

Multifunctional advanced coatings based on ZnO/M obtained by nanocasting method

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Nanocoating has attracted a lot of attention as a simple and cost-effective method of enhancing coating properties by the addition of a small amount of properly designed and dispersed nanometer fillers. In this research, we applied a nanocasting route for synthesis of ZnO nanoparticles on the mesoporous silicate supports. In the first step, mesoporous silica (SBA-15 structure) was prepared using a soft template and in the second step, this material was used for impregnation of ZnO nanoparticles. The obtained nanocomposites were morphologically and structurally characterized by XRD diffraction, SEM, IR and AFM investigations. The new obtained material was investigated as an additive in two coating systems: acrylic and polyurethane. With the goal to see how the new material improves the film characteristics of the coatings, different amounts of ZnO/M composite were introduced by ultrasound shaking for 2 hours in the acrylic and polyurethane coating system. SEM and AFM were used to investigate dispersion of ZnO/M nanocomposite and the changes in the surface behavior of the modified coatings. The results showed an improvement of the optical and mechanical properties, UV resistance of the new coatings at lower concentration (0.1% by wt), indicating the positive effect of addition of ZnO/M nanocomposite in the coatings. These composites will be investigated as an additive for improve weathering resistance of the coatings.

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1. Introduction

In recent years, more and more investigators have focused on controlling the properties of ZnO particles. Few works have been concerned by the applications of nano-ZnO in coatings system with multi-properties. The nanocomposite system coatings can be obtained by the traditional coatings technology, i.e., by filling with nanomaterials. Both structure and function property of coatings can be modified by filling with nanomaterials.[1].

Nanocoating has attracted a lot of attention as a simple and cost-effective method of enhancing coating properties by the addition of a small amount of properly designed and dispersed nanometer fillers.

Addition of nanoparticles to coatings can upgrade many properties of coating system and can produce multipurpose coatings.

Until now, various techniques have been used for the preparation of zinc oxide particles. The most commonly used method, i.e., the chemical route [2,3], has difficulty in finding the proper chemical reactions and processing conditions and in controlling the shape of the particles [4,5].

The application of the nanocasting technique to the fabrication of inorganic compounds implies that the fabrication of these products takes place in the nanospaces provided by the pores of a porous solid (hard template). After the synthesis of the material, the template framework is selectively removed and the inorganic product is obtained.

In commercial use there are large requirements on the synthesis process. The process should be of low cost, easy to make small or large batches and effective and not a hazard to the environment or employees. SBA-15 is a product that is not very expensive and it is easy to change the batch size. The material has many applications such as catalysts, drug delivery system [6], as hard templates for nanocasting of oxide nanoparticles [7] and also as a template for making mesoporous replicas [8].

There are four main steps in the preparation of SBA-15. The first step is the synthesis of the mesoporous structure using a block copolymer, P123 and TEOS as silica precursor. The second step is the hydrothermal treatment at a higher temperature. Filtration and washing the samples are the third step and the fourth step is removing the polymer by calcinations.

For SBA-15 the triblock copolymer P123 is used as a the surfactant. The P123 forms spherical micelles in the solution. When the silica precursor is added, it hydrolyzes and bonds to the micelles forming a silica network that will be the walls in the particles. At this step the micelles becomes elongated from spheres to cylinders [9]. Between the cylindrical pores, there are micropores which connect the cylinders to each other.

Inorganic nanocrystalline metal oxides are particularly interesting because they can be prepared with extremely high surface areas. Nanoparticles have been shown to improve the mechanical properties even at low loadings and due to their small particle size, they do not affect the transparency of clear coats. Scratch resistance also improved further due to homogeneous distribution of nanoparticles in polymers. Even a small amount can retain

the appearance of surface without any negative impact on coating and its gloss.[10].

In this work, we investigate the formation of zinc oxide nanoparticles inside mesoporous silica (SBA-15) matrix. Zinc oxide has been known as a luminescent material for a century and today it is used for various applications.

2. Experimental

2.1 Materials

2.2.1 Preparation of nanocomposite

The ZnO/SBA-15 nanocomposite was prepared by incorporating zinc nitrate precursor into the channels of mesoporous silica SBA-15 and subsequent calcination. Parent mesoporous silica SBA-15 was synthesized according to the reported process [9,10,11].

A typical synthetic procedure was carried out as follows: 6 g of triblock copolymer Pluronic P123 was mixed with 30 g of hydrochloric acid (HCl) 35 % and 180 mL of deionized water. The mixture was stirred at 35 °C until P123 was completely dissolved. A total of 13.5 mL of tetraethyl orthosilicate (TEOS) was added to this solution under vigorous stirring. The final mixture was stirred at 35 °C for 24 h, then transferred into an autoclave and kept in the autoclave at 90 °C for 24 h under static condition for hydrothermal treatment. Finally, the formed white precipitates were filtered, washed with water for several times and dried at room temperature. The SBA-15 was obtained by calcining the dried product at 550 °C for 4 h at a heating rate of 1 °C/min in air. In this way the organic surfactant P123 was removed.

P123, $[\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}]$ abbreviated as $[\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}]$ is an amphiphilic molecule where the PEO parts are hydrophilic and PPO part is hydrophobic. The PEO parts are referred to as EO chains and PPO as PO chain. The amphiphilic behaviour of P123 makes it form spherical micelles in water with the EO chains towards the water and the PO chains in the core of the micelles.

The procedure of incorporating ZnO into the channels of SBA-15 is as follows [12]. A total of 0,5 g of extracted mesoporous silica SBA-15 was impregnated with 0,61 g $\text{Zn}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$ and 21 mL ethanol $\text{C}_2\text{H}_5\text{OH}$ under vigorous stirring and then filtered and washed for several times with ethanol.

The paste-like product was dried for 24 h in air at room temperature. Finally, ZnO/SBA-15 nanocomposite was obtained by calcining the dried (pastelike) product at 550 °C for 1 h at a heating rate of 1 °C/min in air.

Before any characterisation of the product it was crushed in a mortar.

Nanocomposites based on organic polymer generally have many advantages such as long-term stability and good processability. The inorganic nanoparticles possess very good optical, catalytic, electronic and magnetic properties. By combining the functionalities of both components, the new nanocomposites could potentially provide many applications in automotive, aerospace, optoelectronics or coatings industry [13].

2.2 Preparation of acrylic coating system

Model paint materials based on an acrylic resin were formulated using the pearl mill Turbomil. Different amounts of ZnO/SBA composite were introduced in the paint system and the samples were denoted as A1, A2 and A3 respectively. The sample A1 does not contain the nanoparticles and was kept as standard model for comparison. The acrylic coatings so prepared were applied with doctor blade applicator onto cleaned glass panels 100 x 200 x 5 mm and onto plasterboard panels 300x150x10 mm.

2.3 Preparation of polyurethanic coating system

Conventional polyurethane lacquer was stabilized with ZnO/SBA-15 composite in different concentrations by Ultrasonic probe dispersion equipment for about 2 hours until a clear coat was obtained. Before the adding the nanocomposite in the coating system, the powder of the nanocomposite was dispersed in propylene glycol in order to avoid the agglomeration. The coating systems thus formed were denoted as P1, P2 and P3 respectively. The sample P1 does not contain the nanoparticles being kept as standard model for comparison.

The lacquers so prepared were applied with doctor blade applicator onto cleaned glass panels 100 x 200 x 5 mm and onto steel panels 150 x 75 x 5 mm. All the samples applied onto the panels were kept under standard conditions in a climatized laboratory (temperature 23 °C, relative air humidity 50 %).

Mechanical properties were studied by cupping test, pencil hardness and cross-cut tape test methods. Optical property was studied using UV-Vis spectrophotometer, surface morphological studies were carried out using Scanning Electron Microscopy and Atomic force microscopy.

2.4 Characterization techniques

In order to characterize the obtained ZnO/SBA composite and the acrylic and polyurethane coatings prepared with these, a series of analyses were performed: XRD diffraction, SEM, AFM and IR, investigations.

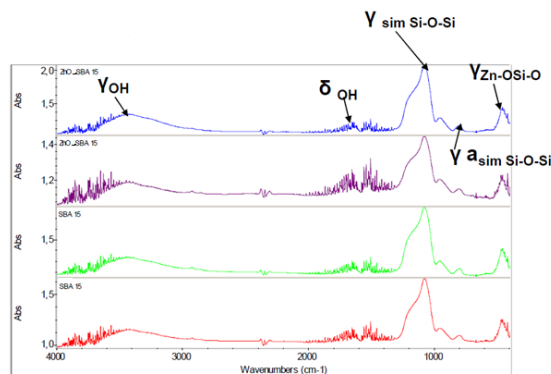


Fig. 1. IR spectrum of SBA-15 and ZnO/SBA-15

For X-ray diffraction studies was used a Bruker D8 Advance.

IR spectra were recorded using a Karl Zeiss Jena UR device 20 and EQUINOX 55 using for plotting the spectrum, KBr on the range $400\text{--}4000\text{ cm}^{-1}$.

The SEM images were recorded on a Hitachi S2600N, the samples being covered with a 10 nm thin layer of gold.

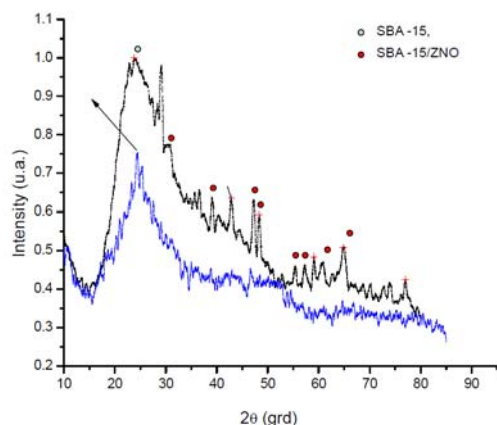


Fig. 2. XRD diffractogram for a) SBA-15 (blue), ZnO/SBA-15 (black).

Interpretation of IR spectrum of ZnO deposited on silica support (SBA-15) has been compared with that of the substrate. From IR spectra recorded it can observe the presence of the vibration bands characteristic to the γ as links $\text{Si-O-Si} = 792\text{ cm}^{-1}$, and $\gamma_{\text{sim}} \text{Si-O-Si} = 1051\text{ cm}^{-1}$, and the-OH group remained incondensable (left the network at 3400 cm^{-1}) also.

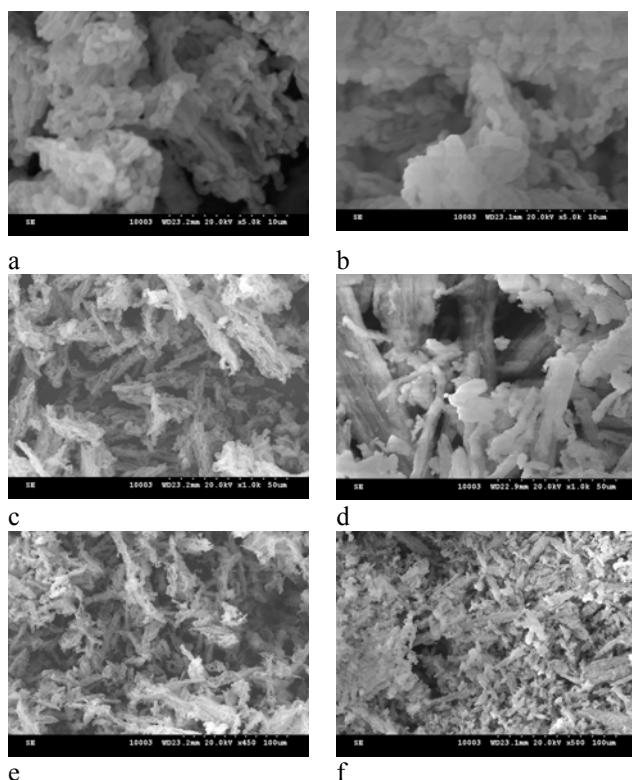


Fig. 3 SEM images of SBA-15 and ZNO/SBA-15 composite: a) SBA-15 10 μm ; b) ZnO/SBA-15 10 μm ; c) SBA-15 50 μm ; d) ZnO/SBA-15 50 μm ; e) SBA-15 100 μm ; f) ZnO/SBA-15 100 μm

The micrographs of acrylic and polyurethane coatings, SBA-15 and ZnO/SBA-15 particles taken by scanning electron microscope are shown in Fig 3. It is evident from these micrographs that the SBA-15 structure remains even after ZnO impregnation and ZnO is distributed uniformly inside the entire SBA-15.

2.5 Mechanical tests

2.5.1 Determination of degree of dryness the paint films

The time necessary for reaching a specified degree of non-tackiness of the paint film (the drying time) was determined using a paint applied onto a glass panel; each measurement was carried out on a different part of the film surface.

A square of special paper is carefully put onto the film surface; a rubber ring is then placed on the paper and weights of 20, 500 and 1000 g are then placed in the centre of the rubber ring; the weight and the ring are removed after 60 seconds.

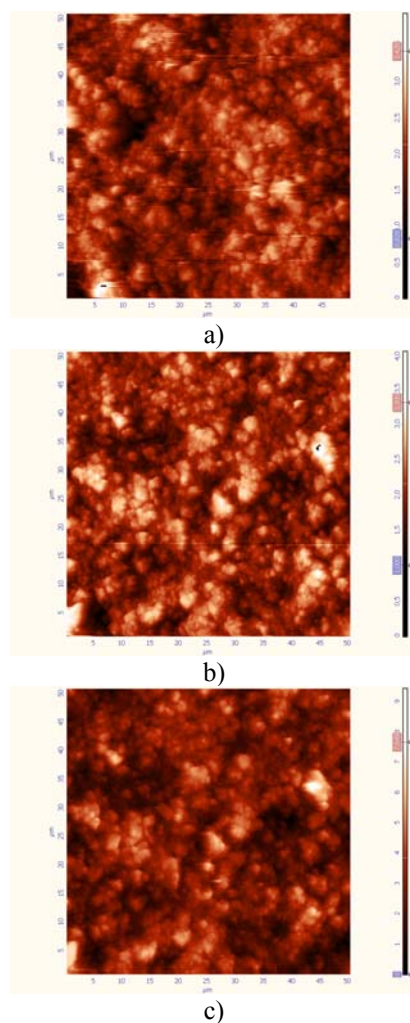


Fig.4 AFM images of acrylic coating surface : a) sample A1; b) sample A2; c) sample A3

The tested panel is then allowed to fall freely by the longer edge from a height of 30 mm. Stage of drying is reached when the paper square falls off the film after the impact and the surface is not damaged. The determination is repeated each 5 minutes. The results are shown in Table 3.

2.5.2 Determination of surface hardness of the paint film

The hardness of coating films applied onto the glass panels according to SR EN ISO 1522 Pendulum damping test – was carried out with Persoz Pendulum Hardness Rocker Model Ref.707 KP from Sheen. A pendulum resting on a coating surface is set into oscillation and the time for the oscillation amplitude to decrease (from 12° to 4°) is measured. A sample presenting a shorter damping time has a lower hardness. The results are shown in Table 3.

2.5.3 Determination of the resistance to cracking and/or detachment from a substrate of the paint film (cupping test)

The method was carried out with the Cupping teste apparatus from Sheen and was performed by gradually increasing the depth of indentation to determine the minimum depth at which the coating cracks and/or becomes detached from the substrate.

The elastic properties of the paint film are determined by first placing the coated panel between two rings, namely the retaining ring and the drawing die. The panel is then pushed by hemispherical intender at a steady rate into the die so as to form a dome shape with the coating on the outside. The deformation is increased until the coating cracks and/or detaches from the substrate and the result is then assessed. The results are shown in Table 3. In Fig. 9, b), is depicted the dome shape with the polyurethane coating on the outside undamaged.

2.5.4 Determination of adhesion of polyurethane coatings

We evaluated the adhesion of these polyurethane coatings to steel panels using the cross-cut tape test method (SRENISO 2409-2007). The test measures the percentage area where flaking occurs due to removal of an adhesive tape. The results are classified as follows: 0 (0% or none); 1 (<5%); 2 (5–15%); 3 (15–35%); 4 (35–65%); and 5 (>65%).

The results are shown in Table 3.

2.5.5 Determination of the wet scrub resistance of the acylic coating film

Method for determining the wet scrub resistance of the paint according to the SRENISO 11998-2007 has been used to determine the coating's ability to resist damage caused by repeated washing operations.

The ability of a dry film to lose in the thickness less than the loss specified on a defined area, when it is subjected to 200 cycles of wet scrub is expressed through coating mass loss per unit area L , in g / m^2 and it is calculated using the equation:

$$L = \frac{m_1 - m_2}{A} \quad (1)$$

where: A - is the area crossed by abrasive sponge (m^2), m_1 - is the initial mass (g) of the test film and dry film, and m_2 - is the mass (g) of the test film and dry film after the 200 cycles of friction.

The dry film thickness loss, $L_{p_{fu}}$, is calculated in micrometers using the equation:

$$L_{p_{fu}} = \frac{m_1 - m_2}{A * \rho_{fu}} = \frac{L}{\rho_{fu}} \quad (2)$$

where: ρ_{fu} - dry film density (g/cm^3) and A , m_1 , m_2 and L have same meanings as above.

The results are shown in Table 1.

Table 1 Assessment of the wet scrub resistance of the acrylic coatings through the loss in thickness of dry film

Sample	Loss in thickness of dry film, μm
A1	3.64
A2	2.32
A3	1.58

2.5.6 Determination of the photocatalytic effect

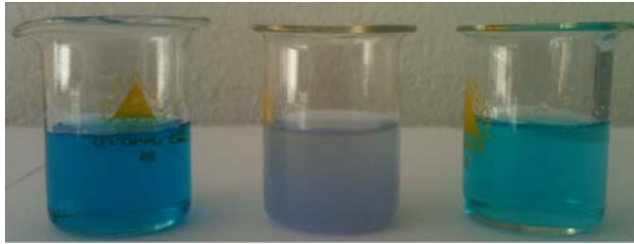
The photocatalytic activities of the ZnO/SBA-15 samples were evaluated by the degradation of MB in aqueous solution and depending on the degree of the methylene blue solution discoloration, the self-cleaning properties of the films were appreciated.

Methylene blue (MB) has been used as a model organic compounds to evaluate the photocatalytic activities of the as prepared composite.

A beaker containing only 100 ml of 1 % methylene blue aqueous solution and another containing 100 ml 1% aqueous methylene blue solution and 0.1 g composite were exposed to the sun light.

The degree of discoloration of the solution was assessed after 12 hours and after 24 hours.

The results are shown in Fig. 5 and 6.



a) 1 % methylene blue aqueous solution unexposed to the sun light
 b) 1 % methylene blue aqueous solution and 0.1 g composite exposed to the sun light
 c) 1 % methylene blue aqueous solution exposed to the sun light

Fig.5 After 12 hours exposure to the sunlight



a) 1 % methylene blue aqueous solution unexposed to the sun light
 b) 1 % methylene blue aqueous solution and 0.1 g composite exposed to the sun light
 c) 1 % methylene blue aqueous solution exposed to the sun light

Fig.6 After 24 hours exposure to the sunlight

In parallel, 1 % methylene blue aqueous solution was sprayed on the surface of plasterboard plates covered with samples A1, A2 and A3 and were exposed to the sunlight for one month.

The results are shown in Fig. 7 and Table 2.

Table 2 Assessment of the self cleaning effect of the acrylic coatings

Sample	Self cleaning effect
A1	null
A2	strong
A3	strong

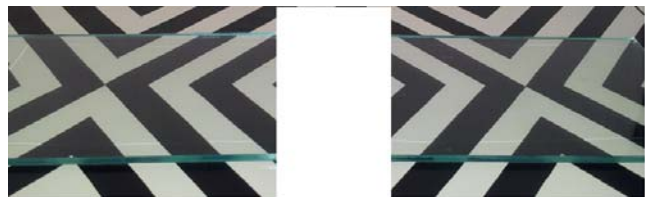


Acrylic coating with ZnO/SBA-15 composite before exposure Acrylic coating without ZnO/SBA-15 composite before exposure



Acrylic coating with ZnO/SBA-15 composite after 30 days exposure to sunlight Acrylic coating without ZnO/SBA-15 composite after 30 days exposure to sunlight

Fig.7 Assessment of the self cleaning effect of the acrylic coatings with and without ZnO/SBA-15 composite



a) Coating without ZnO/SBA nanocomposite; b) coating with ZnO/SBA nanocomposite

Fig. 8. Comparison between the transparency of the coating system with and without adding ZnO/SBA nanocomposite

3. Results and discussion

The structure of the composite and the coatings are followed from FT-IR spectra, and the results are shown in Fig. 1.

The SEM images of ordered mesoporous silicate support SBA-15 and its composites are shown in Fig. 3. As it can be seen the SEM images show that the morphology of composites does not change compared to SBA-15.

The AFM images of the acrylic coatings (samples A2 and A3) reveal the homogeneity of the composite powder dispersion in the polymer matrix.

The images depicted in Fig. 8, b) and 9, a) indicate that the transparency of the coating system is not much affected by the addition of the nano particles. This means that the nanoparticles do not affect the clarity of the coatings. This may be because of the fact that, particles in nanodimension are smaller than the wavelength of visible light and so no scattering and reflecting occurs in the visible light range leading to transparent nanocomposite.

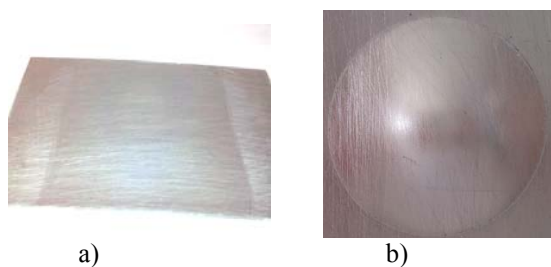


Fig. 9. Images with polyurethane coating system with ZnO/SBA nanocomposite a) Polyurethane coating on the metal ; b) The dome shape with the polyurethane coating on the outside undamaged

At higher loading level the increase in the number of particles form agglomerates because of their high surface activity introducing defect in coatings. These defects act as site for electrochemical reaction affecting the coating performance [14].

The photocatalytic activities of the the nanocomposite are depicted in Fig.5 and 6. When the nanocomposite was introduced directly in the methylene blue aqueous solution the discoloration has occurred after only 12 hours. After 24 hours the discoloration was complete.

When methylene blue aqueous solution was sprayed on the plasterboard which was covered with acrylic coatings the discoloration was slower but still effective for the samples which contain nanocomposite (Fig.7). This may be possible due the fact the nanocomposite which was incorporated in the polymer matrix. The discoloration has not occurred in the case of the sample without nanocomposite.

The adding of the nanocomposite in the acrylic system makes these coatings be more resistant to the wet scrub. As we can see in Table 1, the loss in thickness after 200 cycles of wet scrub was decreased from 3.64 to 1.58 μm ,

which means a bigger resistance of the coatings to the scrub.

Table 3 Mechanical properties of the polyurethane coatings.

Sample	Dry time (hours)	Adhesion	Elasticity (mm)	Hardness (sec)
P1	6	1	5	148
P2	4	0	10	198
P3	2	0	12	213

By adding the ZnO/SBA-15 composite in the polyurethane system, the mechanical properties as the adhesion, elasticity and hardness, were also improved. The results are shown in Table 3.

4. Conclusions

In this work we have synthesized successfully ZnO/SBA-15 composite by nanocasting method.

This composites were investigated as additives in acrylic and polyurethane coatings in order to demonstrate if they can improve the mechanical properties of the coatings.

It was demonstrated that only a small amount of this composite in the coating system gives the photocatalytic activities and improves the wet scrub resistance of the coating system.

The adding of only 0.1 % nanocomposite ZnO/SBA-15 into the polyurethane system improves the mechanical properties as: adhesion, flexibility or hardness.

The ZnO/SBA-15 nanocomposite will be tested to the weathering resistance of the coatings.

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References

- [1] T. Xu, C.S. Xie, Progress in Organic Coatings **46**, 297 (2003).
- [2] D.W. Yuan, et al., J. Mater. Sci. **34**, 1293 (1999)
- [3] M.G. Kakazey, et al., J. Mater. Sci. **34**, 1691 (1999).
- [4] Y. Suyama, Y. Tomkyo, et al., J. Am. Ceram. Soc. **71**(5), 391 (1988).
- [5] A. S. Edelstein, R. C. Cammarata, Nanomaterials: Synthesis, Properties and Applications, 1996, Institute of Phys. Publisher, Bristol, Philadelphia, PA, USA.

- [6] T. P. B. Nguyen, J.-W. Lee, W. G. Shim, H. Moon. Microporous and Mesoporous Materials **110**, 560 (2008).
- [7] N. El-Hassan, E. Delahaye, V. Escax, P. Beaunier, M.-D. Appay, and A. Davidson. Annales de Chimie: Science des Matériaux, **30**, 315 (2005).
- [8] M. Kand, S. H. Yi, H. I. Lee, J. E. Yie, J. M. Kim. Chem. Comm., page 1944, 2002.
- [9] Emma Johansson, Design Of Mesoporous Silica Templates For Nanoparticle Growth, Thesis for the degree of Master of Science, 2008
- [10] A.S. Khanna, Nanotechnology in High Performance Paint Coatings, Asian J. Exp. Sci., **21**(2), 25 (2008)
- [11] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Frederickson, B.F. Chmelka, G.D. Stucky, Science **279**, 548 (1998). doi:10.1126/ science.279.5350.548
- [12] M. Imperor-Clerc, D. Bazin, M.-D. Appay, P. Beaunier, A. Davidson, Chem. Mater. **16**, 1813 (2004). doi:10.1021/cm035353m
- [13] In-Yup Jeon, Jong-Beom Baek, Nanocomposites Derived from Polymers and Inorganic Nanoparticles Materials, **3**, 3654 (2010) doi:10.3390/ma3063654.
- [14] S. K. Dhoke¹, Narayani Rajgopalan, A. S. Khanna Effect of Nano-Zinc Oxide Particles on the Performance Behavior of Waterborne Polyurethane Composite Coatings, IJMSCI **2**(2), 47 (2012)

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