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Development of self-cleaning bricks surfaces by $CaCO_3$modified nano-TiO_2 composite coatings

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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 CaCO3 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/%6TiO_2/1g$CaCO_3$ coatings, could give promised effect in modification of bricks surfaces from superhydrophilic substrates to Superhydrophobic with higher contact angle 167.3987$^{o.}$ These results will encourage the future research in surface engineering of bricks surfaces using CaCO3 particles for self-cleaning and environmental applications.
Keywords: TiO_2 nanoparticls, $CaCO_3$, 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 $CaCO_3$ particles with TiO_2 nanoparticles-based polymer composite coatings in surface engineering of bricks by spin process for environmental and self- cleaning applications.

2.Experimantal work

2.1 Materials

The titanium oxide used in this work was a nano anatase type (TiO_2) 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 ($CaCO_3$) 98%,purchased from Sinopharm chemical reagent Co.,Ltd was used for the enhancement of coatings.

Table1. Ratios of the polymer matrices in the coating solutions

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 mm^3.

Before coating, all the samples' surfaces were washed, polished, cleaned with ethanol, and dried in oven at 100^o 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 TiO2 modified composite coatings (TMCC).

Table2. Ratios of TiO_2 additions in the composite coating solutions

Samples No.	Additives	
	Matrix	TiO_2(g)
TMCC1	PS(2g)+ DMF(8g)	0.02
TMCC 2	PS(2g)+ DMF(8g)	0.04
TMCC 3	PS(2g)+ DMF(8g)	0.06

Table 3. Ratios of $CaCO_3$ modified composite coating solutions

Samples No.	Additives	
	Composites	$CaCO_3$(g)
CTMCC 1	TMCC 3	0.5
CTMCC2	TMCC 3	1

Finally, Calcium carbonate particles were added to the composite coating solutions according the ratios shown in [table 3], to investigate the properties of CaCO3and 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 100º 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-TiO2 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).

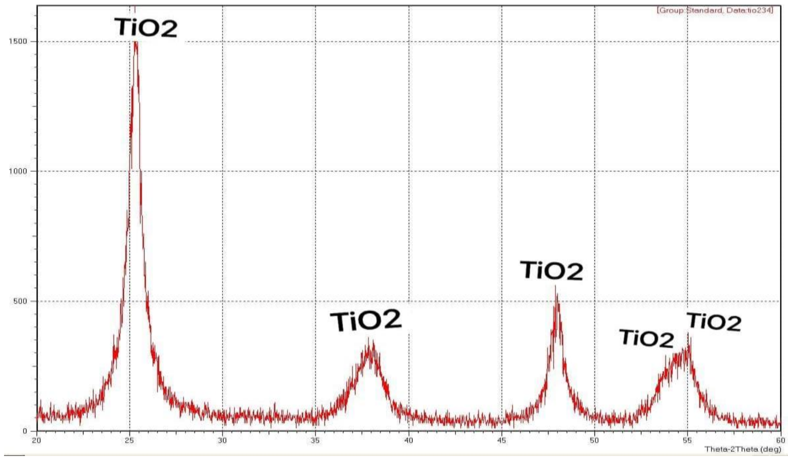


Figure 1.XRD patterns of nano-TiO2 particles

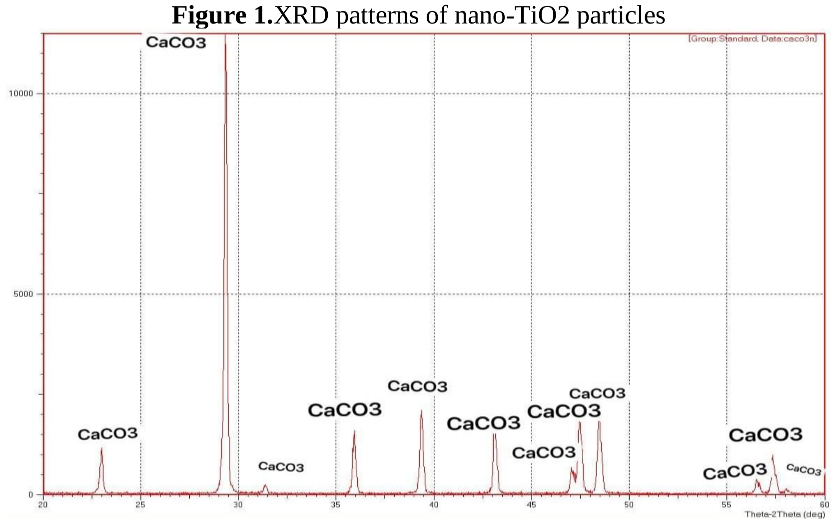
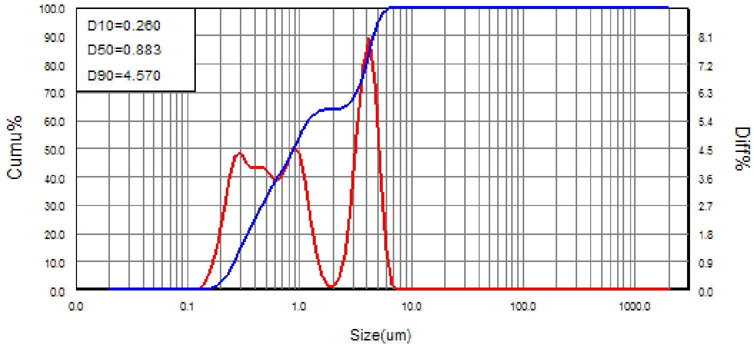


Figure 2.XRD patterns of $CaCO_3$ particles

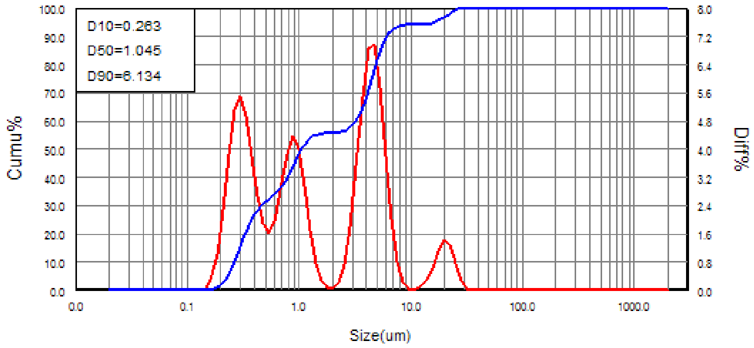
3.2 PSA Results

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 (0.202µm-5.350µm) with a mean value of (0.883µm). Also, the size of particles for $CaCO_3$ powder distributed in the range of (0.213µm-19.94µm) with a mean value of (1.045µm). Such results are necessary to better understand the behavior of the hydrophobized TiO_2/$CaCO_3$coatings.



Diam um	Percent
0.100	0.00
0.200	2.80
0.500	32.00
1.000	54.59
2.000	63.85
5.000	94.92
10.000	100.00
20.000	100.00
45.000	100.00
75.000	100.00

Figure 3.particle size of nano-TiO_2 powder



Diam um	Percent
0.100	0.00
0.200	1.77
0.500	31.13
1.000	48.46
2.000	55.85
5.000	81.66
10.000	94.13
20.000	97.03
45.000	100.00
75.000	100.00

Figure 4.particle size of $CaCO_3$ powder

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^o for CTMCC2 samples (T 0.6%1 $CaCO_3$)

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.

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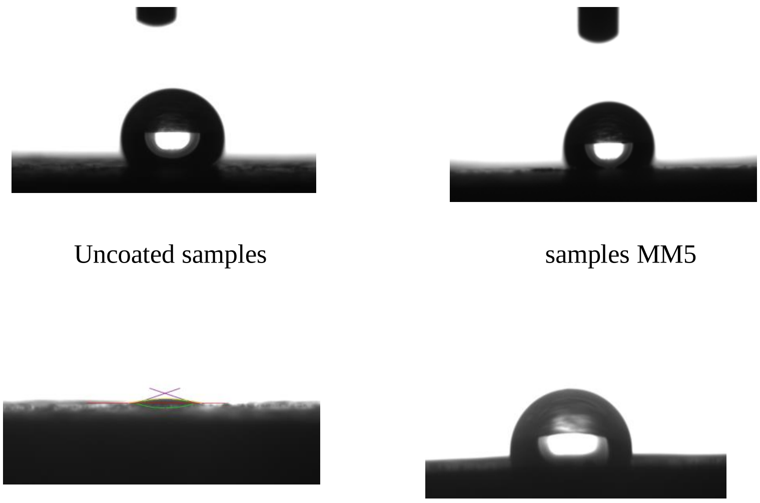
Table 4. CA results

Samples No.	CA
Uncoated sample	0.000
MM5 (PS 20%)	94.4771^{o}
TMCC3 (T 0.6%)	154.9627^{o}
CTMCC2 (T 0.6%1 $CaCO_3$)	167.3987^{o}



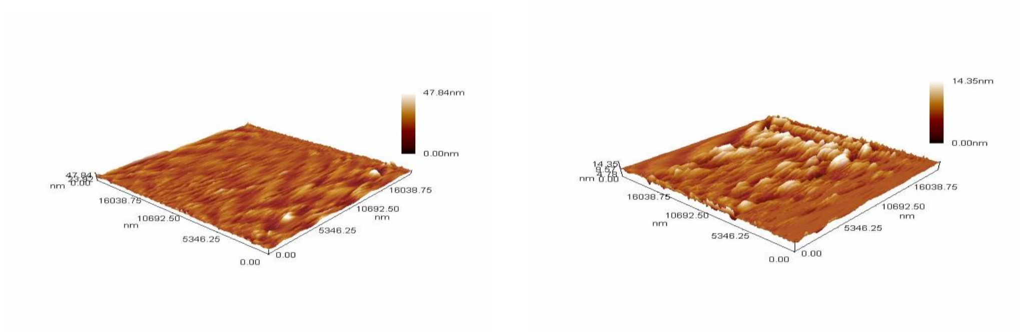
Uncoated samples   samples MM5

samples TMCC3   samples CTMCC2

Figure 5. Contact angle results

3.4 Atomic Force Microscopy

Fig (6) show the topographic structure in 3D view for T 0.6% and T 0.6%1C 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%1 CaCO3) is (2.97nm) Furthermore, that is the roughness increased with increased the CaCO3 addition .



(a) (b)

Figure6.AFM results (a) sample TMCC3 (b) sample CTMCC2

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° , 167.3987º are the subject of great interest because these super-hydrophobic films, are resulted by combining appropriate surface roughness of the modification particles with matrix surfaces of probably low surface energy.

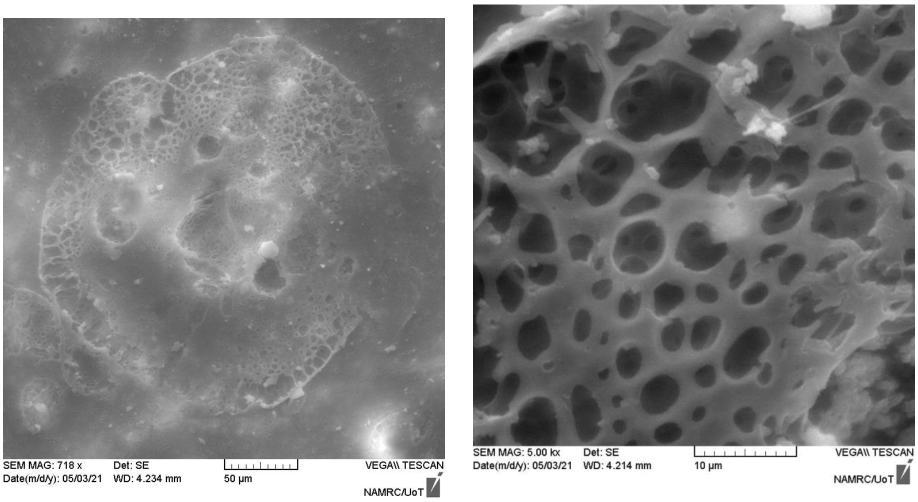


Figure7.SEM. images of the sample CTMCC2

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-$TiO_2$and $CaCO_3$ particles.

2- After modifying, the contact angle value CA of %20PS/%6TiO2/1gCaCO3 is 167.3987º .

3- CA values increased with the increasing of additions of nano-TiO_2 and $CaCO_3$.

4- AFM results proved that the composite coatings have dens topography with roughness increased with increasing of the $CaCO_3$ addition.

5- SEM observations showed porous morphology characterized by clear distribution of the nano TiO_2 particles 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.

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