Physicochemical Properties of Advanced Nanostructured Materials for Dental Microimplant Coatings

GEORGETA ZEGAN[1], DANIELA ANISTOROAEI[1], LOREDANA GOLOVCENCU[1], EDUARD RADU CERNEI[1], CRISTINA GENA DASCALU[2]*, ELENA MIHAELA CARAUSU[3]

[1] Grigore T. Popa University of Medicine and Pharmacy, Faculty of Dental Medicine, Department of Surgery, 16 University Str., 700115, Iasi, Romania

[2] Grigore T. Popa University of Medicine and Pharmacy, Faculty of Medicine, Department of Medical Informatics and Biostatistics, 16 University Str., 700115, Iasi, Romania

[3] Grigore T. Popa University of Medicine and Pharmacy, Faculty of Dental Medicine, Department of Management and Public Health,16 University Str., 700115, Iasi, Romania

An important aspect of orthodontic microimplants is represented by biocompatibility and avoidance of infection development at living tissue surrounding it. Therefore, nanotechnology has the ability to improve this issue by coating microimplants with metal oxides type nanomaterials possessing antimicrobial effect. Some features of advanced nanostructured materials used as implant coatings, such as composition, structure, specific surface area, porosity, shape and size are factors that make them suitable as antimicrobial agents. The present work deals with the structural and morphological studies of ZnO and TiO_2 *nanoparticles used to combat oral diseases. Coating microimplants with nanosized titanium oxide (*TiO_2*) and zinc oxide (ZnO) may improve conditions for osseointegration in accordance with preventing oral infection. These metal oxides nanopowders were synthesized using sol-gel method. Structural and morphological investigation were carried out by XRD and FTIR spectra, SEM-EDX and TEM images respectively. XRD and FTIR analyses confirmed metal oxides crystallization and metal oxide bonds. SEM-EDX and TEM features confirmed elemental composition of these nanoparticles and their textural characteristics such as shape, size, porosity and agglomeration degree.*

Keywords: dentistry, dental implants, orthodontic microimplants, nanoparticles, morphology

Nanodentistry refers to the science that includes diagnosis, treats and prevents of dental diseases, pain, preserving dental health using nanomaterials. A wide variety of dental products is available, ranging from oral hygiene products to implants that need nanoscale features. The major interest in this field is to design biocompatible and antimicrobial implants [1]. Although the nanotechnology in dentistry is developing very fast there are many issues to be resolved such as minimally invasive dentistry without side effects. In the past few years, dental implant longevity implies a multidisciplinary system using structural and morphological surface characteristics [2, 3].

Dental implants are frequently used as an adjunctive therapy to young people which show a congenital lack of upper lateral incisors (hipodontia), in order to improve aesthetic dentistry.

Microimplants are often used in orthodontics to obtain maximum anchorage or dental movements or or group of teeth during multi-brackets fixed treatments of teens.

A significant purpose in implantology is to achieve the osseointegration and to maintain an intimate contact of tissue with the microimplant thereby preventing the multiplication of bacteria [4]. Nanotechnology can create antimicrobial nanoparticles for implant coatings with controlled structural and morphological properties and biological interactions [5].

Nanoparticles refers to the insoluble particles smaller than 100 nm in size possessing specific properties such as composition, structure, dimension, morphology, porosity, pore size distribution, specific surface area, uniformity and agglomeration degree [6].

Due to their biocidal property some of these advanced materials are explored in order to prevent biofilm formation in the oral cavity. Nanoparticles can interact efficiently with microbial membranes thus proving their antimicrobial activity. Several researchers related that metal or metal oxides nanoparticles have shown the most effective antibacterial activity leading to the idea that they can be used as microimplant coatings [7, 8]. Some of them like ZnO, titanium dioxide (TiO_2), gold, silver, silica (SiO_2) and Cu/CuO can be coated on either microimplants or brackets in orthodontics as antimicrobial agents [9-11].

For example, ZnO and TiO_2 type nanoparticles are commonly used as antimicrobial coatings for implants and microimplants [12, 13].

Although these types of metal oxides are accepted as antimicrobial agents, they must be safe and very efficient without compromise the integrity of the dental microimplant [14].

The major goal of dental implant coatings with metal or metal oxides is to provide a high effective rate after initial microimplant fixation avoiding bacterial infection.

This study includes ZnO and TiO_2 nanoparticles synthesis by sol-gel route for their subsequent use in dental microimplant coatings.

As synthesized metal oxides were structurally and morphologically analyzed using XDR, FTIR, SEM-EDX and TEM physicochemical characterization advanced techniques.

Experiemntal part

Materials and methods

Sol-gel synthesis of metal oxides nanoparticles allows the deposition of these nanosized materials on the microimplant surface. This technique offer a size and morphology control of nanoparticles altering their textures

---

*email: cdascalu_info@yahoo.com

and enabling fabrication of thinner coatings with biological applications [15, 16].

The experimental procedures were carried out in accordance with the mandatory principles of the ethics [17-22].

ZnO synthesis

Zinc oxide (ZnO) nanoparticles synthesis was carried out using sol-gel method [23-29]. Thus, 4.3 g $ZnSO_4 . 7H_2O$ and 1.2 g diethylene glycol were added to a mixed solution containing 10 mL pure ethanol and 300 mL double distilled water.

The entire solution was vigorously stirred at 85°C for 2 h leading to gel formation. After this stage the obtained gel was sunjected to drying step at 220°C for 2 h .

The obtained product was ground into fine particles and finally treated at 500°C for 5 h for getting ZnO nanoparticles.

As synthesized samples was structurally characterized using XRD and FTIR techniques and morphologically using scanning electron microscopy (SEM-EDX) and transmission electron microscopy (TEM).

TiO_2 synthesis

TiO_2 nanoparticles were obtained by sol-gel route [30-34]. 20 mL of $TiCl_4$ were added gradually in a 40 mL HCl solution of 37% concentration.

The mixed solution was cooled in an ice bath at 5°C. the obtained sol was added to 600 mL double distilled water. To precipitate the amorphous TiO_2, the reaction mixture was treated with an aqueous solution of ammonia till *p*H value reached at 8.

The suspension was subjected to ageing stage for 48 h at room temperature then dried at 80°C for 24 h.

The final white powder was ground for thermal treatment at 550°C.

Advanced techniques such as XRD, SEM and AFM were also used for structural and morphological highlighting.

Results and discussions

XRD analysis was used to highlight crystalline phase of ZnO and TiO_2 nanopowders presented in figure 1 and figure 2. For ZnO sample are presented the diffraction peaks at angles 2θ and their corresponding reflections of 31.36°(100), 34.03°(002), 35.8°(101), 47.16°(102), 56.26°(110), 62.54°(103), 67.64°(200), 68.79°(112), 69.45°(201), 72.82°(004) and 77.33°(202) demonstrating crystalline structure of zinc oxide.

For TiO_2 sample are presented the diffraction peaks at angles 2θ of 25.27°, 36,91°, 37.77°, 38.52°, 48.01°, 53.84°, 55.03 and 62.64° correspond to the reflection from (011), (012), (002), (102), (112), (013), (112) and (111) crystal planes of TiO_2 structure.

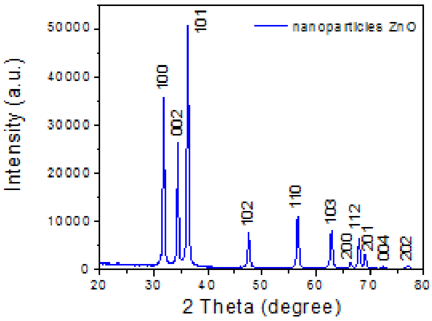


Fig. 1. XRD patterns of ZnO nanoparticles

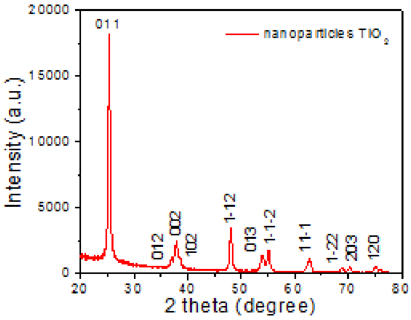


Fig. 2. XRD patterns of TiO_2 nanoparticles

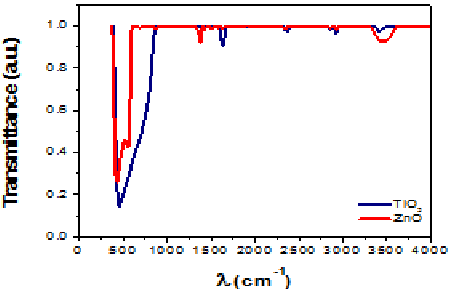
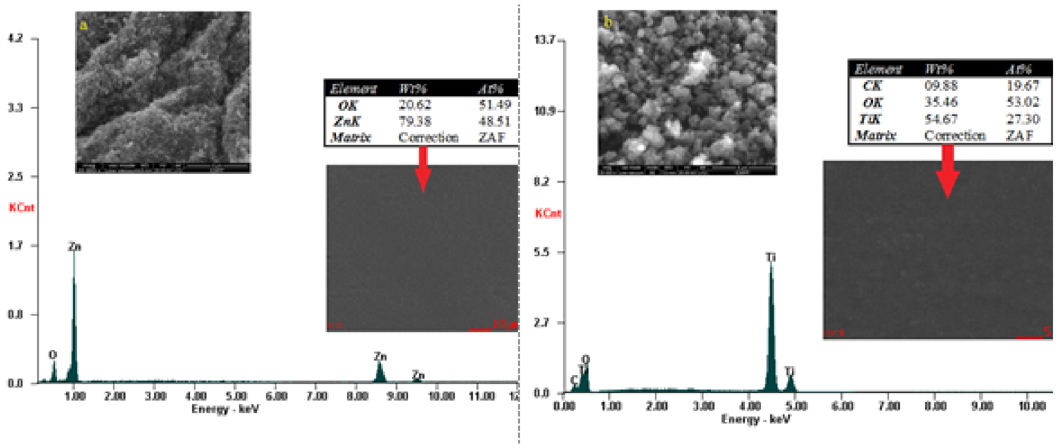


Fig. 3. FTIR spectra of ZnO and TiO_2 nanoparticles

FTIR spectra shown in figure 3 of ZnO and TiO_2 nanocristals aquired in the range of 4000-400 cm^{-1} exhibited a strong absorption peak at around 3500 cm^{-1} for stretching vibration belonging to OH group nonchemical bonded and at around 1600 cm^{-1} associated to H-O-H bending vibration. Peaks exhibited at around 500 belong to ZnO and TiO_2 bonds.

SEM-EDX patterns reveal elemental composition of the samples and morphological characteristics of ZnO and TiO_2 nanopowders. From figure 4(a) and 4(b) it can be observed a high omogenity, spherical shape of nanoparticles and the absence of particle agglomeration. ZnO nanocrystals size is in the range 5-20 nm while TiO_2 nanoparticles size in in the range 5-10 nm.

TEM analysis confirm the size of TiO_2 and ZnO nanoparticles and the uniformity of nanopowders as shown in figure 5(a) and 5(b).



Element	Wt%	At%
OK	20.62	51.49
ZnK	79.38	48.51
Matrix	Correction	ZAF

Element	Wt%	At%
CK	09.88	19.67
OK	35.46	53.02
TiK	54.67	27.30
Matrix	Correction	ZAF

Fig. 4. SEM - EDX a) ZnO b)TiO_2

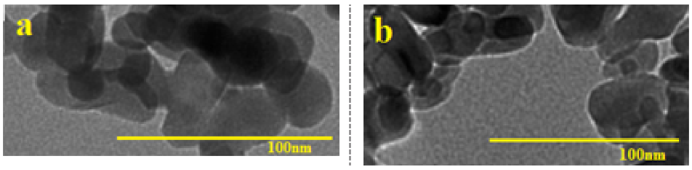


Fig. 5. TEM images of a)ZnO, b) TiO_2

Conclusions

Nanotechnology in dentistry faces significant challenges in achieving its potential. It requires solving different issues at nanoscale levels.

Dental implants, usually used to replace missing teeth, can alter their nanofeatures by different procedures in order to enhance their osseointegration avoiding infections development. Nanostructures coatings for dental microimplants increased researcher's attention in last few years. Owning specific structures and morphologies, nanosized metal oxides type titanium dioxide and zinc oxide have a large potential in their use in dentistry.

Synthesis and characterization of these materials offer information about their specific structural and morphological properties, giving the possibility of using them as dental microimplant coatings with peculiar biological properties due to their efficient bactericidal features. We can conclude that controlling their size makes these biocompatible nanomaterials good candidates for further researches on a large range of oral germs.

References

1.SHARMA, S., CROSS, S.E., HSUEH, C., WALI, R.P., STIEG, A.Z., GIMZEWSKI, J.K., Int. J. Mol. Sci., **11**, 2010, p. 2523.

2.ADELL, R., LEKHOM, U., ROCKLER, B., BRANEMARK, P.I., Int. J. Oral Surg., **10**; 1981, p. 387.

3.ZARB, G.A., SCHMITT, A., J. Prosthet. Dent., **64**, 1990, p. 185.

4.ROZE, J. BABU, S., SAFFARZADEH, A., GAYET-DELACROIX, M., HOORNAERT, A., LAYROLLE, P. Clin. Oral Implants Res., **20**, no.10, 2009, p. 1140.

5.MENDONÇA, G., MENDONÇA, D.B.S., ARAGAO, F.J.L., COOPER, L.F., Biomaterials, **29**, 2008, p. 3822.

6.PANCHALI, B., MUSHTAQ, A., JAHIRUL, M., MERYAM, S. MIGLANI, R., Advances in Dentistry and Oral Health, **2**, no. 2, 2016, p.1.

7.ALLAKER, R.P., J. Dent. Res., **89**, no. 11, 2010, p. 1175.

8.AHN, S.J., LEE, S.J., KOOK, J.K., LIM, B.S., Dent Mater, **25**, no. 2**,** 2009, p. 206.

9.SODAGAR, A., BAHADOR, A., KHALIL, S., SHAHROUDI, A.S., KASSAEE, M.Z., J. Prosthodont. Res., **57**, no. 1, 2013, p. 15.

10.SPENCER, C.G., CAMPBELL, P.M., BUSCHANG, P.H., CAI J., HONEYMAN, A.L., Angle Orthod., **79**, no. 2, 2009, p. 317.

11.RAMAZANZADEH, B., JAHANBIN, A., YAGHOUBI, M., SHAHTAHMASSBI, N., GHAZVINI, K., et al., J. Dent., **16**, no. 3, 2015, p. 200.

12.VIDIC, J., STANKIC, S., HAQUE, F., CIRIC, D., GOFFIC, R., VIDY, A., JUPILLE, J., DELMAS, B., J. Nanopart. Res., **15**, 2013, p. 1.

13.JUILLERAT-JEANNERET, L., DUSINSKA, M., FJELLSBO, L. M., COLLINS, A. R., HANDY, R. D., RIEDIKER, M., Introduction to the NanoTEST Project. Nanotoxicology, **16**, 2013, p. 16.

14.CHEN, M. H., J. Dent. Res., **89**, 2010, p. 549.

15.IVANOFF, C.J., HALLGREN, C., WIDMARK, G., SENNERBY, L., WENNERBERG, A., Clin Oral Implants Res, **12**, 2001, p. 128.

16.BEN-NISSAN B., CHOI A.H., Nanomed, **1**, 2006, p. 311.

17.TOADER, E., TOADER, T., Revista Romana de Bioetica, **10**, no. 3, 2012, p. 66.

18.TOADER, E., Revista Romana de Bioetica, **8**, no. 2, 2010, p. 157.

19.BALAN, G.G., TRIFAN, A., SAVIN, C., BALAN, A., GOLOGAN, E., Revista de Cercetare si Interventie Sociala, **55,** 2016, pp. 244-259.

20.BALAN, G.G., MITRICA, D.E., IACOB, M., BALAN, A., ZETU, I., Revista de Cercetare si Interventie Sociala, **49,** 2015, pp. 229-238.

21.BALAN, A., SAVIN, C., BALAN, G.G., ZETU, I., Revista de Cercetare si Interventie Sociala, **45,** 2014, pp. 160-174.

22.TOADER, E., Revista de Cercetare si Interventie Sociala, **37**, 2012, p. 144.

23.SUCHEA, M., TUDOSE, I.V., IONITA, S., SANDU, I., IACOMI, F., Rev. Chim. (Bucharest), **66,** no. 12, 2015, p. 2044.

24.SUBLI, M.H., OMAR, M.F., SANDU, I.G., ZULKEPLI, N.N., ABDULLAH, M.M.A., SANDU, A.V., Mat. Plast., **51,** no. 4, 2014, p. 391.

25.BACHVAROVA-NEDELCHEVA, A.D., GEGOVA, R.D., STOYANOVA, A.M., IORDANOVA, R.S., COPCIA, V.E., IVANOVA, N.K., SANDU, I., Bulgarian Chemical Communications, **46,** no. 3, 2014, p. 585.

26.COPCIA, V.E., HRISTODOR, C.M., DUNCA, S., IORDANOVA, R., BACHVAROVA-NEDELCHEVA, A., FORNA, N.C., SANDU, I., Rev. Chim. (Bucharest), **64,** no. 9, 2013, p. 978.

27.COPCIA, V.E., GRADINARU, R., MIHAI, G.D., BILBA, N., SANDU, I., Rev. Chim. (Bucharest), **63,** no. 11, 2012, p. 1124.

28.IRIMIA, M., IACOMI, F., RAMBU, A.P., SANDU, A.V., DOROFTEI, C., SANDU, I., Rev. Chim. (Bucharest), **63,** no. 8, 2012, p. 803.

29.SANDU, I., POPESCU-CIOCIRLIE, I., GRUIA, I., CALANCIA, O, COSMA, D.G., SANDU, I.G., COZMA, D.G., Rev. Chim. (Bucharest), **49,** no. 11, 1998, p. 756.

30.ADOMNITEI, C., Cornei, N., LUCA, D.,SANDU, I. VASILACHE, V., DOBROMIR, M., MARDARE, D., Journal of Optoelectronics snd Advanced Materials, **17,** no. 5-6, 2015, p. 889.

31.POIANA, M., DOBROMIR, M., NICA, V., SANDU, I., GEORGESCU, V., Journal of Superconductivity and Novel Magnetism, **26,** no. 10, 2013, p. 3105.

32.ADOMNITEI, C., LUCA, D., GIRTAN, M., SANDU, I., NICA, V., SANDU, A.V., MARDARE, D., Journal of Optoelectronics snd Advanced Materials, **15,** no. 5-6, 2013, p. 519.

33.BALAN, A., SAVIN, C., SANDU, A.V., STOLERIU, S., Mat. Plast., **53**, no. 1, 2016, p. 100.

34.GEANTA, V., STEFANOIU, R., VOICULESCU, I., DAISA, D.D., Journal of Optoelectronics and Advanced Materials, 13, 2011, p. 921.

Manuscript received: 3.02.2017