



Luminescent siliceous materials based on sodium silicate, organic polymers and silicon analogs



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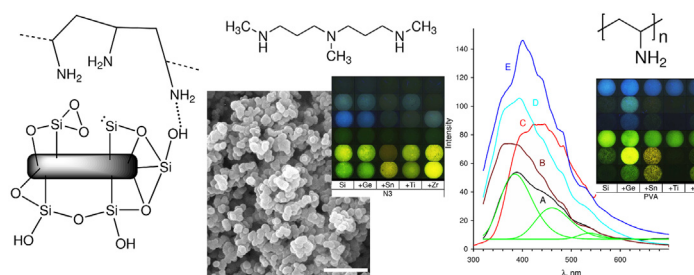
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HIGHLIGHTS

- New composites were obtained from silicic acid, organic polymers and silicon analogs.
- The composites show considerably intensive luminescence comparing with pure silica.
- The luminescence spectra and lifetimes are similar to pure silica.
- The additives allows to control morphology of the highly luminescent particles.

GRAPHICAL ABSTRACT



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ABSTRACT

A new composite materials of various particle morphology were obtained by silicic acid condensation in the presence of oligomeric polyamine, poly (vinyl amine) or co(1-vinylimidazole - acrylic acid). These organic compounds are the models of biopolymers which participate in synthesis of siliceous structures in living organisms. Hydroxides of silicon analogs (Ge, Ti, Zr and Sn) were also applied as additives in the composite synthesis. The obtained materials show greatly more intensive luminescence comparing with pure silica without essential changes in luminescence spectra and lifetimes. We suppose the increase in emission intensity under the action of organic and inorganic additives is connected with increase of concentration of the luminescence-active defects which present in pure silica. Our results show possibility to obtain bright luminescent siliceous materials with controllable nano- and micro-level morphology by the action of polymeric amines and silicon analogs.

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1. Introduction

Fluorescent and photosensitive materials are actively studied nowadays in the connection with production of various electronic

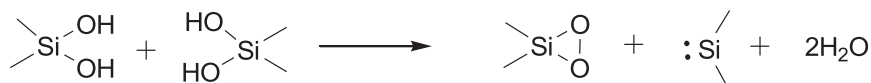
devices, displays, elaboration of new visualization approaches in medicine and biology. Photocatalytic decomposition of the water is a promising way to effective utilization of the solar energy [1,2]. Siliceous materials and composites are considered as highly promising compounds because inorganic matrix is stable and cheap and silica morphology is controllable by the means of sol-gel methods [3–6]. The nanosized silica particles having high surface-volume ratio demonstrate peculiar properties such as bright visible

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photoluminescence under ultraviolet (UV) excitation [7]. Therefore silica nanoparticles are promising for medical nanoprobes without need to doping with bright extrinsic fluorophores [8].

Pure non-doped silica is capable of photoluminescence in blue, green and red regions of the electromagnetic spectrum due to defects present in its structure. Particularly, a weak photoluminescence within about 430–600 nm ($\lambda_{\text{exc}} = 390$ nm) was observed for polysilicic acid [9]. Under the excitation of 325 nm high purity pristine silica samples gave a photoluminescence spectrum, which after mathematical processing revealed the existence of two luminescence bands centered at 550 nm and 450 nm [10]. Uchino et al. in paper [7] proposed a model of the blue-light-emitting center in silicon and silica-based materials on the basis of the density functional theory calculations and experimental results. There are several types of luminescent centers in silica and siliceous composites. The first type of the centers is various defects in the silicon dioxide structure, including nonbridging oxygen hole centers (NBOHC, Si–O•) and two types of oxygen-deficient centers (ODCs, Si•, Si••Si) [10–13]. The luminescence spectra of porous material and nanoparticles is similar to the ones in bulk silicon dioxide. The second type is surface defects in silicon and silica nanoparticles. There are defect structures arising under heating of the siliceous materials, e.g. dioxasilirane, =Si(O2) and silylene = Si: obtained from hydrated silicon [7,14–16]:



Photoluminescence from these centers is characterized with short lifetimes (<20 ns) which points on singlet-singlet transitions. There are no definite assignment of the luminescence band to defects in silica structure, moreover the bands positions are often calculated from the Gaussian model fitting [17].

The third type of luminescent centers was observed in silica doped with silicon analogs such as carbon [18–21], germanium [22–29] or tin [4,27,30,31] ions which increase luminescence in violet-blue region due to developing of the defect structures similar to structures in pure silica. Introducing of silicon analogs (Ge, Ti, Zr and Sn) can give five- or sixfold oxygen atoms which were described for titanium and zirconium [32–35]. The presence of organic compounds in composites can results in luminescence of these compounds or products of their thermodestruction, e.g. 2–3 nm carbon nanoparticles [36].

Morphology of the luminescence siliceous material is an important factor for its application. Alkoxysilanes are used for a long time as precursors for synthesis of uniform silica particles [3, 4, 37 and references in these works]. Water-based systems applying sodium silicate become promising last decades because of cheapness and ecology friendliness. Some living organisms can build fine skeletons from silicon dioxide (practically pure melting quartz glass), the most known of them are frustules of diatom algae [38] and spicules of siliceous sponges [39]. Study of the silicifying organisms resulted in an increased attention to polymeric amines as the substances which catalyze condensation of silicic acid and control morphology of the obtained silica or composite particles. These polymers and oligomers are probably play an important role in silicon assimilation by the living cells and in building of the resulting biosilica [40]. Synthetic polymeric amines are considered as models of biopolymers and as reagents

for bioinspired production of siliceous materials with controllable structure [41–43]. Recently [44] we have found that Ti(IV), Ge(IV), Zr(IV) and Sn(IV) influence on the silicic acid condensation in the presence of polymeric amines. These elements belong to the same group in the short variant of Periodic Table as silicon and so they are considered as silicon analogs. Interaction between organic polymer and primary silica nanoparticles is enhanced in the presence of these elements which was explained with their “metallic” properties and high activity (compared to silicon) to form complexes with a coordination number greater than four [45].

The aim of this work is to synthesize siliceous materials doped with the silicon analogs and to study their luminescent properties. Poly(vinyl amine) (PVA), co(1-vinylimidazole - acrylic acid) (VI-AA) and N-methyl-N,N-bis[3-(methylamino)propyl]amine [tri(1-methylazetane) (N3) (Fig. 1) were applied as reagents capable to control morphology of the siliceous particles. Silicic acid condensation in the presence of these reagents in aqueous medium has been studied previously and results in <100 nm nanoparticles (PVA [40], VI-AA [46]) and 200–300 nm spherical particles (N3 [47]). Silicon analogs Ti(IV), Ge(IV), Zr(IV) and Sn(IV) were added with the objective to enhance possibilities to the morphology control and to influence on luminescence of the obtained materials.

2. Materials and methods

2.1. Materials

The inorganic salts (Na_2SiO_3 , ZrCl_4 , TiCl_4 , Na_2GeO_3 , Na_2SnO_3) and other chemicals were purchased from Sigma Aldrich, Fisher or Acros Chemicals and used without further treatment. Silicon and other Group IV elements were used as 100 mM stock solutions of Na_2SiO_3 , Na_2GeO_3 , TiCl_4 and ZrCl_4 and 10 mM stock solution of Na_2SnO_3 . Polyamine N3 was obtained according to [48]. PVA was obtained by alkaline hydrolysis of poly(vinyl formamide) [43,49] and VI-AA copolymer (44 mol.% VI units) was synthesized by radical copolymerization [50]. Molecular weight of the PVA and VI-AA samples was 231,000 and 1,060,000 respectively.

2.2. Composite synthesis and characterization

The composite precipitates were obtained by mixing of a polymer (N3, PVA or VI-AA) stock solutions with sodium silicate and dopant solutions. The silicon analogs were added in the amount corresponding to 10 mol % from total silicon and dopant concentration. Water was added up to the desired volume (10 mL) and pH was adjusted to 7, 5.5 and 5 for N3, PVA and VI-AA systems respectively using concentrated and 1 M HCl. The solutions with precipitates were stored for two days at room temperature, centrifuged (3500 g, 20 min), washed with water (3 times) and freeze-dried. Details of the composite synthesis and yields of the products are summarized in Table 1. Composites were calcinated at 550 °C during 10 and 30 min, the obtained samples are labeled by addition “\10” or “\30” to the initial sample abbreviation.

Composition of N3-based composites was determined with FTIR spectrometry using Si–O–Si (1090 cm^{-1}) and alkyl (1465 cm^{-1}) bands. Calibration mixtures were prepared from N3 and silica gel

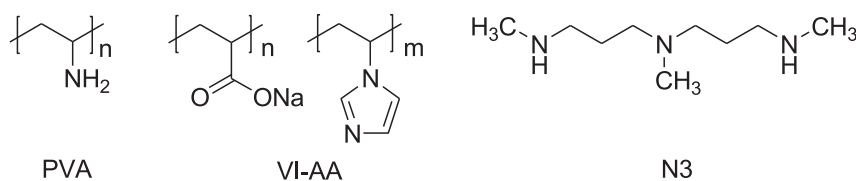


Fig. 1. Structures of poly (vinyl amine) (PVA), co(1-vinylimidazole - acrylic acid) (VI-AA) and N-methyl-N,N-bis[3-(methylamino)propyl]amine [tri(1-methylazetane) (N3)].

Table 1
Synthesis of the composites.

Label	Polymer	Dopant	Concentration of the components, mM			HCl added, mL ^a		pH	Yield, %
			Na ₂ SiO ₃	Dopant	Polymer ^b	Conc.	1 M		
N3-0	N3	–	13.0	–	13.0	–	0.434	7.13	41.4
N3-Ge	N3	Ge	11.9	1.3	13.2	–	0.347	7.16	36.6
N3-Sn	N3	Sn	11.9	1.3	13.2	–	0.343	7.17	54.4
N3-Ti	N3	Ti	12.0	1.3	13.3	–	0.255	7.18	45.3
N3-Zr	N3	Zr	12.0	1.3	13.3	–	0.274	7.13	52.1
PVA-0	PVA	–	22.5	–	15.0	–	0.442	5.76	21.8
PVA-Ge	PVA	Ge	20.3	2.2	15.0	–	0.449	5.70	54.5
PVA-Sn	PVA	Sn	16.9	1.9	12.5	–	0.389	5.50	78.3
PVA-Ti	PVA	Ti	20.2	2.3	15.0	–	0.321	5.70	73.5
PVA-Zr	PVA	Zr	20.2	2.3	15.0	–	0.365	5.60	73.0
VI-AA-0	VI-AA	–	28.4	–	19.2	0.016	0.511	4.80	81.7
VI-AA-Ge	VI-AA	Ge	25.7	3.0	19.5	0.024	0.435	4.89	78.2
VI-AA-Sn	VI-AA	Sn	25.8	2.9	19.3	0.021	0.430	4.94	83.2
VI-AA-Ti	VI-AA	Ti	25.98	2.92	19.48	0.007	0.371	5.05	83.8
VI-AA-Zr	VI-AA	Zr	25.97	2.89	19.48	0.014	0.369	4.84	82.9

^a Total volume of the solution with sodium silicate, dopant and polymer was 10 mL.

^b Calculating on the monomer units.

(Panreac, silica gel 60, 63–200 μm). Composition of PVA-based precipitates was determined by dissolving of 3–5 mg in 1 ml of 0.3 M NaOH at 60 °C during 3 h. Silicon concentration in the resulted solutions was measured by the molybdate method [51]. Silica content in the precipitates was calculated based on silicon content in silica obtained from 0.1 M Na₂SiO₃ by precipitation with 1 M HCl at pH 5.5. Composition of the material based on VI-AA copolymer was determined in Ref. [46] by the same way. FTIR spectra of the doped and non-doped samples (Fig. 1 in SM) do not show influence of the silicon analogs on the composition of the products obtained with PVA and VI-AA.

Elemental analysis of the samples was performed with ICP-MS method using an Agilent 7500ce quadrupole mass spectrometer. Samples of the composites (1 mg) were treated with concentrated HF (50%, 3.5 μl), HNO₃ (70%, 110 μl) and 30% H₂O₂ (10 μl) in a closed 15 ml polypropylene tubes (Falcon type) at 80 °C for 2 h. After cooling the tubes 0.165% EDTA was added up to 4 ml. A blank samples were prepared from composites without silicon analogs and pure reagents without any composites.

2.3. Instrumentation

Scanning electron microscopy (SEM) was performed using an FEI Quanta 200 instrument. An acetone suspension of the composite precipitate was placed on aluminum sample holder and then sputter coated with gold using an SDC 004 (BALZERS) device. The coating settings (working distance 50 mm, current 15 mA, time 75 s) correspond to 12 nm of gold coating, according to the device manual.

Qualitative study of the luminescence was performed with Axiovert 200 epifluorescence microscope with excitation at 365 and 470 nm. Samples (3 mg) were placed into 96-well flat-bottom cell culture plates (Nunclon, Cat. No. 167008). Semi-quantitative estimation of the luminescence intensity was performed by

calculation of the average pixel brightness. Study of organic luminescent admixtures in the composites was performed by dissolution of the sample (1 mg) in 0.1 mL of 44% HF. 0.05 mL of the obtained solutions were placed into 96-well flat-bottom cell culture plates and studied with epifluorescence microscope.

Photoluminescence spectra were obtained with Perkin-Elmer LS-55 instrument at 25 and -196 °C. The width of monochromator slits was 15 (input) and 6 (output) nm. All excitation spectra were recorded using the wavelength of the emission maximum as the emission wavelength. Emission is presented without spectral correction due to flat response of the detection channel in the measured spectral range. Powder samples were filled in high purity quartz tubes and placed in an ESR quartz cold-finger. The dewar was mounted into the spectrofluorimeter so as to block a pathway of the excitation light scatter.

The lifetimes for blue luminescence were measured with a FluoTime 200 luminescence lifetime spectrometer (PicoQuant GmbH). Semiconductor picosecond laser with $\tau_0 \approx 180$ ps pulse duration (FWHM), 20 MHz repetitions frequency, and wavelength of $\lambda_{\text{exc}} = 375$ nm was used as an excitation source, emission was recorded at 450 nm. The luminescence decays were fitted by the FluoFit Pro 4.5.3 (PicoQuant GmbH) software package using common multiexponential model.

The lifetimes for blue and green-red luminescence were also measured using nitrogen laser and argon discharge lamp operated on 337 and 470 nm respectively, 12.6 ns pulse duration, 50 Hz repetitions frequency, 50 ns impulse delay from the synchronization signal. The signal recording at 440 and 530 nm was performed with a grating monochromator MDR2, a photomodule Hamamatsu H6780-04, and an oscilloscope Rigol DS1202CA.

3. Results and discussion

The siliceous materials doped with Ge (IV), Sn (IV), Ti (IV) and Zr

(IV) were obtained similar to our previous works [43,46,48] by neutralization of aqueous solution of sodium silicate and organic component. Introduction of the silicon analogs was performed by substitution of 10 mol % of sodium silicate with the dopant hydroxide. Yields of the composites (Table 1) change from 22 to 84% depending on the polymer and silicon analog nature. PVA is known as polymer capable of stabilizing silica nanoparticles in the solution [40] which explains low yield of the composite based on sodium silicate. The addition of the silicon analogs to PVA-based system increases yields especially with Zr, Ti and Sn in accordance with metallic properties of these elements and their ability to interact with PVA by donor-acceptor bonds. Coordination of PVA chains with metal ions can result in cross-linking and precipitation of the soluble nanoparticles. N3 is not a long-chain polymer and it acts as catalyst of silicic acid condensation [45] but it is not involved into the precipitates in a considerable amounts which results in a low influence of the silicon analogs on the yields of composites. VI-AA copolymer provides a high yield of the siliceous composite without any dopant and the addition of silicon analogs does not influence on the yield. Elemental analysis (Table 1 in Supplementary Materials (SM)) confirms including of the dopants

into the materials. Content of tin, titanium and zirconium corresponds to inclusion of the whole amount of the dopant into composite which is in agreement with the possibility of these ions to form complexes with nitrogen-containing ligands. According to our previous data [46], composite based on sodium silicate and VI-AA contain 57% of the organic polymer. PVA composite contains 60% PVA according to silicon analysis with the molybdate method [51]. IR spectra of the samples obtained with the addition of silicon analogs (Fig. 1 in SM) do not show influence of the dopants on composition of PVA and VI-AA-based materials. According to FTIR data, the products with N3 contain 3.5, 5, 10, 18 and 6% of N3 for non-doped system and Ge, Sn, Ti, Zr respectively.

The composite precipitates obtained by silicic acid condensation in the presence of organic additives consist of submicrometer particles ≈ 150 and 70 nm in diameter for N3 and PVA systems respectively and of merged nanoparticles in the case of VI-AA (Fig. 2).

Introduction of Ge (IV) into N3-based composites does not influence on the particle morphology, the other dopants decrease particle size to 60–90 nm and in the case of Sn (IV) ≈ 400 nm particles are observed (Fig. 2 in SM). The dopants do not change

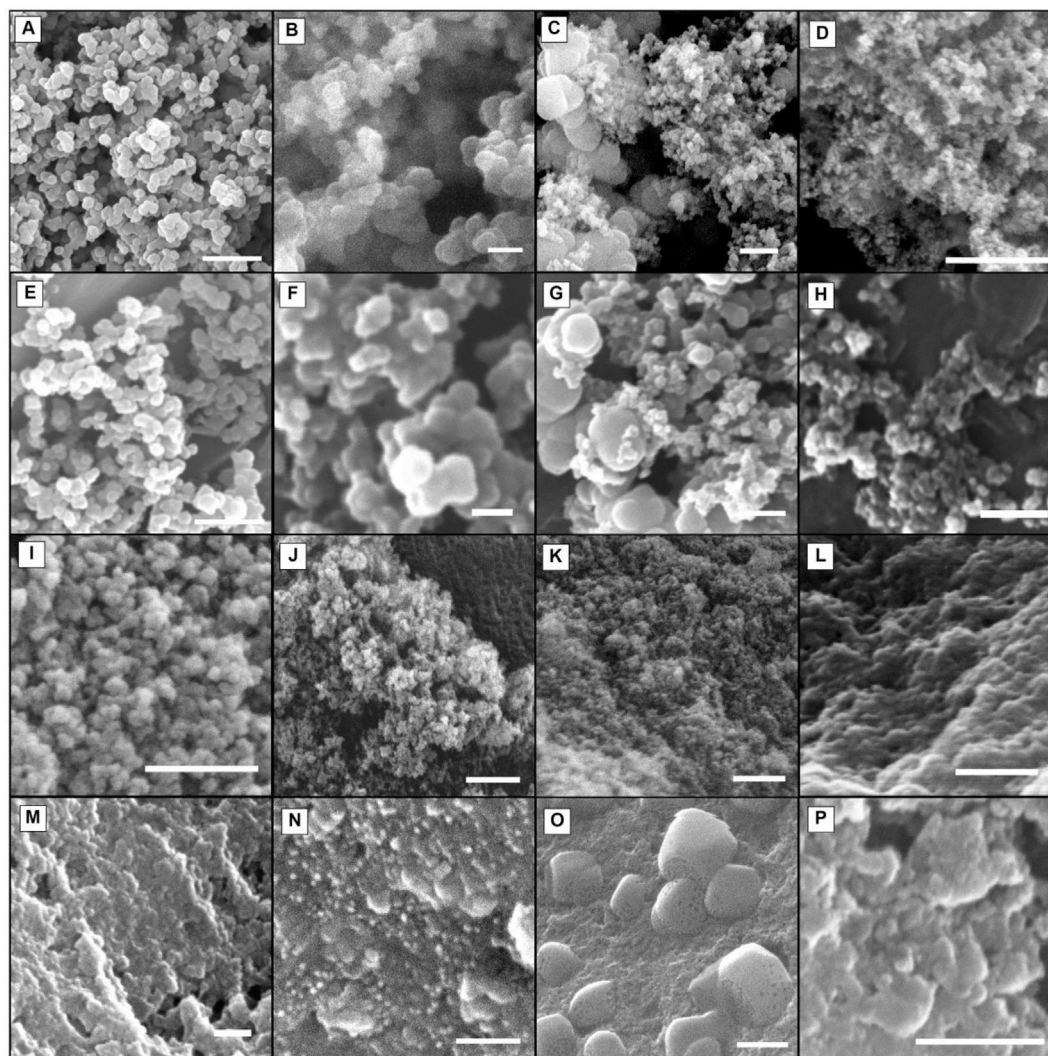


Fig. 2. SEM images of composites N3-0 (A), N3-Ge (B), N3-Sn (C), N3-Zr (D), N3-0/30 (E), N3-Ge/30 (F), N3-Sn/30 (G), N3-Zr/30 (H), PVA-0 (I), PVA-Ge (J, K), VI-AA-0 (L), VI-AA-Sn (M), VI-AA-Sn/30 (N), VI-AA-Ti (O), VI-AA-Ti/30 (P). The samples with “/30” in the label were heated at 550 °C for 30 min. Scale bar represents 1 μm (A, D and P), 500 (G-L and O) and 250 (B, C, F, M and N) nm.

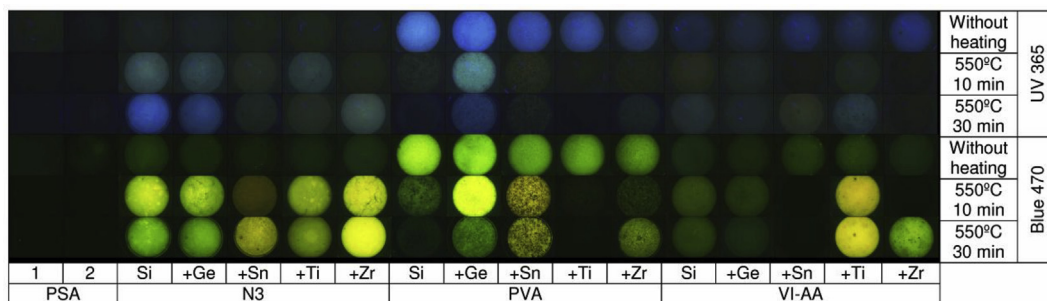


Fig. 3. Luminescent images of the composite precipitates placed into 96-well array plates. Excitation – 365 and 470 nm. PSA: 1 – silica gel for flash chromatography (PSA-1); 2 – silica precipitated from 100 mM sodium silicate with 1 M HCl at pH 5.5 (PSA-2). The conditions of microphotography (power of the lamp, diaphragm, and exposure) were identical in all cases.

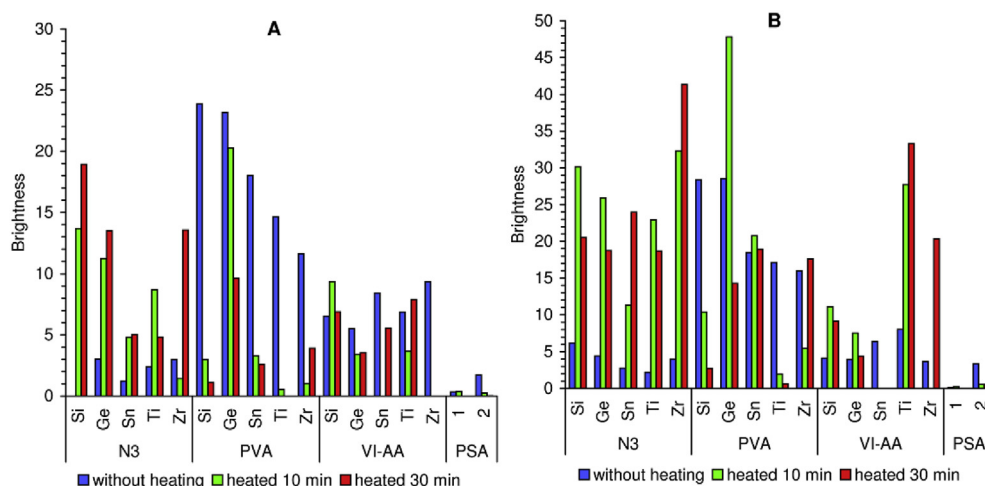


Fig. 4. Semi-quantitative data of the luminescence intensity under 365 (A) and 470 (B) nm excitation. Without heating – composite precipitates without thermal treatment, heated 10 min – samples after 10 min heating at 550 °C, heated 30 min – samples after 30 min heating at 550 °C. PSA: 1 – silica gel for flash chromatography (PSA-1); 2 – silica precipitated from 100 mM sodium silicate with 1 M HCl at pH 5.5 (PSA-2).

considerably the particle size in PVA composites with the exception of Ti (IV) which increases diameter from 50 to 60 nm to 70–130 nm (Fig. 3 in SM). In the case of VI-AA composites, Sn (IV) and Zr (IV) do not influence on the precipitates morphology but Ge (IV) and Ti (IV) stimulate formation of large 500–1000 nm particles (Fig. 4 in SM). The formation of these large particles is probably caused with large aggregates found in silicic acid solutions in the presence of poly-ampholyte and germanium or titanium additives [44]. Calcination of the samples results in merging (sintering) of the particles and destruction of the large particles observed in VI-AA system (Fig. 2).

Epifluorescence microscopy was applied for screening of the obtained composite materials (Figs. 3 and 4). Silica samples do not show visible luminescence comparing with the composite precipitates. PVA considerably increases emission of the composites and doping with the silicon analogs slightly decreases luminescence brightness. Heating of the samples influences on the emission in an ambiguous manner. PVA-based composites decrease the excitation with the exception of Ge-doped sample after 10 min heating. The precipitates obtained with N3 show low excitation which increases with heating and becomes comparable to PVA non-heated samples. The same is true for VI-AA composites doped with titanium and zirconium. Green-luminescent samples show high blue emission too but yellow-luminescent composites are not so active under UV-excitation. We can not see any specific influence of the silicon analogs on the photoluminescence, e.g. N3 and PVA based composites show high emission without any dopants. The

change of the luminescence color from green to yellow can not be attributed to a dopant nature too. N3–Zr/30 sample is yellow, VI-AA–Zr/30 is green, N3–Ge/30 is green, PVA–Ge is also green but become yellow after heating.

As mentioned above, the luminescence of organo-silica composites may be caused by luminescence of the organic components [36]. With the objective to find such compounds in the studied samples, we dissolved them in 36% HF and measured luminescence of the solutions (Fig. 5, Fig. 5 in SM). Non-calcinated composites do not give luminescent solutions in HF. There are six annealed samples containing soluble organic fluorophors which include Sn and Zr-based systems. The organic fluorophors were not found in composites which showed bright luminescence in the solid state which confirms participation of the inorganic component in luminescence of the composite materials.

Excitation and luminescence spectra of the composite samples were recorded and data are discussed mainly for the brightest samples. The luminescence spectra obtained with 280 nm excitation (Fig. 6) represent broad lines with maximum near 400 nm and several pure resolved bands in long-wave area. PSA-2 sample gives a broad complex spectrum which consists of several lines possibly attributed to various luminescence centers similar to data obtained in Ref. [17]. Luminescence spectra of some composites differ from the silica spectrum but they also look like a superposition of several lines and the observed shifts of the spectra maximum can be attributed to change of the relative intensity of luminescence from

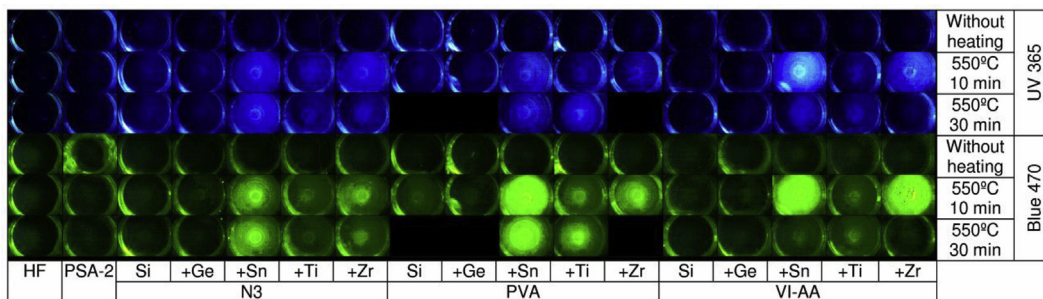


Fig. 5. Luminescent images of HF solutions of the composite precipitates placed into 96-well array plates. Excitation – 365 and 470 nm. PSA – silica precipitated from 100 mM sodium silicate with 1 M HCl at pH 5.5. The conditions of microphotography (power of the lamp, diaphragm, and exposure) were identical in all case and exposure was two times longer than in Fig. 3.

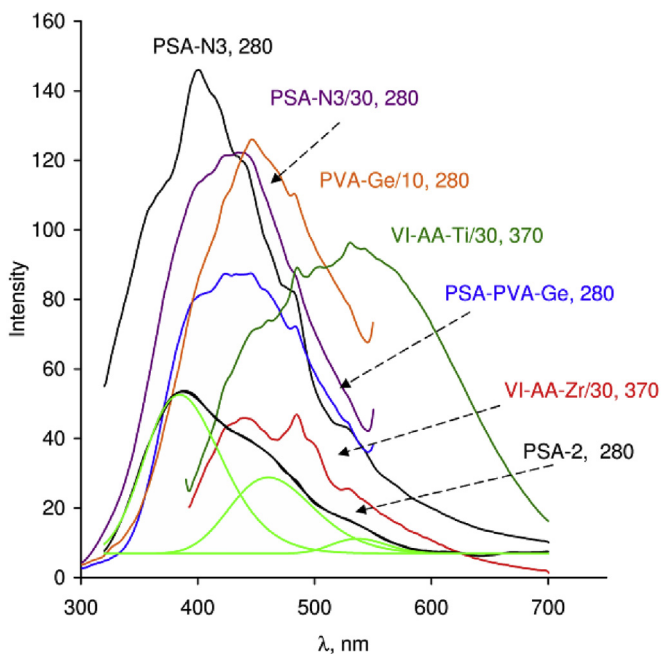


Fig. 6. Luminescence spectra of PSA-2 and composites. Numbers in the curve labels designate excitation values, nm. Green curves represent decomposition of the PSA-2 spectrum by the use of Gaussian model fitting which was applied to intensity vs energy (eV) data. Intensity of VI-AA-Zr/30, 370 spectrum was increased by factor 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

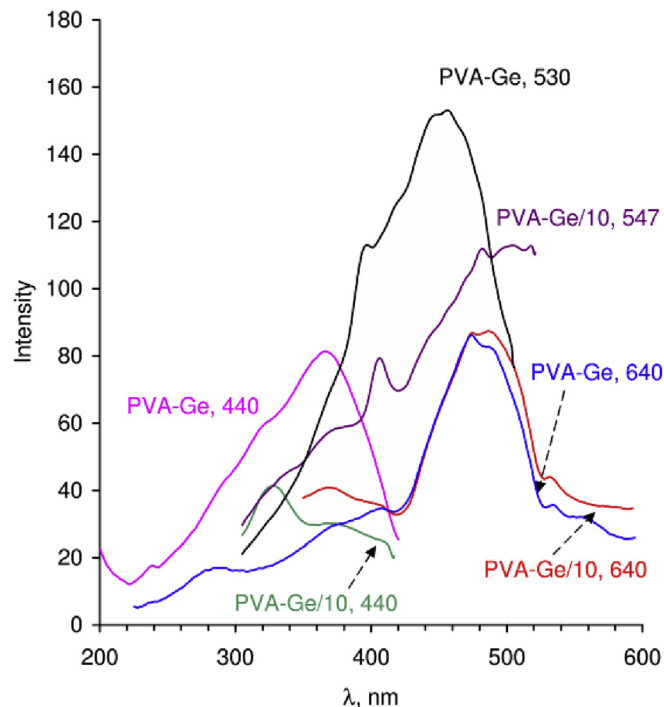


Fig. 7. Excitation spectra of PVA-Ge and PVA-Ge/10 composites. Numbers in the curve labels designate luminescence values, nm.

the centers present in pure silica. The spectra obtained with more long-wave excitation do not show considerable peculiarities comparing with 280 nm excitation (Figs. 6 and 7 in SM).

As mentioned above, two groups of samples were found with epifluorescence microscopy: green and yellow luminescent composites. For example, green emission of PVA-Ge sample becomes yellow after ten minutes at 550 °C (Fig. 3). The change of the luminescence color does not accompanied by considerable change of the luminescence spectra (Fig. 8 in SM), peaks of the curves do not change their position but change the relative intensity. The decrease of blue emission (under 365 nm excitation) after sample heating is not connected with change of the luminescence spectrum too.

Analysis of excitation spectra of PVA-Ge and PVA-Ge/10 samples (Fig. 7) show decrease of 360–370 nm band (440 nm luminescence) relative to 320–330 band after heating which explains the decrease of blue luminescence under 365 nm excitation (Fig. 3). Excitation spectra of 530 nm luminescence (green area) show

maximum at 440–460 nm in the case of PVA-Ge sample which corresponds to green luminescence of this sample under 470 nm excitation with the epifluorescence microscope (Fig. 3). Heating of this sample decreases 440–460 nm band and excitation of 640 nm luminescence (red area) is not changed which results in yellow luminescence of PVA-Ge/10 sample under 470 nm excitation (Fig. 3). Excitation spectra of the PVA-Ge and other samples (Fig. 9 in SM) show main excitation bands at 270–290, 320–330, 365–395 and 470–490 nm which relative intensities vary from sample to sample.

Lifetimes of the luminescence (Table 2 in SM) are close for all samples including pure silica and their values (several ns) correspond to singlet-singlet transitions. The luminescence decay curves for the green-red area were almost identical with the blue luminescence data. The small differences in lifetimes (Table 2 in SM) are explainable with redistribution of the contribution from several luminescent centers into the resulting spectrum. The increase of luminescence intensity at liquid nitrogen temperature (Fig. 10 in SM) confirms the singlet-singlet transition.

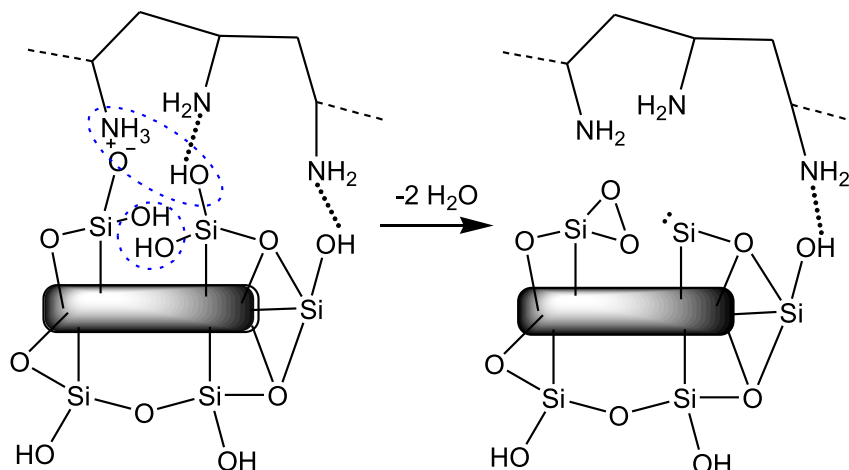


Fig. 8. Schematic model of the formation of the emission centers at surface of primary oligosilicates in PVA-silica nanoparticles.

Thus, the spectral data confirms observations from fluorescent microscopy: composites obtained with organic polymers and silicon analogs do not show new luminescence features, we see increase of the emission only. We suppose that in the presence of organic polymers the number of defects in silica structure increases. PVA catalyzes condensation of the silanol groups by stabilization of $\sim\text{Si}-\text{O}^-$ groups and the polymer chains are tightly mixed with silica phase in the composites [43]. This can provoke formation of the defects, such as silylene and a dioxasilirane groups due to the appearance geminal = $\text{Si}(\text{OH})(\text{O}^-)$ groups on the silica nanoparticles surface (Fig. 8). N3 is involved into composites in the lesser amount than PVA but heating of the samples allows migration of this low-molecular polyamine along the sample giving rise the defects such as in case of PVA systems. VI-AA copolymer inhibit condensation of the silanol groups by stabilization of $\sim\text{Si}-\text{OH}$ moieties [46] through hydrogen bonds in contrast to PVA and N3, and the corresponding composites do not show considerable luminescence without heating and addition of silicon analogs which can coordinate with imidazole groups releasing silanol groups.

On the other hand, the observed increase in the emission and changes in the luminescent spectra of the composites are similar to the effects observed with Al^{3+} doped silica [9]. It was supposed that the aluminum ions capture oxygen which increases amount of ODCs in the silica and this effect was enhanced after heating at 500°C . We can hypothesized that in the case of our composites the organic substances and silicon analogs act as the oxygen acceptors and increase concentration of the siliceous ODCs.

4. Conclusion

Silicic acid condensation in the presence of polyamine and organic polymers gives rise to composite particles of various morphology. The addition of silicon analogs Ge, Sn, Ti or Zr allows further change of the particles morphology. The obtained composite materials show considerably more intensive luminescence comparing with pure silica without essential changes in luminescence spectra and lifetimes. Our results show possibility to obtain bright luminescent siliceous materials with controllable nano- and micro-level morphology by the action of polymeric amines and silicon analogs. We suppose the increase in emission intensity is connected with increase of the luminescence-active defects which present in pure silica. Our data point to the necessity of a cautious analysis of the luminescent data from composite siliceous material

because the spectral peculiarity can arise not only from new luminescent centers but also from an increase of luminescence-active defects which are inherent for the pure silica.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.matchemphys.2016.10.006>.

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