OBTAINED OF NANOCOMPOSITES: Cu, CuO and $Cu(OH)_2$ - CNF BY SOL-GEL METHOD

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Abstract: Copper oxides (Cu, CuO and $Cu(OH)_2$ nanocrystals with carbon nanofiber (CNF) have been successfully prepared by sol gel method from copper acetate and copper sulfate. Synthesis techniques such as: chemical reduction, hydrothermal, sol–gel, direct electrochemical reduction, have been reported for the synthesis of copper nanoparticles. Sol-gel process can be described as a polycondensation reaction forming an oxide network of a molecular precursor in liquid. The synthetized samples were characterized using: X-Ray diffraction (XRD) and Energy-dispersive X-ray spectroscopy (EDX). Morphological structure was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Experimental results demonstrated that the sizes of the prepared copper oxides are in the range of (34-40) nm, and Cu is in the range of (24-28) nm, calculated according to the Scherrer equation.
Key words: nanocomposites, carbon nanofibers, copper oxides, characterization

1. INTRODUCTION

Copper oxides are materials widely studied being used in fabrication of catalysts, in metallurgy posed high temperature thermal barriers, in metallization of integrated microelectronics components, preparation of high-temperature superconductors etc. [1, 2] .
In the last years there is an increasing need of developing new materials with high conductivity and thermal dilatation coefficient, compatible with ceramic materials. The thermal conductivity of carbon fibres and copper's making its the ideal nanocomposite for use in the electronic modules applications [1, 2]. Synthesis methods such as: chemical reduction [3], hydrothermal [4], sol–gel [5], sonochemical [6], microemulsion [7], direct electrochemical reduction from CuO nanoparticles [8], mechano-chemical [9], polyol [10,11,12], in-situ synthesis in polymers [13], electro-exploding wire 14], ion beam radiation [15] etc. have been reported for the synthesis of copper nanoparticles.
Nanoparticles research is gaining increasing interest due to their unique properties, such as increased electrical conductivity, toughness and ductility, increased hardness and strength of metals and alloys, luminescent efficiency of semiconductors, formability of ceramics. CuO is one of the potential p-type semiconductors with excellent optic, electric and magnetic properties. CuO with a narrow band gap of 1.2 eV is widely used, especially as a catalyst [16], solar energy conversion [17], gas sensors [18] and field emission [19].
The sol-gel process involves the formation of colloidal suspension (sol) and gelatine of the sol to form a network in continuous liquid phase (gel). Only sol-gel synthesis can produce materials at low temperatures, synthesize almost any material, cosynthesize two or more materials simultaneously, precisely control the microstructure of the final products, and precisely control the physical, mechanical, and chemical properties of the final products etc. The sol-gel method is currently used for obtained nanocomposite materials with CNF [20]. The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive legends [21].
In this paper, we reported the methods of chemical synthesis of nanoparticles and their characterization. For obtaining the nanocomposites we used the sol-gel method.

2. EXPERIMENTAL

For the experiment were used the following materials: copper sulfate ($CuSO_4 \cdot 5H_2O$) (produced

by Panreac,) copper acetate $(CH_3COO_2)\cdot H_2O$, ethylene glycol ($C_2H_6O_2$) (produced by Scharlau), ammonia (NH_3), ethanol (C_2H_6O), sodium hydroxide pearl 98-100% (NaOH) and hydrazine (N_2H_4) 98% (produced by Panreac). All analytical grades were used without purification.
The carbon nanofibers (CNF) were supplied by Grupo Antolin Engineering S.A. and their properties are presented in Table 1.

Table 1. Physical and mechanical properties of CNF

Properties	Value
Fibre diameter (TEM)	20-80 nm
Fibre length (SEM)	>30 µm
Real density	>1970 kg/m^3
Apparent density	60 kg/m^3
Specific surface area BET (N_2)	150-200 m^2/g
Superficial energy (purified and fluidized)	~120 mJ/m^2
Graphitization degree	~70%
Young modulus (theoretical)	230 GPa
Tensile strength	2.7 GPa

Morphological structure was examined by SEM and TEM divices. The JEOL 6400 with an Oxford Link EDX microanalyser and Pentafet light sensing was used. The TEM - JEOL JEM-2100, with a resolution of 0.14nm 0.25nm between lines and points and may reach 1.200.000 increase times was used. Furthermore, the coupled EDS X-max is Oxford Instruments equipment. The cristallinity material characterization was realized by XRD method, whith Philips model X`Pert PDP3040 with a $K_{\alpha 1}$ Cuα source, 40 kV and 40 mA. The diffraction patterns was analized with X`Pert HihgScore Plus PANalytical (version 2.0). The crystals size was calculated according to Scherrer equation using XRD results:

$$d=0.94\cdot\lambda/(ß\cdot\cos\theta) \quad (1)$$

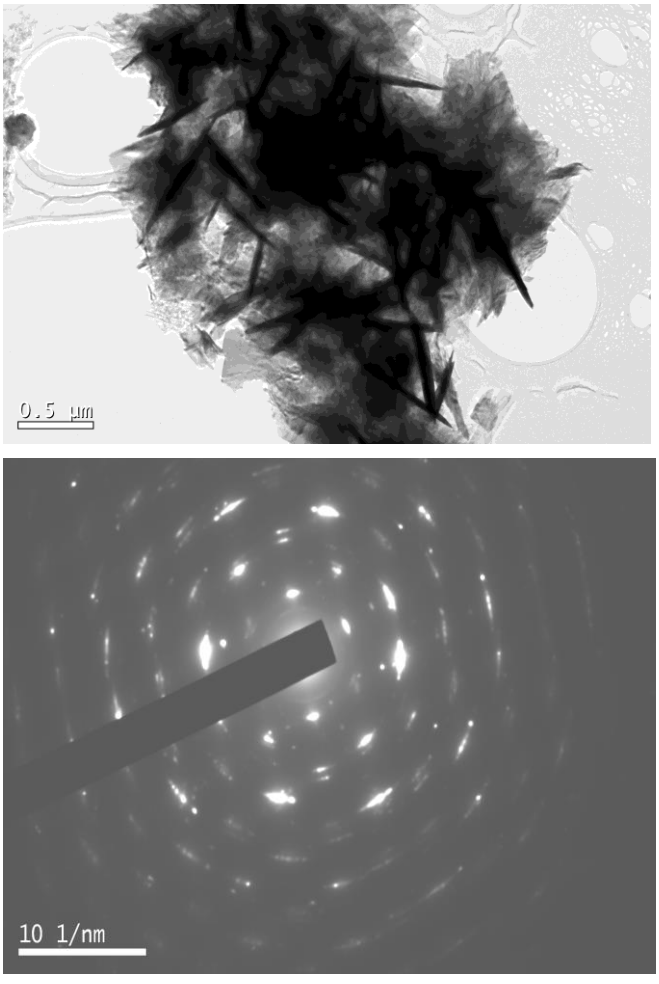
where: λ is the X-ray wavelength; ß is full width at half maximum value; θ is the diffraction angle.

Preparation method

The samples were preparated in following experimental conditions:
1. sample 1: 400 mL of $CuSO_4$ (0.1M) + 2mL of NH_4OH (added drop by drop) and stirred for 24h. After 24h were added 10 g of NaOH tablets and 3 g of CNF, stirred for 4 h at 50°C. Then, 10mL of N_2H_4 (0.8 M) were added and stirred for 24 h. After stirring we added 2 g of NaOH + 1 mL of NH_4OH, and stirred for 24h.
2. sample 2: 10 g $CuSO_4\cdot 5H_2O$ (in solid state) + 3g of CNF + 150 mL $C_2H_6O_2$ + 100mL H_2O stirred for 24h at 50°C, added 5 g of NaOH and stirred for 4 h, then 2 mL of pure N_2H_4 and stirred for 24h. Finally was added 2mL of pure hydrazine and stirred for 24h.
3. sample 3: 150 mL of $C_2H_6O_2$ + 3g of CNF + 15g copper acetate + 100mL H_2O and stirred for 24h at 50°C. Then 5g of NaOH were added and stirred for 4h with 2mL of H_4N_2 and stirred it for 24h at the same speed and temperature.
4. sample 4: 15g of $Cu(CH_3COO)_2\cdot H_2O$ + 150g of $C_2H_6O_2$ + 250 g of C_2H_6O + 3 g of CNF and stirred for 24h at 25°C.
All the samples were washed with deionized water and dried at 110°C for 24h.

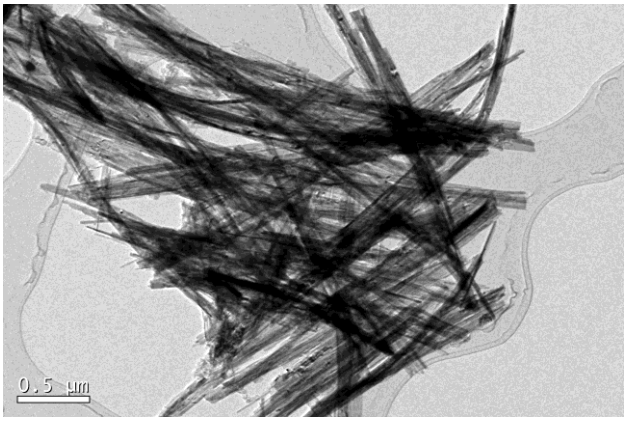
3. RESULTS AND DISSCUSSION

Figure 1 presents the TEM images for obtained samples. In Figure 1a is the sample from the first experiment. The electron diffraction pattern is presented in Figure 1a with the ring that indicates the polycrystalline nature of the particles and an agglomerate that contains CNF and $Cu(OH)_2$ nanoparticles confirmed by XRD.
Figure 1b shows the TEM images of the sample from experiment 2 with agglomerate containing fine graphite particles and CuO nanofibers (seen better at higher magnitude).



a

Fig. 1a. TEM micrographs of sample 1



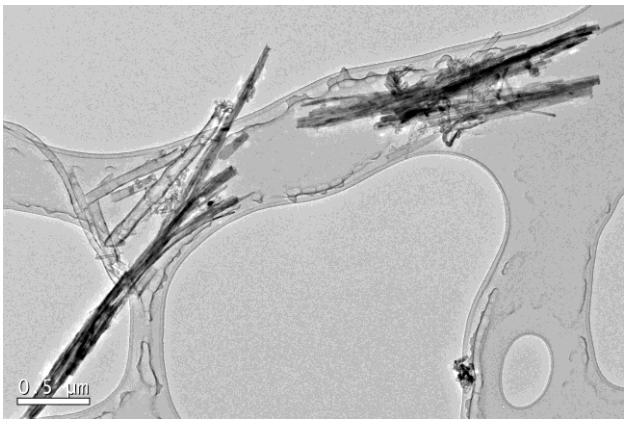
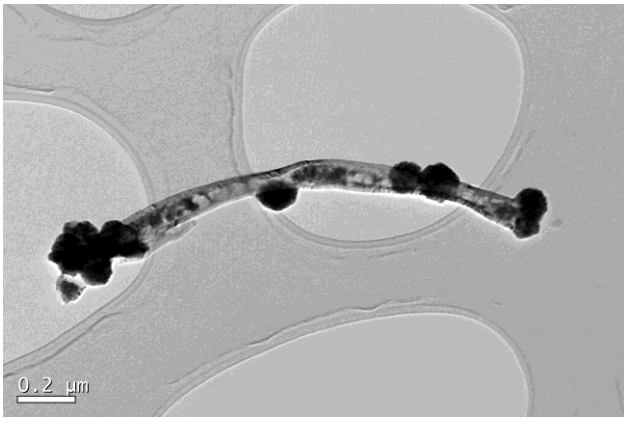


Fig. 1b. TEM micrographs sample 2



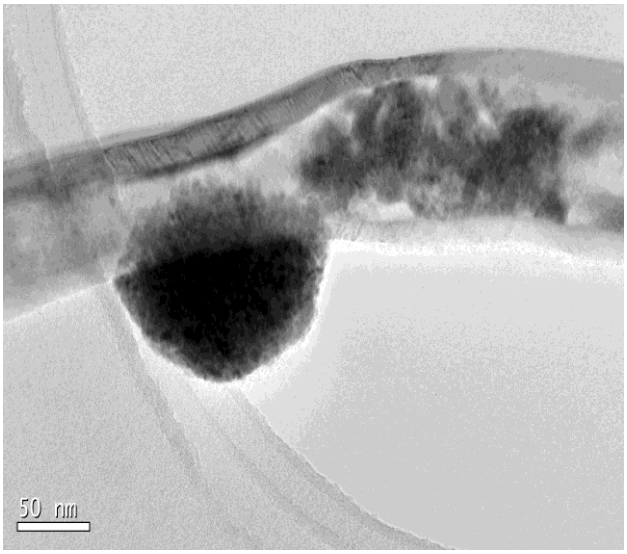
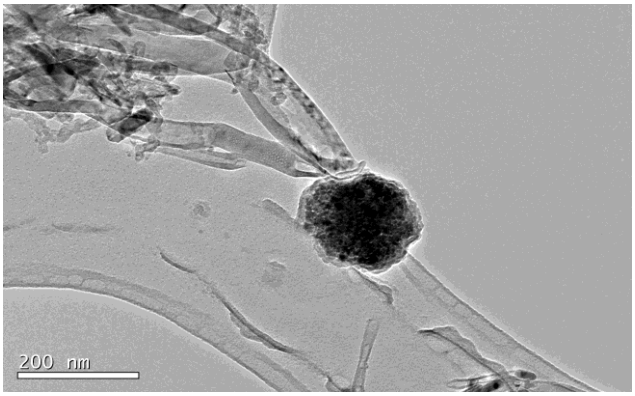


Fig. 1c. TEM micrographs sample 3



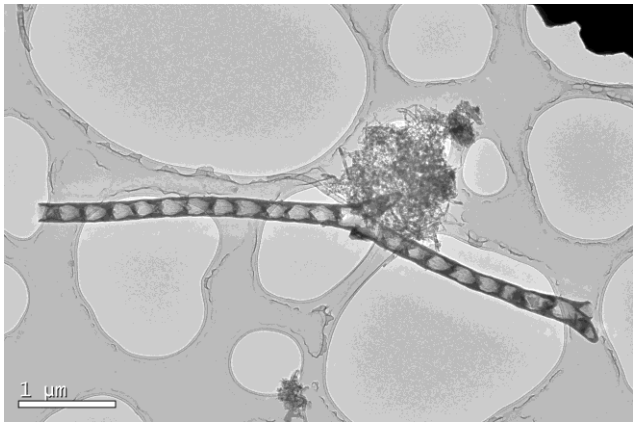
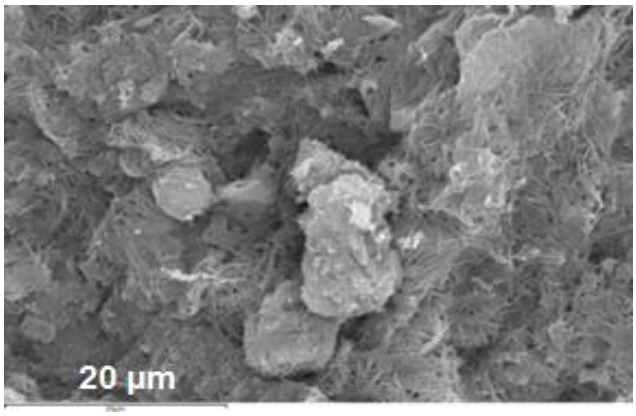


Fig. 1d. TEM micrographs sample 4

Figure 1c shows the TEM images of sample 3 with the fine particles deposited on the nanofiber. The last figure (1d) shows the sample from sample 4. It can be seen that they have a bamboo-like structure. CuO particles can be seen at higher magnification on the surface of CNF.



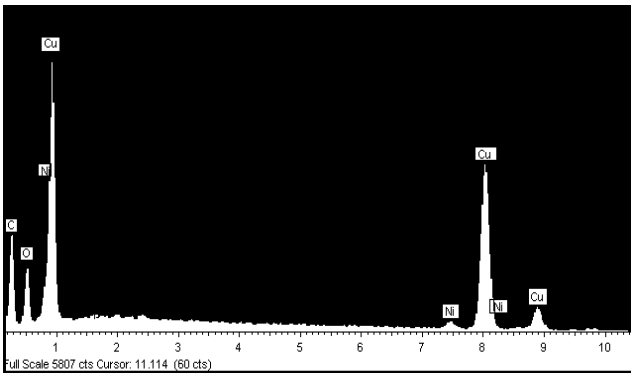
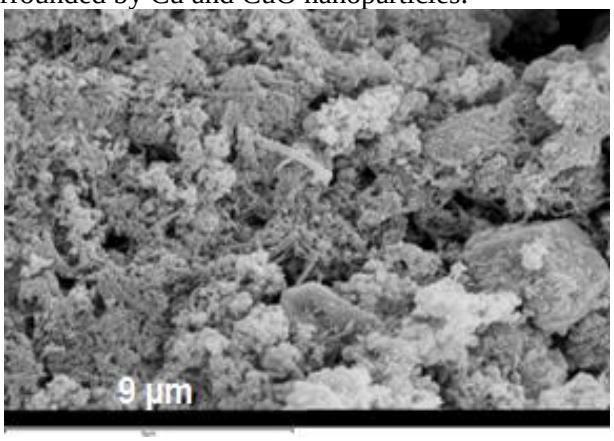


Fig. 2a. SEM and EDAX of sample 1

Figure 2a shows the morphology of the nanoparticles from sample 1. In EDAX spectra C, copper in different oxides and Ni, from CNF, can be observed. In Figure 2b we can see the results of experiment 2, in which ethylene glycol was used, so we can see a change in nanoparticle's morphology. It is observed that the particles are nanosized and are irregular form, so from SEM-EDX analysis, presence of C and Ni means that the nanofibers are present.

In Figure 2c we can see a different morphology and that the nanofiber is surrounded by nanoparticles, thus the presence of nanofibers can be deducted from the SEM-EDX analysis.

The last figure (2d) shows how the nanofibers are surrounded by Cu and CuO nanoparticles.



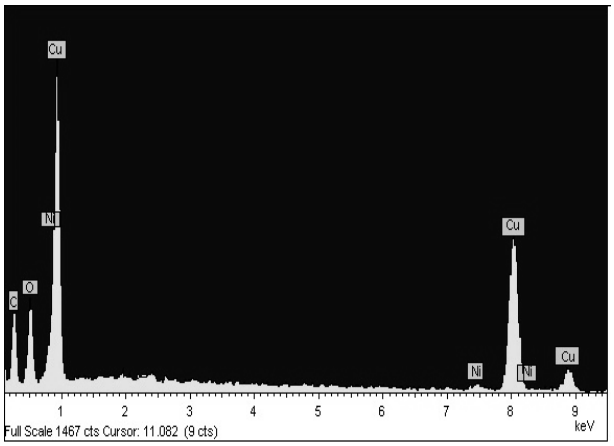
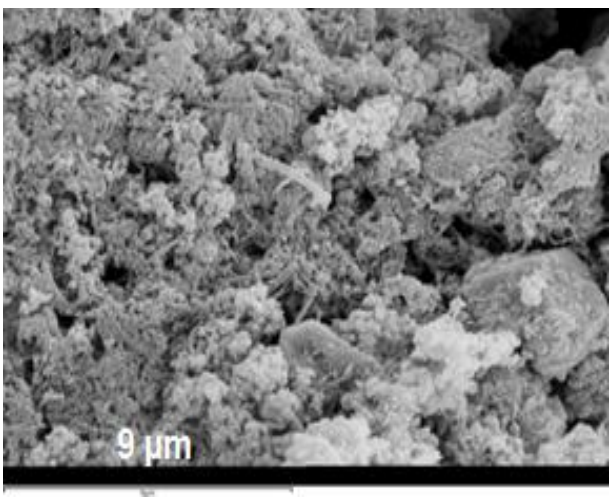


Fig. 2b. SEM and EDAX of sample 2



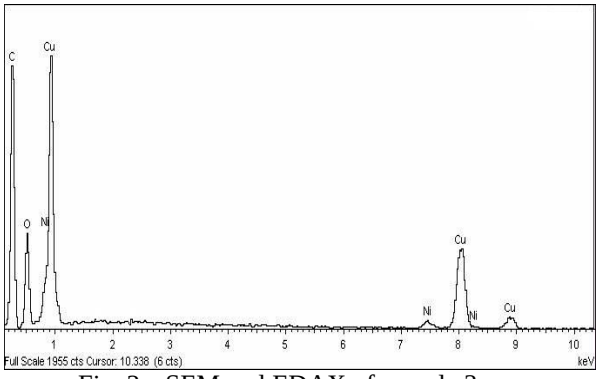
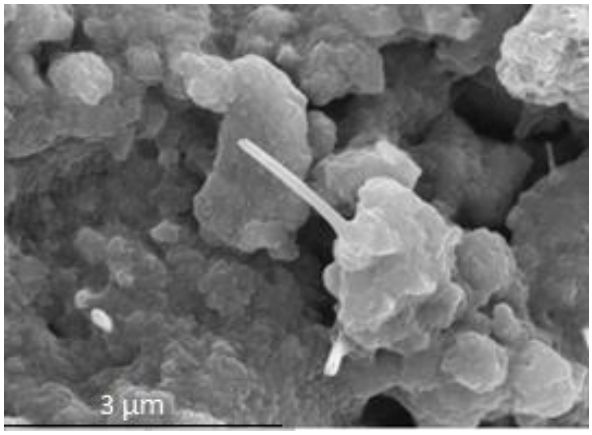


Fig. 2c. SEM and EDAX of sample 3



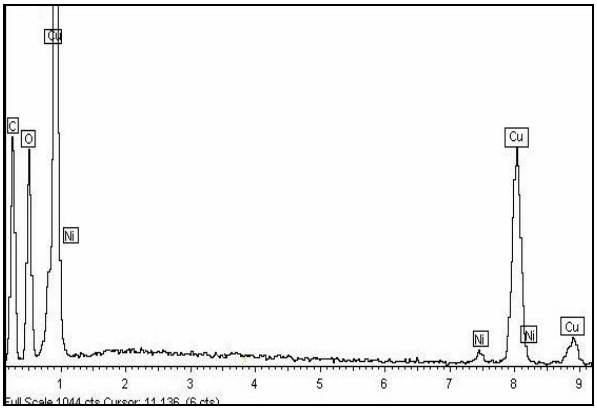


Fig. 2d. SEM and EDAX patterns of sample 4

The XRD patterns consist from the spectrum of Cu, CuO and $Cu(OH)_2$ nanoparticles, Fig. 3.

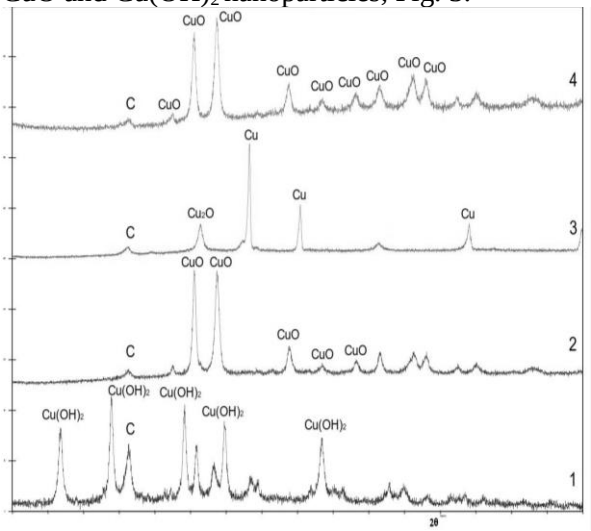


Fig. 3. XRD patterns of samples

The size of the nanoparticles was calculated by Scherer equation. The peaks of sample 1 confirm the orthorhombic crystal structure of the copper hydroxide. The multitude of peaks present in the pattern is due to the used analysis technique. Sample 2 shows the characteristic peaks located at 2θ = 32.58°, 35.47°, 38.97° and 48.74° of CuO. The XRD pattern for sample 3 confirms the presence of copper oxide and copper.

XRD of these nanoparticles sample show that all of the peaks match well with Bragg reflections of the standard cubic structure of copper. XRD pattern at 2θ value of 43.6°, 50.7° and 74.45° representing (111), (200) and (220) planes of fcc structure of cooper.

The crystallite size of the prepared $Cu(OH)_2$ is in the range of 34-40 nm, CuO particles size is in the range of 30-35 nm, for Cu it is in the range of 24-28 nm, which was calculated according to Scherrer equation.

4. CONCLUSIONS

After all four experiments we obtained nanocomposites that contain nanofibers. The obtained analysis results confirm that ethylene glycol has an effect on changing the morphology of the nanoparticles. TEM and SEM analysis reveal the agglomerates that contain cooper oxides and carbon nanofibers. It can be seen that the nanofibers are surrounded by nanoparticles. The crystallite size of the prepared $Cu(OH)_2$ is in the range of (34-40)nm, CuO is in the range of (30-35)nm, Cu is in the range of (24-28)nm, which was calculated according to Scherrer equation.

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