SYNTHESIS AND CHARACTERIZATION OF PbS/ZnS CORE/SHELL NANOPARTICLES BY MICROWAVE METHOD

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PbS/ZnSnanoparticles were synthesized via colloidal and microwave methods. First PbS nanoparticles with size of 11 nm and absorption in the visible range with higher luminescent properties were generated by microwave method. Then PbS/ZnS nanoparticles were obtained when the PbS:ZnS ratio was kept to 1.0:0.1 during the synthesis, leading to nanoparticles with PbS core of 12 nm and shell of approximately 3 nm. PbS/ZnS nanoparticles present a dramatically increase of PL intensity, confirming the confinement of the PbS core. In this case, the synthesis by microwave method allows obtaining nanoparticles with enhanced optical characteristics than those of nanoparticles synthesized by colloidal method.

1. Introduction

The study of semiconductors in the nanometric scale has been increased in the past few years, due to quantum confinement. This phenomenon comes along with an enhancement of the luminescent properties of the nanoparticles, making the material an interesting component for photovoltaic devices.

Lead sulfide (PbS) nanoparticles exhibit a large Bohr radius of PbS (18 nm) and a small band gap (0.41 eV),[1,2] therefore, it is relatively easy to prepare particles with size smaller than the Bohr radius that show strong quantum confinement effects. This effect, besides other interesting properties such as photomultiplication of charges [3], makes PbSa semiconductor widely studied and applied in photovoltaic, bio-analytical and micro-electronic device; nevertheless, PbSnanoparticles are very unstable in oxidizing conditions. One of the approaches to stabilize PbSnanoparticles isto cover them with an outer shell of a more stable component. Kumar *et al* reported the surface modification ofZnS and PbS by interfacing PbS on ZnS and ZnS on PbS nanoparticles, generating In this way core–shell nanocompositesZnS/PbS and PbS/ZnSby the colloidal method and varying the amount of shell precursor. They conclude that the nucleation of ZnS on PbS produces a core–shell structure, which induces the separation of charge and enhances the lifetime. The optical, photophysical, and electronic properties of the generated nanoparticles can be manipulated by changing the surface environment. [4]

It is well known that the heating method during the synthesis has a significant influence in the final properties, size and shape of the desired material.[5] One of the properties strongly influence by the heating method is the photoluminescence, due to changes in the surface defects of the material that may act as exiton traps.Microwave radiation allows a selective heating of compounds in the reaction mixture with reaction rate acceleration as a consequence of high heating rates, obtaining smaller particles with high homogeneity.[6] In addition, this method has

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proved to be environmental friendly, as shorter reaction times are used, compared to the traditional method, saving energy.

This work present the results of the synthesis of PbS/ZnS core/shell system by microwave heating and their comparison with the optical properties of the same material synthesized by colloidal method under reflux conditions.

2. Experimental procedure

2.1. Material and reagents

The chemical reagents used in this work, such as thioacetamide (TAA, CH_3CSNH_2), lead chloride ($PbCl_2$), 3-mercaptopropionic acid (MPA), zinc acetate($Zn(OAc)_2$), potassium hydroxide (KOH) and sodium citrate ($C_6H_5O_7 Na_3$), were obtained with purities above 99.0%, therefore no further purification was made; all of the solutions were prepared using distilled water.

2.2 PbS/ZnSNanoparticles traditional colloidal method

In a typical synthesis, 50.0 mL of sodium citrate 3.0 mM were prepared, then2.0 mL of $PbCl_2$ 30.0mM and 2.0 mL of TAA 30.0mM were added to the reaction vassel. The pH was adjusted to 7.0 with NaOH 1.0 M. The reaction mixture wasplaced under reflux conditions for 30min, obtaining a dark brown solution. Next, 1.0 mL of MPA 0.18 M was added to the PbS previously synthesized, and kept under stirring for 10 minutes; the solution turned to a light brown. After that, 10.0 mL of TAA 1.0 mM were added and pH adjusted to 8.0 with NaOH. The solution was kept into reflux conditions for 30min; meanwhile $Zn(OAc)_2$ 1.0mM was added with a constant flux of 0.3 mL/min. The mixture was kept under reflux conditions for six hours. The obtained nanoparticles were centrifuged, washed with acetone and acetonitrile, and then re-dispersed in water for further characterization.

2.3.PbS /ZnSnanoparticles by microwave method

The synthesis was carried out under the same experimental conditions as in the traditional method.2.0 mL of $PbCl_2$ 30.0 mM and 2.0 mL of TAA 30.0 mM were mixed with a previous prepared solution of 30.0 mM sodium citrate. The pH was adjusted to 7.0 with NaOH 1.0 M then the microwave heating was performed on the reaction mixture in cycles of on/off radiation with a total heating time of 60 s, Table 1 show the different heating rates performed on the experiments. Then 1.0 mL of MPA 0.18 M was added to the PbS previously synthesized, and it was kept under magnetic stirring for 10 minutes; the solution turned light brown. The pH adjusted to 8.0 with NaOH 1.0 M. The solution was placed into the microwave system and $Zn(OAc)_2$ and TAA 30.0 mM were added in portions of 2.0 mL during the on/off cycling the total microwave heating time was 15 min, Table 1 shows the experimental conditions for the synthesis. The obtained nanoparticles were centrifuged, washed with acetone and acetonitrile, and then re-dispersed in water for further characterization.

Table 1. Heating methods used for the experiments of PbSand PnS/ZnS nanoparticles synthesized by microwave method.

PbS nanoparticles		PbS/ZnS nanoparticles			
Experiment	Microwave on/off profile (s)	$[Zn^{2+}]$ (mM)	[TAA] (mM)	Microwave on/off profile (s)	Pb:Zn ratio
PbS1	10/5	–	–	–	–
PbS2a	20/5	1	1	10/50	1.0 : 0.1
PbS 2b		2	2		1.0 : 0.3
PbS3	60/0	–	–	–	–

2.4 Characterization methods

The microwave system used for the synthesis of the desired nanoparticles operates at 1100W, 2.45 GHz, working at 80% of power under the described conditions (see Table 1). UV-vis absorption spectra were obtained using a Perkin Elmer UV-vis Lambda 12 spectrophotometer from the dispersion of the nanoparticles in water.Fluorescence experiments were performed using a Perkin Elmer PL Lambda 12 spectrofluorimeter using a wavelength of excitation of 250nm. All optical measurements were performed at room temperature under ambient conditions. DSL analyses were performed with a Zetatrac NPA 152 from Microtrac in order to determine the size distribution of the obtained nanoparticles. Synthesized samples were examined via Scanning Electron Microscope (SEM) to analyze morphology and size of the obtained material.SEM images were obtained using a FE-SEM JEOL 67013.

3. Results and discussion

3.1. PbSnanoparticles

Fig. 1a shows the UV-Vis spectrafor the PbS nanoparticles synthesizedby different profiles of microwave heating, andit compares the results with the spectrum obtained for the PbS synthesized by colloidal method. It is well known that the absorption edge is blue-shifted when the size of semiconductor nanoparticles decreases.[7] For PbS nanoparticles, it was reported that the UV-vis absorption edge shows a marked blue-shift from that of the bulk PbS crystals which is expected around 1200 nm.[8] UV-Vis spectroscopy was applied to obtain information about the size and the light interaction of the PbS nanoparticles. The absorption of the colloidal PbS nanoparticles starts at around 800 nm and it increases with decreasing the wavelength, three salient shoulders are present around 600, 400, and 300 nm and they are attributes to exciton peaks of $1s_e$-$1s_h$, $1s_e$-$1p_h$, and $1p_e$-$1p_h$ transitions, respectively.[9-10] This is due to quantum confinement, because the average size of the PbS nanoparticles is smaller than the exciton Bohr radius of bulk PbS (18 nm).
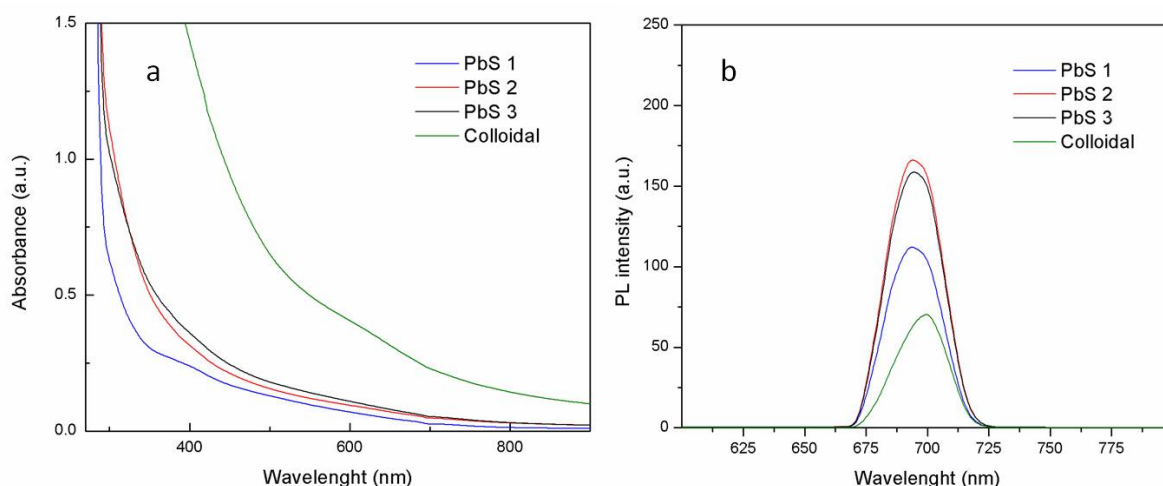

Fig. 1.a) UV-Vis and b)PL spectra for PbS nanoparticles synthesized by different methods.

For the nanoparticles synthesized by the microwave method at different heating profiles, it was observed that absorption edge shifts to 520 and 550 nm; this blue shift confirms the generation of smaller nanoparticles than those synthesized via traditional method. The confinement signals are still presents for the different exciton transitions. The Eg values of the PbS nanoparticles synthesized by both methods are listed in Table 2 and they vary from 1.55 to 2.4 eV. Those values

are similar to the Eg values of the most used semiconductor nanoparticles in photovoltaic devices,[11-12] in addition, all those values range into the visible region of the electromagnetic spectra. The use of microwave heating cycles allows to the diffusion of the nuclei into the preformed nanoparticles, giving more chemical stability in order to obtain better optical characteristics.

Tabla 2.EstimatedEg values for the different PbS nanoparticles synthesized in the present work.

Experiment	Absorption wavelength, λ(nm)	Optical band gap, E_g (eV)
PbS 1	520	2.38
PbS 2	542	2.29
PbS 3	550	2.25
Colloidal	800	1.55

Fig. 1b shows the room temperature photoluminescence spectrum of samples PbS nanoparticles obtained with traditional colloidal synthesis and microwave heating, all prepared at pH=7. It can be appreciated that the emission bands of the PbS nanoparticles fall within the visible region and they are centered ca. 700 nm. In microwave experiments, the line width is slightly blue shifted, what can be related to the decrease of the particle size. It is clear than the particles obtained by microwave heating present higher luminescence behaviour than those obtained by colloidal method. The sharp luminescence obtained by particles with cycling heating profiles is a dramatic example of the efficiency of the synthesis method and capping stabilizer in electronically protecting the structures from chemical degradation and size increase[13-14]. The effect observed for the microwave heating experiments is the result of a combination of relaxation into shallow trap states, the size distribution and crystal shape. As it was observed, the experiment labelled as PbS 2 was the one to obtain the maximum luminescence intensity, what make evident the desirables characteristics from the material. For further experiments, the synthesis conditions will be fixed to the PbS 2 experiment (Table 1).

Figure 2a shows a FESEM image of PbS nanoparticles with an average size of 20 nm for the PbS synthesized by colloidal method, those particles form agglomerates with size above 50 nm. Figure 2c shows the particle size distribution of the PbS synthesized by colloidal method with a disperse distribution obtained by DSL analysis. The wide distribution could be attribute to the synthesis method, since in the colloidal synthesis, the walls of the reactor are heated by convection or conduction and the center of the flask filled with the reaction mixture needs longer time to achieve the reaction temperature, resulting in a non-homogeneous temperature profiles within the reaction flask.[6] This gives different size of the particles and a wide size distribution.
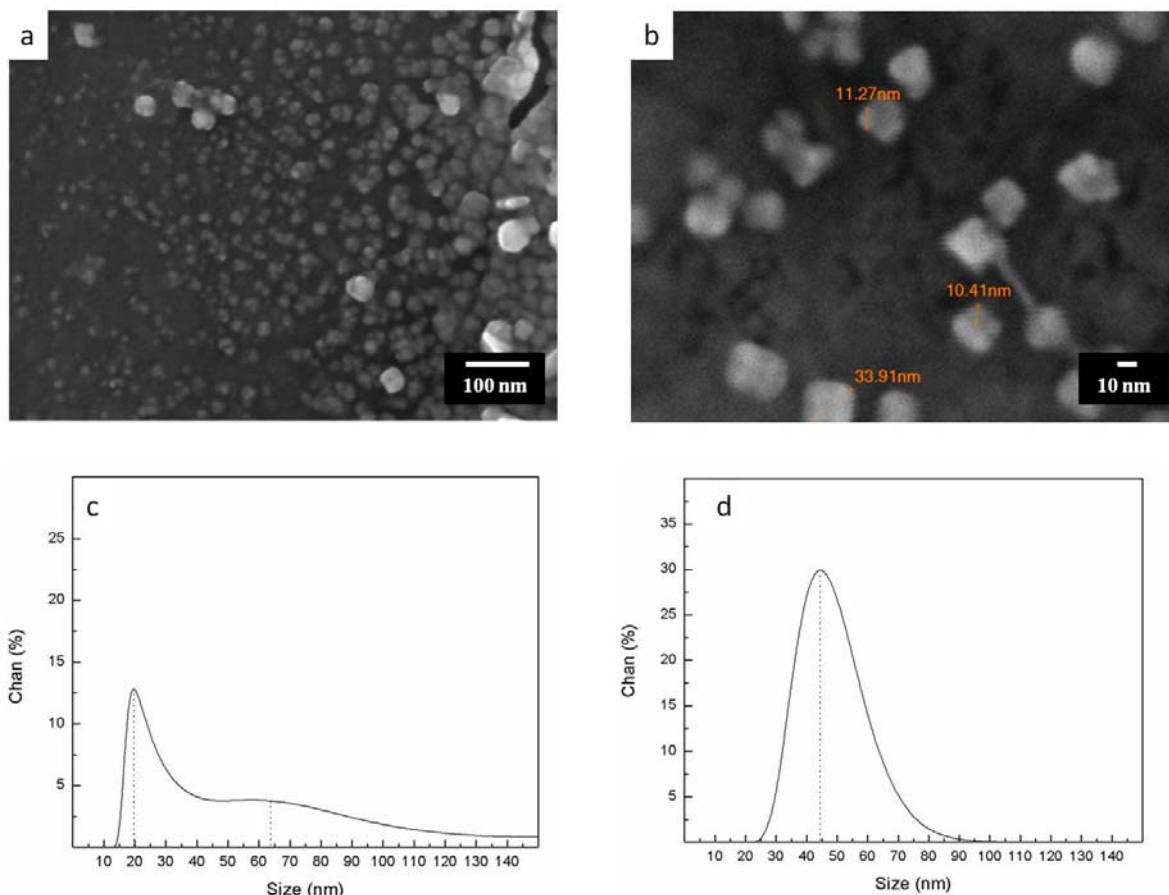
Fig. 2. SEM images and particle size distribution for PbS nanoparticles synthesized by a), c) colloidal synthesis and b), d) microwave synthesis methods for PbS 2 experiment.

Fig. 2b shows an image of nanoparticles synthesized by microwave heating with an average size of 11 nm. Those particles are interacting among them in order to form agglomerates of four particles with an average size of 33 nm. Figure 2d shows the particle size distribution of the PbS synthesized by microwave heating method acquired by DSL analysis. The distribution for the microwave method is narrower than the one for colloidal synthesis and it's centered around 40 nm, which correspond to the size of the agglomerates observed by FESEM. Microwave process induces a rapid and homogeneous heating of the reaction mixture to the desired temperature, which saves time and energy because of the faster energy transfer mechanism. This allows to the formation of smaller nuclei and the presence of the sodium citrate which acts as complexing and electrostatic stabilizer helps to segregate the particles and maintain the size of the particle constant giving a better size distribution.

3.2 PbS/ZnS NPs

Figure 3 shows the UV-Vis spectra of PbS/ZnSnanoparticles synthesized by both methods. An important blue shift is clearly observed forPbS/ZnSnanoparticles in comparison to the absorption edge of PbS pure nanoparticles which is attributed to the presence of the ZnS shell. ZnS nanoparticles absorbs in the UV region, around 300 nm when are in the nanoparticles size. Nanoparticles synthesized by microwave method present the characteristic absorption of PbS nanoparticles, with the presence of the exiton signals around 600 and 400 nm with an additional absorption at 300 nm corresponding to the ZnS effect. Otherwise, PbS/ZnS nanoparticles synthesized by the colloidal method present absorption from 400 nm and it overlap with the signal at 300 nm corresponding to the ZnS. This may be explained by the ZnS shell thickness, expected to be larger for the colloidal particles due to the slow heating method that allows the diffusion of the ZnS nuclei on the surface of the PbS nanoparticles, leading to a larger shell for the material.
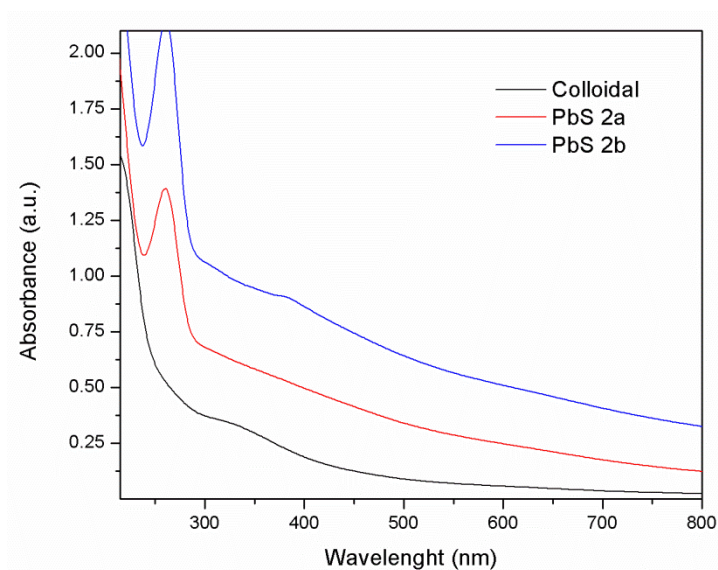
Fig. 3. Absorption spectra for PbS/ZnS nanoparticles synthesized by colloidal and microwave method.

Fig. 4a shows the room temperature photoluminescence spectrum of samples PbS/ZnS nanoparticles obtained with colloidal synthesis and microwave heating with two different PbS:ZnS ratio. It can be appreciated that the emission bands of the PbS/ZnSnanoparticles still fall within the visible region and they are slightly blue shifted than those of pure PbS. In microwave experiments, it is clear higher luminescence behaviour than those obtained by colloidal method due to the interaction between PbS nanoparticles and the ZnS shell, this last material well known for its highly luminescent properties when it is in the nanoscale. In addition Figure 4b shows the PL spectra for pure PbS and PbS/ZnS nanoparticles where a dramatically increase of the PL intensity is obtained after the formation of the ZnS shell. The sharp luminescence obtained by particles with cycling heating profiles is an evidence of the efficiency of the ZnS shell for stabilizesthe PbS core by decreasing the surface traps and confining the charge carries generated during the exciton formation. [15]
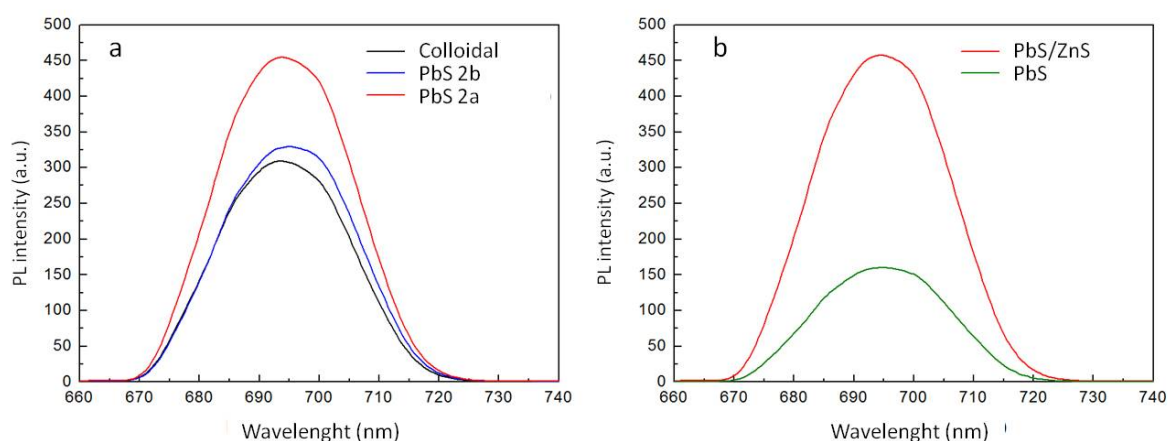

Fig. 4. a) PL spectra for PbS7ZnS synthesized by colloidal method and microwave method (PbS:ZnS ratio were 1.0:0.3 and 1.0:0.1). b) PL spectra comparing the pure PbS 2 nanoparticles and the PbS/ZnS nanoparticles generated from the PbS 2 core with PbS:ZnS ratio of 1.0:0.1.

PbS 2a system samples were analyzed byscanning electron microscopy in order to confirm thatPbSnanoparticles were successfully covered by a ZnS layer. For that, a sample of the obtained material in the PbS 2a experiment was analyzed firstly with a secondary electron detector (Figure 5a) and then with a backscattered electron detector (Figure 5b), both images from the same location. When a secondary electron detector is used, sample surface images are obtained; on the other hand, backscattered electrons give an idea of where the heavy and light atoms are located. Using this contrast method,nanoparticles with an approximate diameter of 17 nm are observed in Figure 5a using a secondary electron detector, which correspond to the PbS/ZnS nanoparticles. Those nanoparticles kept the original agglomeration of 4 particles and the agglomerates have a size of 50 nm.Figure 5b shows smaller nanoparticles with diameter of around 12 nm, which correspond to the PbS, as Pb is a heavier atom than Zn. This measurement is in good agreement with the observation made by SEM from the pure PbS 2 sample, which present an average diameter of 11 nm. These observations allowconcluding that ZnS shell grew up onto the surface of the PbS nanoparticles, forming a shell of around 3 nm.

Fig. 4a also shows that the system with better optical characteristic is the one labelled as PbS 2a, where the PbS:ZnS ratio was kept to 1.0:0.1 during the synthesis. This fact could be attributed to the amount of ZnS in the system, leading to the formation of a thinner shell which helps to confine the PbS core without masking its properties. In addition the ZnS shell of approximately 3 nm have a size which is near to the exciton Bohr radius of bulk ZnS (3 nm) provides a confined shell for the generated material.
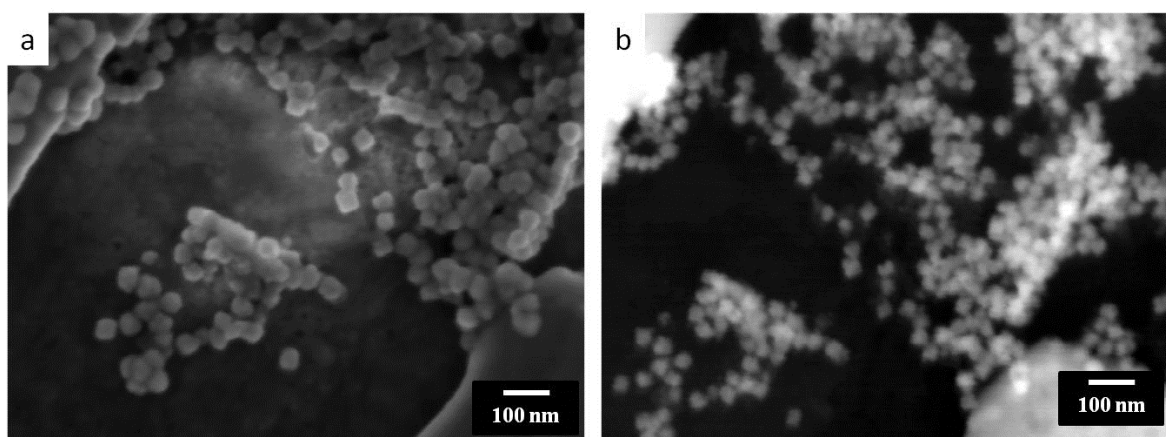

Fig. 5a SEM image of PbS 2a nanoparticles using a) secondary electron detector and b)backscattered electron detector.

4. Conclusions

The synthesis of PbSnanoparticleswas achieved by both, colloidal and microwave heating methods, where the synthesized PbS nanoparticles presented the best optical characteristics when they were synthesized at pH = 7 and on/off heating profile of 20/5 s. Those nanoparticles present absorption in the visible electromagnetic spectra and they present higher luminescent properties than those particles generated by colloidal method. The particles size was 11 nm for the PbS nanoparticles. The generated PbS nanoparticles were used as core, in order to produce PbS/ZnS nanoparticles. The best optical characteristics were obtained when the PbS:ZnS ratio was kept to 1.0:0.1 during the synthesis, leading to nanoparticles with PbS core of 12 nm and shell of approximately 3 nm. PbS/ZnS nanoparticles present a dramatically increase of PL intensity, confirming the confinement of the PbS core. In this case, the synthesis by microwave method allows to obtain nanoparticles with enhanced optical characteristics.

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