doi:10.1017/S1431927621008382
Microsc. Microanal. 27 (Suppl 1), 2021

FCC and 4H structure coexistence in Ag nanoparticles determined through TEM imaging and a diffraction pattern indexing program (DPIP)

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Silver nanoparticles (AgNP) have been widely utilized over the last decades in different areas, ranging from the biomedical to the optoelectronic fields. The great importance of AgNP relies upon their outstanding optical absorption, leading to surface plasmon resonance-related phenomena and their excellent antibacterial effect [1, 2]. In recent years, the crystallization of different nanoparticles of traditional FCC metals into unusual non-FCC structures has been reported [3], with exciting properties differing from the cubic structure. Hence, the study and determination of their internal structure provide information on the effect that synthesis methodologies have on the final features. In this regard, transmission electron microscopy (TEM) is a suitable technique for analyzing nanoscale materials since its spatial resolution provides local information and fine structural information. The crystal phase's determination can be done statistically by selected-area electron diffraction (SAED) over a group of nanoparticles or locally using nano-area electron diffraction or high-resolution TEM (HRTEM). The latter case permits the analysis of the defects and fine structure at the single-particle level.

Herein, we have synthesized AgNP through a fast and straightforward soft-chemistry methodology, using only synthetic tannins and a silver precursor [4]. Usually, it is reported the production of AgNPs with the traditional FCC structure when using tannin-assisted methodologies. However, in our case, it was observed that AgNPs crystallized in both cubic and hexagonal phases, and the ratio between one and the other phase depends on the initial parameters of synthesis. AgNPs were produced in aqueous solution using tannic acid as both the reducing and capping agent, driving a fast reduction and a high nanoparticle production, providing them with stabilization and biocompatibility. The nanoparticles were collected by centrifugation and redispersed in distilled water. Nanoparticle's characterization was performed by TEM, and phase determination was done using a home-made computer program based on measurements on the digital diffractograms of HRTEM images [5]. The diffraction pattern indexing program (DPIP) enables a fast comparison between multiple structures, providing calculated lattice distances and interplanar angles matched with the experimental data. The program storages crystallographic data from multiple candidate structures such as the space group, lattice parameters, and lattice distances and planes [6]. The experimental necessary entry data are the coordinates of two non-collinear lattice spots from the digital diffractogram generated by the fast Fourier transform (FTT) of HRTEM images. The DPIP displays the calculated interplanar distances and angles of two sets of crystallographic planes for each candidate structure that best match the experimental entries within a given tolerance.

Figure 1A shows an HRTEM image of a single AgNP from which the FFT was calculated (Figure 1B). The coordinates of two non-collinear spots were acquired and entered into the software. The matching database consisted of the crystallographic data of the FCC structure, the 4H phase, the 2H phase, and common silver oxides. Figure 1C corresponds to a screenshot of the program, displaying the calculated interplanar distances and angles and a delta value, which corresponds to the difference with the experimental measurements. In this case, the AgNP was identified as a 4H-phase nanoparticle. The calculated and experimental data are shown for comparison.

In summary, we determine the structure of AgNP synthesized through a tannin-mediated method. We found that the synthesis method yields a mixture of cubic and hexagonal phases coexisting in the prepared samples. Furthermore, our DPIP permits a quick comparison between different structures and identifies the best match according to the experimental data. These results give insights into the growth process during tannin-mediated synthesis of AgNP, which is essential for understanding and optimizing synthesis protocols seeking to generate stable and biocompatible nanoparticles.

Acknowledgments: R. Mendoza-Cruz thanks PAPIIT-UNAM for grant IA102020 to support this work.

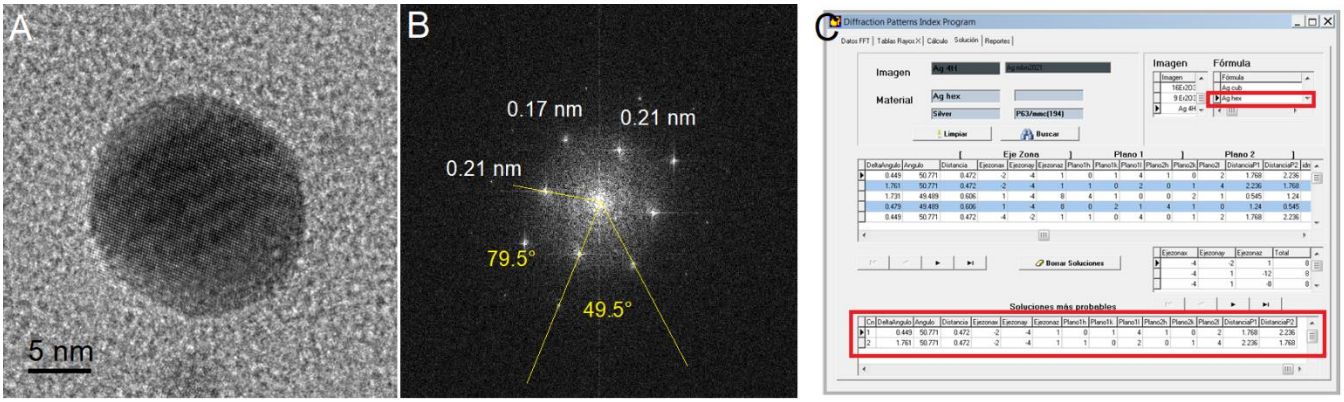

Figure 1. (A) HRTEM image of a single AgNP, and (B) its FFT. The measured interplanar distances and angles are shown. (C) A screenshot of the DPIP interface displaying the calculated interplanar distances and angles.

References

1. Tran QH, Nguyen VQ, Le A-T (2013) Silver nanoparticles: synthesis, properties, toxicology, applications and perspectives. Adv Nat Sci Nanosci Nanotechnol 4:033001. https://doi.org/10.1088/2043-6262/4/3/033001
2. Evanoff DD, Chumanov G (2005) Synthesis and optical properties of silver nanoparticles and arrays. ChemPhysChem 6:1221–1231. https://doi.org/10.1002/cphc.200500113
3. Sow C, P S, Mettela G, Kulkarni GU (2020) Noble Metal Nanomaterials with Nontraditional Crystal Structures. Annu Rev Mater Res 50:345–370. https://doi.org/10.1146/annurev-matsci-092519-103517
4. Ascencio F, Estevez JO, Rangel-Gamboa L, et al (2020) A comparative study of the synthesis and cathodoluminescence of BiOCl nanostructures using synthetic tannins. Mater Today Commun 25:101614. https://doi.org/10.1016/j.mtcomm.2020.101614
5. Galicia R, Herrera-Becerra R, Rius-Alonso JL, et al (2012) A program for phase identification using diffractograms obtained from TEM structure images. Rev Mex Fis 59:102–106
6. Miguel F, Aguirre A, Bazán-Díaz L, et al (2015) Nano Phase Characterization by Transmission Electron Microscopy: Experimental and Simulation. Mater Sci Appl 6:935–942. https://doi.org/10.4236/msa.2015.611094