CREATION AND SOME PRACTICAL APLICATION OF HYBRID TiO_2 AND SiO_2 SOL-GEL NANOCOMPOSITES

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Multifunctional hybrid TiO_2 and SiO_2 nanocomposites (films, powders) with new, unusual, properties are attracting a lot of attention as the latest nanomaterials for use in various areas of opto- and nanoelectronics, catalysis, biosensorics, fuel cells etc. Significant progress in this direction was achieved thanks to the application of controlled sol-gel synthesis, which opened up new technological possibilities for the creation of such materials.

Main idea of work: Develop of controlled sol-gel synthesis of hybrid TiO_2 and SiO_2 nanocomposites and demonstrated their practical application.

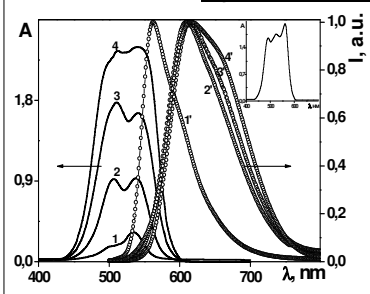
Experimental

The hybrid films were prepared by the one pot template sol–gel technique. Tetraethoxysilane or tetraisopropoxide titanium which served as a precursor of matrix was dissolved in ethanol and stirring. Pluronic P123 or CTAB served as template. These chemicals were dissolved in ethanol, distilled water and hydrochloric acid. The rhodamine 6G (Rh6G) dye was added to the obtained solution with different concentrations and ultrasonic mixed to form sol that was used for film formation. The hybrid films were prepared on different substrates (glass, mica, silica etc.) using spin- or dip-coating technique. After preparation, the films were aged at ambient temperature for 48 h.

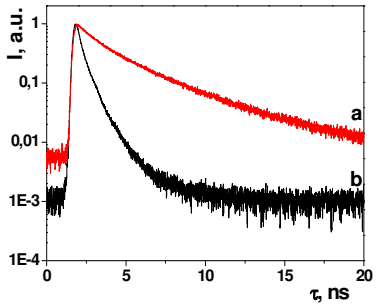
Doped by sulfur TiO_2 nanocomposites, labeled as TiO_2-S nanocomposites, were prepared using a method based on the controlled hydrolysis of titanium butoxide by water molecules produced by the esterification reaction between acetic acid and ethanol under catalyst of H_2SO_4 at different content with subsequent hydrothermal treatment. Composite membranes Nafion/TiO_2-S were prepared by spin-coating solution of polymer Nafion mixed with TiO_2-S nanocomposites using ultrasounds.

Obtained materials were characterized by FT-IR, XRD, SEM, TPD-MS, XPS, AFM, nitrogen adsorption/desorption, proton conductivity measurement, quartz crystal microbalance, thermogravimetric analysis, UV-VIS, stationary and time-resolved absorption and fluorescence spectroscopy.

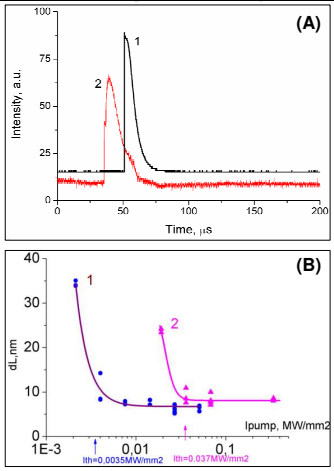
Hybrid films: spectral-luminescence properties and possibility of the useful application

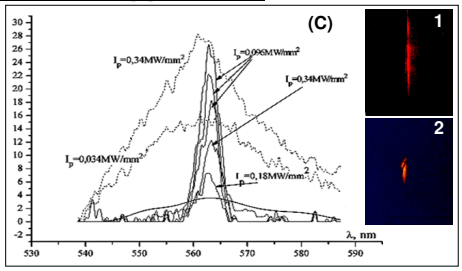


Absorption spectra and normalized fluorescence spectra of hybrid mesostructured films with different concentration of Rh6G, M:
1 - $2{\cdot}10^{-3}$, 2 - $2{\cdot}10^{-2}$, 3 - $1{\cdot}10^{-1}$, 4 - $1{,}5{\cdot}10^{-1}$.
The differential absorption spectra 4 are shown in the inserts.



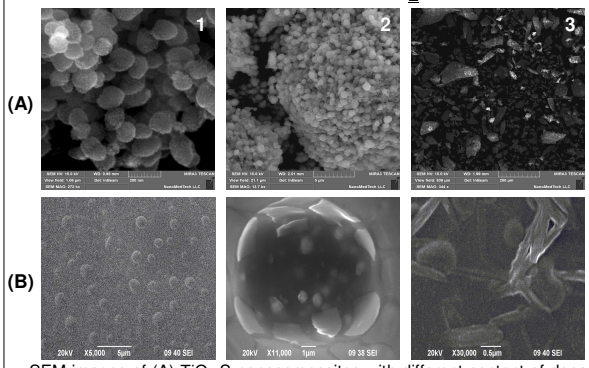
Fluorescence lifetimes of rhodamine 6G incorporated in body of hybrid film (a) and in water solution (b).



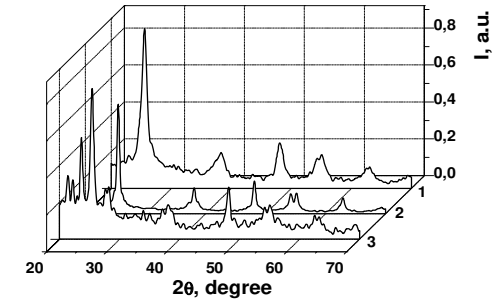


(A) Oscillogram of output intensities in first diffraction orders: 1 - probe beam, 2 - self-diffracted beam.
(B) Narrowing of the radiation spectrum under pumping increase of the hybrid films TiO_2/P123/Rh6G (1) and SiO_2/P123/Rh6G (2).
(C) Laser emission from surface of doped mesostructured film as planar waveguide and photos of lasing without (1) & with short focus lens (2).

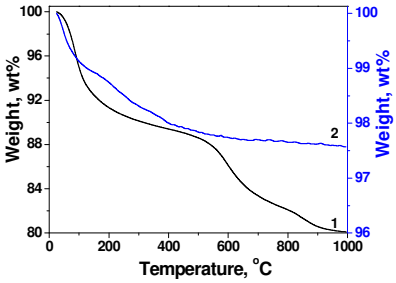
TiO_2-S nanocomposite and Nafion/TiO_2-S composite membrane



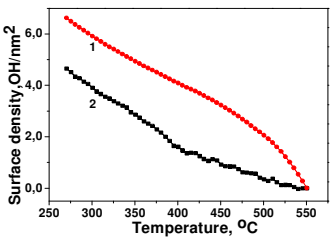
SEM images of (A) TiO_2-S nanocomposites with different content of dopant: 1 – 0,75; 2 – 1,5; 2 – 3,0 and (B) composite membrane Nafion/TiO_2-S.



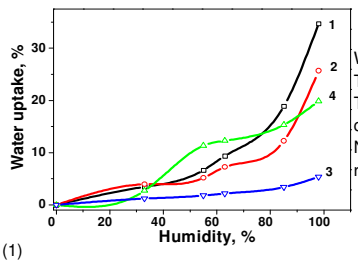
XRD pattern of TiO_2-S nanocomposites with different content of dopant: 1 – 0,75; 2 – 1,5; 3 – 3,0.



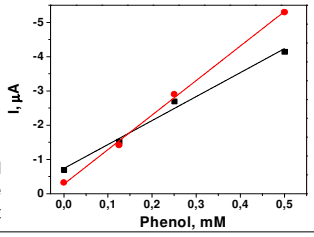
Thermogravimetric analysis of TiO_2-S nanocomposite (1) and TiO_2-Degussa (2).



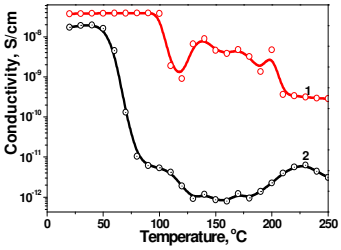
OH surface density of TiO_2-S nanocomposite (1) and TiO_2-Degussa (2).



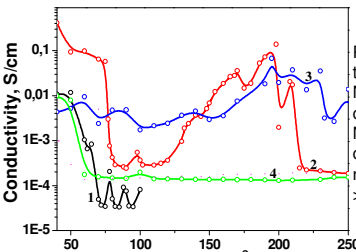
Water uptake of the: Nafion (1), TiO_2-S nanocomposite (2), TiO_2-Degussa (3) and composite membrane Nafion/TiO_2-S (4) under different relative humidity.



The calibration curves for biosensor analysis of phenol in the spiked communal wastewater samples using a "standard addition mode": (red) the sample diluted 40 times, (black) the sample diluted 10 times.



Conductivity of TiO_2-S nanocomposite (1) and TiO_2-Degussa (2).



Proton conductivity in medium temperature region of the Nafion membrane (1) and composite membrane Nafion/TiO_2-S at various concentration of TiO_2-S nanocomposite: 1% (2), 3% (3), >>3% (4).

Conclusion

The sol-gel technique was elaborated for successful fabrication of the high-quality hybrid sol-gel mesostructured films, doped by Rh6G and TiO_2-S nanocomposites.

Established that increasing of the concentration of dye in films don't lead to dimerization and strong fluorescence quenching. In our case, fluorescence yield is about 36 times higher in comparison with solutions. In tested regime, we had shown the successful ability of hybrid films for exploration as the photonic layer in all-optical time-to-space converters. We have obtained the recording of a dynamical grating in a single-pulse regime. The hybrid sol-gel films were studied as waveguide laser medium.

Established, that the modified TiO_2-S nanocomposites due to the nature of their composition and structure have a strong capacity for coordination of water molecules on the surface due to polarization of water molecules on the acid group of titanium surface. Preliminary tests of proton conductivity (the direct injection of protons) that was carry out on the Nafion/TiO_2-S composite membrane, has highlighted the benefit of doped titanium nanocomposites introduction on the conductivity in the temperature range up to 240 °C, that maintained at 10^{-5}-10^{-2} Cm, compared to the commercial Nafion membrane.

The results may be a prerequisite for the efficiency of composite polymer membranes Nafion/TiO_2-S in conditions close to operating parameters of the PEM fuel cell in middle temperature range.

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