Rare earth dual-doped multifunctional hydroxyapatite particles for potential application in preventive medicine

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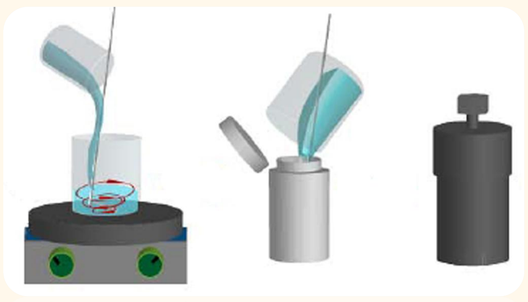
Bioluminescence
(*Coconut Octopus*)

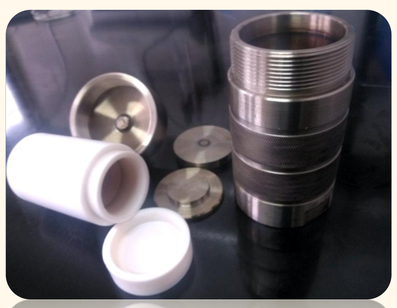
Photograph by Mario Neumann (scuba.hamburg on Flickr)

Introduction: Composite biomaterials based on nano hydroxyapatite (HAp) are the subject of numerous studies in reconstructive medicine. Multifunctional and nanoparticulate systems based on HAp and biodegradable polymers are successfully designed as systems for controlled and systemic drug delivery suitable for use in reconstructive medicine [1, 2]. Thanks to the stability and flexibility of the apatite structure, Ca ions can be replaced with various elements (Zn, Sr, Mg, Co, *etc*.) [3, 4]. Doping the apatite structure enables potential application of this material in preventive medicine, too. Multimodal imaging (MI) is a new and promising technique for improved diagnosis and it is patient-friendly because it saves time. MI has recently attracted much attention due to the advantageous combination of various imaging modalities, such as computer tomography, photoluminescence and magnetic resonance imaging.

Aim: For such a promising approach, we devised new multimodal agents using the doping of a HAp matrix with rare earth (RE) ions.

Materials and methods:

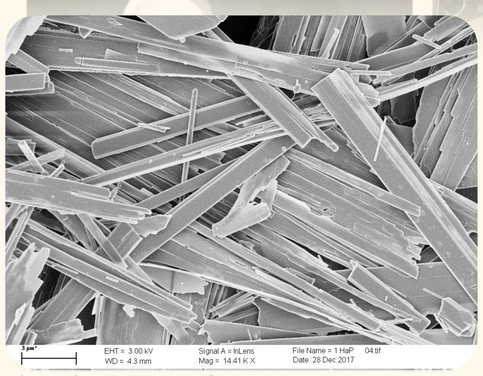




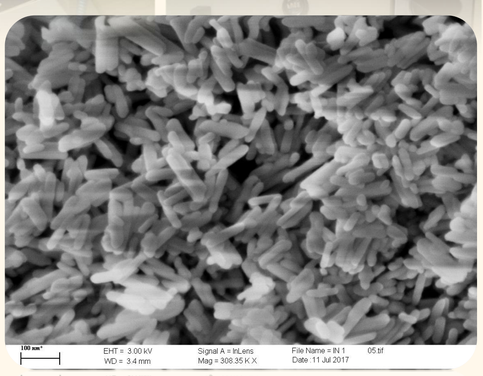
The first stage: a) Ca-nitrate+NH_4OH+H_3PO_4, b) Gd-nitrate, c) Yb-nitrate/Tm-nitrate, d) Eu-nitrate, e) EDTA;
I: a), II: a)+b), III: a)+b)+c)+e), IV: a)+b)+d)+e) at 60°C, 1h with mixing.
The second stage: The hydrothermal reaction, at 200 °C, 12h with mixing.

Results and Discussion:

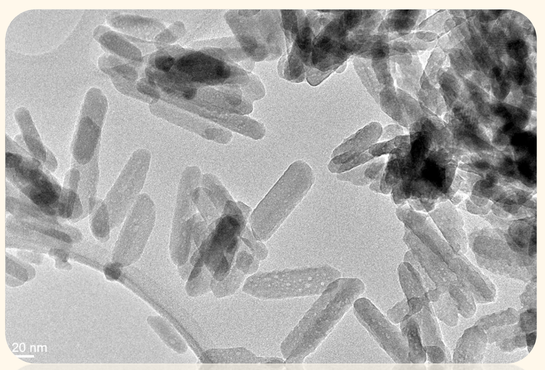
I HAp:
$Ca_5(PO_4)_3(OH)$
II HAp:Gd:
$Ca_{4.85}Gd_{0.15}(PO_4)_3(OH)$
III HAp:Gd,Yb/Tm:
$Ca_{4.85}Gd_{0.03}Yb_{0.1}Tm_{0.02}(PO_4)_3(OH)$
IV HAp:Gd,Eu:
$Ca_{4.94}Gd_{0.02}Eu_{0.04}(PO_4)_3(OH)$



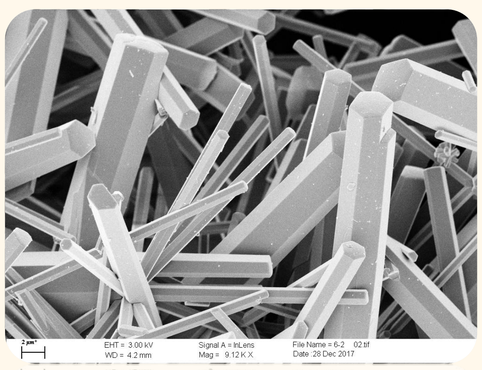
SEM of HAp



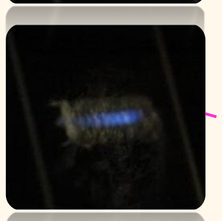
SEM of HAp:Gd

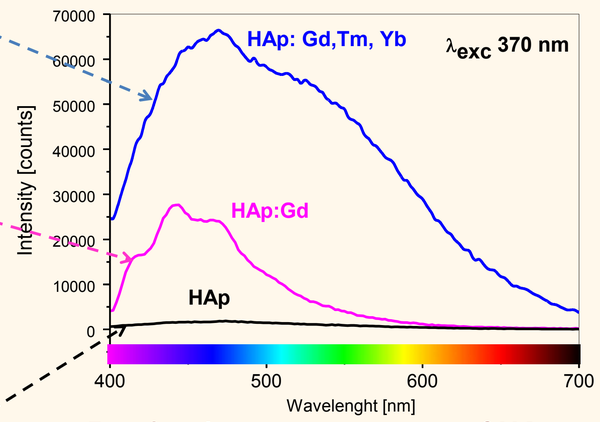


TEM of HAp:Gd

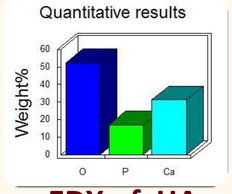


SEM of HAp:Gd,Yb/Tm

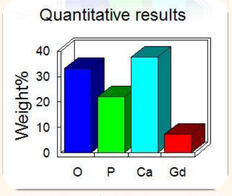




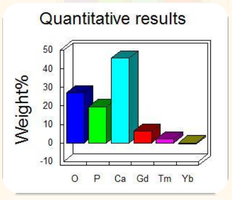
Fotoluminescence spectra of HAp, HAp:Gd and HAp:Gd,Yb/Tm excited at 370 nm



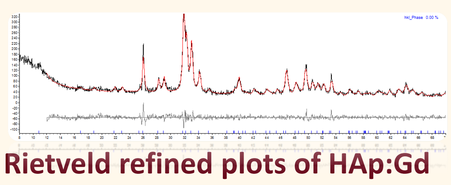
EDX of HAp



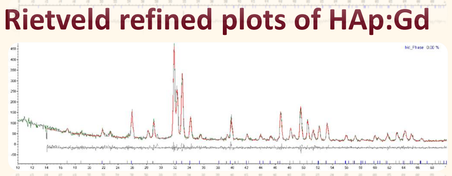
EDX of HAp:Gd



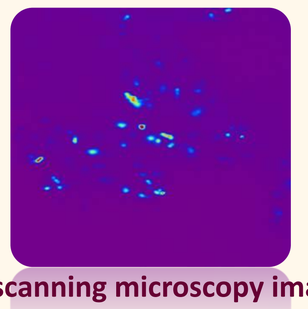
EDX of HAp:Gd,Yb/Tm



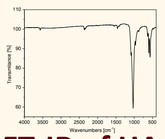
Rietveld refined plots of HAp:Gd



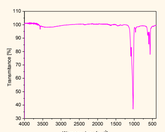
Rietveld refined plots of HAp:Gd,Yb/Tm



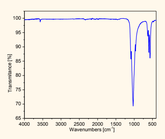
Laser scanning microscopy image of HAp:Gd,Yb/Tm particles fluorescence upon CW excitation at 977 nm



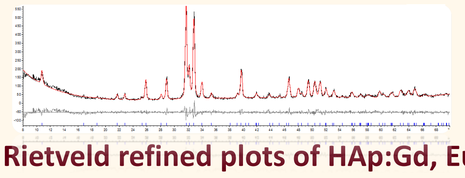
FT-IR of HAp



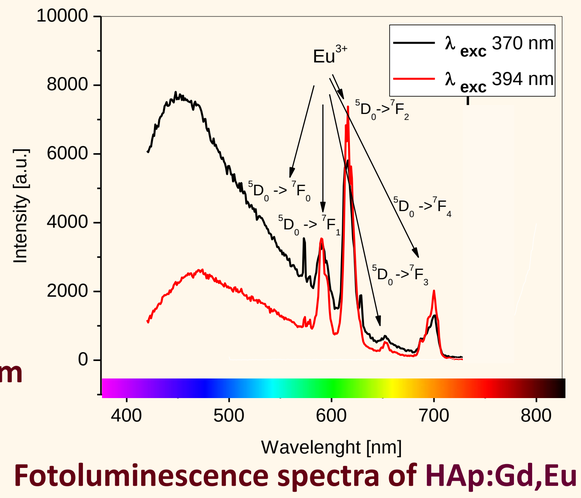
FT-IR of HAp:Gd



FT-IR of HAp:Gd,Yb/Tm



Rietveld refined plots of HAp:Gd, Eu



Fotoluminescence spectra of HAp:Gd,Eu excited at 370 and 394 nm

Conclusion:

Pure HAp ($Ca_5(PO_4)_3(OH)$), magnetic HAp:Gd ($Ca_{4.85}Gd_{0.15}(PO_4)_3(OH)$), down-converting HAp:Gd,Eu ($Ca_{4.94}Gd_{0.02}Eu_{0.04}(PO_4)_3(OH)$) and up-converting HAp:Gd,Yb/Tm ($Ca_{4.85}Gd_{0.03}Yb_{0.1}Tm_{0.02}(PO_4)_3(OH)$) were synthesized using a hydrothermal procedure.

Acknowledgments

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References:

[1] N. Ignjatović et. al., *Mater Sci Eng C*. 2018;89:371-377
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[4] Lj. Veselinović et. al., *J. Appl. Cryst.*,2010; 43:320-327