman et al. and Borghain et al. reported the optical absorption properties of CuO and Cu\(_2\)O nanoparticles of different sizes, respectively.\(^{33,52}\) A comparative study of optical absorption between nanoparticles and near-monodisperse nanospheres of Cu\(_2\)O has been reported by Zhang et al.\(^{53}\) They found that the nanospheres of Cu\(_2\)O have a wide absorption peak at 520 nm while Cu\(_2\)O nanoparticles have an absorption edge at 550 nm.\(^{53}\)

Mayer et al. have reported that CuO is nonluminescent.\(^3\) This is despite a few reports demonstrating the photoluminescence (PL) of CuO films, however the purity of such films is questionable (the presence of Cu\(_2\)O is a possibility). Nevertheless, Zhang et al. reported a detailed analysis of the PL properties of CuO nanostructures. They found that the PL properties of nanostructured CuO can be controlled via altering their shape, dimension and morphology.\(^1\) The QC effect and the specific surface effect are the two most reported mechanisms which can

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**Fig. 2** (i) Electronic band structure and density of states from hybrid functional DFT calculations and (ii) Brillouin zones with special high symmetry \( k \) points of the three copper oxide compounds to: (a) Cu\(_2\)O, (b) CuO and (c) Cu\(_4\)O\(_3\). Reprinted figure with permission from (M. Heinemann, B. Eifert and C. Heiliger, Phys. Rev. B, 2013, 87) copyright (2013) by the American Physical Society.

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result in the blue shift and red shift of the PL peak, respectively.\(^5,6\) On the other hand, Cu\(_2\)O shows a weak PL effect due to the fact that optical transitions require parity change, which does not exist between the energetically highest valence band and lowest conduction band of the Cu\(_2\)O direct transition band.\(^2\) In bulk Cu\(_2\)O, there are three peaks or shoulders that can be assigned to doubly charged oxygen vacancies (\(V_{\text{O}^2}\)) at 1.72 eV (720 nm), singly charged oxygen vacancies (\(V_{\text{O}^+}\)) at 1.53 eV (810 nm) and copper vacancies (\(V_{\text{Cu}}\)) at 1.35 eV (920 nm).\(^2\) In nanostructured Cu\(_2\)O, these peaks and shoulders can be tuned via shape, dimension and morphology alterations as observed by Shi \textit{et al.}\(^5,56\)

### 2.4 Vibrational properties

The lattice dynamics of Cu\(_x\)O materials have been studied using IR, Raman and photoluminescence spectroscopy.\(^57-61\) These studies provided insight into the nature of the electron phonon interaction and the negative thermal expansion (NTE) in Cu\(_x\)O. These methods also provided information about spin-phonon interaction and size dependent electron phonon scattering.\(^61\) Debbichi \textit{et al.} reported an extensive study of vibrational properties of Cu\(_x\)O via Raman spectroscopy where they clearly distinguished the different types of vibrational modes either by Raman or IR spectroscopy.\(^61\) Recently, Shih \textit{et al.} have reported studies on the size effects of spin-phonon coupling in in-plane Cu\(_x\)O nanowires.\(^62\) They employed low-temperature Raman spectroscopy for probing the local atomic vibrations of nanowires. They found that the spin-phonon mode varies with the size of the Cu\(_x\)O nanowires due to the increase in the strength of the spin-phonon coupling.\(^62\)

The IR spectroscopy modes are associated with the relative motion of both copper and oxygen atoms which consist of asymmetric Cu–O stretching and asymmetric O–Cu–O bending modes. In contrast, Raman active modes only involve the relative motion of oxygen atoms.\(^61\) Fig. 4 shows Raman spectra of Cu\(_x\)O with calculated frequencies of Raman active vibrational modes.\(^61\) The symmetries of the zone-center modes are given by the following representations:\(^61\)

\[
\Gamma_{\text{Cu}_2\text{O}} = A_{2u} + E_u + 3T_{1u} + T_{2u} + T_{2g} \tag{2}
\]

\[
\Gamma_{\text{CuO}} = A_g + 2B_g + 4A_u + 5B_u \tag{3}
\]

\[
\Gamma_{\text{Cu}_4\text{O}_3} = 3E_g + A_{1g} + 2B_{1g} + 9E_u + 6A_{2u} + 5B_{2u} + 2B_{1u} + 2A_{1u} \tag{4}
\]

#### 2.5 Electrical properties

The electrical conductivity and hole density of p-type Cu\(_2\)O films vary with copper vacancy density, which act as shallow acceptors.\(^2\) Similarly in CuO, copper deficiencies account for the intrinsic p-type semiconducting behaviour.\(^64\) Suda \textit{et al.} and Young \textit{et al.} have studied the effect of temperature on electrical conductivity of CuO and Cu\(_2\)O films, respectively (Fig. 5(a) and (b)).\(^65,66\) They have shown that an increase in temperature increases the conductivity of CuO and Cu\(_2\)O due to an increase in the hole concentration.\(^65\) Similar findings were also reported by Gopalakrishna \textit{et al.}\(^67\) using Hall effect studies. They revealed a significant increase in conductivity, mobility and carrier concentration of nanocrystalline CuO after annealing.\(^67\) Apart from temperature, electrical properties of Cu\(_x\)O also relied on grain dimensions, grain boundary, film thickness, specific phase and dopants.\(^1,1,8-72\) Shao \textit{et al.} reported an electrical conductivity of individual single CuO nanowires grown by thermal oxidation.\(^69\) The electrical transport measurement has shown that the CuO nanowire has a conductivity of \(7.8 \times 10^{-4} (\Omega \text{ cm})^{-1}\).\(^69\) Additionally, Liao \textit{et al.} reported that individual Cu\(_2\)O nanowires have a high mobility of >95 cm\(^2\) V\(^{-1}\) s\(^{-1}\).\(^79\) It is possible to tune the electrical properties (resistivity, carrier concentration and mobility) of Cu\(_x\)O by changing the stoichiometry and crystallinity of the Cu\(_x\)O films during the deposition process. Deposition parameters, such as pH of the solution in electrodeposition and hydrothermal methods and ion pressure and concentration in RF sputtering techniques, significantly contribute to changes in stoichiometry and crystallinity.\(^73-75\)

#### 2.6 Thermal properties

A limited number of studies have been carried out on the thermal properties of pristine copper oxide films. However, great interest has been shown for the development of nanoparticles of Cu\(_x\)O suspensions in fluids (nanofluids) due to the significant enhancement of thermal conductivity that they grant to the fluid in which they are suspended.\(^76-79\) The relatively high thermal conductivity of CuO (76.5 W mK\(^{-1}\)) makes it an excellent candidate for enhancing the efficiency and reliability...
CuO has a rather low thermal conductivity of the order of 4.5 W mK⁻¹. It has been shown that the thermal conductivity enhancement of both CuO and Cu₂O nanofluids corresponds to an increased particle volume fraction and temperature.

The variations in the Seebeck coefficient (S) of CuO and Cu₂O as a function of temperature are shown in Fig. 5(a) and (c) for which both oxides show decreasing trends. It has been shown that at 500 K, CuO and Cu₂O exhibit a maximum value of 200 μV K⁻¹ and 1050 μV K⁻¹, respectively.

The presence of a wide gap in the phonon spectra between low frequency (due to acoustic and optical phonon modes that involve the motion of Cu atoms) and high frequency (due to the optical modes of oxygen vibrations) bands are reflected in the temperature dependence of heat capacity. The calculated and experimental heat capacities (C_p) of CuO and Cu₂O as a function of temperature are shown in Fig. 5(d) and (e).

2.7 Magnetic properties and superconductivity

The copper-oxygen covalent bond is the prominent factor governing the properties of high transition temperature (High-Tc) superconducting CuO compounds. Both CuO and Cu₂O₃ have an antiferromagnetic ground state. For CuO the antiferromagnetic unit cell has twice the size of the primitive unit cell of the crystal. In the case of Cu₄O₉, it was suggested that the antiferromagnetic unit cell doubles the crystallographic unit cell in all three special directions. Bulk CuO is antiferromagnetic with Néel temperatures from 213 K to 230 K. The CuO antiferromagnetic transition takes place in two stages: near 230 K it leads to incommensurate antiferromagnetic order and near 213 K by a first order transition to a commensurate antiferromagnetic order. As mentioned in Section 2.1, the copper atom of CuO is surrounded by four coplanar oxygen atoms, resulting in two sets of one dimensional Cu-O-Cu chains. The magnetic interaction due to super exchange leads to antiferromagnetic order in the Cu-O-Cu chains along the [10-12] direction with a bond angle of 146°. Magnetic properties of nanostructured CuO significantly rely on their grain dimensions, morphology as well as anisotropy of the nanostructures.
A diameter of 10 nm is the critical size for CuO nanoparticles to show ferromagnetic behaviour. Interestingly, there are reports regarding room-temperature ferromagnetism of pure CuO nanostructures. The room-temperature ferromagnetism is due to oxygen vacancies at the surface/or interface of the nanoparticles.

A neutron diffraction study revealed that Cu$_3$O$_4$ undergoes a magnetic phase transition below 42.3 K leading to a pyrochlore lattice. The amplitude of the magnetic moment carried by Cu$^{2+}$ is ~0.46 $\mu_B$ which indicates the strong covalent character of the Cu–O bonds and the presence of strong fluctuations even at low temperatures.

Compounds made of Cu and O are the base of a famous class of high-$T_c$ superconductors. Superconductivity in these materials is observed when they are strongly doped away from their ideal stoichiometry. It has been shown that spatial changes in carrier density and the superconducting gap produce local inhomogeneity, which strongly affects their superconductivity.

High-$T_c$ was first discovered by Bednorz and Müller in 1986 using Cu and O compounds such as La$_2$CuO$_4$ doped with Ba. A few months later it was found that doping the same material with Sr raised the superconducting critical temperature to nearly 40 K. Recently, the performance of high-$T_c$ copper and oxygen based materials was further enhanced with the inclusion of extra oxygen atoms as mobile “holes” into the copper oxide planes as illustrated in the Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ and YBa$_2$Cu$_3$O$_{6+x}$ systems. Apart from providing charge carriers, the role of oxygen dopants is still debatable and being investigated.

### 2.8 Doping

It is possible to modify the chemical and physical properties of Cu$_2$O through doping. It has been shown that doping has the capability to alter the conduction type of Cu$_2$O (from p to n). Based on the valencies of Cu and O, which are +1 and –2 in Cu$_2$O, some n-type dopants including group VII elements such as halogens (O sites) (and possibly group II elements (Cu sites)) allow this transition to occur. The typical reported halogen dopants include fluorine (F), chlorine (Cl) and bromine (Br) which can be intercalated into the structure of Cu$_2$O during the synthesis process. Theoretically, F is the best match for O given the similarity in the size; however, CuF is soluble in water. Recently, Scanlon et al. have demonstrated that intrinsic n-type defects or defect complexes in Cu$_2$O created during an electrodeposition process cannot be the source of any n-type behaviour. They have suggested that the n-type conduction is due to an inversion layer which was attributed to a shallow donor level being formed during the electrodeposition process or due to external impurities (dopants).

Generally, the hole density of native p-type Cu$_2$O films is poor, uncontrollable and sensitive to the preparation methods and experimental conditions. It has been reported that nitrogen (N) and silicon (Si) doped Cu$_2$O via a RF sputtering process can significantly reduce such instabilities. These dopants were found to act as acceptors, which are incorporated into the oxygen lattice without converting the conduction type of Cu$_2$O. To further stabilize the films Ishizuka et al. and Okamoto et al. investigated the effect of passivation using hydrogen (H) and crown-ether cyanide of the N doped Cu$_2$O films. The improvement after the treatment indicates that hole traps are passivated by cyanide or protons. These hole traps are generally due to oxygen vacancies or dangling bonds of Cu.$^{115}$

For solar cell applications, the intrinsic photoconductivity of Cu$_2$O can be limited by minority charge carrier recombination caused by native defects acting as trap states. Isseroff et al. used first principles DFT calculations to study these trap states and demonstrated that substitutional cation doping reduces the recombination effect. They found that split vacancies are the source of trap states that inhibit the minority carrier diffusion in Cu$_2$O. Dopants such as lithium (Li), magnesium (Mg), manganese (Mn), and zinc (Zn) prevent the formation of the split vacancies for a single cation vacancy which resulted in an electronic structure that exhibited no trap states within the band gap.

### 3. Nanostructured Cu$_x$O synthesis

Many different approaches for the synthesis of nanostructured Cu$_2$O have been implemented using both vapour and liquid-phase-based methods. In this section, we present the most common synthesis methods and describe how they can be employed for engineering and tuning the morphologies and properties of Cu$_2$O.

#### 3.1 Vapour phase synthesis

Vapour phase synthesis methods can be divided into two different categories: (i) physical vapour deposition (PVD) and (ii) chemical vapour deposition (CVD). The main difference between them is the process they employ, in which PVD uses physical forces to deposit films, while CVD uses chemical processes.

##### 3.1.1 PVD methods

Many of the common PVD synthesis techniques such as RF sputtering, direct current (DC) sputtering, thermal evaporation, thermal oxidation, molecular beam epitaxy (MBE), pulse vapour deposition (PLD) and electron beam epitaxy (EBE) have been used for the deposition of nanostructured Cu$_2$O. A PVD process is purely physical, starting with either Cu$_2$O or Cu as the source material in the form of a solid target or powder, which is evaporated or sputtered with the application of ion bombardment, thermal heating, electron beam impingement or laser irradiation.

##### 3.1.1.1 Sputtering

Amongst the PVD techniques, sputtering has, thus far, been the most common technique to synthesize thin film Cu$_2$O due to the ease of control over the deposition parameters. The as-synthesized films usually exhibit a nanometer-sized tightly packed columnar structure. Sputtering is a process in which atoms are ejected from a solid target material by bombarding it with energetic particles. It offers a high degree of control over a film’s crystallinity and stoichiometry. The crystallinity, grain dimension and stoichiometry of the copper oxide films can be controlled by varying the sputtering parameters such as applied power, oxygen flow rate,
oxygen partial pressure and concentration as well as annealing temperature.\textsuperscript{32,120–122,124–128} For example, Chu et al. reported crystallite sizes of Cu$_2$O thin films varying from 16.8 to 8.8 nm when oxygen partial pressures increased from $1.1 \times 10^{-3}$ to $1.8 \times 10^{-3}$ Torr. This indicated that the higher the oxygen partial pressure, the smaller the crystallite size in the nano-crystalline Cu$_2$O thin films.\textsuperscript{120} In contrast, Elfadill et al. reported that the crystallite size of CuO increased from 12 to 24 nm as the oxygen pressure increased.\textsuperscript{125}

Generally in an oxygen rich sputtering chamber, at relatively low sputtering powers, only a small number of Cu atoms are sputtered, which effectively react with oxygen in the plasma, resulting in the deposition of films with high oxygen content such as CuO films. Conversely, Cu$_2$O films are formed at high sputtering powers, due to a large number of sputtered Cu atoms.\textsuperscript{122,126} However, relatively high sputtering powers can also adversely affect the stoichiometry of the films, resulting in the presence of unreacted metallic copper and undesirable stoichiometric ratios between copper and oxygen.\textsuperscript{122}

Although Cu$_4$O$_3$ was discovered during the late 1870s, the synthesis of single phase Cu$_4$O$_3$ thin films has rarely been reported. Pierson et al. and Richthoven et al. have successfully demonstrated the synthesis of single CuO, Cu$_2$O and Cu$_4$O$_3$ phases by varying the oxygen flow rate using a reactive magnetron sputtering technique.\textsuperscript{32,128} They used a Cu target with the RF power maintained at 600 W. It was suggested that conductive Cu-rich copper oxide (Cu$_4$O$_3$) thin films tend to form at an oxygen flow rate $R$(O$_2$) < 30%, whereas insulator O-rich copper oxide (CuO) thin films tend to form at $R$(O$_2$) $\geq$ 30%.\textsuperscript{128} This is in contrast to the work of Blobaum et al. who also successfully synthesized Cu$_4$O$_3$ films via sputtering, but with a CuO target and at a lower sputtering power of 200 W.\textsuperscript{127}

3.1.1.2 Thermal evaporation. Deposition of Cu$_x$O films using thermal evaporation is achieved by vaporizing a source material of Cu or Cu$_2$O (in either powder or condensed form) using heat either in a vacuum or in a controlled gaseous environment at a low pressure.\textsuperscript{25,45,130–133} The vaporized Cu or Cu$_2$O that emanates from the material source interacts with the gas molecules in the environment of the deposition chamber before condensing onto a substrate. Processing parameters such as evaporation temperature, substrate temperature, substrate type, gas environment and pressure all play important roles in achieving the desirable Cu$_x$O thin films.\textsuperscript{25,131,134} It has been reported that the as-synthesized Cu$_x$O films from these methods are usually compact thin films, which are textured by nanocrystallites (25–30 nm).\textsuperscript{25,45,132,133}

3.1.1.3 Thermal oxidation. Thermal oxidation techniques offer a simple, convenient and fast method to synthesize nanostructured Cu$_x$O with various morphologies including nanowires, nanoribbons and nanorods.\textsuperscript{125–139} In this method

![Fig. 6](image_url)
nanostructured Cu$_2$O is directly grown on the surface of a Cu substrate. Thermochemical oxidation is performed by simply heating a Cu substrate to a high temperature (typically between 200 and 800 °C) in an oxygen rich environment. Generally, the morphology and stoichiometry of the Cu$_2$O can be controlled by tuning the deposition parameters. For instance, the diameter and density of Cu$_2$O nanowires can be altered by changing the oxidation temperature. However, very high oxidation temperatures (>900 °C) are not suitable for nanowire formation as Cu$_2$O nanostructures can be fused together, as observed by Huang et al. Valladares et al. have studied the effect of oxidation temperature in altering the stoichiometry of the Cu$_2$O films. They have observed that pure Cu$_2$O films are obtained at 200 °C, whereas CuO films are obtained above 300 °C.

Unfortunately, mechanical adhesion between the as-deposited nanostructured Cu$_2$O and the substrates synthesized by the thermal oxidation method is very weak. Cracking and flaking of the Cu$_2$O films or even exfoliation from the substrates poses a big challenge which severely affects the properties and practical applications of the nanostructured Cu$_2$O. Several methods have been proposed to alleviate the cracking and flaking problem including pre-deposition of a ZnO layer on copper foil, synthesis of Cu$_2$O nanowires on other foreign substrates such as silicon or glass and synthesis of Cu$_2$O nanowires on porous substrates such as the porous copper substrate or nickel foam as shown in Fig. 6. Zhang et al. have successfully demonstrated non-cracked and flaked Cu$_2$O nanowires synthesized on porous copper substrates. The porous substrates managed to reduce thermal stress during the oxidation process and as a result eliminate cracking and flaking issues.

### 3.2 CVD methods

CVD processes have become the popular deposition techniques owing to their inherent flexibility and potential to tailor the Cu$_2$O phase composition by simply varying the operating conditions and precursors. Many forms of CVD have been used for depositing different Cu$_2$O stoichiometries, including atmospheric pressure CVD, aerosol assisted CVD, and plasma assisted CVD. Such films are typically of a compact structure, consisting of micro- or nanometer-sized grains.

Generally, precursors such as bis(2,4-pentanedionato) copper(II) or Cu(acac)$_2$ (acac = acetylacetonate) are used due to their high sublimation rate (activation energy of 105.6 kJ mol$^{-1}$) and low melting temperature between 140 and 190 °C. Valtierra et al. have demonstrated the synthesis of nanostructured Cu$_4$O$_3$ and CuO thin films with a crystallite size of 6.5 to 8.4 nm on fiberglass substrates using Cu(acac)$_2$ as a precursor and oxygen as a carrier-reactant gas via atmospheric pressure CVD. The deposition temperature of CuO and Cu$_2$O was recorded as 315 °C and 345 °C, respectively. In addition, thin films of Cu$_2$O have also been synthesized on fiberglass substrates using a similar technique and precursors by Ortiz et al. at a deposition temperature of 320 °C.

However, precursors such as Cu(acac)$_2$, Cu(dpdm)$_2$ (dpdm = dipivaloylmethanate) and Cu(hfa)$_2$ (hfa = hexafluoroacetylacetonate) may present drawbacks in terms of poor thermal characteristics, reduced shelf life, halide incorporation or instability upon prolonged utilization due to aging phenomena. Therefore, a second generation of adducts of the type M(hfa)$_2$ tetramethylethlenediamine(TMEDA) (M = Cu(i) or Cu(ii)) have been successfully adopted as alternative precursors. They have favourable properties in terms of improved long-term stability and volatility with respect to conventional β-diketonate.

Barreca et al. were the first group to successfully demonstrate the deposition of nanostructured CuO and Cu$_2$O using the Cu(hfa)$_2$ adduct with TMEDA via CVD. They successfully demonstrated morphological evolution from continuous films to 1D hyperbranched nanostructures.

Spray pyrolysis is a typical aerosol-assisted chemical vapour deposition, which is utilized in the glass industry and in solar cell production to deliver film coatings of various thicknesses. This method has the benefit of forming large-scale thin films by using a simple apparatus that can lead to increased productivity. Moreover, the film thickness and stoichiometry are easy to control and the resulting films are generally dense. During film deposition, the precursor's solution is pumped to an atomizer, and then sprayed onto heated substrates. Subsequently the droplets undergo evaporation, solute condensation and thermal decomposition, which results in film formation.

The composition of these thin films is highly dependent on the solvent, morphology of the substrate as well as the deposition temperatures. Cu$_2$O films generated by the spray pyrolysis method are generally produced from copper acetate or copper nitrate as precursors dissolved in alcohol based solutions such as ethanol, propanol or methanol. Alcohols are used to increase the wettability of the sprayed solution on the substrate and to improve the homogeneity of the deposited films. It has been reported that Cu$_2$O nanostructures are formed with the addition of glucose or sucrose to the solution. These sugars are used as reducing agents in the precipitation of the Cu$_2$O nanostructures. Waser et al. demonstrated synthesis of CuO nanoparticles via flame spray pyrolysis with various diameters from 6 to 50 nm by varying the precursor solution and the oxygen flow rate.

Apart from CuO and Cu$_2$O films, CuO$_2$ films can also be obtained via spray pyrolysis techniques. Albores et al. have successfully demonstrated the deposition of CuO$_2$ films on ZnO nanorods. The formation of CuO$_2$ films is a gradual process. Initially, the possible lattice matching of ZnO and CuO promotes the growth of CuO. In the presence of methanol, at elevated temperatures, the Cu$_{2+}$ in CuO is reduced to Cu$^+$ forming Cu$_2$O as.
\[
\text{CH}_3\text{OH} (g) + 6\text{CuO} \rightarrow 3\text{Cu}_2\text{O} + \text{CO}_2 (g) + 2\text{H}_2\text{O} (g) \quad (5)
\]

Then at these elevated temperatures, the solid reaction between CuO and Cu2O results in parmelaconite phase formation which can be described by:

\[
2\text{CuO} + \text{Cu}_2\text{O} \rightarrow \text{Cu}_4\text{O}_3 \quad (6)
\]

3.3 Liquid phase synthesis

Liquid phase techniques include methods such as electrodeposition, hydrothermal/solvothermal and sol-gel. These methods are generally chosen due to their low capital cost and better control of the material’s morphology in comparison to vapour phase deposition techniques as well as the deposition at relatively low temperatures, which is crucial for low-heat-tolerant substrates. Among a variety of liquid phase synthesis methods, hydrothermal/solvothermal and chemical precipitation techniques have been widely used to synthesize Cu3O nanostructures.

3.3.1 Electrodeposition. Electrodeposition is a process in which metal ions in an electrolyte are reduced at a conducting electrode under potential control. The process uses electrical current to reduce Cu2+ ions from an aqueous solution. The electrolyte generally contains a mixture of a Cu salt such as copper sulphate, copper acetate or copper nitrate and a chelating agent such as lactic acid, ammonium nitrate, amino acids or tartaric acids.\(^{29,173-177}\) The deposition is carried out in an alkaline environment with the addition of sodium hydroxide or ammonia to control the pH level. The electrodeposition technique is commonly used for depositing CuO and Cu2O films.\(^{1,2,29,173-175,177-180}\) Such films are typically of a compact structure, consisting of micro- or nanometer-sized grains. The stoichiometry of the electrodeposited films is very much dependent on the type of the chelating agent and applied potential used during the electrodeposition process. Generally, CuO films are obtained upon the application of a positive voltage/current bias, where oxidation of Cu is expected and this process is well known as anodic electrodeposition. Inversely, Cu2O films are deposited at a negative bias, in which the reduction process occurs (cathodic electrodeposition).\(^{173,174,181}\)

Synthesis of CuO films via anodic electrodeposition in an alkaline solution containing copper(II) nitrate, ammonium nitrate and ammonia has been reported by Izaki et al.\(^{174}\) Sasano et al. demonstrated that CuO films formed by applying potential pulses are more crystalline than the ones deposited using a constant potential.\(^{175}\) The mechanism for the electrodeposition of CuO films is outlined in eqn (7)–(10). The reaction starts via electrolysis of water to generate oxygen and protons (reaction (7)). Consequently, these protons react with ammonia Cu(II) complexes to yield free Cu(II) ions in the vicinity of a substrate’s surface (reaction (8)). The free Cu(II) ions are then hydrolyzed to form CuO films on the substrate (reactions (9) and (10)).\(^{174,181}\)

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (7)
\]

\[
\text{Cu(NH}_3\text{)}_4^{2+} + 4\text{H}^+ \rightarrow \text{Cu}^{2+} + 4\text{NH}_4^+ \quad (8)
\]

\[
\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 \quad (9)
\]

\[
\text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O} \quad (10)
\]

Similarly, syntheses of Cu2O films have been reported via cathodic electrodeposition using an alkaline aqueous solution containing copper(II) sulphate or copper(II) acetate and lactic acid as the chelating agent.\(^{10,173,177,179,180,182}\) Zoolfakar et al. have

---

**Fig. 7** SEM images of deposited octahedral Cu2O crystals that display systematically varying degrees of branching with (100) planes parallel to the substrate (a–d) and with (111) planes parallel to the substrate (e–h). These crystals were obtained at a constant temperature (60 °C) and concentration of Cu2+ (0.02 M) and by applying deposition conditions of 0.10 mA cm\(^{-2}\) ≤ I ≤ 0.12 mA cm\(^{-2}\) and 0.08 V ≤ E ≤ 0.12 V. All figures have scale bars of 1 μm. Reprinted with permission from (M. J. Siegfried and K. S. Choi, Angew. Chem. Int. Ed., 2005, 44, 3218–3223) copyright (2012) by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
demonstrated the electrodeposition of Cu_2O films onto ZnO for forming heterojunction solar cells. The electrodeposition process was carried out at \(-0.55\) V vs. Ag/AgCl. Cu_2O was formed according to the following electrochemical reaction:

\[
2\text{Cu}^{2+} + 2e^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (11)
\]

Apart from depositing thin films of Cu_2O, electrodeposition techniques have been used to synthesize various morphologies of nanostructured CuO and Cu_2O including leaf-like, nanospindles, nanocubes, nanorods, nanoribbons, nanotubes, microspheres and macrowhiskers. Various morphologies including spherical, ellipsoidal and needle-shaped CuO. Wu et al. prepared CuO nanoparticles with different sizes and morphologies in organic solvents such as dimethylacetamide (DMAC). They found that the nucleation and growth kinetics of CuO nanoparticles can be tuned by varying the processing parameters including the volume ratio of DMAC and water, increasing the temperature of the solution and the molar ratio of Cu^{2+} and OH^-.

### 3.3.2 Hydrothermal and solvothermal

Hydrothermal and solvothermal processes are facile and cost-effective deposition techniques. They have the capability of producing nanostructured CuO of different morphologies including nanodendrites, nanowires, nanorings, nanorods, nanoribbons, nanotubes, microspheres and macrowhiskers.

The synthesis of nanostructured CuO has been hydrothermally achieved using various precursors such as copper(II) chloride, copper(II) acetate or copper(II) sulphate. Generally, a lower concentration of Cu(OH)_2/f^2- precursors favours tubular formation, whereas a higher concentration leads to rodlike morphologies. In most cases, the hydrothermal synthesis of CuO starts with the preparation of a solution that contains copper salts, sodium hydroxide and solvents, typically deionized water. Such a solution is then kept at an elevated temperature (100–300 °C) for a certain period of time, allowing the nucleation and growth of CuO crystallites.

Solvothermal methods are almost identical to hydrothermal methods except that organic solvents are used instead of water. In comparison with the hydrothermal method, the solvothermal method exhibits many advantages such as easier morphological control, free foreign anions and macroscopic quantity. Recent reports have shown that the high-aspect ratio of CuO nanostructures can be synthesized via solvothermal methods. Zhao et al. have demonstrated a facile method to synthesize pure polycrystalline CuO microspheres using copper(II) nitrate as the precursor in the presence of N,N-dimethylformamide and ethanol. They have successfully manipulated the CuO/Cu_2O stoichiometry ratio to generate CuO films with the reaction of (2CuO + Cu_2O \rightarrow Cu_3O_2) in a closed system.

### 3.3.3 Solution-based chemical precipitation methods

In most cases, the chemical precipitation synthesis of CuO nanoparticles starts with the preparation of a solution that contains copper salts, sodium hydroxide and solvents, typically deionized water. In order to avoid agglomeration of the CuO nanoparticles, an external energy such as ultrasonic or high pressure needs to be applied during the synthesis process. Zhu et al. prepared highly dispersed CuO nanoparticles of 6 nm with various morphologies including spherical, ellipsoidal and nanocube-like CuO. This journal is © The Royal Society of Chemistry 2014

concentration of the surfactant.\textsuperscript{217} Zhang et al. reported synthesis of monodisperse Cu$_2$O and CuO nanospheres. It has also been shown that by modulating the concentration of solvent, the diameter, crystallization and monodispersity of Cu$_2$O nanospheres can be kinetically controlled.\textsuperscript{21} Interestingly, various groups have reported a facile method for the synthesis of Cu$_2$O nanocrystals with systematic shape evolution (Fig. 9).\textsuperscript{220–223} Recently, Susman et al. demonstrated precise morphology control of Cu$_2$O nanocrystals covering the entire range of morphologies from complete cubes, via the intermediate morphologies truncated octahedral, cuboctahedra and truncated cubes, to complete octahedral.\textsuperscript{220} The highly effective morphology control is attributed to competitive adsorption of hydroxide and citrate anions on the [100] and [111] planes of the growing crystallite.\textsuperscript{220}

### 3.3.4 Other film formation methods

A sol–gel process involves the formation of a colloidal solution (sol) from selected chemicals that acts as a precursor for an integrated network.

![Diagram](image.png)

**Fig. 9** (i) Schematic illustration of the procedure used for growing Cu$_2$O nanocrystals of different shapes. (ii) (a–d) Respective SEM images of the Cu$_2$O nanocrystals synthesized in sample containers A, B, C and D with increasing amounts of NH$_2$OH·HC added to the solutions. The particle morphologies are (a) truncated cubic, (b) cuboctahedral, (c) truncated octahedral and (d) octahedral in shape. Insets show the enlarged views of individual nanocrystals. The scale bars in the insets are 100 nm. Reprinted with permission from (C.-H. Kuo and M. H. Huang, J. Phys. Chem. C, 2008, 112, 18355–18360) copyright (2007) American Chemical Society.
(gel) of either discrete particles or connected networks. During gelation (aging process), various forms of hydrolysis and polycondensation processes can take place. Film deposition is generally carried out during the gelation process via dip-coating, spin coating or drop-casting onto the substrates. Armelao et al. have reported Cu$_2$O thin films via sol–gel synthesis, using ethanolic solutions of copper(u) acetate.$^{225}$ Films were obtained by dip-coating at room temperature in air and were subsequently heat-treated at different temperatures (100–900 °C) in oxidizing (air), inert (N$_2$) or reducing (4% H$_2$ in N$_2$) atmospheres to observe different crystalline phases of Cu$_2$O as a function of the annealing conditions with an average crystallite size lower than 20 nm.$^{225}$ Ray has also reported a similar technique, however he experimented with methanolic solutions of cupric chloride. Heteroepitaxial growth of Cu$_2$O on Cu nanostructures is possible by controlling the diameters, lengths and densities of the nanowires.$^{227}$ At the end of the deposition process, the templates must be removed either by chemical reactions$^{229}$ or a selective burn-away at high temperatures.$^{228}$ Consequently, this procedure may prolong the process as well as degrade the quality of the Cu$_2$O.$^{141}$

4. Applications of Cu$_x$O

Cu$_x$O has been employed for a variety of applications ranging from optical devices to high thermal conductivity systems. In this section, some of the most common applications of Cu$_x$O materials are presented. Particular emphasis is placed on the enhancements that can be achieved by exploiting the nanostructured forms of Cu$_x$O.

4.1 Solar cells and light emitting diodes

Cu$_x$O films are possible candidates for developing different types of optical devices, including solar cells based on dye-sensitized and heterojunction architectures as well as organic light emitting diodes.

The quest and need for a clean and economical energy source have increased interest in the development of solar applications. Amongst various metal oxide materials for solar energy applications, Cu$_x$O has attracted increasing interest due to its theoretical power conversion efficiency (PCE) of 18% and an absorption coefficient higher than single crystalline Si.$^{173,231}$

As described previously Cu$_x$O is an intrinsically p-type material. However, self-compensation problems and dopant solubility have inhibited the synthesis of n-type Cu$_x$O to produce efficient homojunctions for photovoltaic applications.$^{172,232}$ Therefore, heterojunction architectures have been employed with other n-type semiconductors such as ZnO,$^{10,173,175}$ CdO,$^{233}$ TiO$_2$,$^{234–236}$ Ga$_2$O$_3$ (ref. 237) and GaN.$^{2}$ Amongst the aforementioned n-type semiconductors, ZnO has been found to be the most stable and exhibit relatively low lattice mismatch of 7.6% between the {002} ZnO and {111} Cu$_2$O phases.$^{3,175,177}$

Despite the predicted PCE value of 18%, in practice the ZnO–Cu$_2$O solar systems have yet to reach high efficiencies.$^{3,10,238}$ To date, the highest efficiency ever reported for bilayer ZnO–Cu$_2$O heterojunction solar cells has been 3.83%.$^{239}$ This is due to the fact that theoretically their intrinsic electronic band structures do not permit an open circuit voltage larger than 0.7 V.$^{238}$ To date, the largest ever short circuit current that has been reported by Zoolfakar et al. using electrodeposited ZnO and Cu$_2$O films was 12.7 mA cm$^{-2}$ (Fig. 10).$^{173}$

Apart from heterojunction cells, Cu$_2$O has also been widely used in dye-sensitized solar cell (DSSC) technology. CuO is commonly used as a blocking layer that prevents recombination reactions by forming a potential barrier between the anode and the electrolyte which enhances the PCE of the device.$^{240–241}$ Yet in other experiments, the use of Cu$_2$O at the photoanode of a DSSC was found to decrease the overall PCE.$^{241}$ This is due to the dissociation of Cu$_2$O in liquid-based electrolytes, inducing numerous extrinsic defects that increase carrier recombination, resulting in photovoltaic performance degradation.$^{244}$

Cu$_2$O has also been used in organic light emitting diodes (OLEDs).$^{134,245}$ In order to construct efficient OLEDs, it is important to optimize the carrier injection ability at the interface of the active layer and anode materials. The Cu$_2$O films are commonly used as hole injection layers (HILs) to lower the hole injection barrier.$^{134,246,247}$ Kim et al. have reported the advantage of using a mixed stoichiometry of CuO and Cu$_2$O for increasing the performance of OLEDs as illustrated in Fig. 11.$^{134}$ Mixed stoichiometry of Cu$_2$O contains high density of defects such as oxygen vacancies or unbounded oxygen atoms, which act as an

Fig. 10 (a) 3D schematic of the electrodeposited ZnO–Cu$_2$O heterojunction solar cells. (b) J–V characteristic curves of ZnO–Cu$_2$O heterojunction solar cells. Reproduced from ref. 173 with permission from The Royal Society of Chemistry.
extra energy state within the energy gap of the Cu₃O layer. Interestingly, when the energy levels of these gap states are aligned with the highest occupied molecular orbital (HOMO) level of the hole transporting layer, no potential barrier is produced at the anode interfaces, which can lead to an increase in the hole injection efficiency.²⁴

4.2 Photo-catalytic applications

Cu₃O is a promising photo-catalyst that is used in many chemical processes, such as organic contamination degradation and water splitting under visible-light irradiation owing to their small band gap and low cost.¹³,²⁴⁸–²⁵⁵ Under illumination, Cu₃O produces electron/hole pairs that can generate hydroxyl radicals (·OH) from water. This radical is capable of mineralizing most organic molecules.²⁵⁶ For water splitting applications, the majority charge carriers of the Cu₃O (holes) oxidize water to oxygen gas (O₂), while the photo-generated minority charge carriers (electrons) reduce water to hydrogen gas (H₂).²⁴⁸,²⁵⁴,²⁵⁵ Significantly, the Cu₃O conduction band is more negative than the redox potential of H⁺/H₂, which allows sunlight to produce H₂ from water.²⁵³

Unfortunately, the general photo-instability of Cu₃O greatly hinders its direct application in photo-catalysis.²⁴⁸,²⁵⁶ To overcome this photo-instability effect, Cu₃O is typically coupled with other semiconductors to form heterojunctions and it has been reported that TiO₂ is one of the best candidates for this purpose.²⁵⁶,²⁵⁷ Additionally, nanostructuring of Cu₃O can also significantly improve overall stability.²⁵⁶ Fortunately, the large surface area to volume ratio, which is provided by nanostructuring, significantly increases the effective surface area available for photo-catalytic reactions.²⁴⁹,²⁵⁰,²⁵²

It has also been reported that the photo-catalytic production rate of H₂ can be significantly improved in the presence of alcohol, which provides suitable electron donors (also known as sacrificial agent/reagent).²⁵⁸–²⁶⁰ Barreca et al. have successfully demonstrated excellent performance of Cu₃O photo-catalysis for generating H₂ in the presence of methanol.¹³ They have suggested that methanol inhibits electron–hole recombination and acts partially as a hydrogen source.¹³ However, efficient photo-catalytic activity of Cu₃O for H₂ production has not been reported. This is despite the fact that the band gap of Cu₃O is 1.2 eV, which makes Cu₃O an efficient material to absorb sunlight. However, the position of the conduction band level limits its activity. Therefore, introducing a sacrificial agent is crucial to enable it to be used as a photo-catalyst. For example, Yao et al. have reported that Cu₃O exhibits high photo-catalytic activity in oxalic acid solutions.²⁵¹ Oxalic acid, which is a common pollutant in industrial wastewater, is a strong reductive agent and acts as an electron donor.²⁴¹,²⁴²

4.3 Antimicrobial applications

The antimicrobial properties of Cu₃O, in particular Cu₃O, have attracted growing research interest. Nanostructured Cu₃O commonly offers a strong degree of chemical and physical stability. Most bacterial cells have cellular membranes that contain pores in the nanometer range. Cu₃O, with dimensions less than 20 nm, have shown antibacterial properties.¹¹,²⁶⁰ The antimicrobial activity of Cu₃O has been attributed to the production of reactive oxygen species (ROS) such as ·O₂⁻, ·HO₂⁻, ·OH and H₂O₂ which can also occur without exposure to any visible light owing to the small band gap of Cu₃O.²⁶⁴,²⁶⁵ The generated ROS interact with outer cell walls to generate free radicals. The radicals penetrate into the inner cell membranes which lead to the disruption of the internal contents of the cell.²⁶⁴,²⁶⁵ The effectiveness of the antimicrobial agent appears to be related to the nature of the cell wall structures.²⁶³,²⁶⁵,²⁶⁷ S. aureus is composed of multiple layers of peptidoglycan with
numerous pores, which are suggested to be more susceptible to intracellular transductions. In contrast, the cell walls of *E. coli* are relatively thin, mainly consisting of peptidoglycan and outer layers of lipopolysaccharide, lipoprotein and phospholipids, which are less prone to being attacked by CuO nanoparticles. As a result, nanostructured CuO has a higher antimicrobial activity against *S. aureus* than *E. coli.*

It has been demonstrated that nanostructured CuO antimicrobial activity can be enhanced by exposing it to light. As described in Section 4.2, light irradiation generates excited electron–hole pairs in the CuO and deactivation of the bacteria is possible via a photo-catalytic process. Akhavan et al. have reported an improvement of 22% of CuO antibacterial activity under illumination.

### 4.4 Electrochemical applications

The electrochemical properties of nanostructured Cu$_2$O as electrodes for lithium ion batteries (LIB) have also been of growing research interest. Cu$_2$O has many attractive advantages over conventional materials including high theoretical capacity (>600 and >350 mA h g$^{-1}$ for CuO and Cu$_2$O, respectively) and low cost. One of the major issues with the use of Cu$_2$O in LIBs is its large volume variation during the Li$^+$ ion insertion/extraction processes, which leads to severe mechanical strains and a rapid decay in capacity. Recently, there have been various reports demonstrating LIBs with high reversible capacity and cycling stability by synthesising Cu$_2$O/graphene nanocomposites. Mai et al. reported an excellent reversible capacity of 583.5 mA h g$^{-1}$ with high cycling stability by incorporating CuO nanoparticles (~30 nm) onto graphene sheets. Wei et al. have discussed and listed three main advantages of hollow structures as anode materials for LIBs. Zhou et al. have reported excellent LIB performance by integrating hollow nanostructures of CuO with graphene. The composites exhibited a durable lifetime with reversible capacities as large as 640 mA h g$^{-1}$.

### 4.5 Electrochromic devices

Nanostructured Cu$_2$O electrochromic based systems, such as smart windows and optical displays, have been studied since the 1990s. It has been found that Cu$_2$O exhibits cathodic electrochromism, being transparent under visible illumination in their oxidized state and almost black when switched to their reduced state in the presence of an electrolyte containing positive ions such as H$^+$, Li$^+$ and Na$^+$. Generally, it has been found that the electrochromic process corresponds to the conversion of Cu$_2$O (transparent) to CuO (black) in a reversible reduction–oxidation process (redox). To date, the best coloration efficiency obtained by Cu$_2$O nanostructures has been up to 37 cm$^2$ C$^{-1}$, which is only one-fourth of the best of those made from nanoporous WO$_3$ (141.5 cm$^2$ C$^{-1}$). Unfortunately, nanostructured Cu$_2$O requires high coloration voltage and shows poor stability, and further work should be carried out to solve such important issues.

### 4.6 Sensing applications

Cu$_2$O offers great potential for the development of highly sensitive, yet low cost sensors. This includes optical, gas and bio sensors. Photodetectors are important devices that can be used in various applications, including thermal imaging systems, free-space communications, navigator aids and ozone-layer...
monitoring.\textsuperscript{283,284} Among the semiconductor materials, $\text{Cu}_x\text{O}$ has proven to be an attractive material for making photodetectors due to its relatively low band gap and remarkable optoelectronic properties.\textsuperscript{70,284–287}

Sahoo et al. have demonstrated excellent performance of the photodetector based on $\text{Cu}_2\text{O}$ nanowires.\textsuperscript{285} They adopted the metal–semiconductor–metal (MSM) technique for photon sensing under dark and illumination conditions. Fig. 13(a)–(d) illustrated SEM micrographs of four such MSM devices with channel lengths (i.e. spacing between the electrodes) of 210, 260, 580 and 720 nm, respectively.\textsuperscript{285} They observed that the channel length significantly influenced the photocurrent and the bias dependence of the photo-to-dark-current ratio (Fig. 13(e)–(h)).\textsuperscript{285} Liao et al. reported the photoconductivity of $\text{Cu}_2\text{O}$ nanowires measured under dark and blue (488 nm) laser illumination and the conductance of nanowires increased from 0.7 to 4.3 $\mu$S under illumination. Remarkably, the photoconductivity response time was less than three seconds with good reversibility and stability.\textsuperscript{70} $\text{Cu}_2\text{O}$ has also been extensively used in photodetector applications under visible and IR illumination (due to its relatively low band gap).\textsuperscript{284,286–288} Recent comprehensive reviews on the usage of $\text{Cu}_2\text{O}$ in photodetection are found elsewhere.\textsuperscript{1}

$\text{Cu}_x\text{O}$ also offers a great possibility for developing highly sensitive semiconductor-based gas sensors. The sensing properties of $\text{Cu}_x\text{O}$ can be improved by decreasing its size to nanoscale dimensions (comparable to twice of the Debye length) and by adding appropriate dopants.\textsuperscript{126,289} Catalytic nanoparticles such as $\text{Pd},$\textsuperscript{290} $\text{Pt},$\textsuperscript{291} $\text{Ag}$\textsuperscript{292} and $\text{Au}$\textsuperscript{291,293,294} attached to the $\text{Cu}_2\text{O}$ surface further increase its sensitivity, mainly due to spill-over effects.\textsuperscript{299} $\text{Cu}_2\text{O}$ thin films have been demonstrated to be highly sensitive towards various gas species including $\text{C}_2\text{H}_5\text{OH},$\textsuperscript{14,126,294–298} $\text{CO},$\textsuperscript{296,299,300} $\text{NO}_2$ (ref. 14 and 300) and $\text{H}_2\text{S}$\textsuperscript{53,290,301} (Fig. 14). The ability to tune the shape and dimensions of $\text{Cu}_2\text{O}$ thereby creating superior chemical and physical properties can be exploited for chemosensors and biosensors. They also show unique surface chemistry, thermal and electrical properties and a high surface-to-volume ratio which enhance the sensitivity and response of electrochemical sensors.\textsuperscript{302}

$\text{Cu}_2\text{O}$ has been used as a working electrode in electrochemical based biosensors including glucose sensors.\textsuperscript{303} Most electrochemical glucose sensors involve the use of the enzyme glucose oxidase. However, the greatest drawback of enzymatic sensors is their lack of stability due to the intrinsic nature of enzymes.\textsuperscript{304,305} Development of non-enzymatic sensors, using $\text{Cu}_2\text{O}$ as the working electrode, has been reported.\textsuperscript{306–308} Though non-enzymatic sensors are, by design, quite selective, $\text{Cu}_2\text{O}$-based glucose sensors have fast response times, possess a high degree of repeatability and are extremely stable.\textsuperscript{303}

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**Fig. 13** (a–d) SEM micrographs of $\text{Cu}_2\text{O}$ nanowire based devices having electrode spacings of 210, 260, 580, and 720 nm, respectively. The electrodes are 3.2 $\mu$m wide for all of the devices. The scale bars are 100 nm. The current–voltage ($I$–$V$) measurements are carried out at dark and under illumination conditions for all four samples. Depending on the interelectrode spacing, the samples are categorized into two sets, set I: sample-1 and sample-2; set II: sample-3 and sample-4. (e and f) $I$–$V$ characteristics of set I and set II, respectively. (g and h) Plot of the ratio of photocurrent ($I_{\text{photo}}$) to the dark current ($I_{\text{dark}}$) vs. bias voltage for set I and set II, respectively. Insets of (g) and (h) represent the photocurrent as a function of bias for set I and set II, respectively. Reprinted with permission from (S. Sahoo, S. Husale, B. Colwill, T.-M. Lu, S. Nayak and P. M. Ajayan, ACS Nano, 2009, 3, 3935–3944) copyright (2007) American Chemical Society.
roles in tribology in monitoring the friction and anti-wear properties. Recently, Gaujan et al. have revealed that lubricity enhancement is attributed to the synergistic effect of uninterrupted supplies of CuO nanorods under contact surfaces and their rolling mechanism.80

In addition to the enhancement of tribological properties, nanofluids with dispersed CuO nanoparticles have great potential for improving heat transfer especially in improving the efficiency of chillers, refrigerators and air-conditioners.81,810,811 Many studies have reported that mixtures with suspended CuO nanoparticles have higher thermal conductivity than the conventional host fluid.81 This is due to the thermal conductivity of CuO (76.5 W m K⁻¹ which is much higher than ethylene glycol that has a value of 0.26 W m K⁻¹). Lee et al. have compared the thermal conductivity of CuO and Al₂O₃ nanoparticles suspended in ethylene glycol and found that the thermal conductivity of the CuO suspensions is 7% higher than the Al₂O₃ system.812

4.8 Field emission applications

The field emission (FE) properties of CuO are far less reported than other oxide materials such as ZnO, SnO₂ and In₂O₃. Due to its relatively narrow band gap, nanostructured CuO offers an attractive alternative to serve as a FE emitter.811–815 In a FE system the emitting capability is believed to be highly dependent on both the properties of the material and configuration of the cathode.84 It is known that materials with higher aspect ratios and sharp edges generally produce higher FE currents.55,813,815 Zhu et al. have reported FE measurements of CuO nanowire films with a low turn-on field of 3.5–4.5 V μm⁻¹. They obtained a large current density of 0.45 mA cm⁻² at an applied electric field of 7 V μm⁻¹.814 Nanostructured Cu₂O also exhibits relatively high FE performance. Shi et al. have demonstrated Cu₂O microporous cubes with a low turn-on field of 3.1 V μm⁻¹. They showed a high current density of 1 mA cm⁻² at an applied electric field of 11 V μm⁻¹.55 It has also been reported that Cu₂O can be coupled with other metal oxides such as ZnO or TiO₂ to enhance its FE performance (Fig. 15).815–817 This enhanced FE is attributed to the alteration in electron affinity of CuₓO by the other metal oxides forming a nano-heterojunction.817 Additionally, the presence of the heterojunctions promotes charge separation, where the electrons move to ZnO or TiO₂ and the holes move to Cu₂O, which reduces the recombination of electron–hole pairs.817

4.9 Other applications

Nanostructured Cu₅O has also been reported for many applications other than those presented in Sections 4.1 to 4.8. Of note, nanostructured Cu₅O has been used in ceramic resistors818 and supercapacitors.819,820 Nanostructured Cu₅O has also been incorporated in memristors,821–823 heterogeneous catalysis,824–828 anti-fouling829,830 and thin-film transistors.8,822,823 Of course, there are other applications for which Cu₅O has been used, but these are beyond the scope of this review paper.
5. Conclusions and future outlook

In this article, we have presented a comprehensive review of nanostructured Cu$_2$O focusing on their properties, preparation, processing and device applications. An overview of the material properties, including crystal structures, electronic band structures, optical, vibrational, electrical, thermal and magnetic as well as superconductivity were presented. The effect of doping on the band gap and the enhancement in electrical properties was also detailed. Though much effort has been channeled in producing n-type Cu$_2$O, the reproducibility and quality issues of the generated films are still questionable. This is potentially due to strong self-compensation effects and dopant solubility issues when n-type dopants are involved. Clearly, these issues must be overcome before high efficiency photovoltaic devices, based on homojunction Cu$_2$O devices, will be realized.

Numerous synthesis techniques were reviewed, focusing on methods that produce nanostructured Cu$_2$O. Different synthesis techniques provide flexibility within the constraints of any particular application needs. Therefore, it is essential that exploration of nanostructure Cu$_2$O synthesis continues and more innovative and low-cost routes are found in order to improve the future of the nanostructured Cu$_2$O and its many applications.

Additionally, we have discussed the major applications of nanostructured Cu$_2$O in optics, sensing, tribology, refrigeration, electrochemistry, photocatalysis, high-$T_c$ superconductivity, electrochromics and antimicrobial devices. Due to the versatility of nanostructured Cu$_2$O, many more applications can be explored and are yet to be investigated.

To date, the majority of work in the area of Cu$_2$O has been devoted to CuO and Cu$_2$O, whilst the number of reports on Cu$_2$O$_x$ are significantly lower. Despite the fact that there is a very limited number of reports available, the authors believe that the study of nanostructured Cu$_2$O$_x$ might provide possible new material insights and unique opportunities for incorporation into a wide-range of applications. Like other copper oxides, nanostructured Cu$_2$O$_x$ has the potential to be used in tribology and heat transfer applications as well as antimicrobial devices. As with the other copper oxide structures, the potential gains from developing a low-cost, nanostructured material, like Cu$_2$O$_x$ for any of these applications are extremely enticing and expected to be explored.

Notes and references
