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GAS SENSITIVITY OF SOME NANOPARTICLES ENSEMBLES IN POROUS GLASS

The importance of substances' surface development suitable for sensor technology by dispersing them to the level of nanoparticles' ensemble within a certain matrix has been demonstrated. It has been proven that the best matrix for the formation of the specified ensemble of nanoparticles is porous silicate glass. Methods of formation of ensembles of nanoparticles of some compounds in porous glass are briefly considered. The applicability of the mentioned systems for sensors is demonstrated by the example of their luminescent response sensitivity to the presence of ammonia or HCl vapours in the environment.

Introduction

The luminescence centers of materials useable as active elements of luminescent gas sensors are mostly located near the surface, and just the near-surface substance layers are affected by gas composition changes of the environment. Hence, the best registration of the specified changes, is in the maximum possible developement of the substance active surface which is achieved by dispersing the specified substance to nanometer sizes. As soon as it is inconvinient to operate with individual particles of nanometer sizes, it is reasonable to place them in a system of the appropriate size"tubes", which can be a matrix containing small cavities in the form of through pours. In this case an ensemble of nanoparticles is formed, consisting of the indicated small particles of the substance and the matrix itself, in which they are placed. The matrix properties must meet certain restrictions, due to which it will not affect the gas sensitivity of the studied substance and, moreover, will positively influence its luminescent properties. Such limitations include chemical inertness, mechanical durability, and its luminescent response may be present only in the spectrum regions that are not essential for the substance under investigation. Some authors use polymers [1-2] or gelatin [1, 3] as a matrix. These compounds do not luminesce and are quite chemically inert. Thanks to the peculiarities of their structure, they are able to keep the clusters of the studied substance formed inside them. However, these clusters can have arbitrary sizes and shapes, and their growth will not be restrained by polymer or gelatin, but on the contrary, they will uncontrollably form the backbone of the matrix by themselves. Sparse silicate glass with voids of nanometer size is free of this defects. The sizes of interpenetrating pours can vary from few nanometers to several hundred nanometers. In addition, the quartz skeleton of the compound is quite durable, so it limits the size of the particles that are formed, because they cannot exceed the size of the pours. The columnar structure of the glass allows to influence both the inner surface of the pours and the nanoparticles created inside them. In the most cases, such nanoparticles can be conveniently created by saturating the matrix with solutions of suitable substances. Thus, porous silicate glass perfectly meets the requirements formulated to the matrix, inspite of the fact that it does not exist in nature. It can be obtained from two-phase sodium-borosilicate glass by a not very complicated technology [4].

Types of porous silicate glass and the technology of their production

Two-phase sodium borosilicate glass has the complex chemical formula $SiO_2 \times [Na_2O \times B_2O_3]$. The melting temperature of such glass exceeds 750°C. In addition, the melting point of the silicate component of the glass is much higher than the melting point of the sodium borate complex, and therefore there is a temperature at which the sodium borate component of the glass is in a liquid state, while its silicate component is simply very heated. A temperature of 650°C corresponds to this condition. If the charge for boiling two-phase glass, which has been brought to 750°C, is cooled adiabatically to 650°C, then the separation of phases occurs at the indicated temperature, the sodium-borate complex will still melt, forming large bubbles that will form the silicate skeleton. Due to the viscosity of the melt, it is kept in such conditions for several hundreds of hours, until both phases mutually completely dissolve in each other, and then it is slowly cooled to room temperature. The two-phase glass obtained is quite large (up to hundreds of nanometers) areas of mutually intertwined silicate and sodium borate phases. These phases, in particular, show unequal chemical stability, thanks to which a mixture of hydrofluoric, nitric and glacial acidic acids can be used to completely etch the sodium borate phase, while almost not affecting the silicate phase, which forms a quartz skeleton with through-through cavities in places of the etched sodium borate phase. These cavities have quite large dimensions, however, due to mutual dissolution, the rather small, powder-like particles of SiO_2 also got inside the sodium borate phase, and after its etching off should settle inside the resulting cracks. Such settled powdery particles are called residual silica gel. Chemically, they are completely identical to quartz skeleton and differ from it only in their fineness. The glass produced in such a way is conventionally called porous glass of type C. Such glass is unsuitable for a number of applications, because due to sufficiently large pours, particles of the investigated substance of significant size will form in it. Therefore, the sufficient expansion of its surface will remain impossible.

For the formation of smaller pours in the glass, the technological modes of two-phase glass production should be slightly changed. The charge for its melting must be cooled adiabatically to a lower temperature, which is close to the melting point of the sodium borate phase, but lower than it (about 490 °C). If the charge is kept at such a temperature for hundreds of hours, it will lead to the formation of rather small bubbles in the sodium borate phase and, after cooling to room temperature, phase separation will occur, as a result of which the two-phase glass will be small (about tens of nanometers) areas of interwoven silicate and sodium borate phases. After the etching of the unstable sodium borate phase in the above-described manner, a rather fine-cracked silicate glass will be formed, which will also contain residual silica gel in the pours. Glass created in such a way is conventionally called porous glass of type A.

The presence of silica gel inside the pours, depending on the conditions of a specific scientific problem, can be both desirable and harmful. Thus, the presence of silica gel makes the glass more finely porous, but at the same time reduces the free space for the formation of nanoparticles of the studied substance. On the other hand, the presence of silica gel improves the adsorption properties of glass, but worsens its mechanical properties (deformation of the sample may occur due to the swelling of the gel in a humid environment [5-7]). It is true that special treatment can improve the mechanical properties of glass, but this will not always have a positive effect on its other properties [8]. Within the scope of the surface development problem for a substance suitable as an active element of a certain sensor, the separating ability of silica gel is definitely useful, which prevents the process of aggregation of particles ensemble formed in the gaps [1, 9]. Nevertheless, for cases where the presence of silica gel in cracks is harmful, the method of leaching silica gel developed in [10] is quite applicable, which impoverishes the glass from this formation, or completely eliminates it. According to this technique, the finished glass is etched in an alkaline etchant based on KOH. This etchant interacts with the finely dispersed silica gel rather quickly and acts much more slowly on the continuous (at least spongy) walls of the matrix. Due to this, the majority of the silica gel is removed, while the walls of the matrix backbone are only slightly etched [4, 11]. Type A glass treated in this way is conventionally called type B glass, and type C glass is called type D glass.

The results of studying the structure of all 4 above-mentioned types of glasses using an electron microscope are shown in Fig. 1. It is clearly visible that the glasses of types A and B are finely porous, while the pours in glasses of types C and D are much larger. Particles of residual silica gel appear as white spots in the images corresponding to glasses A and C. In type C glass they are larger, in type B glasses they are almost invisible (this confirms that the leaching technique leads only to impoverishment of the glass with silica gel [4, 11]), and in type D glasses they are absent at all.

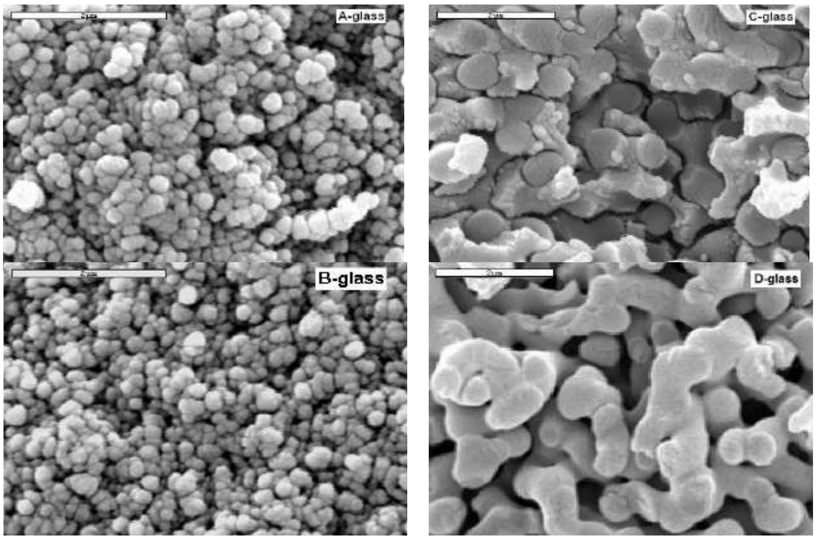

Fig. 1. Electron microscopic images of four poures types glass structures

Figure 2 shows the size distribution of pours for all specified types of glass. One can make sure, that in each of the glass types there are mainly two fractions of pours sizes, but any of the types contain small amounts of any pours from about 10 to over 100 nanometers.

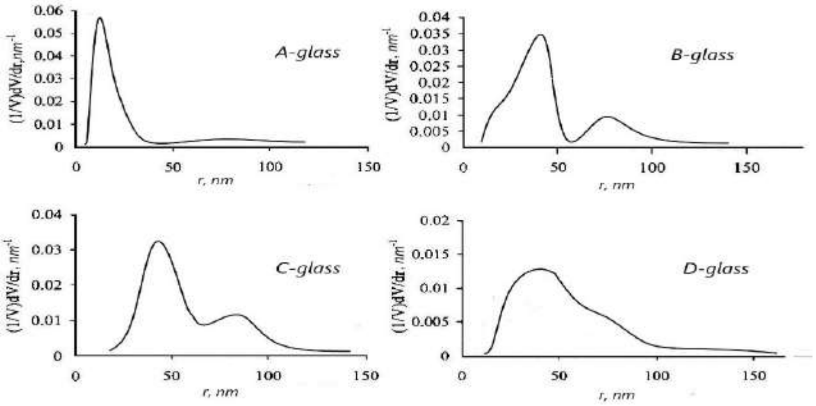

Fig. 2. Typical pours sizes distribution for four types of slotted glass

Formation of nanoparticles ensembles.

The formation methods of nanoparticles' ensembles in the porous glass matrix depend on a number of factors. The first of them, is the chemical composition of the particles' substance, the ensemble is to be formed. It should be taken into account that porous glass is almost pure quartz SiO_2, therefore the formation of silicon nanoparticles' ensemble, which are the component of the matrix, is possible through their chemical treatment [12-13]. For this, it should be based on the fact that silicon is the main chemical component of both the framework of the porous glass and the residual silica gel in the pours. Both formations are chemically identical and differ only in dispersion. And since carbon in its chemical properties is similar to silicon, but more active, it is able to squeeze it out of the oxide at the appropriate temperatures. Thus, if the pours are saturated with carbon, under the right conditions it will push silicon out of the oxide, primarily from silica gel, as a more dispersed formation. Silicon will be in an energetically disadvantageous atomic state, and since carbon will turn into carbon dioxide, which is heavier than air and will prevent the re-oxidation of atomic silicon, the latter will have time to turn into silicon clusters, which will settle on the walls of the silicate skeleton, during the time required to remove CO2 from the pours like grape formations. In the future, the surface of these clusters will oxidize and a porous glass will be formed, enriched with silicon along the walls of the pours. This process is called carbon processing.

If it is necessary to form the nanoparticles' ensemble of a substance whose components are not included in the chemical composition of the matrix, but the specified substance is well soluble in water, alcohol or a special solvent that does not destroy the matrix, then the ensemble of nanoparticles can be formed by immersing the matrix into the appropriate solution. This will lead to the matrix impregnation with the subsequent formation of nanoparticles inside the pours. A classic example of such a substance is a group of dyes based on tetravalent stannum [4, 14]. These rather complex organic compounds are actually an aggregation of interwined benzene rings with nitrogen bridges and they are perfectly soluble in the organic solvent dimethylformamide (CH3)2NCO (abbreviated DMFA). By varying the concentration of the solution, the duration of the immersion and the temperature of the process, it is possible to obtain a whole nanoparticles' ensemble series of the specified molecular crystals with quite diverse properties, which can be particularly used in sensors.

In some cases, the substance itself is poorly soluble or insoluble in matrix-safe solvents. However, it can be synthesized as a result of the reaction of soluble substances. In this case, the specified synthesis should be performed directly inside the pours of the matrix. At the same time, after saturation of the matrix with a soluble component of the reaction, it is not necessary to interact with another substance, and sometimes it is enough to perform a thermosynthesis (as in the case of SnO_2 [15]) or coprecipitation (as in the case of RuO_2 [16]). It is worth to note that the above-mentioned carbon treatment , consisting of two stages, at the primary stage also represents the thermosynthesis of glucose, which is renewed to carbon in the form of graphite.

And finally, in some cases, after saturating the matrix with a soluble component of the reaction, it is necessary to place the saturated matrix in the solution of the second component of the reaction. This occurs when an ensemble of CdS [17] or AgBr [18] nanoparticles is formed. In these cases, after the completion of the reaction, the surface should be thoroughly cleaned so that the ensemble of nanoparticles does not shunt through it.

The nanoparticles' ensembles application in sensor technology

Highly dispersed ensembles of nanoparticles with a well-developed surface should be useful, first of all, as active elements for gas sensors. Nanoparticles' ensembles of dyes based on tetravalent stannum are especially applicable in this sense [19-20]. The molecules of these substances consist of two parts: a coordination node, which is a complex set of benzene rings, and a hydrazone fragment, which consists of one benzene ring located outside the coordination node and connected to it by an ordinary C-C bond. One of the hydrogen atoms of the hydrazone fragment is replaced by a certain group of atoms (e.g., the amine group NH3), which is analogous to a substitution impurity in semiconductors. At the same time, a ligand consisting of stannum and chlorine is contained inside the coordination unit, and is analogous to an impurity penetration in semiconductors. Both of these formations can be centers of light emission

Our studies demonstrate that the intensity of the dye with an amine ligand luminescence depends on the concentration of the solution impregnating during the formation of nanoparticles' ensemble. This dependence is non-linear and has a maximum at a certain concentration, exceeding of which leads to a sharp decrease in luminescence [21]. Basing on this property, it is possible to register the presence of ammonia in the environment. In fact, if an ensemble of nanoparticles is created at a concentration that provides maximum luminescence, then in the presence of ammonia in the environment, the system will begin to behave as if it was formed at an overestimated concentration of the impregnating solution and its luminosity will drop sharply. This is the operation principle basis of the proposed ammonia transducer [22].

The coordination unit ligand itself is not enough active, for it is protected from all sides by a set of benzene rings. There are two types of ligands, $SnCl_4$ and $SnCl_3$. Both of them form a certain distribution of negative charge inside the dye molecule. In this case, the SnCl3 ligand corresponds to a more intense glow. The presence of HCl vapours in the environment enriches the coordination node with negative Cl- ions. This changes the charge distribution in the molecule to that typical for a dye with the $SnCl_4$ ligand, and the luminescence intensity of the system decreases sharply again. This property is the basis of the established action principle for the suggested hydrogen chloride vapor sensor [23].

After the actuation of both of these sensors, they should be subjected to low-temperature short-term annealing. to restore their performance This is the main drawback of these devices. This drawback does not occur in the case of using an ensemble of SnO_2 nanoparticles. This system is not sensitive to HCl vapors, but in the presence of ammonia in the environment it also sharply reduces the intensity of its emmitance. However, after being transferred to a clean atmosphere, within a short time it completely restores itself its performance . [24].

Conclusions

Porous silicate glass is the best matrix for creating ensembles of nanoparticles of all kinds of substances due to its durability, chemical inertness and separation properties of powder-like formations inside slots.

The molecular structure peculiarities of dyes based on tetravalent stannum make it possible to use them as active elements for some gas sensors.

In the dye molecule of the specified structure, there are two types of luminescence centers: a substituent in the hydrazide fragment, which is analogous to a substitution impurity in a semiconductor, and a ligand in the coordination node, which plays the role of a penetration impurity. The substituent is responsible for sensitivity to ammonia, and the ligand is responsible for sensitivity to HCl vapors.

The sensitivity principle of dye nanoparticle ensembles to the presence of these gases in the environment is manifested in their luminescence intensity decrease.

References

1. Meshkovsky I.K., 1998. The composite optical materials based on porous matrices, Sankt- Petersburg, 332 p.
2. Smyntyna V.A., Skobeeva V.M., Malushin-N.V., The boundary influence on the optical and luminescent properties of the quantum dots of the CdS in a polymer// Fizika i khimiya tverdogo tela-2011-V12,N2-pp.355-358.
3. Smyntyna V.A., Skobeeva V.M., Malushin N.V. Influence of the Surface on the Spectrum of Luminescence NC CdS in Gelatine Matrix // Photoelectronics – 2012 – No.21 – pp.50-56.
4. Doycho I.K. Study of the photoluminescent properties of nanoparticles ensembles of dyes In the book: Non equilibrious processes in the sensor structures, Editor V.A.Smyntyna, p.p.120-170, ONU (Odessa Mechnikov national university),Odessa (2015).
5. Gevelyuk, S.A., Doycho, I.K., Rysiakiewicz-Pasek, E., Marczuk, K., Relative changes of porous glass dimensions in humid ambiance, Journal of Porous Materials, 7 (2000) 465-467.
6. Gevelyuk, S.A., Doycho, I.K., Lishchuk, D.V., Prokopovich, L.P., Safronsky, E.D., Rysiakiewicz-Pasek, E., Roizin, Ya.O., Linear extension of porous glasses with modi-

fied internal surface in humid environment, Optica Applicata, 30 (4) (2000) 605-611.

7. Gevelyuk, S.A., Doycho, I.K., Prokopovich, L.P., Rysiakiewicz-Pasek, E., Safronsky, E.D., Humidity dependencies of porous sol-gel and silica glass linear sizes, Material Science, 20 (2) (2002) 23-27.
8. Rysiakiewicz-Pasek E., Vorobyova V.A., Gevelyuk S.A., Doycho I.K., Mak V.T., Effect of potassium nitrate treatment on the adsorption properties of silica porous glasses, Journal of Non-Crystalline Solids 345–346, 2004, pp. 260–264.
9. Tyurin O.V., Bercov Y.M., Zhukov S.O., Levitskaya T.F., Gevelyuk S.A., Doycho I.K., Rysiakiewicz-Pasek E., Dye aggregation in porous glass, Optica Applicata, 40 (2) (2010) 311-321.
10. Mazurin O.V., Roskova G.P., Averianov V.I., Antropova T.V., 1991. Biphasic glasses: structure, properties, applications, NAUKA, Leningrad., 276 P.
11. *I. K. Doycho, V. S. Grinevych,* and *L. M. Filevska*. Porous Silica Glasses as a Model Medium for the Formation of Nanoparticles Ensembles: Review. Advanced Nanomaterials for Detection of CBRN, NATO Science for Peace and Security Series A: Chemistry and Biology, 2020, 283-294; https://doi.org/10.1007/978-94-024-2030-2_21
12. S.A.Gevelyuk, I.K.Doycho, L.P.Prokopovich, E.Rysiakiewicz-Pasek, K.Marczuk. The influence of anneal of incorporated carbon on the photoluminescence properties of porous glass and porous silicon // Polish Ceramic Bulletin 19, Ceramics 57 / Porous and Special Glasses (Proceedings of the 4-th International Seminar PGL'98) / edited by L.Stoch. – Polish Ceramic Society, Krakow: 1998. – p.59-64.
13. Gevelyuk, S.A., Doycho, I.K., Prokopovich, L.P., Rysiakiewicz-Pasek, E., Safronsky, E.D. Influence of carbon multiple treatments on the photoelectrical properties of porous glasses. Radiation Effects & Defects in Solids, 2003, Vol.158, pp.427-432. Doi: 10.1080/1042015022000037292
14. *I.K.Doycho*, *S.A.Gevelyuk, E.Rysiakiewicz-Pasek.* Photoluminescence of tautomeric forms of nanoparticle ensembles of dyes based on the 4-valence stannum complexes in porous silica glass // Photoelectronics. – 2015. – Vol.**24**. – pp.30-37.
15. *Gevelyuk S. A.; Grinevych V. S.; Doycho I. K.; Lepikh Ya.I.; Filevska L. M.* Photoluminescence of SnO_2 nanoparticle ensemble in porous glass with column structure // 2019 IEEE 8th International Conference on Advanced Optoelectronics and Lasers (CAOL). – 2019, – pp.416-419; doi: 10.1109/CAOL46282.2019.9019433
16. *Doycho I.K., Gevelyuk S.A., Filevska L.M., Grinevych V.S.* Catalysis of Wastewater Pollutants by Ruthenium Nanooxide in Porous Glass. Book of Abstracts of the 9th International, Conference Nanotechnology, and Nanomaterials (NANO 2021), August 25-27, 2021, Lviv, p.37. (если уже вышла отправленная в декабре статья в Шпрингере, можно заменить на неё)
17. Rysiakiewicz-Pasek, E., Polańska, J., Gevelyuk, S.A., Doycho, I.K., Mak, V.T., Zhukov, S.A., The photoluminescent properties of CdS clusters of different size in porous glasses, Optica Applicata, XXVIII (1) (2008) 93-100.
18. Doycho, I.K., Gevelyuk, S.A., Ptashchenko, O.O., Rysiakiewicz-Pasek, E., Tolmachova, T.N., Tyurin, O.V., Zhukov, S.O., Photoluminescence features of AgBr nanoparticles formed in porous glass matrixes, Optica Applicata, 40 (2) (2010) 323-332.
19. *Дойчо І.К., Гевелюк С.А., Лепіх Я.І., Рисякевич-Пасек Е..* Особливості газочутливості барвників на базі комплексів 4-валентного станууму // SEMST– 2017– Vol.14, № 1 – pp. 31-40.
20. *I.K.Doycho*, *S.A.Gevelyuk, Ya.I.Lepikh, E.Rysiakiewicz-Pasek.* Nature of gas sensitivity of dyes on the base of Sn(IV) complexes // Optica applicata. – 2019. – Vol. **49**. – No.3. – pp.427-436.
21. *S.A.Gevelyuk, E.Rysiakiewicz-Pasek, I.K.Doycho.* Dependence of photoluminescence of nanoparticle ensembles of stannum (IV) complexes in silica porous matrix on concentration of saturating solution // Photoelectronics. – 2016. – Vol.**25**. – pp.40-47.
22. Патент України на винахід №119092, Сенсор аміаку: МПК G01N 21/64 (2006.01) / *Гевелюк С.А., Дойчо І.К.,*

Лепіх Я.І.; зареєстровано у Держреєстрі патентів на винаходи 25.04.2019.

23. Патент України на винахід №118415, Сенсор парів хлористого водню: МПКG01N 21/76 (2006.01) / *Лепіх Я.І., Дойчо І.К., Гевелюк С.А.*; зареєстровано у Держреєстрі патентів на винаходи 10.01.2019.

24. *Gevelyuk S.A., Grinevych V.S., Doycho I.K., Filevska L.M.* The active environment influence on the luminescence of SnO_2 nanoparticles' ensembles in a porous matrix// Applied Physics A, 2020, 126(12) 919; DOI:10.1007/s00339-020-04101-4

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Summary The importance of substances' surface development suitable for sensor technology by dispersing them to the level of nanoparticles' ensemble within a certain matrix has been demonstrated. It has been proven that the best matrix for the formation of the specified ensemble of nanoparticles is porous silicate glass. Methods of formation of ensembles of nanoparticles of some compounds in porous glass are briefly considered. The applicability of the mentioned systems for sensors is demonstrated by the example of their luminescent response sensitivity to the presence of ammonia or HCl vapours in the environment.

Key words: gas sensitivity, photoluminescence, porous glass, ensembles of nanoparticles.

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ГАЗОЧУТЛИВІСТЬ ДЕЯКИХ АНСАМБЛІВ НАНОЧАСТИНОК У ШПАРИСТОМУ СКЛІ

Реферат Продемонстровано важливість розгортання поверхні речовин, придатних для використання у сенсориці, шляхом диспергування їх до рівня ансамблю наночастинок всередині певної матриці. Доведено, що найкращою матрицею для формування зазначеного ансамблю наночастинок є шпаристе силікатне скло. Коротко розглянуто способи формування ансамблів наночастинок деяких сполук у шпаристім склі. Застосовність зазначених систем у сенсориці продемонстровано на прикладі чутливості їхнього люмінесцентного відклику до наявності аміаку або парів HCl у довкіллі.

Ключові слова: газочутливість, фотолюмінесценція, шпаристе скло, ансамблі наночастинок.

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ГАЗОЧУВСТВИТЕЛЬНОСТЬ НЕКОТОРЫХ АНСАМБЛЕЙ НАНОЧАСТИЦ В ПОРИСТОМ СТЕКЛЕ

Реферат Продемонстрирована важность развертывания поверхности веществ, пригодных для использования в сенсорике, путем диспергирования их до уровня ансамбля наночастиц внутри определенной матрицы. Доказано, что наиболее предпочтительной матрицей для формирования указанного ансамбля наночастиц является пористое силикатное стекло. Кратко рассмотрены способы формирования ансамблей наночастиц некоторых соединений в скважистом стекле. Применяемость указанных систем в сенсорике показана на примере чувствительности их люминесцентного отклика к наличию аммиака или паров HCl в окружающей среде.

Ключевые слова: газочувствительность, фотолюминесценция, пористое стекло, ансамбли наночастиц.

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