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Hybrid silica luminescent materials based on lanthanide-containing lyotropic liquid crystal with polarized emission

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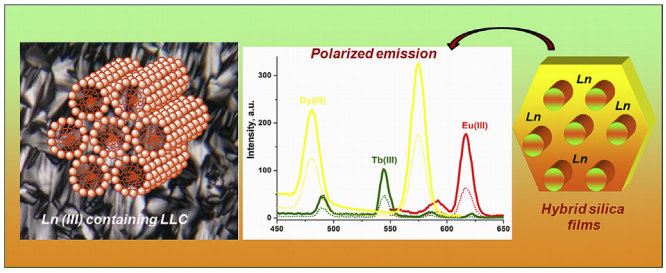
HIGHLIGHTS

- We suggest a new simple approach for creating luminescence hybrid silica films.
- Ln-containing hybrid silica films demonstrate yellow, green and red emissions.
- Tb(III)-containing hybrid film have a high lifetime.
- We report effects of linearly polarized emission in hybrid film.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper represents the template method for synthesis of hybrid silica films based on Ln-containing lyotropic liquid crystal and characterized by efficient luminescence. Luminescence films were prepared *in situ* by the sol–gel processes. Lyotropic liquid crystal (LLC) mesophases $C_{12}H_{25}O(CH_2CH_2O)_{10}H$/$Ln(NO_3)_3 \cdot 6H_2O/H_2O$ containing Ln (III) ions (Dy, Tb, Eu) were used as template. Polarized optical microscopy, X-ray powder diffraction, and FT-IR-spectroscopy were used for characterization of liquid crystal mesophases and hybrid films. The morphology of composite films was studied by the atomic force microscopy method (AFM). The optical properties of the resulting materials were evaluated. It was found that hybrid silica films demonstrate significant increase of their lifetime in comparison with an LLC system. New effects of linearly polarized emission revealed for Ln-containing hybrid silica films. Polarization in lanthanide-containing hybrid composites indicates that silica precursor causes orientation of emitting ions.

1. Introduction

The hybrid organic–inorganic materials are intensively investigated today, in particular, their synthesis and properties. The difference of the organic and inorganic components in nature as well as diverse combinations of their properties offer promising ways for the creation of multifunctional materials with a broad range of new properties. The chemistry of the soft materials provided opportunities for the synthesis of a new family of the mesoscale (50–100 nm) two-phase hybrid networks by a template synthesis involving the ordered directing agents. The structural diversity of the lyotropic liquid crystals (LLC) makes them potentially suitable for these agents in the synthesis of nanostructures with various spatial organizations: nanoparticles, nanowires, nanorods, nanoplates and mesoporous materials [1–6]. Among the most prominent advantages of the LLC templates, the following

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ones should be underlined: their soft synthesis conditions, the opportunities for the synthesis of porous materials with uniform pore sizes and their homogeneous distribution in a material, as well as the opportunities to control the material macroscopic properties by the mesophase type variations. The interest in the synthesis of the mesoporous silica structures by an LLC template has been growing since the first publications by Kresge et al. [7] appeared due to the fact that this method can be modified to be used for synthesizing functionalized nanostructures [8–23]. For example, the modification of the silica materials was reported to have been carried out through introducing various transition and noble metal ions [9–17], doping the lanthanum binary oxides (Na/La, K/La, Rb/La, Cs/La) [18], Ni–Co [19] and Sn–Mo [20] clusters, Ru (II) complexes [21–23]. The hybrid organic-inorganic composites based on the lanthanide ions are of a special interest. The unique photophysical properties of the lanthanide ions make these hybrid materials highly promising for such applications as optical amplifiers, optical waveguides, light emitting diodes and chemical sensors. The authors have shown [24,25] that these luminescence hybrid materials demonstrate excellent mechanical properties, processability and thermal stability.

Koen Binnemans [26] gave a detailed review of various approaches to the synthesis of the lanthanide-based hybrid luminescent materials, including the sol–gel technology based composites where some well-known silica precursors (MCM-41 with a hexagonal structure and 20–100 Å pores) are used as the host matrix. There are three basic methods for introducing the luminescent lanthanide complexes into the sol–gel glasses: impregnation, doping and chemical immobilization. We offer a new approach to creating the silica hybrid lanthanide-containing materials. Our earlier studies were dedicated to the lyotropic liquid-crystalline systems based on the nonionic and zwitter-ionic surfactants containing lanthanide ions [27–32]. The binary $C_{12}EO_{10}$/$Ln(NO_3)_3 6H_2O$ and tertiary $C_{12}EO_{10}$/$Ln(NO_3)_3 6H_2O$/H_2O systems in the Ln (III) – La, Nd, Eu, Tb, Dy, and Er series were shown to form a hexagonal mesophase in a broad concentration and temperature range. The systems containing the Eu (III) and Tb (III) ions demonstrate highly photostable and efficient luminescent media properties, while the luminescence efficiency depends on the type of the formed liquid crystalline phase [33]. This paper is the continuation of our previous research as it represents the new approach to the synthesis of hybrid silica films with the above-mentioned Ln-containing LLCs as the main structuring agents. In contrast to known methods of lanthanum encapsulation into silica, that are based on either as an *ex situ* prepared complex with a siloxane-based ligand or on *in situ* complexing with chelating groups attached to the silica [34], we used a priori luminescence lyotropic liquid crystal structuring matrix. Hereinafter this LLC phase interacted with silicate precursor. Optical properties data provide discussion points on the influence of the structure of hybrid silica films on their luminescence and polarization properties.

2. Experiment

The following commercial products of "Aldrich" were used: monodecyl ether of decaethylene glycol $C_{12}H_{25}O(CH_2CH_2O)_{10}H$ ($C_{12}EO_{10}$) as a surfactant, phenyltriethoxysilane $Si(C_6H_5)(OC_2H_5)_3$ (FTEOS) as a silica precursor and crystalline hydrates of lanthanide nitrates: $Eu(NO_3)_3 \cdot 6H_2O$ (Eu (III)), $Tb(NO_3)_3 \cdot 6H_2O$ (Tb (III)), $Dy(NO_3)_3 \cdot 6H_2O$ (Dy (III)).

The calculation of the number of components for the synthesis of hybrid systems was carried out in the following way. The molar ratio $C_{12}EO_{10}$/Ln (III) was 1:2 and constant for all the systems. The total percentage of water was 40 wt% of the $C_{12}EO_{10}$/Ln (III), Ln (III)=Tb, Dy complex mass and 50 wt% for system containing Eu (III) (for example, in the $C_{12}EO_{10}$/Dy (III)/H_2O system: a 0.0699 g of salt and 0.0333 g of water were taken for 0.05 g of $C_{12}EO_{10}$).

The hybrid systems were synthesized in several stages. At the first stage, a silicate precursor was hydrolized at the ratio of 1:3:0.2 ratio of FTEOS:EtOH:HCl components, while the water content was a half of the total amount (m H_2O = 0.0167 g). The FTEOS: $C_{12}EO_{10}$ ratio of 0.2:1 was constant (m FTEOS = 0.0038 g). The pH value of this solution was in the range of 2–3. The mixture was homogenized by an ultrasonic stirrer in the mild heating conditions ~30°C for 3 h. The next step was the addition of the aqueous solution of salt (m H_2O 0.0167 g and m $Dy(NO_3)_3 \cdot 6H_2O$ 0.0699 g) and the calculated amount of surfactant (m $C_{12}EO_{10}$ = 0.05 g). This system was homogenized by an ultrasonic stirrer for one hour. An important prerequisite for the creation of luminescent hybrid films was the sustainability of a mesophase at this stage, that was detected by the POM method. At the second stage, the condensation reaction at the temperature of ~60–80 °C occurred for 6 h. Finally the homogeneous mixture was uniformly deposited on a glass support and left to complete the sol–gel reaction and solvent evaporation. Then, the product was kept in vacuum at 40 °C for 10 h before a further study. The film thickness was 40–50 microns.

The LC properties were studied, and the mesophases were identified using the polarized optical microscopy (POM) on the Olympus DX 51 microscope with the Linkam heating system.

The X-ray studies were carried out on the automatic X-ray Bruker D8 Advance diffractometer with the Vario attachment and the Vantec coordinate detector. The radiation type used was the CuKα1 radiation monochromated by the curved Johansson monochromator (λ = 1.54056 Å), the X-ray tube operation mode was: 40 kV, 40 mA. The experiments were performed using the Bragg–Brentano geometry for the planar sample at the room temperature. The LLC sample was placed on a glass support.

The surface morphology was studied on the MultiMode V scanning probe microscope by Veeco in the atomic force mode.

IR spectra were obtained in a film on a Bruker Tensor-27 spectrometer in the frequency range of 4000–400 cm^{-1} and on the Bruker IFS-113v spectrometer in the range of 700–100 cm^{-1}.

The luminescent properties were studied on the Cary Eclipse spectrofluorimeter by Varian on thin films. The luminescence kinetics was detected at the maximum emission wavelength of the respective ion: Eu (III) λ = 617 nm, Tb (III) λ = 544 nm, Dy (III) λ = 575 nm. The experimental curves were approximated by the exponents in the Origin software.

Polarization studies were carried out using the set of polarizers (Manual Polarizer Accessory 00-100761-00, Varian) placed between a sample, the emission chromatograph and the detector.

The light transmission of silicate films was measured by the double-beam Instrumental Lambda 35 UV/VIS Spectrometer by Perkin Elmer. The measurements were carried out at the 25 °C temperature.

3. Results and discussion

3.1. Structure of Ln-containing thin films

As Raimondi and Seddon summarized in review [35], the best results for template synthesis of hybrid mesoporous materials were obtained for exactly hexagonal mesophases, not for cubic or lamellar. Previously, we found [28] that the nonionic surfactant $C_{12}EO_{10}$ forms a hexagonal mesophase in the concentration range 38–78 wt% in water. Introduction of crystalline hydrates of lanthanide nitrates leads to shifting of hexagonal mesophase concentration range towards larger values of $C_{12}EO_{10}$/Ln (III) the complex content (50–100 wt%). In this regard, 50 wt%/50 wt% $C_{12}EO_{10}$/H_2O ratio is required for optimal synthesis of hybrid films.