

08.1

Semiconductor vanadium compounds as a template for the formation of microporous particles of various morphologies

© D.A. Eurov, E.Yu. Stovpiaga, D.A. Kirilenko, A.N. Smirnov, D.A. Kurdyukov

Ioffe Institute, St. Petersburg, Russia
E-mail: edan@mail.ru

Received June 23, 2023

Revised November 3, 2023

Accepted November 7, 2023

Vanadium compounds — V_2O_5 and NH_4VO_3 — are used as a template to obtain porous silica. Both submicron spherical microporous SiO_2 particles and hybrid core–microporous shell particles are obtained in a single technological cycle. Selective etching of the core material (α - V_2O_5) results in obtaining SiO_2 particles with a hollow core.

Keywords: V_2O_5 , NH_4VO_3 , silica, micropores, template, core-shell, hollow core.

DOI: 10.61011/PJTF.2024.03.57038.19661

Obtaining and researching high-capacity, non-combustible and environmentally safe microporous dielectric materials is an urgent technological task [1]. Such materials find applications such as low dielectric permittivity insulators [2], thermal insulators [3], gas separation and storage devices [4], and in catalysis [5]. Among microporous materials, crystalline zeolites and $AlPO_4$ containing a system of interconnected pores less than 2 nm in size, with a specific surface area (SSA) up to 600 m²/g and a pore volume (V_p) up to 0.4 cm³/g are widely used [6].

Amorphous silica (α - SiO_2), which has such advantages as simplicity and rapidity of synthesis, high chemical and thermal stability, low toxicity, appears to be an alternative for the creation of microporous materials [7]. A number of applications (targeted drug delivery [8], chromatography [9], catalysis [10]) utilize spherical particles. The main method for synthesizing spherical particles α - SiO_2 is the Stöber method [11], but such particles are obtained non-porous. As a rule, to form a porous structure inside the particles, liquid crystals whose molecules act as a soft template are added to the reaction mixture [12]. This approach allows to achieve large porosity values (SSA \sim 1200 m²/g, $V_p \sim$ 1 cm³/g), but causes the formation of meso- rather than micropores.

There are two approaches to form micropores in α - SiO_2 particles: post-synthetic treatment of non-porous particles and modification of the Stöber method [13,14]. The difficulties in synthesizing microporous silica particles with high values of SSA and V_p are due to the fact that in the resulting particles the micropores are often isolated from each other and such closed pores are not included in the usable volume of the particles. In the present work, a simple and technological method for the synthesis of silica particles with interconnected micropores, core–microporous shell particles and microporous particles with a hollow core is proposed. Vanadium semiconducting compounds: vanadium pentoxide (α - V_2O_5) and ammonium metavanadate

(NH_4VO_3) were used as templates for pore formation in silica.

To obtain a saturated solution and synthesize ammonium vanadate particles, which subsequently serve as template, powdered vanadium pentoxide was dissolved under the action of ultrasound (ultrasonic bath „Sapphire with digital timer and thermostat“) in a mixture of $C_2H_5OH-NH_3-H_2O$ at 60°C. Due to the reaction of V_2O_5 and NH_3 , a saturated aqueous-alcoholic solution NH_4VO_3 was formed. It is known that NH_4VO_3 is poorly soluble in alcohol and better soluble in aqueous ammonia, with the solubility increasing with the temperature rise [15]. Upon cooling down, the vanadate solution became supersaturated and colloidal particles were formed in the mixture. After sedimentation of the coarse fractions for 24 h, the concentration of particles in the suspension, determined gravimetrically, was 4 g/L. This suspension was used to obtain core–shell type particles. A saturated solution of NH_4VO_3 , obtained by purifying the suspension from colloidal particles by centrifugation, was used to synthesize microporous spherical silica particles ($mSiO_2$).

The developed methodology for the synthesis of $mSiO_2$ particles using NH_4VO_3 as template is based on the Stöber method [11]. Tetraethoxysilane (TEOS) of mass 2 g was added to a concentrated solution of (0.5 L) NH_4VO_3 in a mixture of $C_2H_5OH-NH_3-H_2O$ (with concentrations of NH_3 and ethanol 4.5 and 11.0 M, respectively) with stirring under normal conditions. After 5 h, the obtained particles were centrifuged, washed with deionized water, dried at 100°C for 1 h and annealed for 5 h at 550°C to remove water and organics.

To obtain core–shell type particles ($V_2O_5-mSiO_2$), TEOS was added dropwise to the NH_4VO_3 particle suspension (4 g/L). The technique for coating particles with $mSiO_2$ shell is similar to the procedure described above for synthesizing microporous silica particles. The particles were

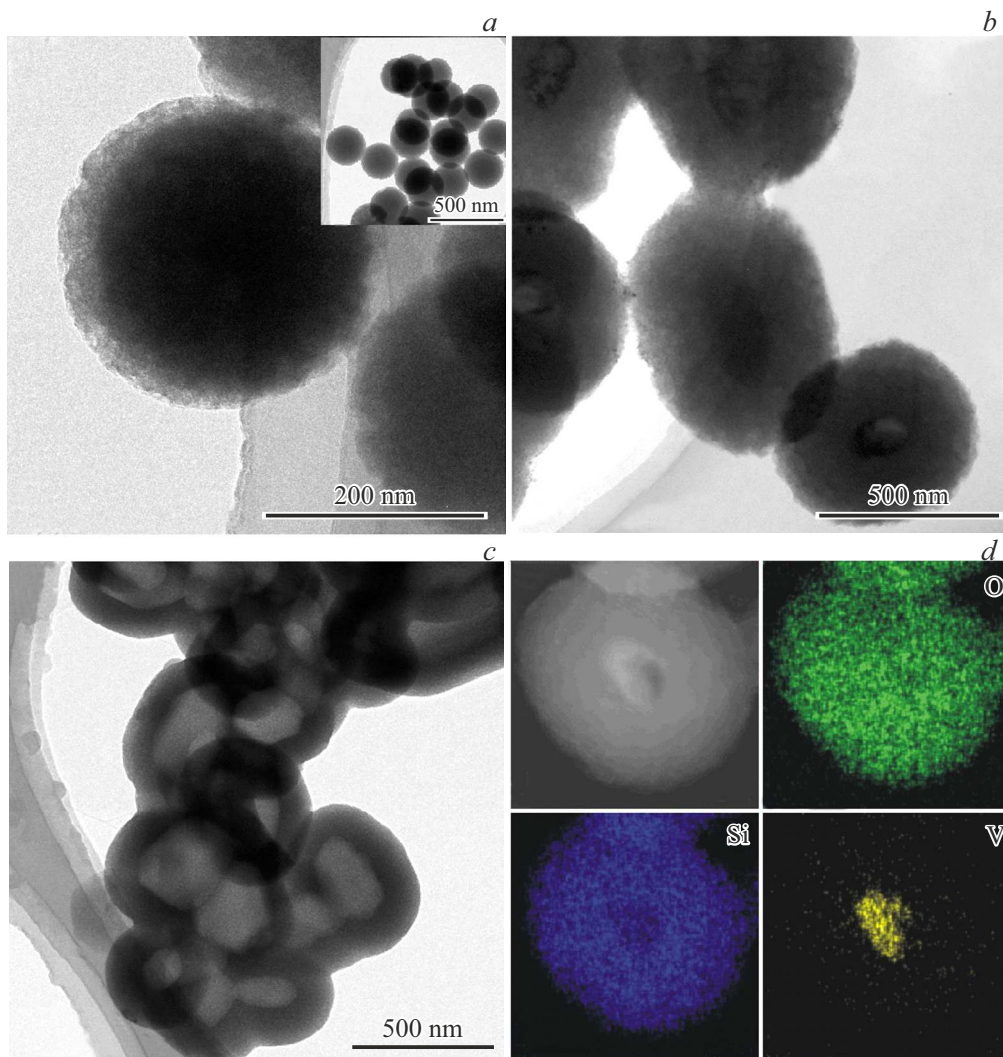


Figure 1. *a–c* — TEM images of the obtained particles: spherical microporous $m\text{SiO}_2$ particles (inset — image of a group of particles) (*a*); core-shell $\text{V}_2\text{O}_5\text{--}m\text{SiO}_2$ particles (*b*); hollow-core HC- $m\text{SiO}_2$ particles (*c*). *d* — enlarged TEM image and elemental EDX maps of O, Si, V for core-shell $\text{V}_2\text{O}_5\text{--}m\text{SiO}_2$ particles (size of images on the panel *d* — $0.55 \times 0.55 \mu\text{m}$).

then annealed in air at 550°C for 5 h to form crystalline V_2O_5 .

In order to obtain particles with hollow core (HC- $m\text{SiO}_2$, HC — hollow core) for etching of the core material (vanadium oxide), a weighed portion of $\text{V}_2\text{O}_5\text{--}m\text{SiO}_2$ particles was placed in 5% solution $\text{NH}_3 \cdot \text{H}_2\text{O}$ for 24 h. After dissolution of V_2O_5 , the particles of HC- $m\text{SiO}_2$ were separated by centrifugation, washed twice with deionized water, and dried at 100°C for 1 h.

Particle morphology was investigated using a Jeol JEM-2100F transmission electron microscope (TEM) equipped with a Bruker XFlash 6 T-30 X-ray energy dispersive (EDX) spectrometer. Fig. 1, *a–d* shows the results of TEM- studies for all types of synthesized particles. It can be seen that the particles $m\text{SiO}_2$ have a spherical shape and a small size deviation (inset in Fig. 1, *a*). According to dynamic light scattering (DLS) data obtained using a Malvern Zetasizer Nano ZS analyzer, the hydrodynamic

particle diameter is $270 \pm 20 \text{ nm}$. The enlarged image of the particles (Fig. 1, *a*) shows a loose structure, indicating the presence of pores uniformly distributed throughout the volume of the particles. In this case, the template is NH_4VO_3 dissolved in the reaction mixture. Probably, during the formation process, silica can interact with groups $\equiv\text{V}\text{--}\text{O}^-$ and $\equiv\text{V}\text{--}\text{OH}$ (horizontal dashes refer to the remaining four bonds of pentavalent vanadium) to form $\text{V}\text{--}\text{O}\text{--}\text{Si}$ bonds. A similar interaction was observed in the preparation of V_2O_5 catalysts on the surface of silica carriers [16]. In addition, the partially formed SiO_2 can adsorb VO_3^- and NH_4^+ ions from solution. After synthesis, the particles were washed with water, apparently resulting in dissolution of the template material, in place of which pores were formed.

The results of nitrogen adsorption porosimetry performed using a Micromeritics 3FLEX analyzer at the temper-

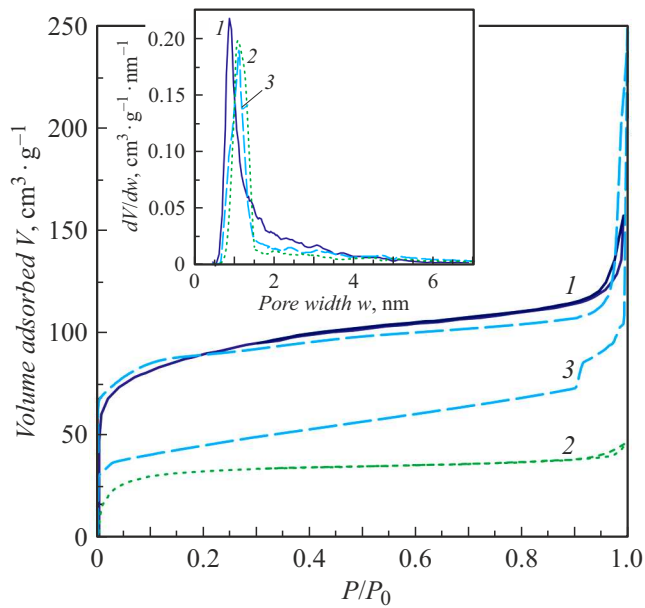


Figure 2. Nitrogen adsorption and desorption isotherms at 77 K and pore size distribution calculated by the NLDFT method (inset). 1 — spherical microporous particles $m\text{SiO}_2$, 2 — core-shell particles $\text{V}_2\text{O}_5-m\text{SiO}_2$, 3 — hollow-core HC- $m\text{SiO}_2$ particles.

ature of 77 K confirm the presence of micropores in the particles. Figure 2 (curve 1) shows the nitrogen adsorption and desorption isotherms for particles $m\text{SiO}_2$. The isotherms are of type I [17] and have the typical shape for microporous materials. The SSA value calculated by the Brunauer–Emmett–Teller method in the relative pressure range $0.05 \leq P/P_0 \leq 0.20$ (P_0 — saturated vapor pressure over a flat surface) was $320 \text{ m}^2/\text{g}$, and the pore volume (at $P/P_0 = 0.994$) was $0.25 \text{ cm}^3/\text{g}$. The inset to Fig. 2 (curve 1) shows the pore size distribution calculated using nonlocal density functional theory (NLDFT) for the obtained particles $m\text{SiO}_2$. The average size of micropores was $1.0 \pm 0.2 \text{ nm}$. A small number of larger pores, formed probably in place of adsorbed associates of VO_3^- and NH_4^+ ions are also observed, with little effect on the pore volume of the particles.

When obtaining hybrid particles with core-shell structure, the particles NH_4VO_3 present in the reaction mixture act as nucleation centers in the formation of SiO_2 . As a result, the coating of template particles with the shell of microporous $\alpha\text{-SiO}_2$ occurs, the mechanism of V–O–Si bond formation is probably similar to that in the synthesis of $m\text{SiO}_2$ particles. TEM images (Fig. 1, b) show that the almond-shaped nuclei are covered by a shell, which, as in the case of $m\text{SiO}_2$, has a loose structure. The almond-shaped core is due to the fact that it consists of rather large crystallites of NH_4VO_3 [18]. Indeed, the calculated size of the coherent X-ray scattering region was $\sim 55 \text{ nm}$ [18], which is on average $\sim 20\%$ of the particle core size. Therefore, the number of crystallites

forming the core is relatively small: from several tens to hundreds. Orthorhombic crystals of NH_4VO_3 tend to have an elongated shape. Obviously, the shape of particles assembled from large nonspherical crystals will also be different from spherical. The technique of coating NH_4VO_3 particles with the $m\text{SiO}_2$ shell was optimized versus [18] to increase its thickness, resulting in a particle shape closer to spherical.

Apparently the SiO_2 shell formed during synthesis adsorbs ions in solution, which are then dissolved at the washing stage with the formation of micropores in their place. The presence of the microporous shell allows the gaseous products of ammonium vanadate decomposition to be effectively removed during the $m\text{SiO}_2$ heat treatment process and to preserve the shape and size of the particle core during the transformation of NH_4VO_3 into V_2O_5 [18]. The average size of the obtained composite particles according to DLS data was $700 \pm 200 \text{ nm}$. The nitrogen adsorption-desorption isotherms for $\text{V}_2\text{O}_5-m\text{SiO}_2$ particles (curve 2 in Fig. 2) are also of type I [17]. The SSA and V_p values for the obtained particles were $170 \text{ m}^2/\text{g}$ and $0.1 \text{ cm}^3/\text{g}$, respectively. The pore size distribution (curve 2 in the inset to Fig. 2) shows that the particles contain micropores with an average size of $1.2 \pm 0.2 \text{ nm}$. The number of larger pores in $\text{V}_2\text{O}_5-m\text{SiO}_2$ particles is less compared to $m\text{SiO}_2$ particles. This may be due to the lower content of VO_3^- and NH_4^+ in the reaction mixture, as a result of which the formed shell probably adsorbs mainly single ions.

In Fig. 1, d the distribution maps of basic elements in the $\text{V}_2\text{O}_5-m\text{SiO}_2$ particle are presented, which confirm the formation of hybrid particles with the core-shell structure. It is seen that the shell also contains vanadium inside, the ions of which are obviously not completely removed at the stage of washing the particles in water. As indicated earlier, the microporous shell provides effective removal of gaseous decomposition products of metavanadate at the particle annealing stage and allows the transformation of the core material into V_2O_5 , as well as into V_2O_3 [18]. Fig. 3 (curve 2) shows the Raman spectrum for composite particles $\text{V}_2\text{O}_5-m\text{SiO}_2$ measured at room temperature on a Horiba Jobin Yvon T64000 spectrometer using Nd: YAG laser ($\lambda = 532 \text{ nm}$, $P < 3 \text{ kW}/\text{cm}^2$) as a second harmonic emission source. The spectrum contains a set of reflections typical for $\alpha\text{-V}_2\text{O}_5$ [19]. The spectrum for particles $m\text{SiO}_2$ (curve 1 in Fig. 3) is also given, which has a set of bands typical for $\alpha\text{-SiO}_2$ [20], while no phonon modes corresponding to V_2O_5 are observed. This indirectly confirms the completeness of the removal of vanadium compounds during the $m\text{SiO}_2$ particle washing from the template material. At the same time, when obtaining particles $\text{V}_2\text{O}_5-m\text{SiO}_2$, complete removal of vanadium from the shell pores is difficult due to the presence of a vanadium-containing core. As vanadium compounds dissolve from the micropores, they are „refueled“ by the partial dissolution of the core material, resulting in vanadium inside the shell of $\text{V}_2\text{O}_5-m\text{SiO}_2$ (Fig. 1, d).

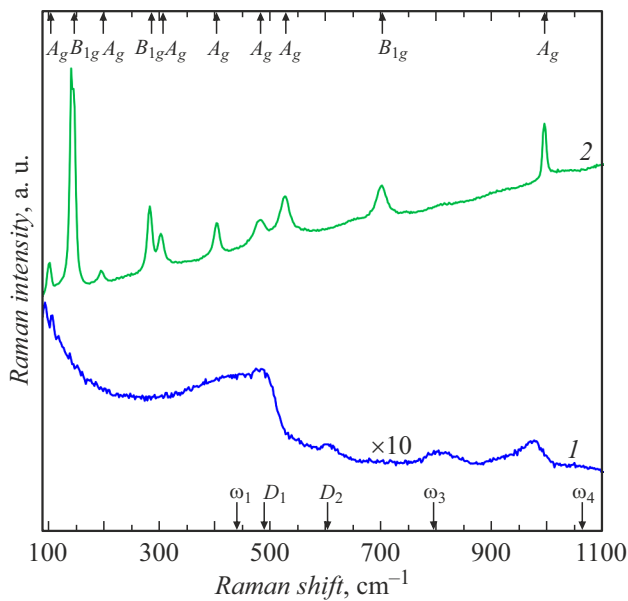


Figure 3. Raman spectra. 1 — spherical microporous particles $m\text{SiO}_2$, 2 — core-shell $\text{V}_2\text{O}_5\text{-}m\text{SiO}_2$ particles. Arrows indicate Raman-active phonon modes in $\alpha\text{-V}_2\text{O}_5$ [19] and $\alpha\text{-SiO}_2$ [20].

The presence of pores in the shell allows not only modification of the core material, but also its complete removal. Therefore, microporous silica particles with hollow core were obtained by dissolution V_2O_5 . Fig. 1, c shows TEM images of such particles. It can be seen that their size does not change much after the removal of the core. According to the DLS data, the average particle size of $\text{HC-}m\text{SiO}_2$ was 700 ± 200 nm, which correlates with the particle size of $\text{V}_2\text{O}_5\text{-}m\text{SiO}_2$. Fig. 2 (curve 3) shows the nitrogen adsorption-desorption isotherms for the obtained particles $\text{HC-}m\text{SiO}_2$. The values of specific surface area and pore volume were $150 \text{ m}^2/\text{g}$ and $0.35 \text{ cm}^3/\text{g}$ (at $P/P_0 = 0.996$), respectively. The pore size distribution (curve 3 in the inset to Fig. 2) shows that after removing the core V_2O_5 , the average size of micropores in the shell remains the same and is 1.2 ± 0.2 nm. The adsorption isotherm shows a sharp rise in the relative pressure region $P/P_0 > 0.9$ due to capillary condensation of nitrogen in a hollow core of ~ 480 nm in size (calculation by Kelvin equation at $P/P_0 = 0.996$), which correlates with TEM data. There is a wide hysteresis between the adsorption and the desorption isotherms up to relative pressures $P/P_0 \sim 10^{-5}\text{--}10^{-6}$. This is probably due to the fact that at relative pressures $10^{-5} < P/P_0 < \sim 1$ micropores of ~ 1 nm in size in the shell are completely filled with nitrogen, which hinders its desorption from the particle core at decreasing pressure.

Thus, this work proposes a simple and technologically advanced method for the synthesis of microporous particles of $\alpha\text{-SiO}_2$ based on the traditional Stöber technique using NH_4VO_3 as a template for the formation of micropores. The method allows to obtain spherical $m\text{SiO}_2$ particles with a size standard deviation not exceeding 7%. The

use of submicron particles NH_4VO_3 as a template allows the synthesis of hybrid particles, in the form of a V_2O_5 core covered by a shell of $m\text{SiO}_2$, containing a system of interconnected micropores that provide access of liquids and gases to the core. A method for selective etching of core material from $\text{V}_2\text{O}_5\text{-}m\text{SiO}_2$ particles has been developed. As a result, microporous SiO_2 particles with submicron-sized hollow core were obtained. At the same time each type of particles has its own advantages: $m\text{SiO}_2$ particles have the highest specific surface area and monodispersity, $\text{V}_2\text{O}_5\text{-}m\text{SiO}_2$ particles contain an active component for catalysis, and $\text{HC-}m\text{SiO}_2$ particles have the largest pore volume, which when used as nanocontainers for drug delivery will allow loading more of the target substance into them, as well as provide prolonged action due to slower drug release through the microporous shell. Note that all obtained particles have sedimentation and aggregation stability and form a stable aqueous suspension. The microporous structure determines the prospects of their application, for example, as adsorbents, in catalysis and medicine.

Acknowledgments

Transmission electron microscopy studies were carried out using the equipment of the Federal Center for Collective Use „Materials Science and Diagnostics in Advanced Technologies“.

Funding

The study was supported by the Russian Science Foundation grant № 23-79-00018.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] E. Doustkhah, Y. Ide, *New J. Chem.*, **44**, 9957 (2020). DOI: 10.1039/C9NJ06222J
- [2] M. Xie, M. Li, Q. Sun, W. Fan, S. Xia, W. Fu, *Mater. Sci. Semicond. Process.*, **139**, 106320 (2022). DOI: 10.1016/j.mssp.2021.106320
- [3] A. Headley, M. Hileman, A. Robbins, E. Piekos, P. Fleig, A. Martinez, C. Roberts, *Int. J. Heat Mass Transfer.*, **135**, 1278 (2019). DOI: 10.1016/j.ijheatmasstransfer.2019.02.073
- [4] R.-B. Lin, S. Xiang, W. Zhou, B. Chen, *Chem.*, **6**, 337 (2020). DOI: 10.1016/j.chempr.2019.10.012
- [5] W. Khan, X. Jia, Z. Wu, J. Choi, A.C.K. Yip, *Catalysts*, **9**, 127 (2019). DOI: 10.3390/catal9020127
- [6] *Handbook of porous solids*, ed. by F. Schüth, K. Sing, J. Weitkamp (Wiley, Weinheim, 2002).
- [7] A.J. Schwanke, R. Balzer, S. Pergher, in *Handbook of ecomaterials* (Springer, Cham, 2019), p. 3379–3399. DOI: 10.1007/978-3-319-68255-6_43

- [8] M. Vallet-Regí, *Int. Sch. Res. Notices*, **2012**, 608548 (2012). DOI: 10.5402/2012/608548
- [9] R. Hayes, P. Myers, T. Edge, H. Zhang, *Analyst*, **139**, 5674 (2014). DOI: 10.1039/C4AN01428F
- [10] J. Li, L.-S. Li, L. Xu, *Mater. Lett.*, **193**, 67 (2017). DOI: 10.1016/j.matlet.2017.01.091
- [11] W. Stöber, A. Fink, E. Bohn, *J. Coll. Interface Sci.*, **26**, 62 (1968). DOI: 10.1016/0021-9797(68)90272-5
- [12] D. Zhao, Y. Wan, W. Zhou, *Ordered mesoporous materials* (Wiley, Weinheim, 2013).
- [13] P.A. Bazuła, P.M. Arnal, C. Galeano, B. Zibrowius, W. Schmidt, F. Schüth, *Micropor. Mesopor. Mater.*, **200**, 317 (2014). DOI: 10.1016/j.micromeso.2014.07.051
- [14] R. Vacassy, R.J. Flatt, H. Hofmann, K.S. Choi, R.K. Singh, *J. Coll. Interface Sci.*, **227**, 302 (2000). DOI: 10.1006/jcis.2000.6860
- [15] M. Trypuć, K. Białowicz, *J. Chem. Eng. Data*, **42**, 318 (1997). DOI: 10.1021/jc960259q
- [16] F.J. Feher, J.F. Walzer, *Inorg. Chem.*, **30**, 1689 (1991). DOI: 10.1021/ic00008a005
- [17] S.J. Gregg, K.S.W. Sing, *Adsorption, surface area and porosity*, 2nd ed. (Academic Press, London, 1982).
- [18] D.A. Eurov, D.A. Kirilenko, L.V. Sharonova, A.V. Shvidchenko, A.N. Smirnov, M.V. Tomkovich, M.A. Yagovkina, D.A. Kurdyukov, *Mater. Today Commun.*, **35**, 106047 (2023). DOI: 10.1016/j.mtcomm.2023.106047
- [19] R. Baddour-Hadjean, J.P. Pereira-Ramos, C. Navone, M. Smirnov, *Chem. Mater.*, **20**, 1916 (2008). DOI: 10.1021/cm702979k
- [20] D.J. Little, M. Ams, P. Dekker, G.D. Marshall, J.M. Dawes, M.J. Withford, *Opt. Express*, **16**, 20029 (2008). DOI: 0.1364/OE.16.020029

Translated by D.Kondaurov