



Self- Cleaning Materials: Review of Recent Progress and Innovations

Aniedi E. Nyong¹*, Idara O. Peter¹, Joachim J. Awaka-Ama¹, Godwin J. Udoh¹

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Abstract

This paper is a review of some of the trends in the theoretical conception and development of self-cleaning materials for various applications. This review is significant as it highlights briefly the various research activities in the area of selfcleaning materials. Beyond the Wenzel, Cassie-Baxter and Young's Models that are used in theoretically examining the concept of selfcleaning, there is advancement of modelling and simulation of contact angles behaviour to include the effect of gravitational forces.

Aniedi E. Nyong: <u>aniedinyong@aksu.edu.ng</u>

¹ Department of Chemistry, Akwa Ibom State University, Ikot Akpaden, Akwa Ibom State Furthermore, research trends in three (3) different areas, namely; self-cleaning glasses, self-cleaning fabrics and self-cleaning cements have been discussed in some details. It has been noted that researches have focused on the use of photocatalyst, mainly TiO_2 and SiO_2 , to generate self-cleaning surfaces that are capable of photodegrading organic matter. These photocatalysts are added *in-situ* to the materials or coated on to the materials' surfaces. Different methods of coating of these photocatalysts on to the surfaces of the materials have been developed. Some of these coating methods that have seen great interest recently are the pad-dry cure and sol-gel coating methods.

Keywords Self-cleaning; Photocatalyst; Superhydrophobic; Superhydrophilic



1.0 Introduction

Self-cleaning materials have over the years, garnered considerable attention in the areas of Chemistry, Materials science as well as Engineering both in research and in commercial applications. The potential applications of the self-cleaning materials include self-cleaning clothes and textiles (Diaa and Hassabo, 2022); smart automotive coatings and concretes (Tupcu et al., 2020); agricultural tools, glasses, optical appliances and aerospace gadgets (Dodiuk and These Kenig, 2009; Gunnarsson, 2012). materials require less mainte-nance and are aesthetically pleasing for a longer period of time compared to normal materials.

The various self-cleaning technologies, as with several man-made technologies, derive their inspiration from nature. Self-cleaning activity is predominant in nature, as in the cases of the lotus plant (Nelumbo nucifera), butterfly wings (Bhushan and Jung, 2011), as well as in fish scales (Banerjee et al., 2015) etc. The lotus effect, which is attributed to the botanist -Wilhelm Barthlott, is derived from the lotus flower's unique ability to keep itself clean. Investigation of the chemistry and morphology of the lotus flower's surface reveals that it possesses a special nano-structured surface, made up of micro-sized projections and a layer hydrophobic nano-structured of waxy, crystalloids (Dodiuk and Kenig, 2009). The waxy surface of the lotus leaves combined with the presence of the micro-nanostructures result in an extremely hydrophobic surface. Consequently, it is the hydrophobicity that repels.

Broadly, self-cleaning surfaces can be categorized into two types namely the hydrophobic surfaces and the hydrophilic surfaces. The surfaces showing water contact angles greater than 90° are termed as hydrophobic whereas those surfaces with water contact angles greater than 150° are termed as super hydrophobic. A super hydrophobic surface is considered to be a surface that repels water almost perfectly and causes water drops to assume a near- spherical shape along with a low roll-off angle. Similarly, a surface showing water contact angles less than 90° is called a hydrophilic surface and if the water contact angle is less than 10° , it is called a superydrophilic surface (Sivakumar et al., 2013).

This review paper is necessary as it will highlight briefly the various research activities in the area of self-cleanning materials. This review is therefore an overview of the recent progress in self-cleaning technology with emphasis on the theoretical conceptions, selfcleaning fabric, glasses, smart coatings and concretes.

2.0 Theoretical Conceptualization of Self-Cleaning Phenomena

The primary parameter that is used in the conceptualization of the wettability of a material is the static contact angle, which is the angle that a liquid makes with a surface. The contact angle has been found to be dependent on some factors namely the surface energy and surface roughness (Bhushan and Jung, 2011). The static contact angle, θ , is determined by the tangent angle between the smooth solid surface and the liquid meniscus outline.



Using the Young's equation, the surface wettability is expressed in terms of cosine value of the static contact angle, θ by equation (1).

$$\cos\theta = \frac{Y_{SG} - Y_{SL}}{Y_{LG}} - - - - \quad (1)$$

where γ_{SG} , γ_{SL} and γ_{LG} are the interfacial surface tension at the solid/gas, solid/ liquid and liquid/gas interfaces respectively (Sun and Bohringer, 2019).

From literature however, it has been shown that the contact angle (θ) measurement is not always highly reproducible. The real contact angle θ therefore can take any value within the range of $\theta_R \le \theta \le \theta_A$, (where θ_A and θ_R are defined as the advancing and receding angles, respectively). The difference between θ_A and θ_R is termed as hysteresis, and both θ_R and θ_A are characteristics of the surface-chemistry, texture and topography (Banerjee *et al.*, 2015).

The Young's model of determining contact angle expressed in equation (1) is valid only for ideal solid surfaces, which are chemically homogenous, inert, rigid and smooth. Beyond the Young's model, the Wenzel model considers that the wetting of a rough surface by a liquid droplet involves contact with the entire surface and complete penetration into the cavities on the surface. For such a rough surface, the "apparent" contact angle θ_{app} for a liquid droplet is related to the "true" contact angle θ_s of the droplet on a smooth surface by Equation [2].

$$\cos\theta_{app} = r \cos\theta_s \quad \dots \quad (2)$$

where the surface roughness factor r is defined as the ratio of geometric surface area to the actual surface area. The Wenzel model predicts that a hydrophobic surface (θ >90⁰) becomes more hydrophobic with an increase in surface roughness r while a hydrophilic surface ($\theta <$ 90°) becomes more hydrophilic with an increase in r (Bhushan and Jung, 2011). The Cassie-Baxter model on the other hand does not postulate complete penetration of a liquid droplet into the surface cavities and heterogeneities as can be seen in figure 1. Accordingly, in the Cassie- Baxter model, the "apparent" contact angle θ_{app} for a liquid droplet on a rough surface is related to the "true" contact angle by equation (3);

$$\cos \theta_{app} = f_s \cos \theta_s + f_v \cos \theta_v - \dots$$
(3)

where f_s and f_v are the area fraction of the liquid droplet in contact with the solid surface and the area fraction of the liquid droplet in contact with the vapour trapped in the cavities on the rough surface, respectively, and θ_v is the contact angle of the liquid in air. For $\theta_v = 180^\circ$, and $f_{s+} f_{v}=1$, equation (3) becomes (4) (Sun and Bohringer, 2019).

$$\cos\theta_{ann} = 1 + f_s(\cos\theta_s + 1) \quad ----- \quad (4)$$

The illustration of the water droplet behaviour on the surface structure for the Wenzel and the Cassie-Baxter models is presented in Figure 1. As can be seen Figure 1 (A), the water droplet completely wets the surface and the apparent contact angle is given by the Wenzel model in equation 2 while in Figure 1 (B) the wetting of the surface is not complete and the apparent contact angle is derived from the Cassie-Baxter model in equations 3 and 4. It should be noted however that the above models do not take into consideration the effect of gravitation on the form of the contact angles. These models therefore lead to a certain level of imprecision in the estimation of the water contact angles.



Thus, the recent trend in the simulation of the behaviour of contact angles/contact angle hysteresis involves the consideration of the gravitational force factor (Xu et al, 2016; Karim et al., 2021). Based on these theoretical

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concepts, the various applications to which these ideas have been put to and the advances recorded in these applications are discussed below under self-cleaning glasses, self-cleaning fabrics, self-cleaning coating and paints.



Fig. 1: Effect of the surface structure on the wetting property of a solid surface. (A) Wenzel wetting model (B) Cassie-Baxter wetting model

3.0 Research Trends in Developing Self-Cleaning Glass, Self-Cleaning Fabrics and Self-Cleaning Cements and Concretes

3.1 Self- Cleaning Glass

Self- cleaning glasses are superhydrophillic glasses made from very thin layer of titanium dioxide (TiO_2) or silicon dioxide (SiO_2) nanoparticles, which are in the order of 10-25nm (Worasukhkhung et al, 2012). Beyond being self-cleaning in nature, these glasses are known to be multifunctional in nature with other inherent properties for anti-fogging, antireflective and anti-abrasive uses. The selfcleaning effect is achieved through a series of photocatalytic reactions within the titanium dioxide (TiO_2) thin film coating. The thin film of TiO₂ must be activated through exposure to ultraviolet (UV) radiation where the TiO₂ reacts with the oxygen and water molecules in the air leading to oxidative species that result in photo generated electrons and holes.

When dirt and dust deposit on the surface of the glass as a result of natural weathering, the generated electrons will reduce oxygen to water (vapour) and the holes will oxidize the organic matter, thereby deteriorating the dirt and dust (Sun and Bohringer, 2019). Depending on the wettability of the surface, which is characterized as either hydrophilic or hydrophobic, the dust is washed away when it rains.

TiO₂ thin films embedded with plasmonic gold nanoparticles interacted effectively with visible light. The results showed water contact angle value of $(12 \pm 3)^{\circ}$ for a 0.5 wt % AU- embedded TiO₂ coating under dark conditions and contact angle of $(5 \pm 2)^{\circ}$ under ultra-violet light irradiation, proving the superhydrophilic nature of the films (Peeters et al, 2020). In a related study, the formation of hybrid assembly of inorganic-organic layers based on sol-gel derived titania (TiO₂)/dodecylamine was reported (Kartini et al., 2014). In the study, onestep and layer-by-layer dip-coating approaches were compared, as well as the effect of film annealing rates on the hydrophobicity of the glass surfaces. The results showed that slow annealing rate combined with layer-by-layer sol-gel dip-coating produced robust coating with reasonable transparency although the report also indicated that the film transparency decreased with increasing coating times.

Superhydrophobicity with water contact angle of 155.5 ° was observed for translucent hybrid film after three-time coating at C/Ti mole ratio of 7.

Detailed research has also revealed that TiO₂/carbon nanotube (CNT) composite would a promising candidate to enhance be photocatalytic performance of self-cleaning glass. Beyond the direct use of carbon nanotube additives, a polymer-assisted approach to synthesize TiO₂/CNT thin films has been developed (Yi et al., 2016). Polyethylenimine was used to effectively combine Ti⁴⁺ with CNTs for film formation of TiO2/CNT. The water contact angles (WCA) of pure TiO₂ thin films and TiO₂/CNTs thin films indicated 7.2 $^{\circ}$ and 3.6 ° respectively, which are indicative of the superhydrophilic nature of the surfaces.

3.2 Self-Cleaning Fabric

Textile products play an important role as one of man's basic needs. There has been continuous improvement and innovation in the area of Chemistry in regards to textile finishing. Recent scientific interest has grown enormously in areas such as fabric softness, durability, breathability, water repellence, flame resistance and anti-microbial property (Afzal et al, 2014). To this end, concerted efforts have been made to produce finished products with multiple characteristics. The dip-pad-dry-cure process has been used to create bonds between nanoparticles and fabrics. For instance, nano-TiO₂ pre-treatment to enhance the self cleaning capacity has been investigated with cotton fabric (Chaudari et al, 2012). The cotton fabric was treated with nano- TiO₂ by pad-dry-cure method.

Similarly, TiO_2 nanosol has been applied directly on textiles by pad-dry-cure method. The fabric was dipped in TiO₂ nanosol and left for 3 minutes, then passed through a two-roller laboratory padder, oven dried and cured for 10 minutes at 130°C. SiO₂ was used as a binder since it prevents textile from degradation during the photocatalytic activity of TiO₂ (Ortelli et al., 2015). High-resolution transmission electron microscopy infrared (HRTEM) and spectroscopy of the materials showed that corrosion of the upper layers of cotton would occur under daylight irradiation, if there was no SiO₂ as a binder.

Afzal et al., (2014) prepared a superhydrophobic cotton fabric exhibiting selfcleaning properties under visible light by stepwise deposition of anatase TiO₂, meso-tetra (4carboxyphenyl) porphyrin (TCCP) and trimethoxy (octadecyl) silane (OTMS). The exhibited modified cotton excellent superhydrophobicity with WCA of 156[°] as well as photocatalytic degradation of methylene blue under visible light irradiation. Yuranova et al., (2007) used a different approach of surface modification to modify polyester and wool (90%-polyamide, 10% wool) to achieve selfcleaning activity. This involved introducing negative groups such as -COO⁻, O-O⁻ by radiofrequency plasma (RF-Plasma), microwave plasma (MW-plasma) and vacuum - ultraviolet irradiation. The fabrics were exposed under visible light in reasonable time to allow the TiO₂ coatings to discolor wine and coffee stains.



The results obtained indicated that the nanoparticles of TiO_2 remained fairly stable on the textile surface after the photochemical discoloration of the stains showing high photo-activity.

3.3 Self Cleaning Cements and Concretes

Environmentalists as well as other researchers have been working on different techniques that can be used in controlling indoor and outdoor pollutants. These cements possess environmental benefits for the reduction of pollutants (Topcu et al, 2020). Trends in research on the development of self-cleaning cement, from 2015 are briefly discussed in the following paragraphs.

The self-cleaning capability of mortars and concrete containing TiO₂ has been a subject of investigation. The effect of the contact with dyes showed that the concrete effectively decolourized specific organic dye up to 90% self-cleaning efficiency, signifying its effectiveness (Mendoza al. 2015). et Furthermore, photocatalytic concrete with very smooth surfaces have been created to determine the self cleaning effectiveness. The cement consisted of calcium silicate hydrates and TiO₂ nanoparticles (Shen et al, 2015). This research showed that the TiO₂ nanoparticles found in the concrete caused the photodegradation of methyl-blue dye and due to the ultra smoothness of the surface, hydrophillicity was achieved.

The use of self cleaning cements with photocatalytic properties for the maintenance of external features and facades of buildings have been studied (Andalora et al, 2016). In this case, TiO_2 based coatings were applied directly to concretes used for building facades. After preliminary laboratory measurements to determine the water contact angles, outdoor evaluation for a 36 months duration, showed that the coated concrete facades were cleaner after exposure to the environment.

The use of sol-gel chemistry to generate metal oxides such as TiO_2 and SiO_2 has been extended to cement for self-cleaning purpose. For instance TiO_2 and SiO_2 photocatalysts generated via the sol-gel method have been used as coating on hardened concrete for self-cleaning effect (Koli et al, 2019). Equally, composite catalysts consisting of a mixture of different photcatalyts have been loaded into cement matrix to enhance their self-cleaning qualities. For example, a composite photocatalyst consisting of nano TiO_2 was loaded into recycled clay, bricks and recycled glass and the self- cleaning behaviour studied (Chen et al, 2020).

Based on the above, research into self-cleaning concrete has seen a vast use of photocatalyst such as TiO_2 and SiO_2 both as *in-situ* additives or external coatings. These photocatalysts are used either individually or as mixtures/composites. Research has equally been scaled up beyond the laboratory as can be seen in self-cleaning concrete facades being studied for their environmental friendliness.

4.0 Conclusion

Self-cleaning technology is a novel view that is witnessing enormous interest due to the various eco-friendly, time and energy conserving applications. Therefore, a proper understanding of the underlying scientific basis of this phenomenon is vital in enhancing its use in other potential areas of application such as antibiofouling paints, anti-fouling glasses that can be used in various areas. In this review, the



research direction is in the development of selfcleaning glasses, self-cleaning fabrics as well as self-cleaning cements/concretes, which have been highlighted. We have seen that the research emphasis is on the use of photocatalysts of various kinds to induce selfcleaning via photodegradation. Although great progress has been recorded in the synthesis of superhydrophobic and superhydrophilic selfcleaning materials, there are still many obstacles that need to be eliminated to make them commercially useful.

5.0 References

- Afzal, S., Daoud, W. A. and Langford, S. J. (2014). Superhydrophobic and Photocatalytic Self-cleaning Cotton. Journal of Materials Chemistry A, 2, 18005 18011.
- Andalora A., Mazzucchelli E.S., Lucchini A., Pedeferri M.P., (2016), Photocatalytic selfcleaning coatings for building facade maintenance. Performance analysis through a case-study application, Journal of Facade Design and Engineering, 4, 1115- 129.
- Banerjee, I., Dionysiou, D. D., and Pillai, S. C. (2015). Self-cleaning Applications of TiO₂ by Photo-induced Hydrophilicity and Photocatalysis. *Applied Catalysis B: Environmental*, 176, 396-428.
- Bhushan, B and Jung, Y. C. (2011).Natural and Biomimetic Artificial Surfaces for Superhydrophobicity, Self-cleaning, Low Adhesion and Drag Reduction. Progress in Materials Science, 56, 1-108.
- Chen X., Kou S., Poon C., (2020) Rheological behaviour, mechanical performance, and NOx removal of photocatalytic mortar with

combined clay brick sands-based and recycled glassbased nano- TiO_2 composite photocatalysts, Construction and Building Materials, 240. 117698.

- Diaa, M. and Hassabo, (2022).Self-cleaning Properties of Cellulosic Fabrics - A Review.Biointerface Research in Applied Chemistry, 12(2), 1847-1855.
- Dodiuk, H. and Kenig, S. (2009). Self-cleaning Coatings. Surface Engineering, 25(2), 89-92.
- Gunnarsson, S. G. (2012). Self-cleaning Paint: Introduction of Photocatalytic Particles into a Paint System. Technical University of Denmark.
- Karim, A. Fujii, K. Kavenhpour, H. (2021). Contact line dynamics of gravity driven spreading of liquids. Fluid Dynamics Research.53(2), 035503.
- Kartini, I. Santoso, S. J., Febriyanti, E., Nugroho, O. R., Yu, H., and Wang, L. (2014).Hybrid Assembly of NanosolTitania and Dodecylamine for Superhydrophoboc Self-cleaning Glass.Journal of Nanoparticle Research, 16, 2514.
- Koli V.B., Mavengere S., Kim J. (2019) An efficient one-pot N doped TiO₂-SiO₂ synthesis and its application for photocatalytic concrete, Applied Surface Science 491, 60–66.
- Mendoza, C., Valle, A., Castellote, M., Bahamonde, A., Faraldos, M., (2015). TiO₂ and TiO₂-SiO₂ coated cement: Comparison of mechanic and photocatalytic properties, Applied Catalysis B: Environmental, 178, 155-164.



- Ortelli, S., Costa, A. L. and Dondi, M. (2015). TiO₂ Nanosols Applied directly on Textiles using different Purification Treatments. Materials, 8, 7988-7996
- Peeters, H., Keulemans, M., Nuyts, G., Vanmeert, F., Li, C., Minjauw, M., Detavernier, C., Bals, S., Lenaerts, S. and Verbruggen, S. W. (2020). Photocatalytic Self-cleaning Coatings with Embedded Plasmonic Gold Nanoparticles.
- Shen W., Zhang C., Li Q., Zhang W., Cao L., Ye J., (2015) Preparation of titanium dioxide nano particle modified photocatalyticselfcleaning concrete Journal of Cleaner Production, 87, 762-765.
- Sivakumar, A., Murugan, R., Sundaresan, K. and Periyasamy, S. (2013). UV Protection and Self-cleaning Finish for Cotton Fabric using Metal Oxide Nanoparticles. Indian Journal of Fibre and Textile Research, 38, 285-292.
- Sun, D. and Bohringer, K. F. (2019). Selfcleaning: From Bio-inspired Surface Modification to MEMS/Microfluidics System Integration. Micromachines, 10, 101.

- Topcu, I. B., Akkan, E., Uygunoglu, T. and Caliskan, K. (2020). Self-cleaning Concretes: An Overview. Journal of Cement Based Composites, 2, 6-12.
- Worasukhkhung, S., Pudwat, S., Eiamchai, P., Horprathum, M., Dumrongrattana, S. and Aiempanakit, K. (2012). Hydrophilic Property of TiO₂ Films Sputtered on Glass/ITO for Self-cleaning Glass and Heat Mirror Application. Procedia Engineering, 32, 780-786
- Xu, Q. Zhang, W. Dong, C. Sreeprasad, S. (2016). Biomimetic Self-cleaning Surfaces: Synthesis, Mechanism and Application. Interfaces, 13, 20160300
- Yi, Q., Wang, H., Cong, S., Cao, Y., Wang, Y., Sun, Y., Lou, Y., Zhao, J., Wu, J., and Zou.
 G. (2016). Self-cleaning Glass of PhotocatalyticAnatase TiO₂ and Carbon Nanotubes Thin Film by Polymer Assisted Approach. Nanoscale Research Letters, 11, 457.
- Yuranova, T., Laub, D., Kiwi, J. (2007).Synthesis, Activity and Characterization of Textiles showing Selfcleaning Activity under Daylight Irradiation. Catalysis Today, 122, 109-117.

