INNOVATIVE SYNTHESIS OF SILVER NANOWIRES AND TITANIUM NANOCRYSTALS FOR FUTURE APPLICATIONS IN OPTOELECTRONIC DEVICES

https://doi.org/10.22533/at.ed.797112404112

Data de aceite: 04/11/2024

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ABSTRACT: Silver nanowires (AgNWs) and oxide semiconductors such as titanium oxide (TiO_2) nanocrystals are nanomaterials that have advantages in both; their physical and chemical properties. Due to these advantages, these nanomate- rials have the potential to be applied in optoelectronic devices, both for the manufacture of electrodes and in the construction of devices such as solar cells, photodiodes, sensors, and transistors. The performance of these opto- electronic devices depends on the synthesis method, which influences the size of the nanostructures, crystallization, purity, and phase composition. In this ar- ticle, we present a simple and rapid synthesis of nanostructures such as AgNW and TiO_2 nanocrystals, which use the Polyol and Sol-Gel methods respectively, to obtain optimal dimensions for their applications. The nanostructures were deposited using the spin coating technique; on glass and silicon substrates for their characterization, which was carried out using X-ray diffraction, scanning electron microscopy, and UV-Vis spectroscopy.

KEYWORDS: Nanomaterials, AgNWs and TiO_2 nanocrystals

INTRODUCTION

In recent decades, there has been a great deal of interest in metallic nanostructures, especially those of copper (Cu), silver (Ag), gold (Au), and TiO_2 nanocrystals; showing great potential in their electrical, optical, and mechanical properties, applying them in optoelectronic devices, such as transistors, nanosensors and solar cells [1]. In this sense, various nanomaterials have been developed, such as networks of metallic nanowires, in par- ticular AgNWs; being produced on a large scale and deposited in environmental conditions, allowing their application in flexible devices. In addition, they offer very high conductivity and transmittance, essential properties for the development of nanostructured, electrodes capable of replacing commercial ITO [2]. Therefore, this research studies and develops a simple and rapid synthesis, obtaining nanomaterials with high purity, morphology, and sizes suitable for future applications; in the case of AgNWs, they depend mainly on their length, diameter, and aspect ratio, critical factors to achieve high transparency with low turbidity, low resistance, and high mechanical strength [3]; however, it is difficult to achieve these factors simultaneously. Yang et al. claimed that a reaction time of 2 hours can synthesize AgNWs with a diameter of 62.5 nm and a length of 13.5 μm [4]. Xia group. used a simple polyethylene glycol process to obtain very long AgNWs, adjusting the stirring rates [5]. Therefore, the search for a synthesis that allows controlling the length and diameter of AgNWs is still under investigation. After searching the literature, it was found that the varieties and quantities of nucleates are crucial. The results showed that, when using NaCl, chloride ions interact with silver ions, affecting the growth and morphology of Ag- NWs. The reaction between Ag^+ and Cl^- leads to the formation of silver chloride (AgCl), these ions help the formation of the nanowire [6]. However, the lifespan of these nanostruc- tures in an electrode is shorter than that of ITO when left to the environment, as AgNWs change their surface, leading to the formation of silver sulfate (Ag_2SO_4) nanoparticles due to their sulfidation [7]. This contributes to the degradation of the AgNWs that make up the electrode, a problem that is overcome by depositing a thin film of TiO_2 nanocrystals on the AgNWs to protect them from the environment, providing them with good stability and durability.

EXPERIMENTAL

Materials

Silver nitrate ($AgNO_3$, 99.8 %), ethylene glycol (EG), polyvinylpyrrolidone (PVP), sodium chloride (NaCl, 97 %), titanium isopropoxide ($C_{12}H_{28}O_4Ti$, 97 %), isopropyl alcohol (C_3H_8O, 99.84 %), nitric acid (HNO_3) and ethyl alcohol, were obtained from Aldrich Chemical, Ltd.

Synthesis of silver nanowires

In this synthesis, ethylene glycol (EG) is selected as a solvent of both silver nitrate ($AgNO_3$) and polyvinylpyrrolidone (PVP), considering its boiling point of 197 ℃, allow- ing synthesis at high temperatures. Another agent used is sodium chloride (NaCl), which affects the morphology of metal nanoparticles, decreasing the concentration of silver chlo- ride (AgCl), reactions that facilitate the formation and growth of nanowires. The synthesis of AgNWs, shown in Figure 1, was performed using the Polyol method [8]. In the first step, 0.094 moles of $AgNO_3$ were dissolved in 15 ml of EG until a homogeneous solution was obtained. In the second step, the solution obtained was mixed with another solution containing 0.110

moles of PVP and 0.100 moles of NaCl, previously dissolved in 15 ml of EG. The latter solution was kept under magnetic agitation at 58 °C until a cloudy solution was obtained. In the third step, this obtained solution is placed in a preheated oven at 100 °C for 2 hours. After this period, the AgNWs obtained were purified through washes with ethyl alcohol, followed by centrifugations at 2000 rpm for 45 minutes. This process was repeated three times, removing the excess liquid to discard the EG, the PVP, and the nanoparticles present. Approximately 450 mg of AgNWs were obtained, storing them in ethanol at 4 °C.

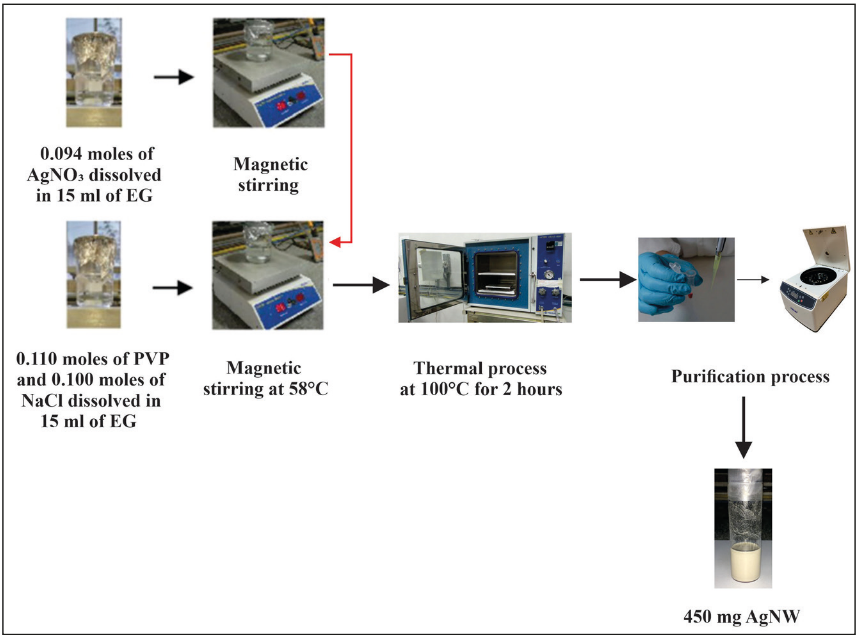


Figure 1: Silver nanowire synthesis process.

Synthesis of titanium oxide nanocrystals

To synthesize TiO_2 nanocrystals, shown in Figure 2, the Sol-Gel method was used [9] the precursor solution (solution 1) was prepared, by mixing 3.13 ml of titanium isopropoxide ($C_{12}H_{28}O_4Ti$) with 0.5 ml of isopropyl alcohol (C_3H_8O); a solution that was combined, in a covered container, due to its crystallization with air, solution magnetically stirred for 10 minutes. In a separate container, 37.5 ml of ultrapure deionized water was mixed with 0.5 ml of nitric acid (HNO_3) (solution 2), adjusting the pH to 6; the mixture was magnetically stirred, at 65 °C for 10 minutes. Solution 1 was then slowly added to solution 2, forming a milky solution and initiating the hydrolysis process. The Solution continued to be stirred at the same temperature for 1 hour and 30 minutes, then cooled to room temperature, precipitating TiO_2 nanocrystals. Finally, the mixture was centrifuged at 2000 rpm for 5 minutes to extract the liquids, preserving the 400 mg of TiO_2 nanocrystals in a hermetically sealed flask.

Techniques for characterizing

TiO_2 and AgNWs nanocrystals were deposited on glass substrates for UV-Vis measurements and microscopy images and on silicon for XRD measurements, using the Spin

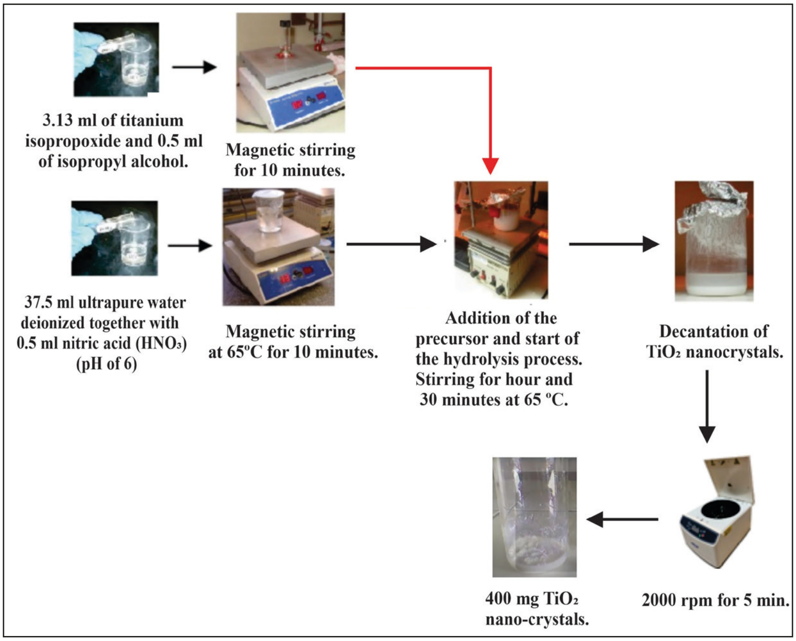


Figure 2: Synthesis of TiO2 nanocrystals process.

Coating method. Before the deposition of the nanostructures, they were dispersed in 20 ml of ethanol at a concentration of 1% for further dispersion. Finally, these depositions were subjected to heat treatment at 160 ℃ for 10 minutes in a horizontal tube furnace, to evaporate the liquid waste. X-ray diffraction patterns were recorded on a Shimadzu XRD-7000 diffractometer operating at 40 kV and 20 mA monochromator (Cu-Kα radi- ation λ = 1.5418Å) (scan rate of 2° min^{-1}) in the 2θ angle range from 20° to 62°, to determine the crystal phase and sizes of the nanocrystals. A Tescan Vega 3 scanning electron microscope was used at an electron acceleration voltage of 10 kV, and a JEOL JEM transmission electron microscope operated at a voltage of 120 kV and a resolution of 0.5 nm, allowing magnifications of up to 20.000x which allows the morphology and size of the nanostructures to be observed. Images were analyzed using Image J. UV-Vis transmittance spectroscopy was performed using a Perkin Elmer Lambda 1050 UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the synthesized AgNWs shown in Figure 3(a), corresponding to the deposition of AgNWs on a silicon substrate; it reveals the characteristic silver (Ag) peaks at 2θ angles of 38° and 44.7°, corresponding to the crystallographic planes (111) and (200), respectively. No traces of other compounds, such as Ag_2O, were detected, indicating high crystallinity and purity. In addition, the high intensity of the plane (111) that the AgNWs obtained has great length; in addition, diffraction shows peaks of very low intensity generated by the silicon substrate, observed at 2θ angles of 32° and 46°, corresponding to the planes (220) and (400), respectively. Figure 3(b) shows the diffract grams of TiO_2 nanocrystals deposited on a silicon substrate. This analysis confirmed the formation of the anatase phase, revealed by the 2θ angles of 260°, 38°, 47°, and 54°, corresponding to the planes (101), (004), (200), and (211), respectively; additionally, a peak associated with the silicon substrate was observed at an angle 2θ of 32°, corresponding to the plane (220). On the other hand, the size of the crystallographic plane was calculated using the Debye–Scherrer equation [114], obtaining a size of (4.33 ± 0.02) nm, confirming the high precision in the TiO_2 nanocrystals. To facilitate a clear view of the isolated nanowires and to appreciate their elongated morphology, they were dispersed in isopropyl alcohol. TEM microscopy allows us to observe a minimal presence of nanoparticles, which failed to form as nanowires, and also a thin layer of polyvinylpyrrolidone (PVP) on the surface of these nanostructures, as shown in Figure 4. This polymer layer formed during synthesis through the polyol method remains adhered to its surface even after purification, a layer that is not uniform. This varies from (20 to 40) nm in thickness, a measurement obtained using the "ImageJ" software. The presence of this layer influences their optoelectronic properties due to their insulating characteristics, which leads to these nanostructures being exposed to a thermal process to evaporate the polymeric layer using SEM microscopy, allowing us to observe AgNWs in greater detail, revealing their smooth, elongated, and cylindrical morphology with a high ratio.

Figures 5(a) and 5(b) show well-defined nanowires free of structural defects; the mea- surements of both the diameter and length obtained using the "ImageJ" software, taking into account its scale as a reference the diameter measurement scale was 1 μm while its length was 10 μm; the results obtained through a frequency distribution, represented by a histogram show that the diameter is 72 nm and its length is (27 ± 0.7) μm, demonstrating

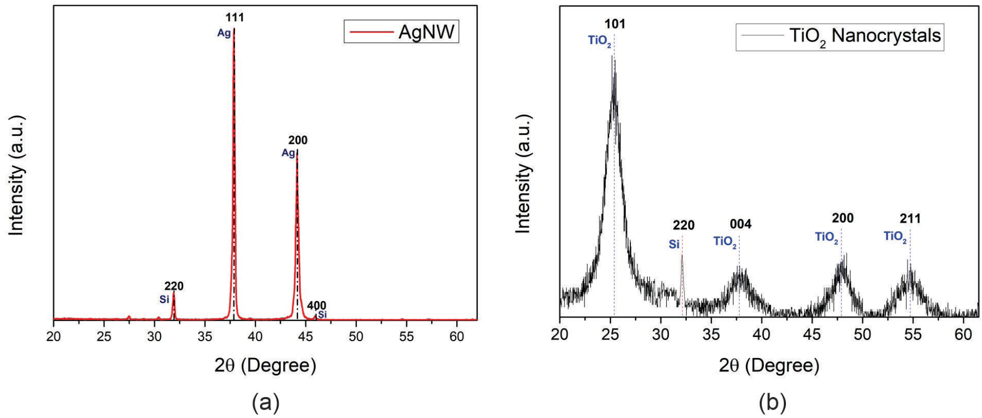


Figure 3: Diffractograms obtained by (XRD) a) AgNWs and b) TiO_2 nanocrystals.

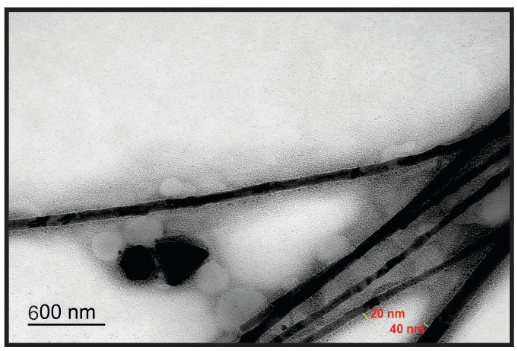
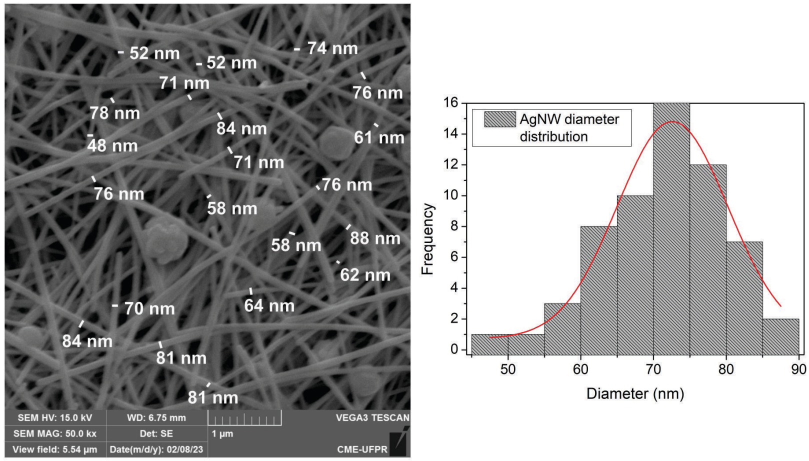


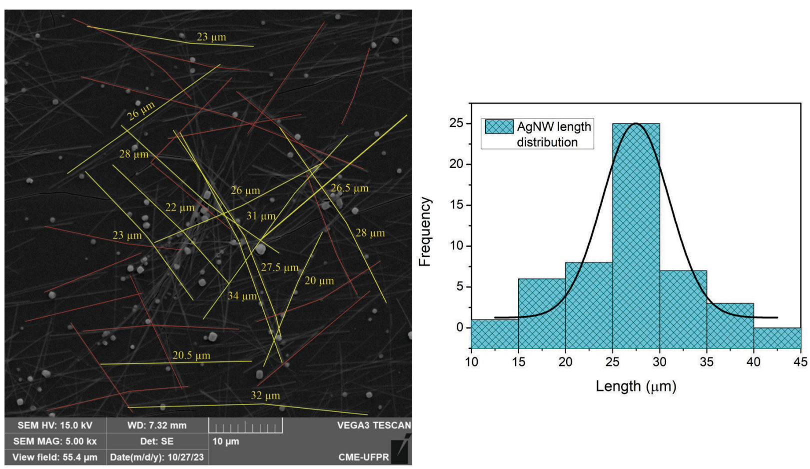
Figure 4: Image obtained by (TEM) of the AgNW, showing the thin layer of PVP thick- ness (20 to 40) nm.

that the length of these nanostructures is up to three orders of magnitude greater than their diameter. A recent study by Elif Sumeyye [10] reported AgNWs with a diameter of approximately 70 nm and lengths of up to 20 μm, synthesized using the polyol method, achieved optimal results in the devices; a finding that is comparable to those obtained in this work, which highlights the reliability of the synthesis process.

To observe the morphology of TiO_2 nanocrystals synthesized using the Sol-Gel method, transmission electron microscopy (MET) was used, an image captured at a scale of 50 nm, as shown in Figure 6, this analysis reveals that the nanocrystals exhibit an almost spherical morphology, with minimal agglomeration due to the Van der Waals forces, acting between the nanocrystals, leading to low dispersion. To counteract these attractive forces and im- prove the dispersion of these nanostructures, they were suspended in ethyl alcohol, a solvent that is compatible with nanostructures and minimizes their interaction, which is why they were dispersed at a high concentration of ethyl alcohol, achieving better distribution; as can be seen in Figure 7 through a MET image at a scale of 100 nm, the measurements



(a)



(b)

Figure 5: Images obtained in SEM, with their measurements and respective relative frequency distributions, a) diameters and b) lengths of the AgNWs.

of their diameters obtained, using the “ImageJ” software, using the microscope scale as a standard reference. The resulting data was represented using a histogram, which facilitated the calculation of frequency distributions for the measurements, the analysis shows that the diameter of TiO_2 nanocrystals is (15 ± 9) nm.

Figure 8(a) illustrates the UV-visible spectra taken before and after the purification process. The black graph represents the spectrum of the product obtained before purification, showing two peaks: one at 358 nm, indicating a high concentration of AgNW, and another at 424 nm, associated with the presence of Ag nanoparticles within the nanomaterial. In contrast, the blue graph represents the characterization of the sediment collected

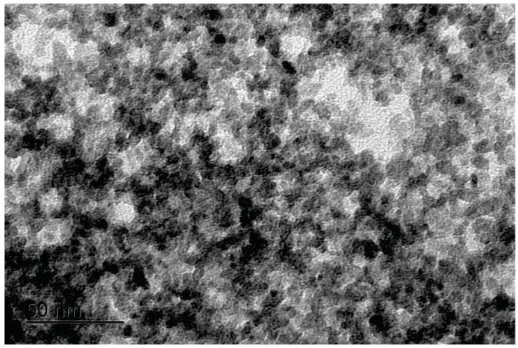


Figure 6: TEM image of TiO_2 sin- gle crystals, showing small agglomera- tions.

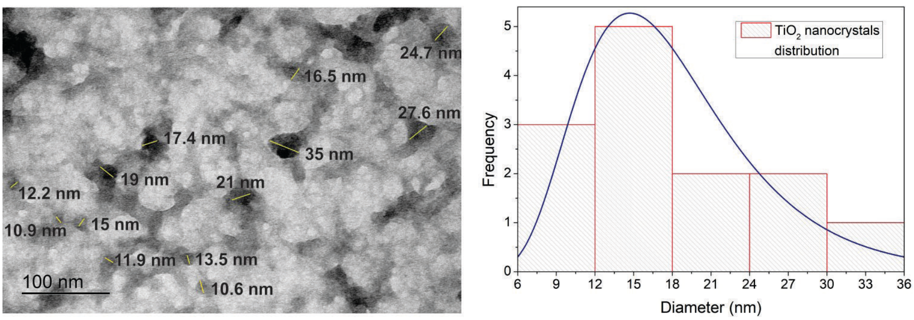
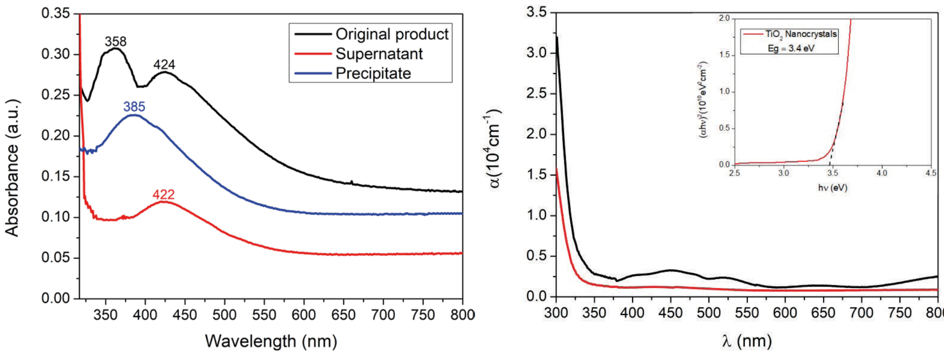


Figure 7: SEM images of the TiO_2 nanocrystals, their measurements, and their respective relative frequency distributions.

after centrifugation of the nanomaterial; this spectrum shows a single prominent peak at 385 nm, corresponding to the high AgNW concentration, confirming the successful removal of most nanoparticles. The red graph represents the spectrum of the supernatant obtained after centrifugation, which shows a significant peak at 422 nm, indicating a high presence of Ag nanoparticles and a large absence of AgNWs [11].

The absorption spectrogram of the TiO_2 nanocrystals was analyzed within the wave-length range between 300 nm and 800 nm, as shown in Figure 8(b). The spectrum shows a greater absorption in the ultraviolet region, corresponding to wavelengths below 350 nm, due to its wide bandwidth of approximately 3.4 eV, corresponding to the anatase phase of TiO_2. The black curve represents the absorption coefficient of the nanocrystals showing small peaks in the visible region, corresponding to wavelengths of 450 nm and 525 nm, due to the transition of electrons from a metallic orbital (Ti) to an organic ligand (O), characteristic of TiO_2 nanocrystals. These nanostructures have an absorption coefficient of 0.16×10^4 cm^{-1}, which is higher than the absorption coefficient of a glass of 0.08×10^4 cm^{-1} measured at a wavelength of 550 nm. This higher absorption coefficient indi- cates that the nanocrystals, having smaller diameters, have shifted their absorption peak



(a) (b)

Figure 8: a) UV-vis characterization of the AgNWs obtained before and after the purifi- cation process and b) Absorption coefficient of TiO_2 nanocrystals (black curve) and glass (red curve).

towards shorter wavelengths, thus demonstrating improved optical properties suitable for various applications.

CONCLUSION

In summary, AgNWs were synthesized using the Polyol method following the processes that led to long, thin nanostructures (diameter 72 nm and length 27 μm) during two hours of processing. These exceptional results combining a high aspect ratio nanowire morphology and a short synthesis time, were achieved through an in-depth experimental study of the synthesis parameters. The second nanomaterial synthesized was TiO_2 nanocrystals, using the Sol-Gel method, obtaining nanostructures of 15 nm in diameter with a perfect morpho- logical relationship. This last nanomaterial aims to protect AgNWs from the environment, as they are deposited on any substrate, providing them with high stability and durability for future applications in optoelectronic devices.

ACKNOWLEDGEMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES) — Finance Code 001 and the Conselho Nacional de De- senvolvimento Científico e Tecnológico — Brasil (CNPq). The authors thank the Centro de Microscopia Eletrônica (UFPR) for providing access to the SEM facilities and Laboratório de Óptica de Raios X (UFPR) for providing access to the XRD facilities.

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