Technical Leaflet

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Titanium Dioxide Based Nanotechnology for Smart and Functional Coatings

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Abstract

Nano titanium dioxide produced from the sol-gel method forms an easy route to waterborne sols that can be directly applied as a coating following commonly used application methods. Coatings based on sol-gel prepared nano titanium dioxide were applied on to glass showing minimal effect on the transparency of the glass. SEM (Scanning Electron Microscopy) and AFM (Atomic force microscopy) showed that the coating had an open structure with a particle size of 16nm and an average rugosity of 29nm. These coatings are superhydrophilic upon light activation, which results in decreased water contact angle and demonstrate antistatic behaviour. Moreover, the coating was able to breakdown organic and inorganic matter according to ISO27442 and ISO1096-5 standards for the breakdown of these types of materials. In a real-life performance test coated solar panels were able to produce on average 1% more power.

Introduction

Nanomaterials and their use

Nanotechnology is defined as the systematic manipulation, fabrication, or modification of structures, systems, materials, or components in the range of atomic or molecular dimensions between 1 nm and 100 nm (1 nm = 10^{-9} m) (Goedicke et al., 2008,[i]).

Nanotechnology is often referred to as the bottom-up method of manufacturing (Figure 1), as opposed to the 'traditional' top-down method, which uses high-energy processes such as grinding and milling. As a matter of fact, even with high energy processes, it is hardly possible to get to particles less than 100nm, due to the difficulty to breakdown the thermodynamically favourable crystal structure. Nanotechnology, on the other hand enables the creation of smaller particles with greater control and energy efficiency. Nanomaterials can be processed into a variety of applications and are found back in pharmaceuticals, smart sensors, smart textiles and smart coatings.

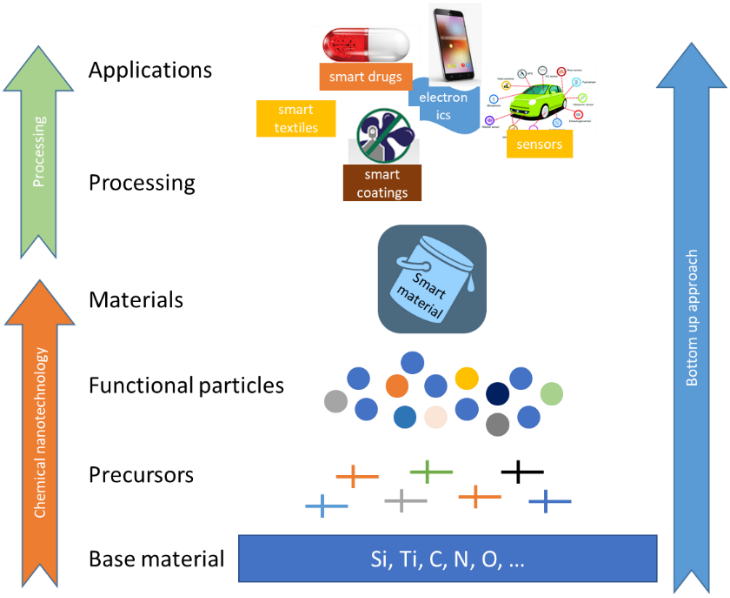

Figure 1. Bottom-up approach Nanotechnology

Sol-gel method to particles

The sol-gel method is a process used to create nanoparticles or other types of small particles by converting a solution (sol) into a solid (gel) network. The method involves 2 main steps:

1. Hydrolysis: The precursor chemicals, usually metal salts or metal alkoxides, are dissolved in a solvent, typically an alcohol or water, and then subjected to hydrolysis. In this step, the precursor molecules react with water molecules to form metal hydroxide species.
2. Condensation: The metal hydroxide species produced in the hydrolysis step start to polymerize, or condense together, to form a three-dimensional network of molecules known as a sol. This network is still in a liquid state, but it contains small particles of the desired material.

The sol can be further dried and (force) cured to obtain a strong, high, density network of metal oxides.

The sol-gel method offers several advantages over other particle fabrication methods, including precise control over particle size and shape, and the ability to incorporate a wide range of chemical elements into the particles. It is widely used in applications such as catalysis, smart coatings, and optics.

Sol-gel method to prepare nano titanium dioxide

The sol-gel method can be used to create nano-sized titanium dioxide particles, which is an ideal process to obtain highly defined particles. This method involves hydrolysis, condensation, aging, and drying steps, as summarized below, and depicted in Figure 2:

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1. Preparation of titanium precursor: A titanium precursor such as titanium isopropoxide or titanium butoxide is dissolved in a suitable solvent such as ethanol or water.
2. Hydrolysis: The titanium precursor is hydrolyzed by adding water to the solution. This leads to the formation titanium hydroxide species.
3. Condensation: The hydrolyzed species then start to condense to form a three-dimensional network of particles, the titanium dioxide sol. The size of the particles can be controlled by adjusting the concentration of the precursor and the amount of water added during the hydrolysis step.
4. Aging: The sol is allowed to age for a period of time, typically a few hours to a few days, to allow the particles to grow and the gel network to become more stable.
5. Drying: The gel is then dried at a low temperature, typically around 100-200 °C, to remove the solvent and create a solid material.

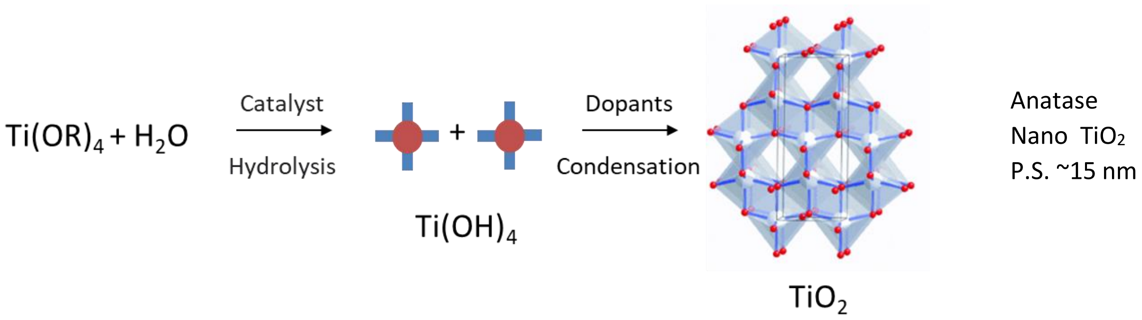

Figure 2. Sol gel method to nano titanium dioxide

The resulting material is composed of nano-sized titanium dioxide particles, predominantly in its anatase form, which have a high surface area and unique properties due to their small size. These particles can be used in a variety of applications, such as smart coatings and photocatalysis, where they catalyze chemical reactions under light irradiation. They are also used in cosmetics, where they act as a UV filter to protect the skin from harmful UV radiation.

Sol-gel titanium dioxide: from precursor to coating

The sol-gel method is commonly used as a direct process to create titanium dioxide coatings on various surfaces. After the preparation of the sol, the solution can be directly applied to the surface. The nanoparticles are dried and cured, and the resulting titanium dioxide coating exhibits several desirable properties, including high transparency, photo-activity, and good adhesion to the substrate. It is commonly used in applications such as self-cleaning, air purifying, and antimicrobial coatings. The sol-gel method provides an effective way to produce titanium dioxide coatings with precise control over their thickness and properties.

Nano titanium dioxide photocatalyst

Nano titanium dioxide photocatalysis is a process in which organic matter is decomposed under light radiation using nano-sized titanium dioxide particles as a catalyst. The mechanism of this process can be described as follows (Figure 3):

1. Absorption of light: When light is absorbed by the nano titanium dioxide particles, electrons in the valence band are excited to the conduction band, leaving behind electron holes in the valence band.

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2. Formation of reactive species: The excited electrons and electron holes can react with adsorbed oxygen and water molecules on the surface of the titanium dioxide particles to generate highly reactive species, such as hydroxyl radicals (•OH) and superoxide ions (•O^{2-}).
3. Adsorption of organic matter: The highly reactive species generated in step 2 can react with organic matter adsorbed on the surface of the titanium dioxide particles or in the surrounding solution, breaking it down into smaller, harmless molecules such as CO_2 and H_2O.
4. Regeneration of titanium dioxide: Finally, the electron holes left behind in the valence band can react with the adsorbed hydroxyl ions to form hydroxyl radicals, which in turn can react with the excited electrons to regenerate the original titanium dioxide particles.

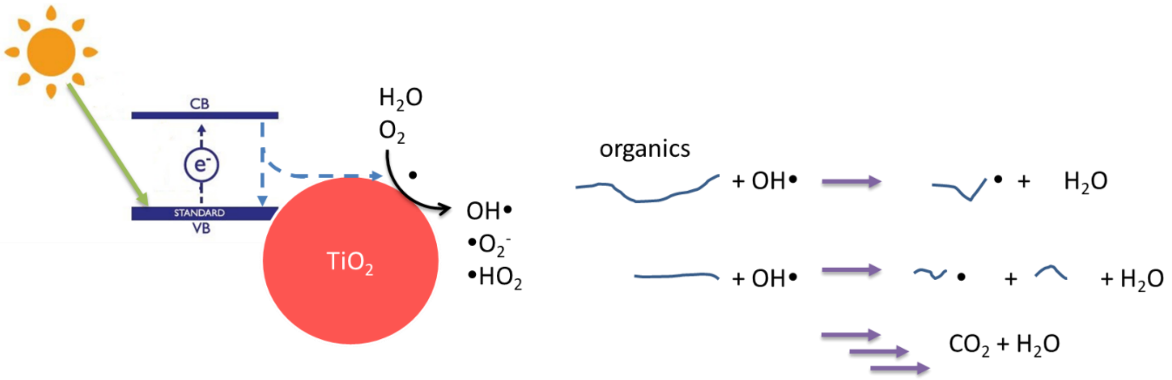

Figure 3. Mechanism Nanotitanium dioxide

Overall, the mechanism of nano titanium dioxide photocatalysis involves the generation of highly reactive species, which can oxidize and break down organic matter. This process is highly effective in removing organic pollutants from water and air and has potential applications in a variety of fields such as air purification, self-cleaning surfaces, antibacterial, antiviral and antimould coatings.

Modification – Doping

Doping of nano titanium dioxide involves the introduction of small amounts of foreign atoms into the titanium dioxide lattice, which can modify the properties of the material. In the sol-gel process there are several ways to dope nano titanium dioxide. Doping can be achieved using small amounts of metal atoms (Ag, Fe, Pt) or adding small amounts of organic species like nitrogen, phosphorus or sulphur elements. The advantage of the sol-gel process is that doping can be achieved by adding dopant precursors to the titanium dioxide sol-gel precursor solution before application. This method produces a homogeneous distribution of dopant atoms throughout the titanium dioxide lattice.

The function of doping nano titanium dioxide is to modify its electronic and optical properties, which can lead to improved performance in various applications. Doping with elements such as nitrogen, carbon, or sulphur can increase the visible light absorption of titanium dioxide, leading to enhanced photocatalytic activity[ii].

On the other hand, doping with metals such as platinum, silver, or gold promotes charge separation in titanium dioxide, which results in the improvement of its performance in applications such as water splitting or dye-sensitized solar cells[iii].

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In general, doping of nano titanium dioxide can be an effective way to tailor its properties to specific applications and improve its performance in various fields such as photocatalysis, solar energy conversion, and sensors.

Results

Application on Glass

Nano titanium dioxide sols were prepared and coated on to glass using a conventional spray gun (Krautberger) at 3 bars pressure and a nozzle size of 1mm. The objective was to create an invisible and evenly coated surface shown, by systematically zigzagging from one upper corner to the opposite lower as shown in Figure 4a. This process was repeated 2 to 6 times to obtain plates of coated glass with increasing layer thickness (Figure 4b-c).

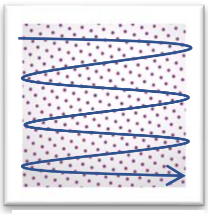

Figure 4a

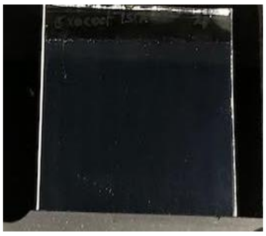

Figure 4b. 2 passes

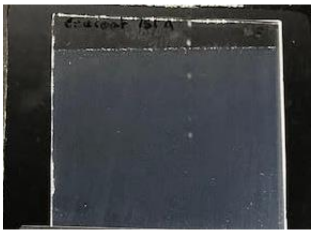

Figure 4c. 6 passes

Increasing the number of passes reduced the transparency of the plate, which could be assessed by the haze test. Haze is defined as Haze = $T_{diffuse}/T_{total}$. The haze level remained under 1% for 2 passes, which is acceptable for most applications of see-through glass. However, increasing the number of passes decreased the transparency, and the haze level increased to an average of 4% for 6 passes.

SEM and AFM analysis

Porosity of the nano titanium dioxide coating is believed increase in the travel time of organic molecules throughout the layer, which as consequence enhances their breakdown via the photocatalytic process. By utilizing SEM (Scanning Electron Microscopy) and AFM (Atomic force microscopy), we were able to inspect the surface structure and roughness of the glass plate coated with 2 passes nano titanium dioxide coating (Figure 4b) as shown in Figure 5a, b.

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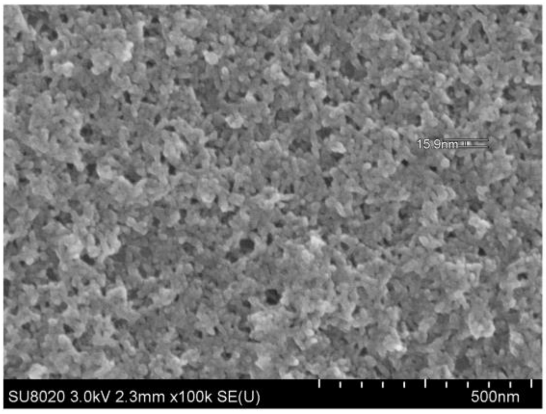

Figure 5a. SEM picture, 500nm

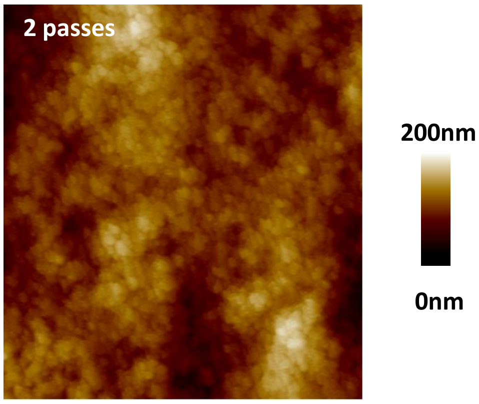

Figure 5b. AFM analysis. Scanned region: 6x6µm²

The SEM picture shows a relatively unclustered structure, allowing us to analyze a particle size of 16nm. The AFM analysis revealed an average roughness of 29nm with amplitudes reaching up to 201nm.

Antistatic and superhydrophilicity nano titanium dioxide

Under the influence of light, photocatalytic nano titanium dioxide exhibits superhydrophilicity, which can be measured by the contact angle with water. The contact angle (CA) is the angle formed by a water droplet on the surface, as shown in Figure 6. A typical contact angle for water on a coated surface, such as an acrylic-based coating, would be around 70°, whereas a superhydrophilic surface is characterized by a contact angle below 10°.

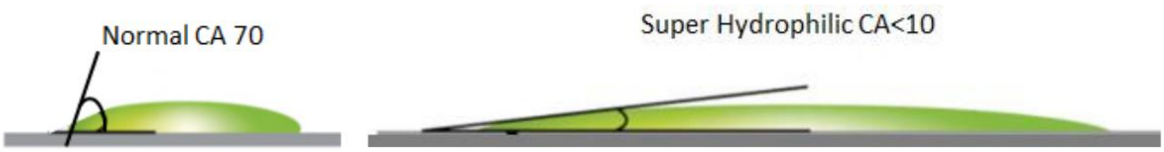

Figure 6. Contact angle.

The superhydrophilicity of activated nano titanium dioxide can be attributed to the activation of the titanium-oxygen bond, which occurs through the generation of electron-holes resulting from photo-activation. This process weakens the bond between the titanium atom and the lattice oxygen, allowing it to react with water molecules from the surrounding air and create new hydroxyl groups. As a result, the wettability of the titanium dioxide surface is transformed to a more hydrophilic state, which is referred to as photo-induced hydrophilicity[iv],[v].

Figure 7 provides a schematic of the titanium dioxide surface according to the above-mentioned mechanism.

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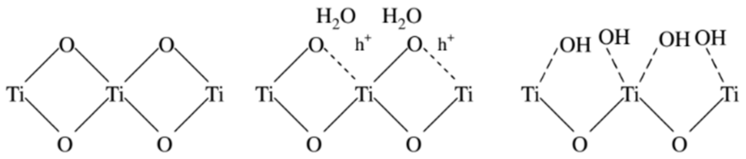

Normal Light Activation Superhydrophilic

Figure 7. Superhydrophilic nano titanium dioxide

A 4-probe surface resistance analyzer is a tool used to measure the electrical resistance of a thin film or coating on a surface. The basic principle behind the 4-probe surface resistance analyzer is the four-point probe technique, which involves placing four probes in contact with the material being measured. The two outer probes apply a constant current to the sample, while the two inner probes measure the voltage drop across the sample. The analyzer consists of four evenly spaced probes, which are typically made of tungsten or stainless steel. To use the analyzer, the sample is placed on a flat surface and the probe head is positioned on top of it. The probes are gently pressed into the material to make contact, and the current is applied to the outer probes. The voltage drop across the sample is then measured by the inner probes, and the analyzer calculates the surface resistance of the material.
A thin film of nano titanium dioxide sol-gel was subjected to the 4 probe analyzer and the results showed a resistance of 2.3 10^8 Ω/□. This indicates that the layer of nano titanium dioxide sol-gel behaves antistatic and may be expected to repel dust.

Practical test

1. A practical way to observe the impact of the surface treatment is to evaluate its response to a powder substance that would typically cause fouling, as well as its reaction to water spray. An activated surface will have a lower static charge, resulting in less attraction to dirt. As illustrated in Figure 8a, carbon powder was applied to both a plate coated with sol-gel nano titanium dioxide and a non-coated plate. The coated side (left) showed less powder adhesion. Furthermore, when the coated plate was sprayed with water, it demonstrated full wetting and self-cleaning due to the water sheeting effect (Figure 8b, left).

Figure 8a. Left side Sol-gel nano titanium dioxide, right side not treated. Throwing a powder against the plate.

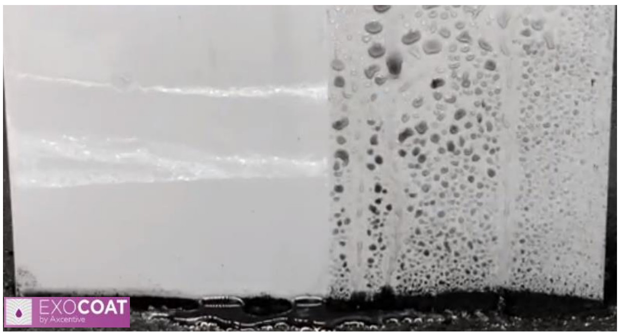

Figure 8b. Left side Sol-gel nano titanium dioxide, right side not treated. Spraying the plate with water.

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ISO27448 - Photodegradation test

ISO-Norm EN27448 describes the degradation of oleic acid with the use of photocatalytic coatings. This international standard determines the self-cleaning performance of non-porous surfaces by a measurement of the contact angle under activation with UV light. In the test a thin layer of oleic acid is applied to the sol-gel nano titanium dioxide photocatalyst-coated surface by dip coating in a 0.5% solution of oleic acid in n-heptane. After withdrawal, the surfaces are dried at 70°C (160°F) for 15 minutes. Contact angles of samples coated with oleic acid are measured before the start of light-activation and noted as initial contact angles. By exposing the samples to UV light (1 mW/cm^2 or 450 mW/sq ft), the sol-gel layer degrades the organic layer of oleic acid causing contact angles to drop as we would move to a surface only containing nano-titanium oxide which have contact angles close 0º. In (Figure 9) the water contact angle was followed at regular intervals which caused a clear drop in the case of the plate coated with nano titanium dioxide (red line) and remained the same with the non-coated reference plate (blue line).

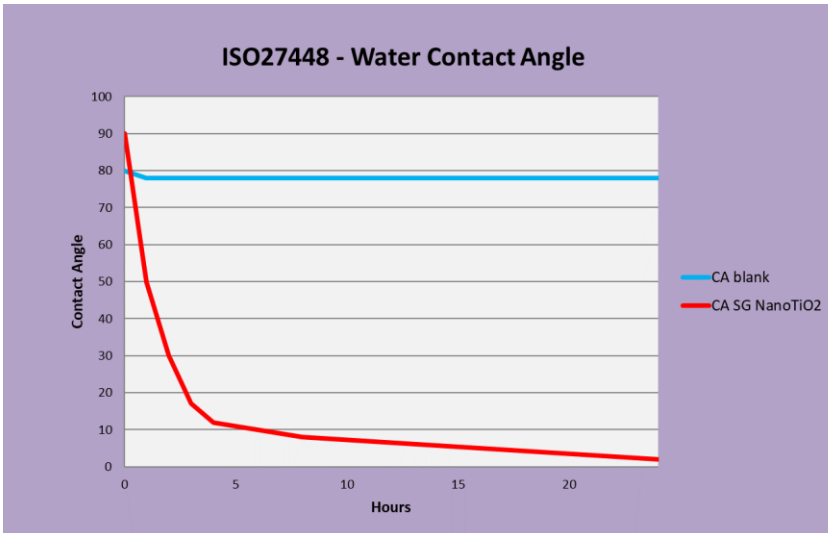

Figure 9. Photodegradation test.

The graph clearly shows the effect of sol-gel coated glass (red line). Initially the contact angle was 90º due to the hydrophobicity of oleic acid coated over glass. The contact angle decreases rapidly, within several hours below 10º, the initial value of the sol-gel coated glass surface. This decrease in contact angle can only be explained by the complete degradation of oleic acid to its components H_2O and CO_2 which are consequently released from the substrate. The reaction scheme would be:

$$\text{Oleic acid } (C_{16\text{-}18})COOH \xrightarrow{\text{hv, nano titanium dioxide}} H_2O + CO_2$$

Wet dirt pick up ISO1096-5:2016

ISO1096-5:2016 is a part of the ISO1096 standard that provides a method for testing the resistance of paint and varnishes to dirt pickup (DPU). This test is designed to evaluate the ability of a coating to resist the accumulation of dirt, dust, and other contaminants on its surface, which can affect the coating's appearance and performance.

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The ISO1096-5 dirt pickup test involves applying a thin film of the coating being tested to a smooth substrate (glass for example) and allowing it to dry. After the coating has dried, a layer of dirt is sprayed on the surface. The dirt is composed of oleophilic substances mixed with inorganic salts.

A modification of the test involved rinsing the plate with water, simulating a rain effect, to remove the dirt. Following this, the glass plate was dried, and the haze was measured. A glass plate coated with sol-gel nano titanium dioxide was compared to a blank glass plate. Figure 10 shows the difference after the dirt pick up test. The sol-gel coated panel shows to be nearly clean and the haze levels of average 1% proof the self-cleaning effect whereas the noncoated panel shows increased haze level and has become less transparent.

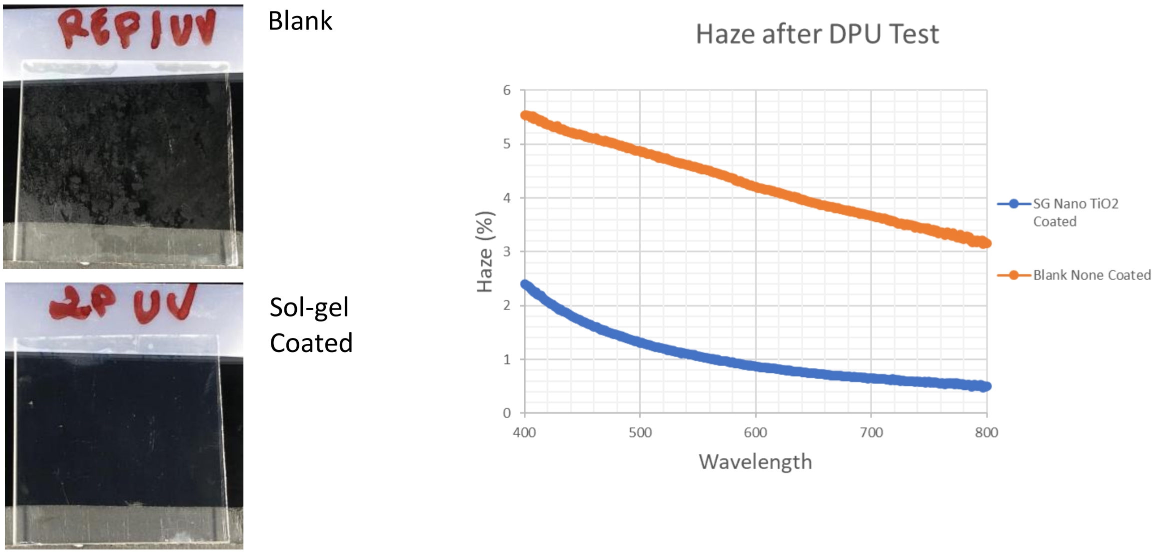

Figure 10. ISO1096-5 DPU Test.

Practical use Self-Cleaning Coatings: Solar Panels

The self-cleaning performance of sol-gel nano titanium dioxide is of great interest to solar panel farms as it can be expected that cleaner panels generate more energy and need less maintenance throughout their service life. In a real-life experiment solar panels were coated with sol-gel nano titanium dioxide (Figure 11; String 1) and their energy output was compared to blank solar panels (Figure 11; String 2). The power output was plotted as relative number: String 1 over String 2. Initially the power output of String 1 is slightly inferior to String 2 which can be attributed to the fact that the coating has a minor effect on the transparency, which was earlier assessed in haze experiments. After about 3 months the self-cleaning effect kicks in and String 1 starts to produce more energy than String 2.

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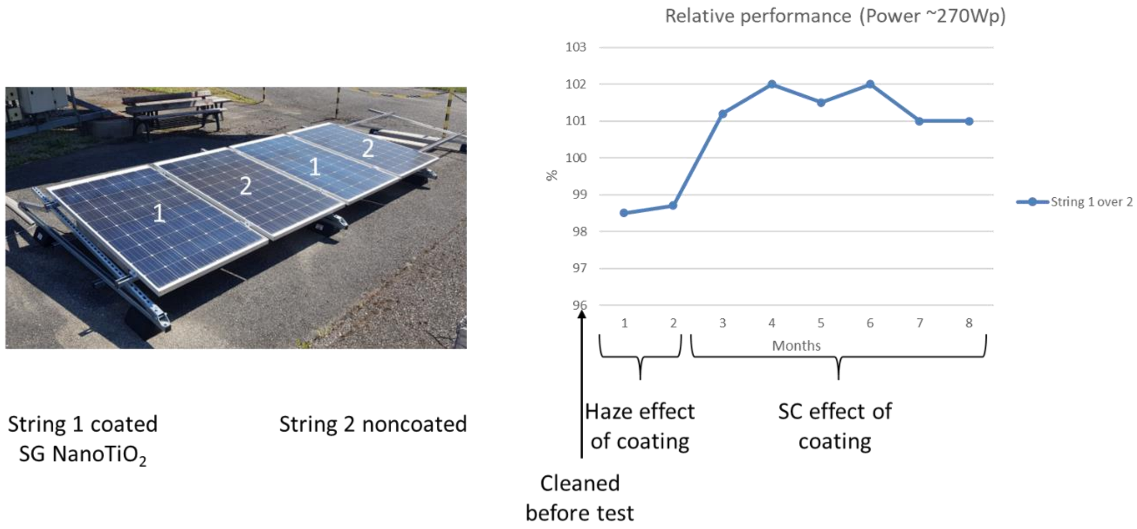

Figure 11. Solar panel test.

Conclusion

Nano titanium dioxide was prepared using the so-called sol-gel method, a wet chemistry technique that produces particles in the nanometer range. In this study, we have presented a method for synthesizing such nanoparticles and demonstrated their effectiveness as coatings. Thin films of nano titanium dioxide can be easily applied to any surface and exhibit remarkable photodegradation, superhydrophilicity, and self-cleaning properties.

To gain insight into the factors contributing to these properties, we conducted mechanistic studies including SEM and AFM analyses, which revealed the small particle size, open structure, and surface roughness of the nano titanium dioxide. The 4-probe test demonstrated the antistatic properties of the coating and which consequently showed its ability to repel dirt.

Furthermore, practical tests showed that sol-gel-based nano titanium dioxide coatings can effectively clean surfaces and improve the performance of solar panels.

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[i] Nanotechnology, 2008, Gross, Goedicke, Sepeur by Vincentz Network, Hannover, Germany
[ii] Shahzad Abu Bakar, Caue Ribeiro, Journal of Photochemistry and Photobiology C: Photochemistry Reviews Volume 27, June 2016, Pages 1-29
[iii] Lim, S., Pandikumar, A., Lim, H. et al. Boosting Photovoltaic Performance of Dye-Sensitized Solar Cells Using Silver Nanoparticle-Decorated N,S-Co-Doped-TiO2 Photoanode. Sci Rep 5, 11922 (2015).
[iv] Wang R et al 1997 Light-induced amphiphilic surfaces, Nature, 388-431
[v] Anandan S et al 2013 Superhydrophilic graphene-loaded TiO2 thin film for self-cleaning applications ACS Applied Materials & Interfaces 5 207–12

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