Synthesized Nanoparticles Based on Functionalized Metal Oxides with Chiral ligand

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Abstract

The research reports the synthesis of α–MnO2 and CuO nanoparticles obtained from laser ablation method. Based on the properties as semiconductors, the oxides as bactericity systems for Escherichia coli ATCC 11229 and Staphylococcus aureus ATCC 6538 have been tested. The influence on plasmon was evaluated, in relationship to the energy, time and wavelength of the laser used. The dispersion of nanoparticles for manganese oxide were in function of the energy, and its frequency oscillation is greater than copper oxide, due to the effects of charge transfer. The effect of a chiral organic compound was estimated in situ, generating stability and reproducible biocidal properties. Finally, it is important to mention that the biological activity was mediated by the semiconductor capacity. Control experiments will be necessary for to continue for the understanding of the mechanism.

Keywords: Metallic oxides, sputtering method, electronic properties.

1. Introduction

Nosocomial infections are the main cause of a prolonged stay of infected patients in the hospitals. NS aggravate the imbalance between the allocation of resources for primary and secondary care at divert scarce funds towards the treatment of potentially preventable conditions [1]. A study conducted in Colombia by the Ministry of Health and Social Protection, showed that in samples of patients from different hospitals for locations, such as: pediatric and neonatal were found microorganisms (12 % K. pneumoniae, 10.7% S. aureus and 5.4% to E.coli), corresponding to 1,010 insulations. In urine samples 405 microorganisms were isolated associated with 33.1% E. coli and 15.3% to K. pneumoniae [2][3] High resistance to carbapenems (> 11.6%) and third generation cephalosporins (> 25.6%) in Enterobacteria were found.

The importance of combating this microorganisms give to place to synthesize new materials that allow control contagion vectors in hospital implements. Previous studies have shown that the use of metal oxide nanoparticles (NPs) can be an alternative to combat this type of microorganisms. In 2018 Atacan and et al, synthesized nanoparticles of Ag/CuFe2O4 functionalized with tannic acid and immobilized in papain, which presented remarkable antibacterial activity against Escherichia coli and Staphylococcus aureus [4]. In 2015 Kooti and collaborators impregnated NPs of CoFe2O4/SiO2/ Ag with Streptomycin, increasing its antibacterial properties [5]. The combination of NPs of metallic oxides with molecules organic increase their respective potentials, and provide others magnetic and optical properties. The aim of this research is to synthetise...
MnO₂ and CuO nanoparticles obtained from Pulsed Laser Deposition, evaluating the best parameters in order to stabilization in colloidal suspension, and the decrease of GAP for to be deposited in polylethylene terephthalate (PET) substrate, as potential biocide materials. The effect of organic molecule was evaluated in situ with L-proline, in the microbiological activity for *Staphylococcus aureus*.

2. Experimental details

MnO₂ and CuO nanoparticles were synthetized from MnO₂ and CuO target by conventional Pulsed Laser Deposition (PLD) technique. **figure 1**.

![Figure 1. Synthesis of MnO₂ and CuO nanoparticles](image)

The target was obtained from sintering method by Zhou in 2011 [6]. The rust was pressed in a 2 ton mechanical press, then it was taken to the flask and subjected to temperature for 12 hours at different heating ramps (0-100°C in 2 hours, 100-300°C 2 hours, 300-500°C 3 hours, 500-800°C 5 hours). PLD of MnO₂ and CuO target was carried out using Q-switched Nd:YAG laser operating at wavelength of 1064 nm, pulse duration variable, pulse energy different values and methanol and water as solvents, **table 1**. The laser fluency was kept at 0.89 J/cm². The Band Gap (eV) for nanoparticles in suspension were calculated using Tauc’s method (Eq 1).

\[(\alpha h\nu)^2 = k(h\nu-E_g)\]

Where:

- \(h\) is Planck constant,
- \(\nu\) photon frequency,
- \(\alpha\) absorption coefficient and
- \(K\) energy independent constant.

UV-Vis spectra performed with Perkin Elmer Lambda 9 UV/VIS/NIR spectrometer, covering and extended wavelength range of 190 to 800 nm. For RAMAN shifts was used RAMAN scattering (CCD) spectrophotometer with 532 nm laser, 50 μm slit, 900 lines/nm, estimated resolution 5.5 – 8.3 cm⁻¹ and focus 2524.

The MnO₂ nanoparticles synthetized were evaluated in Tryte Soy Agar, in the presence of bacterial communities of industrial origin, *Escherichia coli* (ATCC 11229) and *Staphylococcus aureus* (ATCC 6538). The bacterial inoculum with 100 μL of the bacterial solution at 0.1 Absorbance, was made. To evaluate the compounds, blank discs made with filter paper were sterilized to which 50 μL of each nanoparticle solution, controlling contamination of the materials or reagents. Continuing this, the discs were deposited in Petri dishes, in where these were exposed to UV-C (200-280 nm) radiation by 2 h. Subsequently, each essay was incubated during 12 h and 24 h, as incubation time. It was used as control, test in the absence of light UV-C. The inhibition was measured reporting the best conditions for the samples with the lowest GAP value, finally. The chiral effect on nanoparticles was estimated in solution, a specific concentration (1 x 10⁻³ M) was added to the systems, which improved the dispersion of the nanoparticles and therefore the estimation of the properties.
Table 1. Experimental conditions for MnO$_2$ and CuO nanoparticles

| Metallic oxides | Wavelength (nm) | Solvent | Energy (mJ) | Time (min) |
|-----------------|-----------------|---------|-------------|------------|
| MnO$_2$         | 1064            | Methanol | 25, 50, 80 | 5, 10      |
|                 | 1064            | Water   | 25, 50, 80 |            |
| CuO             | 1064            | Methanol | 25, 50, 80 | 5, 10      |
|                 |                 | Water   | 25, 50, 80 |            |

The microstructural analysis were analyzed through scanning electron microscopy (SEM). Using an SEM JEOL de Mesa JCM 50000. They were submitted to a gold coverage using PVD, in a high vacuum and a 10 kV voltage was used. The magnifications were $x1000$ to determine the dispersion, $x10000$ to assess the general morphology. It is worth to mention, that for every analysis the sample were conditioned to 25 °C in an environment of relative humidity of 50±5% during 48 h.

3. Results and discussion

3.1 Optical and electronic properties

In relation to the table 2, the higher the energy used to obtain nanoparticles, the value of GAP decreases. This behavior indicates that the laser- induced sputtering near threshold fluencies presents effect of dense electron- hole plasma. Likewise, there is adiabatic stability at 80 mJ in relationship to 25 mJ, when the electron with the exciton, is trapped. The semiconductor requires minor energy at 80 mJ. The strong optical absorption is characteristic of MnO and CuO direct band gap transition and indicating good quality of the synthesized nanoparticles with low reflectance. However, changes in the reflectance in the UV region are observed, in relation to fluency time. This behavior might be associated to the influence of numerous factors such as structural parameters and carrier concentrations. The optical behavior is attributed mainly to the sp-d spin exchange interaction between the band electrons and the localization d electrons Mn$^{4+}$ ions, figure. 2(a)-2(b). On the other hand, the colloidal solutions in methanol and water as solvents, were obtained. This behavior showed that water does not participate effectively in the stabilization of nanostructures. The solvent water present major electrodeonator capacity than methanol. The water can to establish coordination bonds on the surface nanoparticle. However, the methanol suggested that the presence of aliphatic groups stabilize the nanoparticles. Likewise, water as solvent has a high dielectric constant that can affect the dispersion and oxidation states of manganese, figure. 2 (c).

In the figure. 3 the RAMAN spectrum, was observed. Initially, between 200-3250 cm$^{-1}$ Raman shift is associated with the presence of PET corresponding to: 628.5 cm$^{-1}$, 859.3 cm$^{-1}$, 1099 cm$^{-1}$, 1278.8 cm$^{-1}$, 1608.3 cm$^{-1}$, 1717 cm$^{-1}$, 2968.3 cm$^{-1}$, and 3077.9 cm$^{-1}$. The intensity of carbonyl shifted to 1717 cm$^{-1}$ is assigned, band large and acute. The weak peak at 3077.9 cm$^{-1}$ corresponding to benzene ring, skeleton vibration and the 1099 cm$^{-1}$ band to symmetric and asymmetric C-O-C vibration is related. The absorption peak below 900 cm$^{-1}$ is assigned to C-H bending vibration peak, with adjacent hydrogen and hydrogen bonds isolated in the benzene ring. Fluorescence effect in presence of PET overlaps some vibrations are observed.[7] On the other hand, MnO$_2$ provides different types of vibrations. The spectra showed three peaks in all cases for α-MnO$_2$ around 183, 574 and 635 cm$^{-1}$ varying only the width of these. The spectrum obtained from the synthesized MnO$_2$ nanoparticles presented split to 180 cm$^{-1}$ and 650 cm$^{-1}$, which corresponds to α-MnO$_2$.[8]
| Oxide | Time (min) |  |  |  |  |
|---|---|---|---|---|---|
|  | 5 | 10 |
| Energy | 25 | 50 | 80 | 25 | 50 | 80 |
| GAP (eV) | 5.79 | 5.61 | 3.99 | 5.86 | 4.03 | 3.77 |

Table 2. GAP calculated using Tauc’s method

![Graph a](image1)

![Graph b](image2)

![Graph c](image3)
Figure 2. Optical and electronic properties of MnO$_2$ nanoparticles. a). 5 min, 80 mJ, Methanol; b). 10 min, 80 mJ, Methanol; c). 5 min, 50 mJ, Water; d). Graphical GAP

Figure 3. Shift RAMAN of MnO$_2$ nanoparticles

The electronic properties for CuO showed a major stabilization using methanol as solvent. The electronic transition associated with Cu$^{2+}$ tetrahedral, at 600 nm in methanol, was found. This band corresponds to exciton recombination linked to oxygen vacancies. The plasmon is favoured for 10 min and 80 mJ. The same manner that MnO$_2$ nanoparticles, the methanol does not overlap the copper band, possibly due to the formation of coordination compounds in the periphery from metallic oxide.[9] figure. 4.
For CuO nanoparticles the behaviour of GAP presented the same tendency in relationship with MnO₂. The higher the energy used to obtain nanoparticles, the value of GAP decreases, using as solvent methanol. **Figure 5 (b).**
Figure 5. a). 5 min, 80 mJ, Water; b). Graphical GAP

Table 3. GAP of NPs CuO in Methanol calculated using Tauc’s method

| Oxide | Time (min) 5 | Time (min) 10 |
|-------|--------------|--------------|
| CuO   | Time (min) 5 | Time (min) 10 |
| Energy | 25          | 50          | 80          | 25          | 50          | 80          |
| GAP (eV) | 5.74  | 5.71  | 5.62  | 6.08  | 5.71  | 5.44  |
The Figure 6 shows the electron microscopy images for the MnO$_2$ and CuO nanoparticles. The size nanoparticle is

![Image](image_url)

**Figure 6.** Nanoparticles corresponding to a). MnO$_2$ 10-80 mJ; b). CuO 10-80 mJ

This research has allowed to development new materials, which as antimicrobial systems can be used. The following is describes the results with two microorganisms *Escherichia coli* ATCC 11229 and *Staphylococcus aureus* ATCC 6538. **Tables 4 and 5.**

The best antimicrobial properties were observed for 10 min and 25 mJ in *Escherichia coli* ATCC 11229 and *Staphylococcus aureus* ATCC 6538. The results showed that the microorganisms are attacked according to order of the GAP value. The UV-C lamp is shortwave which better excites the samples with a higher GAP. On the other hand, for *Escherichia coli* there is major activity, which suggested that the mechanism is discriminated in relation to the type of microorganism. For 10 min and 80 mJ no antimicrobial activity was observed whitout ligh, which suggested the is essential to activite the nanoparticle as a semiconductor.

| Nanoparticles MnO$_2$ | % Inhibition region 24 h | Escherichia coli ATCC 11229 | Staphylococcus aureus ATCC 6538 |
|-----------------------|--------------------------|-----------------------------|------------------------------|
| **C1** 10 -80 mJ      | 20%                      | 2%                          |
| **C5** 10 -25 mJ      | 40%                      | 3%                          |
| **C6** 10 –50 mJ      | 5%                       | 3%                          |
| **C7** 5- 80 mJ       | 3%                       | 2%                          |
| **C8** 5 -50 mJ       | 4%                       | 0%                          |

**Conclusions**

The size dispersion of nanoparticles for manganese oxide, is in function of the energy. The frequency of plasma oscillation for copper oxide is greater than manganese oxide, due to the effects of charge transfer. There are solvent effects on the stabilization of the nanoparticles, in consequence with charge transfer and solvation capacity. The antimicrobial activity is closely related to the activation of GAP with energy in the orden of its magnitude. It is necessary to continue with studies that allow finding the best synthesis conditions related to best antimicrobial activity. Also complementary studies in order to understand the discriminatory mechanism on microorganisms and chiral effect.

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