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Preparation of multicolor luminescent cellulose fibers containing lanthanide doped inorganic nanomaterials

Aleksandra Erdman [a], Piotr Kulpinski [a,*], Tomasz Grzyb [b], Stefan Lis [b,**]

[a] Department of Man-Made Fibers, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland
[b] Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland

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ABSTRACT

In this paper, the UV sensitive optically active cellulose fibers contained of 0.5% w/w Sr_2CeO_4, $Gd_4O_3F_6$:5% Eu^{3+} and CeF_3:5%Tb^{3+} with respectively blue, red and green emission are described. The fibers were formed from an 8% by weight cellulose spinning solution in N-methylmorpholine-N-oxide (NMMO). The modifiers were chosen because of their specific color of emitted light. Photoluminescent particles were introduced into the polymer matrix during the dissolution process of cellulose in NMMO. The emission intensity and excitation energy of the final cellulosic luminescent products were examined by photoluminescence spectroscopy. The degree of dispersion of the nanoparticles in the polymer matrix was evaluated using transmission electron microscopy (TEM). The influence of modifier's particles on the mechanical properties of the fibers was determined.

1. Introduction

Nanomaterials doped with lanthanide ions (Ln^{3+}) are intensively investigated in the last years due to their applications in the fields of material sciences (new materials with luminescent properties), physics (diodes and lasers techniques) and medicine (diagnostic and therapy) [1–5]. From the many years their unique properties have been used for designing phosphors, lasers, optoelectronics, security markers, solar cells or catalysts [6–12]. Nowadays also life sciences, i.e., biology and medicine, use the spectroscopic properties of nanomaterials doped with Ln^{3+} ions [4,13–15]. The main reasons of applications of these materials are the spectroscopic properties of the Ln^{3+} ions and character of f–f transitions that are responsible for the observed luminescence. These transitions are partially forbidden, by selection rules, which results in relatively long luminescence lifetime (ms), narrow line width (several nm) and low absorption cross section of the Ln^{3+} ions. Shielding properties of 5s and 5p outer orbitals have additional effects on these transitions. Furthermore, emission of Ln^{3+} ions is characterized by high quantum yields and the possibility of a large difference between the wavelengths of absorbed and emitted radiation what also influences their applications [3,9,16]. The wavelength of emitted light is strongly depended on the Ln^{3+} ion used and the most of these ions can emit in the visible region. Therefore, nanocrystalline materials doped with Ln^{3+} ions were chosen as good candidates for luminescence activators in cellulose fibers. As the hosts for luminescent Tb^{3+} and Eu^{3+}, ions, inorganic compounds were chosen: CeF_3 and $Gd_4O_3F_6$. As the blue emitting material, Sr_2CeO_4, was used, without any Ln^{3+} dopants. These materials were previously investigated and were selected as stable phosphors with the high emission intensity [17–19]. The use of above mentioned Sr_2CeO_4 compound and two Ln^{3+} ions gave the possibility to cover the visible range by the three basic colors: blue, green (Tb^{3+}) and red (Eu^{3+}).

Present research describes a method of obtaining luminescent cellulose fibers. This kind of optically active material can be produced by an NMMO method which is well known as a method of manufacturing “Lyocell” and “Tencel” type fibers [20]. The use of N-Methylomorpholine-N-Oxide (NMMO) as a direct solvent of cellulose is one of the newest, promising and environmental friendly method of making regenerated cellulose fibers. One of the most important advantages is the possibility of modification of Lyocell fibers. It can be achieved by introduction of the modifier into the spinning dope during the cellulose dissolution process in NMMO [21]. The conditions of the cellulose dissolution process are relatively rigorous (highly alkaline environment with relatively high temperature), so the chosen modifier must be stable and inert for them. In present research, added modifiers contains the lanthanide ions, which according to our study [22] seems to be very promising materials for obtaining photoluminescent cellulose fibers and fulfills the strict conditions of the preparation of the solution and fibers formation. The modifiers are chosen as to obtain fibers with different colors of emitted light. This paper

* Corresponding author. Tel.: +48 42 631 3359.
** Corresponding author. Tel.: +48 61 829 1679.
E-mail addresses: piotr.kulpinski@p.lodz.pl (P. Kulpinski), blis@amu.edu.pl (S. Lis).

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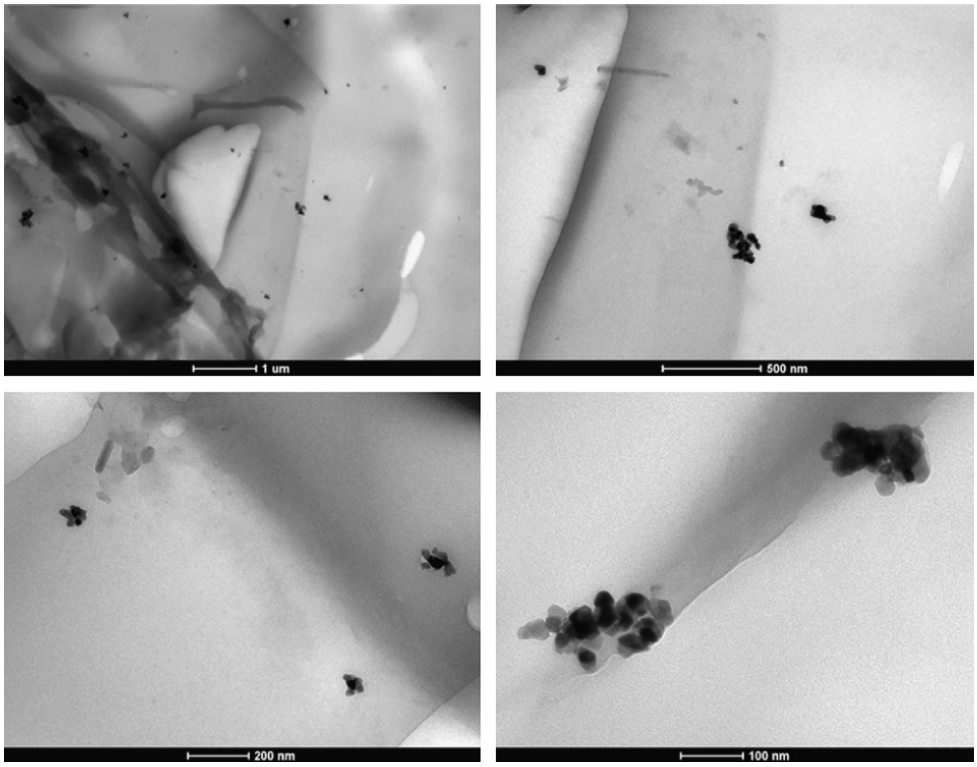

Fig. 1. TEM images of $Gd_4O_3F_6$:5%Eu^{3+} nanocrystals in polymer matrix.

describes the criteria of choosing the proper modifiers and methods of preparation of them. Also method of making photoluminescent cellulose fibers and their properties is described.

The inspiration of present research was the system of protection for garments and papers that is still not perfect nowadays. The luminescent Lyocell fibers that are presented in this paper can be also used as unique and advanced material to manufacture yarns and threads for textile protection. These fibers can be incorporated into fabrics in small amounts and in addition, may be a useful tool in the management of production to mark the batch production in different plants with similar range. The luminescent fibers are excellent materials for documents protection. It is possible to produce a paper containing certain amount of staple or filament fibers with luminescent properties. Such materials are relatively difficult to be counterfeited and therefore can be used for production of special purpose papers (notes, passports, ID tags etc.). The authenticity of such documents can be easily proven by simple lighting them up with UV radiation. Under UV irradiation the luminescent fibers appear as gloving lines. The additional advantage of the cellulose fibers is their high compatibility to the paper pulp. It means that the fibers can be very well bonded to the paper, what makes them extremely hard to be removed from the product during e.g. printing, processing and handling.

2. Materials and methods

2.1. Instrumentation

The cellulose solutions were obtained on the high efficiency laboratory-scale IKAVISC kneader type MKD 0.6 H60 and the fibers were formed with the use of a dry–wet spinning method on the laboratory-scale piston-spinning device with spinneret equipped with 18 orifices of 0.4 mm diameter.

The mechanical properties of fibers were checked on a Zwick Z2.5/TN1S tensile testing machine, in accordance with ISO standard ISO 5079:1995. The linear density of the fibers was measured according to ISO standard ISO 1973:1995.

The evaluation of size and distribution of modifiers' nanoparticles in the polymer matrix were performed with the use of the transmission electron microscope (TEM) technique. TEM images were measured at JEM 1200 EXII, JOEL electron transmission microscope, using an accelerating voltage of 80 kV.

The excitation and emission spectra of all samples were recorded on a HITACHI F-7000 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Excitation and emission spectra were corrected for the instrumental response.

3. Experimental

3.1. Preparation of the modifiers

3.1.1. Blue luminescent Sr_2CeO_4 nanocrystals

To prepare the Sr_2CeO_4, $Sr(NO_3)_2$ (POCh S.A., ACS grade 98+%, Poland), $CeCl_3 \cdot 6H_2O$ (Sigma-Aldrich, 99.9%, Poland) the 1 M solutions of the reagents were prepared and their stoichiometric amounts (volumes) were dissolved in distilled water in order to synthesize 1 g of the product. Then the citric acid monohydrate (CHEMPUR, p.a. grade, Poland) and ethylene glycol (CHEMPUR, p.a. grade, Poland) were added to the solution, as chelating and polymerizing agents, respectively (12 g citric acid and 2 mL of glycol per 1 g of the final product). The total volume of 100 mL of the final mixture was heated and stirred on the electric stove for about 30 min. Afterwards, solution was concentrated by slow evaporation (about 8 h) in drying oven, hence a transparent brown gel was obtained. The precursor was fired at 1000 °C for 3 h in

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