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Resumen.

En los últimos años, se ha despertado interés en la comunidad científica por estudiar nanopartículas (NPs) y explorar la amplia diversidad de aplicaciones que tienen, incluso como una alternativa a los materiales utilizados convencionalmente. Un paso clave en el estudio de las nanopartículas es el análisis de sus propiedades ópticas, ya que estas revelan información sobre su estabilidad, pureza e interacciones con radiación UV-vis, y ayudan a confirmar la identidad de la naturaleza de las nanopartículas. En este proyecto, se sintetizaron y estudiaron muestras de nanopartículas de óxido de cobre y manganeso con el objetivo de comprender puntos clave en el comportamiento de estas partículas. Los picos observados en los espectros UV-Vis permitieron confirmar la identidad de las nanopartículas producidas, con resultados que mostraron una alta estabilidad para las nanopartículas de CuO sintetizadas en agua y metanol; se encontró que las nanopartículas de MnO_2 eran inestables en agua debido a la aglomeración de las partículas. El análisis de los picos de resonancia de plasmones superficiales mostró la presencia de reacciones de oxidación durante el proceso de ablación. Se estimaron valores de la brecha de banda de 5,44 eV y 3,77 eV para las nanopartículas de CuO y MnO_2, respectivamente, lo que descarta cualquier posible aplicación de estas nanopartículas como materiales semiconductores. Las nanopartículas de CuO tienen potencial aplicación como material antibacteriano debido a su alta estabilidad en agua y la citotoxicidad natural del cobre.

Palabras Clave: Nanopartículas, Propiedades Ópticas, Aglomeracion, UV-Vis

Optical properties of metal oxide nanoparticles: UV-Vis study of CuO and MnO_2 NPs.

Abstract.

In recent years, interest has been found by the scientific community in studying nanoparticles (NPs) and exploring the vast diversity of applications they have, even as an alternative to materials used conventionally. A key step in the study of nanoparticles is the analysis of their optical properties, since these reveal information on their stability, purity, and interactions with UV-vis radiation, and help to confirm the identity of the nature of the nanoparticles. In this project, samples of copper and manganese oxide nanoparticles were synthesized and studied, with the aim of understanding key points in the behaviour of these. Observed peaks on UV-Vis spectra allowed to confirm the identity of the nanoparticles produced, with results showing high stability for CuO NPs synthesized in water and methanol; MnO_2 NPs were found to be unstable in water, due to nanoparticle agglomeration. The analysis of surface plasmon resonance peaks showed the presence of oxidation reactions during the ablation process. Estimated band gap values were 5,44 and 3,77 eV, for CuO and MnO_2 nanoparticles respectively, which rules out any possible application of these NPs as semiconductor materials. CuO nanoparticles have a potential application as an antibacterial material, due to its high stability in water and copper's natural cytotoxicity.

Key Words: Nanoparticles, Optical Properties, Agglomeration, UV-Vis

1. Introduction

The use of metallic nanoparticles (NPs) in different fields and applications has led to theoretical and experimental studies on their stability and their optoelectronic, thermal, catalytic and magnetic properties. The optical properties of metallic NPs are related to their semiconductor and conductive capacity, as well as giving valuable information regarding nanoparticle stability and purity. In metallic NPs with semiconductor characteristics the conduction band is partially filled with electrons, therefore, there is no difference in the electronic excitation. The electrons that are conducted in a metal form a plasma state since the electronic transition within the conduction band is a collective movement of free electrons. This repetitive oscillation of the electrons to protect the polarization caused by external fields such as electromagnetic radiation forms an oscillatory wave that is expressed as a particle and is called a surface plasmon resonance (SPR) (Goyal, 2017). There is evidence that plasmon is related to the shape and possibly even the size of nanoparticles (Li, 2018).

Plasma laser ablation in liquids (PLAL) is an alternative for nanoparticle synthesis which is characterized by its low complexity and by being efficient and relatively cheap and has been implemented in a wide variety of applications. (Naito,2018; Noguez, 2007; Valverde-Alba, 2015; Dowding, 2010; Kanakkillam, 2020; Kabashin, 2003; Tsuji, 2002; Tsuji,2008) PLAL uses a liquid medium for nanoparticle synthesis, where it has been reported that the medium in which nanoparticles are synthesized will have a direct impact on the stability, size and shape of the produced nanoparticles; the choice of this medium must be made taking into account the application that is being targeted, an example of this situation is the use of NPs as an alternative to conventional antibiotics, where it is key to use a liquid medium that is not harmful or toxic for cells, because as this application is performed on living organisms, it can not only destroy damaged or unwanted cells but also healthy tissues.

2. Methodology

2.1. Target sintering

To obtain targets from metal oxides, the sintering method reported by Zhou (2011) was used, a steel mold was used to give the required shape to the targets, for it to be used in the ablation process. Ten grams of each metal oxide (CuO and MnO_2) were used for this process, which were deposited in a press at a pressure of 2 ton/m^2 to obtain a solid target with a defined shape. For pressing, a hydraulic press from TESSI Dental was used, which has a manometer to regulate the pressure. The metal oxide was subjected to this pressure for 2 min. Finally, the materials were subjected to temperatures of 800 ° C for 12 hours, to finish with the sintering process.

2.2. Nanoparticle synthesis process.

Nanoparticles were synthesized using the laser ablation method, using a Nd:YAG (neodymium-doped yttrium aluminum garnet, Nd:Y3Al6O12) laser, operating at a wavelength of 1064 nm, 9 ns and different energy pulse values. The set up for the synthesis process is as shown in figure 1 and the experimental conditions used for the synthesis is shown in table 1.

Figure 1. Nanoparticle synthesis using laser ablation set up.

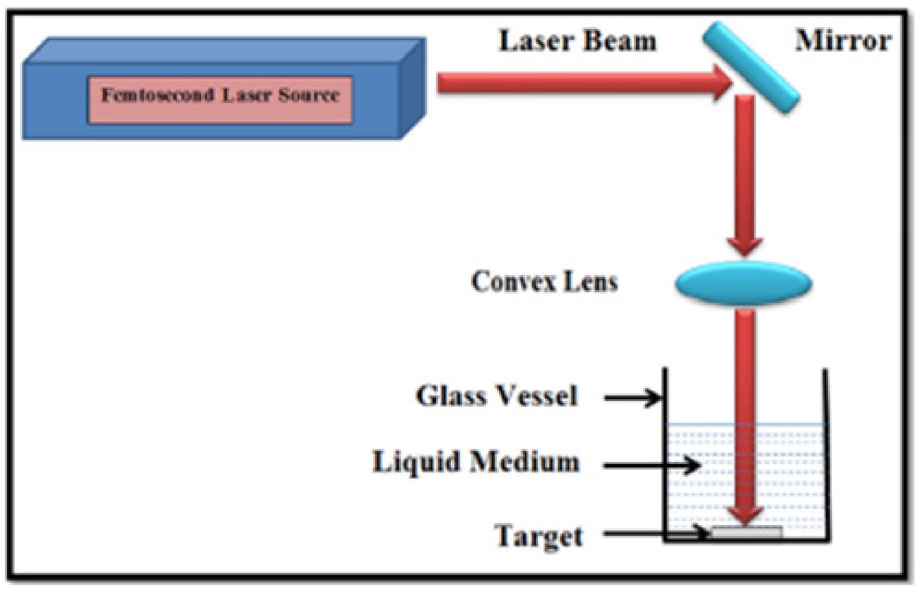

Table 1. Experimental parameters for nanoparticle synthesis

Metal Oxide	Wavelength (nm)	Liquid Medium	Energy (mJ)	Ablation time (min)
MnO_2	1064	Methanol, water	25, 50, 80	5, 10
CuO	1064	Methanol, water	25, 50,80	5,10

Revista EIA https://doi.org/10.24050/reia.v21i42.1773

2.3.Determination of UV-Vis properties.

To carry out the optical analysis of the nanoparticles, UV-Vis spectra of the NPs was taken with Perkin Elmer Lambda 9 UV/VIS/NIR spectrometer, with a wavelength range of 180 up to 800 nm. The estimated band gap value (eV) for NPs in suspension was calculated using Tauc's plot method based on the equation (1)

$$(\alpha hv)=\alpha(hv-E_g)^{1/r} \qquad (1)$$

3. Results and discussion.

It is important to note that the liquid mediums used during this project were water and methanol, which have different dielectric constants, 80.1 and 33.0 respectively. It has been reported that the medium in which nanoparticles are synthesized will have a direct impact on the stability, size and shape of the produced nanoparticles (Jyothi, 2015)

3.1. Optical properties of CuO nanoparticles

Figure 2. UV-Vis spectra of CuO NPs in Methanol a) 80mJ – 10min. b) 80mJ – 5 min.

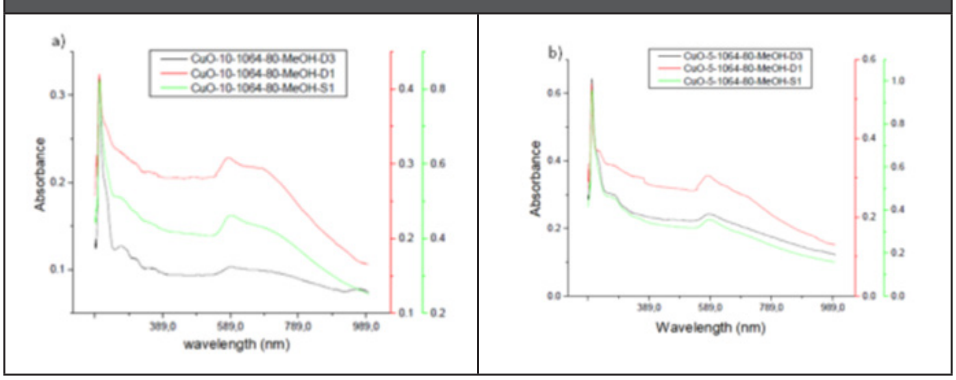

Figure 2 shows the optical absorption spectra of CuO synthesized in methanol for two values of deposition time and 80 mJ laser energy. The positions of the peaks registered in the UV-Vis spectra are 270 and 618 nm approximately. The peak at 270 nm can be attributed to the interband transition between copper atoms and its oxide (Rawat, 2019; Nath & Khare, 2011). The peak at 618 nm corresponds to the surface plasmon resonance peak (Baruah, 2018). This peak, at 618 nm, manifest the presence of copper NPs in the suspension, a sign that, when using methanol as a solvent, the oxidation of Cu NPs into CuO NPs doesn't occur completely. Broadness of peaks can be attributed to a wide distribution on the nanoparticles size (Al-Jumali, 2018; Gondal; 2013; Sahai, 2016; Chen, 2012). In order to analyze the NPs stability, measurement of the UV-Vis spectra was taken three times: first day of synthesis (red line), third day after synthesis (blue line) and one week after the synthesis (green line). Because no displacement of the absorption peaks was found in terms of wavelength, it can be concluded that the synthesized nanoparticles count with an acceptable stability. Comparing figures 2a and 2b is possible to note a widening of the absorption bands at longer ablation times (10 min), which allows to state that the longer the deposition time is, the smaller the size of the nanoparticles formed is going to be.

Figure 3. UV-Vis spectra of CuO NPs in water c) 80mJ – 5min.

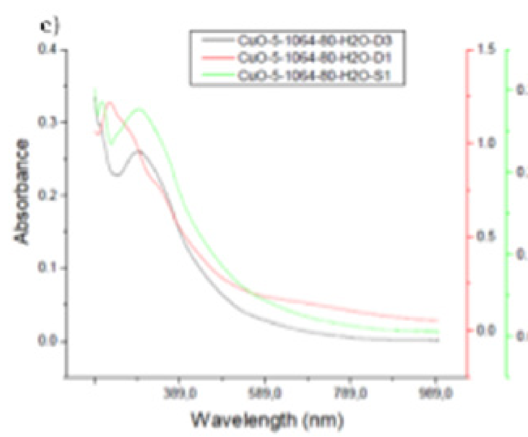

Figure 3 shows the spectra of CuO synthesized in water at 5 min of deposition time and 80 mJ laser energy. Stability was measured in the same way as with methanol, finding that, likewise, nanoparticles

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synthesized with water show acceptable stability over time. It is important to note the absence of the surface plasmon resonance peak, which is an indicator of the absence of copper nanoparticles, due to the complete oxidation of these to copper oxide nanoparticles. Another peak can be observed at 310 nm, which is assigned to the copper oxide NPs absorption band; its intensity is due to charge transition from O_2 to Cu ions during the oxidation process (El-Trass, 2019).

Figure 4. Band GAP estimation for NPs in Methanol at 80mJ and 10 min.

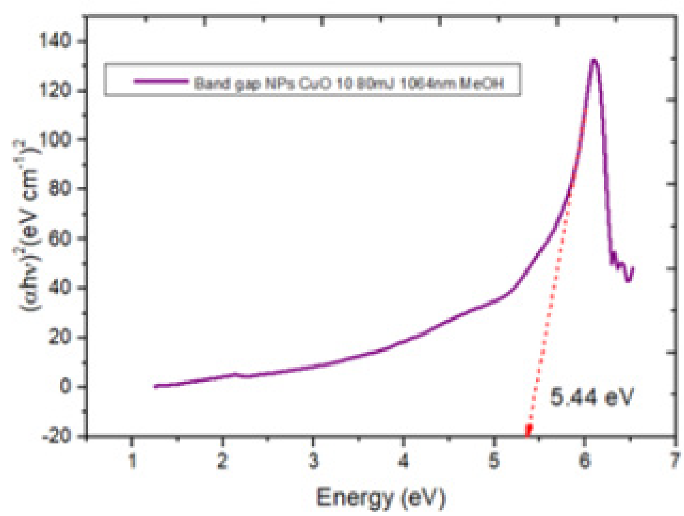

Figure 4 shows the band gap estimation for CuO NPs in methanol using Tauc's method. The estimated band GAP for nanoparticles synthetized in Methanol is 5.44 eV; this value is considerably high and rules out the possibility of considering the use of these nanoparticles as a semiconductor material. A tendency was observed that as the energy used in the ablation process increases, the lower the estimated band GAP value is.

3.2. Optical properties of MnO2 nanoparticles

Figure 5. UV-Vis of MnO2 NPs in water and methanol at the first day and first week of synthesis.

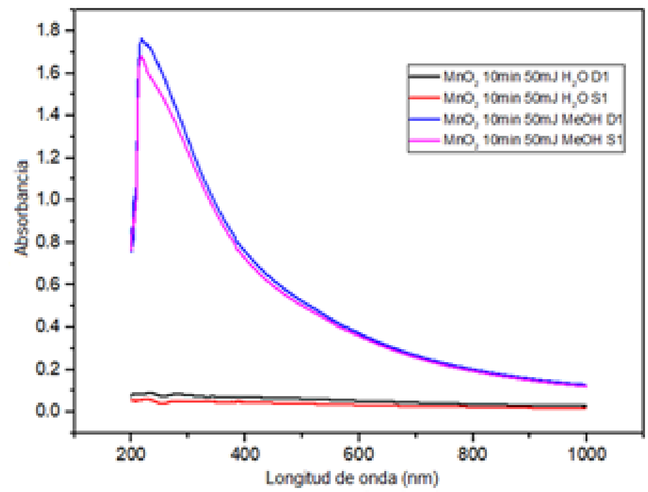

Figure 5 shows the spectra of MnO_2 NPs synthesized in water and methanol at 10 min of deposition time and 50 mJ laser energy. It is observed that the optical activity decreases drastically when water is used as the medium of synthesis. MnO_2 NPs prepared in methanol showed different behavior, indicating that the solvent has a considerable effect on the optical activity of MnO_2 NPs prepared by laser ablation. This change in optical activity could be due to a greater dipole moment of water (1.85D) versus methanol (1.70D) (Rahmat, 2019) and the dielectric constant (Rawat, 2019) and the rapid agglomeration of the NPs in the medium, since when water is used as a liquid medium, it generates the oxidation of the metallic NPs more easily.

Revista EIA https://doi.org/10.24050/reia.v21i42.1773

Figure 6. Band GAP estimation for NPs in Methanol at 80mJ and 10 min.

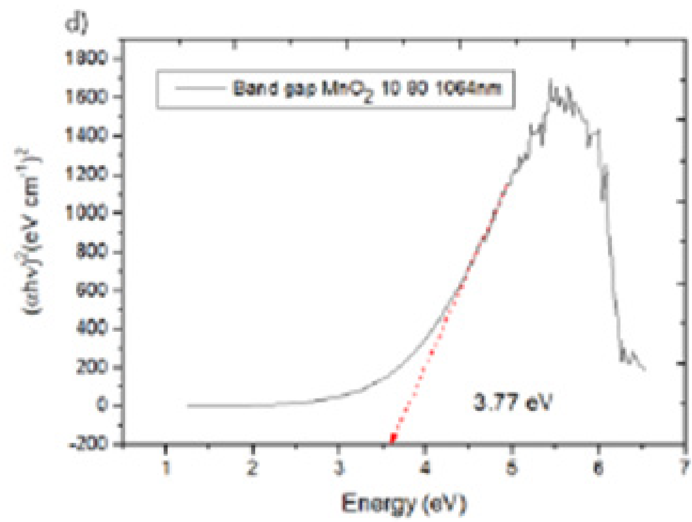

Figure 6 shows the band gap estimation for MnO_2 NPs in methanol using Tauc's method. The estimated band gap value in these conditions is 3.77 eV. These values do not show a trend with the variation of energy or time. Given the values obtained it can be deduced that the use of this material as a semiconductor material is not suitable (due to the large band gap).

4. Conclusions

CuO and MnO_2 were synthesized and their optical properties were studied. Observed peaks on UV-Vis spectra allowed to confirm the identity of the nanoparticles produced, with results showing high stability for CuO NPs synthesized in water and methanol; MnO2 NPs were found to be unstable in water, due to nanoparticle agglomeration. The analysis of surface plasmon resonance peaks showed the presence of oxidation reactions during the ablation process. Estimated band gap values were 5,44 and 3,77 eV, for CuO and MnO_2 nanoparticles respectively, which rules out any possible application of these NPs as semiconductor materials. CuO nanoparticles have a potential application as an antibacterial material, due to their high stability in water and copper's natural cytotoxicity.

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Revista EIA | https://doi.org/10.24050/reia.v21i42.1773

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