

Metal enhanced luminescence of Cerium Oxide (IV) Hollow Sub-microspheres with Au, AuPd and Pd Nanoparticles

Mario Guzmán, PhD.¹, Dalia Chávez-García, PhD.¹, Amanda Nieto, M.Sc. ¹, Karla O. Juárez-Moreno^{2,4}, PhD and Andrey Simakov, PhD.³

¹ Centro de Enseñanza Técnica y Superior (CETYS), México, mario.guzman@cetys.mx, dalia.chavez@cetys.mx, amanda.nieto@cetys.mx.

² Departamento de Bionanotecnología, Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, México, kjuarez@cnyn.unam.mx.

³ Departamento de Nanocatálisis, Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, México, andrey@cnyn.unam.mx.

⁴ CONACYT-CNyN-UNAM, Ensenada, México

This work reports an analysis of the luminescent properties of Cerium oxide (IV) hollow sub-microspheres (CeO₂-HS) as well as the effect of the presence of Au, AuPd and Pd NPs over the mentioned properties. CeO₂-HS were synthesized via hydrothermal method, then the CeO₂-HS were impregnated with the metal precursors and by a reduction process the metal nanoparticles (NPs) were obtained. CeO₂-HS were characterized by XRD, Raman, UV-Vis and TEM. The CeO₂-HS with metal NPs deposited on them were analyzed using UV-Vis and TEM. All samples luminescent excitation and emission spectra were recorded. It was observed that the presence of metal NPs dramatically increases the emission intensity compared to the CeO₂-HS without metal NPs. Finally, it was also observed a clear slight but evident displacement of the main emission peak between samples with and without metal NPs

Keywords: Ceria, Hollow spheres, Metal enhanced luminescence, Noble metal NPs

I. INTRODUCTION

Cerium oxide (IV) (CeO₂) is a rare earth oxide that presents a considerable variety of applications. CeO₂ can be used as adsorbent material for pollutant compounds (1), support for heterogeneous catalysts (2), antimicrobial (3–5), cancer treatment (6), magnetic material (7,8) and as a luminescent material (9–11). The interest on the CeO₂ as a nanomaterial has recently increased due, not only to its remarkable properties, but also, to the variety of morphologies at the nanoscale such as cubes, rods, wires, particles and spheres (2,3,9,12); that can be obtained via relatively easy methods. Among these structures, hollow nanospheres (1,13,14) are a very promising material due to their possible application as nanoreactors (15), as drug delivery systems (16–18) and as drug carrier (19).

It has been previously reported that the luminescent intensity of the CeO₂ is related with the content of Ce³⁺ species which is also associated with the corresponding crystal sizes (20), but even when the CeO₂ presents photoluminescent properties, it does not present a high luminescence (9). Recently an interesting and useful strategy has been used for

the enhancement of the luminescent properties of the lanthanides (21,22), which involves the addition of metal nanoparticles that presents a surface plasmon resonance which allows to increase the intensity of the photoemission. One of the most studied metal nanoparticle system is the gold nanoparticles (Au NPs). It is well known that the plasmonic resonance for the Au NPs depends on their shape and size as well as the nature of the media in which the Au NPs is dispersed. On the other hand, Palladium nanoparticles (Pd NPs) do not exhibit a plasmonic resonance in the visible spectrum. However, due to their similar atomic size and crystal structure it is possible to form bimetallic systems and, as a consequence, modify in a controlled manner the properties of such combination.

It is proposed that the interaction between the CeO₂ hollow spheres and the metal nanoparticles depends directly on the nature of these nanoparticles and that, the luminescence properties of these systems will be also affected by their metallic composition.

In the present work, we report the synthesis and characterization of cerium oxide (IV) hollow sub-microspheres with and without Au, AuPd and Pd nanoparticles, as well as an analysis of their luminescent properties and the enhancement effect of the metal nanoparticles over the ceria sub-microspheres luminescence.

II. MATERIALS AND METHODS

A. Synthesis of materials

Cerium chloride (CeCl₃*7 H₂O), urea (N₂H₄CO) and trisodium citrate anhydride (Na₃C₆H₅O₇) were purchased from Sigma Aldrich, hydrogen peroxide (H₂O₂ 30%) was received from Fisher Chemical. Trichloroauric acid 99% (HAuCl₄) and Palladium Chloride (II) 99 % (PdCl₂) were purchased from Alfa-Aesar. All reagents were used without further purification.

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Cerium oxide (IV) hollow sub-microspheres (CeO₂-HS) were prepared as reported by Qi et al. (23). In a typical synthesis 0.52 g of urea was dissolved in 85.5 ml of deionized water and stirred until obtain a clear solution. Then 36 ml of a 10 mM solution of Na₃C₆H₅O₇ was added to the previous solution, the mixture was stirred for 10 minutes. Subsequently, 0.89 g of CeCl₃*7H₂O was added to the mixture under stirring for 15 minutes. Then 5 ml of H₂O₂ 30 % was added dropwise during 30 minutes, turning the solution to a light-yellow color. The mixture was transferred to stainless steel autoclave. The system was heated to 100°C and maintained at this temperature for two hours; subsequently, the temperature was raised again up to 180°C and maintained for 18 h. The autoclave was cool down and a light-yellow powder was obtained. The powder was centrifuged and washed three times with deionized water, and finally dried at 80°C in air for 12 h.

Noble metal supported on the CeO₂-HS were synthesized as reported by (14) et al. In a typical synthesis, 0.2 g of the previous prepared CeO₂-HS was dispersed in 10 ml of deionized water. Then, 3.0 ml of a 10 mM solution of HAuCl₄ was added to the previous dispersion. The mixture was magnetically stirred for 12 hours and the centrifuged at 4000 rpm for 10 minutes. The precipitate was separated and re-dispersed in 10 ml of deionized water. At that point, 10 ml of a 0.1 M solution of NaBH₄ was added to the mixture and vigorously stirred for 15 minutes. Finally, the previous suspension (light purple color) was centrifuged at 4000 rpm for 10 minutes and washed with deionized water by triplicated. The solid obtained was dried at 80°C for 12 hours, having a light purple powder as a final material (Au/CeO₂-HS). The procedure was repeated varying the metallic content (1.5 ml of HAuCl₄ 10 mM +1.5 ml of PdCl₂ 10 mM for the AuPd/CeO₂-HS sample, and 3.0 ml of PdCl₂ 10 mM for the Pd/CeO₂-HS sample).

B. Materials characterization:

Transmission electron microscopy (TEM) was used to analyze the structure of the CeO₂-HS with and without noble metal nanoparticles, using a JEOL JEM-2010 microscope with XMAX OXFORD detector. Previous for the analysis the samples were dispersed in propan-2-ol and dropped on a copper grid coated with carbon film. The crystallographic phases of CeO₂-HS were studied by X-Ray diffraction with a Philips X'pert MPD diffractometer, applying CuKα (0.154 nm) radiation. Crystallite size and crystalline strain were estimated from the Williamson-Hall (W-H) plot as reported by (24). W-H plot was obtained from the equation 1.

$$\beta_{hkl} \cos\theta = \frac{K\lambda}{D} + 4\epsilon \sin\theta \quad (1)$$

Where:

θ : The diffraction angle

β_{hkl}: The peak's broadening

K: Shape's factor (equal to 0.9)

D: Crystallite size

Noble metal content (Au and Pd) in the samples was estimated by inductively coupled plasma-optical emission spectroscopy (ICP-OES), using a Vista pro (varian) equipment. Three different pattern solutions (1, 5 and 10 ppm) were used to calibrate the analysis.

Samples were prepared once as it follows. First, 20 mg of a sample was digested for 24 hours in an acid solution (1 ml of HNO₃ 70% and 1 ml of HCl 30 %). Then, 1 ml of the previous solution was diluted in deionized water at a volume ratio of 1:25. Metal content was determined using the diluted solution.

The optoelectronic properties of all samples were studied UV-Vis spectroscopy in a diffuse reflectance mode. UV-visible spectra were collected using an Avaspec-2048 UV-visible spectrometer (Avantes) equipped with AvaLight-DHS light source and AvaSphere-30 integrating sphere. MgO was used as a reference. CeO₂-HS at different thermal treatments were studied by Raman System AvaSpec-ULS2048LITEC-USB2 (Avantes) equipped with two temperature-controlled diode lasers (power 500 mW, 785 nm excitation wavelength) were used. Luminescence analysis was performed using a Cary Eclipse Fluorescence Spectrometer, using an excitation wavelength of 510 nm and an emission wavelength of 254 nm, all samples were analyzed in aqueous media. The samples were dispersed in deionized water previous for the analysis (0.7 mg/ml).

III. RESULTS AND DISCUSSION:

The Cerium oxide (IV) hollow sub-microspheres (CeO₂-HS) were successfully obtained. Figure 1 (a) shows the TEM images for de CeO₂-HS (Fig. 1a), ceria spheres present a diameter around 250 nm. HR-TEM for all samples (Fig. 1e, f, g and h) shows an interplanar distance typical of the fluorite-type ceria (JCPDS No. 34-0394), corresponding to the (2 0 0) plane (d= 0.271 nm) and (2 0 0) plane (d= 0.192 nm). Metal nanoparticles have a quasi-spherical shape and sizes between 4.1 nm and 8.8 nm.

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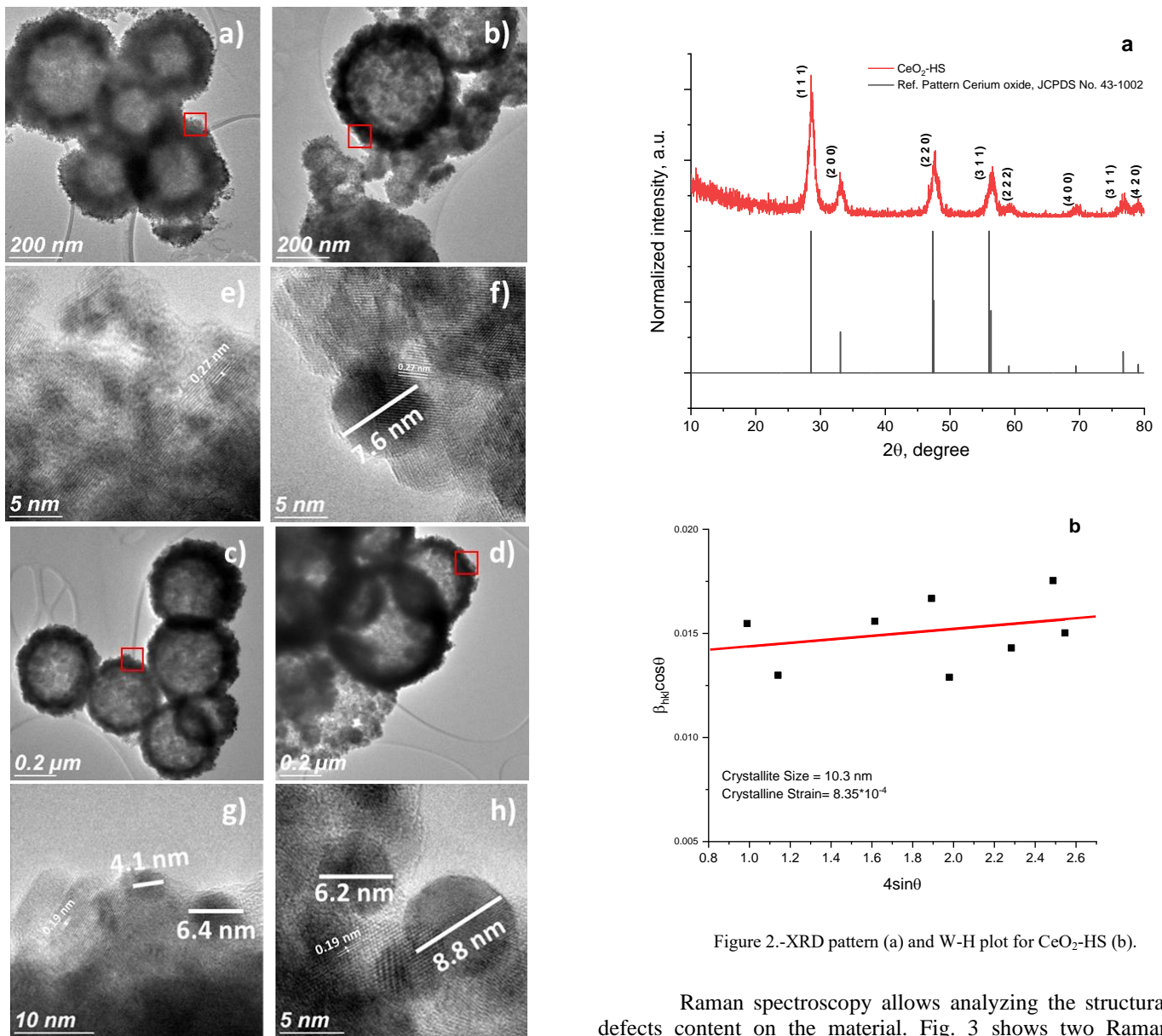


Figure 2.-XRD pattern (a) and W-H plot for CeO₂-HS (b).

Figure 1 Typical TEM and HR-TEM images of CeO₂-HS (a and e), Au/ CeO₂-HS (b and f), AuPd/ CeO₂-HS (c and g) and Pd/ CeO₂-HS (d and h). High resolution TEM images correspond to the areas selected by red box.

The XRD pattern (Fig. 2 a) for the CeO₂-HS presents diffraction peaks at 28.62, 33.13, 47.61, 56.46, 59.33, 69.60, 76.90 and 79.06 values for the 2θ angle. The diffraction pattern corresponds to the ceria fluorite-type crystal structure (JCPDS 34-0394). The Fig. 2 (b) presents the W-H plot for the CeO₂-HS after thermal treatment at 500°C for 6 hours. The crystallite size and the crystalline strain were estimated by the intercept and the slope of the W-H plot respectively. The crystal size for the CeO₂-HS sample was about 10.3 nm and the crystalline strain equal to 8.35*10⁻⁴.

Raman spectroscopy allows analyzing the structural defects content on the material. Fig. 3 shows two Raman spectra for CeO₂-HS before and after heat treatment. Both spectra, presents a characteristic peak centered around 464 cm⁻¹ which corresponds to the symmetric mode F_{2g} for the CeO₂ (25). Raman spectroscopy for CeO₂-HS (Fig. 3) presents a typical F_{2g} peak centered at 464 cm⁻¹ which is associated to the Ce-O bonding. The sample treated at 500° C has a remarkable higher intensity than the sample treated at 300° C, according to (26,27) the phase transition from Ce(OH)₄ to CeO₂ occurs about a temperature of 400° C which explains the increase in the intensity of the spectrum signal of the sample treated at 500° C. Also, there is a shoulder of the F_{2g} peak at 602 cm⁻¹. This shoulder is associated with oxygen vacancies in the material (3). The oxygen vacancies is commonly associated with the presence of Ce³⁺ species, that are usually linked to different properties such as compound adsorption (28), magnetic (29) and luminescent properties (9).

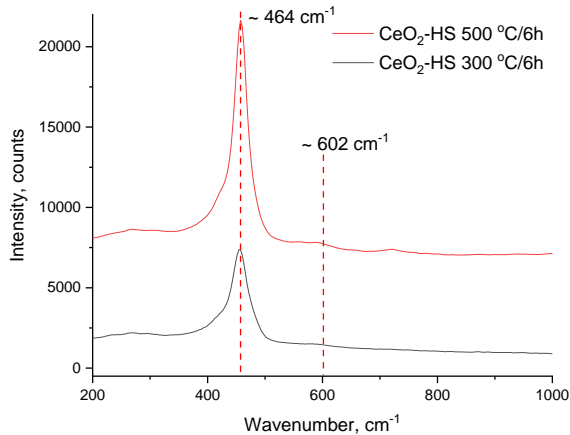


Figure 3.-Raman spectra of CeO₂-HS under different thermal treatments

Chemical composition of samples loaded with metal nanoparticles (Table 1) presents very similar metal content in each of the sample analyzed. Most of the metal employed during the synthesis remained present in the samples.

TABLE 1
CHEMICAL QUANTIFICATION OF METAL CONTENT IN SAMPLES WITH METAL NANOPARTICLES

Sample	Ce, % weight	Au, % weight	Pd, (% weight)
Au@CeO ₂	80.80	0.73	-
AuPd@CeO ₂	80.54	0.53	0.52
Pd@CeO ₂	80.57	-	1.02

The optoelectronic properties of the CeO₂-HS were studied by diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis) (Fig. 4). The ceria spheres present a band gap around 3.1 eV which is similar to the value reported by (8), also Bazhukova (9) reported the same band gap with CeO₂ NPs suspension. The Ceria hollow spheres with Au NPs supported on it (Au/CeO₂-HS) presents a plasmonic resonance centered on 550 nm, which is an evidence of the presence of Au NPs in the material. It has been reported that AuNPs with diameter about the size of our system presents a plasmonic resonance around 521 nm (30,31). Nevertheless, the plasmon position depends on the dielectric function of the media which is in direct contact with the nanoparticles (32), which indicates that the difference between the plasmon position in the Au/CeO₂-HS and the position reported by (30,31) is associated with the electronic interaction between the cerium oxide (IV) and the Au NPs.

On the other hand, the spectrum for the bimetallic system (AuPd/CeO₂-HS) shows an evidently lower intensity on the gold's plasmon in comparison with the one observed for the Au/CeO₂-HS system. Chen et al. (33) reported that, for

bimetallic AuPd NPs, the coating of Au NPs with Pd causes a gradual decrease over the intensity of the plasmonic resonance for the gold; based on this is possible to conclude that the AuPd/CeO₂-HS consists in bimetallic AuPd NPs instead of Au and Pd NPs. Finally, the Pd/CeO₂-HS system doesn't have any main features in the UV-Vis range that can be related to the presence of the Pd species, nevertheless there is a slightly change in the profile of the CeO₂ in comparison with the CeO₂-HS spectrum. Such difference might be associated with a modification of the semiconductor behavior of the CeO₂ due to the interaction with the Pd NPs.

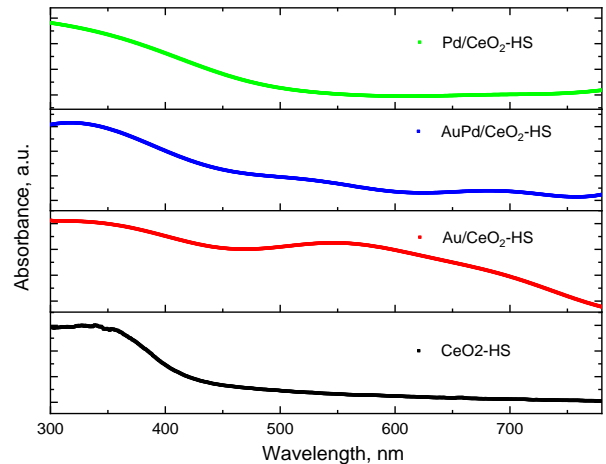


Figure 4. DR UV-Vis for CeO₂-HS (—), Au/CeO₂-HS (—), AuPd/ CeO₂-HS (—) and Pd/ CeO₂-HS (—).

To improve the photoluminescence (PL) intensity for CeO₂-HS NPs, we used the strategy of metal-enhanced luminescence (MEL) [21] this technique is based on the localized plasma effect of precious metal NPs, such as Au-NPs or Ag-NPs. This phenomenon happens when luminescence material is placed near metal NPs, in this case, the phosphors bring a mirror dipole in the metal NPs and it radiates the coupled quanta high efficiency that produce enhanced luminescence.

The PL spectra for CeO₂-HS NPs, Au/CeO₂-HS, AuPd/ CeO₂-HS and Pd/ CeO₂-HS is shown in figure 6, the excitation wavelength was 510 nm, the emission spectra of the CeO₂-HS NPs is 254 nm due to the electronic transition ²F_{5/2} → 5d₂ with low intensity (figure 6A), as characteristic of nanoceria, with the addition of Au, Pd and Au/Pd the enhancement of the PL emission spectra is depicted. Au-NPs had the inherent ability to produce plasmonic resonance on the surface [34] and Pd tends to have more stability to bonds with surface oxygen atoms than surface metal atoms, this is correlated to the position of the d electron density center of Pd atom [35].

MEL phenomenon was explored by [21] with Ag@SiO₂ nanoparticles; they demonstrated that the luminescence intensity and quantum yield of the lanthanide complexes can be enormously enhanced by the Ag@SiO₂ with optimized size

under proper excitation wavelength. In figure 6B the enhanced luminescence is shown for nanoceria NPs and Au with excitation at 510 nm wavelengths, the emission spectra were measured and depicted in figure 7B at 508-510 nm.

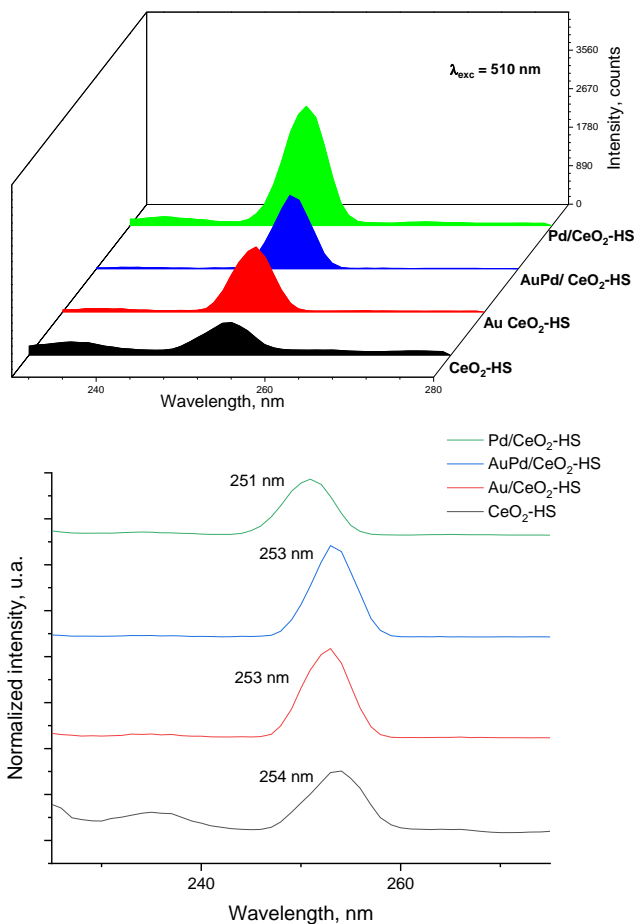


Figure 6.-PL spectra (Emission) for CeO₂-HS (A), Au/CeO₂-HS (B), AuPd/ CeO₂-HS (C) and Pd/ CeO₂-HS (D).

For Au-Pd/ CeO₂-HS and Pd/ CeO₂-HS NPs the emission spectra is shown in figures 6C and 6D, according to [34], they analyzed the binding energy for Au and Au/Pd core shell NPs and found a dependency of binding energies of Pd (3d_{5/2}) and Au (4f_{7/2}), with the increase of Pd content, the interaction between Au and Pd atoms gradually weakens and the dominant role of Pd atoms tend to determine the electronic structure. In figure 6D is observed that the enhanced luminescence is in the presence of Pd atoms into the nanoceria and in figure 6B it is observe that the combination of Au/Pd is similar to the Au-nanoceria NPs.

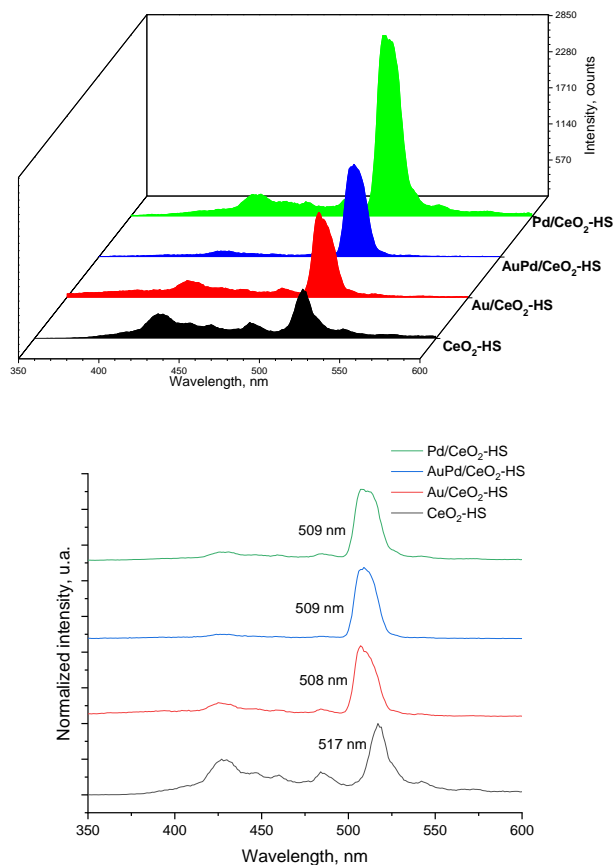


Figure 7.-PL spectra (Excitation) for CeO₂-HS (A), Au/CeO₂-HS (B), AuPd/ CeO₂-HS (C) and Pd/ CeO₂-HS (D).

IV. CONCLUSION:

The Cerium oxide (IV) hollow microspheres were successfully obtained via hydrothermal synthesis. CeO₂-HS photoluminescence presents an enhancement by the addition of Au, AuPd and Pd NPs on their surface. It was also observed that, the excitation peak centered around 517 nm presents a blue shift to the presence of the metal NPs. The observed blue shifts varied depending on the nature of the metal NPs (Au NPs > AuPd > Pd), same behavior was observed for the emission spectra, were the system containing Pd NPs presented a blue shift from 254 nm to 251 nm. The NPs, with the addition of Au, Pd and Au/Pd, observed enhancement of the PL emission spectra. Au-NPs produce plasmonic resonance that produces this enhancement. Finally based on the previously reported, we may conclude that Metal NPs-CeO₂ are promising materials for biomedical applications such as cancer detection via photoluminescence and photo-thermal cancer treatment.

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