Contract Nº: NMP4-ct-2007-033168

PHOTONANOTECH

PHOTOZYME NANOPARTICLE APPLICATIONS FOR WATER PURIFICATION, TEXTILE FINISHING, PHOTODYNAMIC BIOMINERALIZATION AND BIOMATERIAL COATING

SPECIFIC TARGETED RESEARCH PROJECT

Nanotechnologies and nanosciences, knowledge-based multifunctional materials and new production processes and devices

Publishable Final Activity Report

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Start date of project: 1st April 2007 Duration: 3 years

Executive Summary

According to the description of work, the investigations were concentrated on:

- synthesis and characterization of new photozymes,
- photoactivity tests of the synthesized photozymes, including photostability tests,
- preparation of hybrid photozymes by incorporation of organic photozymes in polymeric hydrogels and hydrogel nanocomposites (including zwitterionic ones), liposome bilayers and layers adsorbed on phthalocyanine pigment with further investigation of their properties,
- photoactivity tests of photozymes included in matrices from hydrogels and organized layers ,
- photozyme tethering to different kinds of textile fabrics,
- boosting the performance of washing/bleaching bioformulations,
- photodegradation and mineralization tests of a model contaminant (phenol and pesticides) in order to determine photozyme activities,
- screening of photozyme biomineralisation potentials,
- establishing of protocols for coating of breast prosthetic materials with zwitterion-containig photozymes,
- analysis of the achievements of recent research on the mechanism of excited energy transport and conversion in natural photosynthetic system (including the recently revealed quantum coherence in this system) and derivation of the principal direction for photozyme chromophore composition, fixation and mutual orientation,
- protocols for the purification of waste oil-containing cooling liquids using photozyms,
- specific aggregation of zwitterion-containing photozymes and estimation of their cytotoxity.

0.1. PROJECT EXECUTION

PhotoNanoTech is to develop new classical type photozymes (amphiphilic copolymers containing comonomers with chromophoric groups) based on zwitterionic comonomers, and to investigate their long-term innovation potential as:

- photocatalysts in solar wastewater detoxification and disinfection;
- finishing agents for textile;
- a new approach to control the biomineralization process (photodynamic biomineralization), and
- new biomedical coatings and materials with suppressed inflammatory response.

PhotoNanoTech is divided into 6 scientific workpackages. In the period reported here, in workpackage 1 (WP1) photozymes with targeted properties have been synthesized and characterized in order to supply all further work and respectively all other WPs. The photozymes produced have been used to prepare materials in WP2, and have been investigated for solar wastewater detoxification (WP4), textile (WP3) and biomedical materials (WP6) and coatings areas in workpackages (WP5).

The contractors of the PhotoNanoTech consortium are the following:

SUN: Sofia University St. Kliment Ohridski, Bulgaria

UPC: Technical University Of Catalonia, Spain

3B's-UM: Universidade Do Minho, Portugal

PSA: Plataforma Solar de Almería, Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas (CIEMAT), Spain

UKL: Institut Für Verbundwerkstoffe Gmbh (University of Kaiserslautern), Germany

PTO: Politecnico Di Torino, Italy

SPO: Specialni Polimeri Ltd., Bulgaria

TIN: Tinfer, S.L., Spain

COL: Color-Center, S.A., Spain

TBS: Tecnologie Biomediche Srl, Italy

INO: Inotex Spol. S R.O., Czech Republic

PER: Perca Ltd., Bulgaria. The relation with this contractor was terminated during the last 6 months in connection with the financial crisis and with a special decision of EC.

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0.1.1. WP1 Photozyme Synthesis and Characterization

SUN's and SPO's efforts during the 3rd year period were concentrated on the synthesis and characterisation of hybrid photozymes. In addition to the chemical composition, molecular weight and size distribution characteristics of these photozymes (Deliverable D2), the second direction of the WP1 research work was the determination of the photooxidation activity of these photozymes towards different pesticides under homogeneous and heterogeneous conditions. The efficiency of photozymes for accomplishing this project task was demonstrated, opening new possibilities for the application of solar energy for an easy and cheap approach to purification of water from toxic pesticides. Among the 12 investigated pesticides, the best results were obtained for Chlorpyrifos, Quizalofop-p-ethyl, Diflubenzuron, Triallate and Lambda Cyhalotrone. It is noteworthy that all promising results of photozyme photoactivity were obtained for hybrid photozymes, consisting of a combination of an organic copolymer and a phthalocyanine pigment. The efficiency of these photozymes in their immobilized (in polyacrylamide gel) state was also demonstrated. It is worth noting that some of these photozymes are more effective in an immobilized state than in their free (homogeneous) state. The comparison between the activities of these photozymes under homogeneous and heterogeneous conditions is important not only for the photozymes produced and the project tasks, but also for the better understanding of the photosynthetic mechanism and for easier separation of purified water from the photozyme after treatment.

During the last third year the WP1 team prepared and distributed among the other contractors 54 photozyme samples and 16 polyzwitterinised silicone breast prosthesis membranes. Poly(SSA-co-VBC/HemPorph-co-VBA) photozyme was produced (by SPO team) in large quantities (around 400 g) and was used for pilot-scale industrial textile finishing experiments at TINFER. Another 7 were supplied in medium quantities (10-15g), intended for extended laboratory testings. 10 of the photozyme samples were of a new hybrid type that combined photozymes with phthalocyanine pigments in their composition. Original methods for the determination of the composition of xanthene-, porphyrin- and phthalocyanine-containing photozymes were developed and used.

According to the Deliverable D4, some thermal characteristics and microhardness of the zwitterion-containing amphiphile copolymers were determined. The synthesis was performed by an original emulsifier-free emulsion copolymerization, which opens possibilities to use the copolymers obtained for the preparation of different types of drug forms with controlled release. In addition, a nanosized latex was produced with a very narrow size distribution; the latex microsphere diameter was 205±0.6 nm. By scanning electron microscopy (SEM) of the tablet fracture surfaces it was proved that the nanospheres (grains) were conserved under the agglomerate surface. This fact confirms the desicive role of drug inclusion in the copolymer nanospheres for its release. DSC thermograms of the copolymer tablets show the relationship between the copolymer glass (Tg) and melting (Tm) temperatures and their compositions. The influence of copolymer composition on the microhardness of the drug tablets was also demonstrated. By this way, the correlation between the zwitterion-containing copolymer composition and copolymer thermal characteristics (Tg and Tm), swelling ability, microhardness and drug release ability of copolymer tablets was demonstrated during this period.

According to Deliverable D3, an analysis of the latest achievements in the study of the mechanism of high effficiency energy transport and conversion in natural photosymyhetic systems was made and discussed. 6 fundamental principles and 4 consequences of them for synthetic photozymes were derived. The long-lasting quantum coherence phenomenon (discovered during the last two years) tells that the classical photozyme concept, based on an effective antenna effect due to the high chromophore concentration in the photozyme core is not productive. The close coupling between the photozyme chromophores and an organised molecular environment has to be provided to overcome this shortcoming. The prepared and tested hybrid photozymes and the more positive results obtained with them indicate that this direction of photozyme development is correct. The optimisation of the photozyme chromophore coupling with its close environment, providing the long-lasting electronic quantum coherence mentioned above, is the main challenge for the preparation of a new generation of photozymes with an energy conversion efficiency close to that of natural photosynthetic systems.

According to Deliverable D5, chemical composition of the photozymes produced was determined by chemical (elemental) analysis. NMR-, FTIR-, Raman, UV and fluorescent spectral analysis were successfully used as well. For the prosthesis materials and hydroxyapatite coating with photozymes, energy-dispersive X-ray analysis was applied. Gel-permeation chromatography and static and dynamic laser scattering methods were used for the characterisation of the molecular weight distribution of the photozyme copolymers. HPLC and HPLC-MS methods were used for the determination of the photozyme-stimulated pesticide photooxidation under visible light.

A universal photozyme nomenclature was also accepted. It is in corresponedence with the UPAC recommendations for copolymer designation, and reflects the copolymer nature of photozymes. The type and mole fraction of the different types of the monomer units are included in the photozyme formula. The type of the photozyme chromophore is also denoted, and its bond to the correspondig monomer units is underlined by the inclusion of the chromophore symbol in brackets, immediately after the monomer unit to which the chromophore is bonded.

An four-steps protocol for the purification of waste oil-contaminated cooling liquid was developed. The last step of this method is the irradiation with visible light of the cooling liquid that had beeb pre-treated with acid, sodium chloride and sorbent. It provides an efficient purification, sufficient for recommendation of this method for industrial verification.

The chemical method for surface polyzwiterionisation of silicon breast prosthesis membranes was extended and improved. Samples of these modified membranes were prepared and sent to PTO and TBS for the appropriate testings.

The main contractors involved were SUN and SPO.

0.1.2. WP2 Zwitterionic Photozyme-based Materials Production and Characterization

During the PhotoNanoTech project the main activity of WP2 was devoted to the development and investigations of hydrogel materials with good mechanical and tribological performance. They include several types of hydrogel matrices: acrylic and polyurethane based individual gels, natural polymer-hybrid networks and double networks (Interpenetrating Polymer Networks). For the reinforcement of gels, different water dispersible and water swellable nanofillers including layered silicates, hydroxyl-aluminates, in situ produced polysilicate, bioactive hydroxyapatite and photoactive titanium dioxide have been used for the synthesis of nanocomposite hydrogels.

Zwitterionic hydrogels are a very promising type of smart biomaterials. Sulfobetaines belong to the group of polyzwitterions; they are the most biocompatible synthetic polymers found so far due to their similarity to phospholipids, the main biomembrane components. Considering these factors, development of sulfobetaine hydrogel materials was a primary topic of the research work.

During the 3 years of the project, 12 photozymes synthesised by Sofia University and Specialni Polimeri were supplied to UKL and were tested and characterised by several methods to investigate their structure, self-assembling ability and photoactivity. Several photozymes have been used for the modification of hydrogel systems. It was found that the photoefficiency of photozymes, when incorporated in zwitterionic hydrogels, was higher than that of the non-zwitterionic gels and individual photozyme solutions. These results were explained by the improvement of the antenna effect generated by photozymes due to the strong self-assembly of the zwitterionic hydrogel matrix. The hydrogels developed were non-toxic, which makes them promising materials for biomedical applications.

The Interpenetrating Polymer Network (IPN) technique allows purposeful combinations of different types of polymers (such as polyurethanes and polyacrylates) being cured by different types of reactions (polycondensation and polymerisation, respectively). Hence, the synthesis of hydrophilic polyurethanes with various hard and soft segments and zwitterionic acrylic hydrogels, being biocompatible polymers, and their combinations in IPNs were some of the primary topics of the research work. The high mechanical performance of the gels developed, their non-toxicity and simplicity of modification by photozymes open a wide horizon for use in biomedical applications.

A method for synthesis of natural polymer-hybrid hydrogels with large amounts of hydroxyapatite was developed. The attractiveness of such composites lies in the similarity of their properties to human tissues, which makes them promising materials in bone replacement and regeneration. The synthesis technique utilised for the hydrogel production allows introduction of hydroxyapatite up to 50 wt% without any precipitation in reactive media, resulting in composite hydrogels with a uniform distribution of the mineral within the gels.

Due to the modification with photozymes providing them with photoactivity, and due to their high biocompatibility and non-toxicity, such materials are very promising for photodynamically induced biomineralisation.

The main contractor involved was UKL.

0.1.3. WP3 Photozyme Textile Treatment

The experimental work carried out in WP3 was aimed at activation/functionalisation of textile-based platforms for tethering of photozymes and boosting the performance of washing/bleaching bioformulations.

A number of modifications on cotton and polyester were achieved during the first months of the project, e.g. tosylated, aminated, dialdehyde, carboxylated and cationised cotton fabrics as well as enzymatically activated polyester fabrics and low-temperature plasma pre-treatment. These modifications further allow grafting of photozymes with suitable functional groups. Different approaches for photozyme immobilisation on fabric surfaces were successfully performed and demonstrated by means of spectroscopic techniques. The so treated textiles showed improved UV protection and good antibacterial properties compared with untreated samples.

The self-cleaning effect of several photozymes grafted on natural and synthetic fabrics was tested as it was one of the main objectives of the WP, obtaining satisfactory results. Wine and coffee were chosen as typical coloured stains to perform these experiments. As the last step of this first aim of the WP i.e. fabric functionalisation with PZs, the lab-scale grafting of photozymes on fabric surfaces was scaled up to a kg scale process carried out in Tinfer, one of the WP3 SMEs. This process led to 20kg of a final product with promising self-cleaning properties.

Regarding biobased washing/bleaching formulations, the effect of some new photozymes on lipases (one of the most widely used enzyme in washing formulations) was assessed. As a result, an increase of lipase activity was observed in presence of photozymes.

The study of the self assembling behaviour of photozymes in water solution – forming pseudo-micelles – is a key feature in order to better understand their positive influence in washing formulations. To this aim, previous fluorescence studies were completed with physical characterisation of the pseudo-micelles (size and stability). Furthermore, photozyme interaction with laundry enzymes was studied by means of QCM-D (Quartz Crystal Microbalance with Dissipation).

During this last reporting period one of the basic premises of the project i.e. the use of light energy in order to carry out chemical reactions, was successfully applied on the textile field, leading to a novel application of the PZs. A hematoporphyrin based PZ was used in red wine stains decolouration on cotton fabrics upon light exposure.

The contractors involved were UPC, TIN, COL and INO.

0.1.4. WP4 Solar Wastewater Detoxification

The main objective of this work package was to utilize photozymes present in part per millions concentrations to detoxificate and disinfect wastewater containing persistent, non-biodegradable and hazardous contaminants, e.g. chlorophenols, agrochemical waste (pesticides), dyes, etc. by simple exposure to sunlight. The photocatalytic action of photozymes in the process of solar decontamination of wastewaters directly follows the mechanism of photosynthesis in its light-harvesting as well as in the solar energy transformation into chemical reaction energy phases, by using the enzyme-like structure and performance of synthetic copolymers (photozymes).

During the project more than 60 different photozymes have been tested. Photozymes based on poly (SSA-co-NVC), rose Bengal, chitosan eosin, iron minerals or polyacrylamide gel have been tested for determining their light absorption, stability and efficiency in water treatment using phenol and other contaminants as model compounds.

Several photozymes did not presented an adequate light absorption in the solar spectrum range (λ>300 nm) and others were gradually degraded during illumination, releasing organics into the water, which is not desirable for any decontamination process. In those cases where photozymes had a good overlap with the solar spectrum and were stable under illumination, different tests were done for degrading phenol. In all cases phenol degradation was successful but too slow (no complete degradation after 300 min) and did not lead to mineralisation of the contaminant. This should be compared to other solar treatment processes such as TiO_2 photocatalysis that degrade phenol in 10 times shorter times, obtaining complete mineralisation to CO_2. Other tested contaminants (diuron, pyrimethanil and dichloroacetic acid) gave similar results.

Due to these results it was concluded that all the tested photozymes during the project were not suitable for being used in wastewater treatment.

The contractor involved was PSA.

0.1.5. WP5 Biomedical Coatings and Materials

The main activity of this workpage was focused on the realisation and characterisation of photozyme-based coatings for biomedical applications.

The following biocompatible photozymes were used: (i) xanthene-based photozymes (chitosan-fluorescein and chitosan-rose Bengal) and (ii) photozymes containing chromophores with absorbance in the near-UV region (a zwitterionic photozyme containing vinyl naphthalene and one having vinyl carbazole as a chromophore).

One of the most innovative results from the project was the finding that chitosan-fluorescein (Ch-FL) and chitosan rose bengal (Ch-RB) photozymes have the ability to promote the deposition of hydroxyapatite by photo-stimulation when immersed in simulated body fluid. The process of photodynamic biomineralisation was investigate by PTO and 3B's-UM. For instance, wet-spun fibres of chitosan containing chitosan-fluorescein were produced and characterised by SEM-EDS analysis. Tests in simulated body fluid performed on wet spun fibres showed that only irradiated and photozyme-containing fibres promoted the surface deposition of hydroxyapatite crystals.

Layer-by-layer (LbL) coating was applied on genipin-crosslinked gelatine films (used as model substrates for bone tissue engineering), with the aim to promote scaffold osteointegration by hydroxyapatite precipitation induced by the graft-copolymer photozyme (Ch-FL - cationic photozyme in the LbL coating) and to impart anti-microbial and anti-inflammatory characteristics mediated by the stat-copolymer photozyme (anionic photozyme in the LbL coating). Two different photozymes containing sulphonate moieties were used as polyanions (poly(styrene sulphonate-co-2 aminoethylmethacrylate-co-vinyl carbazole) in one case and poly(vinyl naphthalene-co-styrene sulphonate-co-3-dimethyl(methacryloylethyl)ammonium propane sodium sulphonate) in the other case), whereas CH-FL was used as a polycation. Ten layers were deposited and properties of each layer were characterised by UV-Vis spectroscopy, FTIR-ATR, SEM-EDS, contact angle analysis and fluorescence microscopy (FM). An alternative procedure was also applied for the

LbL coating of genipin-crosslinked gelatine: the coating was developed consisting of three precursor bilayers of commercial polymers (poly(sodium styrene sulphonate)/chitosan) and two final bilayers of the above mentioned photozyme couples. This method has been frequently reported in the literature: the precursor layers based on commercial polymers have the function to generate a homogeneous charge distribution on the substrate. A physico-chemical characterisation was then performed on the coatings by contact angle, SEM-EDS, FTIR-ATR and FM analyses and UV-Vis spectroscopy.

Moreover, silicone model samples for breast prostheses and bladder substitutes were surface modified by plasma treatment in order to find the optimal processing conditions for the treatment. Once optimised parameters for plasma treatment were found, double plasma modification was performed, involving acrylic acid grafting/polymerisation, followed by the grafting of a photozyme (Ch-RB) using carbodiimide chemistry. This functionalisation was performed with the aim to impart photo-antimicrobial activity to the prostheses.

SUN also collaborated with TBS and PTO for the modification of silicone prostheses by hydroxylation and further grafting of zwitterionic functionalities. This functionalisation could be the first step for layer-by-layer modification of the prostheses. PTO performed a surface characterisation of the modified prostheses by contact angle analysis and SEM-EDS analysis: samples were successfully functionalised in some cases, but the coating was not homogeneous.

The main contractors involved were PTO, TBS, UKL, 3B’s-UM and SUN.

0.1.6. WP6 Photodynamic Biomineralization

During this last period, the efforts have been focused on development of a 3D light-responsive system able to induce biomineralization. Based on the previous results achieved by WP5 and WP6, a stimuli-responsive surface was translated into 3D stimuli-responsive fibre mesh scaffolds without loss of responsiveness according to the obtained preliminary results. Scaffolds for bone engineering with incorporated chitosan-Fluorescein and chitosan -Bengal Rose photozymes were produced by a wet spinning procedure. Positive results for light-stimulated hydroxyapatite layer formation on the surfaces of these scaffolds were obtained. Additionally, the possibility to create such systems by incorporation of photozymes into hydrogels was investigated. Studies with new photozymes, active at different wavelength (IR and VIS), were begun. Finally, additional investigations on the ability of zwitterion photozymes to assemble were carried out. By three independent methods (dynamic laser scattering, atomic force microscopy and quartz micro balance), the self-assembling ability of the zwitterion-containing photozymes was demonstrated and its dependence on the low-molecular weight salt concentration was investigated. The new results confirmed the importance of the zwitterion unit in the macromolecule on its ability to form knots.

The main contractors involved are 3B's-UM and PTO.

0.1.7. WP7 Management

The planned PhotoNanoTech project website is on-line at www.photonanotech.eu. Project logos designed for the website and for general use are shown in Figure 0.1 and Figure 0.2

photonanotech

Figure 0.1 The PhotoNanoTech logo, for use on a white background

Figure 0.2 The PhotoNanoTech logo, for use on a green background or as a heading (gradient from RGB (89,106,49) bottom to RGB (151,158,77) top), with border top and bottom RGB (244,197,20)

0.2. DISSEMINATION AND USE

0.2.1. Production process for zwitterionic hydrogels containing photozymes

Hydrogel materials with good mechanical and tribological performance have been developed. They include several types of hydrogel matrices: acrylic and polyurethane based individual gels, natural polymer-hybrid networks and double networks (Interpenetrating Polymer Networks). For the reinforcement of gels, different water dispersible and water swellable nanofillers including layered silicates, hydroxyl-aluminates, in situ produced polysilicate, bioactive hydroxyapatite and photoactive titanium dioxide have been used for the synthesis of nanocomposite hydrogels.

Zwitterionic hydrogels are a very promising type of smart biomaterials. Sulfobetaines belong to the group of polyzwitterions; they are the most biocompatible synthetic polymers found so far due to their similarity to phospholipids, the main biomembrane components. Due to their good biocompatibility and mechanical properties they are widely used as blood-contacting biomaterials. Their properties may be tailored in a wide range depending on the application requirements. Considering these factors, development of sulfobetaine hydrogel materials was a primary topic of the research work.

Several photozymes synthesised by Sofia University and Specialni Polimeri have been used for the modification of hydrogel systems. It was found that the photoefficiency of photozymes, when incorporated in zwitterionic hydrogels, was higher than that of the non-zwitterionic gels and individual photozyme solutions. These results were explained by the improvement of the antenna effect generated by photozymes due to the strong self-assembly of the zwitterionic hydrogel matrix. The hydrogels developed were non-toxic, which makes them promising materials for biomedical applications.

The Interpenetrating Polymer Network (IPN) technique allows purposeful combinations of different type of polymers (such as polyurethanes and polyacrylates) being cured by different types of reactions (polycondensation and polymerisation, respectively). Furthermore, hydrophilic polyurethanes are very attractive hydrogel materials, and their combination with “environmentally sensitive” polyacrylic networks is very promising for tuning the mechanical performance and swelling capacity of such IPN hydrogels. Hence, the synthesis of hydrophilic polyurethanes with various hard and soft segments and zwitterionic acrylic hydrogels, being biocompatible polymers, and their combinations in IPNs were one of the primary topics of the research work. The high mechanical performance of the gels developed, their non-toxicity and simplicity of modification by photozymes open a wide horizon for use in biomedical applications.

A method for synthesis of natural polymer-hybrid hydrogels with large amounts of hydroxyapatite was developed. The attractiveness of such composites lies in the similarity of their properties to human tissues, which makes them promising materials in bone replacement and regeneration. The synthesis technique utilised for the hydrogel production allows introduction of hydroxyapatite up to 50 wt% without any precipitation in reactive media, resulting in composite hydrogels with a uniform distribution of the mineral within the gels. Due to the modification with photozymes providing them with photoactivit, and due to their high biocompatibility and non-toxicity, such materials are very promising for photodynamically induced biomineralisation.

Collaboration partners:

Sofia University and Specialni Polimeri synthesed the photozymes to be incorporated into the hydrogels, while the 3B's Research Group (Biomaterials, Biodegradables and Biomimetics), University of Minho and the Bioartificial System Research Group, Department of Mechanics, Technical University of Turin investigated the cytotoxicity and bioactivity, and tested the systems developed as biomaterials.

0.2.2. Application of photozymes in textiles

Two major achievements were accomplished in the textile field during the Photonanotech projectin the area of improved biobased cleaning formulations and fabrics with self-cleaning properties. These two achievements were possible thanks to the use of photozymes, whose main characteristics are: a) enhanced organic compounds solubilisation, b) light harvesting in the visible or UV part of the spectra and its transduction into chemical energy by the antenna effect, thereby degrading organic dirt entrapped in the micelle and c) stabilization of biomolecules such as enzymes, providing pH stability. These are the reasons why photozymes are suitable boosting components in cleaning and bioremediation formulations, especially in those including bio-agents or those to be used in open-air conditions under sunlight exposure. Furthermore, when grafted on fabric surfaces photozymes can impair self-cleaning properties to the so treated fabrics. These results will lead in a near future to more efficient and eco-friendly products having a positive impact on both cleaning and textile finishing agents markets.

0.2.3. Application of photozymes in biomedical applications

In the biomedical field, the main results of the Photonanotech project were the development of new prosthesis /scaffold materials with improved biocompatibility and biomineralization activity and the realisation of coated scaffolds for bone repair. These results were developed by the coating with suitable photozymes. These innovative scaffolds/prostheses are interesting as the photosensitive properties of photozymes may impart anti-bacterial properties for applications to silicone prostheses used as breast implants or bladder substitutes, and photo-switchable biomineralisation ability to spongy scaffolds for bone regeneration. These interesting results are at an early stage of investigation but they are expected to impact the field of tissue engineering in the next years and to be of interest for Biomedical Industries. Part of the results have been recently published (http://pubs.acs.org/doi/full/10.1021/bm901169v).

0.2.4. Contacts

For zwitterionic hydrogels containing photozymes:

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For biomedical applications:

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For production of photozymes at pilot scale:

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For synthesis of photozymes and all other contacts:

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For photocatalytic and wastewater treatment applications:

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