Structural and Microstructural Analysis for CuO Nanoparticles Prepared by Precipitation Method.

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Copper oxide nanoparticles (CuO-NPs) are being increasingly used in many agrochemicals such as pesticides, herbicide, fertilizers, antimicrobial, additives and growth regulators [1]. The wide use of CuO-NPs leads to their release into the environment, which is of concern due to their potential risk to biological processes [2]. Previous studies have assessed the impact of various NPs including CuO on soil microbial communities, finding that the effects strongly depend on the characteristics of the NPs, such as size, shape, composition, and morphology [3]. Thus, in order to elucidate the effects of NPs on soil microorganisms is quite important the proper characterization of the NPs. The motivation of this work is to describe the structural and microstructural characteristics of CuO-NPs by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

CuO-NPs were prepared according to the simple precipitation method as detailed elsewhere [4], with some modifications. The X-ray diffraction patterns were collected on a PANalytical XPert´PRO diffractometer equipped with an X´Celerator detector, using a Cu K_a (λ= 1.5406 Å) monochromatic radiation. The interpretation of the XRD patterns was performed using the Rietveld method through the Fullprof software [5]. The microscopic analysis of the CuO-NPs was carried out by dispersing the NPs in isopropanol at 10 mgL^{-1} and a drop was placed onto lacey carbon films on a 200 mesh Nickel TEM grid. A JEM-2200FS microscope operated at 200 kV was used to monitor the microstructure and to perform an elemental analysis. The analysis of the selected area electron diffraction (SAED) was made with Process diffraction software [6]. The average grain size and shape as well as chemical composition by EDS were monitored in a field emission scanning electron microscope (FE-SEM, JEOL JSM-7401F) using a 30 kV field emission gun. Bright-field micrographs were acquired in a transmission electron microscope (Hitachi model HT7700) operated at 100 kV. The average size of the nanoparticles was corroborated through the analysis of micrographs obtained by TEM in bright-field mode using the ImageJ software [7].

Rietveld refinement of the XRD patterns was performed considering a monoclinic phase with C2/c space group (Figure 1a). The average crystallite size determined by this method was of 9.17 ± 0.06 nm. Figure 1b reveals that CuO-NPs have a quasi-rounded shape agglomerated like nano-rods. The average particle size of 9.15 ± 0.13 nm obtained by TEM (Figure 1c and e) agrees with the value determined by the Rietveld method. HAADF-STEM micrograph (Figure 1d) confirmed the quasi-rounded shape of nanoparticles. The SAED showed that the nano-rods are polycrystalline and were indexed according to the CuO PDF 00-005-0661 card (Figure 2a). EDS micro-analysis (Figure 2b) revealed peaks for oxygen and copper at 49.2 and 50.8 at. %, respectively, corresponding to pure CuO-NPs. Figure 2c shows two spacing of lattice fringes indexed on a representative HRTEM image, in agreement with SAED. The

characterization results as a whole indicate that high pure CuO-NPs with average size <10 nm were produced by the precipitation method. Likewise, the agglomeration of CuO as nano-rod particles was noted, possibly by pH changes during precipitation. In order to monitor the morphology effects on the CuO-NPs, the pH tune at different values during synthesis is suggested.

References:

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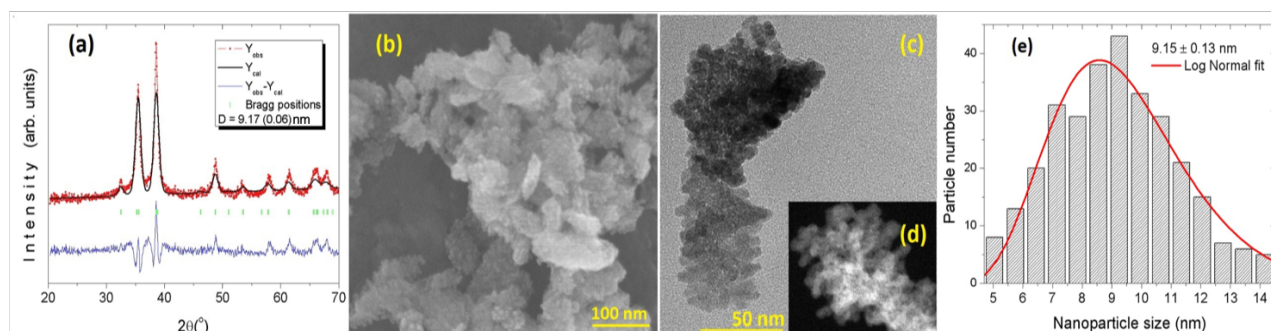
Figure 1. (a) Comparison between the experimental (Y_{obs}) and calculated (Y_{cal}) pattern by the Rietveld method. (b) Nanorods-like observed by SEM micrograph. (c) Quasi-rounded nanoparticles monitored by bright field mode. (d) HAADF-STEM micrograph for the CuO-NPs. (e) Nanoparticle size distribution obtained by recount in TEM in bright field mode.
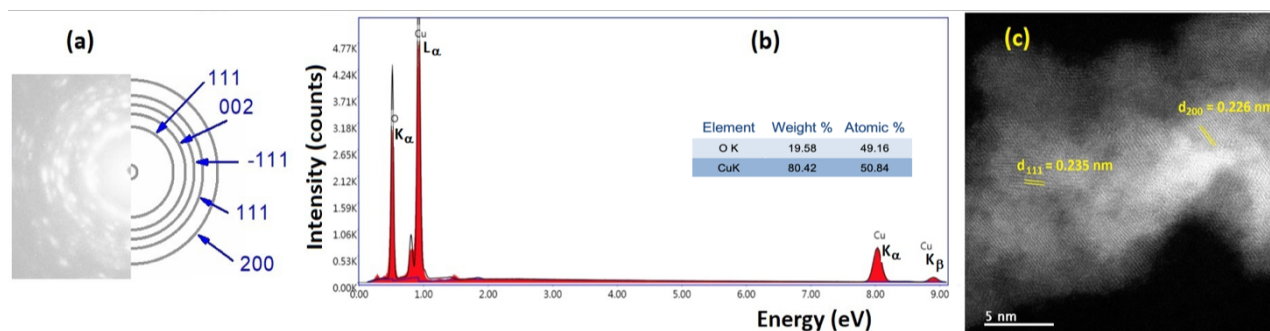

Figure 2. (a) SAED pattern in TEM mode. (b) elemental composition determined by EDS. (c) The crystal space distance determined in the HRTEM for CuO-NPs.