

Preparation of high-performance photocatalytic core-shell lamellar nanostructures ZnO-(Si)-ZnO with high specific surface area

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ABSTRACT

A new preparation method of lamellar core-shell ZnO-(Si)-ZnO nanostructures with high specific surface area and high photocatalytic efficiency is presented in this article. This novel method is based on the application of controlled vacuum sublimation of the frozen liquid dispersion of silicon nanoparticles which were prepared by using the "top-down" process in cavitation Water Jet Mill disintegrator. The particle size of thus disintegrated silicon nanoparticles was measured by dynamic light scattering (DLS). Final product ZnO-(Si)-ZnO was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and amount of ZnO and Si was measured by energy dispersive x-ray spectroscopy (EDAX). Specific surface area was obtained from Brunauer-Emmett-Teller analysis (BET). The photocatalytic activity of ZnO-(Si)-ZnO nanostructure was verified by the decomposition of methylene blue (MB) solution. The Final nanomaterial shows a relatively high specific surface area of 134 m²/g and significantly higher photocatalytic activity compared to standard TiO₂ (Degussa P25). Such procedure based on the controlled vacuum sublimation of frozen liquid of suitable metal salts could be a promising method for obtaining photocatalytic nanomaterials with higher specific surface area. Copyright © 2016 VBRI Press.

Keywords: Nanoparticle; core-shell structure; photocatalysis; sorption.

Introduction

The issue of environmental pollution by industrial pollutants such as nitrogen oxides is currently more actual than ever before. The latest measurements showed that the concentration of nitrous oxide (N₂O) in the atmosphere reaches 612 µg m⁻³ and its concentration is increasing by 0.2–0.3% annually [1]. With the respect to their high stability and negative effects on the ozone layer it is highly desirable to develop processes in which these pollutants will be degraded to neutral elements such as N₂ and O₂. Photocatalytic degradation by using photoactive nanoparticles like TiO₂, ZnS or ZnO seems to be very promising way how to eliminate these pollutants [2-3].

Many methods have been described for the preparation of ZnO nanomaterials for photocatalysis, such as laser ablation [4, 5], hydrothermal methods [6, 7], electrochemical depositions [8, 9], sol-gel method [10-12] and even radiolysis synthesis [13, 14]. With the regard to the Langmuir law of active surfaces [15] the high specific surface area of nanoparticles is important factor in their application in the processes of photocatalytic degradation of pollutants. Due to difficult practical manipulating with very small volumes it is often very advantageous to deposit

nanoparticles on the surface of larger carrier microparticles [16, 17]. At the same time for optimal photocatalytic activity is also very important the morphology of dried powder. This morphology is very strongly dependent on the drying technology.

The aim of this research was to prepare photocatalytic nanomaterial with core-shell structure and with high specific surface area. A new method of preparation of lamellar core-shell nanostructures ZnO-(Si)-ZnO with high specific surface area and high photocatalytic efficiency is presented and further this method could be used for preparation of other photocatalytic materials with high specific surface area.

Experimental

Materials

Zinc acetate dihydrate (≥ 98 %) was obtained from Sigma Aldrich and used without any further purification for preparation of solution for liquid dispersion. Pure polycrystalline silicon ASS., 99.95 % in pieces was obtained from Sigma Aldrich and was then disintegrated in Water Jet Mill disintegrator into the form of

nanopowder. Standard photocatalytic material Aeroxide[®] TiO₂ P25 (≥ 99.5%) was obtained from company Evonik Degussa for the comparison and used without any modification as a benchmark in degradation of methylene blue.

Characterization

An analysis of particle size of silicon and measuring of zeta potential was performed by DLS on a Malvern Zetasizer Nano ZS. Water Jet Mill disintegrator was used for obtaining silicon fraction with lower particle size. TEM was performed on Jeol JEM 1230 microscope operated at 80 kV. Composition of final product was analyzed by using EDAX in SEM FEI Quanta 650 FEG and analysis of the average composition was performed on a region of 50 × 50 microns. Specific surface area was determined by dynamic analysis of BET isotherm on the device HORIBA SA-9600. Concentration of MB was measured by the optical fiber of UV-VIS spectrometer OCEAN OPTICS USB4000 in the range of 660-670 nm.

Preparation of Si nanoparticles

The basic material for carrier particles was polycrystalline silicon ASS, 99.95 % in pieces. After coarse grinding in planetary mill a fraction with particle size below 100 μm was obtained by sieve analysis. This fraction was dispersed in demineralized water and further refined by implosions of cavitation bubbles in Water Jet Mill disintegrator which was developed in our institute [18, 19]. After the disintegration of the primary aqueous microdispersion ($d \leq 100 \mu\text{m}$) was separated from the output dispersion a fraction below 200 nm by turbulent cross-flow filtration method. Subsequently, an analysis of particle size by DLS was performed.

Preparation of lamellar nanostructure ZnO-(Si)-ZnO

In the next stage, in the prepared aqueous dispersion of silicon nanoparticles zinc acetate dihydrate was dissolved in a concentration of 0.01wt% and then this dispersion was sonicated for 30 minutes in ultrasonic field of 50 W/l. Thus prepared nanodispersion of Si particles in zinc acetate solution was then rapidly frozen to -21 °C and subjected to a controlled vacuum sublimation at a pressure of 95 % of the value for saturated steam (at -21 °C). This process is a special application of the patented technology [18] which was previously only used for the preparation of pure lamellar nanoaggregates of various nanoparticles with high specific surface area [19-20]. In our new application the fixation of small nanocrystals of zinc acetate occurs at a surface of silicon carrier particles during sublimation of the water molecules. This process illustrate scheme on Fig. 2a. Particles move gradually during sublimation of the water molecules from the frozen dispersion to sublimation interface on which nanocrystals of zinc acetate encapsulated and simultaneously aggregated into lamellar nanostructures.

In the chamber with frozen nanodispersion (Fig. 1b) the material remains in the form of wool after completely sublimation of water molecules. After controlled freeze-drying sublimation of dispersion, the lamellar

nanoaggregates Zn(OAc)₂-(Si)-Zn(OAc)₂ were further dried for 60 minutes at the temperature 102 °C.

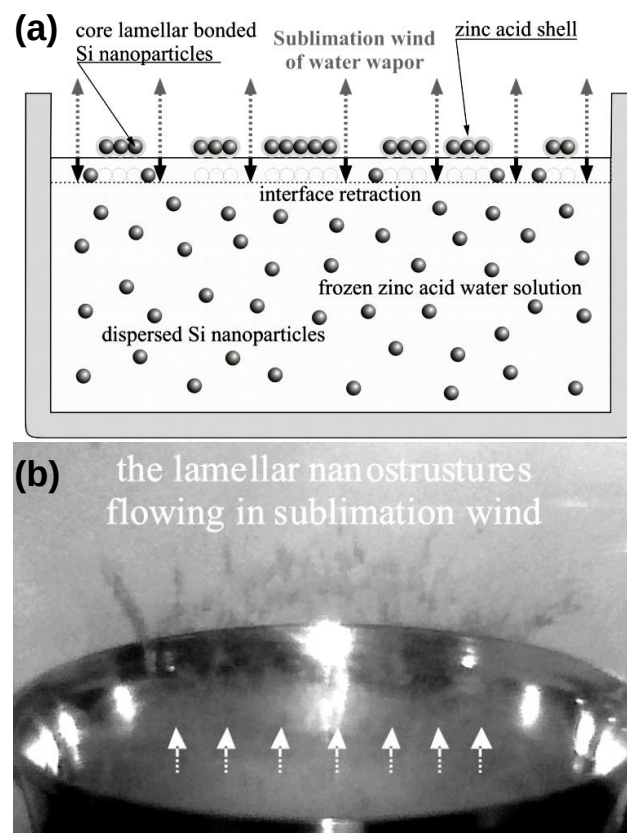


Fig. 1. (a) Scheme of preparation of Si nanoparticles with zinc acid "shell" in frozen liquid dispersion by controlled vacuum sublimation, and (b) image of sublimation interface with lamellar aggregates of Si nanoparticles flying in a "sublimation wind".

The drying temperature was chosen from the reason to gently remove crystalline water with minimal disruption of lamellar nanostructures. Subsequently, the temperature was raised to 300 °C and the material was annealed over 60 minutes in an oxidizing atmosphere. The annealed material was triturated after cooling to a very fine powder.

Photocatalytic tests

The photocatalytic efficiency of the new nanocomposite material ZnO-(Si)-ZnO was subsequently tested in the degradation of methylene blue (MB) in aqueous solution by UV radiation with maximum emission intensity at 365 nm. In a stirred photocatalytic reactor with volume of 250 ml the time dependence of the relative concentration of methylene blue by nephelometric method in the range from 670 to 680 nm was measured. An aqueous solution of MB with concentration 10^{-6} mol/dm^3 was mixed with an equal volume of demineralised water in which microparticles of nanocomposite material ZnO-(Si)-ZnO in a concentration of 0.01 wt% were dispersed by intensive sonication for 30 minutes. For comparison the rate of photocatalytic efficiency of standard material Aeroxide[®] TiO₂ P25 Evonik Degussa was obtained by the same experimental method. Due to the photolysis of methylene blue caused by UV irradiation it was necessary in the first stage to measure the time dependence of the decrease in its relative

concentration $c/c_0 = c(t)/c(0)$ (for $c(0) = 5 \cdot 10^{-6} \text{ mol/dm}^3$) in the radiation field of Hg UV lamp. To determine the concentration of MB a red laser source with maximum wavelength intensity at 763 nm was chosen (**Fig. 2**).

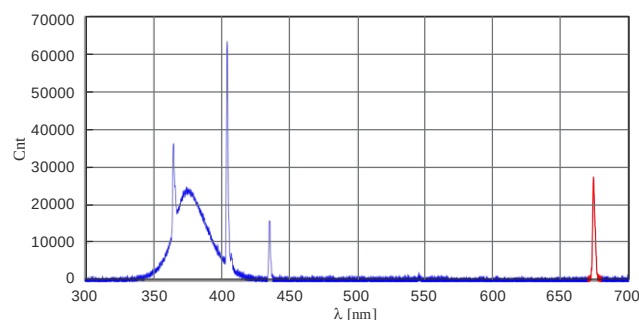


Fig. 2. Basic UV-VIS spectra of light in photocatalytic reactor. The blue - basic UV spectra of UV lamp 365 nm. The red - peak depicts ROI for count integration of red laser light (673 nm) for nephelometric analysis.

Results and discussion

DLS analysis

The result is shown on **Fig. 3** in the form of statistical distribution of the particle volume with mean particle size $d = 109 \text{ nm}$. The liquid nanodispersion of Si nanoparticles showed excellent stability with a value of zeta potential of 23.7 mV.

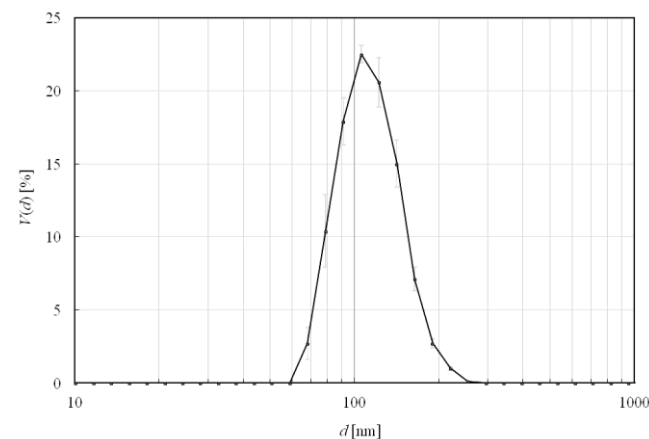


Fig. 3. The statistical distribution of the particle volume of Si nanoparticles with mean particle size $d = 109 \text{ nm}$.

BET analysis

Final product $\text{ZnO}(\text{Si})\text{-ZnO}$ showed relatively high value of specific surface area $134 \text{ m}^2/\text{g}$. This represents a significant advantage of a high value of the reaction area in heterogeneous catalytic reactions and contributes significantly to increase the reaction rate. Prepared material exceeds specific surface area of standard photocatalytic material Aerioxide® TiO_2 P25 Evonik Degussa ($50 \text{ m}^2/\text{g}$) of about 170 %.

TEM and SEM analysis

Detailed appearance of the $\text{Zn}(\text{OAc})_2(\text{Si})\text{-Zn}(\text{OAc})_2$ nanostructure is shown in the micrograph of TEM on

Fig. 4. Bright broken fins in the background match to ground membrane formvar on TEM grid. This material created nanostructure of aggregated silicon carrier particles covered by shell from small zinc acetate nanocrystals with size below 20 nm.

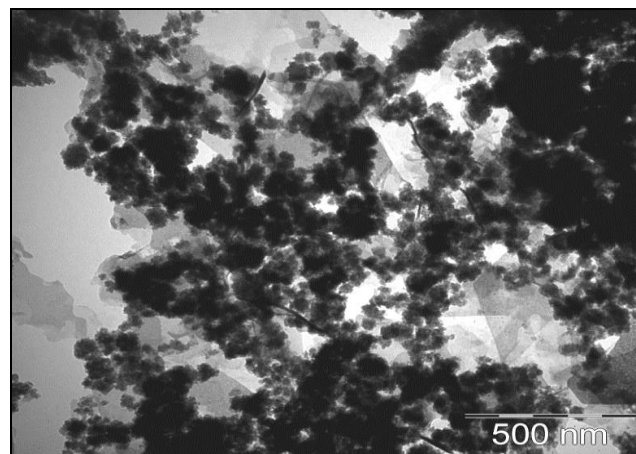


Fig. 4. TEM micrograph of Si nanoparticles with zinc acetate nanocrystalline "shell".

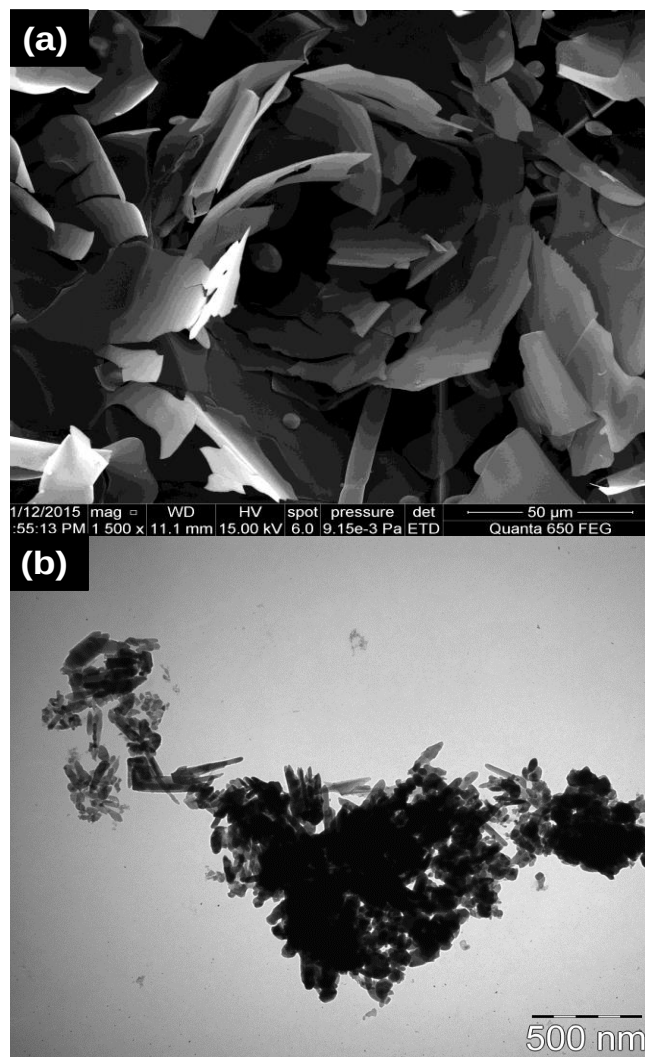


Fig. 5. (a) The SEM micrograph of lamellar self-organized nanostructure $\text{ZnO}(\text{Si})\text{-ZnO}$ after annealing. (b) TEM detail micrograph of fragment of particulate lamellar nanostructure.

Fig. 5a shows lamellar structures, which were obtained after vacuum sublimation, with distinct rod-shaped ZnO nanocrystals on surface-oxidized Si nanoparticles (**Fig. 5b**).

EDAX study

Composition of core-shell ZnO-(Si)-ZnO nanostructure was analyzed using the energy dispersive x-ray spectroscopy in scanning electron microscope. Analysis of the average composition showed a content of 41 wt % ZnO in prepared powder material.

Photocatalytic activity study

On **Fig. 6** is showed the time dependence of the decrease in the concentration of methylene blue as direct photolysis (blue line), thus photocatalytic degradation on the surface of nanoparticles of TiO₂ (gray line) and the new nanocomposite material ZnO-(Si)-ZnO (red line).

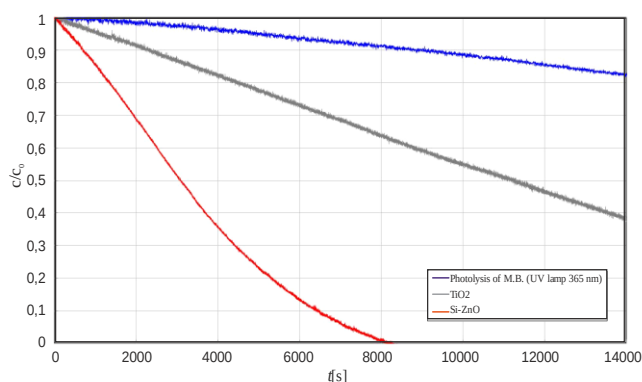


Fig. 6. Comparison of the time dependence of the relative concentration of methylene blue $c/c_0 = c(t)/c(0)$ at its photocatalytic degradation in the radiation field of UV lamps with a maximum emission wavelength at 365 nm.

While half-time $T_{1/2}$ of MB degradation for standard TiO₂ is about 11 300 s, for new material ZnO-(Si)-ZnO is this half-time equal to 3 000 s. Absolute reaction rate of photocatalytic degradation of methylene blue in the initial reaction period $0 \leq t \leq 2500$, related to the same weight of photocatalyst is for new material almost five times higher.

$$\frac{DC_{0,01\%ZnO-(Si)-ZnO}^{(MB)}(t)}{DC_{0,01\%TiO_2}^{(MB)}(t)} = \frac{(1 - 0,688)/(2500 \text{ s})}{(1 - 0,890)/(2500 \text{ s})} = \frac{(0,000215 \text{ s}^{-1})}{(0,000044 \text{ s}^{-1})} \gg 5$$

In this case, when the specific surface area of both photocatalytic materials are significantly different, it is necessary to make a conversion ratio of the two speeds to the same surface.

$$\frac{DC_{0,01\%ZnO-(Si)-ZnO}^{(MB)}(t) \Big|_{S=1}}{DC_{0,01\%TiO_2}^{(MB)}(t) \Big|_{S=1}} \gg \frac{DC_{0,01\%ZnO-(Si)-ZnO}^{(MB)}(t) / (134 \text{ m}^2/\text{g})}{DC_{0,01\%TiO_2}^{(MB)}(t) / (50 \text{ m}^2/\text{g})} = 1,82$$

Result of correction for photocatalytic rate with respect to unit surface of the catalyst confirms almost twice higher

photocatalytic activity of the new photocatalytic nanocomposite material compared to the commonly used standard Aeroxide® TiO₂ P25 Evonik Degussa.

Conclusion

The primary motivation for this work was the application of controlled vacuum sublimation technology [16] for process of preparing a nanocomposite material having a high specific surface area and photocatalytic efficiency. Based on the above experimental results, we can say that new photocatalytic nanocomposite material ZnO-(Si)-ZnO is a promising candidate for further environmental and industrial applications. Further research will be mainly focused on the optimization of technological parameters of preparation method. Experiments performed in this research with final product showed both a high reaction rate in photocatalytic degradation of MB and also higher specific surface area compared with the standard Aeroxide® TiO₂ P25 Evonik Degussa. The outlook for further research will be particularly useful to optimize the concentration of precursor Zn(OAc)₂ in the dispersion liquid and concentration of the dispersed phase of silicon nanoparticles. For the final photocatalytic properties are particularly critical regimes of vacuum sublimation and subsequent annealing of lamellar nanostructures, which significantly affect the morphology of nanostructures.

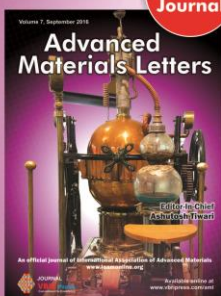
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References

- Pérez-Ramírez, J., Kapteijn, F., Schöffel, K., Moulijn, J.A.: *Appl. Catal. B: Environmental*, **2003**, 44, 117.
DOI: [10.1016/S0926-3373\(03\)00026-2](https://doi.org/10.1016/S0926-3373(03)00026-2)
- Praus, P., Dvorsky, R., Kozak, O., *Advanced Science, Engineering and Medicine*, **2010**, 3, 113.
DOI: [10.1166/asem.2011.1087](https://doi.org/10.1166/asem.2011.1087)
- Dvorsky, R., Praus, P., Trojčková, J., Študentová, S., Luňáček, J., 4th *International Conference NANOCON 2012*, Brno, Czech Republic, Conference Proceedings Book, **2010**, 39.
ISBN: [978-80-87294-35-2](https://doi.org/10.1016/j.matchemphys.2015.06.030)
- Guillén, G. G., Palma, M. M., Krishnan, B., Avellaneda, D., Castillo, G. A., Roy, T. D., Shaji S., *Materials Chemistry and Physics*, **2015**, 162, 561.
DOI: [10.1016/j.matchemphys.2015.06.030](https://doi.org/10.1016/j.matchemphys.2015.06.030)
- Li, B. J.; Huang, L. J.; Ren, N. F.; Kong, X., *Materials Letters*, **2016**, 164, 384.
DOI: [10.1016/j.matlet.2015.11.035](https://doi.org/10.1016/j.matlet.2015.11.035)
- Lam, S. M.; Sin, J. C.; Mohamed, A. R., *Materials Letters*, **2016**, 167, 141.
DOI: [10.1016/j.matlet.2015.12.156](https://doi.org/10.1016/j.matlet.2015.12.156)
- Dai, K.; Lv, J.; Lu, L.; Liu, Q.; Zhu, G.; Li, D., *Materials Letters*, **2014**, 130, 5.
DOI: [10.1016/j.matlet.2014.04.190](https://doi.org/10.1016/j.matlet.2014.04.190)
- Yan, D.; Hu, M.; Li, S.; Liang, J.; Wu, Y.; Ma, S., *Electrochimica Acta*, **2014**, 115, 297.
DOI: [10.1016/j.electacta.2013.10.007](https://doi.org/10.1016/j.electacta.2013.10.007)
- Dai, S.; Li, Y.; Du, Z.; Carter, K. R., *Journal of The Electrochemical Society*, **2013**, 160, D156.
DOI: [10.1149/2.064304jes](https://doi.org/10.1149/2.064304jes)
- Zhong, J.; Zhang, L. J.; Hua, X.; Hu, W.; Bei, Z.; Zhou, X.; Wen, Z.; *Materials Letters*, **2013**, 91, 301.
DOI: [10.1016/j.matlet.2012.10.040](https://doi.org/10.1016/j.matlet.2012.10.040)
- Cittadini, M.; Sturaro, M.; Guglielmi, M.; Resmini, A.; Tredici, I. G.; Anselmi-Tamburini, U.; Martucci, A., *Sensors and Actuators B: Chemical*, **2013**, 213, 493.
DOI: [10.1016/j.snb.2015.03.002](https://doi.org/10.1016/j.snb.2015.03.002)

12. Aksoy, S.; Caglar, Y.; Ilcan, S.; & Caglar, M., *Journal of Alloys and Compounds*, **2012**, 512, 171.
DOI: [10.1016/j.jallcom.2011.09.058](https://doi.org/10.1016/j.jallcom.2011.09.058)
13. Svoboda, L.; Dvorsky, R.; Praus, P.; Matysek, D.; Bednar, J., *Applied Surface Science*, **2015**.
DOI: [10.1016/j.apsusc.2015.11.128](https://doi.org/10.1016/j.apsusc.2015.11.128)
14. Katoch, A.; Choi, S. W.; Sun, G. J.; Kim, S. S., *Journal of Nanoscience and Nanotechnology*, **2015**, 15, 330.
DOI: [10.1166/jnn.2015.8368](https://doi.org/10.1166/jnn.2015.8368)
15. Dvorsky, R.; Luňáček, J.; Slíva, A., *Advanced Powder Technology*, **2011**, 22, 5639.
DOI: [10.1016/j.appt.2010.09.008](https://doi.org/10.1016/j.appt.2010.09.008)
16. Langmuir, I.: The Constitution and Fundamental Properties of Solids and Liquids. Part I. SOLIDS, *J. Am. Chem. Soc.* 38, 2217 (**1916**)
17. Dvorsky, R., Lunacek, J., Slíva, A., Piksová, K.: 2nd *International Conference NANOCON 2010*, Olomouc, Czech Republic, Conference Proceedings Book, **2010**, 144.
ISBN: [978-80-87294-19-2](https://www.isbn-international.org/product/978-80-87294-19-2)
18. Dvorsky, R.; *PCT Patent*: WO2013029576, **2013**
Bibl. data: [Espacenet](https://www.espacenet.com/)
19. Dvorsky, R.; Trojcková, J.; Lunacek, J.; Piksová, K.; Černohorský, O., 3th *International Conference NANOCON 2011*, Olomouc, Czech Republic, Conference Proceedings Book, **2011**, 58.
ISBN [978-80-87294-27-7](https://www.isbn-international.org/product/978-80-87294-27-7)
20. Dvorsky, R., Trojcková, J., Kukutschová, J.; Luňáček, J.; Vodárek, V.; Holešínský, J., *Advanced Science Engineering and Medicine*, **2014**, 6, 449.
DOI: [10.1166/ase.2014.1519](https://doi.org/10.1166/ase.2014.1519)



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