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Preparation and optical properties of colloidal europium(III) diphenanthroline nitrate hydrate

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Preparation and optical properties of $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ colloids with potential application as an attractive UV sensor is discussed depending on preparation conditions. Excitation / luminescence spectroscopy, UV-Vis spectroscopy and AFM – microscopy including roughness analysis are used to characterize the hybrid colloidal microparticles. Luminescence / excitation spectroscopy confirms formation of red emitting hybrid Eu(III) luminescence centers with site symmetry C_{2v} or lower during preparation. A strong energy transfer from the organic ligand to europium at 350 nm excitation is demonstrated.

Key words: Sol-Gel, Europium, Hybrid Composites, UV sensor.

INTRODUCTION

Sol-gel technology is a powerful method for preparation of hybrid materials at room temperature. By variation of synthesis conditions different kinds of amorphous or nanocrystalline materials such as hybrid composites, thin films, xerogels or aerogels can be obtained. The strong luminescence of hybrid materials which contain lanthanide complexes incorporated in sol-gel networks, is based on an efficient energy transfer. These hybrid composite materials usually contain two components – amorphous or nanocrystalline matrix /sol-gel silica or zirconia/ and an optical active complex. Often, rare earth ion complexes are used as an optical active component due to their strong pure emission: Eu^{3+} (615 nm), Tb^{3+} (540 nm), Ho^{3+} (540 nm), Sm^{3+} (590 nm) [1-4].

Lanthanide complexes, however, display some disadvantages which have to be compensated for during sol-gel preparation by variation of pH, temperature and drying conditions. Many lanthanide complexes have very low solubility and low kinetic stability in solid matrices, thus the optical properties of the obtained complexes strongly depend on the preparation procedure which concerns the optical properties of SiO_2:$[Eu(ntac)_3]$[pphendcn] [1-3]. As it was previously described in our prior studies, we proposed a new method for functionalization of Eu^{3+} doped silica nanoparticles with 1,10-phenantroline with a quantum efficiency of 20-40% [1]. The concept of this method was to replace the doping procedure of the complex by a surface functionalization of inorganic oxides, containing lanthanide ions, as SiO_2: Eu or ZrO_2: Eu. The organic ligands (e.g. 1, 10 – phenanthroline) can be used as surface functionalization agents for *in situ* formation of complexes. Thus, by applying the method of surface functionalization of europium doped silica microparticles we achieved a high time stability and improved the luminescent properties of the prepared material SiO_2:$[Eu(phen)_2](NO_3)_3$ [1 - 9].

A third way for preparation of hybrid sol-gel composites is by incorporation into silica or zirconia matrices of functionalized microparticles containing rare earth ions with a high quantum yield [5-8]. Appropriate materials for such an incorporation could be microparticles containing $Eu(phen)_2(NO_3)_3{\cdot}xH_2O$ because of the excellent optical properties of this complex. Such approach, however, requires physico-chemical characterization of colloidal $Eu(phen)_2(NO_3)_3{\cdot}xH_2O$ materials, but also additional efforts for obtaining reproducible results.

The aim of this contribution is to obtain reproducible colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ microparticles starting from Eu_2O_3 and to describe their optical properties depending on the preparation strategy in the framework of preparation and characterization of high-quantum yield hybrid materials.

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EXPERIMENTAL

The preparation of red emitting $Eu(NO_3)_3.xH_2O$ microparticles functionalized with 1,10-phenanthroline was performed in several steps (figure 1). First, a 0.57 M solution with pH = 2-3 was prepared using Eu_2O_3 as precursor and HNO_3 at 40-50 °C. After that, 10 ml of EtOH was added to 10 ml of the initial 0.57 M aqueous solution of $Eu(NO_3)_3$. The so formed solid $Eu(NO_3)_3{\cdot}xH_2O$ was dried at that temperature for 1 h. After this the solid $Eu(NO_3)_3{\cdot}xH_2O$ was dissolved in EtOH. The next step of the preparation of the colloidal solution was to add a mild alkalizing agent – 450 µl of 0.14 M EtOH solution of NH_3. Note that this colloidal solution does not display visible red emission even after excitation with UV light. To achieve a strong red emission at UV light excitation the colloidal $Eu(NO_3)_3{\cdot}xH_2O$ solution was impregnated with EtOH solution of 1.1 M 1,10-phenanthroline for 48 h under constant stirring at room temperature.

The impregnation procedure was done in excess of 1,10-phenanthroline in $n_{Eu}/n_{phen}=9.4{\cdot}10^{-3}$. The final concentration of europium in the functionalized solution was $c_3=0.01$ M.

As a result of the ammonia addition, the composition of the so prepared colloidal particles could be $Eu(OH)_x(NO_3)_{3-x}$. The functionalization with 1,10-phenanthroline leads to a formation of $[Eu(phen)_2](OH)_x(NO_3)_{3-x}$. According to general chemical considerations, and the chemistry of $[Eu(phen)_2](NO_3)_3$, the transformation of $[Eu(phen)_2](OH)_x(NO_3)_{3-x}$ with time to the thermodynamically stable $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ is very probable [5-8]. The exact microcomposition determination, however, needs additional investigations, which will be published in a next contribution.

In a second scheme, Eu_2O_3 micropowders were used instead of $Eu(OH)_x(NO_3)_{3-x}$ microparticles, but the functionalization conditions remained the same. The resulting sol did not luminesce, which means that the process of functionalization has not been successful. This means that the ammonia addition, which led to the formation of $Eu(OH)_x(NO_3)_{3-x}$ microparticles, is an important step in the functionalization process.

A Varian Cary Eclipse spectrophotometer was used for excitation/luminescence spectra measurements of the sol at room temperature. Room temperature UV/Vis absorption spectra of solutions were measured on a Perkin Elmer Lambda 35 spectrophotometer. The Eu content in all prepared samples was checked using an LA-ICP-MS unit.

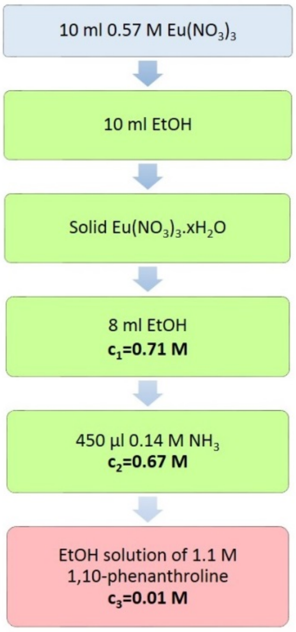

Fig. 1. Preparation of colloidal solution of $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$. The calculated Eu concentration is given in the different steps of preparation.

The sample preparation for AFM imaging involved a deposition of colloidal solution of $Eu(OH)_x(NO_3)_{3-x}$ or $[Eu(phen)_2](NO_3)_3{\cdot}H_2O$ on freshly cleaved mica surface. Freshly cleaved quadratic mica Grade V-4 Muscovite (Structure Probe Inc. / SPI Supplies, West Chester, PA) with sizes 10×10 mm glued to the metal pads were used for the deposition of about 100 µL of colloidal solution. Then the samples were left for 10 min and were gently blown with a flow of nitrogen gas to dry out. AFM imaging was performed on the NanoScopeV system (Bruker Inc.) operating in tapping mode in air at room temperature. We used silicon cantilevers (Tap 300 Al-G, Budget Sensors, Innovative solutions Ltd, Bulgaria) with 30 nm thick aluminum reflex coating. According to the producer's datasheet the cantilever spring constant was in the range of 1.5–15 N/m and the resonance frequency was 150 ± 75 kHz. The tip radius was less than 10 nm. The scan rate was set at 1 Hz and the images were captured in height mode with 512×512 pixels in a JPEG format. Subsequently, all the images were flattened by means of Nanoscope software.

RESULTS AND DISCUSSION

In Figure 2, absorption, excitation and luminescence spectra of the prepared colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ are shown. The absorption spectrum shows peaks at 231 nm (strong), 265 nm (strong), 324 nm (weak) and 350 nm (shoulder). The absorption peaks of the colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ in this study are close to those of the SiO_2: $[Eu(phen)_2](NO_3)_3$ and ZrO_2: $[Eu(phen)_2](NO_3)_3$ [1-3]. More details about the optical properties of this complex are given in [5].

There are significant differences in the excitation spectrum of colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ compared to that of bulk $[Eu(phen)_2](NO_3)_3$ or hybrid sol-gel materials containing $[Eu(phen)_2](NO_3)_3$. In the excitation spectra of $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$, only one sharp excitation band at 350 nm is visible and it is in agreement with the absorption spectra shoulder at the same wavelength. The excitation channels at $\lambda<330$ nm are closed in the case of colloidal solution (figure 2).

In the excitation spectra of the bulk polycrystalline powders a broad excitation window down to 270 nm has been described [1]. In the excitation spectra of ZrO_2:$[Eu(phen)_2](NO_3)_3$, SiO_2: $[Eu(phen)_2](NO_3)_3$ a broad band between 270 nm and 370 nm, also centered at 350 nm [1-3] has been detected. In this way the as prepared colloids could be an attractive sensor for 350 nm radiation. The differences in the excitation spectra of bulk and colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ require additional theoretical and experimental investigations.

The absorption and excitation spectrum in fig. 2 confirms the occurrence of a strong energy transfer in the colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ solution, where the excitation energy is absorbed by the 1,10 – phenanthroline molecule (T_1 level, 265 nm) followed by inter-system crossing (ISC) to the S_1 level at 350 nm and transfer to the $^5D_2$ term of the Eu^{3+} ion [5,9,10].

The luminescence spectrum of the colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ solution consists of a strong red emission, coming from the well-known Eu^{3+} $^5D_0 \rightarrow ^7F_J$ electronic transitions. We detected one peak in the region of the $^5D_0 \rightarrow ^7F_0$ transition (582 nm), two lines in the region of the $^5D_0 \rightarrow ^7F_1$ transition (594 nm), one peak in the region of the $^5D_0 \rightarrow ^7F_2$ transition (615 nm), one weak peak at 650 nm ($^5D_0 \rightarrow ^7F_3$) and two lines in the $^5D_0 \rightarrow ^7F_4$ transition (684 nm and 700 nm) using second derivative luminescence spectrum analysis. The results of luminescence spectra – structure analysis suggest a site symmetry C_{2v} or lower of europium ions [11-13]. The spectra – structure analysis results in this study are in agreement with our recent results, which suggests that the most probable site symmetry in the case of ZrO_2:$[Eu(phen)_2](NO_3)_3$, SiO_2: $[Eu(phen)_2](NO_3)_3$ and bulk $[Eu(phen)_2](NO_3)_3$ is C_{2v} or D_2 [11-13]. The $^5D_0 \rightarrow ^7F_0$ transition in colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$, however, shows a site symmetry lowering and / or a change of chemical surroundings.

In the luminescence spectrum of colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ a weak blue emission with maximum at about 420 nm, coming from the 1,10 - phenanthroline ligand is visible, which is close to the blue luminescence described in our recent contribution [2,14].

The morphology of the films from nanoparticles deposited on freshly cleaved mica surface was investigated by Atomic Force Microscopy (AFM). Typical topographical images of non-functionalized $Eu(OH)_x(NO_3)_{3-x}$ and functionalized with 1,10 – phenanthroline $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ films are depicted in figures 3A÷C and figures 3D÷F, respectively where the significant differences in topography of the obtained films are easily detectable. In figures 3A÷C are presented typical AFM height images of non-functionalized $Eu(OH)_x(NO_3)_{3-x}$ films where the height images are presented in 2D- (figure 3A) and 3D- format (figure 3C) and also images of functionalized with 1,10 - phenanthroline Eu $(OH)_x(NO_3)_{3-x}$ films (figures 3D, F). The images are accompanied with sections across the films' surface presented in figure 3B and figure 3E, respectively. The films from non-functionalized $Eu(OH)_x(NO_3)_{3-x}$ have relatively flat morphology. Only few individual 3D-structures (white spots in figure 3A) with heights of about 25÷40 nm which are spread irregularly on the film surface can be observed. On the contrary, the films obtained from $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ exhibit a granule-like pattern and are composed of heterodisperse nanoparticles with different shapes and sizes in the range of 40 nm to more than 100 nm.

The roughness analysis of the height AFM images also showed a profound difference in the film structure. It gives reasoning for various non-functionalized $Eu(OH)_x(NO_3)_{3-x}$ films. The main roughness Ra value is 4.5 nm, while for functionalized $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ it is more than 6 times bigger, i.e. Ra= 31 nm.

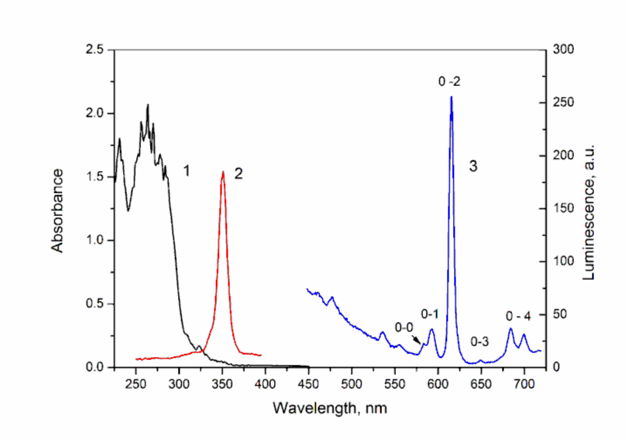

Fig. 2. Optical spectra of [Eu(phen)$_2$](NO$_3$)$_3$·xH$_2$O colloidal solutions. Luminescence spectrum at 355 nm excitation (3) and excitation spectrum monitoring the 615 nm transition (2) are displayed. The $^5D_0 \rightarrow {}^7F_J$ emission transitions of Eu^{3+} ion are denoted as 0-1, 0-2, 0-3 and 0-4. The Eu – concentration is $5 \cdot 10^{-6}$ mol/l in absorption spectra measurements (1) and 0.01 mol/l in excitation / luminescence spectra measurements (2,3).

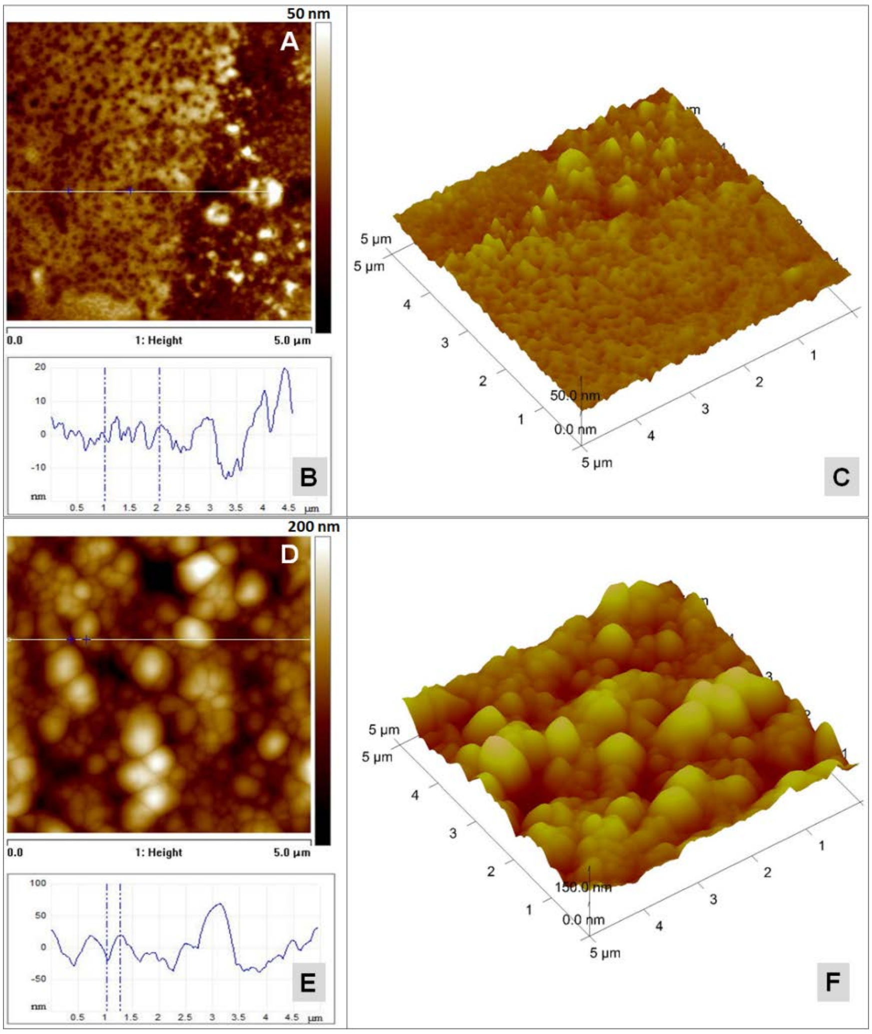

Fig. 3. AFM images of non-functionalized Eu (OH)$_x$(NO$_3$)$_{3-x}$ and functionalized with 1,10 - phenantroline [Eu(phen)$_2$](NO$_3$)$_3$·xH$_2$O films. **(A)** 2D height image of non-functionalized Eu (OH)$_x$(NO$_3$)$_{3-x}$ film with the scanning XY area 5×5 µm^2 and the z-range z=50 nm; **(B)** Cross-section of image (A); **(C)** 3D height image of the same non-functionalized Eu (OH)$_x$(NO$_3$)$_{3-x}$ film; **(D)** 2D height image of functionalized with 1,10-phenantroline [Eu(phen)$_2$](NO$_3$)$_3$·xH$_2$O film with the scanning XY area 5×5 µm^2 and the z-range z=200 nm; **(E)** Cross section of image (E); **(F)** 3D height image of the same functionalized with 1,10 - phenantroline [Eu(phen)$_2$](NO$_3$)$_3$·xH$_2$O film.

CONCLUSIONS

In the present article we demonstrate a promising sol-gel technique for colloidal preparation of a red emitting sol containing $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ with potential application as an attractive UV sensor. The preparation procedure is based on intermediate formation of $Eu(OH)_x(NO_3)_{3-x}$ microparticles. The most probable symmetry of the Eu^{3+} ion in the hybrid colloidal microparticles is C_{2v} or lower. A strong energy transfer from the organic ligand at 350 nm excitation is demonstrated. There are differences in the optical properties of colloidal $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$, compared to that of bulk $[Eu(phen)_2](NO_3)_3$. AFM height images of non-functionalized $Eu(OH)_x(NO_3)_{3-x}$ films exhibit relatively flat morphology with a small number of individual 3D-structures with irregular shapes and sizes of about 25÷40 nm, while the films from $[Eu(phen)_2](NO_3)_3{\cdot}xH_2O$ are composed of nanoparticles with sizes in the range of 40 ÷ 100 nm.

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ПРИГОТВЯНЕ И ОПТИЧНИ СВОЙСТВА НА КОЛОИДЕН ЕВРОПИЕВ (III) НИТРАТ ДИФЕНАНТРОЛИН ХИДРАТ

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(Резюме)

Дискутирана е връзката между условия за получаване и оптични свойства на колоидни микрочастици със състав $[Eu(phen)_2](NO_3)_3.xH_2O$ с потенциално приложение като луминесцентни сензори за ултравиолетово лъчение. Хибридните колоидни микрочастици са охарактеризирани с помощта на луминесцентна спектроскопия и спектри на възбуждане, ултравиолетова спектроскопия и атомно-силова микроскопия. Използваните спектроскопски методи доказват, че симетрията на европиевия йон в получените материали с интензивна червена луминесценция е C_{2V}. Наблюдаван е ефективен енергиен трансфер от органичните лиганди към европиевия йон при 350 nm.