



Photocatalytic and Superhydrophilic TiO₂-SiO₂ Coatings on Marble for Self-Cleaning Applications

Rajaram S. Sutar, Pratiksha B. Patil, Appasaheb K. Bhosale, Saravanan Nagappan, Shital R. Shinde, P. P. Chikode, C. E. Patil, Sunita S. Kadam, P.M. Kadam, C. R. Bobade, Kishor Kumar Sadasivuni, Kang Hyun Park, and Sanjay S. Latthe*

The application of photocatalytic and self-cleaning titanium dioxide (TiO₂) nanomaterials coating on the stone of architectural heritage (particularly on marble) can be used to preserve their aesthetic qualities. The present work describes the effect of dipping time on the wetting property of coatings and the effect of UV irradiation on the coating in terms of hydrophilicity. The suspension of TiO₂-SiO₂ is prepared by adding 30–50 nm in size TiO₂ particles in the sol-gel processed SiO₂ solution. The water contact angle (WCA) decreases with increasing dipping time of piece of marble in TiO₂-SiO₂ suspension. Also the hydrophilicity of coating increases with increasing UV illumination time. The 2D and 3D laser microscope analysis revealed surface structure and stable surface roughness of 1.0 μm. Such type of superhydrophilic TiO₂-SiO₂ coating may be used to protect architectural heritage and buildings.

aesthetic qualities of stone surfaces of historic buildings. Marbles have been extensively used in cultural heritages and historical architectures like statues and monuments. Increasing concentration of pollutants (soil particles, organisms, bird droppings, fire damage, etc.), may cause the deterioration of surface architectures. Photocatalytic and superhydrophilic TiO₂ coating is one of the best solution to avoid this problem. TiO₂ can generate oxidative (●OH) and reductive (●O₂) species under UV light irradiation, which are helps to degrade different organic and inorganic compounds.^[1,2] Recently, Parale et al. have used mesoporous TiO₂ aerogel^[3] and SiO₂-TiO₂ aerogel^[4] for photodegradation of organic pollutants. Moreover, the hydrophilicity enhanced by -OH, which easily

1. Introduction

From last decade, scientific research has been paid many attentions for developing novel surface coatings for the protection of

remove the fouling substances on TiO₂ coated surfaces by flow water film; this is called self-cleaning ability. Munafa et al.^[5] have sprayed colloidal suspensions of TiO₂ on travertine stone to deposit photocatalytic self-cleaning coating. After long-term

R. S. Sutar, P. B. Patil, A. K. Bhosale, S. S. Latthe
Self-Cleaning Research Laboratory
Department of Physics
Raje Ramrao Mahavidyalaya
Jath, Dist
(Affiliated to Shivaji University, Kolhapur)
Sangli, Maharashtra 416404, India
E-mail: latthes@gmail.com
S. Nagappan, K. H. Park
Department of Chemistry
Chemistry Institute for Functional Materials
Pusan National University
Busan 46241, Republic of Korea
S. R. Shinde
Vidnyan Mahavidyalaya
Sangola, Maharashtra 413307, India
P. P. Chikode
Jaysingpur College
Jaysingpur, Maharashtra 416101, India

C. E. Patil
B. V. Matoshri Bayabai Shripatrao Kadam Kanya Mahavidyalaya
Kadegaon
Dist-Sangli
Sangli, Maharashtra, India
S. S. Kadam
Krantisinh Nana Patil College
Dist-Sangli
Walwa, Maharashtra, India
P. Kadam
KWC Sangli
Sangli, Maharashtra, India
C. R. Bobade
Balwant College
Vita. Dist:Sangli
Sangli, Maharashtra 415311, India
K. K. Sadasivuni
Center for Advanced Materials
Qatar University
P. O. Box 2713
Doha, Qatar

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/masy.202100083>

DOI: 10.1002/masy.202100083

aging under UVA irradiation, the microstructure of coating was unaltered but reduced photoactivity and self-cleaning properties. Bergamonti et al.^[6] have applied TiO₂-sol on the stone samples by brush, repeating the procedure for three times to obtain self-cleaning coating. Lettieri et al.^[7] have applied nanostructured TiO₂ as a photoactive coating on two types of the natural stone (a compact limestone and a highly porous calcarenite stone). Luna et al.^[8] have applied sol-gel processed Au-TiO₂/SiO₂ photocatalysts coating on building stone by spray coating. Integrated TiO₂ in a silica matrix can be enhanced its adherence to the substrate and the subsequent coating durability. Au nanoparticles enhance the TiO₂ photoactivity and self-cleaning performance on the coated building stone. Aminian et al.^[9] have deposited nanolayer of TiO₂ on glass substrate by dip coating method and reported that the addition of SiO₂ nanolayer under the TiO₂ layer increase the hydrophilicity due to the increase in the roughness and surface area of the nano-grains.

In the present work, we have deposited TiO₂-SiO₂ coating on white marble by dips coating technique. The sol-gel processed silica sol was prepared by using TEOS and TiO₂ was added to the silica sol to prepare coating solution. The study of photodegradation of methylene blue (MB) revealed that the prepared coating has excellent self-cleaning ability.

2. Experimental Section

2.1. Materials

Tetraethylorthosilicate (TEOS, ≥99.0%) and TiO₂ nanoparticles (<25 nm particle size, 99.7%) were purchased from Sigma-Aldrich, USA. Ethanol and nitric acid (Extra Pure AR) were bought Spectrochem Pvt. Mumbai, India. MB dye was obtained from Poona Chemical Laboratory, Pune, India. A small pieces of white marble (L × W × H, 5 × 2 × 1 cm³) collected from local market.

2.2. Preparation of Superhydrophilic TiO₂-SiO₂ Coating on Marble

The silica sol was prepared by sol-gel processing of TEOS using nitric acid as catalyst. A total of 11.2 mL distilled water and 0.6 mL nitric acid were mixed well using magnetic stirrer, 7.5 mL of TEOS was added drop-by-drop in the above mixture and kept at constant stirring for 500 rotation per minute (rpm). After 5 h of stirring, 10 mL of ethanol was added slowly and stirring further continued for overnight to get silica (SiO₂) sol. Thereafter, 60 mg of TiO₂ nanoparticles were dispersed in the prepared silica sol and stirred for 2 h in order to get uniform coating solution. The marble pieces were washed with laboratory detergent and later by distilled water and dried well under hot air dryer. A cleaned piece of marble dipped in the coating solution with different dipping time. Deposited marble pieces were dried at 110°C in oven for 6 h to rid of solvents. The schematic process of deposition of superhydrophilic TiO₂-SiO₂ coating on marble is shown in **Figure 1**. The dip-withdraw speed and dipping time were controlled by Dip-coater machine. The dipping time varied from 1 to 7 min at constant dip-withdraw speed of 50 mm s⁻¹.

2.3. Characterizations

A laser microscope (KEYENCE, VK-X200 series) was used to characterize the 2D and 3D surface topography of the coated marble. A closed metal box with one open side covered by black napkin was fabricated and UV lamps (Intensity = 1 mW cm⁻²) was fitted onto the ceiling of the box. The photocatalytic property of the coating was confirmed by the decrease in water contact angle (WCA) with UV illumination time. The wetting properties of the coating surface before and after UV, irradiation was confirmed by WCA measurements. A contact angle meter (Kyowa, Drop Master; Saitama, Japan) was used to measure the WCAs. A small water drop was gently placed on the surface by using syringe. The self-cleaning ability of the TiO₂ coating under exposure to UV irradiation was checked using MB as a stain.

3. Result and Discussion

3.1. Surface Topography and Roughness of the Prepared Coating on Marble

The surface topography plays an important role on the wettability of the thin films (**Figure 2**). Generally, the smoother surfaces can have strong adhesion to water droplet because lower surface roughness which delivers the hydrophilic to superhydrophilic properties based on the surface treatments. In contrast, the surfaces with higher roughness can resist water droplet on the surface if it covers a thin layers of hydrophobic coatings, so that these surfaces can deliver hydrophobic to superhydrophobic behaviors based on the surface roughness and hierarchical morphology. In this work, the TiO₂-SiO₂ coating prepared by 1 min dipping showed relatively smooth surface with root mean square (RMS) roughness of nearly 0.74 μm. At the shorter dipping time, a lesser number of TiO₂-SiO₂ nanoparticles were deposited on the coated substrate which is the reason for being a smooth surface morphology with lower roughness (**Figure 2a** and **b**). Whereas, increasing the dipping time significantly alter the thickness as well as roughness of the film. The TiO₂-SiO₂ thin films prepared by 7 min dipping showed remarkably rough surface structure with RMS roughness of 1.0 μm (**Figure 2c** and **d**). At the same, increasing the dipping time would not indicate a significant enhancement in the RMS roughness due to saturation of the coating by full coverage of the coated materials on the substrate in between 1 and 7 min. Whereas, these highly roughness surface helps to achieve the superhydrophilic property because of larger area surface coverage of both hydrophilic TiO₂-SiO₂ nanoparticles as well as photocatalytic property of TiO₂ nanoparticles. The deposition time was further increased to 10 min, however the visible cracks were observed on the thin film due to the deposition of more TiO₂-SiO₂ nanoparticles, which can be easily removed by the gentle fingertip touching owing to reduction of adhesion strength on the coated substrate.

3.2. Surface Wettability, Photocatalytic Activity, and Self-Cleaning property

The coating of TiO₂-SiO₂ thin film were applied on pre-cleaned marble by dipping at different time in coating solution. The

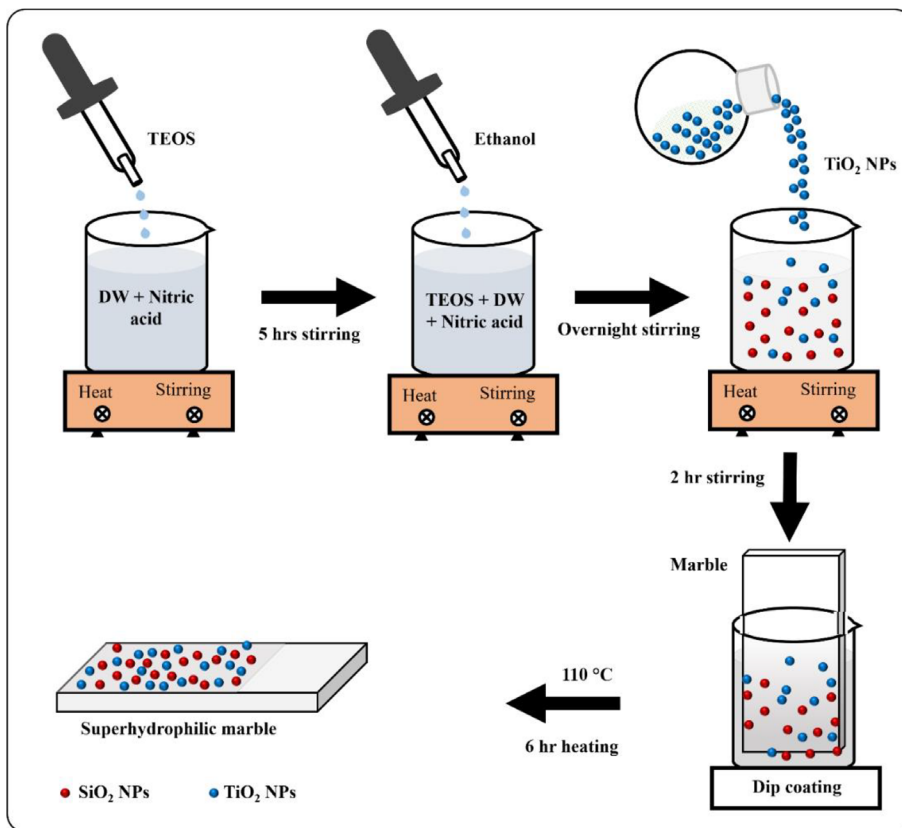


Figure 1. Preparation of superhydrophilic TiO_2 - SiO_2 coating on marble.

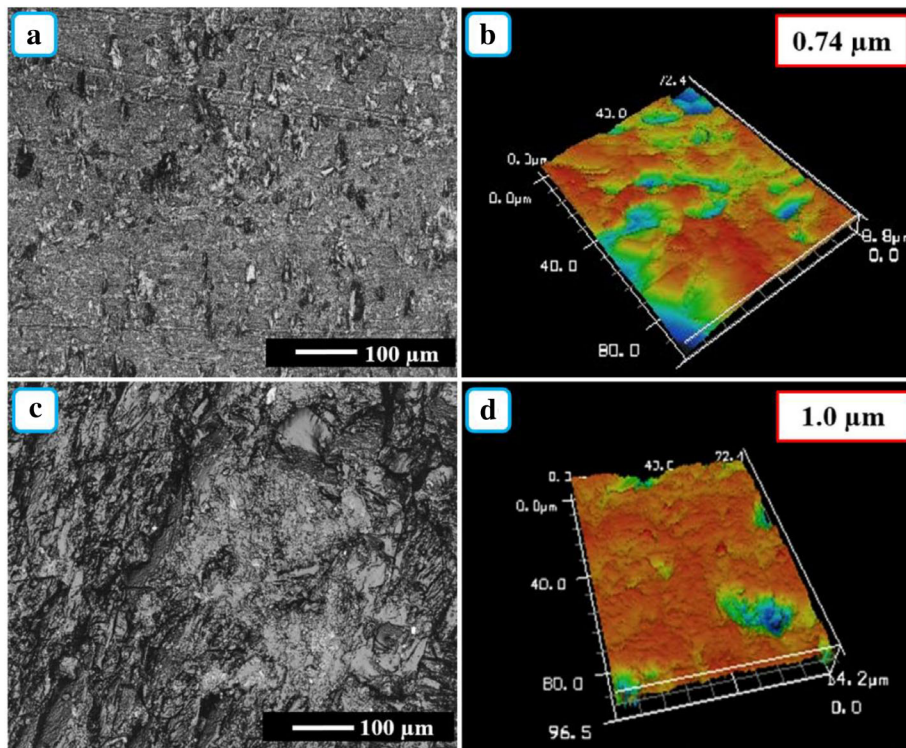


Figure 2. The 2D and 3D Laser Microscope images of the SiO_2 - TiO_2 thin films prepared from a) and b) 1 min and c) and d) 7 min deposition time, respectively.

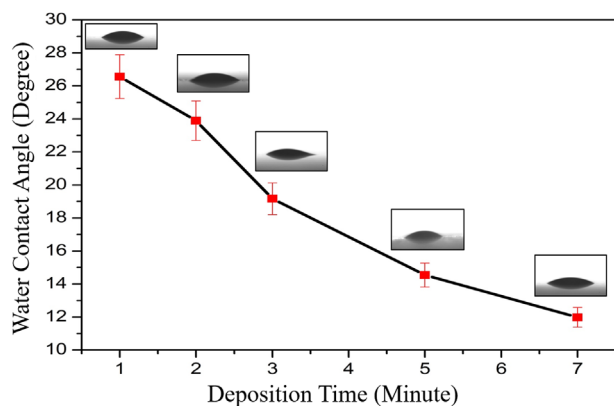


Figure 3. An effect of dipping times on wettability of the coating.

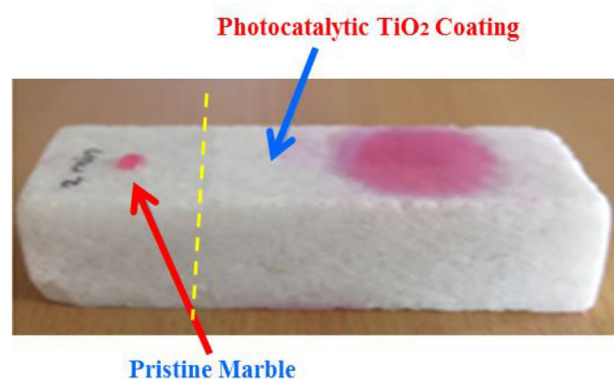


Figure 4. Optical photograph of behavior of water drop on coated and uncoated part of the marble.

dipping time were varied from 1 to 7 min. As usual, 1 min deposited coating showed WCA of 27° due to smoothness of the thin film. However, the WCA gradually decreased to 14° for 7 min deposited TiO₂-SiO₂ thin films. As discussed in the above section, the reduction in the hydrophilic surface contact angle by the increase of dipping time is due to the deposition of more number of hydrophilic TiO₂-SiO₂ nanoparticles on the coated surface which obviously leads to express more water adhesion and penetration on the coated marble surface and lead to more hydrophilic surface property than lesser duration of TiO₂-SiO₂ nanoparticles coating. Furthermore, the photocatalytic property of TiO₂ nanoparticles on the coated marble surface helps to generate more hydrophilic functional groups on the substrate surface which also responsible to enhance the hydrophilic surface property while increasing the coating time as well as by increase of surface roughness. The variations in WCA with respect to dipping time are shown in the **Figure 3**. These due to the increased in roughness as well as the deposition of more hydrophilic TiO₂-SiO₂ thin film layers which eventually helps to decrease the wettability of the coated substrate.^[10]

The optical image of the TiO₂-SiO₂ nanoparticles coated and uncoated marble is shown in **Figure 4**. When a dyed water drop deposited on uncoated marble, water drop stacked on the surface and illustrating the WCA >40° (left side). At the same time, wa-

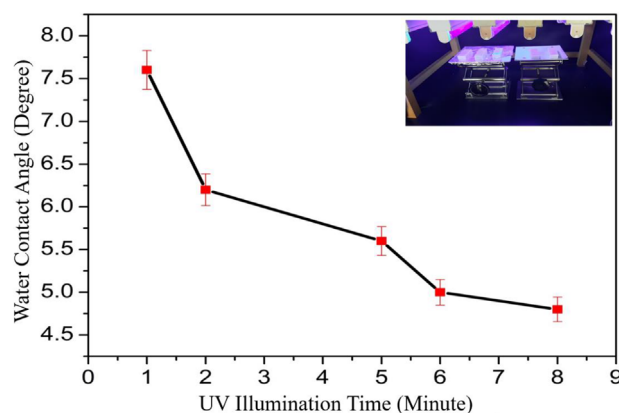


Figure 5. An effect on UV illumination time on the wettability of the TiO₂-SiO₂ coated marble.

ter drop completely spread and penetrate in the coated marble have proved the superhydrophilic surface property of the coated marble.

UV surface treatment can lead to generate more hydrophilic functional groups on a substrate because under UV light illumination, more protons, radicals, surface hydroxyl, or oxygen species are generated at the surface, which have more hydrophilic surface property. In addition, the presence of photocatalytic TiO₂ nanoparticles on the coated surface also induces the surface reactivity to more hydrophilic. We checked the effect of UV irradiation on the dip-coated marble (7 min dipping marble). As expected the hydrophilicity of coating increases with of the increase of UV irradiation time.^[11,12] The variation of WCA with duration of UV irradiation is shown in **Figure 5**. After 8 min of UV irradiation, the WCA of coating reached to <5°, which confirms hydrophilic coating become superhydrophilic. This contradicts to some reports where superhydrophilicity was only achieved after long period of UV irradiation. UV irradiation causes to form stable hydroxyl groups on TiO₂-SiO₂ surface and consequently surface becomes more hydrophilic.^[9] Mostly, fast reducing WCA of hydrophilic coating under UV irradiation, which resulting the development of superhydrophilic self-cleaning TiO₂-SiO₂ coating.

Self-cleaning is one of the most important property in coating applications as well as in various industrial products. In general, self-cleaning property is defined by their ability to clean the surface without any external pressure or sources. Lotus leaf surface was the most common example for self-cleaning behaviors. The presence of micro-nano hierarchical texture with a thin layer of hydrophobic waxy layer in lotus leaf is responsible for the self-cleaning as well as superhydrophobic surface property. In contrast, photocatalytic superhydrophilic coatings can also deliver self-cleaning property. We checked the photocatalytic self-cleaning behavior on the TiO₂-SiO₂ nanoparticles coated superhydrophilic marble. Mostly, white marbles are prone to damage by air and water pollution. The continuous degradation of monuments due to organic pollutants may soon become irreversible. Here, we extensively studied the photocatalytic self-cleaning ability of the MB dye deposited marble surface from the dye degradation behavior under UV irradiation (**Figure 6**).^[6,13]

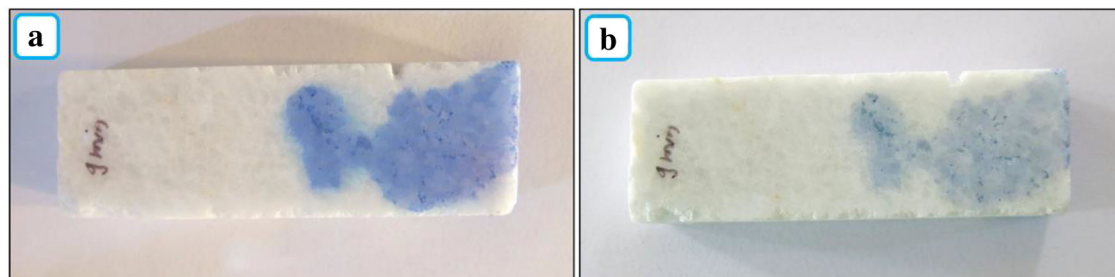


Figure 6. Photograph of self-cleaning photodegradation test by MB, a) before UV exposure and b) after 30 h of exposure to UV irradiation.

We systematically evaluated the self-cleaning activity on the fabricated substrate by adopting standard procedure. A total of 0.5 mL of MB dyed water was poured on the coated marble is shown in Figure 6a. Later, this marble placed at 10 cm from UV source in degradation chamber for degradation of MB. After, 30 h of exposure to UV irradiation, the dye deposited marble can display almost 90% degradation of MB dye on the marble surface (Figure 6b). This result confirms the prepared $\text{TiO}_2\text{-SiO}_2$ coated marble can have excellent photocatalytic activity as well as self-cleaning.

4. Conclusion

In this work, superhydrophilic $\text{TiO}_2\text{-SiO}_2$ thin film coating was successfully applied on marble for photocatalytic and self-cleaning application. We encountered the surface roughness and surface wettability was altered to some levels based on the coated marble by increasing the dip-coating time. The optimized condition of 7 min of deposition time revealed hydrophilic property with contact angle nearly 14° . Whereas, increasing the UV irradiation time to 8 min further reduced the contact angle to $<5^\circ$. At the same, the surface roughness on the coated substrate was also increased with deposition time. Moreover, the transformation of surface wettability of TiO_2 film into superhydrophilic state and subsequent decomposition of organic pollutants by UV exposure leads to self-cleaning phenomena. The fabrication of this simple and cost-effective superhydrophilic and self-cleaning coating can have a wider scope to apply the similar coating formulation on a wide variety of application, especially in the maintenance of the property in architectural buildings.

Conflict of Interest

The authors declare no conflict of interest

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

photocatalytic, self-cleaning and $\text{TiO}_2\text{-SiO}_2$ suspension coating, superhydrophilic

Received: April 7, 2021

Revised: June 6, 2021

- [1] Hoffmann, M. R., Martin, S. T., Choi, W., Bahnemann, D. W., *Chem. Rev.* **1995**, *95*, 69.
- [2] Miyauchi, M., Kieda, N., Hishita, S., Mitsuhashi, T., Nakajima, A., Watanabe, T., Hashimoto, K., *Surf. Sci.* **2002**, *511*, 401.
- [3] Parale, V. G., et al., *J. Mol. Liq.* **2019**, *277*, 424.
- [4] Parale, V. G., et al., *Ceram. Int.* **2020**, *46*, 4939.
- [5] Munafo, P., Quagliarini, E., Goffredo, G. B., Bondioli, F., *Constr. Build. Mater.* **2014**, *65*, 218.
- [6] Bergamonti, L., Bondioli, F., Alfieri, I., Lorenzi, A., Mattarozzi, M., Predieri, G., Lottici, P. P., *Appl. Phys. A* **2016**, *122*, 124.
- [7] Lettieri, M., Calia, A., Licciulli, A., Marquardt, A., *Bulletin Eng. Geol. Environ.* **2017**, *76*, 101.
- [8] Luna, M., Mosquera, M. J., Vidal, H., Gatica, J. M., *Build. Environ.* **2019**, *164*, 106347.
- [9] Khajeh Aminian, M., Sajadi, F., Mohammadzadeh, M. R., Fatah, S., *Prog. Color. Color. Coat.* **2021**, *14*, 221.
- [10] Syafiq, A., Vengadaesvaran, B., Pandey, A. K., Rahim, N. A., *J. Nanomater.* **2018**, *1*, 2018.
- [11] Fateh, R., Dillert, R., Bahnemann, D., *Langmuir* **2013**, *29*, 3730.
- [12] Shayan, M., Jung, Y., Huang, P.-S., Moradi, M., Plakseychuk, A. Y., Lee, J.-K., Shankar, R., Chun, Y., *J. Mater. Sci.: Mater. Med.* **2014**, *25*, 2721.
- [13] Luna, M., Delgado, J. J., Almoraima Gi, M. L., Mosquera, M. J., *Nanomaterials* **2018**, *8*, 177.