Transparent self-cleaning coating applicable to solar energy consisting of Nano-
crystals of titanium dioxide in fluorine doped tin dioxide

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1. Introduction

Energy issues including the limitations on the accessibility of fossil fuels, geopolitical instability and the continued emission of greenhouse gases have been primary drivers for the improvement, development and implementation of renewable energy resources. Advancements have been made due to efforts in improving device and manufacturing efficiency. (Luque, 2011; Allendorf et al., 2006) Continued research on energy capture, storage, conservation and managed use will result in new and greatly improved devices for harvesting sunlight (Green et al., 2013) and for coatings to reduce energy loss in buildings. Accumulation of grime on exposed surfaces is an important issue with regards to solar energy devices and is an area in need of further study. (Al-Hasan, 1998; García, L, 2011; Shin et al., 2011) Studies have verified performance losses due to the accumulation of soiling on the exposed surface of the device. (Elminir, 2006; Machida and Tani, 2001; Hegazy, 2001; Qasem et al., 2011, Kimber et al., 2006) The loss of performance is quite significant for solar power due to particles of dirt blocking from 5 to 30% of available sunlight lowering the amount of solar energy each device delivers. (Cano, 2011, Klugmann-Radziemska, E., 2015; Pavan et al., 2011; Zorrilla-Casanova et al., 2011)
Recently, coatings on glass substrates have been developed to impart a self-cleaning property to the exposed surface and have been found effective when exposed only to outdoor sunlight. (Giolando, 2013; Sakhuja et al., 2014)

Herein is reported a coating on glass substrate consisting of a thin layer of fluorine doped tin dioxide (SnO$_2$:F or FTO) containing photoactive titanium dioxide nanocrystals. Fluorine doped tin dioxide was chosen for its hardness, which provides protection against abrasion by wind-borne particles, transparency to visible light and, most importantly, conducts electricity. An ability to conduct electricity could be used to employ the coating as an anti-static device. Titanium dioxide is an oxidation photocatalyst and constitutes the active coating in commercial self-cleaning window products. However, a coating of titanium dioxide on glass is highly reflective, due to its large refractive index, with a concomitant loss of light transmitted. This limitation is eliminated by embedding 15 nm particles of titanium dioxide in a transparent FTO coating, thereby providing transparency, electrical conductivity and photocatalytic activity. When exposed to sunlight the photocatalyst in the coating maintains the exposed surface in a cleaner state where the build-up of grime is inhibited. In this way a single coating on the exposed surface of either photovoltaics, solar flat plate collectors or concentrated solar power equipment provides increased abrasion resistance, transparency, and self-cleaning properties to enhance and to maintain the performance of the device. Such a coating might result in solar energy harvesting devices delivering increased efficiency for the conversion of sunlight into electricity.
2. Experimental

2.1 Chemicals and Instrumentation

Nitrogen gas (AGA Gas Inc.) was used as a carrier gas. Tin tetrachloride (SnCl₄, anhydrous fuming, Fischer), ethyl formate (97%, Aldrich), ammonium bifluoride (Fluka, 98.5 %) were used as the sources of tin, oxygen and fluorine, respectively. Methylene Blue was purchased from Aldrich, aqueous hydrochloric acid (Certificate A.C.S. Plus) was purchased from Fischer Scientific and anatase-titanium dioxide powder (99.7 %, APS 15 nm) was purchased from Nanostructured and Amorphous Materials. All chemicals were used as received. Solutions containing titanium dioxide nanocrystals were sonicated in a Sharpertek Heated Ultrasonic Cleaner (Model SH80). Soda lime glass substrates (10 cm X 10 cm X 3 mm) were purchased from Bomar Glass and Mirror in Toledo, OH, washed with Microsoap™, rinsed with hot water, blown dried with a stream of nitrogen and stored in an oven at 100 °C prior to depositing films. Coated glass samples were likewise washed.

Sample thicknesses were measured using a DEKTAK³ ST surface profiler. The surface of the samples was examined using SEM, with a JEOL JSM-7500F scanning microscope. The changes in surface composition were examined by GIXRD on a PAN Analytical, X’PertPro PW3020Pro X-Ray diffractometer, at an incident beam angle of 1°. UV-vis spectra were taken on a Hewlett-Packard 8452A diode Array Spectrophotometer. Ultraviolet lamps were purchased from Cole-Parmer (EW-97605-30) using four ft long UV tubes (EW-97605-54), which was used for irradiation of multiple samples, and from Fisher Scientific UVP Model UVGL-58 Mineralight Lamp Multiband UV-254/366 nm. Electrical characterization was performed by determining the sheet resistance (Rₛₗₜ) and resistivity by the conventional 4 point probe measurements and confirmed by Van der Pauw
measurements (MMR Technologies Inc. Model D2500).

2.2 Preparation of coating solution

The complex of cis-[SnCl₄{OC(H)OC₂H₅}₂] was prepared according to Talaty et al., 2009. To a 1 L volumetric flask is added 0.5 L of ethanol, 20 g of cis-[SnCl₄{OC(H)OC₂H₅}₂], 4 g of ammonium bifluoride and 50 mg of titanium dioxide nanocrystals, followed by sonication for 10 min. Ethanol is added to give 1 L of solution.

2.3 Coating FTO/titanium dioxide on glass substrates

2.3.1 Spray-coating application

The reactor chamber consisted a 304 stainless steel six-way ISO cross (MDC# 827005) with 10-inch KF flanges (MDC # 800005) as described in detail elsewhere (Talaty et al., 2009) and modified slightly to allow a mist of the precursor solution to enter the chamber. The mist was generated with an Analtech glass reagent sprayer (Cat # 41-01) that was connected to the reactor chamber by glass tubing in such a way that larger droplets flow back to the glass sprayer receiver. A glass plate was loaded into the chamber, which was flushed with nitrogen gas for 30 min to reduce the level of air in the chamber so as to protect the heater element from oxidation, and then heated to 500 °C for 20 min. A mist of the precursor solution was brought into the reactor chamber for five min using a stream of nitrogen gas. The sample was cooled to room temperature and washed. The coated sample had the same appearance as the uncoated plate of glass, but had a sheet resistance of circa 300 Ω sq⁻¹; further testing as described later demonstrated that a self-cleaning coating was deposited on the surface.
2.4 Testing the photocatalytic activity of the coating

The FTO/titanium dioxide coated sample was irradiated for five min with ultraviolet light to increase the hydrophilic character of the coating, which resulted in water solutions of the dye wetting the surface and drying more uniformly. Two drops of a 0.1 M aqueous solution of Methylene Blue was deposited on the sample, allowed to dry in air at 45 °C and then placed under the ultraviolet lamp. The sample was placed 10 cm from the lamps and on the floor of a fume hood to maintain air flow across the sample, this eliminates the possibility of oxygen radicals generated from the absorption of ultraviolet light by oxygen giving a false positive reading.

3. Results and Discussion

3.1 General Considerations

Self-cleaning coatings (Ganesh et al., 2011) consist of a layer of titanium dioxide on glass. (Sanderson, 2005; Hashimoto et al., 2005; O’Neill et al., 2003) On exposure to ultraviolet light the layer of titanium dioxide generates electron-hole pairs that ionize water and oxygen molecules close to the surface of the coating resulting in the formation of highly reactive oxygen radicals. Organic material adhering to the surface is oxidized to carbon dioxide, water and inorganic residues.

\[
\text{Organic Material} \xrightarrow{\text{h}_\nu} \text{CO}_2 + \text{H}_2\text{O} + \text{Inorganics}
\]

\[
\text{O}_2/\text{H}_2\text{O}
\]
In addition the titanium dioxide surface becomes hydrophilic and the removal of the inorganic matter is facilitated when the surface is rinsed by rain or dew. However, due to the high refractive index of titanium dioxide the amount of sunlight passing through such coated substrates is diminished (O’Neill et al., 2003) and for this reason they may not be appropriate for solar energy application.

A self-cleaning coating useful for solar energy applications will need to fulfill the following criteria: transmission of sunlight similar to the uncoated glass substrate; a surface hardness greater than dust particles such as quartz; and possessing a photo catalyst activated when exposed to sunlight thus generating radicals to remove organic material and renders the surface hydrophilic so wetting action assists in cleaning. In addition a conducting coating could provide a means of dissipating static build-up of dust on the exposed surfaces. A coating meeting these criteria was obtained with a precursor solution of 50 mg of titanium dioxide nanocrystals (15 nm) dispersed in a liter of an ethanolic solution of 20 g of cis-[SnCl₄(OC(H)OC₂H₅)₂] and 4 g of ammonium bifluoride. After sonicating for 10 min the suspension is applied to the glass substrate by spray techniques. The glass substrate was coated while hot (500 °C) for 5 min whereupon an FTO film results. A light layer of dust, identified by powder XRD as FTO, washes cleanly off the surface of the FTO/titanium dioxide coated glass.

Structural and surface characteristics were evaluated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction diagram contained in Figure 1, was obtained for the FTO/titanium dioxide coatings on glass, and compared to XRD of commercially available Tec15 and AFG samples. Inspection of the XRD patterns revealed the presence of polycrystalline films, with no definite preferred orientation for the tin
dioxide tetragonal Cassiterite microcrystallites. The diffraction originating from the (110) planes had the highest relative intensities and strong relative intensities were observed for diffraction involving (101), (200) and (211) planes. This compared well with the randomized orientation of crystallites as listed in the Joint Committee for Powder Diffraction Standards (JCPDS card No. 41-1445). Scanning electron microscopy (figure 2) revealed a uniform coating of tin dioxide exists as microcrystallites, supporting the ERD results.

The uncoated portion of glass is easily scratched with quartz crystal, while the coated sections resist being cut by quartz as might be expected for a FTO coating, which would have a mods hardness close to that of quartz. Exposing the coated substrate to ultraviolet radiation for 15 min results in the coating exhibiting an increase in hydrophilic character. While the uncoated glass exhibited a contact angle for water of circa 45° (before and after exposure to ultraviolet light), the FTO/titanium dioxide coating initially provided a larger contact angle of circa 65° that decreased quite significantly to circa 15° on exposure to ultraviolet radiation. As a control a coated sample was made from a precursor solution that did not contain titanium dioxide nanocrystals and the resultant FTO coating provided a contact angle for water of circa 65° before and after irradiation similar to other results in the literature. (Garškaitė, E., 2013) Samples of glass coated with FTO/titanium dioxide were heated to tempering temperatures (circa 590 °C) without changing any of the properties of the sample. This should prove beneficial for their use as cover plates in solar energy applications since tempered glass plates are used to provide a stronger protective barrier against the elements and debris. Lastly, the suspension does not appear to charge with time when stored at room temperature, suspensions stored for one year in a brown
bottle provide the same film characteristics as freshly prepared suspensions in contrast to conventional sol-gel solutions.

3.2 Preparation of the precursor solution

Tin dioxide is useful in a number of applications and has been deposited onto glass by a variety of technologies such as chemical vapor deposition, sputtering and spray pyrolysis techniques. (Kykyneshi et al., 2010) For this project spray pyrolysis was used because the technology is simple and inexpensive and, more importantly, can be used to transport nanoparticles dispersed in the solution as recently reported for the preparation of titanium dioxide nanoparticles embedded in alumina. (Giolando, 2013) Commonly, tin tetrachloride is used as the tin source but this results in coatings with large highly faceted microcrystalites, which gives rise to an increase in scatter of light. Recently, the ethyl formate complex of tin, \( \text{cis}\left[\text{SnCl}_4\left(\text{OC(H)OC}_2\text{H}_5\right)_2\right] \), was found to give tin dioxide coatings via chemical vapor deposition technology with a higher level of optical transparence than coatings prepared with tin tetrachloride. (Tataly et al., 2009) For this reason the precursor solution was prepared by dissolving the \( \text{cis}\left[\text{SnCl}_4\left(\text{OC(H)OC}_2\text{H}_5\right)_2\right] \) complex in ethanol in the presence of ammonium bifluoride. To this precursor solution was added titanium dioxide nanocrystals (circa 15 nm) with the objective of embedding the nanoparticles in the growing FTO layer. Typically, commercial samples of nanocrystals are aggregated but the aggregation can be broken up to individual nanoparticles by grinding suspensions and/or sonication in an ultrasonic cleaner. The titanium dioxide nanocrystals would then be present on or near to the surface of the FTO/titanium dioxide coated glass to provide a photocatalytic property. Different amounts of titanium dioxide nanocrystals (5, 10, 20, 50, 100 and 150 mg per liter of
solution) were examined. The best photocatalytic activity and optical transparency was obtained with 50 mg titanium dioxide per L suspension; smaller amounts gave a weaker photocatalytic response while higher amounts resulted in a decrease in the %T of the coating.

### 3.3 Characterization of the self-cleaning properties

The FTO/titanium dioxide coated glass exhibits photocatalytic activity on exposure to ultraviolet light. A method for demonstrating self-cleaning properties is to dry a drop of an aqueous solution of an organic dye, such as methylene blue, on to the FTO/titanium dioxide coating and exposing the sample to 254 nm light. (Mills et al., 2006) An advantage is that the dye interacts with, and thereby enhances, the photo catalytic properties of titanium dioxide to provide a rapid assessment of the self-cleaning properties of the coating. The dye also gives a convenient qualitative visual indication of the coating’s photocatalytic properties. Active coatings generate reactive oxygen radicals near the surface of the FTO/titanium dioxide coating, which decompose the organic dye and a decrease in the intensity of the organic dye is observed. A typical example of the photoactive self-cleaning character of an FTO/titanium dioxide coating is shown in the figure 3 and in the data contained in Table 1. The initial intensity of the dried organic dye (labeled A in Fig. 3) measured 0.31 absorbance units at a wavelength of circa 580 nm and after 22 hours of exposure to 254 nm light the intensity decreased to a value of circa 0.10 absorbance units (labeled B in Fig. 3). For comparison the same experiment was performed with a sample of Pilkington Activ for which the organic dye was almost completely eliminated. As a control a drop of the organic dye is also dried on uncoated glass substrate and separately on an FTO coating that does not
contain titanium dioxide, and also exposed to 254 nm light, however the intensity of the organic dye does not change in intensity.

Noteworthy, exposure of samples of dried methylene blue on FTO/titanium dioxide coated glass to natural sunlight, and separately to 365 nm radiation from a handheld lamp, shows a significant decrease in intensity. These observations demonstrate that natural sunlight has sufficient intensity to activate the coating and that application to outdoor conditions is warranted.

A preliminary test in natural sunlight was conducted to ascertain whether the FTO/titanium dioxide coating on glass could provide self-cleaning character under outdoor sunlight conditions. The weather conditions of the local Toledo, Ohio area on average provide two to five cm of rain-fall each week. This is sufficient rainfall to provide a significant cleansing effect of exposed glass surfaces. The objective of this research is to determine whether a self-cleaning coating would be active in outdoor lighting conditions while maintaining high transparency. Such a coating would be useful for all solar energy applications where rainfall is insufficient to maintain clean surfaces. For this reason samples were mounted to provide full exposure to sunlight and the elements but had a cover plate five cm above them to provide protection from rain falling directly onto the samples. Samples of uncoated glass, Pilkington Activ and FTO/titanium dioxide coated glass where placed outdoor side-by-side for six months facing south and in full sunlight. For the FTO/titanium dioxide coated glass samples the %T decreased slightly from circa 88.7 %T (labeled B in Fig. 4) to circa 86.4 %T (labeled C in Fig. 4) at 525 nm. In contrast uncoated glass samples, with circa 89.8 %T (labeled A in Fig. 4), became heavily covered by dust and grime, which resulted in a decrease transmission of light to circa 74 to 67 %T at 580 nm (labeled D in Fig. 4).
Pilkington’s Activ showed a strong self-cleaning effect where the %T only slightly decreased from circa 83 %T at 580 nm when clean to circa 82 %T when “soiled”, the difference may be due to dust adhering via static attraction. These encouraging observation suggest more extensive field test under conditions similar to the environment wherein solar energy is deployed is warranted.

4. Conclusion

Addition of photoactive nanocrystals of titanium dioxide to ethanolic solution of cis-[SnCl\(_4\)(OC(H)OC\(_2\)H\(_5\)\(_2\)\(_2\)]\(_2\), and ammonium bifluoride provides a chemical precursor for the preparation of coatings exhibiting self-cleaning, photoactivated hydrophilic characteristics and transparency to visible light. In addition the coatings are also electrically conducting and potentially could be used to provide anti-static properties to the coated device. Coated glass substrates have characteristics favorable for their being used to increase the performance, and hence lower the cost of implementing, the three major forms of solar energy (photovoltaics, flat plate collectors and concentrated solar power): high transmittance of visible light; increased abrasion resistance; stable to tempering temperatures; electrical conductivity and self-cleaning properties in ambient sunlight.

5. Acknowledgement

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6. References


http://www.osti.gov/glass/Glass%20R&D%20Project%20Final%20Reports/066225_snl_coatings.pdf


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Table 1

Table 1: Absorbance data of aqueous Methylene Blue dried on glass substrates and then exposed to 254 nm light for 22 hr.

<table>
<thead>
<tr>
<th>Absorbance at 580 nm</th>
<th>Before irradiation</th>
<th>After irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated glass</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>FTO coated glass</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>FTO/TiO₂ coated glass</td>
<td>0.31</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Graphical Abstract

H₂O and/or O₂ → Oxygen radicals → CO₂ + H₂O

UV radiation

Glass coverplate

Organic grime

= TiO₂ nanocrystal embedded in SnO₂:F
Figure Captions

**Figure 1:** X-ray diffraction diffractograms obtained for the FTO/titanium dioxide films on soda-lime glass.

**Figure 2:** SEM micrographs of the surface of the FTO/Titanium dioxide film prepared at T = 500 °C by spray pyrolysis.

**Figure 3:** Spectra of absorbance versus wavelength showing the effects of irradiation with 254 nm light on methylene blue, which mimics organic material of soiling, with the initial intensity given by (A) and the intensity after 22 h irradiation by (B). The cleaned coated glass is given in C.

**Figure 4:** Transmittance spectra for (A) uncoated soda-lime glass cleaned after the experiment; and (D) soiled uncoated soda-lime glass; (B) FTO/titanium dioxide coated glass cleaned after the experiment; (C) soiled FTO/titanium dioxide coated glass.
Figure 3

![Graph showing absorbance vs. wavelength with three curves labeled A, B, and C. The absorbance is measured in arbitrary units (au). The graph includes a scale from 475 to 675 nm on the x-axis and from 0.0 to 0.30 on the y-axis.](image-url)
Figure 4