Development of self-cleaning bricks surfaces by CaCO$_3$ modified nano-TiO$_2$ composite coatings

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Abstract Recently, many studies have been carried out on self-cleaning characteristic because it is being regarded as one of the most interesting topics in biomimicry because of its potential applications in energy conversion, and biomedical and environmental protection. In this study, spin coating process has been introduced to coat bricks surfaces with TiO$_2$ nanoparticles-based polymer composite coatings modified using CaCO$_3$ particles for self-cleaning and environmental purposes. The matrix solutions were prepared from Polystyrene. Particle size analyzing PSA and x-ray diffraction XRD were employed for characterization of the particles. The coatings were characterized by SEM and AFM techniques, and contact angle measurement CA. Results proved that CA increased with the increasing of PS ratio and additions of nano-TiO$_2$ and CaCO$_3$. The composite coatings have dense topography with roughness increased with increasing of the CaCO$_3$ addition, and porous morphology characterized by clear distribution of the nano TiO$_2$ particles and larger CaCO$_3$ modification particles. Also, it could be concluded that the %20PS/$6\%$TiO$_2$/1gCaCO$_3$ coatings, could give promised effect in modification of bricks surfaces from superhydrophilic substrates to Superhydrophobic with higher contact angle 167.3987°. These results will encourage the future research in surface engineering of bricks surfaces using CaCO$_3$ particles for self-cleaning and environmental applications.

Keywords: TiO$_2$ nanoparticles, CaCO$_3$, Spin coating, super hydrophobic, Bricks, self-cleaning.

1.Introduction

TiO$_2$ nanoparticles have important role in recent studies because of their unique photocatalysts properties [1-2]. TiO$_2$ nanoparticles are used very common in many applications such as antibacterial and technological agents [3-4]. Anatase TiO$_2$ shows superior photo-catalytic performance than rutile (more stable) and has a wide application in numerous fields such as water splitting, air, water, and wastewater treatment and solar cells [5-6]. Photo-catalysis term in chemistry refers to the acceleration of a photoreaction in the presence of a catalyst [7]. The reaction of photo-catalysis starts when the light is absorbed. The activity of photocatalysts controlled by the ability of the catalyst to create an(electron-hole) pair, which brings the free radicals (OH) to the center [8]. Among the photocatalysts, TiO$_2$ has been show its effectiveness in the degradation of organic pollutants, because of its chemical stability, Superhydrophobic nature, stability for a long time, non-toxic, cheap, and transparency to visible light [9-10].
Self-cleaning property of super hydrophobic materials derived from their high water contact angle which include causing water to form spherical-like droplets on the surface that roll off easily and carrying away all dust and dirt [11]. Spin coating method is increasingly used for producing uniform coatings of different materials on different types of flat substrate surface [12-13]. It can be considered as one of the common deposition techniques due to its superior advantages such as; fast, inexpensive and simple [14-15]. Recently, few works in the literature have been done on surface improvement of bricks for self-cleaning and environmental purposes [16-17]. The objective of the present work is to use CaCO₃ particles with TiO₂ nanoparticles-based polymer composite coatings in surface engineering of bricks by spin process for environmental and self-cleaning applications.

2. Experimental work

2.1 Materials

The titanium oxide used in this work was a nano anatase type (TiO₂) 99%, 30-50 nm, purchased from Hongwu International Group Ltd. Poly styrene was purchased from American polymer service Inc. APS. N,N-Dimethylformamide materials were purchased from Thomas Baker(chemicals) Pvt.Ltd. Calcium carbonate (CaCO₃) 98%, purchased from Sinopharm chemical reagent Co., Ltd was used for the enhancement of coatings.

| Samples No. | Additives | PS(g) | DMF(g) |
|-------------|-----------|-------|--------|
| MM1         |           | 0.1   | 9.9    |
| MM2         |           | 0.5   | 9.5    |
| MM3         |           | 1     | 9      |
| MM4         |           | 1.5   | 8.5    |
| MM5         |           | 2     | 8      |

2.2 Substrates preparation

The substrate samples were prepared by cutting and shaping of Iraqi bricks into square samples with the dimensions of 5 x 20 x 20 mm³. Before coating, all the samples’ surfaces were washed, polished, cleaned with ethanol, and dried in oven at 100° C.
2.3 Preparation of coating solutions

In this process, at the beginning, the PS was solved in DMF by magnetic stir under fume hood with different percentage gradually using electronic balance as shown in [table 1] to investigate the effect of PS on the contact angle results of the matrix material (MM). Then, as shown in [table 2] titanium dioxide TiO$_2$ nano particles was add to the solution of samples MM5 gradually in different percentage in the same way to investigate the effect of TiO$_2$ nano particles on the contact angle results of the TiO$_2$ modified composite coatings (TMCC).

Table 2. Ratios of TiO$_2$ additions in the composite coating solutions

| Samples No. | Additives          | TiO$_2$(g) |
|-------------|--------------------|------------|
| TMCC1       | PS(2g)+ DMF(8g)    | 0.02       |
| TMCC2       | PS(2g)+ DMF(8g)    | 0.04       |
| TMCC3       | PS(2g)+ DMF(8g)    | 0.06       |

Table 3. Ratios of CaCO$_3$ modified composite coating solutions

| Samples No. | Additives  | CaCO$_3$(g) |
|-------------|------------|--------------|
| CTMCC1      | TMCC3      | 0.5          |
| CTMCC2      | TMCC3      | 1            |

Finally, Calcium carbonate particles were added to the composite coating solutions according the ratios shown in [table 3], to investigate the properties of CaCO$_3$and TiO$_2$ modified composite coatings (CTMCC).

2.4 Coating process

The coating process was performed using spin coating machine at the Department of Polymer Engineering/College of Material's Engineering/ Babylon University. In this process, the coating solution was pumped by a syringe to cover the sample surface at 1500 rpm for 20 sec. After coating, the samples were dried in the room temperature for 24 hours, and dried in vacuum furnace at 100°C for 24 hours.

2.5 Characterization and Measurements

The TiO$_2$ and CaCO$_3$ powders were identified with XRD- system type XRD-6000 SHIMADZU, Japan X-Ray Diffractometer, and the particle size analyzing PSA of powders was identified with Laser Particle Size Analyzer Type Better size 2000. The water contact angles of the samples surface were measured by an FTA200 contact angle instrument (first ten angstroms, USA) .The XRD, PSA, and water contact angles tests were done at the
Department of Ceramic Engineering and building materials /College of Material's Engineering/ Babylon University.

The morphology and the structure of coated samples surface were tested with Scanning Electron Microscopy SEM, FEI Company Netherlands Inspect S50-Model, at the Nanotechnology and Advanced Materials Research Center/ University of Technology. The 3D surface topography and measurements of roughness parameters were performed using atomic force microscopy AFM (AFM, contact mode, spm AA3000 Angstrom advanced Inc., USA) at the Department of Chemistry /College of Science/ University of Baghdad.

3. Results and discussion
3.1 XRD Results
Figures (1) and (2) shows the XRD results of nano-TiO$_2$ and CaCO$_3$ powders. The XRD patterns of anatase phase nano-TiO$_2$ powder proved the TiO$_2$ peaks according to standard cards (JCPDS No.01-083-2243). The XRD patterns of CaCO$_3$ powder proved the CaCO$_3$ peaks according to standard cards (JCPDS No.01-072-1937).

![Figure 1. XRD patterns of nano-TiO$_2$ particles](image1)

![Figure 2. XRD patterns of CaCO$_3$ particles](image2)
3.2 PSA Results

Figures (3-4) show the results from PSA for nano-TiO\(_2\) and CaCO\(_3\) particles. It can be observed that the size of titanium dioxide powder distributed in the range of (0.202\(\mu\)m-5.350\(\mu\)m) with a mean value of (0.883\(\mu\)m). Also, the size of particles for CaCO\(_3\) powder distributed in the range of (0.213\(\mu\)m-19.94\(\mu\)m) with a mean value of (1.045\(\mu\)m). Such results are necessary to better understand the behavior of the hydrophobized TiO\(_2\)/CaCO\(_3\) coatings.

![Figure 3. Particle size of nano-TiO\(_2\) powder](image)

![Figure 4. Particle size of CaCO\(_3\) powder](image)

3.3 Contact angle results

The wettability for material surface is defined by contact angle test. The coated and uncoated surfaces were tested to measure contact angle to observe the surface properties; hydrophilic or hydrophobic.

In general, for the matrix solutions CA value increased with increasing PS addition and samples MM5 (PS 20\%) recorded the highest value among the others. After the addition of TiO\(_2\) particles, the CA values increased with increasing TiO\(_2\) addition. Fig.(5) and table (4) show the CA results, where brick substrate before coating have CA (0.000) and show a noteworthy enhancement in the result after coating with composite coatings, 167.3987° for CTMCC2 samples (T 0.6\% CaCO\(_3\))

Commonly, the superhydrophobicity of a surface is depended on its surface morphology and surface energy. Furthermore, to prepare superhydrophobic surfaces: modifying the rough surfaces to lower the surface free energy or enhancing the roughness on the hydrophobic substrate are recommended [21]. The results from CA proved the role of Nano sized TiO\(_2\) particles and CaCO\(_3\) particles with distribution, morphology and topography shown in SEM and AFM presented in figures (6-7) in the preparation of superhydrophobic bricks surfaces.
Table 4. CA results

| Samples No.            | CA       |
|------------------------|----------|
| Uncoated sample        | 0.000    |
| MM5 (PS 20%)           | 94.4771° |
| TMCC3 (T 0.6%)         | 154.9627°|
| CTMCC2 (T 0.6%\ CaCO₃) | 167.3987°|

3.4 Atomic Force Microscopy

Fig (6) show the topographic structure in 3D view for T 0.6% and T 0.6%\ CaCO₃ samples. In general the topography of samples surface can be considered uniform and dense and it can be observed that the roughness average of sample TMCC3 (T 0.6%) is (1.38nm) and the roughness average of sample CTMCC2 (T 0.6%\ CaCO₃) is (2.97nm) Furthermore, that is the roughness increased with increased the CaCO₃ addition.
3.5 SEM results

Fig. 7 gives the SEM images of sample CTMCC2. Further observations can indicate porous morphology characterized by clear distribution of the nano TiO2 particles and larger CaCO3 modification particles. It is well known, that such film whose water contact angle is higher than 150°, 167.3987° are the subject of great interest because these superhydrophobic films, are resulted by combining appropriate surface roughness of the modification particles with matrix surfaces of probably low surface energy.

4. Conclusion

1- In this work, we could develop an inexpensive and facile method to fabricate superhydrophobic coating on the brick surfaces by the composite coating of Polystyrene PS modified using nano-TiO2 and CaCO3 particles.
2- After modifying, the contact angle value CA of %20PS/%6TiO2/1gCaCO3 is 167.3987°.
3- CA values increased with the increasing of additions of nano-TiO2 and CaCO3.
4- AFM results proved that the composite coatings have dens topography with roughness increased with increasing of the CaCO3 addition.
5- SEM observations showed porous morphology characterized by clear distribution of the nano TiO$_2$ and larger CaCO$_3$ modification particles.

6- Because of super hydrophobic property of the coating layer and singular micro/nano structure, nano-TiO$_2$/CaCO$_3$ coatings are predicted to draw tremendous interest and wide practical applications.

References

[1] C. Gomez-Polo, S. Larumbe, A. Gil, D. Muñoz, L. Rodríguez Fernández, L. Fernández Barquín, A. García-Prieto, M.L. Fdez-Guibieda, A. Muela, Improved photocatalytic and antibacterial performance of Cr doped TiO$_2$ nanoparticles, Surfaces and Interfaces 2021.

[2] Elsayed T. Helmy, Elsayed M. Abouellef, Usama A. Soliman, Jia Hong Pan, Novel green synthesis of S-doped TiO$_2$ nanoparticles using Malva parviflora plant extract and their photocatalytic, antimicrobial and antioxidant activities under sunlight illumination, Chemosphere, Volume 271, 2021.

[3] Anaya-Esparza, L.M.; Villagrán-de la Mora, Z.; Ruvalcaba-Gómez, J.M.; Romero-Toledo, R.; Sandoval-Contreras, T.; Aguilera-Aguirre, S.; Montalvo-González, E.; Pérez-Larios, A. Use of Titanium Dioxide (TiO$_2$) Nanoparticles as Reinforcement Agent of Polysaccharide-Based Materials. Processes 2020, 8, 1395.

[4] Ziental, D.; Czarczynska-Goslinska, B.; Mlynarczyk, D.T.; Glowacka-Sobotta, A.; Stanisz, B.; Goslinski, T.; Sobotta, L. Titanium Dioxide Nanoparticles: Prospects and Applications in Medicine. Nanomaterials 2020, 10, 387.

[5] Katal, Reza, et al. “A review on the synthesis of the various types of anatase TiO$_2$ facets and their applications for photocatalysis.” Chemical Engineering Journal 384 (2020): 123384.

[6] Arrigoni, Marco, and Georg KH Madsen. “A comparative first-principles investigation on the defect chemistry of TiO$_2$ anatase.” The Journal of Chemical Physics 152.4 (2020): 044110.

[7] Tahir, Muhammad B., et al. “Role of Nanotechnology in Photocatalysis.” Reference Module in Materials Science and Engineering (2020).

[8] Lasso, H.I.D., Rosales, B.S.: Advances in chemical engineering, photocatalytic technologies. (35), 140–141.

[9] Fujishima, A., Zhang, X.: Titanium dioxide photocatalysis: present situation and future approaches. C. R. Chim. 9, 750–760 (2006).

[10] Nakata, K., Liu, B., Goto, Y., Ochiai, T., Sakai, M., Sakai, H., Murakami, T., Abe, M., Fujishima, A.: Visible light responsive electrospun TiO$_2$ fibers embedded with WO$_3$ nanoparticles. Chem. Lett. 40, 1161–1162 (2011).

[11] Heinonen, Saara, et al. “Antibacterial properties and chemical stability of superhydrophobic silver-containing surface produced by sol–gel route.” Colloids and Surfaces A: Physicochemical and Engineering Aspects 453 (2014).

[12] Moreira, Joana, A. Catávina Vale, and Natália M. Alves. “Spin-coated freestanding films for biomedical applications.” Journal of Materials Chemistry B (2021).

[13] Park, Nam-Gyu, and Kai Zhu. “Scalable fabrication and coating methods for perovskite solar cells and solar modules.” Nature Reviews Materials 5.5 (2020): 333–350.

[14] Hu, Lifang, Weitao Han, and Hao Wang. “Resistive switching and synaptic learning performance of a TiO$_2$ thin film based device prepared by sol–gel and spin coating techniques.” Nanotechnology 31.15 (2020): 155202.

[15] Cheraghcheshm, Fatemehe, and Vahid Javanbakht. “Surface modification of brick by zinc oxide and silver nanoparticles to improve performance properties.” Journal of Building Engineering 34 (2021): 101933.

[16] Alhilouro, E. A., S. A. Kubba, and A. F. Dirweesh. “Nanotechnology use to preserve the durability of archaeological brick buildings in Al-Najaf city.” IOP Conference Series: Materials Science and Engineering. Vol. 1067. No. 1. IOP Publishing, 2021.
[17] JIWEI HUANG, YONGQUAN QING, CHUANBO HU, FALONG WANG, and QIAN MO, "Development of a simple method for the fabrication of superhydrophobic coating of nanoTiO2/CaCO3 Composite" OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS. Vol. 8, No. 11-12, Nov. – Dec. 2014, p. 1225 - 1228