

Research article

Layer formation, morphology and photoluminescent properties of ultrasonic spray of pre-formed $\text{YVO}_4\text{:Eu}$ and SiO_2 coated ZnS:Mn nanoparticles

Eya Hergli^{a,b,*}, Housseem Eddine Sekrafi^{a,b}, Stanislav Ferdov^{a,b}, André Mota^c, Joni Lopes^c, Paulo J.G. Coutinho^{a,b}, Luis Rebouta^{a,b}

^a Physics Centre of Minho and Porto Universities (CF-UM-UP), University of Minho, 4710-057, Braga, Portugal

^b Laboratory of Physics for Materials and Emergent Technologies, LaPMET, University of Minho, 4710-057, Braga, Portugal

^c Sonae Arauco Portugal, SA, Lugar do Espido - Via Norte, Apartado 1129, 4470-177, Maia, Porto, Portugal

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ABSTRACT

In this work, we study the coating process and coating quality of photoluminescent particles deposited on a glass surface in terms of particle distribution and associated film continuity. The dispersion process of commercial ZnS:Mn particles and $\text{YVO}_4\text{:Eu}$ particles synthesized by microwave reactor in aqueous solutions onto solid surface was performed using an ultrasonic atomizer. Two methods of particle deposition were used, one by moving the substrates while spraying and in the second the substrates were not moved. The measured zeta potential values of 42.9 mV and 45.3 mV, respectively, show that the dispersion of $\text{YVO}_4\text{:Eu}$ nanoparticles, in water, is stable at concentrations of 1.2 wt% and 2.4 wt% without the addition of capping agents. It was also found that the dispersion area increases as the flow rate increases from 1 ml/min to 3 ml/min at constant suspension concentration and spraying time. To stabilize the ZnS:Mn particles in solution, either surfactants or a silica capping layer prepared by a sol-gel process were used.

The dispersion area encompassing the major amount of dispersed particles was evaluated, The SEM images demonstrate the effectiveness of the ultrasonic atomizer spraying procedure in the disaggregation nanoparticles, as seen by the reduced mean particle size in the sprayed layer compared to the as prepared powder. Finally, this study suggest that the dispersion process of photoluminescent nanoparticles on a substrate holds the potential for optical traceability.

1. Introduction

Ultrasonic atomization is a technological process by which a thin layer of liquid while spreading on a vibrating surface disintegrates into fine droplets [1–4] forming a spray. Deposition of nanoparticles using sprays has been reported in several studies in which the spraying process is induced by pressurized nitrogen gas flow [5–7], by an electrostatic field [8], or by ultrasonication [9]. Another possibility is spraying appropriate precursors into hot surfaces resulting in various types of inorganic coatings with technological applications such as transparent conducting oxides (TCO) [10]. In this technique the spray characteristics are of utmost importance and ultrasonic atomization has emerged as a valid option [11], and additionally it is highly desirable for large-scale and cost-effective

* Corresponding author. Physics Centre of Minho and Porto Universities (CF-UM-UP), University of Minho, 4710-057, Braga, Portugal
E-mail address: eya.hergli@gmail.com (E. Hergli).

practical applications. When using sprays of pre-formed nanoparticles the process of film growth and the structure of the resulting thin film was also addressed to deposit ZnO nanoparticles for dye-sensitized solar cells (DSSCs) [12], tungsten molybdenum oxide nanoparticles for electrochromic applications [13], silica, TiO₂ and Ag nanoparticles to produce superhydrophobic and antibacterial/self-cleaning surfaces [9,14], Ba_{0.6}Sr_{0.4}TiO₃ nanoparticles for High Capacitance Density Capacitors [7], SiC nanoparticles to fabricate laminate composites [15], ZnS for thin film solar cells [8] and Sn nanoparticles for Na-ion battery applications [16], among others.

Various phosphor materials doped with rare earth ions have been extensively investigated due to their interesting magneto-optical properties such as high luminescence efficiency, and flexible emission colors with different activators [17]. Among these inorganic compounds, rare earth ion-doped yttrium orthovanadate phosphors, such as YVO₄:Eu which is an efficient red-emission phosphor have been extensively used in cathode ray tubes (CRT) and in plasma display panels (PDP) [18,19]. In addition, the ZnS activated with Mn ion is the most efficient cathodoluminescence phosphor extensively used in other displays such as field emission display (FED), PDP and electron luminescence (EL) [20]. These properties make ZnS and YVO₄:Eu appealing materials for deposition studies by ultrasonic atomization. Although the deposition of ZnS particles by ultrasonic atomization has been previously studied [21], the same method to the best of our knowledge has never been applied to YVO₄ nanoparticles.

Ultrafine sprays can be obtained with aqueous dispersions of particles up to 30 % weight, however, it is difficult to disperse ZnS powders in water. In order to stabilize the particles in suspension, different surfactants [22–24] were tested due to their use as agents that inhibit the over-growth of particles and prevent their aggregation. The choice of a suitable capping layer is a key in stabilizing colloidal solutions. Another frequent approach to enhance the stability of ZnS is by covering its surface with a shell such as SiO₂ [25, 26].

Although pulverization is well known technique for deposition of nanoparticles there are systems of particles that are still not explored. As far as we know there is knowledge gap in the pulverization of photoluminescent nanoparticles as YVO₄:Eu and SiO₂ coated ZnS:Mn. Due to the facile preparation of relatively uniform nanoparticles and highly efficient emission [27], YVO₄:Eu is promising material for the pulverization by ultrasonic atomization and optical detection on surfaces. Consequently, the goal of this study is to evaluate the potential of the spraying process by maximizing the deposition of the particles only in a narrow track with the substrate in continuous motion and in one pass, minimizing the consumption of suspension to reduce costs, but enough to detect their presence by photoluminescence measurement. In this evaluation, a static spraying was mainly used, but with parameters that could be used in the above mentioned conditions, such as low probe-substrate distance, high concentration of particles, high flow rate. For example, we would like to evaluate the potential to deposit nanoparticles on a surface area 50 times higher compared to static deposition and still have enough particles to be able to measure photoluminescence. For this reason, we test suspensions with a low and a high particles concentrations and use a spray probe that enables relatively high flow rates. The high particle concentration also has the purpose of reducing the sprayed liquid component. The small distance between probe and substrate would allow not only a narrow track, but also reduce the use of particles to reduce costs. The obtained results support the potential for development of films of photoluminescent nanoparticles on mobile substrate.

Considering that studies on spraying particles on solid substrates provide fundamental knowledge about surface phenomena, we investigate the dispersion of nano-to micron-sized photoluminescent particles on glass slides. With the help of an ultrasonic atomizer, we deposited commercial ZnS and laboratory-made YVO₄:Eu particles and evaluated the dispersion area in terms of amount and distribution of particles as well as the morphology of the obtained coatings.

2. Experimental section

2.1. Materials

2.1.1. ZnS:Mn microparticles and reagents

Experiments were mainly carried out using ZnS:Mn (fine powder) kindly supplied by Nemoto Portugal. Sodium dodecyl sulfate (SDS, 99+%) was purchased from Sigma Aldrich and used as a dispersion stabilizer to get more stable dispersion of nanoparticles. Tetraethylorthosilicate (TEOS, puriss., ≥99.0 %, Fluka), ammonium hydroxide solution (NH₄OH, puriss. ~25 % NH₃ basis, Fluka) and 2 propanol (≥99.9 %, Riedel-de-Haën) were used for the coating of ZnS:Mn. Sodium orthovanadate (Na₃VO₄, 99.98 %, trace metals basis, Sigma Aldrich), yttrium nitrate hexahydrate (Y(NO₃)₃•6H₂O, purity of 99.9 %, Sigma Aldrich), and europium (III) nitrate pentahydrate (Eu(NO₃)₃•5H₂O, purity of 99.9 %, Sigma Aldrich) were used for the synthesis of YVO₄:Eu. Ultra-pure water was used throughout the experiments.

2.1.2. YVO₄:Eu nanoparticles

YVO₄:Eu nanoparticles were synthesized by microwave-assisted hydrothermal method. The preparation method consisted in the following: 1 mmol of Na₃VO₄ was dissolved in 3 ml of distilled water and 1 mmol of Y(NO₃)₃•6H₂O was dissolved in 0.5 ml of distilled water. Then, 0.1 mmol of Eu(NO₃)₃•5H₂O were dissolved in 0.5 ml of water. After stirring the mixture of the three solutions at room temperature for 10 min, it was transferred to a 10 ml borosilicate vial and placed in the Monowave 400 reactor from Anton-Parr. The mixture was heated at 120 °C in 10 min and the temperature was held for 60 min before cooling it at 60 °C for about 3 min. Finally, the sample obtained was separated by filtration using qualitative filter paper (Fisherbrand), washed for several times with distilled water, and dried in air at 50 °C for 10 h.

2.1.3. SiO₂ encapsulated ZnS:Mn microparticles

The ZnS/SiO₂ core/shell spheres were prepared by the hydrolysis of TEOS. Typically, an amount of 4.4 g of ZnS particles was dispersed in 95 ml of 2-propanol. Ultra-pure water (5.5 ml) and a little amount of ammonia solution (0.75 ml) were added in order to motivate the hydrolysis of TEOS. The mixture was then heated to 40 °C, and kept stirring for 30 min. Finally, 10.1 ml of TEOS was added. The mixture was then kept for about 24 h at 40 °C under vigorous stirring. When the reaction completed, the sample was centrifuged. The remaining precipitate was washed several times with ultra-pure water by centrifugation and then dried [25,26].

2.2. Spraying process

An ultrasonic atomizer, whose experimental setup is schematized in Fig. 1, was used in the present study with frequency 40 kHz (Model QA40A-110 procured from Qsonica Sonicators, USA) connected to a probe with a circular irradiating surface. This probe (Part No 4630 from QSonica) allowing flow rates up to 50 ml/min has a section with 8 mm diameter and 19 mm length followed another one with 5 mm diameter and 31 mm long and ending with a flat tip. A low pressure Minipuls 3 Peristaltic pump (procured from Gilson, USA) was used to deliver the liquid sample to the nozzle. The tip of the nozzle was placed at a given distance from the surface of a pre-heated glass slide using a hotplate. With water, the median drop size at 40 kHz is 50 µm. To prevent the formation of coarse agglomerates in ZnS:Mn suspensions, we used first a water bath sonicator and then added dispersion stabilizers [22], as described above. During the spraying process, the suspension was kept under magnetic stirring. Suspension concentrations of 1.2–30 wt% of ZnS:Mn and 1.2–16.6 wt% of YVO₄:Eu particles were used. In all cases, the substrates were held at a temperature of 100 °C throughout the spraying in order to quickly evaporate the solvent in the drops and avoid their coalescence. The wide range of suspension concentrations associated to high flow rates (1 and 3 ml/min) has the purpose of, using the static spraying, to evaluate the potential of the spraying particles only in a narrow track with the substrate in continuous motion and in one pass, but enough to detect their presence by photoluminescence measurement. The small distance between probe and substrate (1.5 cm) would allow the deposition in track with a width of about 1 cm.

Sprayed layers of PL particles were also prepared on glass slides with moving substrates during the spray for 15 s, 30 and 60 s. The distance between the probe and substrates was 1.5 cm and the flow rate was 1 ml/min. The spraying was performed all over the entire surface of the glass slide in a homogeneous way by moving it manually forwards, backwards and laterally.

2.3. Characterization

The zeta potential of the suspensions was measured using Dynamic and Electrophoretic Light Scattering (Litesizer 500 from Anton-Paar) at 25 °C, using a He-Ne laser of $\lambda = 658$ nm. For dynamic light scattering (DLS) the detector was at an angle of 175°, while for electrophoretic light scattering (ELS) the detector was at an angle of 15°. Three measurements were performed for each sample. The photoluminescence was measured with two different equipment: a laboratory fluorometer (SPEX 1680B 0.22m Double Spectrometer), which uses a bifurcated optical fiber to irradiate the glass slide with 320 nm LED light from the equipment excitation channel and collect the sample photoluminescence into the emission channel, and a homemade portable setup (LED M310L1 from Thorlabs, with a peak wavelength of 310 nm) using a CCS200 spectrometer from Thorlabs.

The scanning electron microscopy (SEM) micrographs of the sprayed layers were obtained using a FEI NOVA NanoSEM 200 microscope, which was used to obtain the cross-sectional and surface morphologies. The backside of the sample was marked with a diamond stylus and glass slide was fractured with one end fixed, while the other was pressed with a laboratory spatula. The cross sections were coated by a 2 nm gold-palladium layer to prevent charging of the surface and to promote the emission of secondary electrons.

At the bottom of the SEM images some of the experimental conditions under which they were obtained are indicated: Magnification (mag); High voltage (HV), which gives the energy of the primary electrons; Secondary electrons mode (SE); Through-lens detector (TLD); working distance (WD) and the actual scan range horizontal field of view (HFW).

The surface of the sprayed layers was also characterized by Atomic Force Microscopy (AFM), using a CSI – Nano-Observer Atomic Force Microscope in tapping mode. The powder X-ray diffraction patterns were recorded on a Bruker D8 Discover diffractometer operating with CuK α radiation ($\lambda = 1.5406$ Å) in the Bragg-Brentano ($\theta/2\theta$) geometry in the range of 10°–70° with a step size of 0.04°

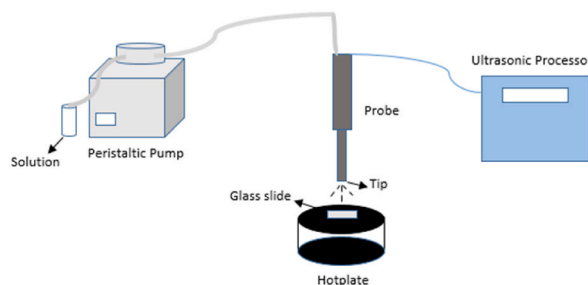


Fig. 1. Schematic representation of the experimental setup.

and an integration time of 1 s. Soller slits were used to limit the divergence of the incident and diffracted X-rays. All characterizations were performed at ambient temperature.

3. Results and discussion

The choice of conditions for particle deposition was based on the existing state-of-the-art [15] and the specific objectives of the present work. Namely, nozzle type, short nozzle to substrate surface distance (1.5 cm), variable particle concentrations (1.2–30 wt%), flow rate (1 ml/min to 3 ml/min), and time (1 and 5 s) for particle deposition were selected aiming to assure narrow but optically detectable area of deposited nanoparticles.

3.1. Sprayed layers prepared from $\text{YVO}_4\text{:Eu}$ suspension

The $\text{YVO}_4\text{:Eu}$ nano powder was analyzed in terms of its crystallographic structure and the XRD pattern is shown in Fig. 2. The diffractogram indicates that this compound has crystallized in tetragonal structure of YVO_4 with space group $I4_1/amd$ (no. 141). All reflections are well consistent with JCPDS 00-016-0250. The crystallite sizes of prepared nanoparticles determined by using Debye Scherrer [28] equation was 11 nm. The Z-average particle size was measured by DLS and a value of 87 nm was obtained. The particle size was also calculated from SEM images of as prepared $\text{YVO}_4\text{:Eu}$ nano powder. The SEM image is illustrated in Fig. 3a, and 3b shows the particle distribution and the mean size. The particle size distribution was determined using “ImageJ” software, resulting in a mean size of 32 nm. From the SEM image is clearly depicted that the synthesized nanoparticles have been agglomerated. As shown later, these synthesized nanoparticles can be separated after the ultrasonication and atomization process.

Suspensions with different $\text{YVO}_4\text{:Eu}$ nanoparticle concentrations (1.2 wt% - 16.7 wt%) were used, which are indicated in Table 1. In the table are also indicated the zeta potential values, measured by Dynamic and Electrophoretic Light Scattering. According to the zeta potential value of suspensions with 1.2 wt% and 2.4 wt% concentrations, we noted that the dispersion is stable without adding any capping agents. In case of 16.67 wt% suspension, the light transmittance though the suspension was very low, which did not allow the measurement of the Z potential.

Fig. 4a exhibits photoluminescence spectra obtained with an excitation radiation with an average wavelength of 310 nm in three different positions of sprayed layer for the spraying time of 1 s. The emission spectrum exhibits six emission peaks, being the two most intense peaks at 619 nm and 622 nm, which were followed to identify the photoluminescence intensity, and the remaining four at about 594, 652, 702 and 707 nm [18]. Fig. 4b shows an image of photoluminescence emission when irradiated by a LED with a wavelength of 310 nm and Fig. 4c presents the intensity of the emission peak at 619 nm obtained in the scan performed along the sprayed layer, being the distance D measured from the center of the sprayed layer (insert of Fig. 4a). The irradiated spot during this scan had a diameter lower than 1 mm. The brighter area in Fig. 4a is about 9 mm, which corresponds to the region with the highest photoluminescence intensity in Fig. 4c (about from -4 mm to $+4$ mm). From the results shown in Fig. 4b and c it is clear that the sprayed layer formed a ring.

The formation of this type of structure, a ringlike stain, known as the coffee-ring effect [29,30], is due to the migration of the dispersed particles to the edge of the drop during the liquid drying [31–33]. The rate of evaporation of the solvent varies along the droplet surface and is increased near the contact line, leading to a convective flow. Thus, during the water evaporation process, the edges of the droplets become attached to the substrate, and capillary flow from the center to the edges of the droplet carries the suspended particles to the edges as evaporation proceeds [34]. This effect is particularly evident in case of spherical particles and can be suppressed by using particles with anisotropic shape [35]. The spray-deposition method involves a complex behavior governed by aggregation, agglomeration, and the formation of clusters of particles during the deposition process.

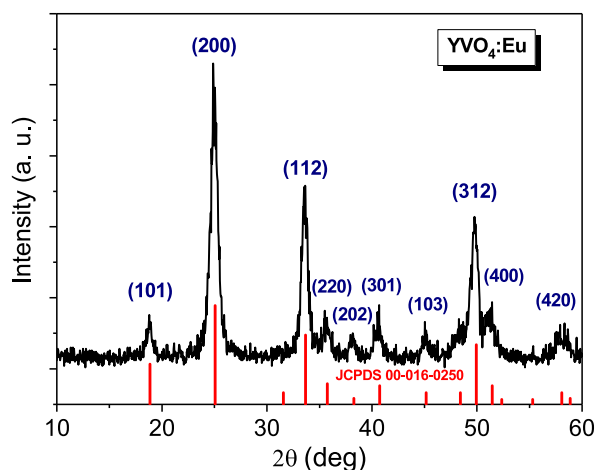


Fig. 2. Indexed powder XRD pattern of $\text{YVO}_4\text{:Eu}$ nanocrystals.

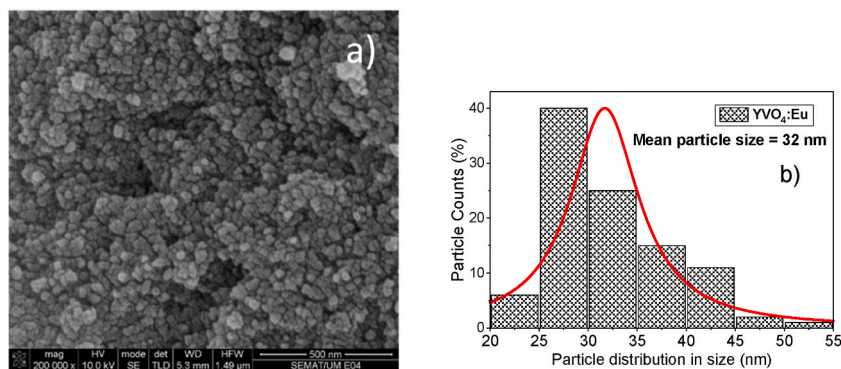


Fig. 3. SEM image of as prepared YVO₄:Eu phosphors. The insert shows the particle size distribution and the mean size calculated from SEM images.

Table 1

Concentrations of YVO₄:Eu suspensions used in this work, and the respective zeta potential.

Suspension	YVO ₄ :Eu concentration	Zeta potential (mV)
C ₁	0.0125 g/ml (1.2 wt%)	42.9
C ₂	0.025 g/ml (2.4 wt%)	45.3
C ₃	0.19 g/ml (16.67 wt%)	–

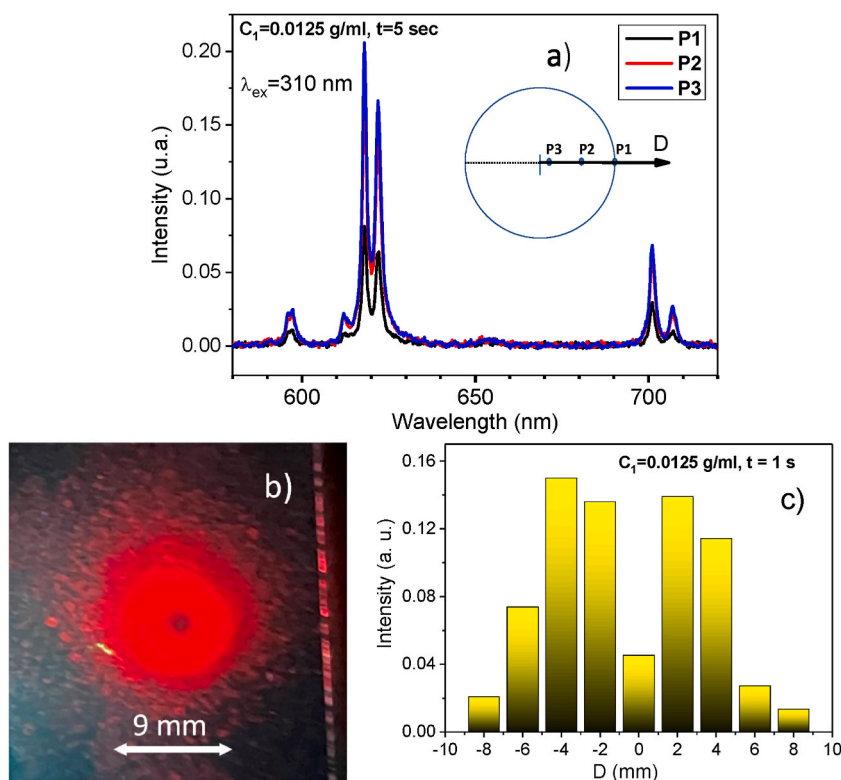


Fig. 4. a) Photoluminescence spectra obtained in three different positions of sprayed layer prepared from YVO₄:Eu suspension; b) Image of photoluminescence emission when irradiated by a LED with a wavelength of 310 nm. c) Intensity of the emission peak at 619 nm obtained in the scan performed along the sprayed layer. The excitation radiation had an average wavelength of 310 nm. The dimensions of the scale in the x-axis were measured in the sample showed in Fig. 4b, with the origin in the center of the area with the sprayed particles.

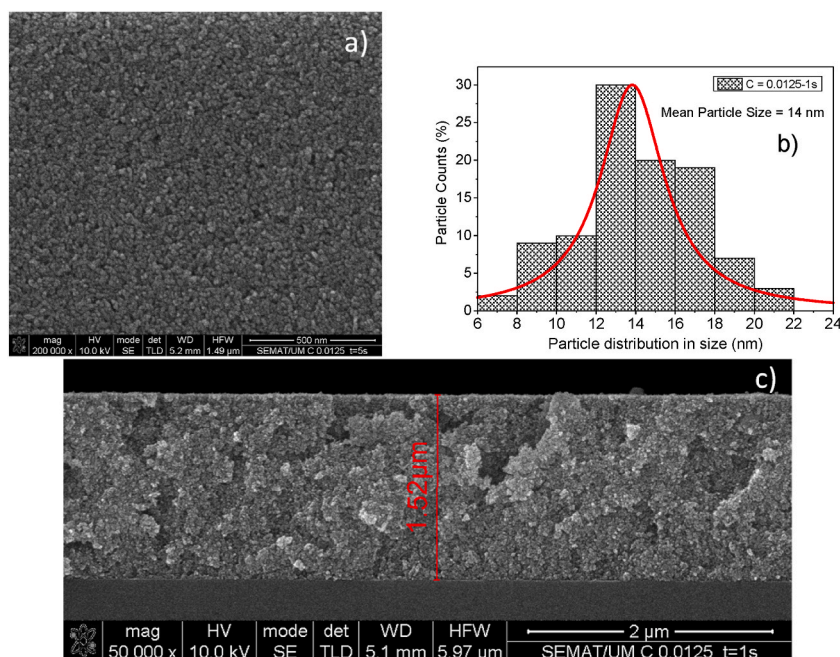


Fig. 5. a) SEM image of the surface of the YVO₄:Eu sprayed layer; b) particle size distribution and the mean size, and c) SEM image of the cross section of the sprayed layer (spraying time = 1 s).

The surface morphology of the deposited structure is shown in Fig. 5a, where the SEM image reveals a uniform structure. The average particle size (Fig. 5b), calculated using the ImageJ software, is about 14 nm, which is significantly lower than the average particle size of 32 nm in as prepared YVO₄:Eu powder and shown in Fig. 3. This shows that the spraying process using an ultrasonic atomizer is effective in the disaggregation of YVO₄:Eu nanoparticles. From the cross section image of the sprayed layer (Fig. 5c), taken from a position deviated from the center of the circle, a well-defined granular shape with irregularities that must come from empty spaces is observed. The large particles lead to decreased relative density due to reduced grain boundary mobility and the increase of voids. From this image, a thickness of about 1.5 μm was extracted.

In the case of spraying time of 5 s, the increase of sprayed particles amount resulted in nanoparticles that are now dispersed in a larger circle with a diameter of about 13 mm. The ring formation is still evident, as shown in Fig. 6, presenting an image of the sprayed layer (Fig. 6a), an image of photoluminescence emission when irradiated by a LED with a wavelength of 310 nm (Fig. 6b) and the intensity of the emission peak at 619 nm obtained in the scan performed along the sprayed layer (Fig. 6c). The surface morphology is similar to that of the previous sample and shown in Fig. 5a. The SEM cross-section image taken in an intermediate region of the circle, 3 mm from the center (Fig. 7 a), shows a thickness with small fluctuations, of about 2.7 μm (Fig. 7b).

AFM images, on a square area of $1 \times 1 \mu\text{m}^2$, of the as prepared YVO₄:Eu sprayed layer surface are shown in Fig. 8. Three surface profiles taken along the lines indicated in Fig. 8a are presented in Fig. 8c. They show a variation in height with an amplitude of about 140 nm, and with a rms surface roughness value of 18.3 nm for the region investigated. The observed range of grain size, or grain agglomerate size, determined by measuring the diameters in the AFM images, has a larger fraction in the range 40–70 nm, which is

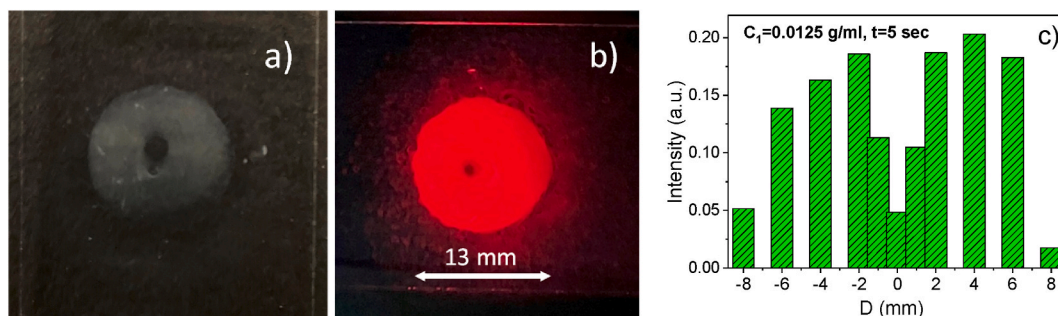


Fig. 6. a) Image of the suspension sprayed onto glass slide with substrate-probe distance of 1.5 cm ($t_{\text{spray}} = 5$ s); b) Image of photoluminescence emission when irradiated by a LED with a wavelength of 310 nm. For the images, the glass slide was placed on a black background to increase contrast; c) Intensity of the emission peak at 619 nm obtained in the scan performed along the sprayed layer.

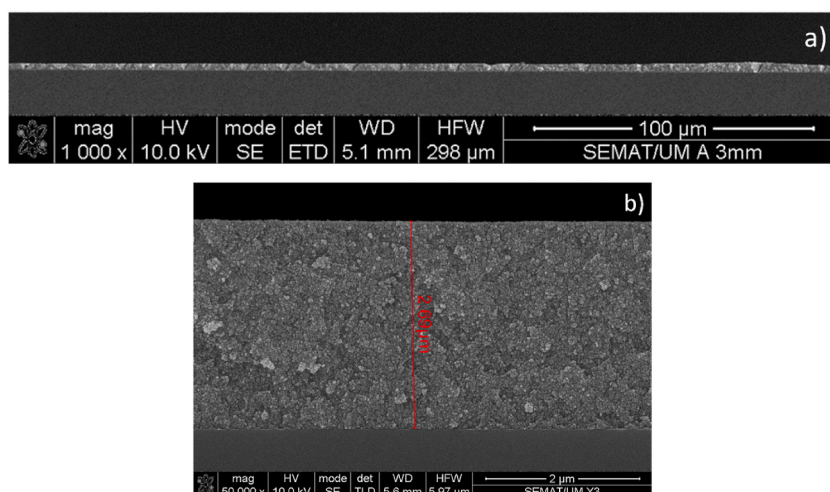


Fig. 7. SEM images of cross section of the sprayed layer (spraying time = 5 s) in the intermediate region of the circle, 3 mm from the center of the circle.

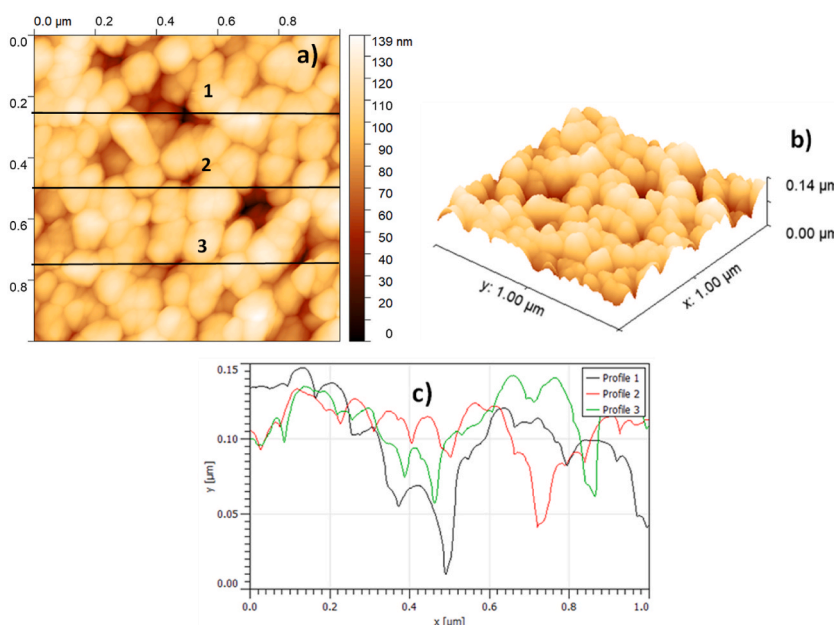


Fig. 8. AFM images (a and b) and three surface profiles (c), obtained along the lines indicated in AFM image (b), of the as prepared YVO₄:Eu sprayed layer surface (spraying time = 5 s and particle concentration of 1.2 wt%).

slightly higher than mean particle size value seen by SEM (Fig. 5).

We tested the feasibility of spraying a suspension of synthesized YVO₄:Eu with a high particle concentration of 0.19 g/ml (16.66 wt %). At a spray time of 1 s and a flow rate of 1 ml/min, the nanoparticles were found to be dispersed in a circle with a diameter of about 13 mm, similar to a concentration of 1.2 wt%, a spray time of 5 s and the same flow rate. The ring formation is still present, but less obvious, as shown in Fig. 9, where an image of the photoluminescence emission is shown when irradiated with an LED with a wavelength of 310 nm. Fig. 10 shows the SEM cross-sectional images of the sprayed layers, taken from a position 3 mm away from the center of the circle. The thickness can change from 3.5 μm (on the right side of Fig. 10a) to 6.4 μm (center of Fig. 10a). The image with higher magnification (Fig. 10b) presents an average thickness of 6.2 μm.

In a second step, two concentrations of a synthesized YVO₄:Eu were prepared ($C_1 = 0.0125$ g/ml and $C_2 = 0.025$ g/ml, which correspond to 1.2 wt% and 2.4 wt%, respectively). Fig. 11 shows the photoluminescence spectra of the sprayed layers using 320 nm excitation wavelength for C_1 and for 15, 30, 60 s spraying times and with moving substrates. The photoluminescence intensity increases as the spraying time increases.



Fig. 9. Image of photoluminescence emission of the sprayed layer (spraying time of 1 s) prepared from $\text{YVO}_4\text{:Eu}$ suspension (0.19 g/ml) when irradiated by a LED with a wavelength of 310 nm.

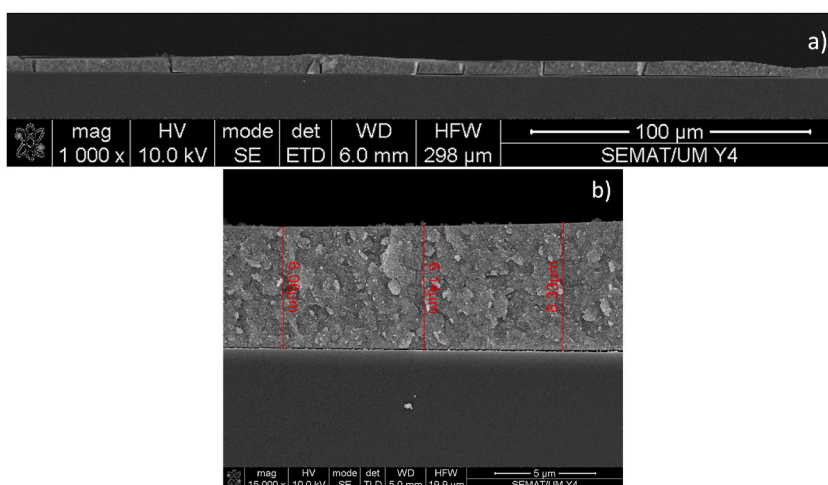


Fig. 10. SEM cross section images of the sprayed layer prepared from $\text{YVO}_4\text{:Eu}$ suspension (0.19 g/ml) and for a spraying time of 1 s, taken from a position deviated 3 mm from the center of the deposited area with low magnification (a) and with higher magnification (b).

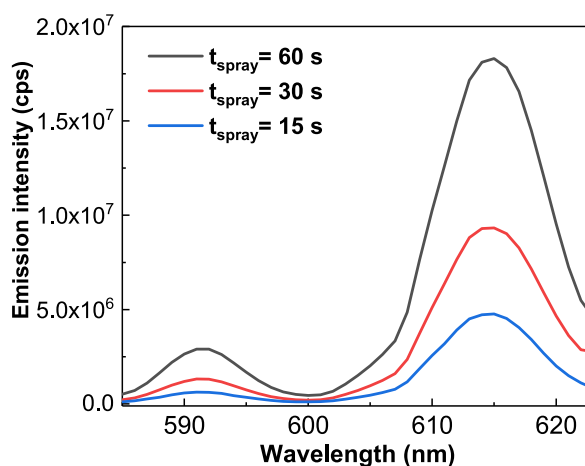


Fig. 11. a) Photoluminescence spectra of the sprayed layers prepared from $\text{YVO}_4\text{:Eu}$ suspensions at 320 nm excitation wavelength for $C_1 = 0.0125$ g/ml and for spraying times of 15 s, 30 s and 60 s, respectively, with moving substrates.

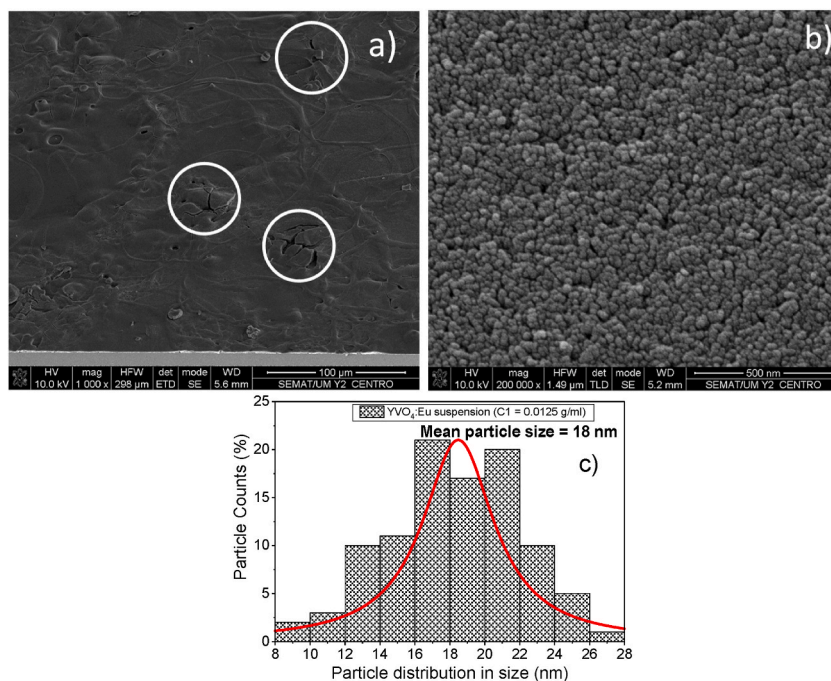


Fig. 12. SEM image of the surface of the sprayed layer prepared from YVO₄:Eu suspension ($C_1 = 0.0125$ g/ml) with moving substrate, and for different magnifications: a) 1000 $\times$; b) 200000 $\times$. The circles in a) identify the surface defects, which may be due to uneven evaporation rates during the drying process. c) particle size distribution and mean size calculated from b).

However, the surface morphology of the sprayed layer has some defects, superficial cracks, when seen with low magnification (identified with circles in Fig. 12a), but fully covering the substrate. These defects may be due to uneven evaporation rates during the drying process. Given the high spray rate, part of the liquid component may remain inside the coating, leading to the subsequent formation of gas bubbles. With the substrate heated, an increase in the amount evaporated increases the pressure exerted on the external layers, leading to their fracture and consequent release of gas.

This layer structure is related with the different processes occurring during the deposition. The dynamics of structural evolution was studied by Sarkar et al. [12] with grazing incidence small-angle X-ray scattering during in situ spraying. According to these authors, during the initial spraying time the main occurrence is the formation of clusters that result from the coalescence of the incoming droplets [12]. Due to the substrate temperature, the droplets evaporate rapidly when they land onto the substrate.

As a result of this rapid evaporation (during the initial spraying stage), the distances between those clusters stay fixed on the substrate. The structure will increase with the deposition of more droplets, and after this stage, the material arriving at the substrate bounds to the nanoparticle layer underneath, rather than clustering with each other to form larger structures [12]. The clusters touch each other and thereby form a closed film and the substrate reaches a considerable coverage, like those shown in SEM cross section (Fig. 13), where the clearly evident surface waviness probably results from the complex thin film growth [12]. The thickness varies from 1.3 to 2.7 μm (Figs. 13a) and 1.6–2.8 μm (Fig. 13b). Fig. 13b suggests that higher particle concentrations can lead to increased

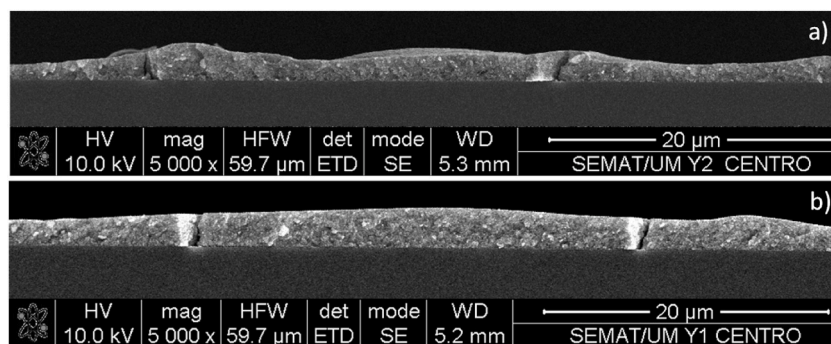


Fig. 13. SEM image of cross section of the sprayed layers prepared from YVO₄:Eu suspensions for a flow rate of 1 ml/min and a: a) concentration $C_1 = 0.0125$ g/ml and spraying time of 60 s; b) concentration $C_2 = 0.025$ g/ml and spraying time of 30 s, with moving substrates.

cracking which may be due to uneven agglomeration across the substrate. When seen with high magnification (Fig. 12b), the surface appears uniform and very similar to the obtained for static spraying as showed in Fig. 5. The deposited mean particle size (18 nm, Fig. 12c) was maintained with the significant increase of the particle concentration in the suspension. The linear relation obtained in the photoluminescence spectra (Fig. 11) is certainly related with the irradiated area of about 3 mm^2 , much higher than the dimension of the fluctuations shown in Fig. 13, allowing to obtain an average value of the photoluminescence intensity for each film.

3.2. Sprayed layers prepared from ZnS:Mn suspensions

The ZnS:Mn particles were analyzed by XRD in order to verify its crystallographic structure. The respective XRD pattern is shown in Fig. 14. The diffractogram indicates that this compound has crystallized in cubic structure with sphalerite space group F-43m (PDF no. 071–5975). The crystallite sizes of commercial nanoparticles determined by using Debye Scherrer [28] equation was 44 nm.

The particle size was also calculated from SEM images (Fig. 15) and using the “ImageJ” freeware. In the case of as received ZnS:Mn particles an average particle size of $0.75 \mu\text{m}$ was calculated. However, from the particle size distribution shown in Fig. 15c, the powder has about 2/3 of the particles with a size around $0.5 \mu\text{m}$ and others ($\sim 20\%$) already with a size in the micrometer range ($>1.0 \mu\text{m}$), what can also be clearly seen in the SEM image. In the case of SiO_2 coated ZnS:Mn particles a smaller mean particles size was measured (Fig. 15d). The ZnS:Mn particles have a faceted morphology, while the SiO_2 coated ZnS:Mn particles this is not so clear.

Suspensions with different ZnS:Mn (uncoated and SiO_2 coated) particle concentrations (1.2 wt% - 30 wt%) were used, which are indicated in Table 2, together with the zeta potential values.

In a first step, commercial ZnS:Mn particles in aqueous suspension with a concentration of 0.0125 g/ml were used. The water bath sonicator was used first to prevent the formation of coarse agglomerates in suspensions [22]. The zeta potential was 13.1 mV . The particle dispersion is still not homogeneous, and the particles were aggregated.

Therefore, the addition of some surfactants was tested in order to prevent the particles from aggregation [22–24]. For the 10 ml of ZnS:Mn suspension, a mass of 6.86 mg of sodium dodecyl sulfate (SDS) was added, which resulted in a suspension with a SDS concentration of 0.407 mg/ml and the zeta potential decreased down to -42.6 mV . The addition of SDS to the suspension increases electrostatic interactions at the surface and induces a more uniform spraying. For comparison, SiO_2 -coated ZnS:Mn particles in aqueous solution with a concentration of 0.0125 g/ml were also prepared. The zeta potential reduced down to -39.2 mV . The SiO_2 shell improved the stability of ZnS. Sprayed layers of these three different suspensions were prepared on glass slides in order to evaluate the dispersion of PL particles. We note that the distance between the probe and the substrates was 1.5 cm and the flow rate was 1 ml/min .

Fig. 16 shows the photoluminescence spectra at 335 nm excitation of sprayed layers of suspensions with colloidal stability, surfactant stabilized ZnS:Mn suspension and SiO_2 -coated ZnS:Mn spheres in aqueous solution, for different spraying times and moving substrates. The measurement positions were approximately in the center of the glass slides. The core/shell ZnS:Mn/ SiO_2 and with surfactant stabilized ZnS:Mn particles have a similar PL intensity. This means that the use of the surfactant can be avoided, and an aqueous suspension can be used when the ZnS:Mn particles are SiO_2 coated. Additionally, the SiO_2 -coated ZnS particles enhance photoluminescence, as already reported in the literature [25,26]. This can be explained by a reduction of the surface defects of ZnS particles reduced the electron-hole recombination on the ZnS surface and reduced nonradiative transition [25,26]. From Fig. 16, we can also conclude that at small concentration of PL particles (1.2 wt%) in the sprayed suspension, the emission intensity is approximately proportional to the spraying time.

In order to test the possibility to spray particles at a higher rate and lower amount of water, the percentage of the solid component was increased. Thus, 4.28 g of SiO_2 coated ZnS:Mn particles were mixed in 10 ml of water, which represents a suspension with 30 wt% of solid component. The zeta potential was not measured because the transmittance through this suspension was very low.

Magnetic stirring was carried out for 1 h before the experiment as well as during the spraying to prevent the formation of agglomerates in the suspension. This level of ZnS:Mn particles concentration in the suspension (30 wt%) was not achievable with uncoated particles and surfactant. Although measurement of the hydrodynamic diameters of nanoparticles in aqueous suspension demonstrated that the particle sizes generally increase with their mass concentration, in the case of SiO_2 particles, the particle concentration has little influence on the particle size [36].

Sprayed layers of PL particles were prepared on glass slides with two different flow rates, 1 ml/min and 3 ml/min , with two different concentrations, $C_1 = 0.0125 \text{ g/ml}$ (1.2 wt%) and $C_4 = 0.39 \text{ g/ml}$ (30 wt%), and with a static substrate. The distance between the probe and the glass slide was 1 cm and the spraying time 1 s for all cases. Fig. 17 displays the image of the sprayed layers onto glass slides for different flow rates and suspensions with different concentrations of solid component. To the right of each image the photoluminescence emission (centered at about 590 nm , which corresponds to orange) when irradiated by a LED with a wavelength of 310 nm is presented. The diameter of the dispersion area increases with the flow rate from 1 ml/min to 3 ml/min , at constant suspension concentration and spraying time.

For high flow rates, more liquid will accumulate and spread out than evaporate on the surface of the glass and the dispersion area increases.

However, for the same flow rate distinct behaviors were found depending on particle concentration. In the case of a lower flow rate (1 ml/min), a small increase of the dispersion area with the particle suspension concentration was observed, whereas at higher flow rate (3 ml/min), the dispersion area decreased with the particle suspension concentration. In C_1 (1.2 wt%) suspension the volume % of the solid component is $0.3 \text{ \%v/v}$, while for C_4 (30 wt%) suspension it is $9.5 \text{ \%v/v}$, meaning that the same volume of C_4 suspension contains about 10 % less water than suspension C_1 .

The sprayed layer obtained with a flow rate of 1 ml/min with lower concentration suspension is very irregular and does not have a

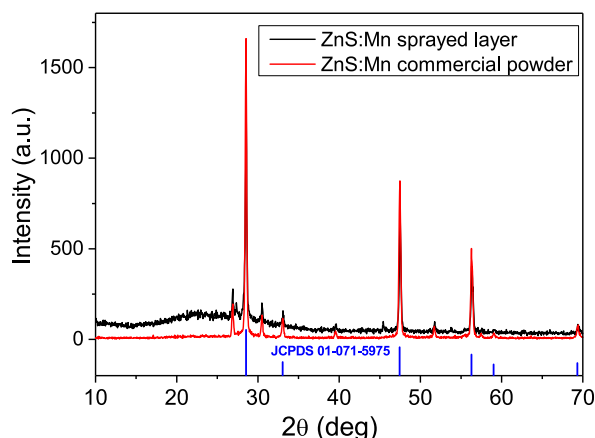


Fig. 14. XRD pattern of ZnS:Mn commercial powder and of the ZnS:Mn particles sprayed layer on a glass slide.

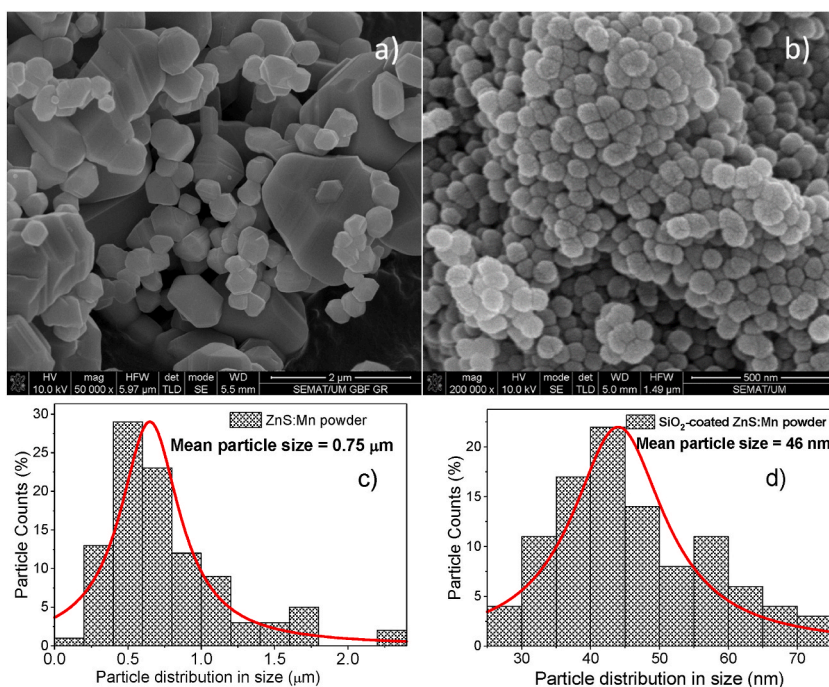


Fig. 15. a) SEM image of as received ZnS:Mn particles; b) SEM image of SiO₂ coated ZnS:Mn particles; c) particle size distribution and the mean size of as received ZnS:Mn particles; d) particle size distribution and the mean size of SiO₂ coated ZnS:Mn particles.

Table 2

Concentrations of ZnS:Mn suspensions used in this work, and the respective zeta potential.

Suspension	Solid component concentration	Zeta potential (mV)
ZnS:Mn	0.0125 g/ml (1.2 wt%)	13.1
ZnS:Mn + SDS	0.0125 g/ml + 0.407 mg/ml SDS	−42.6
SiO ₂ -coated ZnS:Mn	0.0125 g/ml (1.2 wt%)	−39.2
SiO ₂ -coated ZnS:Mn	0.39 g/ml (30 wt%)	–

continuous coverage layer. The increase to a flow rate of 3 ml/min improved the surface coverage but still with significant thickness variations, from 0.9 to 2.3 μm, as shown in the SEM cross section image (Fig. 18). These variations must be related with the irregular shape and the high dispersion of the SiO₂-coated ZnS:Mn particle size, what also causes the coffee ring effect to be greatly reduced [35].

In the case of higher suspension concentration, the surface coverage is more homogeneous, as shown in Fig. 19a. In Fig. 19b the

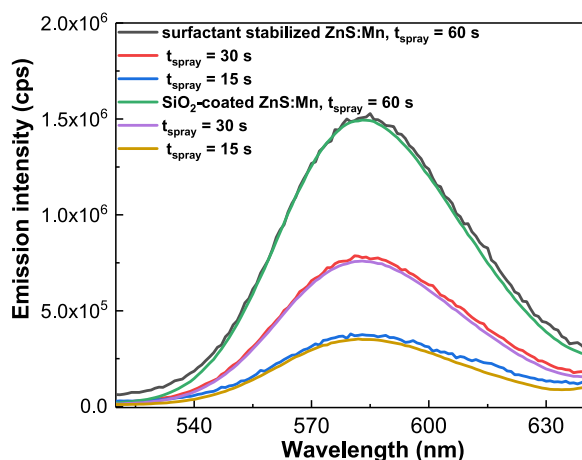


Fig. 16. Photoluminescence spectra of the sprayed layers prepared from surfactant stabilized and SiO₂-coated ZnS:Mn suspensions, at 335 nm excitation wavelength for different spraying times and moving substrates.

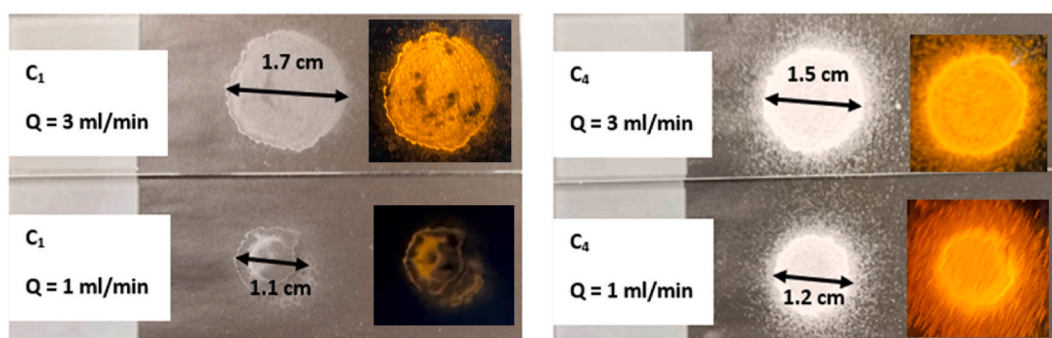


Fig. 17. Images of the sprayed layers onto glass slides obtained from suspensions of different SiO₂-coated ZnS:Mn concentrations ($C_1 = 1.2$ wt% and $C_4 = 30$ wt%) for the indicated flow rates and spraying time of 1 s. On right side of each image is presented the image of photoluminescence emission when irradiated by a LED with a wavelength of 310 nm.

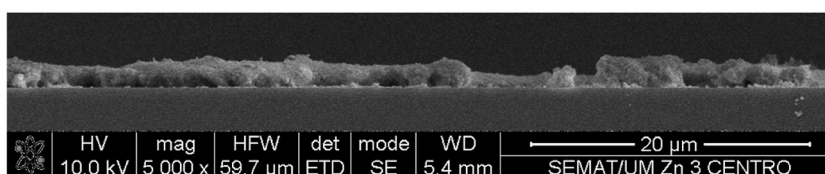


Fig. 18. Cross section SEM image of the SiO₂-coated ZnS:Mn sprayed layer (spraying time = 1 s, flow rate 3 ml/min and 1.2 wt%).

average size of particles is close, ~ 50 nm (Fig. 19c), to those shown in Fig. 15b, ~ 46 nm. Some much larger particles are still present.

The cross sectional SEM image (Fig. 20a) shows rather uniform thickness between 13 and 17 μm , whereas at higher magnification (Fig. 20b), high porosity and large particle size variation is visible.

AFM images on a square area of $1 \times 1 \mu\text{m}^2$, are shown in Fig. 21. Three surface profiles (Fig. 21c) along the lines in the AFM image (Fig. 21a), indicate a height amplitude of about 70 nm and rms surface roughness value of 16.3 nm. The observed range of grain size, or grain agglomerate size, determined by measuring the diameters in the AFM images, range between 50 and 80 nm.

With a higher flow rate (3 ml/min and 30 wt%), the sprayed layer is fully covering the substrate, as expected, with the surface appearing more homogeneous, which is shown in Fig. 22a, but with some features (inverted cone shapes) that can be related with different evaporation rates resulting in localized depressions (Fig. 22b). The distribution of these inverted cones seem to be related with individual clusters. Higher flow rates increase the amount of colloids on the surface of the substrate and the excessive solvent reduces the possibility of effective evaporation during the deposition process. Thus, a liquid layer will accumulate on the glass surface, so particles can migrate with this excessive solvent over the substrate and form initial clusters.

The morphology of the particles (Fig. 22c) are similar to those shown in Fig. 15b, which should be related with the impregnated

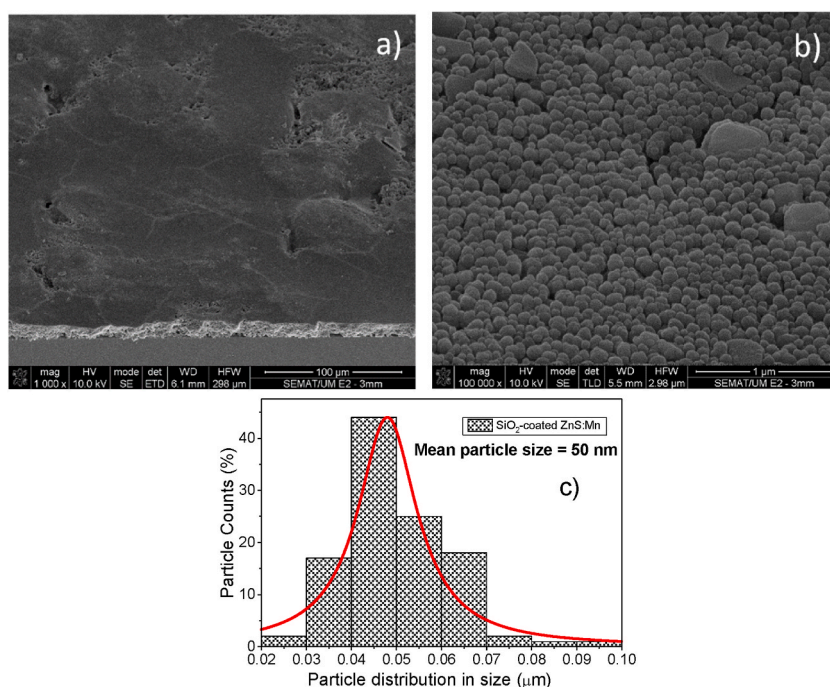


Fig. 19. SEM images with different magnifications of the surface of the SiO₂-coated ZnS:Mn sprayed layer prepared from a suspension with a concentration of 30 wt% and a flow rate of 1 ml/min and a spraying time of 1 s, taken in a position 3 mm from the center of the area where the particles were deposited a) 1000×; b) 100000×. c) particle size distribution and mean size calculated from b).

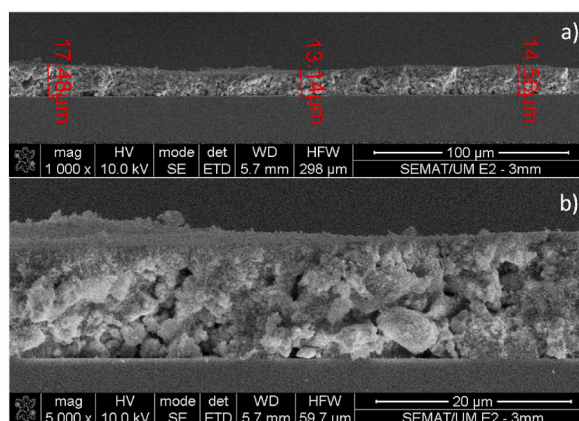


Fig. 20. a) Cross section SEM image of the SiO₂-coated ZnS:Mn sprayed layer (spraying time = 1 s, flow rate 1 ml/min and 30 wt%). b) magnification of the central region of image a).

SiO₂ coating. The cross section SEM image (Fig. 23), also shows the same particle morphology. The particle size decreases from bottom to top layer, as also seen in the previous sample shown in Fig. 20b. The main reason must be that during static spraying the liquid component of the suspension forms a bubble on the glass coverslip and the larger particles end up depositing by gravity, given that the solid component, in volume, is very small.

Additionally, the average particle size of 57 nm, is significantly lower than the average size seen in the commercial powder, of 750 nm, but similar to the as prepared SiO₂ coated ZnS:Mn particles and shown in Fig. 15d, ~46 nm and Fig. 19c, ~50 nm. These values are close to the 44 nm calculated from XRD patterns. Particles with a dimension much larger than the average size are much sparser than in experiments with lower flow rate (Figs. 19 and 20).

Pulverizing water suspension of nanoparticles onto glass without glue and automation imposes several limitations including nanoparticle aggregation, poor adhesion and precision, uneven drying, and formation of cracks. However, the developed experimental setup reveals some critical parameters as the concentration of particle in the suspension and the flow rate of deposition, for the control of the distribution of particles and emission intensity of the deposited particles. In perspective, our study shows that achieving and

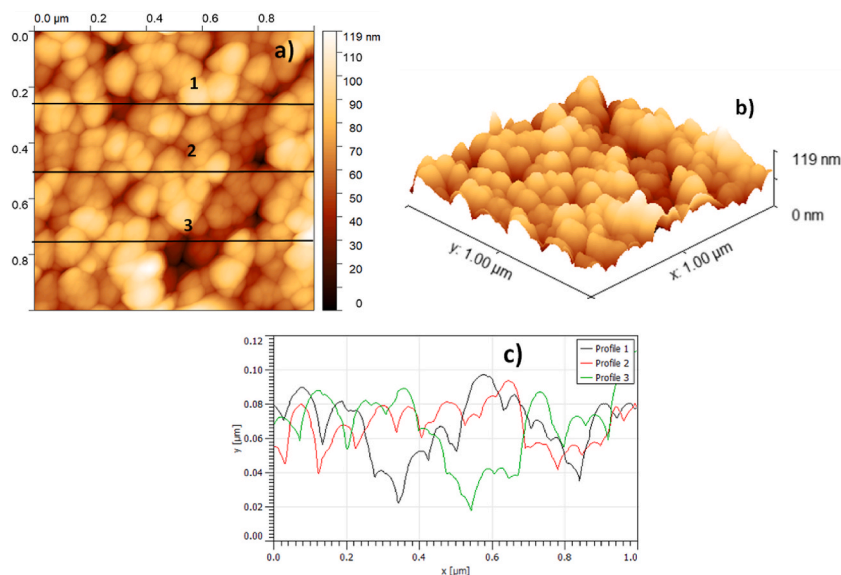


Fig. 21. AFM images (a and b) and three surface profiles (c), obtained along the lines indicated in AFM image (b), of the as prepared SiO_2 -coated ZnS:Mn sprayed layer surface (spraying time = 1 s, flow rate 1 ml/min and 30 wt%).

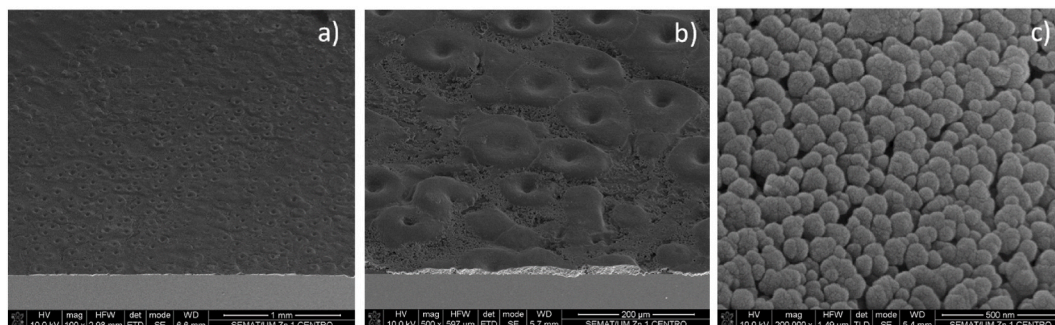


Fig. 22. SEM image of the surface of the SiO_2 -coated ZnS:Mn sprayed layer prepared from a suspension with a concentration of 30 wt% and a flow rate of 3 ml/min and a spraying time of 1s, and for different magnifications.

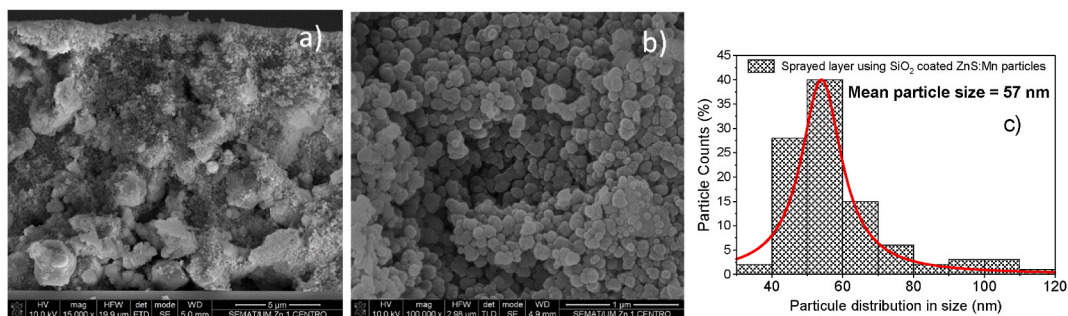


Fig. 23. a) SEM image of cross section of the SiO_2 -coated ZnS:Mn sprayed layer; b) detail of the previous figure in the central region at the top; c) particle size distribution and the mean size (spraying time = 1 s, flow rate 3 ml/min and 30 wt%), calculated from the SEM image with high magnification.

maintaining the desired particle distribution can be challenging and requires precise control over various process parameters.

4. Conclusions

In summary, the nanoparticle spraying process has been developed in order to disperse particles on the surface of a solid substrate, which is a suitable industry-based approach for the mass production of films, as it allows particle deposition in localized areas with a precise rate control. YVO₄:Eu nanoparticles were synthesized by microwave-assisted hydrothermal method and SiO₂-coated ZnS:Mn particles were successfully prepared by using the sol-gel method. Based on zeta potential measurements, the YVO₄:Eu particles are well dispersed and the spraying is stable without dispersion stabilizers. In addition, SiO₂ coated ZnS:Mn particles have significantly improved stability when compared with uncoated ones, and their use is more appropriate than the use of ZnS:Mn particles with surfactant addition especially for high suspension concentration, as no dispersion agents are needed.

The deposition process in a single site showed that the particles dispersed on the glass slides formed a circle with a diameter that increased when the flow rate and the particles suspension concentration increased except for high flow rates. The size of the dispersion area increases with decreasing particle concentration and showed a hole in the middle. However, when using the ultrasonic atomizer with a moving substrate, the sprayed layers have a similar morphology all over the surface. From SEM images, for both YVO₄:Eu and SiO₂ coated ZnS:Mn particles, the mean particle size in sprayed layers is substantially lower than in starting powders, which means the aggregates disintegrated during the atomization process. Cross sections of the films showed a granular structure with varying grain sizes resulting from sedimentation of larger aggregates during film drying. This same process explains the presence of cracks and delamination on the film surface through the build up of pressure from vaporized water molecules and its sudden release. The sprayed surfaces with both types of nanoparticles showed photoluminescence that increased intensity with pumping flow rate and spraying time as a corresponding increase of film thickness occurs as more particles are being deposited. It can be concluded that the YVO₄:Eu and SiO₂ coated ZnS:Mn particles are appropriate materials for photoluminescence labeling of solid surfaces using ultrasonic spray atomization, although the spraying process and the uniformity of the film thickness still need further optimization.

Ethics declarations

This work does not infringe third party rights and respects the Ethics in publishing policy.

Data availability statement for this work

Data will be made available on request.

CRediT authorship contribution statement

Eya Hergli: Writing – original draft, Methodology, Investigation, Formal analysis. **Houssem Eddine Sekrafi:** Writing – review & editing, Investigation, Formal analysis. **Stanislav Ferdov:** Writing – review & editing, Investigation, Formal analysis. **André Mota:** Methodology, Conceptualization. **Joni Lopes:** Methodology, Conceptualization. **Paulo J.G. Coutinho:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Luis Rebouta:** Writing – review & editing, Supervision, Project administration, Methodology.

Declaration of competing interest

All authors confirm that there are no known conflicts of interest associated with this publication and that there has been no significant support for this work that could have influenced the presented results.

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