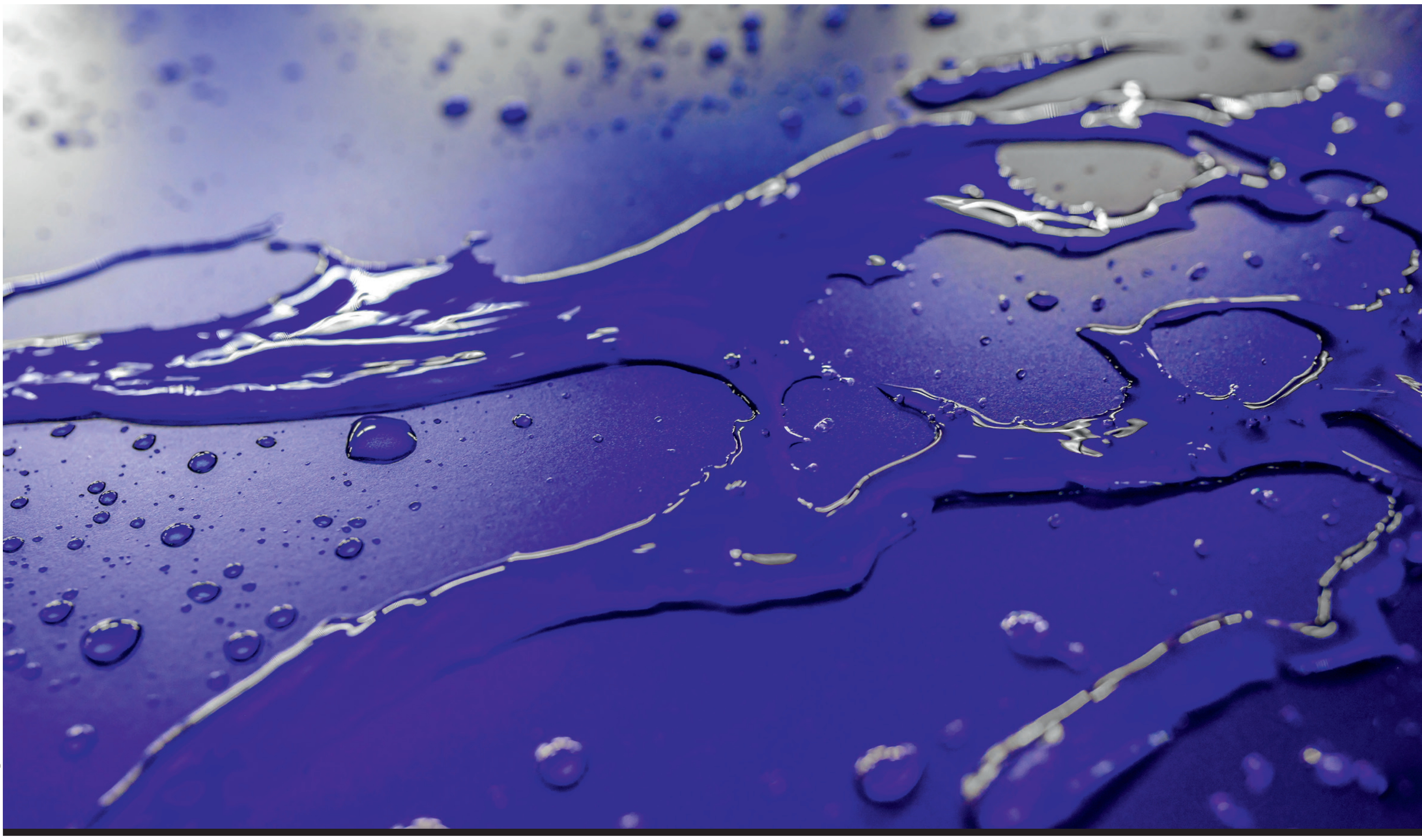

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NANO TITANIUM DIOXIDE-BASED COATINGS

Dirt eradication by nanotechnology-based coatings to increase the power output of solar panels. By Arno Schut, Axcentive and Ahmadou Ly, Driss Lahem and Mireille Poelman, Materia Nova.

We present a nano titanium-based self-cleaning coating technology that allows control of thickness and properties. The technology utilises the sol-gel method to prepare the nano titanium dioxide. We demonstrate that the nano titanium-based technology can be applied to any surface. Furthermore, it exhibits remarkable photodegradation, superhydrophilicity, and self-cleaning properties.

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).[1] It is often referred to as the bottom-up method of manufacturing small particles, as opposed to the 'traditional' top-down method, which uses high-energy processes such as grinding and milling.

The sol-gel method is a process used to create interlinked nanoparticles or other types of small particles by converting a solution (sol) into a solid (gel) network. The method involves two main steps, which are hydrolysis under influence of a small amount of water and condensation 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, like 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 highly defined nano-sized titanium dioxide particles. This method involves hydrolysis and condensation of precursors and aging and drying steps, as summarised below:

- Preparation of titanium precursor solution: A titanium precursor such as titanium isopropoxide or titanium butoxide is dissolved in a suitable solvent such as ethanol or water.
- Hydrolysis: The titanium precursor is hydrolysed by adding water to the solution. This leads to the formation titanium hydroxide species.
- Condensation: under influence of acidic or alkaline catalysis the hydrolysed species then start to condense to form a three-dimen-

RESULTS AT A GLANCE

→ Nano titanium dioxide was prepared using the sol-gel method, a wet chemistry technique that produces particles in the nanometre range.

→ Sol-gel prepared nano titanium dioxide-based coatings are transparent when applied as thin layers.

→ Thin films can be easily applied to any surface, and exhibit remarkable photodegradation, superhydrophilicity, and self-cleaning properties.

→ Outdoor durability tests have shown that sol-gel-based nano titanium dioxide coatings can effectively keep surfaces clean and improve the performance of solar panels, with an average power output increase of 1 %.

sional network of particles, the titanium dioxide sol. The size and shape of the particles can be controlled by adjusting the concentration of the precursor, the pH and the amount of water added during the hydrolysis step.

- Aging: The sol is allowed to age for a period, typically a few hours to a few days, to allow the particles to grow and the gel network to become more stable.
- Drying: The gel is then dried at a low temperature, typically around 100-200° C, to remove the solvent and create a solid material.

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 photocatalysis, where they catalyse 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.
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 specific 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 shown in *Figure 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.
- 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 ($\bullet O^{2-}$) and hydrogen superoxide radicals ($\bullet HO_2$).
- Adsorption of organic matter: The highly reactive species generated in the second step 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.
- 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.

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, 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.[2] 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.

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 (*Figure 2a*). This process was repeated 2 to 6 times to obtain plates of coated glass with increasing layer thickness (*Figure 2b-c*).

Increasing the number of passes reduced the transparency of the plate, which could be assessed by the haze test. Haze is calculated as $T_{diffuse}/T_{total}$. 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 to increase the travel time of organic molecules throughout the layer. Consequently, this enhances their breakdown via the photocatalytic process. By utilising 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 2b*) as shown in *Figure 3a*, *b*.

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

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 4*. 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 characterised by a contact angle below 10°.

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 [3,4].

The hydrophilicity of a surface can be analysed using 4-probe surface resistance analyser that measures the electrical resistance of a thin film or coating on a surface.

A thin film of nano titanium dioxide sol-gel was subjected to the 4-probe analyser and the results showed a resistance of $2.3\ 10^8\ \Omega/\square$. This indicates that the layer of nano titanium dioxide sol-gel behaves antistatic and may be expected to repel dust.

PRACTICAL TEST

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 5a*, 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, due to its antistatic behaviour. Furthermore, when the coated plate was sprayed with water, it demonstrated full wetting and self-cleaning due to the water sheeting effect (*Figure 5b, left*).

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), 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 0 °.
In (*Figure 6*) 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).
The graph clearly shows the effect of sol-gel coated glass (red line). Initially the contact angle was 90 ° due to the hydrophobicity of oleic acid coated over glass. The contact angle decreases rapidly, within several hours below 10 ° and to 0 ° within 24 hours. 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:

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

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.
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 7* 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.

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 8*; String 1) and their energy output was compared to blank solar panels (*Figure 8*; 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. On average it was measured that the coated panels produce about 1 % more energy during the test period. This does not seem a lot but comes down to increased revenue of several hundred thousand euros for an average size solar parc (between 30 and 100 MW).

Arno Schut
Axcentive
a.schut@axcentive.com

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Figure 1: Mechanism nanotitanium dioxide.

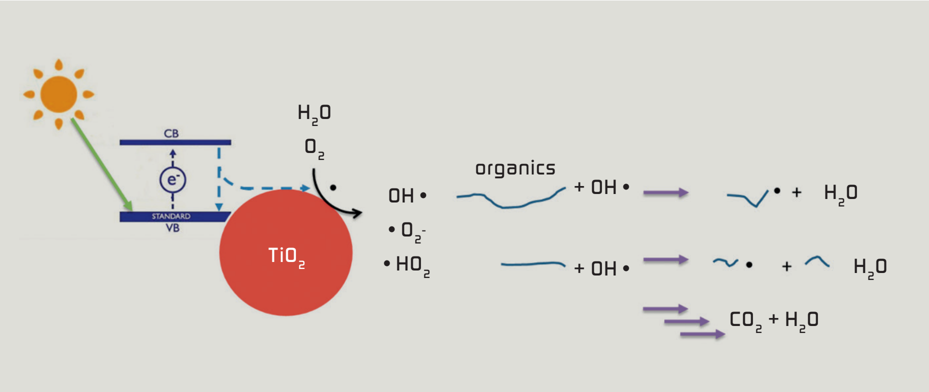

Figure 2: a)Application b) 2 passes c) 6 passes.

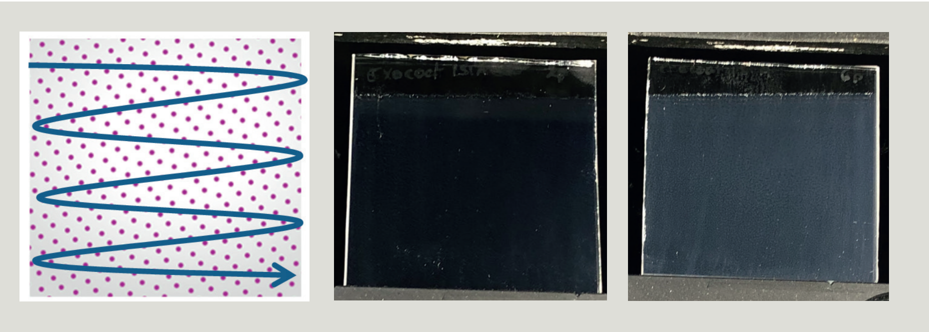

Figure 3: a) SEM picture, 500nm b) AFM analysis. Scanned region: 6x6µm².

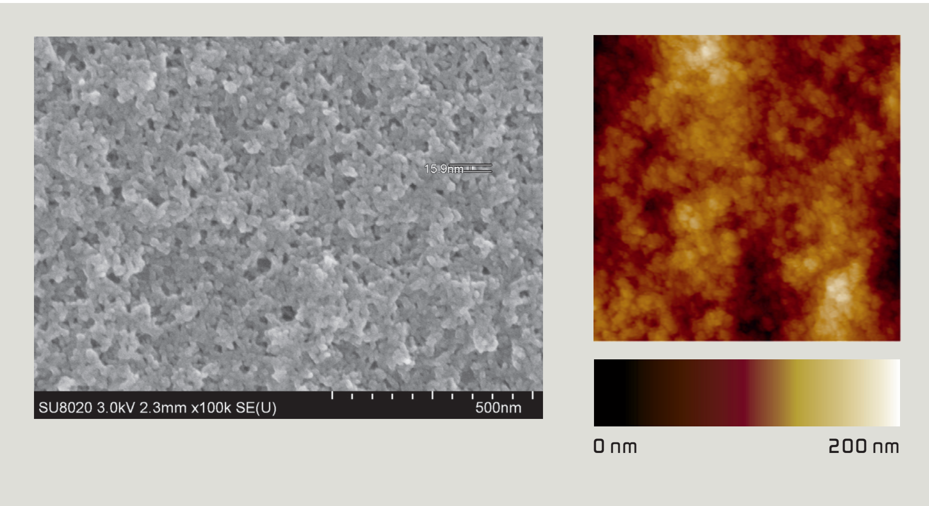

Figure 4: Contact angle.

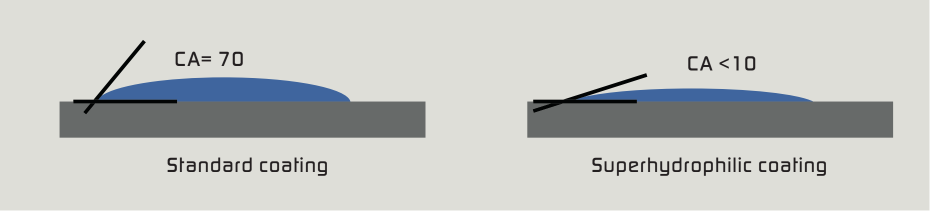

Figure 5: a) Left side Sol-gel nano titanium dioxide, right side not treated. Throwing a powder against the plate b) Left side Sol-gel nano titanium dioxide, right side not treated. Spraying the plate with water.

Figure 6: Photodegradation test.

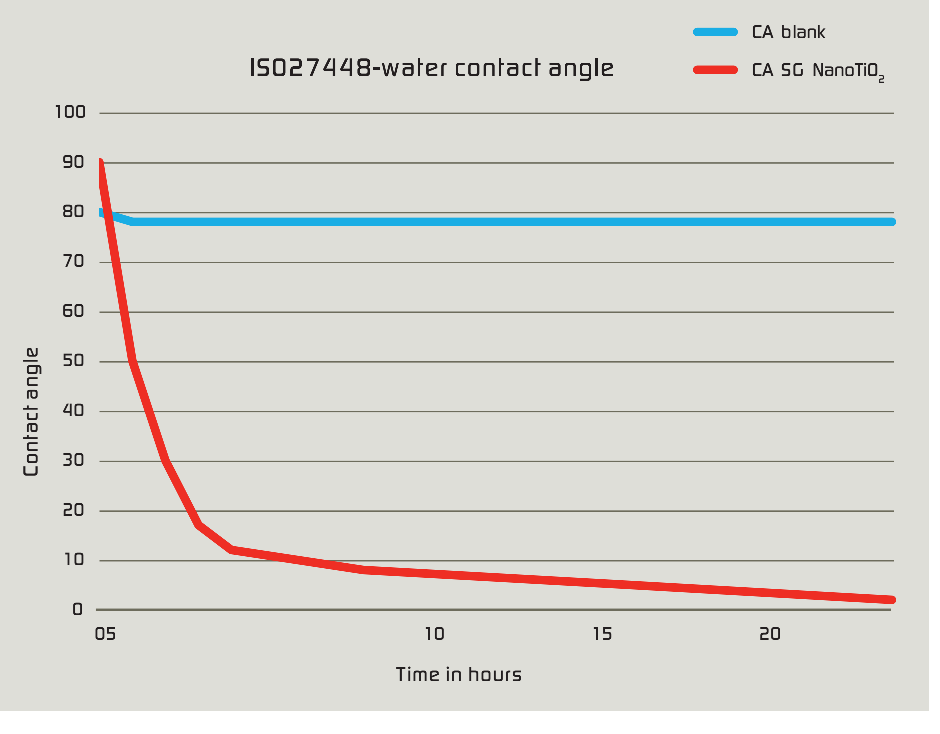

Figure 7: ISO1096-5 DPU Test. a) Sol-gel Coated b) Blank.

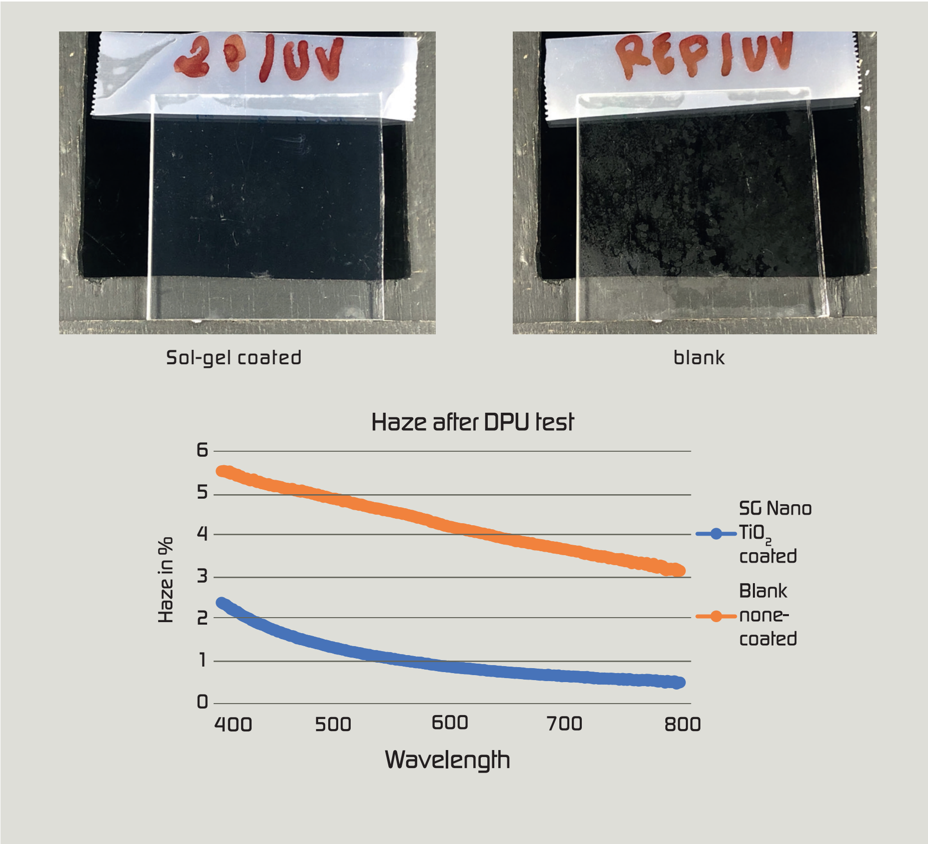

Figure 8: Solar panel test.