

Sonochemical effects on ZnO particles

Efectos sonoquímicos en partículas de ZnO

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Abstract

A variety of technological applications related to oxide semiconductor-based devices have attracted great interest among the scientific community, leading to an increase in studies of these materials during the last years. Among such materials, zinc oxide (ZnO) has applications in several areas, from light-emitting diodes (LEDs) to photovoltaic devices in solar cells. Considering the physical and chemical properties conferred to these materials, the possibilities of application in technological devices depend greatly on the synthesis routes employed. Accordingly, we investigated the morphological modifications in ZnO particles when subjected to sonochemical treatment and the influence of related synthesis method parameters, such as the time and amplitude of sonication. To analyze such effects, four samples were prepared with different sonochemical treatment conditions: in two, the amplitude of sonication was kept constant while varying the time of sonication, and in the other two, the time was kept constant while varying the amplitude. The analysis of the results obtained indicated that sonochemical treatment led to superficial morphological modifications in ZnO particles. Furthermore, these modifications became more apparent when higher amplitude and longer time of sonication were employed in sample synthesis.

-----*Keywords:* Sonochemistry, semiconductors, zinc oxide, nanoparticles

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Resumen

La variedad de aplicaciones tecnológicas relacionadas a los dispositivos basados en óxidos semiconductores nanoestructurados ha despertado un gran interés en la comunidad científica, haciendo con que los estudios relacionados a estos materiales han aumentado en los últimos años. Entre estos materiales, se encuentra el óxido de zinc (ZnO), que presenta aplicaciones en las más diversas áreas, desde diodos emisores de luz (LEDs) a los dispositivos fotovoltaicos en células solares. Con el conocimiento de que las propiedades químicas y físicas que confieren a estos materiales las posibilidades de aplicación en dispositivos tecnológicos son fuertemente dependientes de las rutas de síntesis empleadas para la obtención de los mismos, presentamos en este trabajo una investigación con respecto de las modificaciones morfológicas ocurridas en partículas de ZnO, cuando el mismo es expuesto a un tratamiento sonoquímico, además de las influencias de los parámetros relacionados a éste método de síntesis en la obtención de este material. Para analizar los parámetros presentados anteriormente, tres muestras fueron preparadas, dos de ellas manteniendo la amplitud y variando el tiempo de sonicación y otra manteniendo el tiempo y variando la amplitud de sonicación, durante el tratamiento sonoquímico. El análisis de los resultados obtenidos indica que el tratamiento sonoquímico conduce a modificaciones morfológicas superficiales en las partículas de ZnO, además estas modificaciones se presentaron más evidentes cuando una mayor amplitud y un mayor tiempo de sonicación fueron utilizados en la síntesis de las muestras.

-----*Palabras clave:* Sonoquímica; semiconductores; óxido de zinc; nanopartículas

Introduction

Over the last decade, many efforts were made in the development of semiconductor-based devices with wide band gap. Among these semiconductor materials, zinc oxide (ZnO) has great potential for a variety of practical applications. Many of its properties, such as high electronic mobility, high thermal conductivity, wide band gap (3.37 eV at room temperature) and large exciton binding energy, makes zinc oxide a suitable material for application in a range of devices, including transistors, photodetectors, light emitter diodes (LEDs) and laser diodes [1], piezoelectric transducers, varistors, chemical and gas sensors and UV light emitters, among others [2].

One of the possible applications that have been studied intensively in the last years and that is of great interest to our group, proposes the

replacement of single and polycrystalline silicon in solar cells with semiconductor oxides, such as TiO_2 and ZnO, in photoelectrodes, in so-called dye-sensitized solar cells (DSSC), for the conversion of solar energy into electric energy. However, low efficiencies (global efficiencies of about 0.4-5.8%) for these ZnO-based devices have been reported, suggesting that many improvements must still be made in this field, for a reasonable application [3].

It is important to note, however, that all the applications suggested for zinc oxide, as well as its morphological characteristics, are closely related to the synthesis routes of this material. Furthermore, nanoscale materials usually show different properties compared to their bulk counterparts, mainly due to their higher surface-to-volume ratio and possible surface defects

and consequent modifications in their electronic properties [1].

Many synthesis routes have been applied to obtain ZnO nanostructures, where the most common chemical routes include the sol-gel method [4] and the hydrothermal method [5]. Alternatively, sonochemical synthesis allows the preparation of a great variety of nanostructured materials by ultrasonic wave irradiation in a liquid medium [6], and it can be a useful technique for the creation of new materials with unusual properties.

In this method, sound fields stimulate chemical reactions through the establishment of an extraordinarily high energy density, temperature and pressure conditions [7]. Chemical effects arise from a process called acoustic cavitation, which consists of the formation, growth and implosive collapse of bubbles in a liquid. The implosive collapse of bubble generates overheated points due to adiabatic compression or shock wave formation in the gas phase of collapsed bubble. The conditions at these points were experimentally determined, with transient temperatures nearing 5,000°C, pressures of about 1000 atm and heating and cooling rates over 10¹⁰ K/s [8]. Furthermore, the collapsed bubbles may increase mechanical shocks between the solute particles, possibly causing surface amorphization, which could also result in its sintering [9].

Accordingly, zinc oxide nanoparticles obtained by sonochemical treatment may show special structural and morphological characteristics directly related to the charge carrier dynamics in photovoltaic or photosensor devices [10]. In this paper, we report on the morphological changes in ZnO nanoparticles obtained with the sonochemical method and the modifications that this treatment produces.

Experimental

Four ZnO samples were prepared by the sonochemical method, where the irradiated solution consisted of a mixture of 0.5 g ZnO (Aldrich, 99.99%) and 100 ml of isopropyl

alcohol. The radiation source was an ultrasonic processor, Sonics VCX-750 model, 750 W and 20 kHz.

To investigate the time and amplitude effects of sonication in the samples, these parameters were then varied during the synthesis of the samples under study. Our first, designated ZnO_S10A40, was exposed to ultrasonic irradiation for 10 h, with a fixed amplitude of 40% of the nominal amplitude of the instrument. The second sample, designated ZnO_S17A40, was exposed to ultrasonic irradiation at the same amplitude as the first, but for 17 h.

The third sample, designated ZnO_S10A90, was exposed to ultrasonic waves for 10 h, but the sonication amplitude was modified to 90% of the nominal amplitude. Finally, the fourth sample, designated ZnO_S17A90, was exposed to ultrasonic waves for 17 h, but the sonication amplitude was set to 90% of the nominal amplitude. The time and amplitude used for each sample are shown in table 1.

Table 1 Time and amplitude of sonication for samples and their respective names

<i>Sample Name</i>	<i>Time (h)</i>	<i>Amplitude (%)</i>
ZnO_P	-	-
ZnO_S10A40	10	40
ZnO_S17A40	17	40
ZnO_S10A90	10	90
ZnO_S17A90	17	90

All samples were prepared in an air atmosphere, with five-minute pulses to prevent overheating of the equipment. Furthermore, a cool bath was used to maintain the global temperature constant during the sonication process. After exposure to the ultrasonic wave process, all samples were dried in oven at 80°C for 24 h.

The resultant powder from this process was then submitted to X-ray diffraction (XRD) analysis for the identification of the corresponding crystallographic phases, in a RIGAKU D/MAX 2,100PC diffractometer. The remaining structural

and morphological analyses were performed via transmission electron microscopy (TEM) using a Philips CM200 model, and scanning electron microscopy (SEM) using a Philips XL30 model, with a Schottky-type electron gun. Furthermore, UV-Vis measurements were carried out to determine the possible optical modifications in these particles. The results obtained were then compared to a standard sample of commercial ZnO powder, designated ZnO_P, not subjected to any sonochemical treatment.

Results and discussion

Figure 1 (a) shows the diffractograms for the ZnO_P, ZnO_S10A90 and ZnO_S17A90 samples, where the sonication amplitude was kept constant and the sonication time was varied. Figure 1(b) compares the diffractograms for ZnO_P, ZnO_S17A40 and ZnO_S17A90, and figure 1(c) the diffractograms for ZnO_P, ZnO_S10A40 and ZnO_S10A90 samples, where the sonication time was kept constant and the sonication amplitude was varied. All the observed peaks, for the different diffractograms and all the samples, could be indexed by the hexagonal phase (wurtzite) of ZnO (JCPDS-36-1451). Furthermore, we found a high degree of crystallinity for the ZnO_P sample, with narrow and well-defined peaks, unlike with the treated samples. Especially in the samples exposed to the larger amplitude of sonication (ZnO_S10A90 and ZnO_S17A90), the decrease in intensity and broadening of peaks after the sonochemical treatment were more apparent, indicating the possible occurrence of the amorphization process of the particles and decrease in crystal size. This effect is most evident in the details of figure 1 (a), (b) and (c), which shows the displacement of the peaks for the ZnO_S10A90 and ZnO_S17A90 samples, compared to the ZnO_P sample.

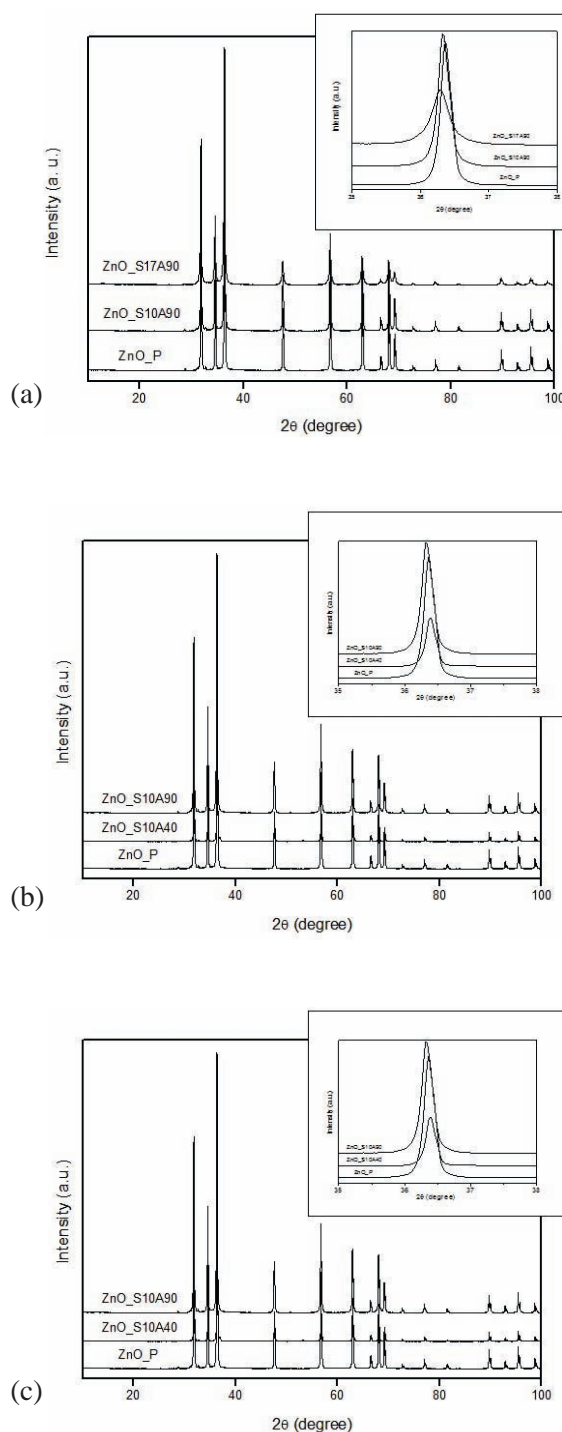


Figure 1 Comparison of X-ray diffraction patterns. (a) ZnO_P, ZnO_S10A90 and ZnO_S17A90 samples. (b) ZnO_P, ZnO_S17A40 and ZnO_S17A90 samples. (c) ZnO_P, ZnO_S10A40 and ZnO_S10A90 samples

These results indicated that the possible structural changes are more clearly dependent on sonication amplitude, since for the same time, it was possible to tell that the higher amplitude produced greater modifications. Otherwise, considering sonication time, keeping the amplitude constant, we determined that a longer time of ultrasonic irradiation led to more structural modifications, despite the hexagonal crystallographic phase being maintained.

To analyze the modifications that occurred in the samples exposed to higher amplitude, scanning and transmission electron microscopy

measurements were made. Figure 2 presents the SEM images for the different samples, (a) ZnO_P, (b) ZnO_S10A40 (c) ZnO_S17A90, where we observed a decrease in particle size for all the samples subject to sonochemical treatment. This result is related to the mechanical shock effect between the particles, caused by implosive collapse of the bubbles during the acoustic cavitation process. Besides the particle fragmentation, figure 2 (d) shows the sintering of the ZnO_S1040 sample, which was attributed to the extreme temperature and pressure conditions during the ultrasonic irradiation process [9].

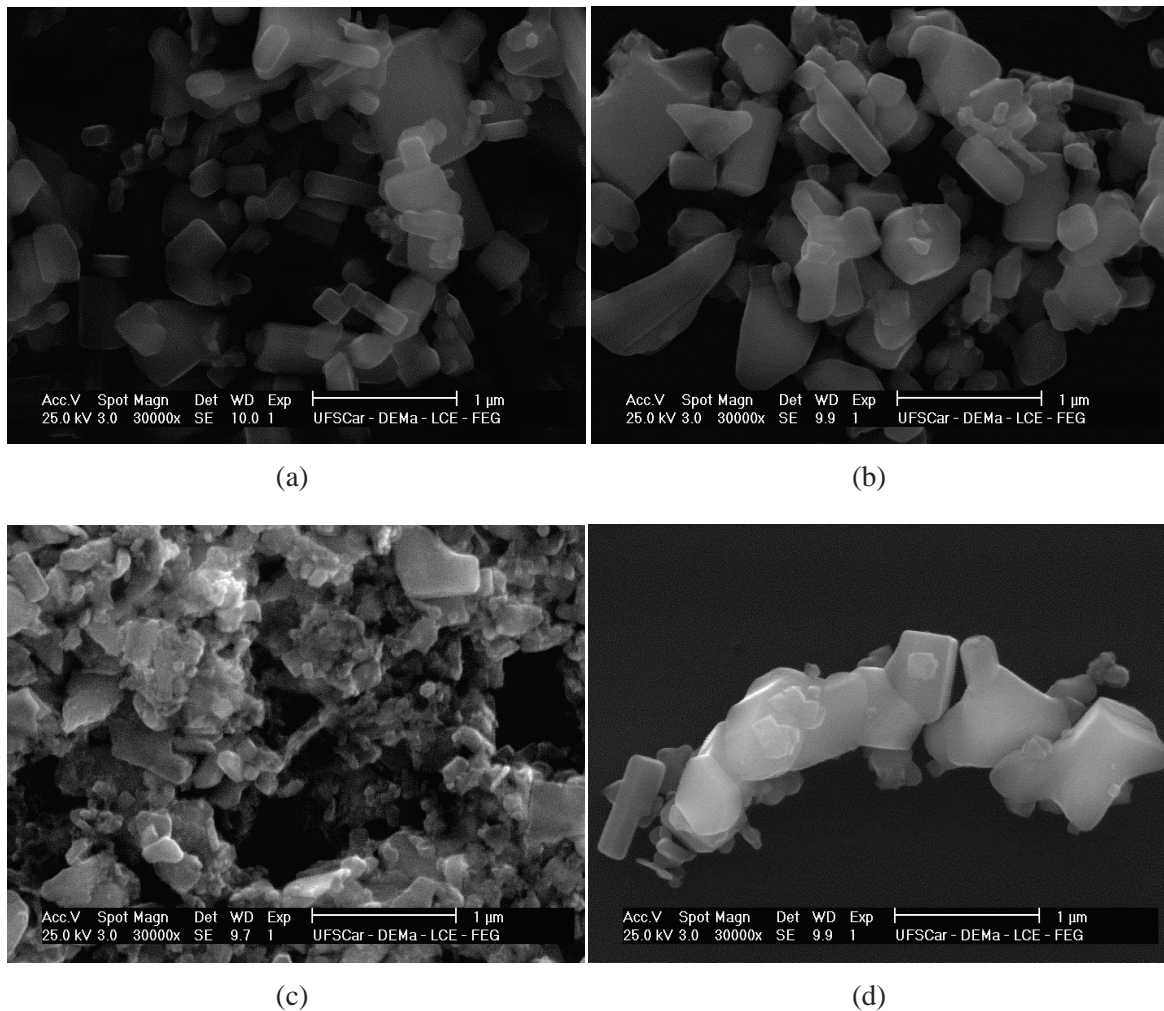
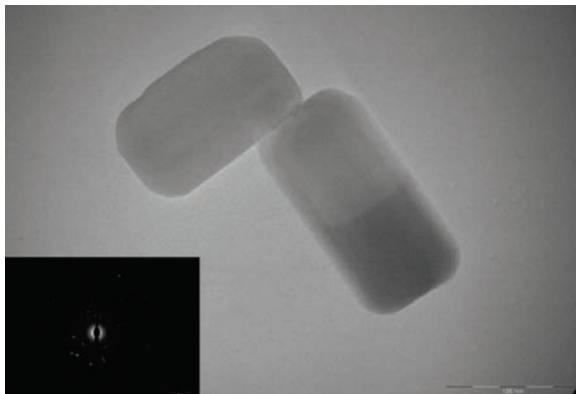
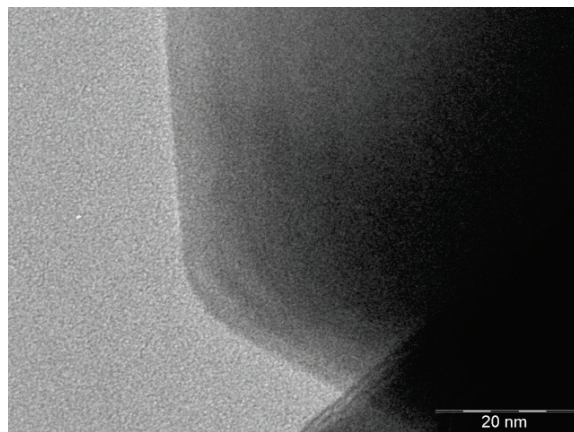


Figure 2 Scanning electron microscopy images of (a) ZnO_P, (b) ZnO_S10A40, and (c) ZnO_S17A90 samples, showing in all cases a decrease in particle size after sonochemical treatment, and (d) ZnO_S1040 sample showing sintering between particles

The transmission electron microscopy images of the ZnO_P, ZnO_S10A90 and ZnO_S17A90 in Figures 3, 4 and 5, respectively, showed very interesting characteristics. Figure 3 (a) shows the TEM image of the ZnO_P particles without sonochemical treatment, as well their electron diffraction pattern, which can be indexed as ZnO and indicates a polycrystalline sample. Figure 3 (b) shows the ZnO particle (standard) surface in detail.



(a)

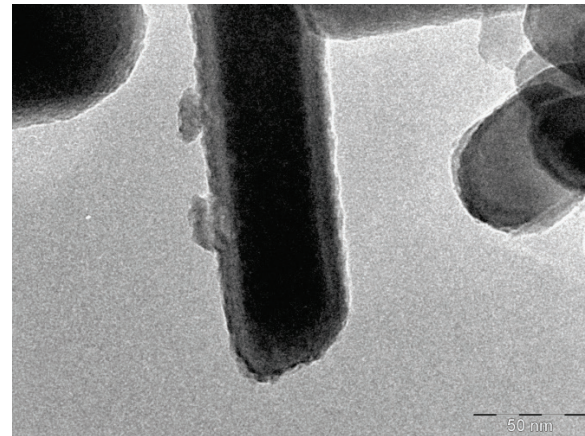


(b)

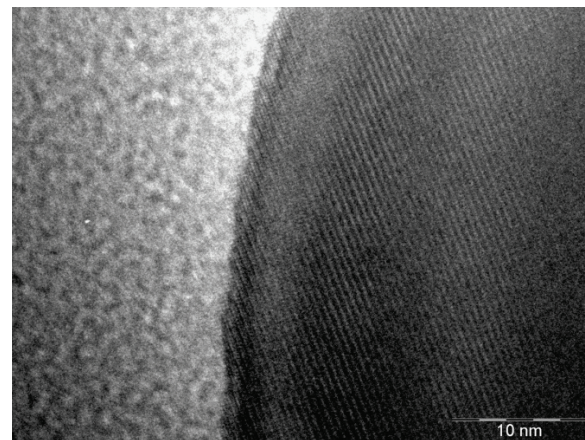
Figure 3 Transmission electron microscopy images of (a) ZnO_P sample with the corresponding electron diffraction pattern and (b) surface detail of ZnO particle

Sonochemical treatment effects were evident when we increased the sonication time as illustrated in figure 4 (a) and (b), which shows

the beginning of a surface amorphization process on the ZnO particles treated for 10 h with a fixed amplitude of 90% of the instrument's nominal amplitude. This was observed as an amorphous shell around the particles, which had already been suggested by XRD analyses. Under these circumstances, a thickness of about 3 nm was estimated for this amorphous shell.



(a)

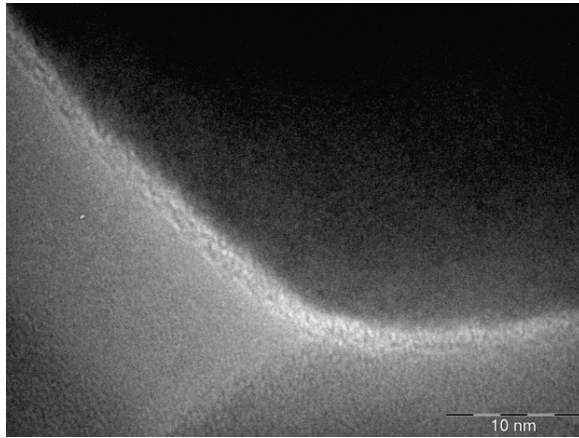


(b)

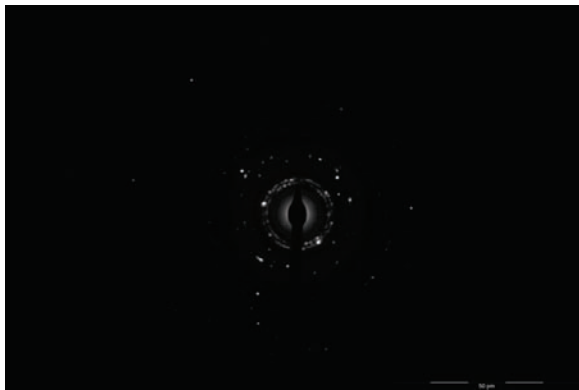
Figure 4 Transmission electron microscopy images of (a) the ZnO_S10A90 sample and (b) the same with higher resolution detail of the particle surface

The amorphization effect on the surface of the particles was more evident in the sample treated for 17 h, with fixed amplitude of 90% of nominal amplitude, where the estimated thickness of

the amorphous shell around the particles was approximately 10 nm. These effects are shown in the figure 5, which displays the increased thickness of the amorphous shell around the particles (a) and the electron diffraction pattern (b) for this sample, where we can emphasize the appearance of halos as evidence of the amorphization.



(a)



(b)

Figure 5 Transmission electron microscopy image (a) of ZnO particle surface exposed to sonochemical treatment for 17 h with amplitude of 90% and electron diffraction pattern (b) for ZnO_S17A90 sample, showing particle surface amorphization

Finally, figure 6 shows the Uv-Vis measurements for the ZnO_P, ZnO_S10A40 and ZnO_S17A40

samples. On the basis of these results, we can conclude that optical transmission is slightly modified but the band gap for all samples remained close to 3.2 eV, which is consistent with that reported in the literature. Furthermore, two bands around 443 and 485 nm could be observed for all samples, as well as one around 585 nm. These bands in the visible region are associated with transitions from shallow-trapped electrons and deeply trapped holes [11]. The superficially photogenerated electrons are trapped by defects on the surface of ZnO (probably Zn^{2+}), while the photogenerated holes are first trapped by surface defects (probably O^{2-}) and then back to the inside of the particle (the holes are deeply trapped by oxygen vacancies), forming emission centers [12]. The literature suggests that ZnO emissions in the visible region depend on superficially defects, while the crystalline internal phase is responsible for emission in the UV region [13-15].

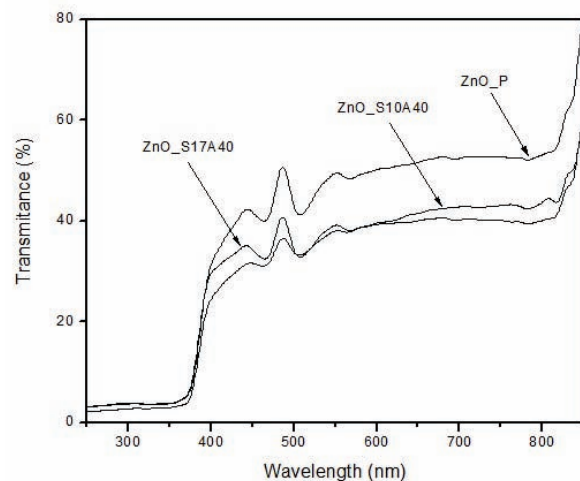


Figure 6 Uv-Vis measurements for ZnO-P, ZnO_S10A40 and ZnO_S17A40 samples

Conclusions

The results obtained allow us to conclude that sonochemical treatment produces some morphological modifications in ZnO particles, such as a decrease in crystal size and their sintering,

which are the result of extreme temperature and pressure conditions and mechanical shocks between the particles during the implosive collapse of the bubbles in the acoustic cavitation process, and that there was surface amorphization, with the appearance of an amorphous shell around the particles. Furthermore, we observed that the time and amplitude parameters of ultrasonic irradiation exercise influenced these morphological modifications. By keeping the sonication time constant and varying the sonication amplitude, we found that more morphological modifications were obtained for the amplitude of 90% of the nominal amplitude of the instrument compared with the amplitude of 40%. When we varied the sonication time and kept the amplitude constant, we found that the longer sonication time produced more morphological modifications, for example, an increase in the thickness of the shell around the particles, from 3 nm for 10 h to 10 nm for 17 h.

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