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Synthesis of Silver/SiO_2:Eu^{3+} Nanocomposites Using Sunlight-Produced AgNPs to Enhance its Photoluminescence.

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In recent decades, there has been a great interest in nanocomposites based on silver nanoparticles (AgNPs) and silica nanospheres due to its properties as luminescent phosphors and their potential applications in bioimaging, among others [1-3]. In this regard, Stöber's method it's the most popular method to synthesize SiO_2 nanospheres because its simplicity and reproducibility [4]. On the other hand, incorporation of plasmonic nanoparticles near a phosphor induce an enhancement of its luminescent properties due to an amplification of the electric field around the noble metal nanoparticle, this process is denominated metal enhanced fluorescence (MEF) [5]. In this work, we synthesized a nanocomposite starting from SiO_2 nanoparticles doped with trivalent europium ions (SiO_2:Eu^{3+}), followed by the growth of AgNPs, obtained *in situ* through direct photoreduction of silver salts in solution, on the silica nanospheres surface.

The synthesis of the nanocomposite was carried out following a two-step method. First, europium doped silica nanospheres were obtained mixing 0.670 mL of tetraethyl orthosilicate (TEOS), 1.035 mL of ammonium hydroxide solution (30%), 0.180 mL of deionized water and 8.115 mL of ethanol. Europium ion was introduced as nitrate in a 1% concentration respect to TEOS. The mixture was left to react during 12h under vigorous stirring. Once the reaction time has elapsed, the as-synthesized nanoparticles were washed three times with ethanol. After the last washing cycle, the samples were dried to obtain white powders. The second step of the method consists of the light triggered synthesis of silver nanoparticles on the surface of silica powders. In a typical experiment, 5 mg of SiO_2 powder were redispersed in water followed by the addition of silver nitrate and sodium citrate to reach final concentrations of 0.1 mM and 3 mM, respectively. Another set of experiments were carried out using a sodium citrate final concentration of 12 mM. The mixture was exposed to sunlight, near noon, for 60 minutes [6]. All syntheses were carried out at ~20 °C. Finally, the obtained nanocomposite was washed and dried as described above. The photoluminescent properties of the samples were studied in the 350 nm to 625 nm interval, using a He-Cd laser (λ = 325 nm) as excitation source. The morphology and composition of the sample were analyzed using a FE-SEM (JEOL, JSM-7800F) equipped with and EDS detector (Bruker, XFlash 6|60) operated at 15 kV.

The synthesized nanocomposites AgNPs/SiO_2:Eu^{3+} present a broad emission spectrum (Figure 1) composed of intrinsic blue luminescence of the silica, centered around 437 nm, associated to a charge transfer process between silicon and oxygen atoms [7], and the sharp lines of trivalent europium ion associated to $^5D_0 \rightarrow {}^7F_J$ transitions (around 612 nm) [8]. The emission spectra of the nanocomposite samples show a marked broadening of the emission band centered around 437 nm respect to the sample without AgNPs. Furthermore, this broadening is larger as the citrate concentration increases.

Nevertheless, the europium emission doesn't seem to be affected in any of the samples. This increase in the intrinsic luminescence may be due to the enhancement induced by the augmented electric field around the nanoparticles causing an increase in the probability of absorption, and finally an enhancement of the fluorescence [5]. Also, the difference observed between the two nanocomposites can be explained as an effect of the size and concentration of metallic nanoparticles, as can be seen in figure 2, where the sample synthesized using more sodium citrate presents larger particles.

This work presents a facile two-step method to incorporate AgNPs on the surface of silica nanoparticles to obtain a luminescent nanocomposite with enhanced emission. Furthermore, this enhancement can be related to the size and concentration of the grown nanoparticles [9].

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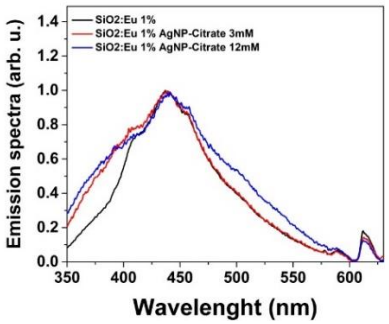

Figure 1. Normalized emission spectra (λ_{ex} = 325 nm) of SiO_2:Eu^{3+} and the two obtained nanocomposites using different concentration of sodium citrate.

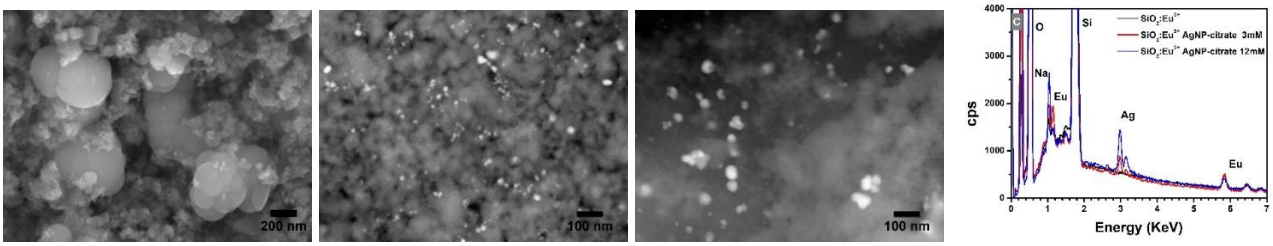

Figure 2. Backscattered electrons micrographies of SiO_2:Eu^{3+} (left), AgNPs/SiO_2:Eu^{3+}/3mM Citrate (middle left), AgNPs/SiO_2:Eu^{3+}/12mM Citrate (middle right) and their corresponding EDS spectra (right).

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