

# Core/shell nanocomposite for biomedicine and environmental safety

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**Abstract.** The two different routes for creation Cu(II) modified zirconia were seen. FTIR and ESR spectroscopy were investigated the influence of synthesis route on features of formation of such structure. It is shown that for both cases the interaction between copper (II) and Zr-OH and Zr=O is occurred and these centres have paramagnetic nature. When the Cu-contained polymer is used for shell formation, only one kind of paramagnetic centres of copper (II) is formed, but when the Cu-contained inorganic complex is used for shell formation two kinds of copper (II) paramagnetic centres are formed.

## 1. Introduction

Task-oriented nanocomposites of core/shell structure (NC) and surface-modified nanoparticles are promising materials for using in biomedical and environmental safety application [1]. These materials must to have pre-determined properties there are catalytic or photocatalytic, antibacterial or fungicide properties [2-3]. CuO, Ag or Au particles are “the oldest” bactericide agents, but in high concentrations the ions of these elements show a high toxicity to living organism [4]. It is also necessary noted that these materials are very expensive. It leads to need developing of a new composite materials in which such bactericide active ions are on nanoparticles surface [5]. That approach allows decreasing of amount of active elements in nanoparticles with safety of their high bactericide properties but to decrease toxicity to living organism and cost of material [5]. The specific features of composite materials are the crucial influence of the interface on their structural and functional properties [6-7]. Efficiency of surface functionalized material in these applications has been achieved due to its high dispersity and homogeneity of components distribution in the complex system [5]. Cu(II) – functionalized zirconia is promising material for creation functional ceramic and inorganic-polymeric composite [8-9]. Composite systems may be inorganic/inorganic and inorganic/organic nature. These composite structures may be different nature, for example, oxide nanoparticles with surface is enriched by Cu (II) complexes or oxide core/Cu-contained polymeric shell [8,10]. The state of copper (II) on surface is a main moment for functionality of such composite structures.

Some routes of creation of functional structures are used in material science technology [11-13]. In practice, the impregnation of Cu salts in oxide surface is a more often used method in catalysts chemistry for creation or enhance catalytic systems [12]. However in this approach often synthesized



the structure with separated chemical components or another words substrate-carrier with high dispersity of active copper oxide components [13].

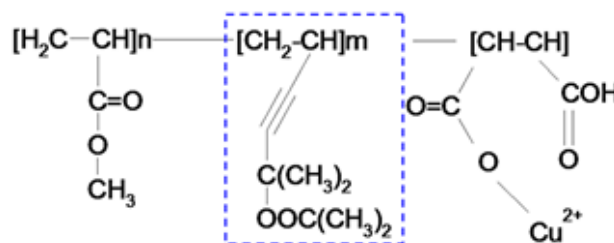
But for some applications the metal ions linked with oxide surface structure are needed [14]. It may be realized due to simultaneously precipitation of oxide matrix and metal hydroxocomplexes and for this case the oxide nanoparticles with copper ions enriched surface is formed [15]. In another approach the creation of oxide core/Cu(II) contained shell structures may be realized modifying of oxide nanoparticles surface by specially developed Cu(II) contained oligomer molecule [16]. It is especially important for forming of polymer compatible nanomaterials. For case of core/shell structure and as core and as shell together determines of functionality of such system [6]. It is noted that for both cases the copper (II) must be linked with zirconia surface.

In this work we show that two routes may be effective use for creation of CuO surface enriched zirconia particles and zirconia core/Cu-contained polymeric shell structure and the linking of copper (II) in these systems will be the same. Preservation of copper (II) in ionic or chelate forms is very important moment for keeping of antibacterial, catalytic and optic properties of composite materials.

## 2. Experimental

Two routes for creation of Cu(II) surface functionalized zirconia were used. First route based on wet co-precipitation technology and only inorganic components are used. Next procedure was used for  $\text{ZrO}_2$ -3 mol. %  $\text{Y}_2\text{O}_3$  core/Cu-contained shell system creation: the mix of 2 mol/L of zirconium chloride [ $\text{ZrOCl}_2$ ] and 0.044 mol/L of yttrium nitrate [ $\text{Y}(\text{NO}_3)_3$ ] salts and 0.09 mol/L of  $\text{Cu}(\text{NO}_3)_2$  in distilled water was used as initial salt solution. Co-precipitation was carried out using 6 wt% solution of ammonia at pH 10-11, and then was precipitate washing to pH 7. The precipitate was drying under microwave irradiation (MW, frequency is 2.45 GHz and power is 700W). Cu(II) functionalized  $\text{ZrO}_2$ -3 mol. %  $\text{Y}_2\text{O}_3$  NPs ( $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ -Cu(II) complex) was obtained.

Second route based on wet co-precipitation method for oxide core creation with follow modification of Cu-contained polymer. Next procedure was used for  $\text{ZrO}_2$ -3 mol.%  $\text{Y}_2\text{O}_3$  core creation: the mix of 2 mol/L of zirconium chloride [ $\text{ZrOCl}_2$ ] and 0.044 mol/L of yttrium nitrate [ $\text{Y}(\text{NO}_3)_3$ ] salts in distilled water was used as initial salt solution. Co-precipitation was carried out using 6 wt% solution of ammonia at pH 10-11 and then the precipitate was washed to pH 7. Precipitate was drying under microwave irradiation (MW) with power of 700 W and frequency of 2.45 GHz.  $\text{ZrO}_2$ -3 mol. %  $\text{Y}_2\text{O}_3$  crystalline NPs ( $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ , zirconia nanoparticles) was synthesized by calcining the dried precipitate. The annealing temperature was 500°C. Coordinated  $\text{Cu}^{2+}$  complex of copolymer of vinyl acetate, 5-tertbutylperoxy-5-methyl-1-hexene-3-yne and maleic acid (OMC) was used for obtaining functional shell via its irreversible adsorption on nanoparticle surface. Complex structure presents in Figure 1.



**Figure 1.** Structure of OMC. The blue square shows the 2-tertbutylperoxy-2-methyl-5-hexene-3-yne fragment (follower BEP).

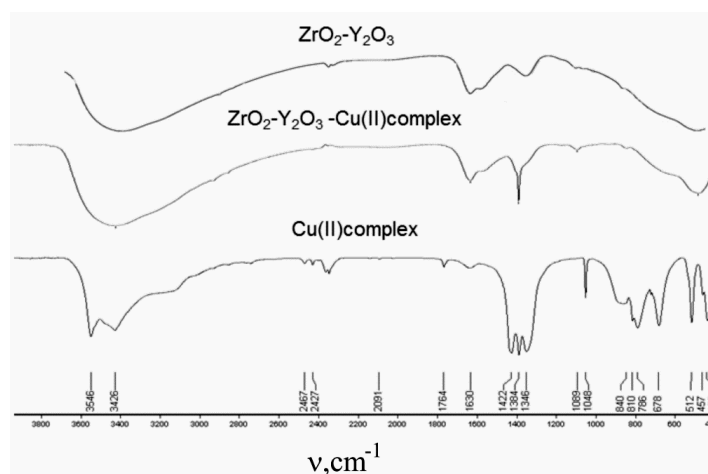
Fourier transform infrared spectroscopy (FTIR spectroscopy) was used to study the initial materials and composite structures. The FTIR spectra of NPs were registered within the range of 375-4000 $\text{cm}^{-1}$  with resolution of 4 $\text{cm}^{-1}$ . FTIR spectrometer “Bruker Tensor 27” was used for measurement.

Electron spin resonance spectra (ESR spectra) of xerogels were obtained at room temperature. The spectrometer CMS8400 with a high-frequency modulation at 9 GHz is used. The ESR measurements were carried out in presence of calibration sample – Mn(II) in cubic MgO. The fifth CTC line of Mn(II)/MgO was chosen as a reference of the paramagnetic centers position. The relative measurement error did not exceed 20%.

### 3. Results and discussion

According to the presented synthesis routes for the first case the Cu(II) are adsorbed on nanoparticles of zirconium hydroxide hydrogel in form complexes with different structures. There are copper ammonia complexes  $[\text{Cu}(\text{NH}_3)_m(\text{H}_2\text{O})_n]^{2+}$  or copper hydroxide complexes  $[\text{Cu}(\text{H}_2\text{O})_m(\text{OH})_k]^{2-k}$  or mix copper ammonia hydroxide complexes  $[\text{Cu}(\text{NH}_3)_m(\text{OH})_n]^{2-n}$  and also the different associates of their complexes may be formed. Realization of determined structure of Cu(II) complex are depended on pH solution and concentration of copper salts and ammonium hydrate [17].

The identification of Cu(II) complex structure which may be realized in conditions of synthesis at pH 8 was carried out by FTIR spectroscopy, see Figure 2. FTIR spectrum shows the presence the set of absorption bands for valence vibrations of O-H bond in hydroxyls and water molecule ( $3546\text{cm}^{-1}$  and  $3426\text{cm}^{-1}$ ) and for valence vibrations of N-H bond of ammonia ligand ( $3125\text{cm}^{-1}$  and  $3050\text{cm}^{-1}$ ) in equatorial and axial positions in a complex, respectively. The set of adsorption bands at  $1354\text{cm}^{-1}$ ,  $1384\text{cm}^{-1}$ ,  $1422\text{cm}^{-1}$ ,  $1635\text{cm}^{-1}$ ,  $1763\text{cm}^{-1}$  in region of deformation vibrations of FTIR spectrum indicates on the presence of ligands with NH and OH bonds in Cu(II) complex and on residual amount of  $\text{NO}_3$  groups. Thus, peaks at  $1635\text{cm}^{-1}$ ,  $1422\text{cm}^{-1}$ ,  $1354\text{cm}^{-1}$  identify  $\text{NH}_3$  ligands, the peak at  $1384\text{cm}^{-1}$  indicate on residual amount of  $\text{NO}_3$  groups, peak at  $1763\text{cm}^{-1}$  is summary from oscillation of both  $\text{NH}_3$  and  $\text{NO}_3$  groups. Peak at  $1048\text{cm}^{-1}$  indicates on Cu-(OH) or Cu-( $\text{OH}_2$ ) groups in complex structure and peak at  $677\text{cm}^{-1}$  corresponds to librational vibration of water ligands. The band at  $858\text{cm}^{-1}$  corresponds to pendulum oscillations of  $\text{NH}_3$ . The band at  $511\text{cm}^{-1}$  corresponds to vibrations of Cu-O bond and vibrations of Cu-N occur at  $456\text{cm}^{-1}$  and  $431\text{cm}^{-1}$  frequencies.



**Figure 2.** FTIR-spectrum of synthesized systems: Cu(II) complex,  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  and precipitated  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Cu(II)}$  complex.

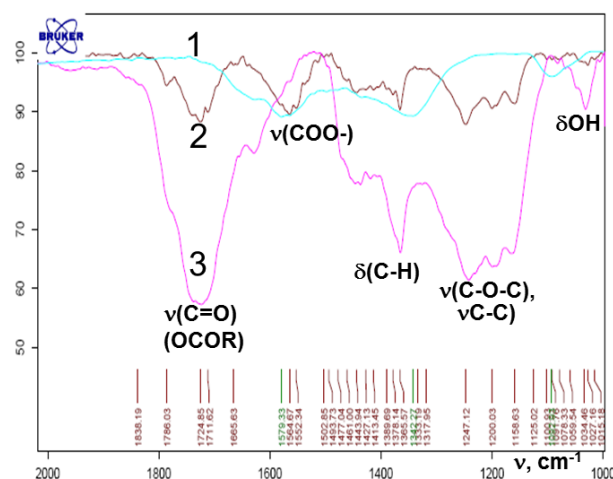
FTIR spectra of  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  amorphous NPs show the presence of surface hydroxyls and water molecules with different extents of connectivity. The wide peak at  $3434\text{cm}^{-1}$  corresponded to terminal hydroxyl and low frequency shoulder corresponds to two and three coordinate hydroxyls and water molecules. The peak at  $1635\text{cm}^{-1}$  indicated physically adsorbed water. The spectra of investigated systems contained an adsorption band at  $1093\text{cm}^{-1}$ . The presence of this adsorption band in the FTIR

spectrum of oxide was found to be associated with the appearance of surface cation-oxygen (or cation-hydroxyl group) vibrations of different strengths [18].

For Cu(II) complex modified  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  in region of valence vibrations of O-H and N-H bonds FTIR spectrum shows the wide bands with central frequency at  $3429\text{cm}^{-1}$ . This adsorption band is shifted in low frequency region on compared with pure Cu(II) complex. FTIR spectrum of this system shows the change of intensities of bands of deformation vibrations of N-H bonds (in range of  $1300\text{-}1400\text{cm}^{-1}$ ). It may be evidence changing in Cu(II) surrounding ligands at adsorption of complex Cu (II) on the surface of  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  nanoparticles. FTIR spectra of Cu(II) modified  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  shows a wide non-divided band at  $400\text{-}1000\text{cm}^{-1}$  in range of lattice vibrations. The qualitative picture of FTIR spectrum of Cu(II) modified  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  may be corresponded to replace some  $\text{NH}_3$  ligands from Cu(II) complex as result of interaction Cu(II) complex with surface oxygen-contained groups ( $\text{Zr=O}$  or  $\text{ZrOH}$ ) and oxygen vacancies.

In the second case the  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  core is first formed and only then copper-contained polymer shell is instilled to it. Synthesis  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  may be divided to same stage. On first stage the amorphous product is formed. On the second stage the heat treatment of amorphous NPs at  $500^\circ\text{C}$  leads to forming tetragonal crystalline NPs with sizes about 10nm. Figure 3 shows the FTIR spectrum of  $\text{ZrO}_2\text{-}3\text{ mol.}\% \text{Y}_2\text{O}_3$  NPs. FTIR spectra of crystalline NPs shows the presence of surface hydroxyls and water molecules with different extents of connectivity. The peak at  $3692\text{cm}^{-1}$  corresponded to terminal hydroxyl groups that were bases. The existence of a wide band at  $3440\text{cm}^{-1}$  indicated the presence of two and three coordinate hydroxyls and water molecules that were acids. The peak at  $1635\text{cm}^{-1}$  indicated physically adsorbed water. The spectra of investigated systems contained an adsorption band at  $1093\text{cm}^{-1}$ . The presence of this adsorption band in the FTIR spectrum of oxide was found to be associated with the appearance of surface cation-oxygen (or cation-hydroxyl group) vibrations of different strengths [18].

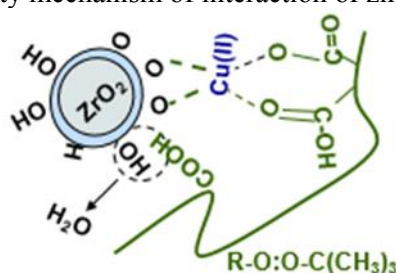
Figure 3 shows the FTIR spectrum of OMC. As one can see, bands on the FTIR spectrum ranged from  $2900\text{-}2930\text{cm}^{-1}$  and were assigned to aliphatic  $\text{CH}_n$  group vibrations.



**Figure 3.** FTIR spectra of (1)  $\text{ZrO}_2\text{-}3\text{ mol.}\% \text{Y}_2\text{O}_3$  crystalline NPs, (2) composite structure  $\text{ZrO}_2\text{-}3\text{ mol.}\% \text{Y}_2\text{O}_3/\text{OMC}$ , (3) OMC.

The presence of weak-intensity peak in range of  $1900\text{-}2000\text{cm}^{-1}$  may be corresponding to  $\text{C}\equiv\text{C}$  bond vibrations. The peak at frequency of  $1728\text{cm}^{-1}$  and shoulder at  $1784\text{cm}^{-1}$  correspond to vibrations of the  $\text{C=O}$  bond of carbonyl groups of different fragments of OMC molecules (Figure 1). The peak at  $3486\text{cm}^{-1}$  was assigned to the associated OH bond of the carbonyl groups. The peak at  $1633\text{cm}^{-1}$  was assigned to the carboxyl ion bound in the chelated complex by  $\text{Cu}^{2+}$  ions. Bands at  $1436\text{cm}^{-1}$  and  $1364\text{cm}^{-1}$  correspond to anti-symmetric and symmetric vibrations of aliphatic  $\text{CH}_2$  or  $\text{CH}_3$  groups, respectively. The wide subminimum in range of  $1100\text{-}1300\text{cm}^{-1}$  (peaks at  $1241\text{cm}^{-1}$ ,  $1199\text{cm}^{-1}$  and

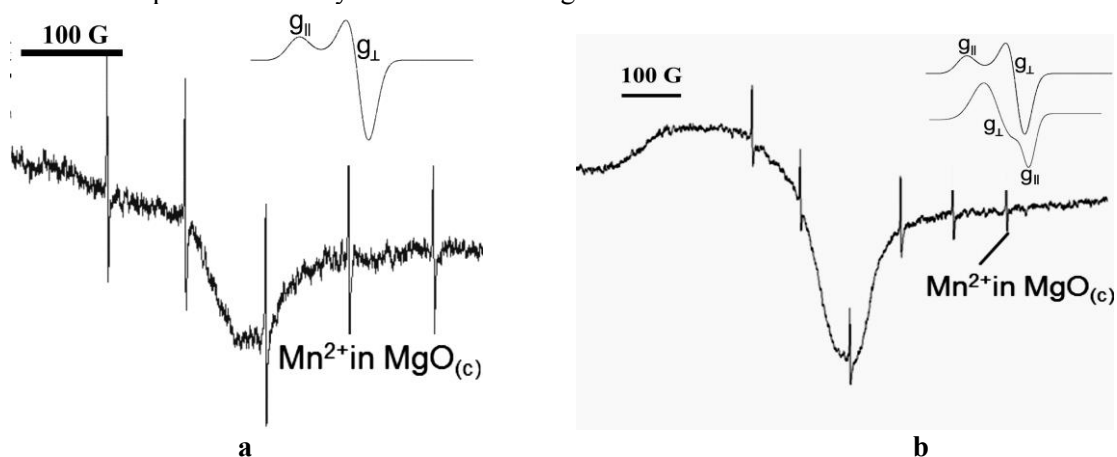
1165 $\text{cm}^{-1}$ ) were ascribed as vibrations of C-O-C and C-C skeleton bonds. The peak at 1032 $\text{cm}^{-1}$  corresponded to a vibration of an OH bond of the carboxylic groups bound to  $\text{Cu}^{2+}$  ions. Figure 3 shows the FTIR spectrum of composite structures of  $\text{ZrO}_2$ -3 mol.%  $\text{Y}_2\text{O}_3$  NPs core/OMC shell. The composites were obtained using 3 wt.% OMC solution. Vibrations of C=O, CH<sub>3</sub>, and CH<sub>2</sub> of functional groups and C-C and C-O-C skeletons of OMC were good appeared in the FTIR spectra. The presence of adsorption band at 1727 $\text{cm}^{-1}$  corresponds to  $\nu(\text{C}=\text{O})$  of carbonyl groups of OMC fragments and also the new band at 1565 $\text{cm}^{-1}$  is appearance. It corresponds to carboxylic groups that are linked with surface. Also the disappearance of adsorption band at 1086  $\text{cm}^{-1}$  (surface Zr-O bonds) is observed in FTIR. The change in band intensity at 1089 $\text{cm}^{-1}$  in the spectra of the modified system was used to estimate the extent of coverage of the organic phase surface. The qualitative picture allows to propose that the interaction OMC with NPs are realized as Cu coordination with Zr=O or Zr-OH. Figure 4 shows the possibility mechanism of interaction of zirconia nanoparticles with OMC.



**Figure 4.** Possible mechanism of interaction OMC with zirconia surface.

Accordingly to noted features of FTIR spectra of zirconia/OMC structure, in particular the shifting of band from 1093 $\text{cm}^{-1}$  to 1086 $\text{cm}^{-1}$  (vibrations of surface  $\text{Zr}=\text{O}(\text{OH})$  groups for zirconia and zirconia/OMC ) and appearance a new band at 1565 $\text{cm}^{-1}$  (vibrations of C=O carboxylic ions), coordination OMC on zirconia surface occurs by linked carboxylic groups and Cu(II) coordination with  $\text{Zr}=\text{O}(\text{OH})$  surface groups.

Figure 5 shows the ESR spectra of Cu(II) modified zirconia which were synthesized by different routes. In ESR spectra of both systems the broad signal are observed.



**Figure 5.** ESR spectra of a) OMC modified  $\text{ZrO}_2$ -3 mol.%  $\text{Y}_2\text{O}_3$  NPs, b) Cu(II) modified  $\text{ZrO}_2$ -3 mol.%  $\text{Y}_2\text{O}_3$  NPs.

Early [19] we show that the ESR signal for pure Cu(II) complex has a complex characters and shows the presence of two kinds of Cu(II) paramagnetic centers ( $g_{\parallel}=2.25$ ,  $g_{\perp}=2.08$  and  $g_{\perp}=2.17$ ,  $g_{\parallel}=2.05$ ). For Cu(II) modified  $\text{ZrO}_2$ -3 mol.%  $\text{Y}_2\text{O}_3$  also two kinds of Cu(II) paramagnetic centers ( $g_{\parallel}=2.24$ ,  $g_{\perp}=2.06$  and  $g_{\perp}=2.15$ ,  $g_{\parallel}=2.03$ ) are observed in ESR spectra. The ESR spectrum of  $\text{ZrO}_2$ -3



mol%  $\text{Y}_2\text{O}_3$  NPs which is modified by OMC show the broad signal with g-factors  $g_{\parallel}=2.17$ ,  $g_{\perp}=2.06$ , which may be corresponded the coordination of Cu(II) on NPs surface as chelate complex.

#### 4. Conclusion

Thus for both routes of formation of Cu(II) modified  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  and  $\text{ZrO}_2\text{-Y}_2\text{O}_3/\text{OMC}$ -shell structures the Cu(II) is linked with zirconia surface via surface oxygen-containing groups ( $\text{Zr=O}$  or  $\text{ZrOH}$ ). The features of formation of Cu(II) modified  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  in presented synthesis conditions led to form surface Cu(II) paramagnetic centers in different environment and as result with different degree of linking with zirconia surface. In case formation  $\text{ZrO}_2\text{-Y}_2\text{O}_3/\text{OMC}$ -shell only one kind of Cu(II) paramagnetic is formed and oligoperoxide shell additional contains the functional peroxide groups as centers of active oxygen forms. The proximity of the values of the g-factors of Cu(II) centers for both kinds of formed structures indicates on approximately equal environment of Cu(II) centers that is linked with zirconia surface.

Using of different synthesis routes may be effective key to controlling of the surface state of composite nanoparticles and kind of their active surface centers. These structures are proposed as active material with antibacterial and catalytic properties in systems of air purification.

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#### Reference

- [1] Ratnasamy P, Srinivas D, Satyanarayana C V V, Manikandan P, Senthil K R S, Sachin M, Vasudev N and Shetti 2004 *J. Cat.* **221** 455-65
- [2] Gawande M B, Goswami A, Asefa T, Guo H Z, Biradar A V, Peng D L, Zboril R and Varma R S. 2015 *Chem. Soc. Rev.* **44** 7540-90
- [3] Shokufeh A 2015 *Res. J. Chem. Environ.* **19**(8) 28-32
- [4] Bondarenko O, Juganson K, Ivask A, Kasemets K, Mortimer M and Kahru A 2013 *Arch. Toxicol.* **87**(7) 1181-200
- [5] Dhanalekshmi K I and Meena K S 2014 *Spectrochimica Acta: Part A. Molecular and biomolecular spectroscopy* **128** 887-90
- [6] Samzadeh-Kermani A, Mirzaee M and Ghaffari-Moghaddam M 2016 *Adv. Biol. Chem.* **6** 1-11
- [7] Levitin E Y, Kryskiv O S and Scoryk M 2015 *Scripta Scientifica Pharmaceutica* **2**(1) 53-9
- [8] Palza H, Quijada R and Delgado K 2015 *J. Bioactive Comp. Polym.* **1** 1-15
- [9] Actis L, Gaviria L, Guda T and Ong J L 2013 *J. Korean Assoc. Oral Maxillofac. Surg.* **39** 43-54
- [10] Samson K, *et al.* 2014 *ACS Catal* **4**(10) 3730-41
- [11] Liu X, Bai S, Zhuang H and Yan Z 2012 *Frontiers of Chem. Sci. and Eng.* **6** 47-52
- [12] Pakharukova V, Moroz E M, Zyuzin D A, Dolgikh L Yu and Strizhak P E 2015 *J. Phys Chem C* **119** 28828-35
- [13] Basahel S N, Mokhtar M, Alsharaeh E H, Ali T T, Mahmoud H A and Narasimharao K 2016 *Catalysts* **6** 57
- [14] Wang G, Ji J, Zhang X, Zhang Y, Wang Q, You X and Xu X 2014 *Sci. Rep.* **4** 5480
- [15] Chen C, Ruan C, Zhan Y, Lin X, Zheng Q and Wei K 2014 *Int. J. Hydrogen Energy* **39** 317-24
- [16] Zaichenko A, Mitina N, Kovbuz M, Artym I and Voronov S 2000 *J. Polym. Sci., Part A: Polym. Chem.* **38** 516-27
- [17] Anufrienko V F, Zenkovec G A, Schutilov R A, Gavrilov V Yu, Vasenin N T, Schublin A A, Ismagilov Z R and Parmon V N 2011 *Phys. Chem.* **440**(5) 651-4
- [18] Davudov A A and Anufrienko B F 1984 *IR Spectroscopy in Oxide Surface Chemistry* (Novosibirsk: Nauka)
- [19] Gorban O, Gorban S, Zarechnaya O, Kharchenko M and Konstantinova T 2016 *Nanophysics*,

*Nanophotonics, Surface Studies and Applications* (Cham: Springer International Publishing AG) pp 543-9