

Electrochemically synthesized biomaterials

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INTRODUCTION: Electrochemical methods were employed for synthesizing composites intended for applications in medicine as antibacterial coatings on titanium bone implants or as highly efficient antibacterial hydrogels for accelerated wound healing.

EXPERIMENTAL: Hydroxyapatite-based coatings were single-step electrophoretically deposited from four-component aqueous suspension containing 1 wt% hydroxyapatite powder (HAP, particles < 200 nm particle size, Sigma-Aldrich), 0.1 wt% poly(vinyl alcohol) (PVA, medium molecular weight, Sigma-Aldrich), 0.05 wt% chitosan powder (CS, medium molecular weight, Sigma-Aldrich), and aqueous gentamicin sulfate solution (Gent, concentration 50 mg/ml, Sigma-Aldrich) on titanium plates (Sigma-Aldrich). Antibacterial activity of HAP/PVA/CS/Gent coating was evaluated against *Staphylococcus aureus* TL (culture collection-FTM, University of Belgrade, Serbia) and *Escherichia coli* ATCC 25922. For poly(vinyl alcohol)/chitosan (PVA/CHI) hydrogel synthesis poly(vinyl alcohol) powder (PVA, Sigma Aldrich, USA), chitosan powder (CHI, Sigma Aldrich, USA), graphene (Graphene Supermarket, USA), glacial acetic acid (Beta Hem), silver nitrate (MP Hemija), potassium nitrate (Centrohem, Serbia) were used. For antibacterial properties evaluation, monobasic and dibasic (Sigma Aldrich, USA) potassium phosphates were used. Cell culture suspensions for cytotoxicity tests were prepared using MTT tetrazolium salt, EDTA, fetal calf serum and antibiotic-antimycotic solution (Sigma Aldrich, USA).

RESULTS AND DISCUSSION: Surface modification of titanium with innovative bioactive coatings enhances biomineralization and reduces post-operation pain and infection risk. Using powerful single-step electrophoretic deposition (EPD) at a constant voltage we have produced various hydroxyapatite-based composite bioceramic coatings in combination with polymers (lignin, chitosan), graphene, and antibacterial agents (silver, gentamicin).

Electrochemical methods enable *in situ* synthesis of AgNPs inside polymer matrices, with the main advantage being the complete absence of any chemical reducing agents that are often toxic and difficult to remove from the material. The electrochemical reduction of Ag⁺ ions is achieved only using electrical current or pure hydrogen gas that is generated at the cathode in aqueous electrolytes, which allows for obtaining completely green and non-toxic product. Modifications in the synthesis process also enable the control of AgNPs properties, such as size and concentration.

CONCLUSIONS: Composite antibacterial coatings were obtained on titanium plates using EPD. Strong antibacterial activity against *E. coli* and *S. aureus* was found. Biocompatibility was confirmed using *in vitro* MTT testing since a non-cytotoxic effect was shown towards healthy human peripheral blood mononuclear cells PBMC, fibroblast cell lines MRC-5 and L929, suggesting high potential for bone tissue engineering and medical applications. Hydrogels composed of physically cross-linked poly(vinyl alcohol)/chitosan with embedded AgNPs were successfully developed for applications as antibacterial wound dressings due to their highly favorable properties of silver release, antibacterial activity, and non-toxicity.

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