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Synthesis and characterization of zirconium oxides for use as antimicrobial additives in paints

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Abstract

Zirconia is a widely used multifunctional material. Its interesting properties, such as high chemical resistance, thermal stability and high mechanical toughness, have turned this material into object of study within fields such as optics, electronics, and magnetism, among others. In recent years, the chemical properties of zirconium oxide have been used, mixed with silicon, in order to obtain more stable and robust mixed oxides, with the final application of toughening ceramics. These properties are related to the degree of mixing of the components at molecular level, therefore, the linking between Si-O-Zr. Considering the effective antimicrobial capacity of silver nanoparticles, their incorporation into different materials is very interesting, acting as biocides. The objective of this work is to obtain zirconium oxides by the sol-gel technique, using zirconium n-propoxide as precursor, and also to study the effect of different solvents (water, ethanol) and the use of various acid catalysts in the synthesis [acetic acid and a heteropolyacid (HPA), as the phosphomolybdic acid ($H_3PMo_{12}O_{40}$)] on the physicochemical properties of the obtained solids. Finally, the addition of a silver salt was carried out into the sample with acetic acid and heteropolyacid as catalyst, in order to incorporate it as antimicrobial filler in paints. The obtained materials were characterized by SEM, XRD, FT-IR, textural properties through the absorption of N_2 (S_{BET}) and potentiometric titration with n-butylamine. Homogeneous solids were obtained in all the synthesis with acetic acid as catalysts. In addition, x-ray diffraction diagrams of amorphous solids were observed. The values obtained of surface areas are influenced by the variables of synthesis. The characteristic bands of zirconia were observed by FTIR in the solids synthesized. The results show that the solids environmentally synthesized are promising additives for use in paints.

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1. Introduction

Green Chemistry should aim to make new chemical processes, or at least turn the already existing ones into a more environmental friendly manner. In this way, the need for a development of clean technologies arises. A sustainable development is obtained through new technologies that provide societies with those products needed using responsible criteria towards the environment (McDonough et al., 2003; Bellotti et al., 2013).

The synthesis of zirconium oxides has been studied in recent decades. Among methods for obtaining this material may be mentioned precipitation (Hu et al., 1998), thermal decomposition (Inaba et al., 1997) and hydrothermal treatment and sol-gel (Kim et al., 2003; Zhao et al., 2000). The latter is considered one of the most promising methods for obtaining materials with high purity and stable paths, through which the chemical and physical properties of the material can be modified varying the synthesis parameters. Due to the interesting properties of the zirconia, such as hardness, chemical stability, mechanical strength and ionic conductivity, among others, it has been studied in the field of optics, electronics, magnetism and biomedicine (Delgado et al., 2003). In ZrO₂ nanoparticles there has been found important abrasive applications, oxygen sensors, implants, catalysts and catalyst supports. Among the various precursors used for the synthesis of zirconium oxide can be named: *n*-propoxide of zirconium (Zr(C₃H₇O)₄), zirconium tetrachloride (ZrCl₄), and hydrated zirconium oxychloride (ZrOCl₂ · xH₂O). We decided to use zirconium *n*-propoxide as a precursor due to its high reactivity to water and for being representative of the metal alkoxides.

Moreover, hygienic paints can be formulated both for easily cleanable surfaces and for the incorporation of active elements capable of preventing bio-contamination (Johns, 2003). The antimicrobial power of Ag nanoparticles makes them attractive to be incorporated in various materials, such as paints (Zielecka et al., 2011). In this paper was carried out the preparation and characterization of various solids from a zirconia precursor at room temperature, using different acid catalysts for the synthesis and evaluating the effect it has on the final solids adding salt silver, for future use as filler in the composition of paints with antimicrobial purposes.

2. Experimental procedure

2.1. Sol-Gel synthesis of samples

The sol-gel method was used to synthesize the solids based on zirconia, under nitrogen atmosphere. The *n*-propoxide of zirconium (Zr(C₃H₇O)₄), was used as precursor zirconia. In order to obtain different structures of gels, acetic acid (99.99%) (AcH), chlorhydric acid (99.99%) (HCl), and molybdophosphoric acid (H₃[P(Mo₃O₁₀)₄].xH₂O) (HPA), were used as catalyst whereas absolute ethanol (CH₂CH₃OH, 99.9%) (EtOH), and distilled water were used as solvents in all the synthesis.

Six samples were synthesized. In the sample Z-Aa, wherein water was added, the hydrolysis ratio (R_h) was 3.7. In a beaker, a portion of the solvent and the corresponding catalyst were placed, the precursor was then incorporated and, preceded to the addition of the remaining amount of ethanol. In the sample Z-AAg was added silver salt with AcH as catalyst and in other sample (Z-HAg), Ag was added in quantity required to occupy half of the acid sites of HPA (H_{1.5}Ag_{1.5}). Subsequently, continuous stirring was performed for 2 h, for all samples. Finally, wet gel particles were dried at room temperature and atmospheric pressure until complete solidification.

Table 1 shows the molar concentration of zirconium propoxide (mol Zr(C₃H₇O)₄/liter of final solution), the mass obtained of dry solid in grams, the catalyst used in each synthesis and, finally the resulting values of the characterization by potentiometric titration and textural properties of the samples were presented.

2.2. Characterization of the synthesized samples

The evaluation of acidic properties of the solids was achieved by potentiometric titration with *n*-butylamine, carried out in a Metrohm 794 Basic Titrino titrator (made in Switzerland), with a double junction electrode. The

amount of 0.025 ml/min of *n*-butylamine in acetonitrile (0.025 N) was added to 0.025 g of sample, previously suspended in acetonitrile (45 ml), and stirred for 3 h. The textural properties of the samples as the specific surface area (S_{BET}), were determined in Micromeritics Accusorb 2100 equipment (USA), using N_2 as absorbable gas. The X-Ray Diffraction (XRD) patterns were obtained in Philips (Holland) PW-1390 (channel control), and PW-1394 (motor control) equipment coupled to a scanning graphical recorder, using $\text{Cu K } \alpha$ ($\alpha=1.5417 \text{ \AA}$) radiation, Ni filter, 20 mA and 40 kV in the voltage source, a 5-60 2θ scanning angle range, a scanning rate of $2^\circ/\text{min}$ and 2000 counts/sec for the amplitude of the vertical scale. Scanning Electron Microscopy (SEM) was achieved to obtain different micrographs of the solids, in Philips 505 equipment (Holland), using a voltage of 15 kV; samples were supported on graphite and metalized with a sputtered gold film. The micrographs were obtained with an ADDAI acquisition device (Soft Imaging System). FT-IR spectra were obtained using Bruker IFS 66 equipment and pellets of the sample in KBr, measuring in a range between 400 and 4000 cm^{-1} .

Table 1. Chemical composition and structural characteristics of the synthesized samples.

Sample	[Zr] M	Obtained weight (g)	Catalyst	E_{initial} (mV)	S_{BET} (m^2/g)
Z-A	1.21	9.9	AcH	-56.4	21.9
Z-Aa	1.12	9.8	AcH	-58.2	11.2
Z-A _{0.5}	0.85	6.1	AcH	-45.9	2.1
Z-AAg	1.21	10.0	AcH	-179.2	201.0
Z-H	1.31	8.2	HPA	19.2	50.3
Z-HAg	1.31	8.8	HPA	-126.4	203.6

3. Results and Discussion

In Fig. 1 digital photographs of the dry solids synthesized are observed. Translucent crystals were obtained with yellowish hue when acetic acid was used. In the sample Z-Aa, the addition of water resulted in an instant hydrolysis of the precursor in the reaction mixture, yielding an opaque solid (Fig. 1b). When the HPA was used as heterogeneous catalyst systems, the presence of different solid phases (Figs. 1e and 1f) were visualized. The weight of dry solid obtained (Table 1) are similar in all synthesis, regardless of the catalyst employed. But it is noted that the grams depends on the amount of precursor used because when the volume of zirconium propoxide used is reduced, the solid obtained decreases in the same amount (see Table 1).

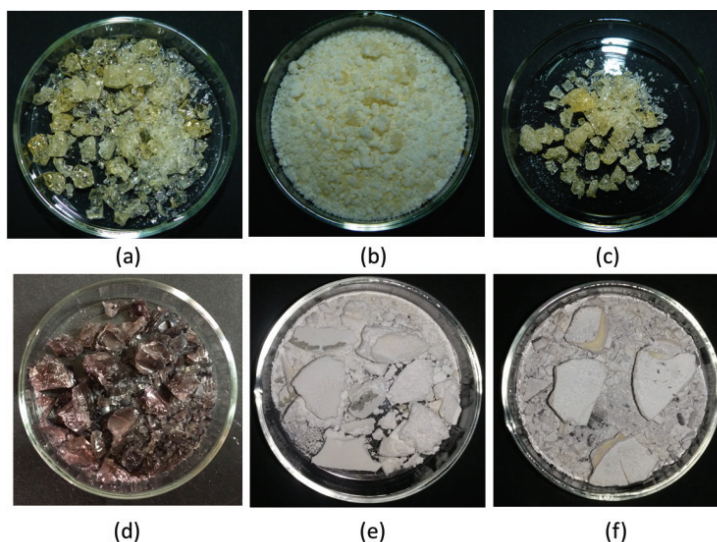


Fig. 1. Digital photos of the synthesized samples, (a) Z-A, (b) Z-Aa, (c) Z-A_{0.5}, (d) Z-AAg, (e) Z-H and (d) Z-HAg

The potentiometric titration with *n*-butylamine was used to determine the acid properties of a dispersion of solid particles by measuring of the electrode potential difference (*E*). Furthermore, interpreting the results, it is known that the potential initial electrode (E_i) indicates the maximum acidic force of surface sites, and values (meq/g solid), wherein the plateau is reached, indicates the total number of acid sites. The acid strength of surface sites can be classified according to the following ranges: very strong sites, $E_i > 100$ mV, strong sites, $0 < E_i < 100$ mV; weak sites $-100 < E_i < 0$ mV, and very weak sites, $E_i < -100$ mV. Acid values of the samples (E_i) are shown in Table 1, and in Fig. 2a can be seen the potentiometric curves obtained for the samples synthesized without the addition of silver. E_i values of Z-A, Z-Aa, and Z-A_{0.5}, indicating the presence of weak acid sites on these solids, whereas those where HPA was used, the strong acid sites are present, possibly due to the superacid properties of the catalyst used as is shown in Fig. 2b ($E_i=800$ mV). Regarding the presence of silver, preliminary results indicate a reduction of Ag^+ cation and potentiometric curves yield values less than -120 mV.

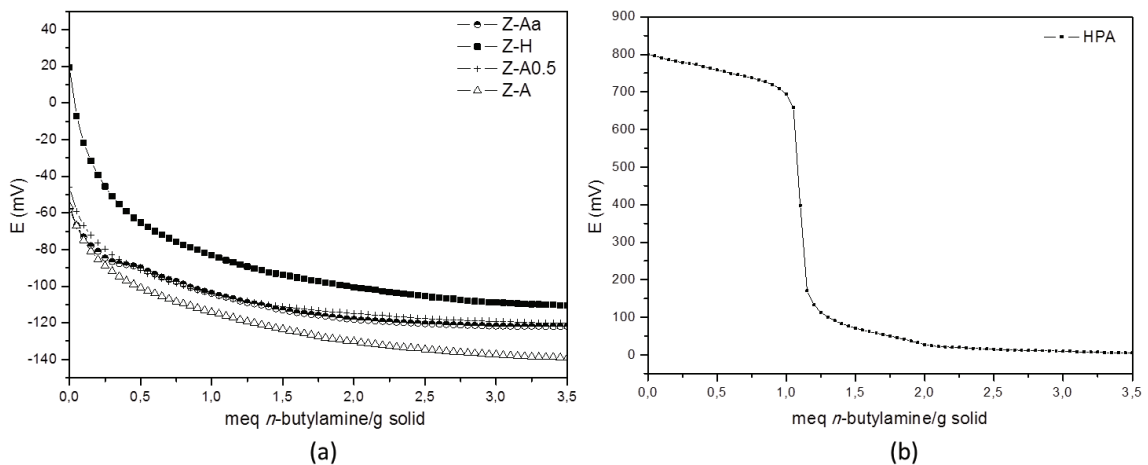


Fig. 2. Potentiometric curves of the synthesized samples.

When analyzing the micrographs obtained by SEM, it should be noted that no appreciated differences were found between samples synthesized with and without water (Figs. 3a and 3b). But there is a difference between the samples synthesized with acetic acid as catalyst and those with HPA. In samples where HPA was used as catalyst (Figs. 3c y 3d) agglomerations were obtained independently of the presence of the silver salt, and this is not observed in the other samples. In all cases, a heterogeneous distribution of particles sizes was observed, with sizes between 1 μ m to 80 μ m.

Then the Infrared spectra of Fourier transform (FT-IR) of the synthesized samples are presented (Figs. 5 and 6). The FT-IR spectrum of Fig. 5 allows to observe the broad band around 3400 cm^{-1} assigned to the symmetric stretching of OH bonds corresponding to physically adsorbed water on the solid; and the signal at 1550 cm^{-1} is attributed to bending OH vibrations of water molecules in the solid retained by hydrogen bonds.

When we analyze the spectra at lower values of wavenumbers, between 1250 and 400 cm^{-1} (Fig. 6), a clear difference between the bands yielded for the samples synthesized with AcH and HPA was observed. In samples with acetic acid appear bands characteristic of zirconia, located at 1050, 1030, 956, 650, 620 and 463 cm^{-1} (Agoudjil et al., 2008; Chavez Granados, 2005). The band around 1030 cm^{-1} indicates the bending vibration of OH end groups of the chemical bond O-Zr-OH in the material structure. On the other hand, broad band at 463 cm^{-1} is produced by bending vibration of the O-Zr-O.

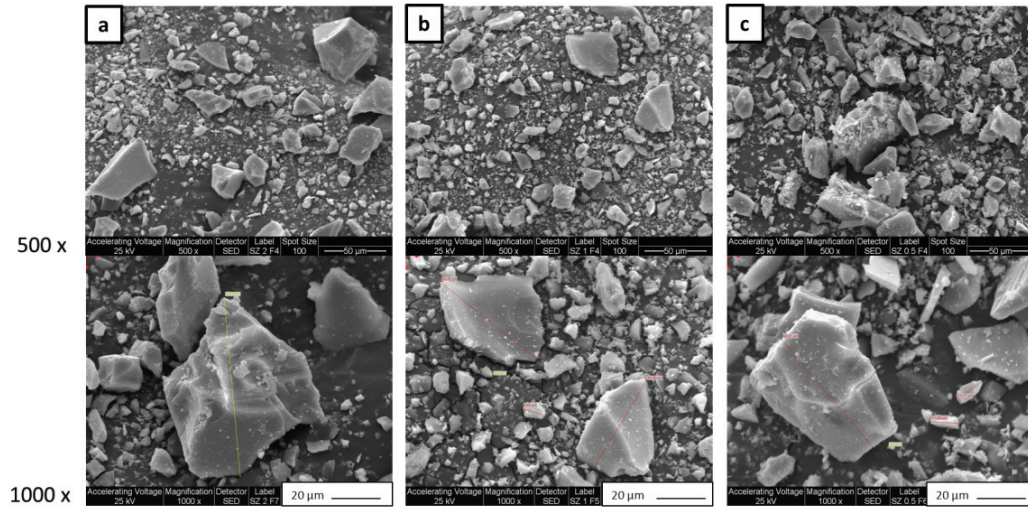


Fig. 3. SEM micrographs of the samples, (a) Z-A, (b) Z-Aa and (c) Z-A_{0.5} with different magnifications.

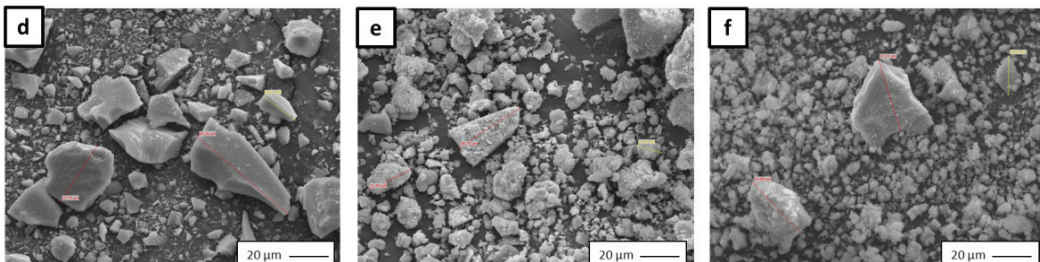


Fig. 4. SEM micrographs of the samples, (d) Z-AAg, (e) Z-H and (f) Z-HAg at magnification 500 x.

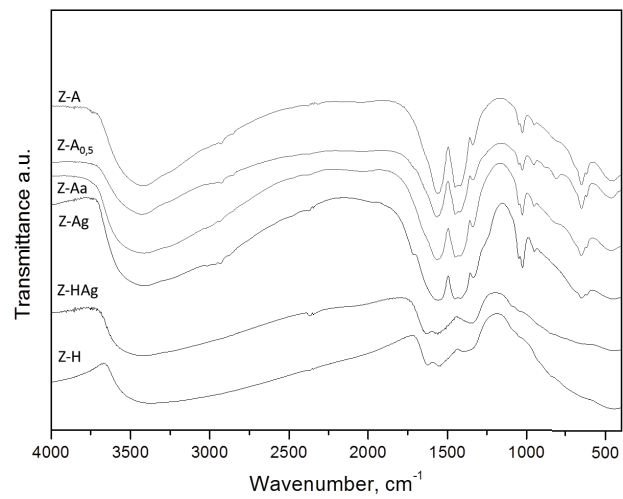


Fig. 5. FT-IR spectrum of the solids between 4000 and 400 cm⁻¹.

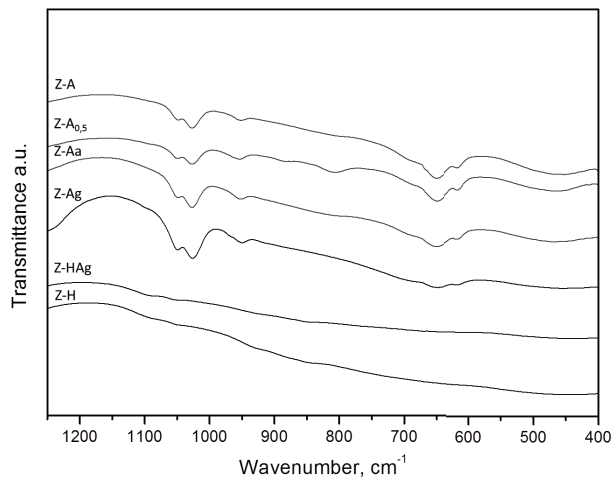


Fig. 6. FT-IR spectrum of the solids at low values of wavenumbers.

In general, the solids presented very low specific areas, calculated by the BET method (See Table 1). The sample with the smallest area was the one with the lowest concentration of zirconium, whose value is within the experimental error of the technique. When the synthesis is performed with HPA, an increase in the area is observed ($\sim 50 \text{ m}^2/\text{g}$). This growth is even greater when the silver salt is added into the synthesis ($\sim 204 \text{ m}^2/\text{g}$), in both cases, probably due to steric effects of the molecule of HPA and HPA-Ag, respectively. Due to increased radius of the compound included, the intra-molecular spaces are larger. For example, the adsorption isotherms obtained for Z-H, Z-HAg and Z-AAg (Figs. 7a and 7b) samples are presented. In these samples, N_2 adsorption isotherms are detected as Type I, corresponding to the classification proposed by Brunauer et al. (1940), characteristics of microporous solids.

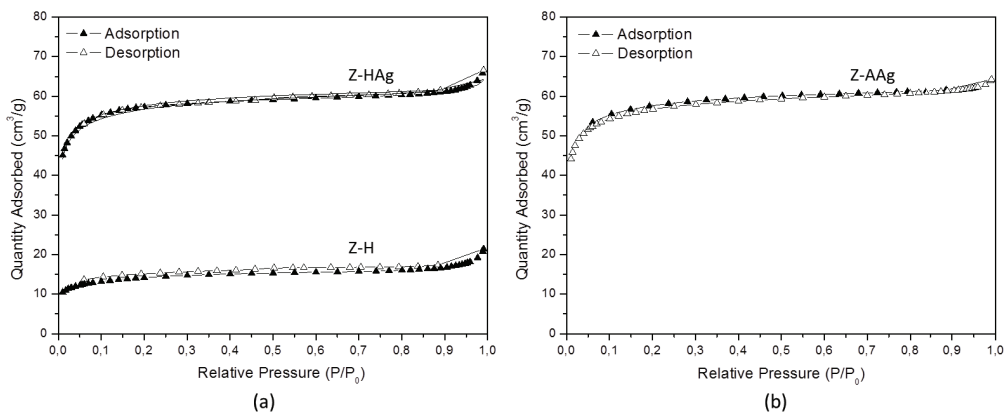


Fig. 7. N_2 adsorption-desorption isotherm of (a) Z-H and Z-HAg samples, (b) Z-AAg sample.

The X-ray diffraction (DRX) diagrams of the solid preparations (Fig. 8) were obtained. In all cases, were observed diffraction patterns with similar characteristics, showing a broad band around $30^\circ 2\theta$, indicating the presence of the amorphous state of the zirconium dioxide (Aguilar et al., 2000). When samples are synthesized with the heteropolyacid catalyst the diffraction patterns obtained have a characteristic distortion band of ZrO_2 .

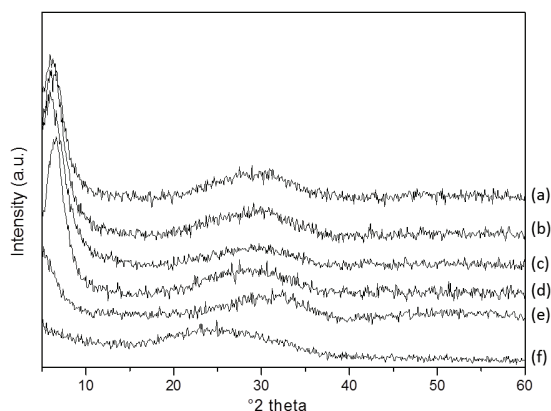


Fig. 8. X-ray diffraction diagrams of the samples, (a) Z-A, (b) Z-Aa, (c) Z-AAg, (d) Z-A_{0.5}, (e) Z-HAg and (f) Z-H.

4. Conclusions

In this work zirconia based solids were prepared by the sol-gel method at room temperature, which consists of a series of reactions of hydrolysis and condensation, modifying the reaction conditions by employing acid catalysts on different synthesis method. This variable was observed that affects the properties of the final material obtained, resulting translucent and homogeneous solid when acetic acid is used and opaque when HPA is used. Amorphous solids were obtained in all cases. The results show that the solids ecologically synthesized are promising for use in paints additives, but will seek to optimize the synthesis to achieve homogeneous materials against all proposals compositions.

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5. References

- Agoudjil, N., Kermadi, S., Larbot, A., 2008. Synthesis of inorganic membrane by sol-gel process. *Desalination* 223, 417-424.
- Aguilar, D. H., Torres-Gonzalez, L. C., Torres-Martinez, L. M., 2000. A Study of the Crystallization of ZrO₂ in the Sol-Gel System: ZrO₂-SiO₂. *Journal of Solid State Chemistry* 158, 349-357.
- Bellotti, N., Salvatore, L., Deyá, C., Del Panno, M. T., del Amo, B., Romagnoli, R., 2013. The application of bioactive compounds from the food industry to control mold growth in indoor waterborne coatings. *Colloids and Surface B: Biointerfaces* 104, 140-144.
- Brunauer, S., Deming, L. S., Deming, W. E., Teller, E., 1940. On a theory of the van der Waals adsorption of gases. *Journal of the American Chemical Society* 62, 1723-1732.
- Chávez Granados, M., 2005. Tesis de Maestría: Métodos de síntesis de óxido de circonio. UAM, México, 2005.
- Delgado García-Menocal, J. A., Morejón, L., Martínez, S., Gil, F. J., 2003. Cerámicas de zircona para aplicaciones biomédicas. *Biomecánica* 11, 46-52.
- Hu, M. Z. C., Harris, M. T., Byers, C. H., 1998. Nucleation and growth for synthesis of nanometric zirconia particles by forced hydrolysis. *Journal of Colloid and Interface Science* 198, 87-89.
- Inaba, M., Mineshige, A., Maeda, T., Nakanishi, S., Ioroi, T., Takahashi, T., Tasaka, A., Kikuchi, K., Ogumi, Z., 1997. Growth rate of yttria-stabilized zirconia thin films formed by electrochemical vapour-deposition using NiO as an oxygen source: II. Effect of the porosity of NiO substrate. *Solid State Ionics* 104, 303-310.
- Johns, K., 2003. Hygienic coatings: The next generation. *Surface Coatings International Part. B: Coatings Transactions* 86, 101-110.
- Kim, K. D., Kim, H. T., 2003. Comparison of the effect of reaction parameters on particle size in the formation of SiO₂, TiO₂, and ZrO₂ nanoparticles. *Materials Letters* 57, 3211-3216.
- Mc Donough, W., Braungart, M., Anastas, P. T., Zimmerman, J. B., 2003. Peer reviewed: Applying the Principles of Green Engineering to cradle-to-cradle design. *Environmental Science & Technology* 37, 434A-441A.

- Zhao, J., Fan, W., Wu, D., Sun, Y., 2000. Synthesis of highly stabilized zirconia sols from zirconium n-propoxide–diglycol system. *Journal of Non-Crystalline Solids* 261, 15-20.
- Zielecka, M., Bujnowska, E., Kepska, B., Wenda, M., Piotrowska, M., 2011. Antimicrobial additives for architectural paints and impregnates. *Progress in Organic Coatings* 72, 193-201.