Optical Materials 36 (2014) 1694–1697

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Aggregation of Rhodamine 6G in titanium dioxide nanolayers and bulk xerogels

Aneta Lewkowicz[a], Anna Synak[a,*], Piotr Bojarski[a], Beata Grobelna[b], Jakub Karczewski[c], Dawid Jankowski[a], Sebastian Mahlik[a]

[a] Institute of Experimental Physics, University of Gdansk, Wita Stwosza 57, 80-952 Gdansk, Poland
[b] Faculty of Chemistry, University of Gdansk, Wita Stwosza 63, 80-952 Gdansk, Poland
[c] Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland

ARTICLE INFO

Article history:
Available online 28 February 2014

Keywords:
Aggregates
Nanolayers
Bulk xerogels
Titanium dioxide
Rhodamine 6G

ABSTRACT

Nanolayers and bulk xerogels of Rhodamine 6G (Rh6G) in titanium dioxide (Rh6G/TiO_2) were prepared using the sol–gel method. The spectroscopic and structural properties of these two types of hybrid matrices were studied as a function of dye concentration.

In both cases absorption, fluorescence and time resolved emission spectra show the formation of fluorescent aggregates. The observed stronger changes in characteristics of bulk xerogels can be explained not only by the formation of aggregates but also by different structure of both materials.

1. Introduction

Titanium dioxide has been recently used in many areas of material science and technology.

This material occurs in three forms: anatase, rutile, and brookite, which leads to a variety of applications in electronics, sensor technology, optics and biomedical applications [1–3]. As a semiconductor with quite large forbidden band gap energy of 3.2 eV it has been used in the process of development of solar cells competitive to the conventional silicon based solar cells and other photovoltaic applications [4].

In this paper, the sol–gel process is applied to obtain and study concentration-dependent fluorescence properties of Rhodamine 6G entrapped in titanium dioxide. Low temperature sol–gel method belongs to the most popular techniques used to produce functional materials in optoelectronic devices, sensors or highly luminescent materials. The bulk xerogels have many advantages such as simple procedure and low cost of production. The mechanism of phase transition from sol–gel has been described in many books and articles [5–9]. Maturation of the gel is the next important process during which the condensation and crosslinking of molecules occurs, while the amount of retained solvent depends on its viscosity and the size of pores formed in the matrix. High porosity favoring the encapsulation of various compounds, the ability to control the shape, biocompatibility, good optical properties, good transparency are the main advantages of materials obtained by this method.

Rhodamine 6G is a strongly fluorescent dye of well defined spectroscopic properties in viscous and aqueous solutions, some polymer matrices or glasses [10–19]. It has been found in several reports that at high concentrations of the dye fluorescent dimers or higher order aggregates of Rh6G appear [15–22]. In the works devoted to hybrid materials containing fluorescent dyes bulk matrices have been prepared and studied. However, it is still not fully clear why in the case of concentrated fluorescent systems the results differ between laboratories [14,18]. In the case of dyes with partly overlapping absorption and fluorescence bands the concentration effects are of special importance for the interpretation of the data because of nonradiative and radiative energy transfer processes. This latter process can affect the results obtained in bulk matrices of high optical density, however, it is absent in matrices of low optical density (below 0.1). Therefore, especially interesting may be the comparison between nanolayers and powdered bulk materials containing dye at its high concentration. The second reason for the disagreement mentioned may be connected with different susceptibility of the dye to aggregate in very thin layers and in bulk materials. The formation of fluorescent or nonfluorescent dimers depends not only on the dye concentration but also on the molecule–matrix surface and molecule–molecule interactions which determines the geometry adopted by the two monomers.

---

* Corresponding author. Tel.: +48 58 5232280.
E-mail address: a.synak@ug.edu.pl (A. Synak).

http://dx.doi.org/10.1016/j.optmat.2014.01.026
0925-3467/

Finally, one has to take into account the time evolution of the physical and chemical properties of the matrix.

In this short report we present our preliminary analysis of these problems based on various steady-state and time-resolved spectroscopic techniques. In this study we will focus on Rh6G in TiO_2 matrix mostly because of quite well known aggregation properties of Rh6G in other media.

2. Experimental

2.1. Materials

All reactants used in this work were of analytical grade. Rhodamine 6G ([9-(2-ethoxycarbonylphenyl)-6-(ethylamino)-2,7-dimethylxanthen-3-ylidene]-ethylazanium chloride) was spectroscopically pure (dye content 99%) and it was purchased from Sigma–Aldrich (Germany). Titanium(IV) tetra(2-propanolate), propan-2-ol, poly(ethylene glycol), Triton X-100 and pentane-2,4-dione were purchased from Sigma–Aldrich (Germany). Ethanol, sodium hydroxide and hydrochloric acid were purchased from POCH Company (Gliwice, Poland). Deionized water was obtained from Hydrolab system installed in our laboratory.

2.1.1. Sample preparation

2.1.1.1. Thin films. The precursor solution for Rh6G/TiO_2 nanofilm was obtained using titanium(IV) tetra(2-propanolate), propan-2-ol, Triton X-100 and hydrochloric acid (37%). Separately, Rhodamine 6G was dissolved in ethanol. Next, both solutions were mixed together. Nanofilms were distributed over a clean piece of microscopic glass using spin-coating technique 90 min after starting the gelation process. A detailed procedure on nanofilms preparation can be found in our earlier work [23].

2.1.1.2. Bulk samples. TiO_2 xerogels were prepared by acid-catalyzed sol–gel method in a non-aqueous solution. Firstly, the precursor solution was obtained using Titanium(IV) tetra (2-propanolate); propan-2-ol and hydrochloric acid. Separately, Rhodamine 6G was dissolved in propan-2-ol. Next, both solutions (precursor and Rh6G solution) were mixed by vigorous stirring. The mixture (sol) was poured into polypropylene containers, which were covered and kept to form stiff gel for one month. Finally the samples were dried at room temperature and powdered.

2.2. Apparatus

The topography of a surface and structure of pores were analyzed using atomic force microscopy (AFM Nanosurf Easyscan 2) by scanning dry sample wafers (Ntegra Aura, NT-MDT), equipped with AFM dry scanner in the semi-contact mode. Images were analyzed using Gwyddion 2.30 software. The absorption spectra were measured with UV–VIS spectrophotometer Lambda 18 Perkin-Elmer equipped with a diffuse reflection holder for crushed samples. These measurements were carried out in the reflection mode. Fluorescence, time resolved emission spectra (TRES) and fluorescence decays were obtained simultaneously from a single measurement with the state-of-the-art pulsed spectrofluorometer of picosecond resolution designed in our laboratory and described earlier in detail [24]. The YAG:Nd pulsed laser together with PG401/SH optical parametric generator producing spectrally tunable light pulses (220–2200 nm) of about 30 ps FWHM serves as the excitation source. The emission signal was analyzed by a Bruker Optics 2501S spectrometer and the Hammamatsu streak camera C4334-01 model.

3. Results and discussion

Fig. 1 shows three-dimensional AFM image of the thin film Rh6G/TiO_2 and the bulk xerogel, respectively. The dimensions of the images are given in each subfigure. The average roughness of the surface of the bulk xerogel is 7.5 nm (without roughness of granules). This result can be compared with that recorded for thin film, for which the roughness is 0.4 nm. The granules visible on the surface of the bulk xerogel can be divided according to their shape into two categories: the slightly larger ones of regular and oval shape and the smaller granules which are geometrically irregular. The linear dimensions of granules in bulk materials are between 20 and 70 nm. In the case of thin films, however, the surface granules are absent. The surface of the bulk xerogel contains nanostructures with a pore size of about 30 nm, whereas the surface of Rh6G/TiO_2 thin films are smoother and more homogeneous.

(Fig. 2a and b) shows absorption spectra of Rhodamine 6G in titanium dioxide thin films (2a) and bulk xerogels (2b) at several selected concentrations of the dye at room temperature $T = 293$ K. It should be stressed that all the results of absorption spectra measurements are not distorted by artefacts. The absorption spectra evolve with concentration. We observed increased halfwidth of absorption spectra at the highest concentration for both types of material. In the case of thin films the formation a new absorption band with a maximum at around 480 nm at the highest concentration is observed. Additionally, the absorption spectra of Rh6G/TiO_2 thin films exhibit the existence of a well defined two isosbestic points at 520 nm and at 558 nm.

However, in the case of Rh6G in titanium dioxide bulk xerogels no well defined isosbestic points were found. These latter results

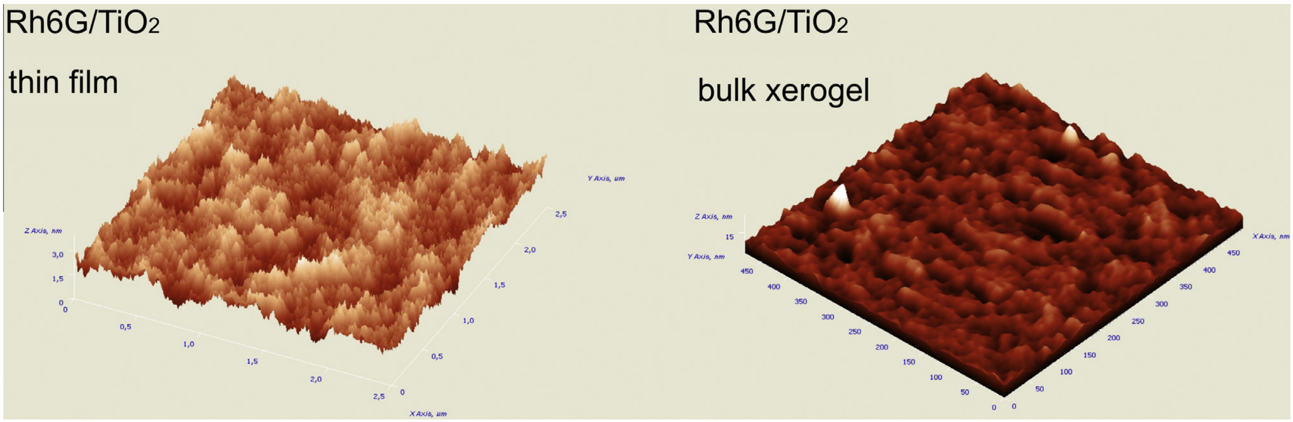

Fig. 1. Three-dimensional AFM images for Rh6G in titanium dioxide thin film and bulk xerogel at $c = 5 \times 10^{-3}$ mol/dm^3.