Conference materials
UDC 544.723
DOI: https://doi.org/10.18721/JPM.153.316

Cetyltrimethylammonium bromide as a soft template for the synthesis of a conductometric gas sensor active substance

G. R. Nizameeva [1,2]✉, R. R. Gainullin [1], I. R. Nizameev [1,3], M. K. Kadirov [1]

[1] A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia;
[2] Kazan National Research Technological University, Kazan, Russia;
[3] Kazan National Research Technical University named after A.N. Tupolev, Kazan, Russia
✉ guliya.riv@gmail.com

Abstract. This paper presents the investigation of cetyltrimethylammonium bromide (CTAB) molecules self-organization at the glass substrate, which is used as a micellar template in the synthesis of metal nanonetworks. These nanonetworks can be used as an active substance of gas sensors for detection of toxic gases. The free surface energy of glass which is used in the work as a substrate, and the free energy of the glass-CTAB interface are calculated.

Keywords: micellar template, metal nanonetworks, gas sensors, cetyltrimethylammonium bromide, surface energy, atomic force microscopy

Funding: The reported study was funded by the government assignment for FRC Kazan Scientific Center of RAS.

Citation: Nizameeva G. R., Gainullin R. R., Nizameev I. R., Kadirov M. K., Cetyltrimethylammonium bromide as a soft template for the synthesis of a conductometric gas sensor active substance, St. Petersburg State Polytechnical University Journal. Physics and Mathematics, 15 (3.3) (2022) 86–92. DOI: https://doi.org/10.18721/JPM.153.316

Материалы конференции
УДК 544.723
DOI: https://doi.org/10.18721/JPM153.316

Цетилтриметиламмония бромид как мицеллярный шаблон для синтеза активного элемента газового сенсора

Г. Р. Низамеева [1,2]✉, Р. Р. Гайнуллин [1], И. Р. Низамеев [1,3], М. К. Кадиров [1]

[1] Институт органической и физической химии имени А. Е. Арбузова КазНЦ РАН, Казань, Россия;
[2] Казанский национальный исследовательский технологический университет, Казань, Россия;
[3] Казанский национальный исследовательский технический университет им. А. Н. Туполева, Казань, Россия
✉ guliya.riv@gmail.com

Аннотация. В данной работе представлены результаты исследования процессов самоорганизации молекул цетилтриметиламмония бромида (CTAB), который используется в качестве мицеллярного шаблона при синтезе ориентированных наносетей металлов. Полученные наносети могут использоваться в качестве активного элемента для обнаружения токсичных газов в газовых сенсорах. Рассчитана свободная поверхностная энергия стекла, которое используется в работе в качестве основы для газового сенсора, и свободная энергия границы раздела стекло – раствор CTAB, на котором формируется мицеллярный шаблон.

Ключевые слова: мицеллярный шаблон, металлические нанопровода, газовый сенсор, цетилтриметиламмония бромид, поверхностная энергия, атомно-силовая микроскопия

Финансирование: Работа выполнена в рамках государственного задания ФИЦ КазНЦ РАН.

Ссылка при цитировании: Низамеева Г. Р., Гайнуллин Р. Р., Низамеев И. Р., Кадиров М. К., Цетилтриметиламмония бромид как мицеллярный шаблон для синтеза активного элемента газового сенсора // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.3. С. 86–92. DOI: https://doi.org/10.18721/JPM.153.316

Introduction

Atmospheric pollution has become one of the most serious problems faced by mankind. In recent years, this problem has attracted more and more attention from a significant part of the scientific community and pushes for the study of various issues of environmental safety. The main cause of air pollution is the release of harmful gases, liquids and chemicals into the air. Air pollutants adversely affect human health and can lead to serious consequences if the maximum allowable concentration is increased. Therefore, to control the content of toxic gases in the atmosphere and monitor the environment, there is a practical need to create productive, accurate and cheap sensors for detecting and measuring the maximum allowable concentration of toxic gases. The importance of creating such devices is quite obvious, because. they will solve the problems of atmospheric monitoring and control of factory conditions, medical problems and problems of the food industry.

To date, nanometer-sized materials are widely used in gas sensors as an active element for detecting harmful gases in the atmosphere. Of particular interest are one-dimensional nanomaterials such as oriented nanonetworks and metal oxide nanowires. Such structures have superior physical and chemical properties compared to thin-film and bulk materials [1]. At present, gas sensors based on nanowires of metal oxides of n-type conductivity are widely studied. However, until recently, insufficient attention has been paid to semiconductor p-type metal oxides. Meanwhile, they have a high specific surface area, sensitivity to toxic gases, low cost and environmental friendliness. Of greatest interest among p-type metal oxides is nickel oxide [2–4]. Oriented nanowires based on nickel oxide NiO, as one of the few materials, are able to detect gases such as ammonia and nitrogen oxides at room temperature, which is the most significant advantage in their application.

Oriented nickel oxide nanowires are obtained by various methods, but from the point of view of economy and scalability, the most promising is the synthesis of nickel nanowires by chemical deposition from a liquid phase using a “soft” micellar template followed by oxidation of the obtained nanowires. Molecules of surface-active substances (surfactants) act as such a template, which, as a result of self-organization, form cylindrical micelles at the “solid-liquid” interface. These cylinders can be used as templates for the synthesis of metal nanonetworks. The characteristics of the micellar template will determine the length, width, and repetition period of metallic nanowires. In this regard, studies of the properties of a micellar template formed at the “solid-liquid” interface are of great practical importance.

In this work, we study the processes of self-organization of CTAB molecules at the glass–surfactant solution interface and the micellar template of CTAB on the surface of a glass substrate made of silicate glass. The obtained data on the processes of self-organization of STAB at the interface “solid body – liquid” allow to more effectively control the chemical deposition of metal networks.

Materials and Methods

In this work, a Levenhuk G 100 round cover glass with a thickness of 0.13–0.17 m and a diameter of 11 mm was used as the basis for the sensor. The glass substrate was preliminarily cleaned and degreased. Cleaning and degreasing were carried out with distilled water and ethyl alcohol, which can be replaced with isopropyl alcohol. The process of final cleaning consisted in immersing the substrate in ethanol and washing due to translational movements in the liquid bulk.

After that, the surface of the glass substrate was washed with distilled water. The surface was dried with an air jet.

Visualization of the surface of the glass substrate was carried out on a scanning probe microscope MultiMode V manufactured by Veeco (USA) in a discontinuous contact mode. For scanning, RTESP (Veeco) rectangular cantilevers with silicon probes were used. The resonant frequency of these cantilevers is in the region of 250–350 kHz, and the radius of curvature of the probe is 10–13 nm. Microscopic images were obtained with a resolution of 512×512 pixels per frame at a scanning speed of 1 Hz. To eliminate distortions associated with the "trembling" of the microscope under the influence of external noise, we used the SG0508 anti-vibration system, which is capable of smoothing vibrations with a frequency of up to 0.5 Hz (lower limit).

To obtain oriented nickel nanowires on the glass surface, we used the method of chemical metal deposition from the liquid phase using a CTAB micellar template. To form a micellar surfactant template, an aqueous solution of CTAB with a concentration of 1 mM was applied to the glass surface. After that, waited for 10 minutes to form a micellar template. Nickel chloride (nickel (II) chloride 6-aqueous) was used as a nickel precursor. Nickel nanowires were synthesized in the presence of a magnetic field.

Microscopic images of the CTAB micellar template on the glass surface were obtained in an AFM liquid cell. Before each experiment, the liquid cell was cleaned initially with bidistilled water and then with acetone. The feedback setting of the integral component during the experiment was in the range of 0.5–1, and the proportional component was in the range of 5–10. The scanning speed was maintained in the range of 1–2 Hz. The calibration of transverse dimensions was performed by scanning a special calibration grid (STR3-1800P, VLSI Standards Inc.) in a temperature range of 20–60 °C. The nonlinearity of the piezo crystal in this range is not observed. The images were obtained by contact AFM. In this case, the pressure force of the probe to the surface of the adsorbed micellar structures of STAB, at the interface of the liquid-substrate transition, was chosen as the smallest possible, at which the micelle structure is not disturbed and, at the same time, clear images can be obtained. Adsorbed CTAB structures have always been studied in regions that did not have surface topology irregularities.

Results and Discussion

Surfactant solutions, which at certain concentrations form cylindrical aggregates at the "solid body – surfactant solution" interface, are of particular interest. They can be used as a "soft template" for metal nanonetworks, which have recently become the subject of intensive research, due to the possibility of using them in many applications. Both anionic and cationic surfactants can be used for the micellar template. The choice of a specific surfactant is determined by the nature of the solid on which the surfactant molecules are adsorbed and a micellar template is formed. Depending on the type of substrate, cylindrical and semi-cylindrical structures of surfactant molecules may form at the "solid-liquid" interface, or they may not form at all. In our case, glass is used as a solid body. The shape of adsorbed surfactant structures, as well as the functional characteristics of gas sensors, will largely depend on the type and quality of the glass working surface, on which oriented nickel oxide nanowires are deposited as an active element. To assess the quality of the substrate surface, a parameter such as roughness is used.

To determine the roughness, the surface morphology of the selected glass substrate was examined by atomic force microscopy (AFM). The surface morphology of the glass substrate, which is used in this work as the basis for the sensor, and the topographic histogram are shown in Figure 1.

According to the obtained data, the surface roughness Ra (arithmetic mean of the absolute values of the profile deviations within the baseline) of the glass substrate is approximately 3.24 nm.

For a more detailed understanding of the processes of self-organization of CTAB molecules at the "glass-liquid" interface, we studied the wetting angles of the glass used in the work as a substrate with water and aqueous solutions of CTAB at various concentrations. As a result of the research, it was found that the contact angle of the glass substrate when wetted with water is 19.30, which indicates the hydrophilicity of the glass substrate.

The properties of glass strongly depend on the density of OH groups on its surface, and their density, in turn, is determined by the concentration of silicon on the surface. The SiOH groups play an important role in the adsorption of organic substances on the glass surface.

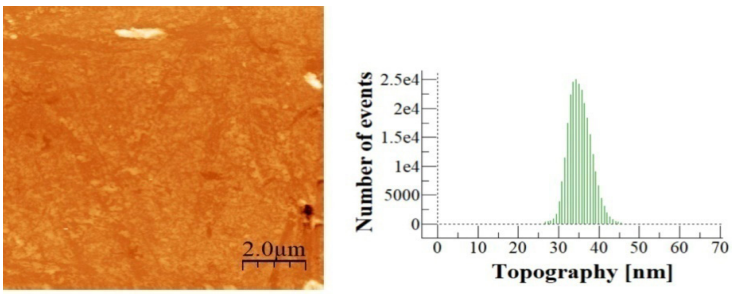

Fig. 1. AFM image of a small area of the glass substrate and the histogram corresponding to the topography

For the numerical characterization of the physicochemical properties of a solid surface, the value of the free surface energy is used. Measuring this value directly is a difficult task. Usually, indirect methods are used (for example, by measuring the contact angle).

Glass has a polar surface. The free surface energy is determined by two components: van der Waals interactions (interparticle interaction) and acid-base interactions:

$$\gamma_{SV} = \gamma_{SV}^{LW} + \gamma_{SV}^{AB}, \tag{1}$$

where γ_{SV} is free surface energy of a rigid body, γ_{SV}^{LW} is Lifshitz-van der Waals component, γ_{SV}^{AB} is acid-base interaction component (includes electron-acceptor and electron-donor parameters of the acid-base free energy component of a solid or liquid).

Various approaches are used to calculate the value of the free surface energy of a solid body. The most common approach in modern literature is the method of Neumann et al. [5, 6]. In these works, the ratio is used to calculate the value γ_{SV}

$$\frac{\cos\theta + 1}{2} = \sqrt{\frac{\gamma_{SV}}{\gamma_{LV}}} e^{-\beta(\gamma_{LV} - \gamma_{SV})^2}, \tag{2}$$

θ is contact angle of wetting of a solid surface by the liquid under consideration (for polar surfaces it must be polar, and for non-polar surfaces it must be non-polar), γ_{LV} is surface tension of a liquid, β is constant independent of surface type (β = 0.000115 $(m^2/mJ)^2$ [265]).

Equation (2) makes it possible to calculate the value γ_{SV} provided that the values and θ are known. However, this equation has no analytical solution. To determine the approximate value γ_{SV} appropriate substitutions are introduced into equation (2) and reduced to the form $f(x) = 0$. Next, Newton's iterative method is used [5].

Let's introduce substitutions:

$$x^2 = \frac{\gamma_{SV}}{\gamma_{LV}}; a = \frac{\cos\theta + 1}{2}; b = \beta \cdot \gamma_{LV}^2, \tag{3}$$

Equation (2) is transformed into the form

$$a = x \cdot e^{-b\left(1-x^2\right)^2} \text{ or } x = a \cdot e^{b\left(1-x^2\right)^2} \tag{4}$$

Because θ is obtained by measuring the system {solid - liquid - gas} with the condition $\gamma_{SV} < \gamma_{LV} \Rightarrow 0 \le x \le 1$. Then the problem is reduced to finding a solution to the equation:

$$f(x) = x - a \cdot e^{b\left(1-x^2\right)^2} = 0 \ , \ (0 \le x \le 1) \tag{5}$$

Newton's method is reduced to finding by successive approximation

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}, (n = 1, 2...) \quad (6)$$

Approximations (iterations) continue until the required degree of accuracy is obtained. In our case, to obtain the accuracy of the value to one decimal place in mJ/m^2, it is enough to reach $x3$.

$$x_{n+1} = x_n - \frac{x_n - a \cdot e^{b\left(1-x_n^2\right)^2}}{1 + 4abx_n\left(1 - x_n^2\right)e^{b\left(1-x_n^2\right)^2}}, \quad (7)$$

For pure water $\gamma_{LV} = 72.8\frac{mJ}{m^2}$, θ = 19.3°.

$$a = \frac{\cos 19.3 + 1}{2} = 0.973; \; b = 0.000115 \cdot 72.8^2 = 0.6095. \quad (8)$$

We choose the initial seed value x equal to 1.0:

$$x_2 = x_1 - \frac{1 - a \cdot e^0}{1 + 0} = a = 0.973, \quad (9)$$

$$x_3 = x_2 - \frac{x_2 - a \cdot e^{b\left(1-x_2^2\right)^2}}{1 + 4abx_2\left(1 - x_2^2\right)e^{b\left(1-x_2^2\right)^2}} = 0.9745, \quad (10)$$

$$\gamma_{SV} = x_3^2 \cdot \gamma_{LV} = 69.1\frac{mJ}{m^2}. \quad (11)$$

According to the calculated data, the free surface energy of the glass turned out to be 69.1 mJ/m^2.

For comparison, similar calculations were carried out for the glass used in the work (θ = 47°) [7, 8]:

$$\gamma_{SV} = x_3^2 \cdot \gamma_{LV} = 55.2\frac{mJ}{m^2}. \quad (12)$$

From the data obtained, it can be concluded that the free surface energy depends on the type of glass.

Further, to determine the concentration of CTAB at which a stable micellar pattern is formed on the surface of the glass substrate, we studied the concentration dependence of the wetting angle of the selected brand of glass with aqueous solutions of CTAB. The results obtained are presented in table 1.

Table 1

Concentration dependence of the contact angle of wetting a glass substrate with CTAB solutions

Concentration, мM	Contact angle θ, °
0.1	19.7
0.25	20
0.5	23.93
1	25.2
2	23.26
5	21.67
10	20.9

In the course of studies on the contact angle of wetting, it was revealed that wetting inversion is observed for the glass substrate. At concentrations below 1 mM, hydrophobization of the glass substrate is observed, and at concentrations above this, hydrophilization is observed. At a CTAB concentration of 1 mM, a transition from hydrophobicity to hydrophilicity is observed, and the formation of a micellar pattern is observed at the glass–CTAB solution interface.

The micellar template is a repeating cylindrical strip suitable for further deposition of oriented nickel nanonetworks. It was determined that the micellar pattern is formed 10 minutes after applying the STAB solution to the glass surface; the band repetition period in such a system is 4.5–5 nm.

To estimate the change in the surface energy of glass after the formation of a micellar template, the free energy of the glass–CTAB solution interface was calculated using the Yang equation (13) (C = 1 mmol/l) γ_{SL}:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos\theta. \quad (13)$$

For CTAB concentration 1 mmol/l $\gamma_{LV} = 41\frac{mJ}{m^2}$ and θ = 25.2°. Then

$$\gamma_{SL} = 69.1\frac{mJ}{m^2} - 0.905 \cdot 41\frac{mJ}{m^2} \approx 32\frac{mJ}{m^2}. \quad (14)$$

The value of the interfacial energy of the glass-surfactant solution calculated by the Yang equation turned out to be 32 mJ/m^2.

Conclusion

The dependences of the wetting contact angle of CTAB solutions on glass on a concentration were studied. It was found that the application of a CTAB solution with a concentration of 1 mM on the surface of silicate glass leads to the formation of a micellar system in the form of repeating cylindrical bands which is suitable for obtaining oriented nickel oxide nanonetworks. The free surface energy of the glass used in this work as the basis for the sensor was calculated. The value of free surface energy is 69.1 mJ/m^2. The free energy of the glass-CTAB solution interface was calculated using obtained for glass data. The value is 32 mJ/m^2. The results show that adsorption of surfactant molecules actually occurs at the glass-CTAB solution interface leading to a decrease in the free surface energy of the glass.

Acknowledgments

The reported study was funded by the government assignment for FRC Kazan Scientific Center of RAS. Nizameeva G. R. performed measurements of contact angle at Arbuzov Institute of Organic and Physical Chemistry and AFM studies at Kazan National Research Technological University. Gainullin R. R. performed liquid sample preparations at Arbuzov Institute of Organic and Physical Chemistry. Nizameev I.R. performed measurements of contact angle at Arbuzov Institute of Organic and Physical Chemistry and topographic studies at Kazan National Research Technical University. Kadirov M. K. performed calculations of surface tension constants at Arbuzov Institute of Organic and Physical Chemistry.

REFERENCES

1. **Barsan N., Weimar U.,** Conduction model of metal oxide gas sensors, Journal of electroceramics, 7 (3) (2001) 143–167.

2. **Hu Z., Chen D., Yang P., Yang L., Qin L., Huang Y., Zhao X.,** Sol-gel processed ytrrium doped NiO as hole transport layer in inverted perovskite solar cells for enhanced performance, Appl. Surf. Sci., 441 (2018) 258–264.

3. **Yu Y., Xia Y., Zeng W., Liu R.,** Synthesis of multiple networked NiO nanostructures for enhanced gas sensing performance, Mater. Lett., 206 (2017) 80–83.

4. **Zhang Y., Zeng W.,** New insight into gas sensing performance of nanoneedleassembled and nanosheet-assembled hierarchical NiO nanoflowers, Mater. Lett., 195 (2017) 217–219.

5. **Spelt J. K., Li D., Neumann A. W.,** The equation of state approach to interfacial tensions, Modern approaches to wettability, (1992) 101–142.

6. **Szymczyk K., Zdziennicka A., Jańczuk B.,** Adsorption and wetting properties of cationic, anionic and nonionic surfactants in the glass-aqueous solution of surfactant-air system, Materials Chemistry and Physics, 162 (2015) 166–176.

7. **Nizameev I. R., Muscat A. J., Motyakin M. V., Grishin M. V., Zakharova Ya L., Nizameeva G. R., Kadirov M. K.,** Surfactant templated oriented 1-D nanoscale platinum and palladium systems on a modified silicon surface, Nano-Structures & Nano-Objects, 17 (2019) 1–6.

8. **Kadirov M. K., Litvinov A. I., Nizameev I. R., Zakharova L. Y.,** Adsorption and premicellar aggregation of CTAB molecules and fabrication of nanosized platinum lattice on the glass surface, J. Phys. Chem. C., 118 (2014) 19785–19794.

THE AUTHORS

NIZAMEEVA Guliya R.
guliya.riv@gmail.com
ORCID: 0000-0002-4991-0502

NIZAMEEV Irek R.
irek.rash@gmail.com
ORCID: 0000-0002-5420-6181

GAINULLIN Radis R.
radis.g@mail.ru
ORCID: 0000-0002-0602-0470

KADIROV Marsil K.
kamaka59@gmail.com
ORCID: 0000-0003-3204-8431

Received 10.08.2022. Approved after reviewing 11.08.2022. Accepted 12.08.2022.