University of Szczecin

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Doctoral dissertation title:

"Outsourcing" of diatoms in the synthesis of 3D structured biosilica functionalized with metal nanoparticles (Ti, V, Nd, Ag)

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Summary of the doctoral dissertation

In the search for innovative solutions for modern technologies, and especially in the design and manufacture of new nanocomposite inorganic materials, micro-organisms functioning as 'natural microtechnologists' can provide significant inspiration. Diatoms represent, in terms of number of species, one of the largest groups of microalgae with the ability to synthesise mineral composites characterised by complex hierarchical structures. Their shells, called frustules, form intricately decorated structures reminiscent of the most sophisticated natural mosaics. Structured pore systems perforate the silica walls of frustules with diameters ranging from nano- to micrometres, creating openworked, three-dimensional silica structures. Exploiting these features is one of the main challenges in developing new technological solutions.

Within the framework of the submitted dissertation, new silica materials with a three-dimensional openwork structure based on diatom biosilica functionalized with nanoparticles of selected metals (Ti, V, Nd, Ag) were successfully synthesized using original

methodologies of metabolic doping of diatom cells grown under laboratory conditions (Ti, V, Nd) and impregnation of pyrolysed diatom biomass with a solution of metal salts (Ag). During the present study, the ability of a selected diatom species (*Pseudostaurosira trainorii*) to metabolically incorporate soluble titanium from the culture medium into the cell wall structure by culturing it under laboratory conditions was determined. Furthermore, AgNPs/TiO_2/pyrolysed diatom biomass (DBP) composites were synthesised by direct impregnation with aqueous silver nitrate solutions. TEM analysis showed epitaxy of AgNPs on the surface of TiO_2 nanoparticles. The antimicrobial potential of the synthesised composites was tested by MIC against the most common drug-resistant microorganisms in medicine: gram-positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumoniae*. The obtained AgNPs/TiO_2/DBP hybrid composites were shown to have high antimicrobial activity. In addition, new $NdVO_4$/DBP composites were obtained using the method of metabolic doping of diatom cells with neodymium and vanadium and pyrolysis of doped diatom biomass at 800°C. The study showed that the surface of the diatom frustule is covered with nanocrystallites (nanoparticles) of $NdVO_4$ with dimensions of 30-40 nm forming clusters of crystallites in the form of monolayer irregular flakes. The synthesised composites produced intense anti-Stokes fluorescence emission in the green, orange and red areas under near-infrared xenon lamp excitation at room temperature and ambient atmosphere.

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Keywords in English: diatoms, diatomaceous biosilica, metabolic doping, titanium-doped biosilica, TiO_2 nanoparticles, silver nanoparticles, neodymium vanadate, heteroepitaxial growth of Ag/TiO_2 nanoparticles, antibacterial activity, photoluminescence properties, anti-Stokes emission, up-conversion luminescence;