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SYNTHESIS OF ZnO/CuO NANOCOMPOSITES WITH CNF AND Ag BY GEL SOL

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Abstract

The synthesis of ZnO/CuO with Carbon Nanofiber (CNF) and Ag nanocomposites have been conducted. Nanocomposites were synthesized using sol-gel method. The nanocomposite products were characterized by SEM, TEM, XRD and DSC. The results of the XRD analysis showed that the CuO-ZnO composite has a nanometer size with the average of 10 nanometer. The SEM-EDX analysis showed that the ZnO has a hexagonal structure whereas the CuO has a monoclinic structure. The importance of impregnating the nanofibers with the precursors has been demonstrated. The hydrazine is a better reducing agent than tannic acid. In this study was synthesized polycrystalline silver as evidenced by XRD. SEM-EDAX analysis indicate presence of oxides, nanofibers and silver.

Keywords*: carbon nanofibers, characterization, sol gel method, nanocomposites, silver*

Introduction

In the recent years, the uses of nanoparticles become very important, in interdisciplinary with chemistry, physics, biology, medicine, material science, etc. (Shchemelinina et al 2017). The most application of the oxidic nanomaterials are catalysis, biomedicine, coatings, semiconductors etc. (Harja et al 2016, Harja et al 2017, Kotova et al 2018, Noli et al 2015). Semiconductor materials are attractive due to their properties reported different potential applications (Mousavi-Kamazani et al 2015, Li et al 2016).

ZnO is recognized as photocatalytic material, it can be activated by UV and visible light to form the electron-hole pairs. The ZnO materials can produce radical compounds and can be used as an antibacterial agent. However, the ZnO material has large band gap of 3.3 eV (Widiarti et al 2017). The addition of CuO to ZnO could form the CuO-ZnO composite that increased particle size and decrease the band gap energy (Sathishkumar et al 2011). The increase of CuO content determines decreasing of band gap energy. It increased the stability can be used CNF, addition of Ag ions conducted to high antibacterial activity (Nutescu Duduman et al 2018). The metal oxides ZnO/CuO have been widely used as adsorbents, conductive materials, photo catalysts etc (Chatkaewsueb et al 2017).

There are various methods reported in literature for preparation of nanocomposite materials such as sol gel, impregnation (El-Shobaky et al 1999, Harja & Ciobanu 2004) co-precipitation in aqueous or organic solutions (Shen et al 1997, Agrell et al 2003) and co-precipitation in an inorganic solvents (Zhang et al 1997, Ning et al 2001). Sol-gel is a simple method for nanomaterial synthesis, which consist in two stages: sol and gel formation. In the sol-gel many parameters could be modified: initial precursor, time of gel formation, type of activator, pH, gel formation conditions etc (Habibi & Karimi 2014).
In this study nanostructure CuO/ZnO oxide mixture was prepared using the sol-gel method using zinc and copper sulphates as precursors under thermal decomposition. Were synthesized 4 samples that were characterized by SEM, TEM, XRD and DSC.

Materials and methods

For synthesis were used: Zinc Sulphate Heptahydrate ($ZnSO_4 \cdot 7H_2O$) by Panreac, Copper (II) Sulphate Pentahydrate ($CuSO_4 \cdot 5H_2O$) by Panreac, hydrazine (N_2H_4) Sigma-Aldrich, tannic acid ($C_{76}H_{52}O_{46}$) Sigma-Aldrich, CNF Grupo Antolín Ingeniería S.A, Silver nitrate ($AgNO_3$) Panreac, deionized water (H_2O) and sodium hydroxide pearl 98-100% (NaOH) Panreac.
The nanocomposite was obtained by the sol-gel method (Nutescu Duduman et al 2016); (Nutescu Duduman et al 2018). The first step was dissolution of $ZnSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$, for obtaining 200 mL from each solution with 0.5M, respectively 0.2 M. After this were added 1.5 g of CNF and stirred 2.5 h, for CNF impregnation. For obtained nanocomposite with silver $AgNO_3$ is added after impregnation. The next step is to add the required amount of NaOH to reach a pH over 12. All of the samples were decanted, filtered, washed for removal reactant excess and dry to constant mass. Sample drying was carried out in the oven at a temperature of 110°C for 24 hours.

Results and Discussion

In the case of obtaining the nanocomposite, samples were synthetized, comparing the results to highlight the route that leads to the obtaining of nanocomposites under optimal conditions. For this purpose, two experiments are equally quantitative, roughly the same conditions differ that the first experiment did not occur without CNF impregnation and in the second experiment it was done. In the SEM and TEM analysis very fine particles are observed, there are copper oxides and zinc oxide leaving the free carbon nanofiber. This is due to the lack of impregnation before CNF (Figure 1).
In the EDX spectrum of this nanocomposite, the formation of ZnO and CuO is verified. If precursors, deionized water and CNF are added and the mixture was allowed to stir for 2.5 hours to impregnate the CNF, analysis SEM can see spheres form of CuO, ZnO is laminated and carbon nanofibers are coated with oxides. The nanocomposite has a compact structure (Figure 2).

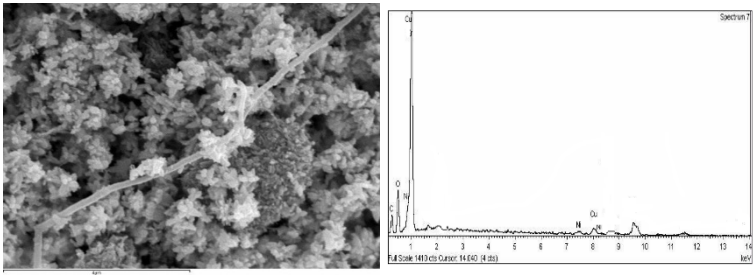

Figure 1. SEM and SEM-EDX analysis for sample 1 that did not impregnate CNF.

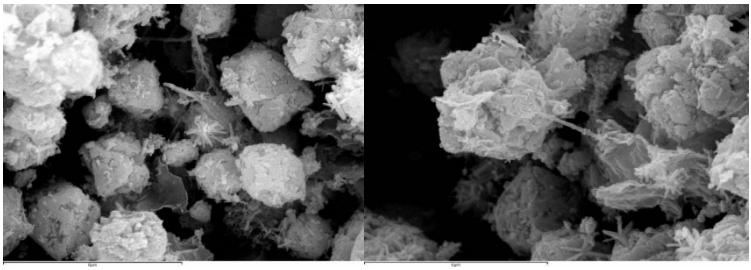

Figure2. SEM analysis for sample 1 with CNF impregnation.

In the TEM analysis of sample 1, agglomerates containing copper and zinc oxides can be observed. Carbon nanofibers are free without being integrated into the structure (Figure 3), as they did not have time to impregnate CNF.

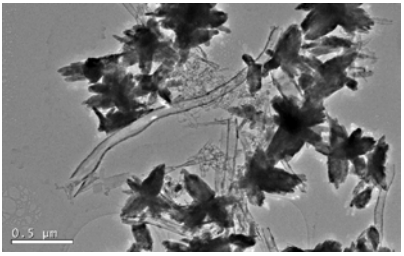

Figure 3. TEM images of the sample 1.

In the TEM analysis (Figure 4) it can be seen that the areas belonging to the agglomerated phases are in the form of nanoparticles and oxides and CNF.

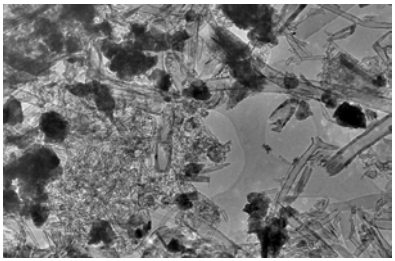

Figure 4. TEM analysis of the sample 2.

Nanofibers are coated with oxides because in this analysis the CNF precursors were impregnated forming a compact structured nanocomposite. EDS analysis confirms the presence of oxides as well as CNF. Therefore, it can be concluded that there is a difference between the two samples, the role of CNF impregnation can be clearly seen. The morphology and structure of the 2 differs, we can see in sample 2 how nanofibers are coated with copper and zinc oxides.
In Figure 5 shows peak X-ray corresponding to the different crystallographic planes of the sample. The crystallinity of the synthesized nanocomposites composed of copper and zinc oxides and CNF is confirmed. JPCDS card files for the CuO monocyclic structure were used through the file JCPDS number 80-1268 and the structure obtained is zinc-shaped with hexagonal structure indexed with JCPDS-36-1451 files.

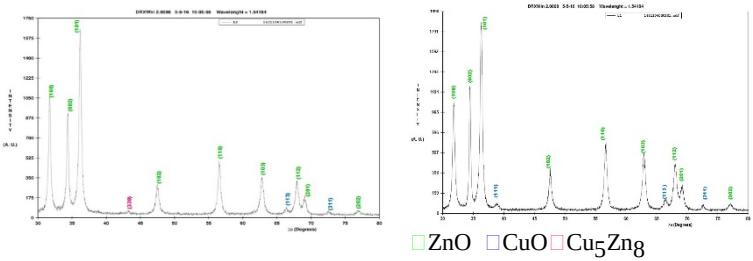

Figure 5. XRD Diffractograms of samples 1 and 2.

A complex of copper and zinc seem to be intermetallic compounds Cu_5Zn_8 showing the degree of reactivity during the process. For samples 3 and 4 the reduction $AgNO_3$ was done with tannic acid and hydrazine. Because the CNF impregnation yielded good results, the two experiments were impregnated.
SEM analysis (Figure 6) shows a morphology consisting of oxides and CNF agglomerates. SEM-EDX analysis shows the presence of Ag, Cu, Zn constituents.

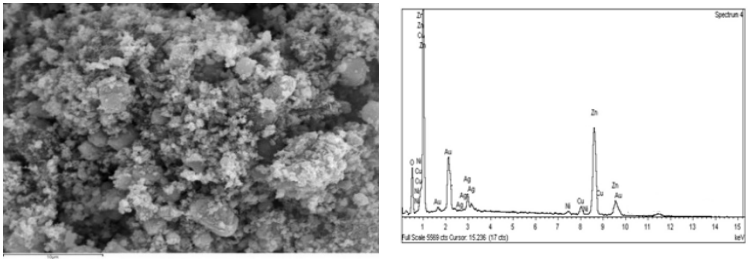

Figure 6. SEM and SEM-EDX analysis of sample 3 using tannic acid.

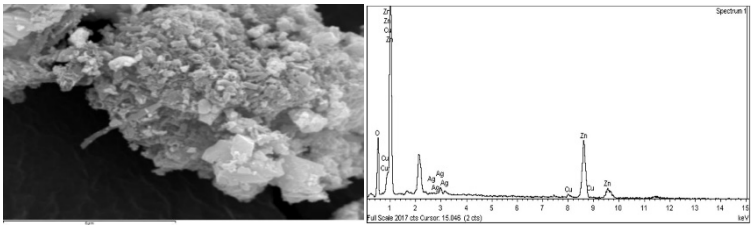

Figure 7. SEM and SEM-EDX analysis of sample 4 using hydrazine.

When hydrazine was used as reducing agent, SEM morphologic analysis shows a larger quantity of irregularity-sized oxides (Figure 7). Ag is observed in SEM-EDX but in SEM images it is not likely to be observed in the matrix of the nanocomposite. In the image obtained by TEM, agglomerates are observed, in the red contour the Ag particle is bounded (Figure 8) which was identified by TEM-EDS analysis. The diffractogram corresponding to the silver crystal is attributed to the Burgers vector. Hydrazine is a stronger reducer than tannic acid and a change in morphology is observed. Separated Electron Diffraction (SEAD) is compared to known structures and we can state the Ag crystal.

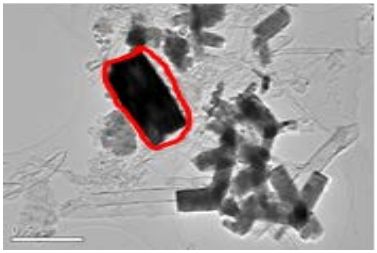

Figure 8. TEM analysis of sample 4.

By the X-ray diffractogram analysis, cubic and orthorhombic crystalline structures are confirmed (Figure 9). There are also peaks attributed to the cubic crystalline structure of Ag read with card files.

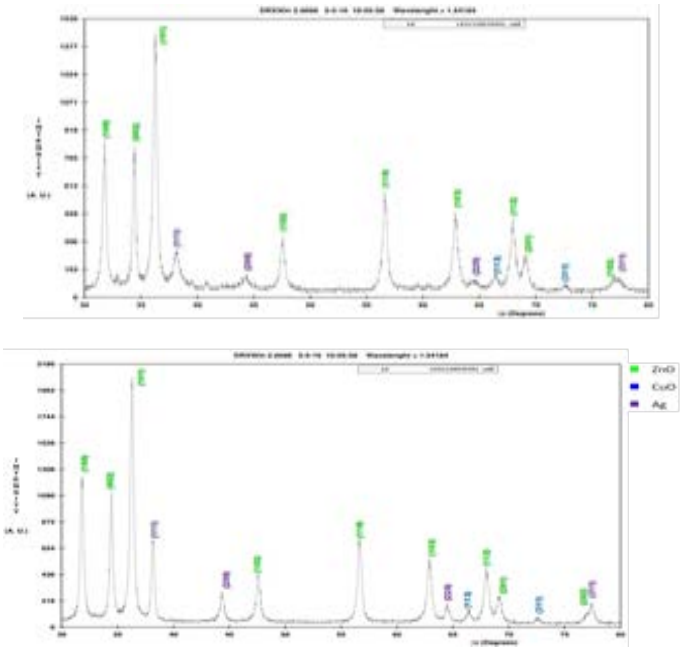

Figure 9. XRD Diffractograms of samples 3 and 4.

In DSC analysis in which tannic acid was used, one exothermically process was observed at 350 ℃, which refers to the elimination of tannic acid, another exothermically process appears around 250℃, refers to the transformation of $AgNO_3$ that did not completely react and the last one around 500 ℃, refers to combustion of carbon nanofibers, Figure 10.

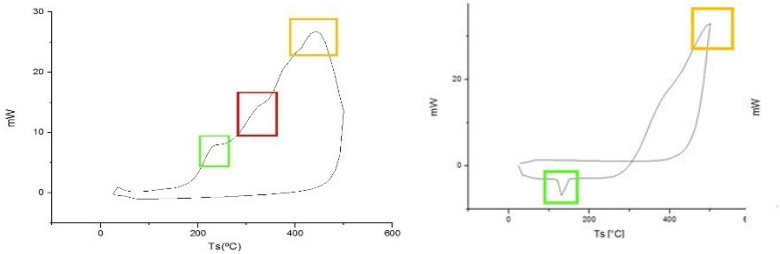

Figure 10. DSC analysis of samples 3 and 4.

DSC analysis (sample 4) of the reduced hydrazine sample the endothermic peak occurring at 140 ℃ corresponds to transforming AgOH into Ag_2O.

Conclusions

The nanocomposite ZnO-CuO-CNF-Ag was obtained by the sol-gel method. To ensure good results, the pH should be over 12. The importance of impregnating the nanofibers with the precursors has been demonstrated and stirred for 2.5 hours. By using the hydrazine, good results are obtained being a better reducing agent than tannic acid. In this study was synthesized polycrystalline silver as evidenced by XRD. SEM-EDAX analysis of samples indicate agglomerate containing oxides, nanofibers and silver.

Acknowledgements

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