PLENARY REPORT

AEROGELS – NEW MATERIALS WITH PROMISING APPLICATIONS

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Abstract

Sol-chemistry is an efficient method for the preparation of porous glassy or nanocrystalline materials with tailored electrical, thermal or optical properties. This presentation focuses on the dependence preparation–structure–physical properties of hydrophobic silica aerogel granules, micro powders and composites all of which prepared under subcritical drying conditions with potential application as optical materials and insulation materials. The so prepared nanoporous hydrophobic silica materials are analyzed with electron microscopy (SEM and AFM), infrared spectroscopy, differential scanning calorimetry, thermal conductivity measurements and luminescence / excitation spectroscopy. It has been proven that a long solvent exchange times and surface hydrophobization lead to aerogel micropowders with a specific surface S_{BET} of about 800-900 m^2/g and a bulk density of about 0.1 g/cm^3.

Keywords: aerogels; composites; optical properties.

INTRODUCTION

Sol-gel chemistry is an efficient method for the preparation of porous glassy or nano-crystalline materials with tailored electrical, thermal or optical properties. This speach focuses on the dependence preparation – structure – physical properties of hydrophobic silica aerogel granules, micro powders and composites all of which prepared under subcritical drying conditions with potential application as optical materials and insulation materials. By changing of the physico-chemical conditions of preparation, a variety of materials with potential application in the field of catalysis, optics and electronics can be created.

EXPOSITION

What are aerogels – the answer is the lightest known materials, with an application as insulation materials, optical materials, water cleaning medium by removing of oil, dyes and other chemicals and also, catalytic medium [1]. How to produce aerogels – the lightest materials in the world? To answer this questions, we need a short introduction in to sol-gel chemistry.

From physico-chemical point of view, the sol-gel process is a heterogeneous chemical reaction, performed in two steps. Starting chemical compounds are metal or silicium alcoxides, the most widely used are tetraethoxysilanes, tributyl aluminium, tetrabutyl zirconium and other, leading to the most used ceramic oxides. The second reagent is pure water. The formation of a gel takes place in two steps [1–4]:

- Hydrolysis, which is acid catalyzed, and leads to a dispersion (sol) consisting the solvent and hydrated nanoparticles of metal oxides of silica
- Condensation, which is basic catalyzed, also called gelation, and leads to a gel formation.

There are two basic reactions, involved in the gelation scheme, water condensation and alchohol condensation, both having different physicochemical constants /equilibrium constants, and rate constants/. Meanwhile, the shape and density of the formed gels can be quantitatively controlled by the chemical composition of the sol, especially the water content, temperature and catalyst type and content. Advantages of the sol-gel technology are the efficient physico-chemical control, and the possibility to prepare composites with a huge application in the ceramic, optical and electrical technologies. The liquid chemical reagents allow preparation of complicated compositions, at low temperatures. The gels contains about 50% water, or other solvent. In other words, we have a possibility to obtain porous materials by drying the wet gel, and to control the density of the products with the temperature and rate of the process.

Disadvantages of the method are the complicated chemistry, long process time and the relative high price of metal and silicium alcoxides (TEOS), compared to that of commercial available oxide powders for ceramic and glassy purposes. The sol-gel composites and aerogels display poor mechanical properties, due to the low degree of densification, compared to the bulk oxide ceramic or glass materials.

On the right part of the figure, the sol-gel process is visualized, together with the main applications of the products of the sol-gel technology. First, we are starting from a metal or silicium alcoxide solution, the next step is of key importance - the disperse system (sol) production. Having a sol, all basic elements of production of a ceramic technology can be realized – powders, xerogels, monodisperse particles, thin films, fibers or even aerogels. Two definitions – xerogel are dried gels, where the porous system has been partially destroyed by the driving force of the drying process. Aerogels, on the other hand, are sol-gel materials where the porous system has been protected, preserved, by soft drying conditions, leading to a very low density, about 0.05 g.cm^{-3}, compared to that of bulk oxide ceramic or glass materials .

After gelation, there is a wet gel, containing about 50% of the solvent used. By changing the drying conditions it is possible to obtain:

a) Aerogels by protection of the initial porous structure of the gels. The pores are in the nanoscale size region.

b) Xerogels, by drying with strong densification, and collapsing of the initial pore architecture.

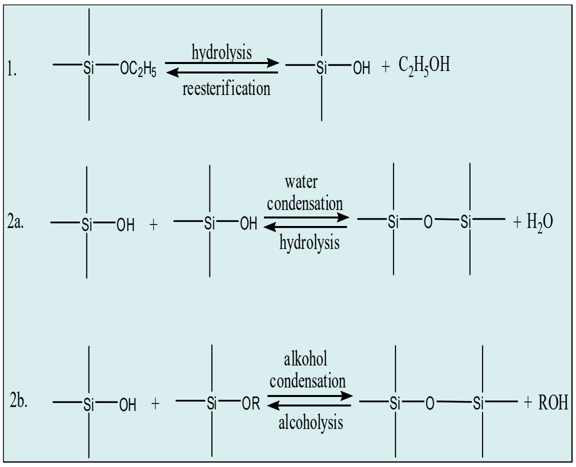


Fig. 1. *Basic chemical rections, included in the sol-gel technique* [4]

Depending on the chemistry and drying condition used, bulk gels, granules, or powders can be obtained. On the other hand, depending on the doping such materials could be either composites, or doped materials. Depending on the chemistry, an additional classification, inorganic, or hybrid gels could be obtained. Summarizing, sol-gel chemistry together with the extension for aerogel production, is an ultimative chemical method for nanomaterials production.

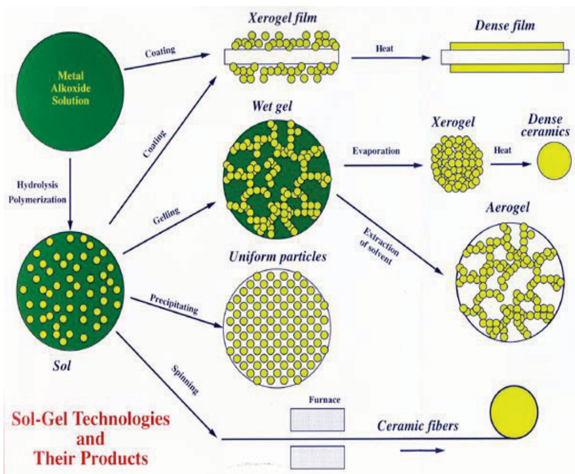


Fig. 2. *Application of the sol-gel technology* [5].

Some examples of our research activities include sol-gel preparation of optical composites. Here, low and heavy doped silica gels are visible. In these inorganic composites, the yellow coloration comes from $Sm(NO_3)_3$ nano-and mycro-crystals, dispersed in the silica matrix. The potential application of rare earth ion doped sol-gel materials are as powder coatings, pigments and UV – filters. Bellow, zirconia gels, containing organic molecules (chromophores), acetic acid and acetyl acetone, are displayed. They also have potential application as pigments, and UV – filtering systems due to their very strong optical absorption. The shape and thickness of the bulky glassy composites are fully reproducible, together with the color intensity, controlled by the doping concentration. In addition, the mean particle size of the dispersed optical active species leads to a "newspaper effect" of the bulky, transparent gels at water addition. Drying of such species can be controlled by reflectance optical spectroscopy, and the rate of densification also can be obtained. By changing the reaction volume and physico-chemical condition, monodisperse silica spheres "Stöbers silica" [6], very suitable for coating production, has been prepared. Sol-gel technology also led to the successful chemical stabilization of cubic cristobalite for glassy industry purposes. The chemical stabilization of cubic cristobalite depend on the concentration of the dopands, and on the sol-gel scheme used for the preparation of powders.

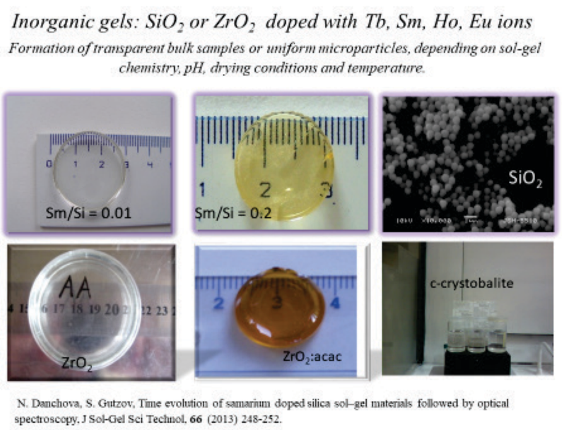


Fig. 3. *Some examples of inorganic hybrid silica and zirconia gels, prepared in the Department of Physical Chemistry, Sofia University "St. Kliment Ohridski"*

As has been pointed out the preparation of aerogels dramatically depends on drying conditions. The first attempt to produce aerogels was performed about 100 years ago by Kistler, who is the inventor of the so called "supercritical drying", by using of a supercritical fluid, carbon dioxide. The idea of this approach is to go around the evaporation line of the p-T diagram of a one component system, and to dry the system by saving its nanoporous structure without pore collapse. The supercritical fluid substitutes the initial solvent in the pores of the gel.

The resulting products can be bulk materials or powders, with a density of about 1/100 of the theoretical materials density [1,7–11]. The idea of such a drying procedure is, that the surface tension of liquids over the critical temperature reduces to zero, so that the supercritical fluid does not destroy the nanopores of the gels.

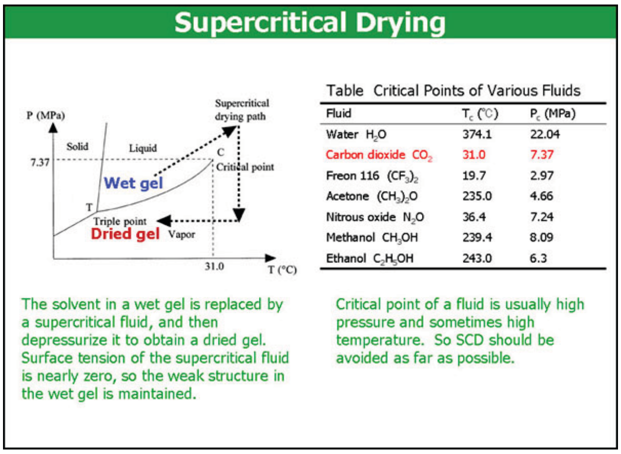


Fig. 4. *Supercritical preparation scheme for aerogel production* [1].

A new direction of aerogel production is the use of 3D printing. An interesting, and expensive approach which seems to have a huge potential in creating of microstructures for electronics, or even for human implants.

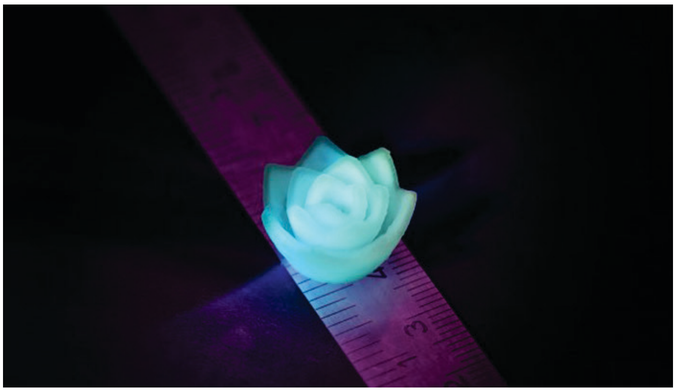


Fig. 5. *Aerogels prepared using 3D - printing* [12].

Here, I am presenting two extremely different kinds of aerogels, according to their thermal and electrical properties, carbon aerogels and silica aerogels. Despite their so different physical and chemical nature, they have a morphological similarity – more than 95% porosity, coming from nanopores. How to produce a natural, organic carbon aerogel – one possibility is to use a watermelon as a precursor, having more than 90% of sweet water and solvent, together with a celluloide like network.

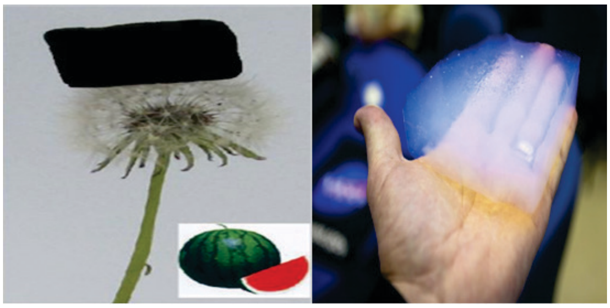


Fig. 6. *Two extreme cases of bulk aereogels concerning the thermal and electrical properties: carbon aerogels, and translucent silica aerogels* [13].

The bulk aerogels, presented in this talk, (Fig. 6) look nice, but they have two significant disadvantages: poor mechanical properties, and a very high price. Even a hydrophobic or hydrophilic silica costs about 30 €, and does not have any interesting functionalities because of their poor mechanical properties. There are, however, technologies allowing the production of materials with improved mechanical properties.

The industry needs aerogel granules or powders, materials with

a) A very high specific surface area, more than a few hundreds m^2/g

b) High porosity, about 95% or more, and a mean pore diameter in the nanometer scale

c) A low density, significantly less than 0.5 g/cm^3 and hydrophobicity, which means that the materials are water repelling

More than 30 years ago, a specific physico-chemical method for the production of such a hydrophobic powders and granules, for example the patent of Brinker and coauthors. The idea of this method is:

a) To protect the pore structure, of the gelated metal oxide medium using a liquid agent with low surface tension, for example, ethanol

b) Creation of a hydrophobic surface, using a hydrophobization agent, for example TMCS, trimethyl chlorosilane, which allows an effective solvent evaporation by protection of the porous system of the materials

c) Drying at subritical conditions, they are softer, compared to that of Kistlers' method

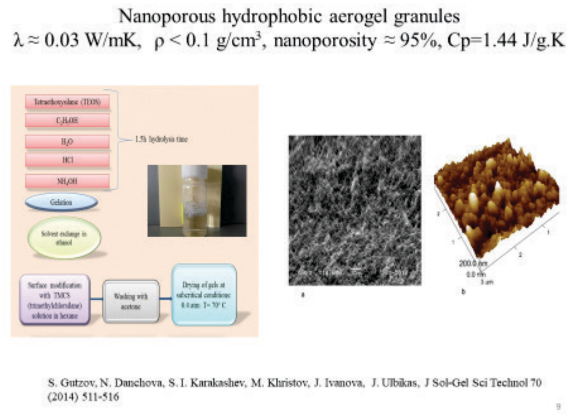


Fig. *7. Laboratory scheme for preparation of aerogel granules and nanopowders using the subcritical metod [4]. Water reppeling properties of granules levitating on the water surface are shown, stable at least 3 years.*

In our Department we created a laboratory physico-chemical technology for preparation of aerogel powders, based on the subcritical approach. More about the preparation conditions, and its variation, are discussed in our papers [9,14,15]. The materials properties of such kind of superhydrophobic powders, levitating on the water surface, are shown here. We created granulated or powdered materials, depending on preparation conditions, with a very low thermal conductivity together with a thermal capacity better than that of the commercial available CABOT hydrophobic aerogel granules. In the laboratory approach, we started from liquid TEOS, followed by water addition, two kind of catalists, an acid and a basic one. The next step is solvent exchange, which can be followed by electrochemical measurements (pH vs time curves), and hydrophobization. The latter step is exothermic, and can be followed by combined (pH + temperature vs time curves). The final procedure is drying, with typical subcritical conditions, room temperature up to 70 °C, and a pressure at about 0.1 atm. SEM and AFM pictures of the materials strongly respond to the morphological definition of aerogels: solid smoke, solid air, cloud like materials. The key element in the developed laboratory approach is the chemical surface hydrophobization with TMCS.

In a recently published paper in Molecules, 2021, we have developed a new spectroscopic method to follow the hydrophobization of our powdres with attenuation IR reflectance spectroscopy, by monitoring the specific IR active Si-OH and Si-O-Si vibration, and its replacement with Si-C vibrations [15].

The texture properties, obtained using liquid nitrogen absorption – desorption isotherms are displayed. Some of the samples are nanopowders, which levitate in air, depending on the preparation condition millimeter scaled granulates can be produced. It is visible, that we have a successful laboratory approach, and that all the material texture properties are reproducible. The texture properties of commercial available CABOT granules also are given for comparison.

Nanoporous hydrophobic aerogel granules – texture properties

Sample	S_{BET}, m²/g	V_t, cm³/g	D_{av}, nm
S1 granules	796	3.40	17
D1 powders	840	2.25	11
D2 powders	950	2.67	11
D11 granules	798	2.53	13
SOF granules	785	3.12	16
Cabot granules	**699**	**3.8**	**21**
Sample	S_{BET}, m²/g	V_t, cm³/g	D_{av}, nm
Y2 granules	871	3.34	15
Y8 granules	756	3.54	19
Y11 granules	787	4.19	21

N. Danchova, D. Paskalev, S. Gutzov, Aerogels – new materials with promising applications, Bulgarian Chemical Communications, **50** (2018), 172 – 177.

Fig. 8. *Texture properties of the prepared aerogel powders and millimeter scaled granules* [15].

The specific applications of aerogel powders and granules are summarized here, together with the characteristic material properties, responsible for the specific applications.

Specific applications of aerogel powders and composites / materials properties

- Thermal insulation materials / low density and thermal conductivity
- Optical composites / optical transparency, possibility for deep doping
- Water cleaning applications / nanoporosity, high specific area
- Catalytic applications / nanoporosity, high specific area, possibility for doping
- Gas capturing (H_2, CO_2) / nanoporosity, high specific area

Fig. 9. *Summary of the basic applications of aerogel powders and composites (black) driven by specific properties (red).*

My lecture continues with optical properties of aerogel composites. Our target is to incorporate optically active molecules into the aerogel matrix. In this way, a typical optical composite is created:

an aerogel matrix, containing an optical center. Lets go now to the formation of the optical center, responsible for light emission and absorption. Our optical properties are based on the luminescent properties of the lanthanide ions (rear earth ions). The optical properties of lanthanide ions are shown here. We have sharp, weak emission lines in the visible and IR spectral region, at UV excitation. The most applied ions europium (red), terbium (green), thulium (violet), neodymium (IR), samarium (orange) emits light after direct or UV (via the charge transfer transition) excitation [16–21]. From physical point of view, we have forbidden electric dipole or magnetic dipole electronic transitions. The emission is very weak, because of the physical nature of the electronic transitions. Thus, we need a way to improve the emission! Here, I am presenting to your attention the concept of the energy transfer, or antenna effect [22,23], in hybrid molecules, organic complex. The UV – energy is absorbed by an organic molecule, for example 1,10 – phenathroline, β-diketonates, acetic acid, acethylacetone, aromatic molecules and other compounds. The physical mechanism is well known as Förster-Dexter energy transfer, its efficiency strongly depending on the physical nature of the ligands (energy of the singlet and triplet state), also on the ligand to central ion distance.

Optical properties of lanthanide (Ln) ions: the optical active center

- Weak, forbidden electric dipole (ED) or magnetic dipole (MD) f-f transitions ($^{2S+1}L_J$), leading to an emission in the UV/Vis and NIR spectral region.
- MD transitions ΔJ=1 : $I_{MD}>I_{ED}$ if Ln(III) occupies a center of symmetry (CS).
- ED transitions $I_{ED}>I_{MD}$, ΔJ=2, 4, 6 if Ln(III) occupies sites without a CS.
- $f_{ED}>f_{MD}$, ED transitions are responsible for luminescence properties of rare earth ions.
- ΔJ=2 ED strong "hypersensitive" transitions, very sensitive for structural.
- Peak number & intensity are related to site symmetry.

I. Georgieva, N. Trendafilova, T. Zahariev, N. Danchova, S. Gutzov, Theoretical insight in highly luminescent properties of Eu(III) complex with phenanthroline, Journal of Luminescence **202** (2018) 192-205

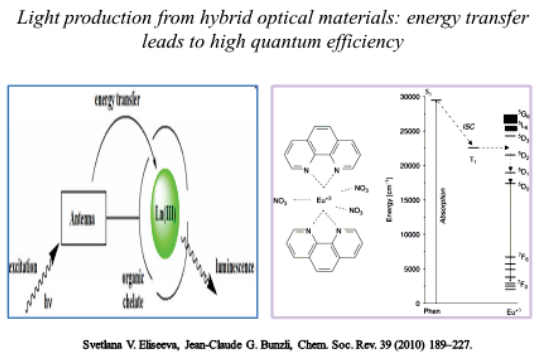
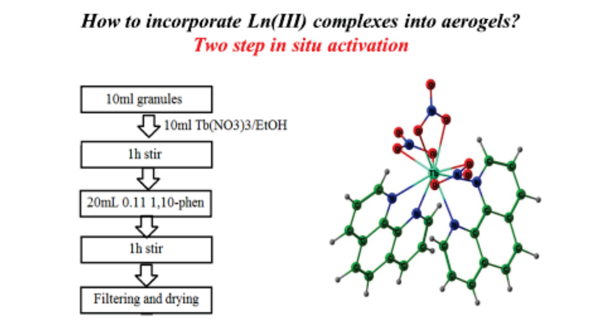


Fig. 10. *Spectroscopic properties of rare earth ions and enetgy transfer scheme from 1,10 – phenanthroline to Eu^{3+} ions* [24,25]

On the next slide, a hybrid molecule, $[Tb(phen)_2](NO_3)_3$ is shown. The antena here is the phenathroline molecule. We are exciting the organic molecule by UV – light, which is transferred to the Tb(III) ion. The Tb(III) ion goes to an excited state, and after that emits his characteristic luminescence (green), In this way, the quantum yield of the terbium emission is increased by one order of magnitude, or more. How to incorporate such an complex into the porous network of the aerogels? It is not easy, one way would be to impregnate the porous matrix with an organic complex solution. But lanthanide complexes are unstable, and very low soluble in organic solvents.



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T. Zahariev, D. Shandurkov, S. Gutzov, N. Trendafilova, D. Enseling, T. Jüstel, I. Georgieva, Phenanthroline chromophore as efficient antenna for Tb3+ green luminescence: A theoretical study, Dyes and Pigments 185 (2021) 108890.

Fig. 11. *Incorporation of $Tb(phen)_2(NO_3)_3$ optical centers into aerogel powders and granules*

Recently we developed a new, two-step procedure for the activation of aerogels with organic ligands, using commercial or self made granules or powders [26]. Fist, we created an inorganic composite, using easy soluble nitrates of the lanthanides. After that, we added a phenathroline solution to the inorganic composites. It is the case of an in situ activation, because a controlled chemical reaction takes place in the nanopores of the aerogel matrix. The complex formation has been confirmed by optical spectroscopy, X-Ray diffraction analysis, and IR – spectroscopy.

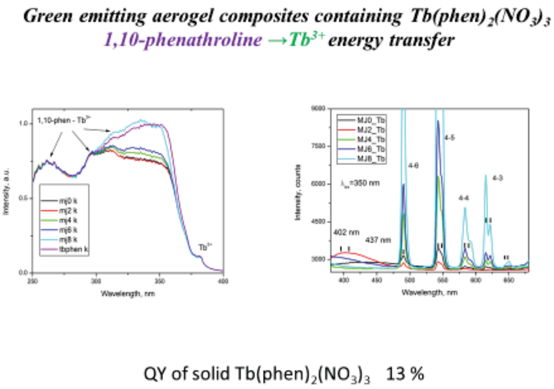

Fig. 12. Optical properites of aerogel composites, containing $Tb(phen)_2(NO_3)_3$. The quantum yield (QY) of the pure solid complexes is also presented.

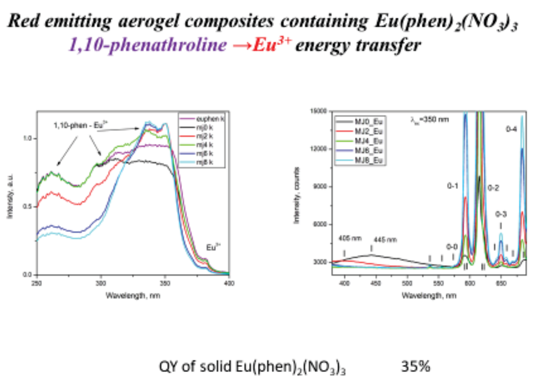

Fig. 13. *Optical properites of aerogel composites, containing $Eu(phen)_2(NO_3)_3$. The quantum yield (QY) of the pure solid complexes is also presented.*

Specific optical spectra, emission and excitation spectra of aerogels, containing $[Tb(phen)_2](NO_3)_3$ or $[Eu(phen)_2](NO_3)_3$. The excitation spectra confirm that a strong, effective energy transfer takes place in the hybrid aerogels prepared. In other word, it is possible to prepare red or green emitting powders, and mix them for a white light production. In such a way, the preparation of materials with potential application as smart optical sensors is possible. Surprisingly, we found out that a weak blue emission, coming from surface complexes or defects is visible in our gels, leading to an additional color change. Our smart sensors give a triple response, red, green or blue to UV – excitation. Repeating, each color is connected with different optical active molecules, so the way for white light production from aerogels is also open. Recently we also found out, that the quantum yield of our aerogel composites dramatically depends on the mean pore diameter of the initial aerogel matrix, opening the way for a control of the chemical reaction, taking place in the nanopores of the aerogel matrix. On the other hand, the results become more complex, and a dependence between nanopore size and quantum yield is visible.

SUMMARY

- Aerogel composites based on hydrophobic silica, displaying a red, green or blue luminescence coming from hybrid molecules are prepared and characterized.
- A new laboratory method for functionalization of doped silica powders and nanoporous aerogel granules with organic ligands is demonstrated.
- Aerogel granules or nanopowders with promising physical properties, low thermal conductivity, increased thermal capacity and specific area are prepared by a laboratory subcritical approach at room temperature and p=0.1 atm.
- The quantum yield of the optical composites strongly depends on the physico-chemical properties of the silica aerogel matrix.

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