Luminescent materials based on nanoparticles of silicon dioxide for solar cells

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Abstract. The report considers luminescent mesoporous silica dioxide particles of activated RE ions and lead sulfide nanocrystals of different sizes. For the purpose of assessing the possibility of converting by lead sulfide nanoclusters of solar radiation into the red-orange light, the following methods will be drawn to the attention: mesoporous silica particles sol-gel synthesis, additional light scattering method as an additional approach for the determination of particle size. The element composition of a particle size of 300 ± 40 nm was identified using the scanning electron microscope with the system of energy disperse analysis. Particle images were obtained using the field scanning electron microscope. Zeta Potential Analyzer was used to measure the surface charge of the particles. Particles in solution were excited by near ultraviolet and visible light. The intensity of intrinsic emission was registered in the range of 400-550 nm. The diagnosis made visible the electron induced energy transmission from the matrix to the Eu³⁺ and Tb³⁺. Emission of Eu³⁺ and Tb³⁺ has been registered at 300K. It is assumed that the identical matrices could work as converters of solar emission spectrum, to which some solar cells are sensitive.

1. Introduction

Luminescent silica (LS) sol-gel materials grade promising environmentally friendly class of phosphors resulting from the carboxylic acid catalyzed condensation of alkoxysilane or aminopropyltriethoxysilane precursors [1]. It is also possible to use luminescent silica as solar emission converters [2, 3]. Conversion of solar emission into electrical energy is performed by semiconductor photovoltaic converter (PVC). Efficiency of conversion is about 25% in the laboratory and 10-15% in the production conditions, which is much inferior to conventional energy sources. Solar silicon cells are sensitive only to a certain spectral range of the continuous spectrum of solar radiation. It amounts 20-30% of the entire spectral range of the solar spectrum. The increase of efficiency based on silicon is carried out follows: luminescent nanocrystalline films of various sizes are placed on the surface of silicon. Luminescence of different energy that occurs during the solar radiation can be collected from each film layer. This increases the overall efficiency of PVC with a set of nanocluster films. Luminescent materials that convert ultraviolet and visible solar radiation into the red light are
placed on the silicon surface in the form of a film. This way the efficiency of PVC based on silicon can be increased.

To produce luminescent silica we used the same synthesis technique as described in previous letter [4]. The paper provides additional information about physical properties of luminescent silica material.

2. Experimental conditions
All photoluminescence measurements of luminescent silica spheres were performed in 3 g of a 30/70 ethanol/toluene mixed solvent. The solvent ratio was chosen to minimize scattering effects with the spheres by refractive index matching. We used LMCS spheres after 6 hours of 200°C calcination. This calcination terms leads to most significant photoluminescence of the LMCS particles relatively to another calcination conditions [4]. Particles concentration was 0.3 mg/ml. 1/10 (lanthanide/LMCS) mass of Eu or Tb chloride was doped into silica spheres suspended in ethanol/toluene solution using ultrasonic bath.

Photoluminescence spectroscopy data were performed with the CM2203 spectrofluorometer. Monochromator slit widths for both the emission and excitation were set to 2 nm band-pass.

For SEM images, LMCS solution was deposited on a doped silicon wafer and the solvent was evaporated. SEM imaging performance assisted with Raith 150 SEM/Leo Gemini Column and JOEL-6460LU with the EDAX system. 10 kV voltage acceleration was applied. Brookhaven Corp. light scattering technique was used as an additional method for the determination of particle size. Brookhaven Corp. Zeta Potential Analyzer was used to measure the surface charge of the particles.

3. Results and discussion.
Mesoporous colloidal silica spheres possess the desirable properties of low polydispersity at the sub-micron level and very high surface area resulting from the mesoscale porosity. The LMCS spheres used in this manuscript had an average diameter of 377 nm and respective standard deviation of 3% (Figure 1).

![SEM of LMCS (TAP6) after calcination.](image)

Energy dispersive analysis results of LMCS particles are in good agreement with the theoretical expectation. The ratio of the intensities of the peaks for silicon (Si) and oxygen (O) is 1:2, as expected for a SiO$_2$ compound. The index shows peaks of carbon and nitrogen impurities. These atomic weights of LMCS based on k(α)-lines intensities are given in Table 1.
Table 1. The atomic content of the elements in LMCS

| Sample# | C k(α) | N k(α) | O k(α) | Si k(α) |
|---------|--------|--------|--------|---------|
| S1*    | 16.56  | 3.67   | 51.09  | 28.69   |
| S2     | 29.19  | 6.00   | 41.57  | 23.24   |
| S3     | 27.10  | 4.92   | 40.05  | 27.86   |
| S4     | 20.55  | 4.61   | 48.77  | 26.08   |

*S1 - TEOS, S2 - TAP noncalcined, S3 - TAP6, S4 - TAP48 [4].

Dynamic light scattering method for TEOS particles [4] gives their sizes with very wide range. Figure 2 shows standard distribution for sizes of given particles. However, SEM analysis demonstrates monodisperse-like distribution. A discrepancy in the data should be attributed to the partial aggregation of the particles in ethanol/toluene solution.

![Figure 2. The statistical distribution of TEOS particles sizes.](image)

Potentiometric measurements indicate the presence of a positive charge on the particle surface. For noncalcined particles, the charge value is $43.5 \pm 0.0216$ mV, for 6 hours at 200°C calcined particles, the value is $48.52 \pm 0.0167$ mV. The positive charge of the noncalcined particles can be attributed to the presence of NH$_3^+$ groups on the particle surface. After doping lanthanides chlorides to the calcined particles, the surface charge increases up to $56.45 \pm 0.0272$ mV.

Photoluminescence spectroscopy data have been collected for different excitation wavelengths. The excitation was fixed at 314, 320, 360, and 378 nm according to luminescence excitation spectra of calcined LMCS (Figure 3).

Figure 3 shows most significant excitation wavelength for calcined particles at 378 nm. As expected, LMCS particles give highest luminescence when exited at 378 nm (Figure 4). Comparing the emission spectra obtained under excitation at 320 nm [4] and at 378 nm, the maximum intensity of the last one is $\sim 7$ times higher.
It is important to note that the high emission intensity of silica dioxide system provides matrix-to-lanthanide energy transfer. Thus, next step of the current research is to provide photoluminescence measurements of LMCS particles doped with lanthanides and excited at optimum excitation energy for matrix.

This research was sponsored by Ministry of Education and Science of the Republic of Kazakhstan, Award #511, from 05.04.2012.

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