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Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

PROTECTIVE TiO_2 COATINGS PREPARED BY SOL-GEL METHOD ON ZINC

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ABSTRACT. The objective of this work was to develop new TiO_2 based coatings for producing an effective barrier as well as an appropriate support for inhibitors in corrosion protection of zinc. For this purpose, compact and mesoporous titania coatings on zinc substrates were prepared by sol-gel method (dip coating). For preparing mesoporous layers, cationic (cetyltrimethylammonium bromide, CTAB) or non-ionic (Pluronic PE 10300) surfactant templates were applied. The corrosion behaviour of the coatings was evaluated by open circuit potential measurements and Tafel interpretation of the polarization curves. The best corrosion resistance was noticed in the case of TiO_2 coated samples prepared in the presence of Pluronic surfactant.

Keywords: *zinc; TiO_2, sol-gel method, dip- coating, corrosion*

INTRODUCTION

The development of new effective anticorrosion pre-treatments for zinc substrates is an issue of great importance for corrosion technology due to the fact that hexavalent chromium conversion coatings are nowadays banished and efforts are made to replace them with other effective, but less toxic protective coatings [1].

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Oxide coatings such as TiO_2 and SiO_2 act very efficiently as corrosion protectors of metals under different temperatures being environmentally - friendly and exhibiting excellent barrier properties as anticorrosive layers [2].

There are several techniques for the deposition of ceramic films and coatings on metal substrates, such as chemical / physical vapour deposition [3], plasma electrolytic oxidation [4], electrolytic deposition [5] and sol–gel process [1].

The sol-gel method is an environmentally friendly technique of surface protection resulting in high corrosion inhibition efficiency that can be used to prepare non-toxic conversion coatings on metals [6]. It involves conversion of small molecules (precursors) into a colloidal solution (sol) and then into an integrated network (gel) consisting of discrete particles and/or inorganic polymers [7].

TiO_2 can be prepared, for example, starting from precursor sols containing alkoxides (*e.g.*, tetrabutylorthotitanate) and diethanolamine dissolved in ethanol [8] and mixing them with water (with or without additives) in a certain ratio.

SiO_2 coatings can be prepared starting from a precursor solution consisting of tetraethylorthosilicate ($Si(OC_2H_5)_4$), H_2O, C_2H_5OH, and HCl, mixed at a certain molar ratio [9]. Different compounds (inhibitors, pigments, etc.) can be added in order to improve the physico-chemical properties of the coating.

Irrespective of the nature of the film, the two main techniques used to apply a sol-gel coating on the surface of a metallic substrate are dip-coating (the substrate is progressively dipped into and is extracted from the sol at a controlled rate) and spin-coating (an amount of sol is placed on the substrate that is rotated at high speed in order to spread the fluid by centrifugal force). In both cases, after the evaporation of the solvent, a thin, homogeneous film is formed on the metallic surface.

Continuing our previous researches in this field [10,11], the objective of this work was the development of new titania based coatings designed to produce an effective barrier as well as an appropriate support for inhibitors in corrosion protection of zinc. For this purpose, compact and mesoporous titania coatings on zinc samples were prepared by dip-coating. For preparing mesoporous layers, cationic (cetyltrimethylammonium bromide, CTAB) or non-ionic (Pluronic PE 10300) surfactant templates were applied. The corrosion behaviour of the coatings was evaluated by open circuit potential measurements and Tafel interpretation of the polarization curves and their performances were compared to those of previously reported SiO_2 coatings [11].

RESULTS AND DISCUSSION

The various types of TiO_2 layers on Zn substrates were obtained by dip-coating method from different precursor sols. The correlations of the coatings with their symbols are presented in Table 1.

Table 1. Summary of sample preparation, the used symbols (P: Pluronic PE 10300; CTAB: cetyltrimethylammonium bromide)

Symbol	*Number of layers*	*Layer thickness* [nm]*	*Type of sample/ templating agent*
TiO_2_K2	2	134 ±4	Compact TiO_2
TiO_2_K5	5	~330	
TiO_2_C1	1	104 ±4	Porous TiO_2/ CTAB
TiO_2_C4	4	~410	
TiO_2_P1	1	134 ±8	Porous TiO_2/ Pluronic
TiO_2_P3	3	~400	

- values estimated from UV-VIS spectra as shown below

Some mono- and multilayered coatings were also deposited on glass substrates for their optical characterization. Figure 1 shows the representative transmittance curves of the double-layered compact TiO_2 coating, the monolayered CTAB and Pluronic PE 10300 templated porous TiO_2 coatings, and their bare glass substrate.

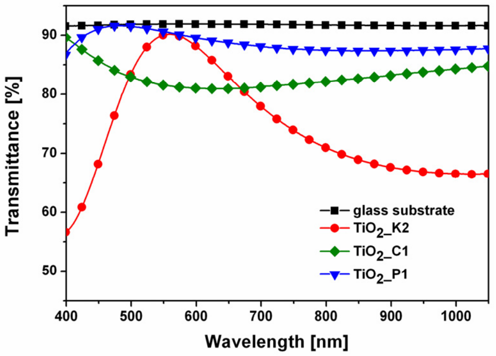


Figure 1. Transmittance spectra of the uncoated glass substrate, of the double-layered TiO_2 (TiO_2_K2), and monolayered CTAB (TiO_2_C1) and Pluronic (TiO_2_P1) templated porous TiO_2 coated samples.

All types of titania coated glass slides show lower transmittance values than their uncoated glass substrates (Figure 1). It can be observed that the Pluronic PE 10300 templated porous coating shows higher transparency then the titania coating prepared without using surfactant additive, in the whole studied wavelength range (Figure 1).

The obtained transmittance curves were analysed in terms of thin layer optical models. Transmittance spectra were fitted with a homogeneous layer model [12] supposing identical homogeneous coatings on both sides of the transparent substrate and perpendicular angle of incidence. The fitting procedures provided coating thickness and effective refractive index values. As the glass substrate had weak absorption, the transmittance spectra were corrected before fitting to eliminate this effect [12-13]. The fitting procedure used a Levenberg–Marquardt algorithm [14]. Porosity of coatings was estimated using the Lorentz-Lorenz formula [15-17]:

$$\frac{n_{eff}^2-1}{n_{eff}^2+2}=\alpha_1\frac{n_1^2-1}{n_1^2+2}+(1-\alpha_1)\frac{n_2^2-1}{n_2^2+2}$$

where the meaning of the used symbols are:

n_{eff}^2- effective refractive index of the layer

n_1-refractive index of anatase TiO_2 (estimated as 2.520, [18]

n_2-refractive index of the air (estimated as 1.00)

α_1-volume fraction of the TiO_2 component

The results of the fitting procedure and the calculated porosity values are presented in Table 2.

Table 2. Fitted effective refractive indices, layer thicknesses, and the calculated porosity values of the double-layered TiO_2 (TiO_2_K2), and monolayered CTAB (TiO_2_C1) and Pluronic (TiO_2_P1) templated porous TiO_2 coatings on glass estimated from UV-VIS spectra

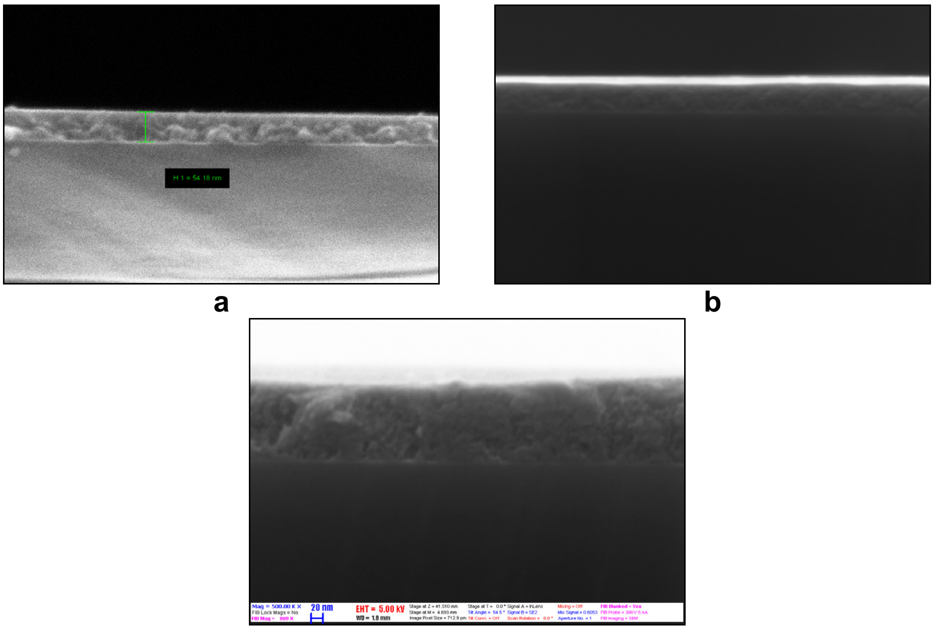
Sample	***Layer thickness [nm]***	***Effective refractive index***	***Porosity [%] (Lorentz-Lorenz)***
TiO_2_K2	134 ± 5	1.945 ± 0.016	25±0.9
TiO_2_C1	104 ± 4	1.662 ± 0.009	42±0.6
TiO_2_P1	134 ± 8	1.590 ± 0.004	47±0.3

It can be observed that the thickness of monolayered porous coatings with Pluronic is about the same like that of the double-layered compact ones prepared on the same way, from a precursor sol without surfactant additive. On the other hand, Pluronic templated coatings porosity is slightly higher than that obtained with CTAB. It is worth mentioning that TiO_2 coatings prepared without surfactant additive (the so-called “compact” layers) show also a considerable porosity (25%) that was further increased by 17% and 22% by using surfactant in the case of CTAB and Pluronic templated porous TiO_2 coatings, respectively.

The titania coated silicon wafers were studied with Field Emission Scanning Electron Microscopy (FESEM) and cross-sectional images were made in order to determine the thickness of the layers (Figure 2). For compact coatings the monolayer thickness was found to be 54 nm. The same parameter for the CTAB templated coating was found to be 94 nm and for the Pluronic templated one 144 nm. These thickness values are in good agreement with those calculated for the layers obtained on the microscope glass slides from UV-VIS spectra. According to our experience the structure of sol-gel coatings doesn't depend on the type of solid substrate (glass, silicon, zinc etc.).

Electrochemical investigations were started with the determination of the open circuit potential (OCP), and were continued with recording of polarization curves in an interval of ± 20 mV vs. OCP (linear polarization) in order to estimate the polarization resistance (R_p). These values are presented in Table 3.

From these values it can be concluded that porous multilayers have the best protection capabilities caused on the one hand by their greater thickness and on the other hand by the better wetting properties of precursor liquid of templating agents.



a

b

c

Figure 2. The FESEM images of the compact (a), CTAB templated (b) and Pluronic templated (c) TiO_2 layers on silicon substrate.

The OCP values of these samples were found to be slightly more positive compared to the reference Zn wafer (without coating) suggesting a possible better corrosion protection.

Table 3. The open circuit potential (OCP) and polarization resistance (R_p) for the TiO_2 layers deposited on Zn

Sample	***R_p*** **[Ωcm^2]**	***OCP*** **[*V vs. Ag/AgCl*/KCl_{sat}]**	***R/N***
Zn	98.5	-0.994	0.9991/ 28
TiO_2_K2	93.1	-1.013	0.9985/28
TiO_2_K5	208	-1.001	0.9980/38
TiO_2_C1	469	-0.948	0.9990/36
TiO_2_C4	352	-0.979	0.9940/74
TiO_2_P1	384	-0.974	0.9990/37
TiO_2_P3	448	-0.968	0.9990/40

Polarization curves were also recorded in the potential range ± 200 mV vs. OCP and are presented in Figure 3 for the compact coatings. The curves for the porous layers are presented in Figure 4.

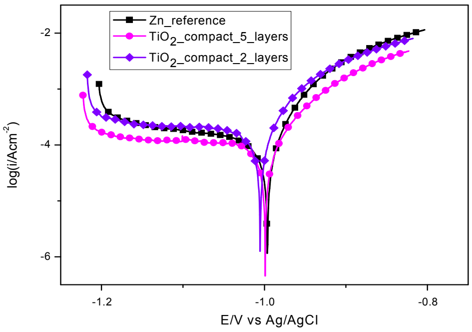


Figure 3. Polarization curves for the compact TiO_2 multilayered coatings on zinc

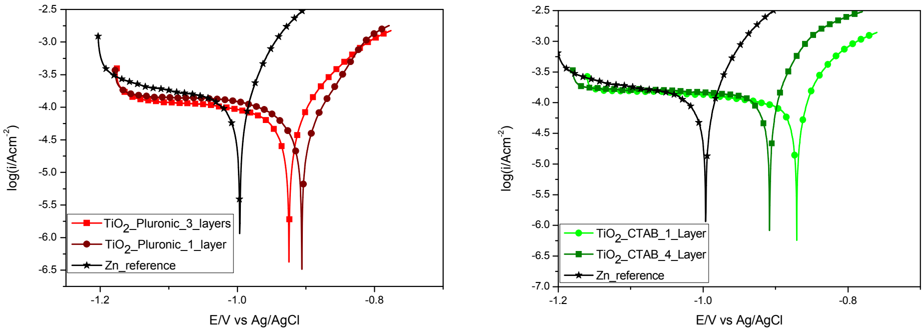


Figure 4. Polarization curves for the porous TiO_2 multilayered coatings on zinc templated with Pluronic (left) and CTAB (right).

The Tafel interpretation was used in order to extract the characteristic corrosion parameters (E_{corr}, i_{corr}, Tafel slopes b_a and b_c, presented in Table 4).

From the corrosion current densities one can conclude, that compact and CTAB templated coatings practically do not modify the corrosion behaviour of the Zn substrate, presumably due to the permeability of coatings. FESEM images revealed previously a granular structure of compact titania coatings [19, 20]. It was also observed that the CTAB template cannot modify the morphology of compact layers significantly [21]. Better results were obtained, however, for porous coatings templated with Pluronic (a triblock copolymer in which the central polypropylene glycol group is flanked by two polyethylene glycol groups); in this case the decrease of the corrosion current density was considerable, possibly due to the improved coating ability of precursor sols containing this surfactant and to the higher thickness of the layer. The lower permeability of Pluronic templated coatings may also be interpreted in terms of the irregular shaped pores in the coating. Using CTAB, the formation of cylindrical shaped pores is expected having a better permeability.

Table 4. The corrosion kinetics characteristic parameters for the TiO_2 coated Zn (E_{corr}-corrosion potential, i_{corr}-corrosion current density, b_c and b_a- cathodic and anodic Tafel slopes)

Sample	E_{corr} (V)	i_{corr} (μA/cm^2)	$-b_c$ (mV/dec)	b_a (mV/dec)
Zn	-0.996	12.15±3.9	36	20
TiO_2_K2	-1.005	16.36±2.3	23	37
TiO_2_K5	-0.999	12.62±0.6	14	11
TiO_2_C1	-0.870	13.63±1.0	16	10
TiO_2_C4	-0.860	15.45±1.2	12	11
TiO_2_P1	-0.906	8.08±0.47	10	8
TiO_2_P3	-0.925	7.87±0.41	12	11

All TiO_2 coatings were less protective than SiO_2 coatings prepared in similar conditions [11] revealing the higher permeability of titania coatings in comparison to the silica ones. For example, i_{corr} in the case of compact SiO_2 coating of 2 layers was almost ten times smaller (1.819 μA/cm^2) than in the case of compact TiO_2 coating of 2 layers (16.36 μA/cm^2). Almost the same finding is noticed in the case of Pluronic templated coatings: porous SiO_2 coating of 1 layer (3.832 μA/cm^2) comparing to porous TiO_2 coating of 1 layer (8.08 μA/cm^2). When CTAB was used the corrosion current density is 2.76 μA/cm^2 and 13.63 μA/cm^2) for porous SiO_2 coating of 1 layer and for porous TiO_2 coating of 1 layer, respectively.

CONCLUSIONS

Among the investigated titania coatings only the Pluronic templated ones showed slight corrosion protection of Zn presumable due to the less-permeable structure and better coating ability of their precursor sols.

As expected, multi-layered coatings were found to be more efficient than single ones. However, the results are inferior to those obtained with SiO_2 coatings on zinc prepared in similar way and reported elsewhere [11].

EXPERIMENTAL

Materials

Titanium (IV) butoxide (TBuOTi, for synthesis, ≥ 98%, Merck), ethanol (EtOH, a.r., > 99.7%, Reanal), nitric acid (HNO_3,special grade, 65%, Lach-Ner), cetyltrimethylammonium bromide (CTAB, cationic surfactant, 99+%, Acros Organics), Pluronic PE 10300 triblock copolymer (non-ionic surfactant, BASF, Ludwigshafen Germany) and distilled water (H_2O, 18.2 MΩ cm, purified with a Millipore Simplicity 185 filtration system) were used as starting materials for precursor sol synthesis.

Distilled water (18.2 MΩ·cm, purified with a Millipore Simplicity 185 filtration system), hydrochloric acid (HCl, purum, 37%, Fluka) and 2-propanol (2-PrOH, a. r., > 99.7%, Reanal) were used for cleaning the surface of the solid substrates.

Zinc wafers (Zn, 76x26x0.65 mm, Bronzker Bt, Hungary), silicon (Si) wafers and microscope glass slides (76×26×1 mm, Thermo Scientific, Menzel-Gläser) were used as solid substrates of the coatings.

In order to obtain the titania coatings three types of precursor sols were prepared. Titania precursor sol of compact coatings was prepared via the acid catalyzed controlled hydrolysis of titanium (IV) butoxide in ethanolic media [19]. Nitric acid was used as catalyst during the synthesis of precursor sol. The molar ratios for TBuOTi:EtOH:HNO_3:H_2O were 1:27.95:0.49:0.82. For obtaining mesoporous titania coatings surfactant containing precursor sols were prepared by adding CTAB or Pluronic PE 10300 surfactant into the mixture of precursor sol. The molar ratios were 1:27.95:0.49:0.82:0.125 for TBuOTi : EtOH : HNO_3 :H_2O :CTAB, and 1 : 27.95 : 0.49 : 0.82 : 0.03 for TBuOTi : EtOH : HNO_3 : H_2O : Pluronic PE 10300. The obtained mixtures were stirred for 2 hours at 60 ^{0}C.

For electrochemical investigation 0.2 g/L Na_2SO_4 (Riedel–de Haën, Germany) solution (pH=5) was used.

Apparatus and methods

In some cases titania coatings were deposited onto glass substrates and the optical properties were investigated by UV-Vis spectrometry. An

Analytic Jena Specord 200-0318 type spectrophotometer was used for taking the transmittance spectra of the bare glass substrates and of the samples at normal incidence. All transmittance spectra were recorded in the range of 400-1050 nm with 1 nm resolution and scanning speed of 5 nm/s.

For the electrochemical investigations a computer controlled potentiostat AUTOLAB, PGSTAT302N (Eco Chemie BV, Utrecht, Netherland) was used. Data registration/interpretation was carried out by a GPES programme. For measurements a classical three-electrode-cell was used, including the Zn wafers (coated and uncoated) as working electrodes, the reference Ag/AgCl/KCl saturated electrode and the Pt wire counter electrode.

Coatings prepared onto silicon wafers were studied with Field Emission Scanning Electron Microscopy (FESEM) as well. Top view and cross-sectional images were taken using a LEO 1540 XB Field Emission Scanning Electron Microscope applying 5.00 keV acceleration voltage. Cross-sectional images were used for the determination of layer thicknesses.

Preparation of TiO_2 coatings

The layers were deposited on microscope glass slides, Zn and Si wafers. Prior to the layer deposition the substrates were preliminarily prepared; Zn wafers were polished with emery paper (grade 1200) and subsequently treated with 0.1 M HCl solution, rinsed with 2-PrOH and Millipore distilled water. The microscope glass slide and Si wafer was cleaned with 2-PrOH impregnated cotton than rinsed with 2-PrOH and distilled water. All the substrates were dried at room temperature.

The sol-gel films were deposited on the above mentioned solid substrates by the dip-coating method. The substrates subsequently their preliminary preparation were immersed in the precursor sols and pulled out with a constant 12 cm/min withdrawal speed. All the deposited films were kept in a drying oven and annealed at 410ºC (coated Zn wafers) and at 450ºC (coated glass substrates).

Multilayer coatings were obtained by the repeated immersion of the wafers in one of the precursor sols. The heat treatment was applied only after the last withdrawal from the precursor sol.

Electrochemical characterization

For the electrochemical characterization in each case the open circuit potential was registered during one hour reaching stabilization.. Subsequently the polarization curves were recorded and Tafel interpretation was made in order to obtain corrosion current density, corrosion potential and Tafel slopes.

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REFERENCES

1. D. Wang, G.P. Bierwagen, *Progress in Organic Coatings*, **2009**, *64*, 327.
2. S. Dalbin, G. Maurin, R.P. Nogueira, J. Persello, N. Pommier, *Surface and Coatings Technology* **2005**, *194*, 363.
3. D. Byun, Y. Jin, B. Kim, J. Kee Lee, D. Park, *Journal of Hazardous Materials*, **2000**, *73*, 199.
4. W. Simka, A. Krzakala, D.M. Korotin, Zhidkov I.S., Kurmaev E.Z., Cholakh S.O., Kuna K., Dercz G., Michalska J., Suchanek K., Gorewoda T., *Electrochim. Acta*, **2013**, *96,* 180.
5. P. Kern, P. Schwaller, J. Michler, *Thin Solid Films*, **2006**, *494*, 279.
6. L. Curkovic, H. Otmacic Curkovic, S. Salopekc, M. Majic Renjo, S. Šegota, *Corrosion Science*, **2013**, *77*, 176.
7. L.M. Muresan, Corrosion Protective Coatings for Ti and Ti Alloys Used for Biomedical Implants in "Intelligent Coatings for Corrosion Control", Eds. A. Tiwari, J. Rawlins, L.H. Hihara, Elsevier, ISBN 978-0-12-411467-8, **2014**, *Chapter 17*, 585
8. Tao FU, Xiao-Ming WU, Feng WU, Meng LUO, Bing-Hui DONG, Yuan JI, *Transactions of Nonferrous Metals Society of China*, **2012**, *22*, 1661.
9. Teng S, Liang W, Li Z, Ma X, *Journal of Alloys and Compounds*, **2008**, *464*, 452.
10. E. Albert, N. Cotolan, N. Nagy, G. Sáfrán, G. Szabó, L.M. Mureşan, Z. Hórvölgyi, *Microporous and Mesoporous Materials*, **2015**, *206*, 102.
11. E. Volentiru, M. Nyári, G. Szabó, Z. Hórvölgyi, L.M. Mureşan, *Periodica Polytechnica Chemical Engineering*, **2014**, *58*, 61.
12. E. Hild, A. Deák, L. Naszályi, Ö. Sepsi, N. Ábrahám, Z. Hórvölgyi, *Journal of Optics A: Pure and Applied Optics*, **2007**, *9*, 920.

13. D.S. Hinczewski, M. Hinczewski, F.Z. Tepehan, G.G. Tepehan, *Solar Energy Materials and Solar Cells*, **2005**, *87*, 181.
14. W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes in C, The Art of Scientific Computing*, Cambridge Univ. Press, New York, **1988**.
15. L.V. Lorenz, *Ann. Phys. Chem.* **1880**, *11*, 70.
16. H.A. Lorentz, *Theory of Electrons*, Teubner, Leipzig, Germany, **1916**.
17. D. Grigoriev, D. Gorin, G.B. Sukhorukov, A. Yashchenok, E. Maltseva, H. Möhwald, *Langmuir*, **2007**, *23,* 12388.
18. A.F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, **1984**.
19. C. Trapalis, N. Todorova, M. Anastasescu, C. Anastasescu, M. Stoica, M. Gartner, M. Zaharescu, T. Stoica, *Thin Solid Films*, **2009**, *517*, 6243.
20. Á. Detrich, E. Hild, N. Nagy, E. Volentiru, Z. Hórvölgyi, *Thin Solid Films*, **2012**, *520*, 2537.
21. E. Albert, P.A. Albouy, A. Ayral, P. Basa, G. Csík, N. Nagy, S. Roualdès, V. Rouessac, G. Sáfrán, Á. Suhajda, Z. Zolnai, Z. Hórvölgyi, *RSC Advances*, **2015**, *5*, 59070.