

Optical properties of nanoporous glass filled with TiO₂ nanostructures

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Titanium dioxide nanoparticles (NP) and nanofibers (NF) were incorporated from polymeric gels into porous glasses. Two types of glasses *A* and *B* with different porosity were chosen for measurements. Optical absorbance and photoluminescence spectra of the samples were measured at the range of 200–1100 nm and 370–800 nm correspondently before and after TiO₂ incorporation. The enhancement of TiO₂ photoluminescence (PL) and short-wave shift of peaks for samples *A* and *B* was found. The obtained results are explained by quantum confinement effects.

Keywords: porous glasses, titanium dioxide, nanofibers, nanoparticles, photoluminescence.

1. Introduction

Titanium dioxide is well-known material, applied for catalytic and photocatalytic oxidation of organic compounds. It is also used in hybrid solar cells to form *p-n* junction with organic semiconductors and in transparent optical coatings. TiO₂ is polymorphic material with two main phases – rutile and anatase, with optical band gap of 3–3.3 eV and absorption edge at 310–330 nm [1, 2]. Adsorptive and photocatalytic properties of titania can be improved by increasing the active surface area within forming particles of a nanometric scale [3]. The decrease in the particle size could lead to quantum confinement effects. The last results in the increase in the band gap value

and declining of operation temperatures. It is known that microcrystalline TiO_2 has no photoluminescent properties at room temperatures [4, 5]. However, a number of papers, concentrated on photoluminescence in TiO_2 nanostructures at room temperatures were published [2, 6]. In these papers photoluminescent properties of titania nanostructures were explained by free excitons in TiO_6 octahedron and oxygen vacancies. We suppose that the luminescence centres concentrate on the surface of titania nanostructures just as it takes place in AgBr nanoparticles [7].

For fabrication titania nanostructures different technologies were proposed such as sol-gel [8], laser ablation [9], and hydrothermal method [10]. The mentioned methods allow to obtain nanopowders with nanocrystallites, having well-defined structural properties. However, under keeping of nanopowder agglomeration processes may occur.

In the presented paper, porous glasses were filled in with TiO_2 nanoparticles and nanofibers to avoid agglomeration. Optical properties of obtained structures were studied. Quantum size effects resulted in shifts of photoluminescence maximums, and an increase in their intensity was observed.

2. Experiment

For optical measurements TiO_2 nanopowder (NP) (Sigma Aldrich, titanium (IV) oxide, anatase 637254 – nanopowder, <25 nm particle size, 99.7% trace metals basis) and TiO_2 nanofibers (NF) were used. TiO_2 nanofibers were prepared by the hydrothermal method. The detailed description of the technology is presented in [11].

Two types of porous glass *A* (with silica gel content) and *B* (cleaned of silica gel) prepared with the technique [12] have been used in the present work.

To fill in the porous glasses with titania nanostructures, TiO_2 nanofibers and nanoparticles were solved in 5% ethanol water solution. Polymeric substance of polyvinyl alcohol was added to a flask and stirred for 2 hours while stable suspension was obtained. The concentration of prepared titania solutions was 0.01 mol/l. Porous glass plates with linear dimensions $1 \times 1 \text{ cm}^2$ were exposed to the solutions of sol-gel for 2 hours. After the exposure the samples were annealed at 300 °C for 1 hour.

Typical pore-size distribution spectra in porous glasses are shown in Fig. 1. These spectra were obtained with the method of adsorption-desorption of water vapour, described in details in [13]. One can see three strongly pronounced fractions with pores radii of 8, 30 nm and more than 120 nm in the pore-size distribution spectra for *A*-glass. So, the pores with big dimensions are present in these glasses as well as the pores with small dimensions. For *B*-glass all the fractions in the pore-size distribution spectra are shifted to higher values of pores radii. TiO_2 nanoparticles had an average size of 30 nm and TiO_2 nanofibers had a diameter at the same range and 300–500 nm in length. Thus, TiO_2 nanoparticles can penetrate into medium sized pores but nanofibers can penetrate into big sized pores, recognized as percolation channels.

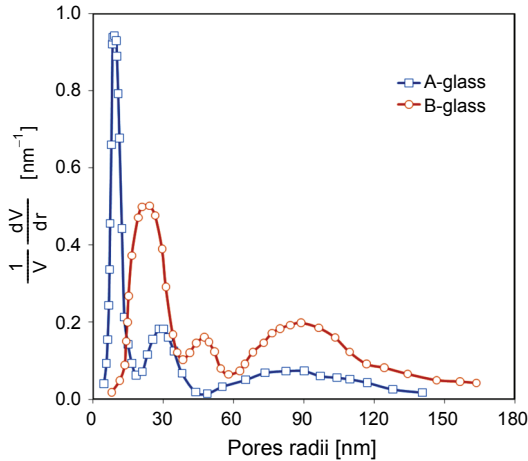


Fig. 1. Pore-sizes distribution spectra for *A*- and *B*-porous glasses.

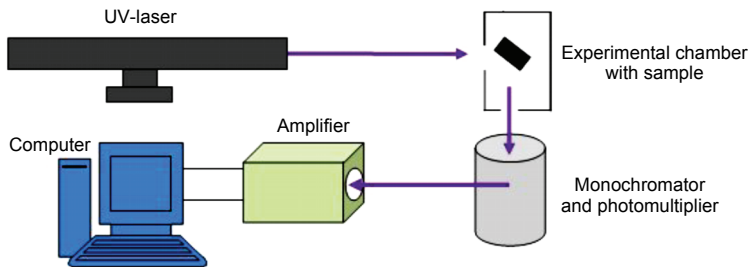


Fig. 2. Photoluminescence setup.

Optical properties were studied with the use of UV–VIS spectrophotometer Shimadzu UV-1700 in the range of 350–1100 nm. Photoluminescence (PL) spectra were measured by a setup, presented in Fig. 2. The photoluminescence was excited by UV laser LCS DTL-382QT with excitation wavelength $\lambda = 266$ nm. The emission spectra were amplified and recorded in the wavelength range of 370–800 nm. The obtained spectra were analyzed in Origin 7.0.

3. Results

Optical absorbance spectra of porous glass *A* and *B*, filled with titania nanofibers and nanoparticles are shown in Figs. 3a and 3b, respectively. From Fig. 3a one can see that the spectrum of porous glass *A* with titania nanoparticles was shifted to shorter wavelengths, whereas the red shift of spectra was observed after filling the porous glass *A* with titania nanofibers. In case of porous glass *B*, the red shift of spectra was observed in all types of titania nanostructures (Fig. 3b).

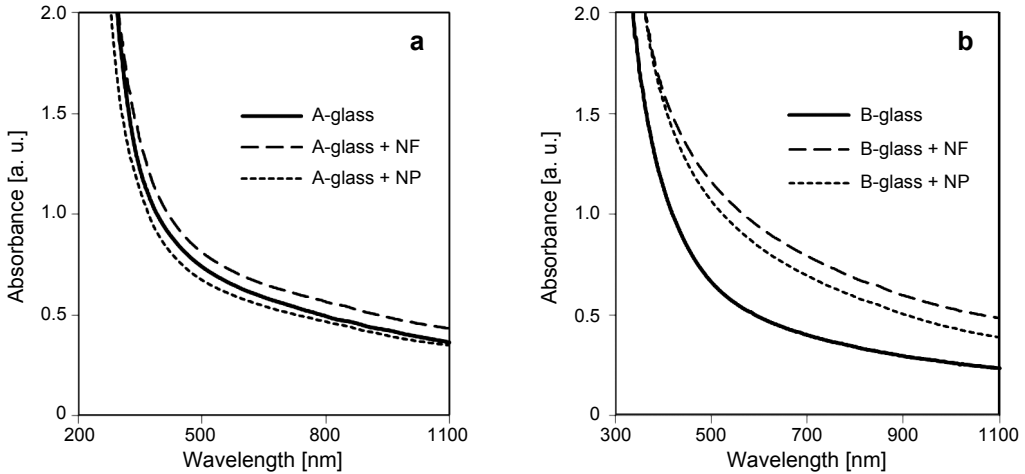


Fig. 3. Absorption spectra of porous glasses with inserted titania nanostructure: porous glass *A* (a), and porous glass *B* (b).

Photoluminescence spectra of porous glass *A*, filled with nanofibers and nanoparticles, are shown in Figs. 4a and 4b, respectively. Figures 5a and 5b show even spectra of porous glass *B*.

It can be seen from Fig. 4a that the insertion of titania nanofibers into porous glass *A* led to the drastic increase in PL intensity. The peak position practically did not change its position (a little shift is associated with the porous glass matrix). On the other hand, after the nanoparticles insertion into porous glass *A*, the peaks' intensity had almost the same values, whereas UV shift of peaks' position was observed (Fig. 4b). In case of porous glass *B*, which had no silica gel, the opposite effect was observed – PL spectrum of glass *B* with nanofibers has not been changed (Fig. 5a), whereas the insertion of titania nanoparticles into porous glass resulted in the increase in spectrum intensity and UV shift of PL peak (Fig. 5b).

4. Discussion

The UV shift of absorption spectra *A*-glass with titania nanoparticles can be explained by the quantum confinement effect (Fig. 3a). Nanoparticles penetration into small sized pores resulted in the UV shift of absorption spectra. Opposite to that, titania nanofibers could penetrate only into big sized pores what caused the IR shift of absorption spectra [1]. In case of *B*-glass (Fig. 3b), the IR shift of absorption spectra was observed for both titania nanostructures. It could be explained by bigger dimensions of pores in *B*-glass.

The analysis of PL spectra confirmed the above mentioned verification. In *A*-glass the concentration of pores with diameter 30 nm is minor. That is why the glow intensity of nanoparticles, which are impregnated into this glass, is also minor (Fig. 4b). In *B*-glass the concentration of pores with a suitable diameter is higher, which causes

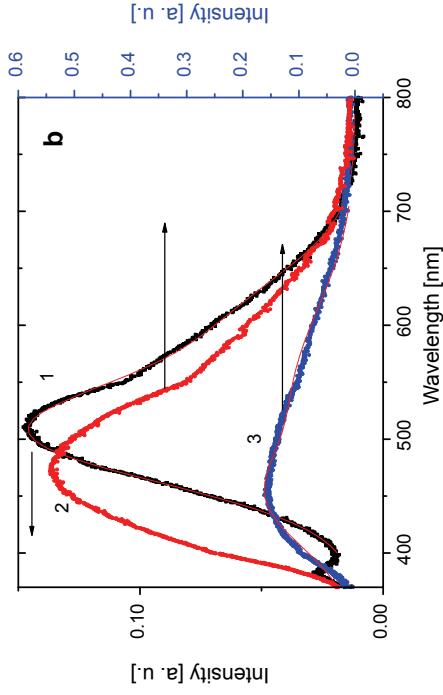
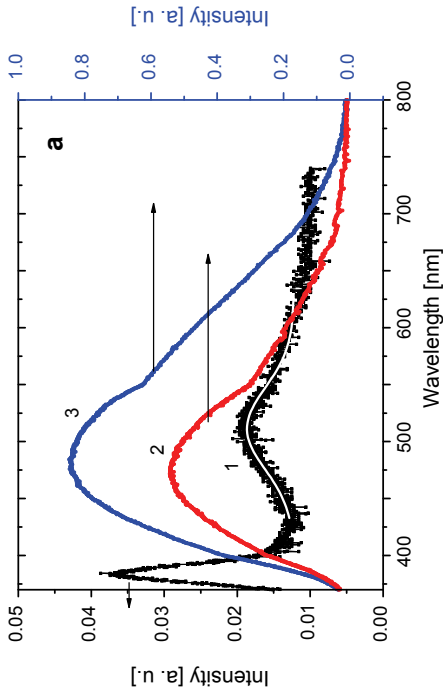


Fig. 4. PL spectra: 1 – TiO₂ NF, 2 – porous glass A with TiO₂ NF (a); 1 – TiO₂ NP, 2 – porous glass A with TiO₂ NP (b).

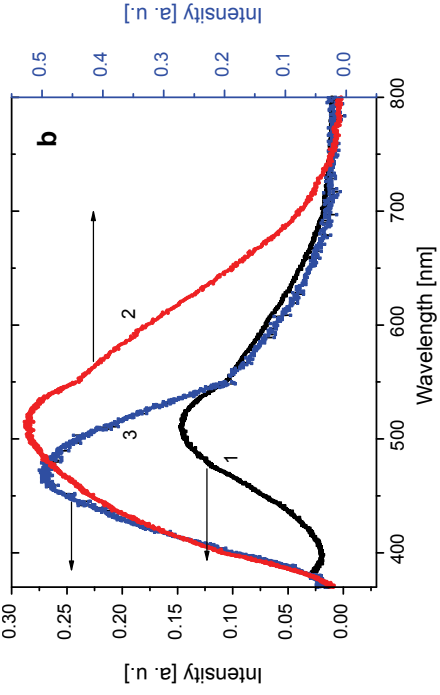
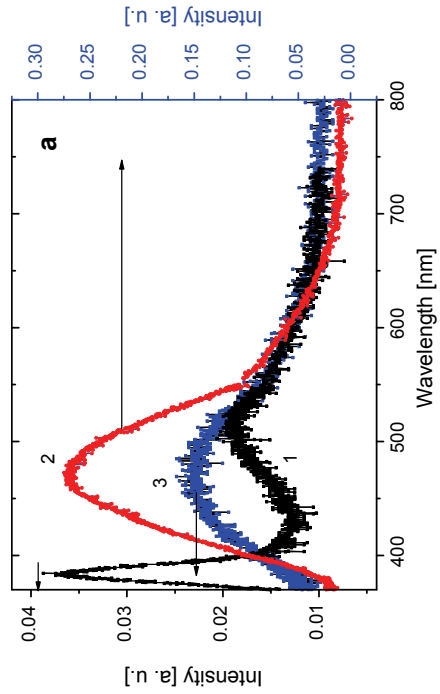


Fig. 5. PL spectra: 1 – TiO₂ NF, 2 – porous glass B with TiO₂ NF (a); 1 – TiO₂ NP, 2 – porous glass B with TiO₂ NP (b).

the PL intensity enhancement (Fig. 5b). In both cases the quantum confinement effect was observed, which appeared in UV shifts of PL peaks.

High intensity of TiO₂ nanofibers in *A*-glass (Fig. 4a) could be connected with silica gel, located in the pores. Titania nanofibers were covered with silica gel, when penetrated into the pore. The contact between neighbor nanofibers was prevented by silica gel insulation. Therefore, the silica gel insulation prevents aggregation of titania nanofibers. As a result of the light propagation effect, this type of surface is more effective for luminescence. In *B*-glass, aggregation of nanofibers may happen. Therefore PL spectrum has not been drastically changed (Fig. 5a).

5. Conclusions

Incorporation of TiO₂ nanostructures into porous glasses improves the investigation of their luminescent properties and makes them suitable for luminescent methods of measurement.

Absorbance spectra shifts after the incorporation of TiO₂ nanostructures into porous glasses are explained by quantum confinement effects.

Photoluminescence intensity of TiO₂ nanofibers and nanoparticles increased in the case of their incorporation into samples *A* and samples *B*, respectively.

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