Copper oxide nanoparticles doped with lanthanum, magnesium and manganese: optical and structural characterization

Maribel Guzman¹, Wei Tian², Chantal Walker² and Jose E. Herrera²

¹Department of Engineering, Pontifical Catholic University of Peru, Avenida Universitaria 1801, Lima 15088, Peru
²Department of Chemical and Biochemical Engineering, Western University, London, ON, N6A 5B9, Canada

Copper oxide (Cu2O) is a promising semiconductor for photovoltaic and photocatalytic applications since this material has a high optical absorption coefficient and lower band gap (2.17 eV). Doped lanthanum (La), magnesium (Mg) and manganese (Mn) Cu2O nanoparticles (Cu2O Nps) were prepared by a displacement reaction. The doped and undoped Cu2O Nps were characterized with scanning electron microscopy–energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and ultraviolet–visible spectroscopy. The EDS results confirm the presence of La, Mg and Mn in the Cu2O Nps. The XRD results confirm the formation a single cubic phase of Cu2O with a cuprite structure. TEM images confirm the formation of Nps with mean diameters between 12.0 ± 6.1 and 30.8 ± 11.0 nm. Doped and undoped Nps present a narrow band gap (2.40 eV), blue shifted with respect to bulk Cu2O.

1. Introduction

In the last two decades, the study of new oxide-based semiconductors has greatly intensified, since these materials can be used in solar cells and transparent electronics [1]. In fact, nanoparticles (Nps) of diverse metal oxides have shown potential applications in optical devices, purification systems, biomedical systems, photocatalysis and photovoltaics. Among promising metal oxide formulations such as tin oxide (SnO2) [2–5], titanium...
dioxide (TiO₂) [6-8], tungsten oxide (WO₃) [9-11], vanadium pentoxide (V₂O₅) [12-14] and zinc oxide (ZnO) [15-19], cuprous oxide (Cu₂O) has emerged as an interesting alternative to study due to its optical properties. Indeed, Cu₂O is an important p-type metal oxide semiconductor with a band gap of 2.17 eV, which makes it a promising material for the conversion of solar energy into electricity [20,21]. Cu₂O exhibits a cubic structure and a p-type conductivity arising from copper vacancies that introduces an acceptor level of approximately 0.5 eV above the valence band [22]. Therefore, Cu₂O is considered a suitable material for photovoltaic applications [1]. In addition to its special optical and electrical properties, Cu₂O has other advantages such as non-toxicity and, compared to other oxides (Fe₂O₃, In₂O₃, NiFe₂O₄, NiO, Sb₂O₅, SnO₂, ZnO, V₂O₅ and others), its low cost [23-28].

In semiconductors and insulators, electrons are confined to a number of energy bands and are forbidden in other regions. The term ‘band gap’ refers to the difference in energy between the top of the valence band and the bottom of the conduction band [29]. Since for semiconductors the band gap can be small, doping with other elements, even in very small amounts, can modify this gap and drastically increase the conductivity of the material. In particular, it is possible to adjust the bandgap by modifying or partially substituting a transition metal with another element. Indeed, doping of p-type (NiO) or n-type (ZnO) semiconductor nanostructures has been previously reported by Das et al. [30], Bhatt et al. [31], Manikandan et al. [32,33] and Shah et al. [15]. However, the exciting physical properties of transition metal oxides arising from the d-electrons can also be affected or disappear with the modification of this band gap [34]. For this reason, researchers have tried to improve the electrical and optical properties of Cu₂O by incorporating various transition metals such as cobalt [35], iron [35,36], manganese (Mn) [22,35,37-40] and nickel [35]. In addition, the incorporation of other elements such as aluminium [41], cerium [42], lithium [43-45], magnesium (Mg) [1,43,46-48], silver [41], sodium [44], samarium [49], titanium [44] and zinc [42,43,50] has also been evaluated.

There are many methods to obtain doped Cu₂O nanostructures, such as biosynthesis [51,52], chemical vapour deposition [46,47], electrodeposition [22], hydrothermal synthesis [37], pulsed laser deposition [40], solvothermal synthesis [38,39] and spray pyrolysis [46,48]. In addition to these methods, the chemical displacement or substitution technique is an interesting but little-explored alternative. This technique involves a reaction in which one element is replaced by another within a chemical compound [53].

The present work reports the preliminary results of the synthesis of Cu₂O Nps doped with lanthanum (La), Mg and Mn through a chemical shift reaction, and the characterization of the resulting materials including the evaluation of their band gap energy.

2. Experimental section

2.1. Materials and methods

2.1.1. Chemicals

Sodium hydroxide, NaOH (97%), was purchased from Alfa Aesar (Toronto, Canada). La(NO₃)₃·6H₂O (99%), Mg, Mg(NO₃)₂·6H₂O (99%), and Mn, Mn(NO₃)₂·nH₂O (98%), were purchased from Sigma-Aldrich (Toronto, Canada). Absolute ethanol, EtOH (99%), was also obtained from Sigma-Aldrich (Toronto, Canada). All chemicals were used as received without further purification. In all the experimental syntheses, Milli-Q water (18 MΩ cm) obtained from a purification system (Millipore, Darmstadt, Germany) was used.

2.1.2. Preparation of doped copper oxide nanoparticles

The modified chemical reduction method proposed by Badawy et al. [54] was used for the synthesis of Cu₂O Nps [55,56]. For the synthesis, ethanolic solutions of sodium hydroxide (20 mM), Mg nitrate (20 mM), Mn nitrate (20 mM) and La nitrate (20 mM) were used. Approximately 100 mg of previously synthesized Cu₂O Nps was suspended in 30 ml of ethanol. The solution containing the dopant element was gradually added to the suspension of Nps under magnetic stirring. The process was carried out for 120 min at 60°C. At the end of the reaction, the colloids were centrifuged at 3000 rpm for 5 min using a microcentrifuge (Thermo Scientific, ST-40R). The Nps were placed in a desiccator. To characterize the samples obtained, the Nps were suspended in absolute ethanol using an ultrasonic cleaning container (Fisher Bioblock Scientific).
2.2. Characterization techniques

2.2.1. Structural characterization

To perform the structural analysis, a Bruker D5000 theta-theta X-ray diffractometer (Karlsruhe, Germany) equipped with a copper anticathode (\( \lambda \text{Cu K}\alpha = 1.5418 \, \text{Å} \)) was used. Data were collected over the range \( 2\theta = 25^\circ \text{–} 80^\circ \) using a step size of 0.02° and a count time of 1 s per step. The X-ray diffraction (XRD) reference intensity ratio methodology was used to assign the phases observed in the diffractograms.

2.2.2. Elemental composition analysis

Chemical composition was determined by scanning electron microscopy (SEM) using an FEI Quanta 650 in secondary electron mode at an accelerating voltage of 3–10 kV (FEI Europe BV; Eindhoven, The Netherlands). Energy-dispersive X-ray spectroscopy (EDS) analysis was performed with an Ametek EDAX TEAM system coupled to an SEM microscope.

2.2.3. Morphological analysis

The size and morphology of the doped and undoped Cu2O Nps were analysed by transmission electron microscopy (TEM). TEM analysis was carried out using a Philips CM10 TEM instrument, upgraded with a digital AMT system and a LaB6 filament. The acceleration voltage used was 80 kV. Before analysis, dried samples were suspended in 2-propanol, and a drop of the suspension was spotted on a copper TEM grid coated with lacey carbon film.

2.2.4. Surface area and pore size distribution

The specific surface area was determined using Brunauer–Emmett–Teller (BET) measurements. Nitrogen adsorption–desorption was developed at 77.35 K in an ASAP 2010 Analyzer. Before each measurement, 150–250 mg of sample was degassed at 200°C for 2 h and until the pressure was below 5 mmHg. Adsorption isotherms were measured within a relative pressure range of 0.001 to 1 at 77.35 K.

2.2.5. Optical properties

Ultraviolet–visible–near-infrared (UV-VIS NIR) spectra were recorded in diffuse reflectance mode using a Shimadzu UV-VIS NIR spectrometer equipped with a Praying Mantis diffuse reflectance cell (Harrick Scientific). The spectra were referenced to a Spectralon standard (DRP-SPR, Harrick Scientific).

3. Results and discussion

The Cu2O Nps doped using a modified displacement reaction were characterized by the techniques described previously.

Elemental analysis of the samples was performed by EDS. The results are shown in figure 1. The EDS spectrum of the undoped Cu2O sample shows all K and L emission peaks for copper and oxygen (figure 1a). Similar results for Cu2O Nps have been previously reported by Mallik et al. [57] and Mancier et al. [58]. The results obtained by the EDS analysis indicate that the synthesized product is composed of Cu2O Nps. Likewise, the calculated Cu : O atomic ratio is approximately 1.2, which is between the values 1.0 and 2.0, theoretical values of CuO and Cu2O, respectively. The EDS spectra of the doped Cu2O samples show, in addition to the Cu and O peaks, the peaks corresponding to La, Mg and Mn. The average atomic percentages of the doped samples were determined to be 2.2% at. of La (figure 1b), 1.1% at. of Mg (figure 1c) and 1.0% at. Mn (figure 1d). The literature reports a similar atomic % for Mn-doped Cu2O Nps obtained by hydrothermal method [37].

By means of XRD, it was possible to obtain information on the crystal structure of the synthesized Nps. The recorded XRD spectra are shown in figure 2. For the analysed samples, the spectra reveal diffraction peaks at \( 2\theta = 29.6^\circ, 36.5^\circ, 42.3^\circ, 61.4^\circ \text{ and } 77.4^\circ \), which correspond to the structure of cubic cuprite (Cu2O) according to JCPDS card no. 005-0667. Therefore, the formation of Cu2O with cuprite structure (space group Pn\overline{3}m, \( a = 4.23 \, \text{Å} \)) is confirmed. Similar XRD results of undoped [20,21,58–64] and Mn-doped [37,38] Cu2O Nps have been previously reported. Likewise, other diffraction peaks were observed at \( 2\theta = 43.3^\circ \text{ and } 50.5^\circ \) arising from Cu (JCPDS card no. 85-1326) [58].
Figure 1. EDS spectra of undoped Cu$_2$O Nps (a), La-doped Cu$_2$O Nps (b), Mg-doped Cu$_2$O Nps (c) and Mn-doped Cu$_2$O Nps (d).
In addition, in some spectra, peaks at $2\theta = 35.6^\circ$ and $38.8^\circ$ are identified, which would indicate the formation of CuO (JCPDS card no. 45-0937). This is evident in the samples of Cu$_2$O doped with Mg (figure 2c) and Cu$_2$O doped with Mn (figure 2d). In addition, no additional diffraction peaks related to impurities of MgO, MnO, MnO$_2$, La$_2$O$_3$, among others, were observed in the doped samples. In this sense, we can affirm that due to the low concentrations of the doping elements used, the La, Mg and Mn ions have been incorporated in the form of ions into the crystal lattice of the Cu$_2$O without changing the cubic structure [38].

The average size and morphology of undoped and doped Cu$_2$O NPs were analysed by TEM. The morphology and particle size distribution of each sample are shown in figure 3. ImageJ software was used to estimate the mean diameter of the NPs. In this case, the diameters of at least 100 particles from each sample were measured. Figure 3a shows the size distribution of undoped Cu$_2$O NPs. Spherical NPs with diameters from 2.0 nm to 26.0 nm and an average diameter of 12.0 nm ± 6.1 nm can be observed. This result is in agreement with that reported by Yin et al. [65], Lai et al. [66] and Liu et al. [67], who obtained semi-spherical Cu$_2$O NPs with similar mean diameters by consecutive oxidation of copper NPs formed in an emulsion. Based on the particle size distribution, we were able to estimate that around 40–45% of NPs could be considered as quantum dots (QDs) (size ≤ 10 nm).

On the other hand, Cu$_2$O NPs doped with different elements show a greater variety of shapes. The sample doped with La shows NPs with semi-spherical, hexagonal, truncated cube and elongated shapes (figure 3b). These particles have various sizes with a bimodal distribution with mean diameters ranging from 2 nm to 78 nm. The estimated mean diameter was 16.8 nm ± 10.6 nm.

A bimodal distribution is also observed for Mg-doped Cu$_2$O NPs (figure 3c). This sample has a mean diameter of 30.8 nm ± 11.0 nm. The particles resemble hemispheres that vary in dimensions from 3 nm to 72 nm. The size distribution is illustrated in the histogram at the top left of this figure.

The size distribution of the Mn-doped Cu$_2$O NPs is shown in the lower right of figure 3d. This figure shows a particle size distribution from 5 to 48 nm with a mean diameter of 20.5 nm ± 7.1 nm. As we can observe, comparing the TEM images, larger semi-spherical NPs are obtained when Mg and Mn are used as doping elements. Likewise, a diversity of forms is obtained when the dopant element is La. The percentages of QDs (size ≤ 10 nm) estimated for the NPs doped with La, Mg and Mn were approximately 37%, approximately 29% and 8%, respectively. A summary of the NP sizes obtained by TEM is presented in table 1.

![Figure 2. XRD patterns of undoped Cu$_2$O NPs (a), La-doped Cu$_2$O NPs (b), Mg-doped Cu$_2$O NPs (c) and Mn-doped Cu$_2$O NPs (d).](image-url)
The surface area determined using the BET method for the undoped Cu$_2$O Nps was determined. The surface area was 11.06 m$^2$ g$^{-1}$. This result is better than the values of 0.76 m$^2$ g$^{-1}$ and 4.5 m$^2$ g$^{-1}$ reported by Bhosale et al. [68] and Mrunal et al. [69] for Nps of similar sizes, respectively. Unfortunately, due to the small amount of doped Cu$_2$O samples, it was not possible to measure their surface area. However, based
on the size distribution of the Nps and assuming that they have hemispherical shapes (except for the La-doped sample), the surface area of the doped samples was geometrically estimated. Though this calculation is based on average distribution sizes, it provides a range of estimated surface areas for the doped Nps. The calculated values were 7.63 m² g⁻¹ (Cu₂O:Mn, ϕ = 20.5 nm), 7.31 m² g⁻¹ (Cu₂O:La, ϕ = 16.8 nm) and 5.09 m² g⁻¹ (Cu₂O:Mg, ϕ = 30.8 nm).

Finally, UV-VIS NIR spectroscopic measurements of each sample at room temperature were recorded (figure 4a). For semiconductor samples, UV-VIS NIR spectroscopy offers a simple and convenient method to estimate the optical band gap, since this technique probes the electronic transitions between the valence band and the conduction band. The optical direct band gap energy (E_g) of the undoped and La-, Mg- and Mn-doped Cu₂O Nps was estimated from the UV-VIS absorption spectra. For this, the variation of the absorption coefficient (α) with the photon energy was used according to the following relationship:

\[ (\alpha h \nu)^2 = A(\nu - E_{\text{gap}}), \]  

(3.1)

where \(E_{\text{gap}}\) is the optical band gap, \(A\) a constant, \(h\) the Planck constant, \(\nu\) the frequency of the incident photons and exponent \(p\) is the transition probability [70, 71]. For \(p = 1/2\), the transition formalism is direct and allowed.

The values of the optical energy gap were estimated by extrapolation of the linear portion of the graph plotted with \((\alpha h \nu)^2\) (figure 4b). The optical direct band gap values are summarized in table 1. The direct band gap of undoped Cu₂O Nps was 2.433 eV, a value higher than the corresponding

\[ \begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Energy (eV)} & 2.0 & 2.2 & 2.4 & 2.6 & 2.8 & 3.0 \\
\hline
\text{Cu₂O} & 1.2 & 1.0 & 0.8 & 0.6 & 0.4 & 0.2 \\
\text{Mn-doped Cu₂O} & 1.2 & 1.0 & 0.8 & 0.6 & 0.4 & 0.2 \\
\text{Mg-doped Cu₂O} & 1.2 & 1.0 & 0.8 & 0.6 & 0.4 & 0.2 \\
\text{La-doped Cu₂O} & 1.2 & 1.0 & 0.8 & 0.6 & 0.4 & 0.2 \\
\hline
\end{array} \]

Figure 4. (a) UV-VIS spectra and (b) direct band gap of undoped and doped cuprous oxide Nps.
methodology and writing produces little structural distortions in the Cu$_2$O lattice, and thus slightly with the doped Nps, being more evident the case of Mn-doped Cu$_2$O Nps. On the other hand, the influence of La on the morphology of Nps is more evident. The energy of the band gap decreases depending on the dopant element. Depending on the dopant element, semi-spherical or elongated Nps similar to nanorods were obtained. In this case, the morphology was changed depending on the identity of doping element. Depending on the mean diameter, the forbidden band decreases slightly when a doping element is added. This may be explained by the effects of a quantum confinement due to the small sizes of the crystallites [73]. However, further analysis should be performed as this trend does not apply for Mn-doped Cu$_2$O.

Indeed, the dopant element can perform two functions: one is to change the size of the Np, which would mean that the forbidden band would change; the other is when the dopant element is incorporated into the electronic structure of Cu$_2$O and thus changes the band gap.

According to the results shown in table 1, we can assume that if the mean diameter increases, the forbidden band decreases, for La-doped Cu$_2$O and Mg-doped Cu$_2$O. This could be explained by the effects of a quantum confinement due to the small sizes of the crystallites [73]. However, further analysis should be performed as this trend does not apply for Mn-doped Cu$_2$O.

4. Conclusion

In summary, we report a method that produces doped and undoped Cu$_2$O Nps. Doped Nps present a larger average size than undoped Nps. The prepared particles have mean diameters of 12 nm (Cu$_2$O), 16.8 nm (La-doped Cu$_2$O), 30.8 nm (Mg-doped Cu$_2$O) and 20.5 nm (Mn-doped Cu$_2$O). It was found that the morphology was changed depending on the identity of doping element. Depending on the dopant element, semi-spherical or elongated Nps similar to nanorods were obtained. In this case, the influence of La on the morphology of Nps is more evident. The energy of the band gap decreases slightly with the doped Nps, being more evident the case of Mn-doped Cu$_2$O Nps. On the other hand, the doped cuprous oxide band gap did not show a significant change that made it widen or narrow and remained within the normal range of cuprous oxide optical band gap around 2.433 eV. The optical properties of doped and undoped Cu$_2$O Nps confirm the potential of this material for low-cost optoelectronic device applications.

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material [74].

Authors’ contributions. M.G.: conceptualization, funding acquisition, methodology, project administration, supervision and writing—original draft; W.T.: formal analysis, methodology and writing—review and editing; C.W.: formal analysis, methodology and writing—review and editing; J.E.H.: resources and writing—review and editing.

All authors gave final approval for publication and agreed to be held accountable for the work performed therein. Conflict of interest declaration. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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