

Институт техничких наука САНУ

Кнез Михаилова 35/IV

Београд

Предмет: Захтев за покретање поступка за реизбор у звање истраживача сарадника  
Магистра техничких наука Зорана Стојановића

### НАУЧНОМ ВЕЋУ ИНСТИТУТА ТЕХНИЧКИХ НАУКА САНУ

Молим Вас да, у складу са Правилником о поступку и начину вредновања, и квантитативном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС, бр. 38/08), и Правилником о стицању звања истраживач сарадник, Научно веће Института техничких наука САНУ покрене поступак за реизбор у звање истраживач сарадник.

За чланове комисије за припрему извештаја научном већу предлажем:

- др Ненад Игњатовић, научни саветник Института техничких наука САНУ
- др Смиља Марковић, виши научни сарадник Института техничких наука САНУ
- др Магдалена Стевановић, виши научни сарадник Института техничких наука САНУ

У прилогу достављам:

1. биографију
2. библиографију са копијом прве стране публикација
3. потврду о пријави теме докторског рада
4. диплому завршених основних студија
5. диплому завршених магистарских студија

У Београду:

15. 05. 2013.

Подносилац захтева:

Зоран Стојановић, Магистар техничких наука

Истраживач сарадник ИТН САНУ

## Биографија Зоран Стојановић

Зоран Стојановић рођен је у Вршцу 02. марта 1978. године. где је завршио основну школу и Гимназију. Дипломирао је јуна 2004. године на Технолошко – металуршком факултету у Београду на Катедри за хемијско инжењерство са темом „Динамика адсорпције/десорпције влаге из ваздуха на пакованом слоју зеолита“, чиме је стекао звање дипломирани инжењер технологије. Магистрирао је на истом факултету на Катедри за конструкционе и специјалне материјале јула 2009. године са темом „Хидротермална синтеза наноструктурних оксидних прахова и њихова карактеризација“, чиме је стекао звање магистра техничких наука. Докторску тезу под насловом „Проучавање процеса синтезе и својстава вишефазних оксидних прахова добијених хидротермалним процесирањем“ пријавио је јуна 2011. године на Технолошко – металуршком факултету.

Од 01. марта 2007. године запослен је као истраживач у Институту техничких наука САНУ. Изабран је у звање истраживача сарадника марта 2010. године. У оквиру стручног усавршавања боравио је 2007. године три месеца на Факултету за хемију и хемијску технологију Универзитета у Љубљани на Катедри за неорганску хемију. Поред овог, провео је такође три месеца 2012. године као гостујући истраживач на Корејском институту за науку и технологију у Сеулу на Институту за биомедицинска истраживања. Ангажован је на пројекту Министарства науке, просвете и технолошког развоја под називом „Молекуларно дизајнирање наночестица контролисаних морфолошких и физико – хемијских карактеристика и функционалних материјала на њиховој основи“ евиденциони број пројекта ИИИ 45004 и билатералном пројекату научне и технолошке сарадње између Републике Србије и Републике Словеније за период 2012. – 2013. год под називом „Наноструктурно дизајнирање вишефункционалних и синтерованих функционално градијентних електричних и биолошких материјала“.

Област његовог интересовања су поступци синтезе наночестица металних оксида, племенитих метала, силицијума, хетероструктурних и хетероморфних наночестица, уопштено проучавање процеса синтезе наночестица хидротермалним и солвотермалним поступцима, као и поступцима колоидне хемијске синтезе, електоро-хемијским и каталитичким реакцијама. Истраживања којима се бави укључују површинска својства нанокристала, функционализација и дизајнирање површине нанокристала, коњугација наночестица са биомолекулима и другим једињењима; проучавање особина хетероструктурних нанокристала и наночестица и њихова употреба у медицини, као и у другим областима, нпр. конверзија енергије, катализа и сепарациони процеси.

**Списак публикација и саопштења Зорана Стојановића**  
**истраживача сарадника у ИТН САНУ**

Радови у часописима од међународног значаја (M21):

1. **Zoran Stojanović**, Mojca Otoničar, Jongwook Lee, Magdalena M Stevanović, Mintai P. Hwang, Kwan Hyi Lee, Jonghoon Choi, Dragan Uskoković, „**The solvothermal synthesis of magnetic iron oxide nanocrystals and the preparation of hybrid poly(L-lactide)-polyethyleneimine magnetic particles**“, *Colloids and Surfaces B: Biointerfaces* 109 (2013) 236 – 243 (<http://dx.doi.org/10.1016/j.colsurfb.2013.03.053>);
2. Ignjatović, N., Ajduković, Z., Savić, V., Najman, S., Mihailović, D., Vasiljević, P., **Stojanović, Z.**, Uskoković, V., Uskoković, D., „**Nanoparticles of cobalt-substituted hydroxyapatite in regeneration of mandibular osteoporotic bones**“, *Journal of Materials Science: Materials in Medicine* 24(2) (2013) 343-354 ([DOI: 10.1007/s10856-012-4793-1](https://doi.org/10.1007/s10856-012-4793-1)).
3. Stanković, A., **Stojanović, Z.**, Veselinović, L., Škapin, S. D., Bračko, I., Marković, S. and Uskoković, D., „**ZnO micro and nanocrystals with enhanced visible light absorption**“, *Materials Science and Engineering: B* 177(13) (2012) 1038-1045 (<http://dx.doi.org/10.1016/j.mseb.2012.05.013>);
4. Lukić, M.J., Veselinović, Lj., **Stojanović, Z.**, Maček-Kržmanc, M., Bračko, I., Škapin, S.D., Marković, S. and Uskoković, D., „**Peculiarities in sintering behavior of Ca-deficient hydroxyapatite nanopowders**“, *Materials Letters* 68 (2011) 331-335 ([doi:10.1016/j.matlet.2011.10.085](https://doi.org/10.1016/j.matlet.2011.10.085));
5. Lukić, M., **Stojanović, Z.**, Škapin, S.D., Maček-Kržmanc, M., Mitrić, M., Marković, S., Uskoković, D., „**Dense fine-grained biphasic calcium phosphate (BCP) bioceramics designed by two-step sintering**“, *Journal of the European Ceramic Society* 31(1-2) (2011) 19-27 ([doi:10.1016/j.jeurceramsoc.2010.09.00](https://doi.org/10.1016/j.jeurceramsoc.2010.09.00));
6. Tadić, M., Čitaković, N., Panjan, M., **Stojanović, Z.**, Marković, D. and Spasojević, V., „**Synthesis, morphology, microstructure and magnetic properties of hematite submicron particles**“, *Journal of Alloys and Compounds* 509(28) (2011) 7639–7644 ([doi:10.1016/j.jallcom.2011.04.117](https://doi.org/10.1016/j.jallcom.2011.04.117));
7. Veselinović, Lj., Karanović, Lj., **Stojanović, Z.**, Bračko, I., Marković, S., Ignjatović, N. & Uskoković, D., „**Crystal Structure of Cobalt-Substituted Calcium Hydroxyapatite Nano-Powders Prepared by Hydrothermal Processing**“, *Journal of Applied Crystallography* 43 (2010) 320-327 ([doi: 10.1107/S0021889809051395](https://doi.org/10.1107/S0021889809051395)).

Радови у часописима од међународног значаја (M23):

8. **Zoran Stojanović**, Ljiljana Veselinović, Smilja Marković, Nenad Ignjatović and Dragan Uskoković, „**Hydrothermal Synthesis of Nanosize Pure and Cobalt-exchanged Hydroxyapatite**“ *Materials and manufacturing processes* 24(10-11) (2009) 1096-1103, ([doi: 10.1080/10426910903032113](https://doi.org/10.1080/10426910903032113)).

Радови у часописима од националног значаја (M52):

9. **Z. Stojanović**, S. Marković, D. Uskoković, „**Merenje raspodele veličina čestica metodom difrakcije laserske svetlosti**“, *Tehnika – Novi materijali* 19 (5) (2010).

Саопштења на међународним скуповима штампана у изводу (M34):

1. **Z. Stojanović**, D. Jugović, D. Uskoković, **Hydrothermal Synthesis of Cathode Materials for Lithium-ion Batteries**, *The Ninth Yugoslav Materials Research Society Conference YUCOMAT 2007*, September 10-14, Herceg Novi, The Book of Abstracts, page 79, ISBN 978-86-80321-11-0;

2. **Z. Stojanović**, Lj. Veselinović, S. Marković, N. Ignjatović, D. Uskoković, **Hydrothermal Synthesis of Cobalt-exchanged Hydroxyapatite Nanoparticles**, *The Tenth Annual Yugoslav Materials Research Society Conference YUCOMAT 2008*, September 8-12, Herceg Novi, The Book of Abstracts, page 159, ISBN 978-86-80321-15-8;

3. Lj. Veselinović, **Z. Stojanović**, S. Marković, N. Ignjatović, D. Uskoković, **XRD Analysys of Cobalt-Substituted Hydroxyapatite Prepared by Hydrothermal Method**, *The Tenth Annual Yugoslav Materials Research Society Conference YUCOMAT 2008*, September 8-12, Herceg Novi, The Book of Abstracts, page 160, ISBN 978-86-80321-15-8;

4. **Z. Stojanović**, M. Jović, D. Uskoković, **Impact of Solvent Mixture Composition and Additive Presence on LiFePO<sub>4</sub> Formation in Water-iso-propanol Solutions at Elevated Temperatures and Pressures**, *The Eleventh Yugoslav Materials Research Society Conference YUCOMAT 2009*, Avgust 31- September 4, Herceg Novi, The Book of Abstracts, page 91, ISBN 978-86-80321-18-9;

5. M. Jović, **Z. Stojanović**, Lj. Veselinović, D. Uskoković, **Hydrothemat Synthesis of LiFePO<sub>4</sub> Powders as Cathode Material for Li-ion Batteries**, *The Eleventh Yugoslav Materials Research Society Conference YUCOMAT 2009*, Avgust 31- September 4, Herceg Novi, The Book of Abstracts, page 91, ISBN 978-86-80321-18-9;



6. Z. Ajduković, N. Ignjatović, **Z. Stojanović**, B. Kaličanin, V. Savić, S. M. Petrović, B. M. Petrović, J. Milićević, D. Uskoković, **Treatment of Osteoporosis Alveolar Bone with Cobalt Substituted Hydroxyapatite Nanoparticles**, *The Eleventh Yugoslav Materials Research Society Conference YUCOMAT 2009*, 31. Avgust - 4. September, Herceg Novi, The Book of Abstracts, page 188, ISBN 978-86-80321-18-9;
7. **Z. Stojanović**, Lj. Veselinović, M. Jović, A. Stanković, M. Jevtić, S. Marković, D. Uskoković, **Laser Diffraction Particle Size Analysis of Non Spherical Particles Synthesized by Hydrothermal Method**, JuniorEUROMAT 2010 24. – 30. July Lausanne Suisse;
8. **Z. Stojanović**, Lj. Veselinović, S. Marković, D. Uskoković, **Synthesis Procedure for the Preparation of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$** , *YUCOMAT 2010* 6. – 10. September, Herceg Novi, The Book of Abstracts, page 91, ISBN 978-86-80321-25-7;
9. **Z. Stojanović**, M. Lukić, Lj. Veselinović, S. Marković, D. Uskoković, **Hydrothermal Synthesis of Zirconium Substituted Hydroxyapatite**, *YUCOMAT 2011* 5. – 9. September, Herceg Novi, The Book of Abstracts, page 74.
10. **Zoran Stojanović**, Miodrag Lukić, Dragan Uskoković, **One – pot synthesis of hydrophobic hydroxyapatite nano particles**, усмено излагање, Tenth Young Researches' Conference Materials Science and Engineering 2011, SASA, 21. – 23. December, Belgrade, Program and The Book of Abstracts, page 2;
11. **Z. Stojanović**, M. Otoničar, S. Marković, D. Uskoković, **Hydrothermal Synthesis of Magnetic Nanoparticles and Fabrication of Magnetic Composite Particles using Poly(L – Lactide)**, постер, конференција *YUCOMAT 2012* 3. – 7. September, Herceg Novi, The Book of Abstracts, page 109;

Саопштења са скупа од националног значаја штампана у изводу (**M64**):

1. **Z. Stojanović**, K. Zupan, M. Marinšek, J. Maček, D. Uskoković, **Uticaј različitih procesa pripremanja oksidnih prahova na karakteristike Ni/YSZ anodnog materijala za keramičke gorivne ćelije**, *VI konferencija mladih istraživača – Nauka i inženjerstvo novih materijala*, 24 – 26. decembar 2007. godine, SANU, Beograd, Program i zbornik apstrakata, strana 18;
2. **Z. Stojanović**, Lj. Veselinović, S. Marković, N. Ignjatović, D. Uskoković, **Hidrotermalna sinteza kalcijum/kobalt hidroksiapatita**, *VII konferencija mladih istraživača – Nauka i inženjerstvo novih materijala*, 22 – 24. decembar 2008. godine, SANU, Beograd, Program i zbornik apstrakata, strana 15;

3. M. Jović, **Z. Stojanović**, Lj. Veselinović, D. Uskoković, **Sinteza katodnog materijala  $\text{LiFePO}_4$  hidrotermalnim postupkom**, *VII konferencija mladih istraživača – Nauka i inženjerstvo novih materijala*, 22 – 24. decembar 2008. godine, SANU, Beograd, Program i zbornik apstrakata, strana 33;
4. **Z. Stojanović**, D. Uskoković, **Hidrotermalna sinteza keramičkih materijala**, *VIII konferencija mladih istraživača – Nauka i inženjerstvo novih materijala*, 21 – 23. decembar 2009. godine, SANU, Beograd, Program i zbornik apstrakata, strana 2, ISBN 978-86-80321-22-6;
5. Lj. Veselinović, Lj. Karanović, S. Marković, **Z. Stojanović**, I. Bračko, N. Ignjatović, D. Uskoković, **Mikrostrukturne i morfološke promene kalcijum/kobalt hidroksiapatita**, *VIII konferencija mladih istraživača – Nauka i inženjerstvo novih materijala*, 21 – 23. decembar 2009. godine, SANU, Beograd, Program i zbornik apstrakata, strana 16, ISBN 978-86-80321-22-6;
6. M. J. Lukić, Lj. Veselinović, **Z. Stojanović**, S. Marković, N. Ignjatović, D. Uskoković, **Master sintering kriva nano kalcijum hidroksiapatita ( CaHAp)**, *VIII konferencija mladih istraživača – Nauka i inženjerstvo novih materijala*, 21 – 23. decembar 2009. godine, SANU, Beograd, Program i zbornik apstrakata, strana 17, ISBN 978-86-80321-22-6;
7. M. Jović, **Z. Stojanović**, Lj. Veselinović, D. Uskoković, **Hidrotermalna sinteza katodnog materijala  $\text{LiFePO}_4$  u prisustvu organske komponente**, *VIII konferencija mladih istraživača – Nauka i inženjerstvo novih materijala*, 21 – 23. decembar 2009. godine, SANU, Beograd, Program i zbornik apstrakata, strana 27, ISBN 978-86-80321-22-6;
8. **Z. Stojanović**, Lj. Veselinović, S. Marković, D. Uskoković, **Synthesis and dielectric properties of calcium copper titanate (CCTO) based ceramics**, Ninth Young Researchers Conference – Materials Science and Engineering 20-22 December 2010, SASA, Belgrade, Serbia, Program and the Book of Abstracts, page 7, ISBN 978-86-80321-26-4;
9. M. Lukić, **Z. Stojanović**, Lj. Veselinović, S. D. Škapin, I. Bračko, S. Marković, D. Uskoković, **The influence of powder characteristics on two-step sintering behavior of hydroxyapatite**, Ninth Young Researchers Conference – Materials Science and Engineering 20-22 December 2010, SASA, Belgrade, Serbia, Program and the Book of Abstracts, page 11, ISBN 978-86-80321-26-4.

ИНСТИТУТ ЗА НУКЛЕАРНЕ НАУКЕ  
"ВИНЧА"  
НАУЧНО ВЕЋЕ  
Број: 401/14  
18. 03. 2010. године  
БЕОГРАД

На основу чл. 59., чл. 70. и чл. 82. Закона о научноистраживачкој делатности ("Службени гласник РС", бр. 110/05), на седници *Научног већа Института за нуклеарне науке "Винча"* одржаној 18. марта 2010. године, донета је

**О Д Л У К А**  
**О СТИЦАЊУ ИСТРАЖИВАЧКОГ ЗВАЊА**  
**Мр Зоран Стојановић**  
стиче истраживачко звање  
**ИСТРАЖИВАЧ САРАДНИК**

**ОБРАЗЛОЖЕЊЕ**

Мр Зоран Стојановић, сарадник Института техничких наука Српске академије наука и уметности, покренуо је поступак за избор у истраживачко звање **ИСТРАЖИВАЧ САРАДНИК**.

На основу извештаја Комисије за оцену научноистраживачког рада именованог кандидата формиране од *Научног већа Института "Винча"* и приложеног изборног материјала, утврђено је да **мр Зоран Стојановић** испуњава услове из чл. 69. Закона о научноистраживачкој делатности за стицање истраживачког звања **ИСТРАЖИВАЧ САРАДНИК**, па је одлучено као у диспозитиву одлуке.

ПРЕДСЕДНИК НАУЧНОГ ВЕЋА  
ИНСТИТУТА "ВИНЧА"



*Z. Radak*  
Др Бојан Радак, виши научни сарадник





Univerzitet u Beogradu



Број: Сл 1  
Датум: 12.05.2013.

На основу чл. 161. Закона о општем управном поступку, а на захтев докторанта, увидом у евиденцију којом располаже, Универзитет у Београду-Технолошко-металуршки факултет, издаје

### ПОТВРДУ

Овим се потврђује да је **мр Зоран (Слободан) Стојановић**, рођен 02.03.1978. године у Вршцу, пријавио тему докторске дисертације 06.06.2011. године на Универзитету у Београду-Технолошко-металуршком факултету.

Наставно-научно веће Факултета донело је Одлуку бр. 35/394 од 20.12.2011. године о одобрењу израде докторске дисертације, а Веће научних области Универзитета у Београду дало је сагласност на предлог теме докторске дисертације Одлуком 02 број: 06-162/12-12 на седници од 30.01.2012. године

Потврда се издаје на захтев докторанта ради конкурисања за избор у звање.

СЕКРЕТАР



Велибор Миросављевић, дипл. прав.



РЕПУБЛИКА СРБИЈА



УНИВЕРЗИТЕТ У БЕОГРАДУ  
ТЕХНОЛОШКО - МЕТАЛУРШКИ ФАКУЛТЕТ

# ДИПЛОМА

О СТЕЧЕНОМ АКАДЕМСКОМ НАЗИВУ  
МАГИСТРА НАУКА

**СТОЈАНОВИЋ (Слободан) ЗОРАН**

РОЂЕН 02.03.1978. ГОДИНЕ У ВРШЦУ, ОПШТИНА ВРШАЦ, РЕПУБЛИКА СРБИЈА,  
УПИСАН ЈЕ 2004/05. ШКОЛСКЕ ГОДИНЕ НА ПРВУ ГОДИНУ МАГИСТАРСКИХ  
СТУДИЈА НА ТЕХНОЛОШКО - МЕТАЛУРШКОМ ФАКУЛТЕТУ У БЕОГРАДУ, А ДАНА  
15.07.2009. ГОДИНЕ ОДБРАНИО ЈЕ МАГИСТАРСКУ ТЕЗУ ПОД НАЗИВОМ  
„ХИДРОТЕРМАЛНА СИНТЕЗА НАНОСТРУКТУРНИХ ОКСИДНИХ ПРАХОВА И  
ЊИХОВА КАРАКТЕРИЗАЦИЈА”.

НА ОСНОВУ ТОГА ИЗДАЈЕ МУ СЕ ОВА ДИПЛОМА О СТЕЧЕНОМ АКАДЕМСКОМ  
НАЗИВУ

**МАГИСТРА ТЕХНИЧКИХ НАУКА**

Редни број из евиденције о издатим дипломама: 948

У Београду, 16. јула 2009. године

ДЕКАН

Проф. др Иванка Ђуповић

РЕКТОР

Проф. др Бранко Ковачевић



~~Потврђује се да је овај препис ~~направљен~~ ~~на~~ са  
~~својим~~ ~~изворником~~ — са његовим ~~овереним~~ —  
простијим преписом који је ~~написан~~ ~~мастилом~~ —  
~~писаћом~~ ~~машином~~ — оловком — \_\_\_\_\_  
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*Ситојановић Слободан Зоран*

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# The solvothermal synthesis of magnetic iron oxide nanocrystals and the preparation of hybrid poly(L-lactide)–polyethyleneimine magnetic particles



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## ABSTRACT

We report a simple and green procedure for the preparation of magnetic iron oxide nanocrystals via solvothermal synthesis. The nanocrystal synthesis was carried out under mild conditions in the water–ethanol–oleic acid solvent system with the use of the oleate anion as a surface modifier of nanocrystals and glucose as a reducing agent. Specific conditions for homogenous precipitation achieved in such a reaction system lead to the formation of uniform high-quality nanocrystals down to 5 nm in diameter. The obtained hydrophobic nanocrystals can easily be converted to hydrophilic magnetic nanoparticles by being immobilized in a poly(L-lactide)–polyethyleneimine polymeric matrix. These hybrid nano-constructs may find various biomedical applications, such as magnetic separation, gene transfection and/or magnetic resonance imaging.

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## 1. Introduction

The high magnetic susceptibility and superparamagnetism found in iron oxide nanoparticles of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and its oxidized form, maghemite γ-(Fe<sub>2</sub>O<sub>3</sub>), have propelled their use in various technological fields, e.g. molecular and cellular magnetic resonance imaging [1], magnetic force-assisted delivery [2], various separation techniques of cells, proteins, viruses, etc. [3–5], AC magnetic field cancer treatment [6], data storage [7], catalysis and adsorbent recovery [8,9], magnetorheological shock absorbers and seals [10,11] are only some of its applications in the biomedical and technical fields.

The physical properties of nanocrystals, and those of iron oxide in particular, are strongly related to their size and shape. In other words, the production of monodisperse high-quality nanocrystals is crucial for scientific research and applications [12,13]. Advances made in high-temperature reactions using organic solutions have led to the production of high-quality monodisperse superparamagnetic iron oxide nanoparticles smaller than 20 nm [14,15].

Although methods based on aqueous solution co-precipitation are advantageous; they confer hydrophilicity to the synthesized nanoparticles; they are non-toxic, cost-effective, and energy-efficient; but they still do not yield high-quality nanocrystals [16]. The microemulsion method is another approach that has shown to be efficient in the synthesis of a wide variety of magnetic nanoparticles but one that is hampered with relatively high polydispersity, and inefficient and non-economic synthesis [17].

Hydrothermal and solvothermal synthesis approaches are based on chemical reactions at elevated temperatures and pressures ranging from ambient temperatures and pressures to above critical conditions. They cover a wide range of chemical and thermodynamic parameters, making them a powerful tool for materials processing in a very broad sense [18,19]. Recent achievements in the solvothermal synthesis of monodisperse nanocrystals are related to a variety of nanocrystals with hydrophobic properties synthesized using different ligands composed of long aliphatic chains and polar coordinating head groups [20]. Magnetite and other ferrite compounds are among those produced using a similar solvothermal liquid–solid–solution (LSS) strategy [21,22]. Several groups have reported the synthesis of iron oxide NPs by hydrothermal method. However, despite distinct efforts to find appropriate ligands to synthesize monodisperse nanocrystals in

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# Nanoparticles of cobalt-substituted hydroxyapatite in regeneration of mandibular osteoporotic bones

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**Abstract** Indications exist that paramagnetic calcium phosphates may be able to promote regeneration of bone faster than their regular, diamagnetic counterparts. In this study, analyzed was the influence of paramagnetic cobalt-substituted hydroxyapatite nanoparticles on osteoporotic alveolar bone regeneration in rats. Simultaneously, biocompatibility of the material was tested in vitro, on osteoblastic MC3T3-E1 and epithelial Caco-2 cells in culture. The material was shown to be biocompatible and nontoxic when added to epithelial monolayers in vitro, while it caused a substantial decrease in the cell viability as well as deformation of the cytoskeleton and cell morphology when incubated with the osteoblastic cells. In the

course of 6 months after the implantation of the material containing different amounts of cobalt, ranging from 5 to 12 wt%, in the osteoporotic alveolar bone of the lower jaw, the following parameters were investigated: histopathological parameters, alkaline phosphatase and alveolar bone density. The best result in terms of osteoporotic bone tissue regeneration was observed for hydroxyapatite nanoparticles with the largest content of cobalt ions. The histological analysis showed a high level of reparatory ability of the nanoparticulate material implanted in the bone defect, paralleled by a corresponding increase in the alveolar bone density. The combined effect of growth factors from autologous plasma admixed to cobalt-substituted hydroxyapatite was furthermore shown to have a crucial effect on the augmented osteoporotic bone regeneration upon the implantation of the biomaterial investigated in this study.

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## 1 Introduction

Osteoporosis is a metabolic disease that affects millions of people around the globe. It is a progressive, systemic skeletal disease characterized by low bone density and micro-architectural bone damage, with the consecutive increase in bone fragility and susceptibility to fracture [1]. Osteoporosis of cancellous bone leads to thinning of trabeculae, widening of marrow and decreased bone density in the center of the bone, while in the cortical region overall thinning occurs at the periphery [1–3]. One of the approaches for treating osteoporosis in oral and maxillofacial areas has involved implantation of different types of biomaterials [3–7]. The quest for materials performing better than those currently in use is, however, ongoing, with a special focus on nanoparticulate biomaterials.





## ZnO micro and nanocrystals with enhanced visible light absorption

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### ABSTRACT

In this paper, we investigate the effect of the particle size and morphology on the optical properties of ZnO. A series of ZnO micro and nanocrystals were synthesized by the hydrothermal processing of zinc acetate dihydrate and sodium hydroxide as the starting materials, and polyvinylpyrrolidone (PVP) as the polymer surfactant. The particle size and morphology were tailored by adjusting the reactant molar ratios  $[Zn^{2+}]/[OH^-]$ , while the reaction temperature and the time remained unchanged. X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution TEM (HRTEM) have shown that the micro and nanocrystals have a high crystalline pure wurtzite-type hexagonal structure with nanosized crystallites. The size and morphology of the ZnO micro and nanocrystals were investigated by field emission scanning electron microscopy (FE-SEM), which showed a modification from micro-rods via hexagonal-faceted prismatic morphology to nanospheres, caused by simple adjustment of the reactant molar ratio  $[Zn^{2+}]/[OH^-]$  from 1:1 to 1:5. The optical properties of the ZnO micro and nanocrystals, as well as their dependence on the particle size and morphology were investigated by Raman and ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy (DRS). The UV–vis spectra showed that the modification of the particle size and morphology from nanospheres to micro-rods resulted in increased absorption, and a slight red-shift of the absorption edge (0.06 eV). Besides, the band gap energy of the synthesized ZnO micro and nanocrystals showed the red shift ( $\sim 0.20$  eV) compared to bulk ZnO. According to the results of a Raman spectroscopy, the enhanced visible light absorption of the ZnO micro and nanocrystals is related to two phenomena: (1) the existence of lattice defects (oxygen vacancies and zinc interstitials), and (2) the particle surface sensitization by PVP.

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### 1. Introduction

Zinc oxide (ZnO) is a versatile, multifunctional material frequently used in high technology such as optoelectronic and electroluminescent devices, UV lasers, solar cells, piezoelectric transducers and gas sensors [1–5]. In addition, ZnO finds application in the areas like rubber industry and plastic processing, cosmetics and pharmacy; it is also used as an antimicrobial agent [6–14]. In many cases, the application of ZnO is based on its direct wide band gap (3.37 eV) and the large excitation binding energy (60 meV) at room temperature [1]. However, an energy gap of 3.37 eV (368 nm) means that ZnO can only absorb UV light [15]. Since solar visible light is a source of clean and cheap energy, while UV light makes no more than 3–5% of the total sunlight, ZnO-based materials capable for visible light photocatalysts are highly desirable [16]. Several approaches have been applied with the aim of

changing the optical absorption properties and improving the visible light photocatalysis; they include the incorporation of transition metal ions into the crystal structure of a ZnO powder (since the presence of various intrinsic defects can give rise to deep acceptors or shallow donors and produce a red shift of the band gap [17]), the treatment of ZnO powders by applying hydrogen plasma technology to create a new absorption band in the visible-light region through the formation of oxygen vacancies, surface sensitization of ZnO particles to extend the spectral response into the visible region, etc.

Since the optical properties of materials are determined by the phase purity, homogeneity, particle size, morphology, as well as crystallinity, the possibility to control the synthesis process is of utmost importance. Several techniques such as precipitation [18], sol–gel process [19], spray pyrolysis [20], hydrothermal/solvothermal synthesis [21], mechanochemical [22], and microwave-hydrothermal processing [23] are used for the preparation of ZnO materials with a controlled morphology. Among them, hydrothermal synthesis is the most attractive especially due to the fact that it allows perfect control of purity, crystallinity,

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## Peculiarities in sintering behavior of Ca-deficient hydroxyapatite nanopowders

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### ABSTRACT

We report unusual sintering behavior of Ca-deficient hydroxyapatite processed with different heating rates; particularly, faster heating resulted in higher densification. We hypothesize that faster heating delays formation of  $\beta$ -tricalcium phosphate which yields to unobstructed densification in intermediate sintering stage, allowing further tailoring of both microstructure and phase composition (hydroxyapatite/tricalcium phosphate).

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### 1. Introduction

Biphasic calcium phosphate (BCP) ceramics, composed of bioactive hydroxyapatite (HAp) and bioresorbable  $\beta$ -tricalcium phosphate ( $\beta$ -TCP), is widely used as hard tissue implant material in the various forms, but it is limited to the non-load bearing application due to the inherent brittleness of ceramic materials. Since the sintering process could improve mechanical properties of materials, knowing of sintering behavior and possibility to control it over the wide range of time-temperature conditions is very important. Final properties of BCPs are strongly influenced by density, grain size, phase composition and crystallinity, so the appropriate processing should yield to the desired final product. By manipulating of HAp/ $\beta$ -TCP ratio, bioreactivity of BCPs could be created, providing dynamic interface and inducing formation of biological carbonated-HAp [1,2]. BCPs can be obtained through physical mixing of HAp and  $\beta$ -TCP, but also through heating or sintering of Ca-deficient HAp (CdHAp) above certain temperature [3,4].

In the studies of producing BCPs through sintering of CdHAp materials, there is no unique opinion concerning the temperature and extent of phase transformation, and its overall impact on sintering behavior. It is accepted that final HAp/ $\beta$ -TCP ratio is determined by the initial Ca-deficiency and sintering temperature [1]. Wide

temperature range for phase transformation is reported, but mainly higher than 700 °C. The amount of  $\beta$ -TCP increases with Ca-deficiency and new phase formed hinders further sintering of HAp matrix [4–8].

According to our best knowledge there is no detailed study on heating rate influence on densification of CdHAp and its phase composition. The aim of this study was to correlate the results of sintering behavior with the phase transformation happening during thermal treatment of CdHAp.

### 2. Experimental part

The CdHAp powder with precursors Ca/P ratio of 1.63 was prepared according to previously published procedure [9]. The phase analysis of the initial and thermally treated powders and pellets was carried out by X-ray diffraction (XRD) using a Bruker D8 instrument. The FTIR measurement was performed on BOMEM (Hartmann & Braun) spectrometer using the KBr pellet technique, in the spectral range of 400–4000  $\text{cm}^{-1}$ . The particle size distribution was determined by the particle size analyzer Malvern Instruments Mastersizer 2000. The morphology and Ca/P ratio of the powder as well as microstructure of the sintered pellets were analyzed by field emission scanning electron microscopy (FE-SEM, Supra 35 VP, Carl Zeiss) equipped with energy dispersive spectroscopy (EDS, Inca 400, Oxford Instruments). Primary particle size and morphology were investigated by transmission electron microscopy (TEM, JEOL 2100, operating at 200 kV). The synthesized nanopowder was uniaxially pressed into pellets of  $\varnothing$  6 mm, 3 mm height and 55% of theoretical density. Non-isothermal sintering was done in heating microscope (New Heating

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## Dense fine-grained biphasic calcium phosphate (BCP) bioceramics designed by two-step sintering

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### Abstract

In this study, dense, fine-grained biphasic calcium phosphate bioceramics were designed *via* the two-step sintering method. The starting powder was nanosized calcium-deficient hydroxyapatite, whose phase composition, average particle size and morphology were characterized by XRD, FTIR, Raman spectroscopy, laser diffraction and FE-SEM. The phase transformations of the initial powder during heating up to 1200 °C were examined using TG/DSC. At first, conventional sintering was performed and the recorded shrinkage/densification data were used to find out the appropriate experimental conditions for two-step sintering. The obtained results show that two-step sintering yields BCP ceramics, consisting of hydroxyapatite and  $\beta$ -TCP, with full dense, homogeneous structure with average grain size of 375 nm. Furthermore, BCP ceramics obtained by the two-step sintering method exhibit improved mechanical properties, compared to conventionally sintered BCP.  
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**Keywords:** Grain growth; Microstructure-final; Apatite; Two-step sintering

### 1. Introduction

Synthetic calcium phosphate ceramics (CaP) are widely studied as implant materials for bone tissue reconstruction because of their chemical similarity with natural bone tissue and excellent biocompatibility. There are different kinds of CaP bioceramics, with different composition and physical properties. Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HAp), represents the stable phase, with very slow bioresorbability rate. Dense HAp is surface-reactive and can be directly attached to the bone through chemical bonding called bioactive fixation. On the contrary, beta tricalcium phosphate, ( $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ ,  $\beta$ -TCP), is a bioresorbable ceramic, on which place, natural bone can ingrow after the implantation. Which type of CaP bioceramics will be used for the implantation depends on whether bioactive or bioresorbable ceramic is needed.<sup>1,2</sup> The concept of biphasic calcium phos-

phates (BCP), consisting of HAp and  $\beta$ -TCP ceramics, was developed by Daculsi et al.<sup>3</sup> The aim of their approach was to provide an optimal ratio of bioactive/bioresorbable ceramics within the implant that would allow natural bone ingrowth (osteogenesis) in the place of the implanted material while making chemical bonds between the implant material and the bone. The contribution of  $\beta$ -TCP is to dissolve faster than HAp in a biological environment, followed by the precipitation of carbonated hydroxyapatite similar to the biological bone mineral at the implant/tissue interface. The events that occur at the bioceramic/bone interface are dynamic physico-chemical processes, including crystal–protein interactions and cell and tissue colonization.<sup>3–6</sup> The presence of  $\beta$ -TCP could be beneficial due to its better protein adsorption capacity compared to pure HAp.<sup>7</sup> By tailoring the HAp/ $\beta$ -TCP ratio, it is possible to control the biodegradation rate, where a larger amount of  $\beta$ -TCP would increase the overall resorbility.<sup>8</sup> BCP ceramics can be prepared by mechanical mixing of HAp and  $\beta$ -TCP or through decomposition of calcium-deficient hydroxyapatite (CDHAp) by sintering above 700 °C.<sup>9</sup> The second procedure seems to be better because the mixture of phases on the atomic level leads

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## Synthesis, morphology, microstructure and magnetic properties of hematite submicron particles

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### ABSTRACT

We report on hydrothermal synthesis, plate-like morphology, microstructure and magnetic properties of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) plate-like particles. The sample is obtained immediately after the hydrothermal process without using any template and without further heat treatment. The so-obtained sample is characterized by X-ray powder diffraction (XRPD), energy-dispersive X-ray spectroscopy (EDX), field-emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and superconducting quantum interference device (SQUID) magnetometer. XRPD confirms the formation of a single-phase hematite sample whereas EDX reveals that iron and oxygen are the only components of the sample. SEM, FE-SEM, TEM and HRTEM show that the sample is composed of plate-like particles. The width of the particles is  $\sim$ 500 nm whereas thickness is  $\sim$ 100 nm (aspect ratio 5:1). The HRTEM images exhibit well defined lattice fringes of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles that confirm their high crystallinity. Moreover, the HRTEM analysis indicates the plate-like particles preferring crystal growth along [0 1 2] direction. Magnetic measurements display significant hysteretic behavior at room temperature with coercivity  $H_C = 1140$  Oe, remanent magnetization  $M_r = 0.125$  emu/g and saturation magnetization  $M_S = 2.15$  emu/g as well as the Morin transition at  $T_M \sim 250$  K. The magnetic properties are discussed with respect to morphology and microstructure of the particles. The results and comparison with urchin-like, rods, spherical, hexagonal, star-like, dendrites, platelets, irregular, nanoplatelets, nanocolumns and nanospheres hematites reveal that the plate-like particles possess good magnetic properties. One may conjecture that the shape anisotropy plays an important role in the magnetic properties of the sample.

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### 1. Introduction

During the last decade iron (III) oxides have been at the focus of a remarkable research interest due to a wide variety of properties, as well as possessing a huge potential for applications [1–20]. Among seven polymorphs of iron (III) oxide,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) in various forms (such as bare nanoparticles, nanowires, microcubes, rods, microspheres, nanorods, nanotubes, and nanoparticles embedded in an inert matrix) has been under extensive investigation in order to understand the influence of size, shape, anisotropy, microstructure, inter-particle interaction and surface effects on its physical properties.

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is the most stable iron oxide with a high resistance to corrosion, low cost, environmentally friendliness and non-toxicity. It is used as a pigment, catalyst, sensor, electrode material, biomedical and magnetic material [1,2,21–23]. Hematite crystallizes in the rhombohedral system space group R-3c (corundum structure) with n-type semiconducting properties (2.1 eV band gap) [1,2]. Despite intensive research, some of its features are still not fully known. Some of these unknowns concern the magnetic properties [24–46]. Hematite's magnetic properties may display three critical temperatures: the Néel temperature, the Morin temperature, and the blocking temperature. In bulk hematite the Néel temperature is  $T_N \approx 960$  K and the Morin transition takes place at the temperature  $T_M \approx 263$  K [1]. Below  $T_M$  the spins are antiparallel and the material behaves as a uniaxial antiferromagnet (AF). Above  $T_M$ , the spins show slight canting and a small net magnetic moment appears (weak ferromagnetism, WF) [1]. As the particle size decreases the Morin temperature

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# Determination of Particle Size Distributions by Laser Diffraction

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Review paper

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*The paper deals with the main principles of the determination of particle size distribution using Mastersizer 2000, Malvern Instruments Ltd., UK. Using several problems as examples we have demonstrated that the method is not a routine one and that the measurement procedure is not limited to entering a sample into the dispersion unit and pressing the button. Furthermore, we have shown that the sample preparation method and, therefore, the accuracy of results conclusively depend on the physical and chemical properties of the analyzed materials.*

**Key words:** Particle size distribution, Mastersizer 2000, Laser diffraction and Light scattering.

## 1. INTRODUCTION

The interest for particle size measurements arises from fact that the properties of dispersed materials are strongly correlated with their particle size and uniformity. From academic and industry researches to the control and production optimization of raw materials, medicaments, food and other products, there is a growing for a fast and accurate on-line method for the determination of particle size distribution. Due to its simplicity and accuracy, the laser diffraction method is nowadays the primary method for the examination of the size distribution in disperse systems such as soles and emulsions. The measurement procedures on modern laser diffraction devices (LD) are fast and fully automated; they are reproducible and can be standardized for certain systems. However, in order to obtain reliable data about the analyzed particle systems it is crucial to understand and take into account several important factors, such as the nature of the material, the instrument, measurement methodology and the verification of results.

## 2. BASICS OF THE LD METHOD

The LD technique is based on the fact that the spatial distribution of scattered light is a function of the particle size of the analyzed sample. The phenomenon of light diffraction on particles is complex, but it can be vividly presented. As a stone hits the water surface, the concentric rings of waves appears.

The waves near the site of impact are intense - higher, while the wave height decreases as moving away. Larger stones will create higher waves in comparison with smaller stones. Waves will also be more intense and clearly separated in the case of larger stones [1].

Generally speaking, a similar occurs when a particle is illuminated as is shown on fig. 1: for smaller particles the diffraction images are more diffuse. Basically, the LD method measures the intensities of diffraction rings and the distance between them (declination angles from the direction of incident light) [2]. It would be an easy method if an additional phenomenon does not occur. Besides diffraction during the illumination of particles other phenomena such as: reflection, refraction, absorption and re-radiation occur.

The phenomena that happen on illuminated particles are called light scattering, shown on figure 2. In contrast to diffracted light, which is emitted at small angles relative to incident light, scattering is more complex because the scattered light is emitted in all directions. The spatial distribution of scattered light is commonly called the scattering pattern of a particle.

The scattering pattern depends on ratio of particle diameter ( $D$ ) and the wave length of incident light ( $\lambda$ ); accordingly, the scattering pattern will change not only with a change in the size of particles but also as result of a change in the wave length  $\lambda$ . Depending on the  $D/\lambda$  ratio it can be distinguished among the Fraunhofer, Mie and Rayleigh scattering.

The Fraunhofer scattering occurs if particle size is at least 5 to 6 times larger the  $\lambda$ . The Rayleigh scattering occurs when the particle size is considerably

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## Crystal structure of cobalt-substituted calcium hydroxyapatite nanopowders prepared by hydrothermal processing

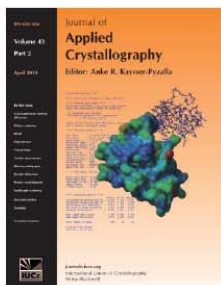
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# Hydrothermal Synthesis of Nanosized Pure and Cobalt-Exchanged Hydroxyapatite

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Pure and cobalt-exchanged hydroxyapatite (HAp and CoHAp) powders were synthesized by hydrothermal method. X-ray diffraction (XRD), Raman spectroscopy, particle size analysis, inductively coupled plasma (ICP) emission spectroscopy, and scanning electron microscopy (SEM) were used to study the microstructural and unit cell parameters, average particle size, particle size distribution, chemical composition, and morphology of the synthesized powders. XRD and Raman spectroscopy confirmed that the samples were free from impurities and other phases of calcium phosphates. It has been found that the increase in the cobalt amount in the crystal structure of HAp reduces unit cell parameters, as well as average crystallite size (from XRD measurements). All of the powders were nano-sized with narrow particle distribution (from particle size analyses). SEM investigations indicated that nano-sized particles were organized in soft micro-sized agglomerates, whose sizes increased with the increase in the content of Co in HAp crystal structure.

**Keywords** Hydrothermal method; Hydroxyapatite; Particle size distribution; Raman spectroscopy; XRD.

## 1. INTRODUCTION

Nowadays, hydrothermal processing of advanced materials is one of the most interesting techniques in the field of nanostructured materials and is also very attractive for large scale production due to its adaptivity, simplicity, low energy consumption, and good environmental aspects. In the past two centuries, hydrothermal technique was mainly applied to processes of single crystal growth and ore leaching, whereas nowadays hydrothermal technology has become one of the most important tools for advanced materials processing. This technique offers many advantages for the processing of nanostructured materials for a wide variety of applications in industry, such as ceramics, biomedical, catalytic, optoelectronics, etc. [1–5].

During the past several decades, there has been an ever increasing interest in materials with apatite structure. General chemical formula of stoichiometric mineral apatites is  $M_{10}(XO_4)_6Y_2$ , where M is a divalent cation, X could be P, V, or Si, while Y is some halogen element or group like  $OH^-$ . Phosphates with molecular formula  $M_{10}(PO_4)_6OH_2$  are used for various medical applications as bone implants, in industry as absorbers for heavy or radioactive elements ions, ion exchangers in chromatographic columns, catalysts, or electrolytes for ceramic fuel cells [6, 7].

Natural calcium hydroxyapatite (HAp,  $Ca_{10}(PO_4)_6(OH)_2$ ) is the main inorganic component of bones and teeth of vertebrates. For medical purposes, synthetic HAp material, with excellent biocompatibility, was produced for the use in

bone and teeth reconstruction. Adequate biodegradation rate and nontoxicity make this material suitable for drug delivery systems providing controlled release [8, 9]. The structure of HAp allows the substitution of  $Ca^{2+}$ ,  $PO_4^{3-}$ , and/or  $OH^-$  with other ions. Calcium ions in an apatite structure can be substituted with various metal ions like K, Na, Mg, Sr, Ba, Pb, Mn, Co, Fe, etc. [10, 11]. Generally accepted affinity of divalent cations for substitution is  $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$  [6]. It enables us to tailor HAp with modified properties, such as lattice parameters, crystallinity, morphology, and additional desired properties for a specific application. Regarding the material's biocompatibility, there is also a possibility of preparing magnetic nanoparticles of HAp by substituting  $Ca^{2+}$  with some magnetic ions such as Fe, Co, etc., for the application in magnetic resonance imaging, hyperthermia treatment, cell separation, and drug delivery [12]. Cobalt-substituted HAp shows catalytic activity for oxidative dehydrogenation of alcohols as well as for the process of styrene epoxidation [13]. Catalytic activity of CoHAp depends on the amount of cobalt substituted in the HAp lattice; moreover, its catalytic activity could be improved by loading with Ru [6, 14].

In this article, a series of pure calcium hydroxyapatite (HAp) and cobalt-substituted calcium hydroxyapatite (CoHAp;  $Ca_{10-x}Co_x(PO_4)_6(OH)_2$ ,  $x = 0.5, 1, \text{ and } 2$ ) powders were prepared by simple hydrothermal treatment of precipitates. X-ray diffraction (XRD), Raman spectroscopy, particle size analysis, inductively coupled plasma (ICP) emission spectroscopy, and scanning electron microscopy (SEM) were used to study the qualitative content, unit cell parameters, degree of crystallinity, average particle size, particle size distribution, chemical composition, and morphology of the synthesized powders.

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