EasyChair Preprint

№ 399

Deposition of sorption and photocatalytic material on nanofibers and fabric by controlled sublimation

Richard Dvorsky, Ladislav Svoboda, Jiří Bednar, Pavel Mancik, Dalibor Matysek and Marketa Pomiklova

August 5, 2018

Deposition of Sorption and Photocatalytic Material on Nanofibers and Fabric by Controlled Sublimation

R Dvorsky[1,2], L Svoboda[1,3], J Bednář[1], P Mančík[1], D Matýsek[4] and M Pomiklová[5]

[1]Nanotechnology Centre, VŠB-Technical University of Ostrava, Czech Republic

[2]IT4-Inovations Nat. Supercomputing Center, VŠB-Technical University of Ostrava, Czech Republic

[3]Institute of Environmental Technologies, VŠB-Technical University of Ostrava, Czech Republic

[4]Institute of Clean Technologies for Mining and Utilization of Raw Materials for Energy Use, VŠB-Technical University of Ostrava, Czech Republic

[5]TEM laboratory, Public Health Institut Ostrava, Czech Republic

corresponding author: richard.dvorsky@vsb.cz

Keywords: controlled sublimation, sorption fabric, sorption capacity, controlled sublimation technology, photocatalytic regeneration, high specific surface area

Abstract. This paper presents a new method of deposition of photocatalytic sorbent on nanofibers. This deposition uses controlled sublimation of water molecules from the vacuum-gel that is patent-protected. Silica gel nanostructures are precipitated by heterogeneous nucleation on the surface of nanofibres from an aqueous suspension of silicate nanoparticles and semiconductor carbon nitride (C_3N_4) or graphene nanosheets. After rapid solidification of gel (at least 10^4 K/s), the nanofibers coated with the silica gel dispersion C_3N_4, or graphene are subjected to controlled sublimation at –41 ^oC. This technology produced a nanofibrous material, which is stably coated with a highly porous silicate sorbent including dispersed photocatalytic nanoparticles. This textile material has a total sorption surface area of the order of hundreds m^2/g. Unlike conventional sorbents, it is capable due to dispersed photocatalytic nanoparticles to regenerate sorption capacity by the absorption of visible light. The results of the preliminary research confirmed the high application potential of new controlled sublimation technology in the production of regenerable photocatalytic sorption fabrics.

Introduction

Current technology uses suitable chemical compounds and materials that have a sorption and degradation effect against industrial pollutants and CBRN military agents. Pollutants are either disposed of with sorbents after sorption, or they are decomposed on the surface of sorbents on non-hazardous components. Just in this area of the combination of sorption and (photo) catalytic decomposition are considerable reserves in current technology.

Information obtained during the research and development of the new technology of controlled sublimation [1] confirms new possibilities of production and increase of sorption and photocatalytic efficiency of nanostructures of environemtntally inert materials such as new type of carbon-silicate and oxidic materials [2], [3] and [4]. Based on the research of self-organization of nanoparticles at the sublimation interface, a new technology for the preparation and modification of special nanomaterials with high values of active surface was created [1]. Based on the study of the collective behavior of the nanoparticles set in the diluted gas (vacuum) an analysis of the self-organization of nanoparticle lamellar aggregates at the sublimation interface was performed. At the same time, a basic mathematical simulation of self-organization of nanoparticles on the sublimation phase interface was carried out in different modes of vacuum sublimation of frozen liquid nanodispersion [5]. An illustrative example of patented technology can be the first application of controlled sublimation technology to the aqueous dispersion of globular nanoparticles. In which a

high specific surface area of lamellar nanoagregates in the order of hundreds m^2/g was achieved compared to m^2/g for the material obtained by the standard method of thermal drying see Fig. 1.

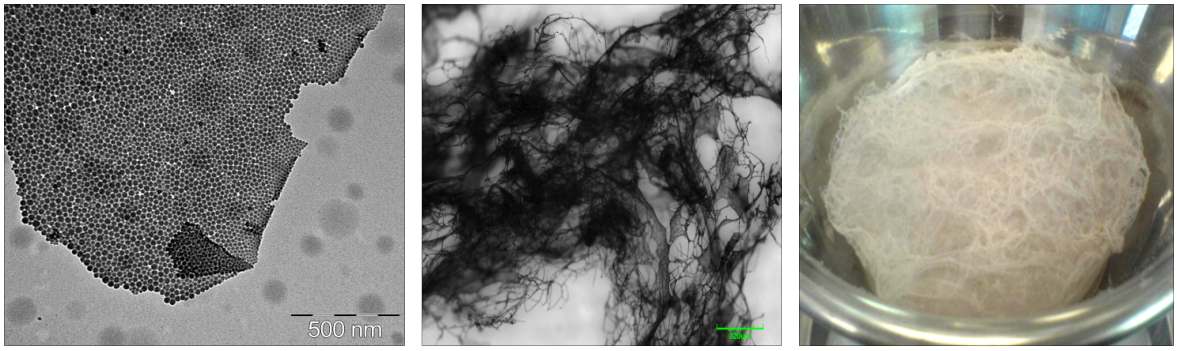

Figure 1. Left: Image of lamellar aggregates of fullerite nanoparticles nC_{60} using the transmission electron microscopy, right: image of lamellar aggregates of silicon nanoparticles obtained by confocal optical microscopy (middle) and "Silicon cotton candy" in macroscopic photograph.

In protecting people and the environment they are currently in the military and civilian sectors used sorption protective fabric and filters. On Fig. 2 is depicted the theoretical dependence of the specific surface for particles, fibers and lamellas on the characteristic dimension *d*.

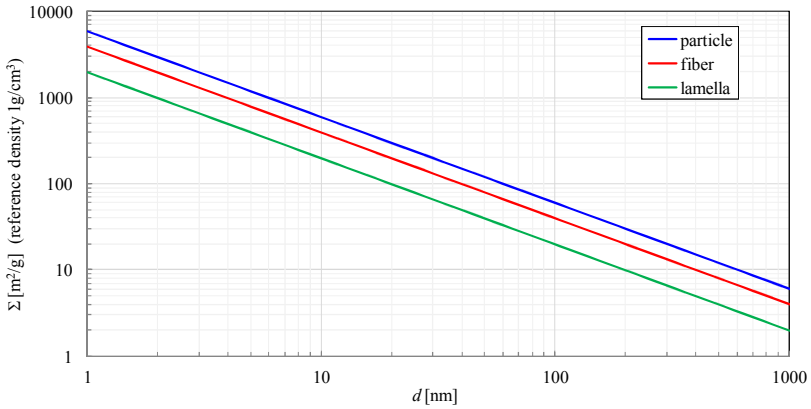

Figure 2. The relationship between the specific surface area and the characteristic size *d* of compact particle, fibre and lamella with reference density 1 g/cm^2

It is clear from the graph in Fig. 2 that the preparation of effective, pure fiber sorption materials with a SSA of hundreds m^2/g is technically unrealistic. An important application potential of ontrolled sublimation technology is the possibility of efficient deposition of active sorption and photocatalytic nanostructures directly onto fibers and fabrics with the intention of obtaining a completely new protective material. This material does not show normal sorption saturation but photocatalytically degrades hazardous chemical forms of pollutants on harmless components directly during sorption exposure. Mentioned ability was checked by repeated exposure and photocatalytic reactivation of laboratory-prepared sorption fabric.

Application of controlled sublimation to sorbent deposition on fibers

Physical background. The physical principle of deposition of the active sorption nanomaterial is based on the synthesis of silica gel porous nanostructure in the presence of dispersed nanoparticles C_3N_4 and PUR nanofibers. Due to the significantly higher probability of heterogeneous nucleation at the interfacial interface, preferential precipitation and growth of the composite solid phase on the surface of the fibers. After rinsing the fabric thereby exposed the material was quickly frozen and subsequently subjected to controlled vacuum sublimation under vacuum at room temperature - 28 ^oC. By applying conventional thermal drying leads to significant degradation of porous structure. By applying the above-mentioned sublimation technology, the porous structure is well preserved and the resulting material exhibits high surface area values.

Materials and chemicals. As carrier material to which photocatalytic sorbent nanomaterials were deposited was nanofibers NnF MBRANE®- PUR 5gsm from the company PARDAM. The final nanocomposite material was synthesized in the reaction of sodium water (M = 3) from the company Vodní sklo, a.s. and zinc acetate dihydrate $Zn(Ac)_2*2H_2O$ (purity >99.9 %) from the company Sigma-Aldrich. The C_3N_4 nanoparticles were synthesized from melamine (purity 99 %, Sigma-Aldrich) by thermal treatment according to our previous work [6].

Instrumentation. The final nanostructures were studied by scanning electron microscopy SEM FEI Quanta 650 FEG and transmission electron microscopy Jeol JEM 1230, operating at 80 kV. To evaluate the sorptive and photocatalytic efficacy of the prepared materials was used UV-VIS spectrometer OCEAN OPTICS USB4000.

Experimental

The microfiber photocatalytic coating by controlled sublimation. By applying the above mentioned controlled sublimation technology to deposit the photocatalytic material on PUR nanofibers, a photocatalytically active sorption fabric fixed on a microfibre support substrate was created. This fixed nanofibers are coated with a sorption photocatalytic nanostructure based on zinc silicate network Si-O-Zn with dispersed nanoparticles 1) graphene Si-O-Zn/C_{graph} (see Fig. 3), 2) carbon nitride Si-O-Zn/C_3N_4 (see Fig. 4.).

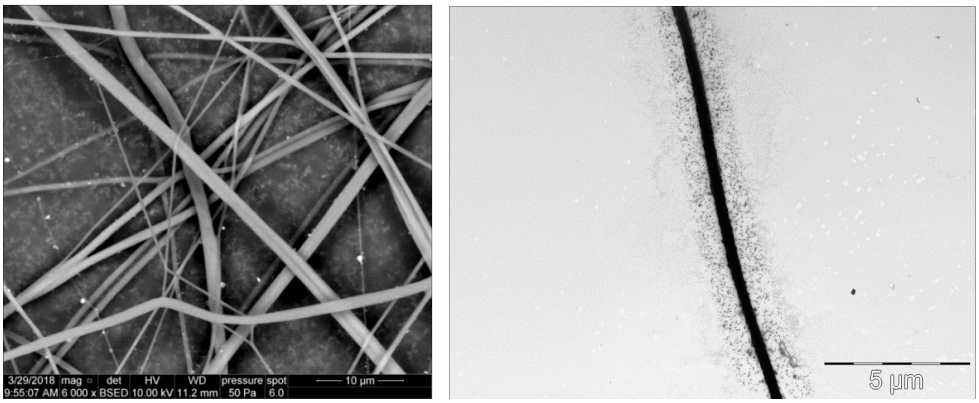

Figure 3. SEM micrograph of the original fiber NnF MBRANE®- PUR 5gsm firmy PARDAM and TEM of the same fiber coated with a porous nanostructure Si-O-Zn/C_{graph} with specific surface area 410 m^2/g, graphene nanoparticles are noticeable and dispersed in the silicate shell.

The EDX analysis determined the elemental representation of the individual components in the silicate nanostructure with the result 4Si: 13O : 3Zn. Such a structure has itself a good photocatalytic properties that were increased by adding graphene nanoparticles Si-O-Zn/C_{graph}. The half-life of photocatalytic degradation of methylene blue at UV 365 nm was about 2000 s.

For practical use, photocatalytic regeneration in the visible spectrum is preferred. For these reasons, further attention was devoted to the second variant of nanomaterial Si-O-Zn/C_3N_4 (see Fig. 4) with an absorption maximum at 417 nm.

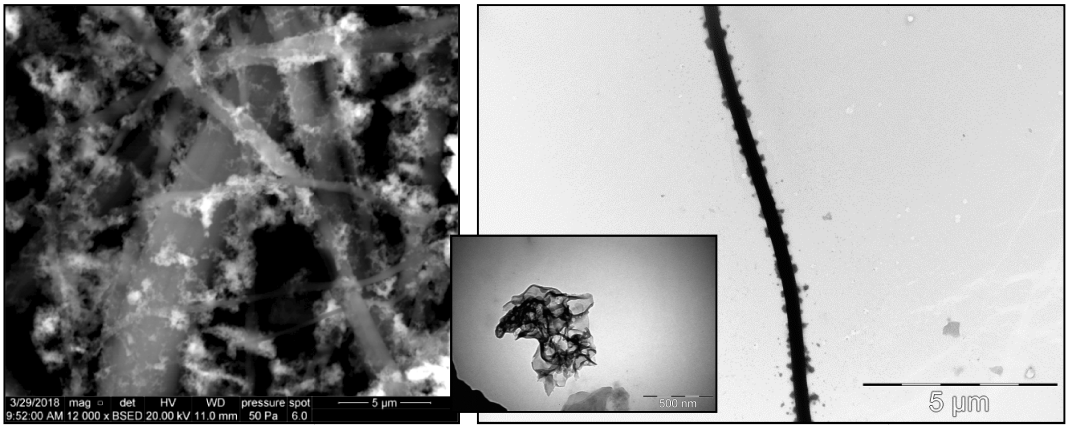

Figure 4. Left: SEM micrograph of original fiber NnF MBRANE®- PUR 5gsm from the company PARDAM, right: TEM image of of the same fiber coated with microporous nanostructure Si-O-Zn/C_3N_4 with SSA ≈ 240 m^2/g and detail of the exfoliated C_3N_4 particle.

EDX analysis also provided an indicative representation of C_3N_4 in the final nanocomposite Si-O-Zn/C_3N_4, which was around 80 wt.%. The final deposited sorption photocatalytic fabric exhibited at area weight 0.3 kg/m^2, the proportion of active material is about 65 %. The specific sorption surface per unit area of fabric was about 110 m^2/m^2. Its sorption and photocatalytic properties are described below.

The photocatalytic sorption capacity regeneration. In our previous work [7] we tested regeneration of sorption capacity of Si-O-Zn/C_3N_4 material. The repeated experiment confirmed the full recovery of sorption capacity as well as the maintenance of sorption kinetics (see Fig. 5.)

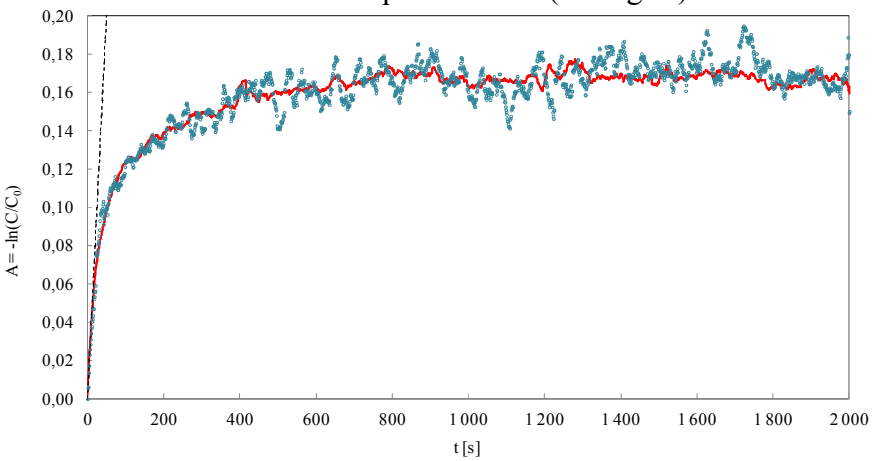

Figure 5. Reaction kinetic of methylene blue sorption on the primary nanomaterial Si-O-Zn/gC_3N_4 is depicted as the blue dot graph and the sorption kinetics of the same material after photocatalytic reactivation is depicted as the red line graph. The dashed linear function corresponds to the value of the kinetic constant $k = 0.004\ s^{-1}$ [7].

The mentioned experiment was performed on a particulate material dispersed in methylene blue solution. Subsequent regeneration of photocatalytic particles was performed by exposure to radiation of 10 W violet LED source with a maximum intensity at 416 nm. The half-time of sorption was only 30 seconds (see Fig. 5.)

For the practical application of sorption fabrics with photocatalytic regeneration, the speed of regeneration is equally important. In tests of the sorptive fabric function, we degraded another simulant, the indigo carmine (IC) dye. Its decomposition was performed in the presence above-mentioned LED source, the layer of fabric was covered by an aqueous solution of IC with initial concentration 12 mg/l. The experiment was carried out in a 3 mm layer of IC solution over the bottom of a flat container that was covered with a sorption fabric. The result of the experiment (see Fig. 6) confirms very good efficiency of photocatalytic regeneration with a half-life about 210 s.

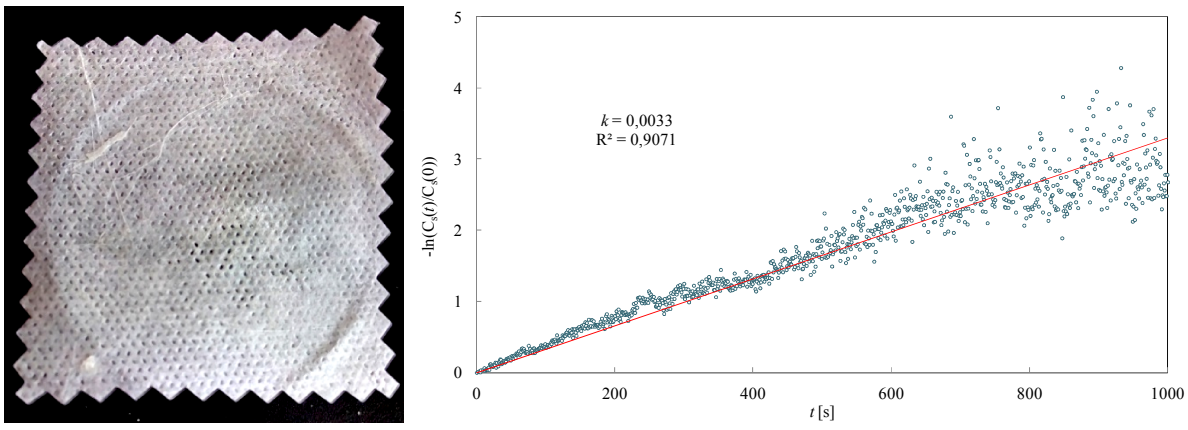

Figure 6. Left: the photograph of the active side of the photocatalytic sorptive fabric, right: the experimentally determined kinetic of IC degradation.

Conclusion

Parameters of sorption fabric with photocatalytic regeneration have proved to be of great interest for practical applications both in terms of stability of fixation and in terms of sorption and photocatalytic efficiency. The achieved results confirm the considerable application potential of the new technology of deposition and fixation of photocatalytic sorbents into nanofibrous structures. On the basis of these results, further intensive research is being carried out in order to achieve a higher sorption capacity and to minimize the economic cost of the technology for the under consideration commercial applications.

Acknowledgments

This work was supported by The Ministry of Education, Youth and Sports from the National Programme of Sustainability (NPU II) project „IT4Innovations excellence in science - LQ1602“, the project Double degree CZ.02.2.69/0.0/0.0/16_018/0002708, this work was also supported by the Grant Agency of the Czech Republic (reg. No. 16-10527S), the Ministry of Education, Youth and Sport of the Czech Republic within the project TEWEP (National Feasibility Program LO1208), by project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic and by the student projects SP2018/79 and SP2018/75.

References

[1] Dvorsky R: Patents: Czech-303513 (2012), USA-US 9,410,739 B2 (2016), Japan-JP5961266 B2 (2016), China-CN 103842755 B (2016), Russia-RU 2599282 (2016), European Patent-EP2751508B1 (2017)

[2] Dvorsky R, Bednář J, Svoboda L, Šollová K, Kukutschova J, Peikertova P, Matýsek D, 2016, Preparation of high-performance photocatalytic core-shell lamellar nanostructures ZnO-(Si)-ZnO with high specific surface area, *Advanced Materials Letters*, **7**(**9**), 730-734

[3] Dvorsky R, Svoboda L, Kočí K, Mančík P, Bednář J, Kostura B, Študentová S, Šihor M, 2017, Preparation of Highly Porous Photocatalytic Nanostructure Containing Graphene Nanoparticles for Exciton Charges Delocalization, *2nd International Conference on Sustainable Materials Science and Technology (SMST2)*, Las Plamas - Spain (2017)

[4] Svoboda L, Dvorsky R, Praus P, Matýsek D, Bednář J, 2016, Synthesis of ZnO nanocoatings by decomposition of zinc acetate induced by electrons emitted by indium, *Applied Surface Science*, **388** (Part **A**), 491-496

[5] Krpelík D, Dvorsky R, Mančík P, Bednář J, Svoboda L, 2018, Mathematical modelling of lamellar aggregation of dispersed globular nanoparticles nC_{60} on the interface upon sublimation of water molecules from rapid frozen dispersion, *Journal of Nanoscience and Nanotechnology*, *in press*

[6] Svoboda L, Prous P, Lima J.M, Sampaio J.M, Matýsek D, Ritz M, Dvorsky R, Faria L.J, Silva G.C, 2018, Graphitic carbon nitride nanosheets as highly efficient photocatalysts for phenol degradation under high-power visible LED irradiation, Materials Research Bulletin, **100**, 322-332

[7] Mančík P, Bednář J, Svoboda L, Dvorsky R, Matýsek D, 2017, Photocatalytic reactivation of g-C_3N_4 based nanosorbent, 9th NANOCON, 2017, Brno, Czech Republic, 289-294.