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Influence of plasmon coupling on the photoluminescence of ZnS/Ag nanoparticles obtained by laser irradiation in liquid

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ABSTRACT

We investigate the photoluminescence, optical absorption and structural properties of ZnS submitted to laser irradiation in water and isopropyl alcohol. Nanoparticles were produced by irradiating micro-sized ZnS particles dispersed in both liquids, with and without the addition of Ag nanoparticles, taking advantage of the laser-assisted fragmentation effect. When ZnS microparticles are irradiated either in pure water or isopropyl alcohol a considerable size reduction is achieved (from micra to few nanometers). The photoluminescence of these nanoparticles mainly occurs in the UV, centered at 350 nm, and with smaller intensity in the visible, centered at 600 nm. Irradiation of ZnS microparticles dispersed in colloidal silver triggers a reaction between both materials, modifying its optical absorption and photoluminescent properties. After irradiation of ZnS in alcohol containing Ag nanoparticles, a giant increase of the UV photoluminescence is observed. Interestingly, when the irradiation is performed in aqueous Ag nanoparticles colloids, the photoluminescence suffers a red-shift towards the violet-blue. The data show that core-shell (Ag-ZnO) nanostructures are formed after irradiation and the visible emission likely originates from the ZnO shell grown around silver nanoparticles. The presence of Ag nanoparticles in the liquid medium promotes a stronger absorption of the laser beam during irradiation due to the coupling with the surface plasmon resonance, fostering intense reactions among ZnS, Ag nanoparticles, and the liquid medium. Our study shows that with a simple change of the liquid medium wherein the irradiation is conducted the photoluminescence can be tuned from UV to visible and core-shell nanostructures can be obtained.

1. Introduction

Nanomaterials of II-VI semiconductors are important to several applications ranging from micro and opto-electronics [1] to nanomedicine [2] and bioimaging [3]. In the latter, the particular interest stems from the size-dependent quantum confinement effect observed in nanoparticles [4]. When the size of the nanoparticles is close to or smaller than the Bohr's exciton radius, they are denominated as quantum dots (QD's) [5]. This class of nanomaterial presents a series of unique physical and chemical properties, namely: size-dependent tunable and intense photoluminescence (PL), high quantum-yield, broad absorption coupled with narrow emission [5–8], etc. Among these compounds, zinc sulfide, a II-VI wide band-gap semiconductor, has been extensively studied. At room temperature, ZnS can be found in cubic (zinc blend) or hexagonal (wurtzite) crystalline structures [9,10]. ZnS is a direct band-gap semiconductor with gap energy $E_g \approx 3.7$ eV, Bohr's exciton radius of about 2.5 nm [11–13], and with a relatively large exciton binding energy (40 meV) [14]. Owing to its wide band gap, ZnS is acknowledged as a very promising material for a great number of optoelectronic applications [15]. For instance, it has been employed in the form of thin film in solar cells [16,17] since it is transparent to the visible and infrared portions of the electromagnetic spectrum and strongly absorbs in the ultraviolet region, a highly desirable feature [17,18].

Photoluminescent QD's are being regularly applied in medicine

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and biology for bioimaging and diagnostics [7]. Nevertheless, most II-VI QD's contain highly toxic heavy metals in their composition, such as Cd, Hg, Te, As, Se and Pb, all of which appear in the World Health Organization's list of the 10 chemicals of major public concern [19]. For instance, *in vivo* and *in vitro* studies showed that cadmium based QD's are particularly toxic and can significantly damage tissues [8,20]. In the search for less toxic QD's, ZnS has attracted much attention due to the potentially low toxicity of its constituents Zn and S [21–23] and may become one of the most important compound semiconductor materials for biological applications. In fact, ZnS has already been used as a biosensor in biological medium, acting as a fluorescence sensor for Cu^{2+}, Hg^{2+}, and Ag^{+} ions [23–26].

Due to the great potential for technological applications of the nanoparticles, the improvement of the synthesis techniques has been a major concern of researches worldwide. In the case of ZnS nanoparticles, a great variety of methods have been reported for its production, such as: wet-chemistry [12,27,28], sonochemistry [29], pulsed electric discharge [30], pulsed laser deposition [31], and laser ablation synthesis in solution (LASiS) [10]. LASiS, the technique employed in this work, has proven to be cost-effective, scalable, and environment friendly [32,33]. Although chemical routes provide, in general, better size distribution control, they generate many byproducts that are, in many cases, difficult to recycle. LASiS, on the other hand, has been classified as a "green technique", since the nanoparticles are obtained directly in the liquid of choice for the irradiation and no purification phase is needed, thus generating a smaller amount of unwanted materials [32]. We applied LASiS for the production of Ag nanoparticles from a bulk target and to induce the fragmentation of ZnS microparticles in order to reduce their size [34,35].

We present a study on the structural and optical properties of ZnS nanoparticles obtained by means of laser irradiation of micro-sized ZnS particles dispersed in two liquids, water and isopropyl alcohol. It is shown that the mean size of a commercial ZnS powder can be reduced from several microns to less than 5 nm taking advantage of the laser-assisted fragmentation process. X-ray Diffraction (XRD) patterns reveal that the ZnS nanoparticles have a cubic structure and show the formation of ZnO when the irradiation is performed in Ag nanoparticles aqueous colloids. The PL of ZnS irradiated in water (without Ag nanoparticles) mainly occurs in the UV region. However, when the irradiation is performed on ZnS dispersed in aqueous colloidal silver, an intense PL in the violet-blue region is observed. We argue that the origin of the PL red shift may be associated to the formation of ZnO, which grows around Ag nanoparticles forming a shell. The intense PL and its tunability are most likely possible due to the coupling of the incident photons with the surface plasmon resonance of Ag nanoparticles. Such coupling leads to two major effects: (i) stronger light absorption from the laser beam and (ii) energy/electron transfer between Ag nanoparticles and nearby photoluminescent structures enhancing the PL intensity.

2. Materials and methods

Colloidal suspensions of ZnS nanoparticles were synthesized making use of laser-assisted fragmentation irradiating aqueous and alcoholic suspensions of micrometric ZnS particles. For this purpose, we used a ZnS powder (Sigma-Aldrich) with 99.99% purity and average (nominal) grain size of 10 μm. A Nd:YAG laser operating at its fourth harmonic ($\lambda = 266$ nm, $\tau = 5$ ns), repetition rate of 10 Hz and 20 mJ/pulse was employed in the synthesis process. Two types of experiments were performed: (i) irradiation of ZnS powder dispersed in pure water/alcohol and (ii) irradiation of ZnS powder dispersed in colloidal suspensions of Ag nanoparticles produced in isopropyl alcohol and water. Fig. 1 shows a scheme of both experiments. The final colloidal suspensions were obtained by adding 1 mg of ZnS powder in 10 ml of liquid (isoprophyl alcohol or bidistilled water). The colloidal suspensions were continuously stirred during the irradiation in order to get homogeneously irradiated samples. The irradiation time varied between 120 and 300 s depending on the liquid. Colloidal suspensions of silver nanoparticles, synthesized in isoprophyl alcohol and bidistilled water, were obtained by LASiS irradiating a solid silver target immersed in water/alcohol. In this case we used a second Nd:YAG laser operating at the fundamental harmonic ($\lambda = 1064$ nm, $\tau = 200$ ns) with repetition rate of 1.5 kHz. For isoprophyl alcohol, the ablation of the Ag target was carried out during eight minutes, resulting in nanoparticles with 12 nm mean size while for bidistilled water ablation lasted 5 min, leading to nanoparticles of 9 nm. In the final suspension, 1 mg of ZnS powder was added to 10 ml of silver nanoparticles colloids and then irradiated during 300 s with the ultraviolet laser ($\lambda = 266$ nm).

The size distributions of the nanoparticles colloidal suspensions were measured using a Dynamic Light Scattering (DLS) equipment (Nanotrac NP 253 Microtrac) able to detect sizes between 0.9 and 600 nm. UV–Vis absorption spectra were acquired using a spectrophotometer (Ocean Optics USB 2000) with 2.5 nm resolution and photoluminescence (PL) was measured with a spectrofluorophotometer (Shimadzu 5301 PC) choosing excitation wavelengths ranging from 220 to 500 nm. Transmission electron microscopy (TEM) images were acquired using a JEOL JEM 1200EX-II microscope operating at 120 kV and the samples were prepared by dripping a small droplet of the solution on a carbon-coated copper grid. X-ray diffraction (XRD) measurements ($\theta - 2\theta$ geometry) were performed using a Shimadzu XRD-7000 diffractometer using copper K_α radiation ($\lambda = 1.5418$ Å). The samples for XRD were prepared by drop casting, depositing a large amount of nanoparticles suspensions on commercial Si(111) substrates. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCA3000 (VG Microtech) equipment operating at 10^{-10} mbar base pressure, with a dual-anode X-ray source (Mg and Al K_α). The hemispherical analyzer coupled to the system had an energy resolution of 0.8 eV and the energy calibration was done by using 1s peak of adventitious carbon of the samples.

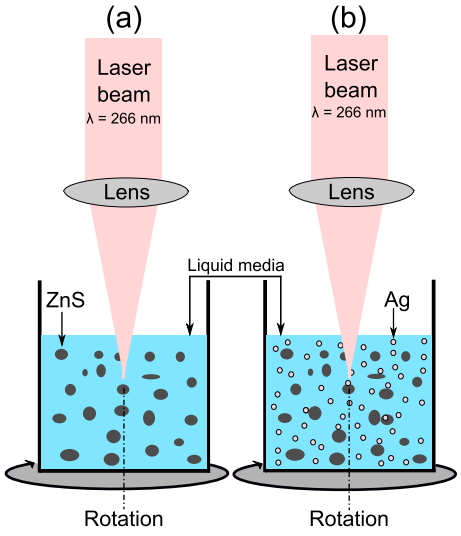

Fig. 1. Schematic drawing representing the experiments performed to obtain ZnS nanoparticles by laser-assisted fragmentation. (a) ZnS dispersed in pure bidistilled water or isopropyl alcohol and (b) ZnS dispersed in colloidal Ag.