A Photoconductivity Technique for the Assessment of Pigment Photoreactivity

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Abstract

Large volumes of titanium dioxide (TiO_2) are utilized each year in coatings, sealants, plastics and paper for opacification and pigmentation purposes. TiO_2 is a photoreactive material that can contribute to the degradation of a material in which it is dispersed. A wide range of photoreactivity exists in commercial TiO_2 pigments, depending on the manufacturing method and surface coating used. At the present time, no standardized, quantitative measurement technique exists in the coatings industry for assessing the photoreactivity of pigments. The primary objective of this research is to develop a scientifically-based technique for the measurement of photoreactivity. One such technique involves measuring the photoconductivity of the pigments under ultraviolet (UV) irradiation. A prototype photoconductivity device as well as preliminary photoconductance measurements on a variety of TiO_2 systems will be presented.

Introduction

Large volumes of titanium dioxide (TiO_2) are utilized each year in coatings, sealants, plastics and paper for opacification and pigmentation purposes. TiO_2 is an effective ultraviolet (UV) radiation absorber, due to its ability to absorb ultraviolet (UV) radiation with energies equal to or greater than its band gap energy: 3.1 eV (rutile) to 3.2 eV (anatase), or correspondingly, wavelengths below 420 nm and 390 nm, respectively [1]. However, TiO_2 is also a photoreactive material, due to the fact that the absorption of UV radiation promotes electrons from the valence band of the TiO_2 into the conduction band, leaving behind a positively charged species, or hole, in the valence band. The resulting electrons and holes are extremely reactive and are capable of participating in oxidation/reduction reactions with any organic materials that they encounter. Alternatively, electrons and holes can undergo interfacial charge transfer with surface or adsorbed species to form reactive species such as hydroxyl radical ($OH^{\cdot}$), oxygen anion (O_2^{-}), and hydrogen peroxide (H_2O_2), all of which are extremely aggressive in degrading organic materials [2].

A wide range of photoreactivity exists in commercial TiO_2 materials, depending on the manufacturing method and post-processing steps used [3]. At the present time, no standardized, quantitative measurement technique exists in the coatings industry for assessing the photoreactivity of pigments. Instead, qualitative or performance-based tests, such as the isopropyl alcohol (IPA) test, are widely utilized. These tests to do not

provide fundamental information on the primary processes involved in charge carrier generation, recombination or interfacial charge transfer reactions.

The primary objective of this research is to develop a fundamental technique for the measurement of photoreactivity, one with a scientific basis that would provide the most direct correlation to end-use performance. One such technique involves measuring the pigment photoconductivity under ultraviolet (UV) irradiation, which could then be quantitatively correlated via conductivity models to the number, mobility and lifetimes of the electron-hole pairs. A prototype photoconductivity testing device and preliminary photoconductance results from a variety of TiO_2 systems will be presented.

Photoconductivity Measurements

Photoconductivity is a complex phenomenon involving competition between charge carrier generation, recombination, and trapping. Measurements of photoconductivity have been used to study electronic transport properties in semiconductors and insulators [4]. Since the generation of electrons and holes is the first step in any photocatalytic process, measurement of photoconductivity provides fundamental information on the density, mobility and the lifetimes of these species generated in TiO_2. Previously, Hermann et al. have studied the photoconductivity of UV-irradiated TiO_2 and related it to photocatalytic reaction mechanisms [5, 6].

As previously stated, under band gap irradiation, valence band electrons are promoted to the conduction band, increasing the population of conduction band, or free, electrons. If an external electric field is applied to a specimen during irradiation, the free electrons are accelerated in the conduction band and migrate to the electrodes, thus generating a photocurrent that can be measured and used to calculate conductance or conductivity [7, 8].   In general, the conductivity of an insulator or semiconductor is related to charge carrier density and mobility via the following relationship:

$$\sigma = e(n\mu_n + p\mu_p). \tag{1}$$

where σ is the conductivity, e is the electronic charge, n and p are the density of free electrons and free holes, respectively and μ_n and μ_p are the drift mobilities of the electrons and holes, respectively.   Changes in conductivity due to irradiation can be related to the increase in the number of free electrons and holes via:

$$\Delta\sigma = e(\Delta n\mu_n + \Delta p\mu_p). \tag{2}$$

TiO_2 is an n-type semiconductor, therefore all conductivity is attributed to electronic transport. Lifetimes of charge carriers can also be measured by pulsed photoconductivity or photoconductivity decay experiments or calculated via electron transport models [7, 9].

Low or no measurable photoconductivity in a TiO$_2$ specimen is indicative of little or low photoreactivity, or in the nomenclature of the pigment industry, high durability or non-chalking. If charge carriers are either not generated in any significant quantities, become trapped in surface states, or recombine rapidly, then they cannot react directly with the organic matrix nor can they undergo subsequent interfacial charge transfer reactions to surface species to generate additional oxidizing or reducing agents. However, high photoconductivity does not always imply high photoreactivity (or low durability), because this type of measurement does not provide information on interfacial charge transfer reactions between the charge carriers and surface species, or nor does it provide any insight as to whether the charge carriers and subsequently produced oxidizing/reducing agents are reactive toward the organic matrix (this type of information can be obtained from Electron Spin Resonance (ESR) experiments or from catalytic probe reactions). However, high photoconductivity in TiO$_2$ does indicate that the *potential* for pigment-initiated degradation reactions exists.

Experimental

TiO$_2$ suspensions were prepared by mixing pigment in absolute ethanol and sonicating the suspension in an ultrasonic bath for 30 min. Suspensions were typically 10 % TiO$_2$ by mass, although lower concentrations were also used in fabricating thinner films. Substrates for the TiO$_2$ films consisted of glass slides masked with 1.6 mm adhesive tape and vacuum coated with an adhesion layer of chromium, followed by approximately 2500 nm of gold. The adhesive tape was removed after vacuum coating to yield a 1.7 mm wide uncoated region. TiO$_2$ suspensions were deposited in the uncoated area and allowed to air dry, yielding a uniform film of pigment particles that made electrical contact with and bridged over the gold electrodes, as shown schematically in Figure 1(b). Additional electrical connections to the gold films were made with 0.254 mm (0.010 in) diameter gold wire and conductive thermoplastic silver-filled adhesive (DuPont 4922N)[*]. One drop of quick-curing 2-part epoxy was applied on top of the silver adhesive/gold wire assembly for additional specimen integrity.

To compare differences in behavior between particulate and bulk materials, photoconductivity measurements were also carried out on vapor-deposited TiO$_2$ on quartz (Spectrum Thin Films) and 10 mm x 10 mm rutile single crystal specimens having (110), (001) and (100) orientation (Princeton Scientific). For these specimens, silver adhesive electrodes were painted directly on the specimen surface, and gold wires were attached as described above. Preliminary measurements were carried out to establish the ohmic nature of the electrode contacts and to provide assurance that the combination of silver adhesive/gold wire/epoxy adhesive was not adding significant resistive barriers to the circuit

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[*] Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such an identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

Photoconductivity measurements were carried out on the prototype device shown in Figure 2. The specimen holder was enclosed in a metal box that serves to shield the specimen from room light and electrical noise. The gold wires on the specimen were connected to a Keithley 6517a electrometer with a resistance range of 2 MΩ to 200 TΩ, and a resolution of 10Ω to 1 GΩ (depending on the measurement range). The 6517a electrometer has a built-in DC voltage source that is used to apply an external bias voltage to the specimen (typically 10 V). Data from the electrometer are transferred to a personal computer for analysis. Polychromatic ultraviolet radiation with an approximate spectral range of 295 nm to 450 nm was provided to the specimen by a 1000 W xenon arc lamp (Oriel) via a collimating tube fitted with a manual shutter. A typical measurement consisted of applying a DC voltage to the specimen, waiting for the dark conductance value to stabilize, and then removing the manual shutter, allowing the UV radiation to irradiate the specimen. It should also be noted that because no corrections are made for specimen geometry, all measurements are reported in terms of the conductance G, which has units of ohm^{-1} (Ω^{-1}), or ΔG, the change in conductance relative to the original dark conductance.

Results and Discussion

Photoconductance measurements on vapor deposited TiO_2 films are shown in Figure 3. The three curves shown represent consecutive measurements made on the same specimen. Each run was carried out within 5 min to 10 min of the run previous to it. In the first run, the conductance curve prior to UV irradiation (termed the "dark" conductance) is initially flat, but displays a large increase in conductance following UV irradiation. It is observed that the dark conductance values for the second and third runs are much higher than in the first run, due to the extremely slow photoconductive decay observed in TiO_2 [10]. However, the conductance following UV exposure is seen to rise to approximately the same level for each run. The uncertainty in the conductance measurements is approximately 12 %.

Changes in conductance exhibited by the rutile single crystal specimens as a function of time after the beginning of UV irradiation (Δt) are shown in Figure 4. The highest change in photoconductance is exhibited by the crystal having (001) orientation, followed by the crystal having (100) orientation, with the crystal having (110) orientation showing the lowest photoconductance. These results are consistent with photocatalytic studies of TiO_2 crystal face reactivity by other researchers, in which the (001) orientation was observed to exhibit the highest photoreactivity [11-13].

Figure 5 shows the changes in conductance for two catalytic grade TiO_2 specimens, both of which are uncoated anatase TiO_2. Both specimens show a significant increase in conductance following UV irradiation. The conductance rise for specimen 1 is similar to that observed for the vapor-deposited TiO_2. Specimen 2, however, shows a rapid rise to a maximum conductance value, after which the conductance begins to drop. This drop in conductance is possibly due to the trapping of the conduction electrons by surface defects in the TiO_2 specimen. The large rise in conductance for both specimens following UV

exposure is indicative of a high concentration of photogenerated electrons and holes, all of which could directly or indirectly participate in a photocatalytic reaction.

Changes in conductance with time for coated pigmentary grade TiO_2 are shown in Figure 6. Pigments 1, 2 and 3 are rutile TiO_2 coated with Al_2O_3, $Al_2O_3/SiO_2/ZrO_2$, and Al_2O_3/organic dispersant, respectively. Very little rise in conductance is observed following UV irradiation; in fact, the photoconductance decreases below the level of the original dark conductance for all three specimens, a phenomenon known as "negative photoconductivity." [14]. Pigment coatings, or encapsulants, are known to decrease photoreactivity by preventing electrons and holes from reaching the pigment surface and reacting further with the polymer matrix [15]. The fact that there is essentially no increase in measured conductance indicates that the charge carriers are either not generated in any significant quantity or that they are recombining at the same rate at which they are generated.

To determine the effect of surface chemistry on photoconductivity, surface hydroxyl groups were removed from the surface of one of the catalytic TiO_2 specimens by calcining at 450 ^{o}C for 2 h. It is believed that holes are trapped by surface hydroxyl groups to form hydroxyl radicals, thereby allowing the electrons to remain free and thus contribute to the measured photocurrent [2, 10]. In the absence of hydroxyl groups, electrons and holes have a greater affinity for recombination, thus leading to a lower density of free electrons in the conduction band. Figure 7 compares the photoconductance of calcined specimens to the non-calcined specimens. Photoconductance is markedly lower after calcination, thus supporting the hypothesis of hole trapping by surface hydroxyls.

Relative humidity is also known to influence the surface hydroxyl concentration as well as the surface concentration of physisorbed water. The effect of relative humidity on the photoconductance of catalytic TiO_2 is shown in Figure 8. The photoconductance is observed to be highest at 46 % RH, and lowest at 16 % RH, where it would be expected that the concentrations of surface hydroxyls and adsorbed water molecules would be lower. To a certain extent, increasing the concentration of adsorbed water on the TiO_2 surface may enhance conductivity by increasing the concentration of surface hydroxyls, which, as discussed above, serve as hole traps [9]. At 60 % RH, however, the high concentration of adsorbed surface water could provide additional sites for electron/hole recombination, thus depressing the concentration of conduction band electrons and hence the measured photocurrent.

Summary and Conclusions

Preliminary measurements of TiO_2 photoconductivity have been carried on a prototype testing device. Measurable differences in photoconductance were observed between vapor-deposited films, single crystal specimens, pigmentary and catalytic TiO_2. Changes in external environmental conditions and surface chemistry were also manifested in differences in measured photoconductance.

Future research will focus on improving environmental control of the test chamber and developing techniques of measuring specimen dimensions so that conductivity, as opposed to conductance, can be calculated. Photoconductivity measurements will be compared to conventional tests of pigment reactivity such as the IPA test and UV weathering studies, as well as more fundamental measurements of charge carrier properties using ESR and terahertz spectroscopy. It is expected that these photoconductivity measurements can ultimately be utilized to calculate charge carrier density, mobility and lifetime, properties that can then be correlated to the photoreactivity of TiO_2.

Acknowledgements
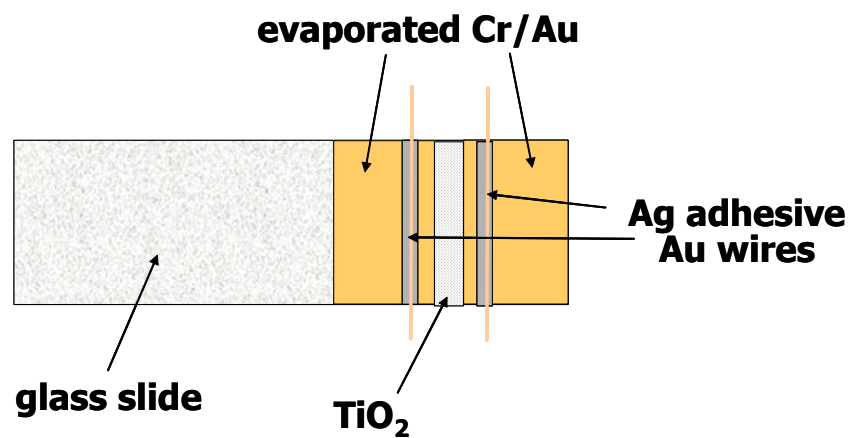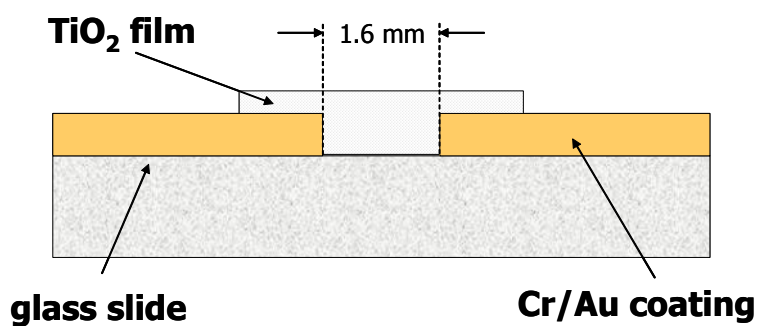
Figure 1: (a) Top, and (b) side views of the TiO$_2$ specimen configuration used in photo-conductivity measurements.

light/noise shield

TiO$_2$ film

UV Source

PC

Keithley 6517a Electrometer
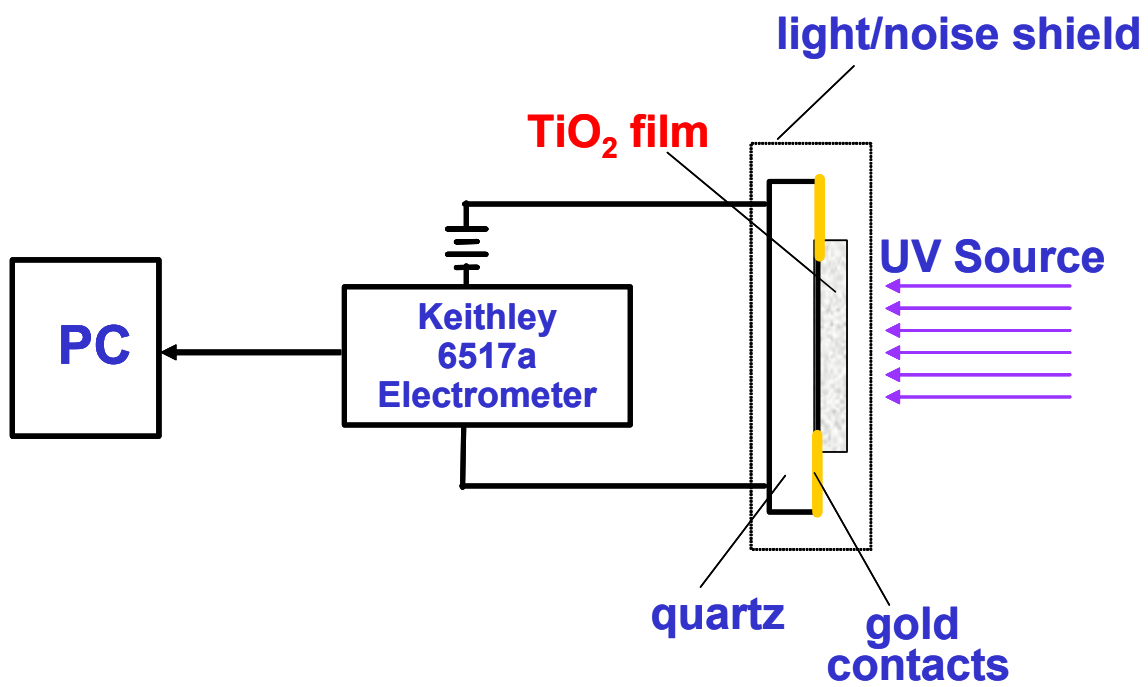
quartz

gold contacts

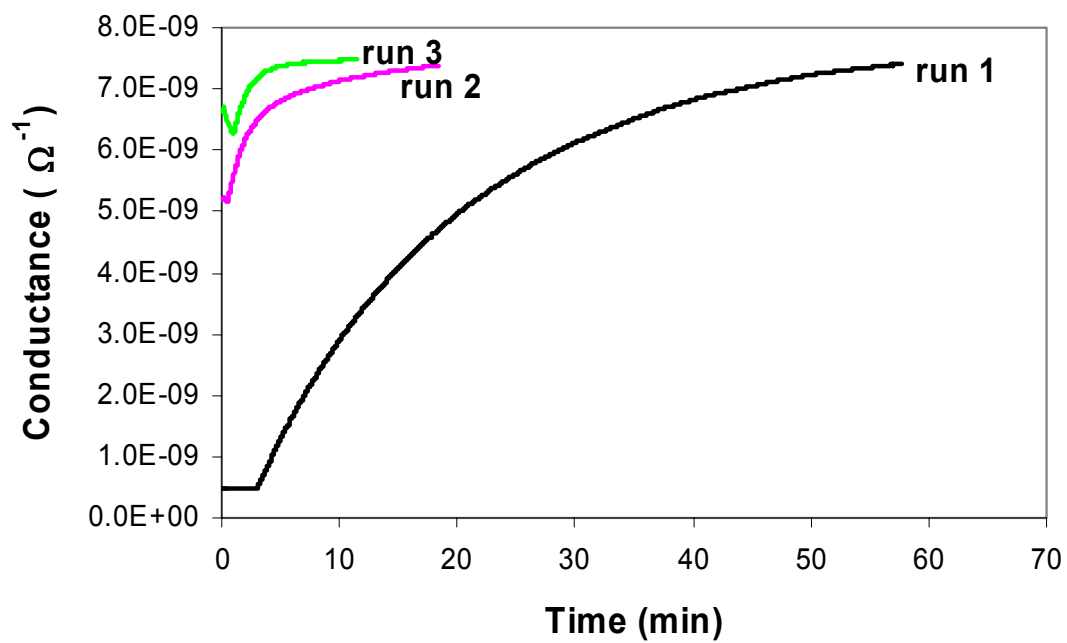**Figure 2:** Schematic diagram of photoconductivity testing device.

Figure (3): Photoconductance of vapor-deposited TiO_2 on quartz as a function of UV irradiation time. Run 1, Run 2 and Run 3 were measurements carried out consecutively on the same specimen.
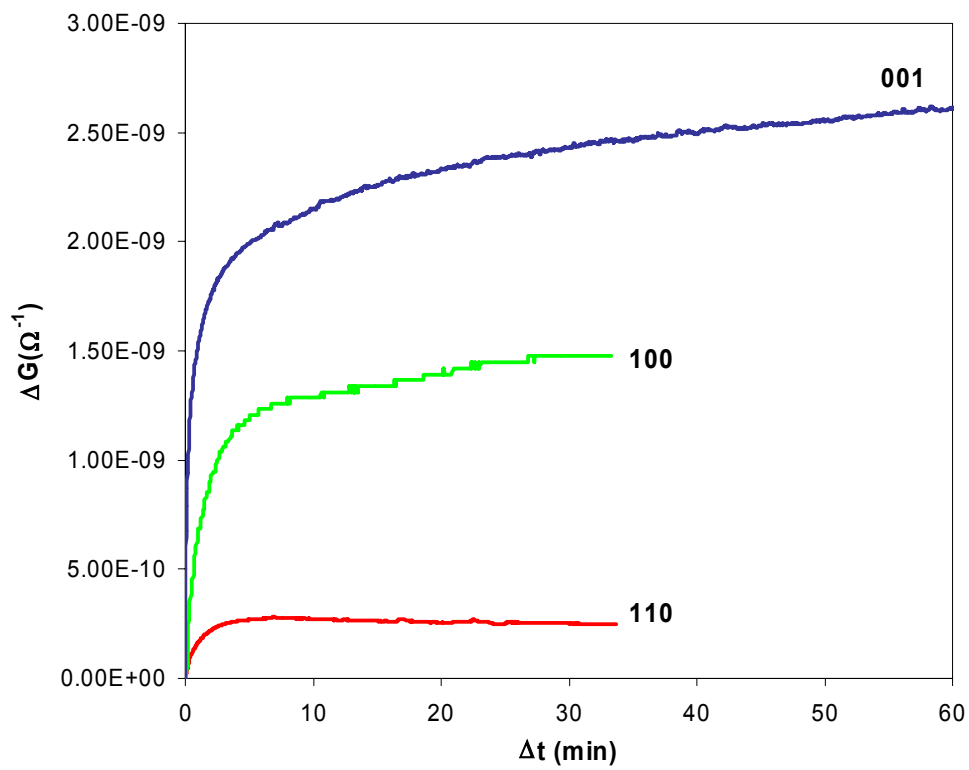
Figure 4: Change in conductance as a function of UV irradiation time for single crystal TiO$_2$ specimens having (001), (100) and (110) orientation.
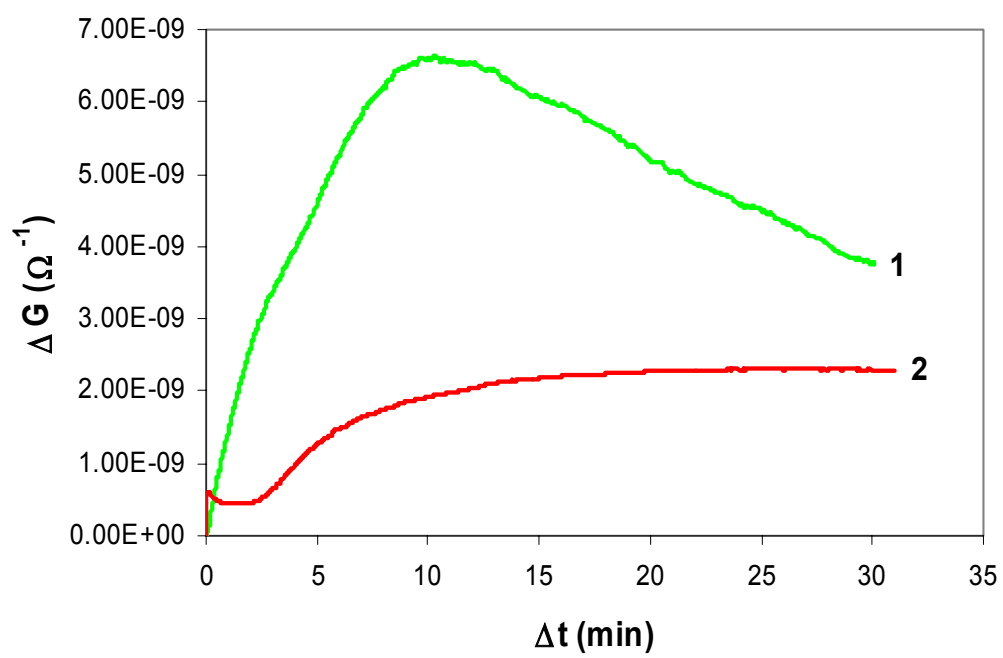
Figure 5: Change in conductance as a function of UV irradiation time for catalytic TiO_2 (uncoated anatase nanoparticles) specimens.
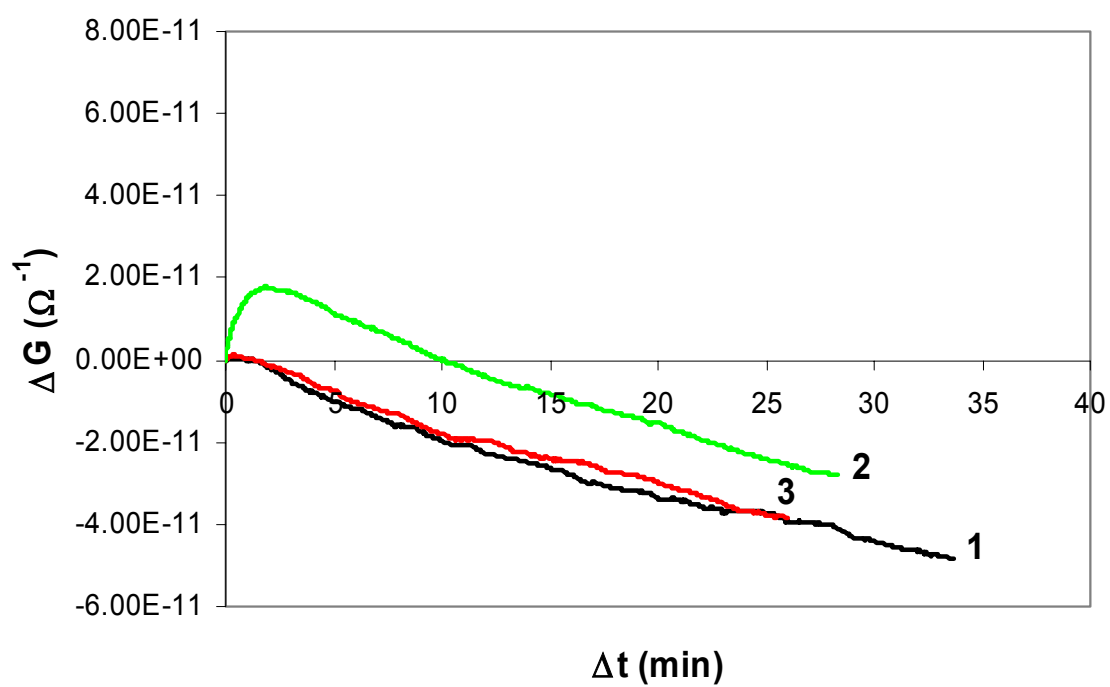
Figure 6: Change in conductance as a function of UV irradiation time for 3 different pigmentary grade (coated rutile) TiO_2 specimens.
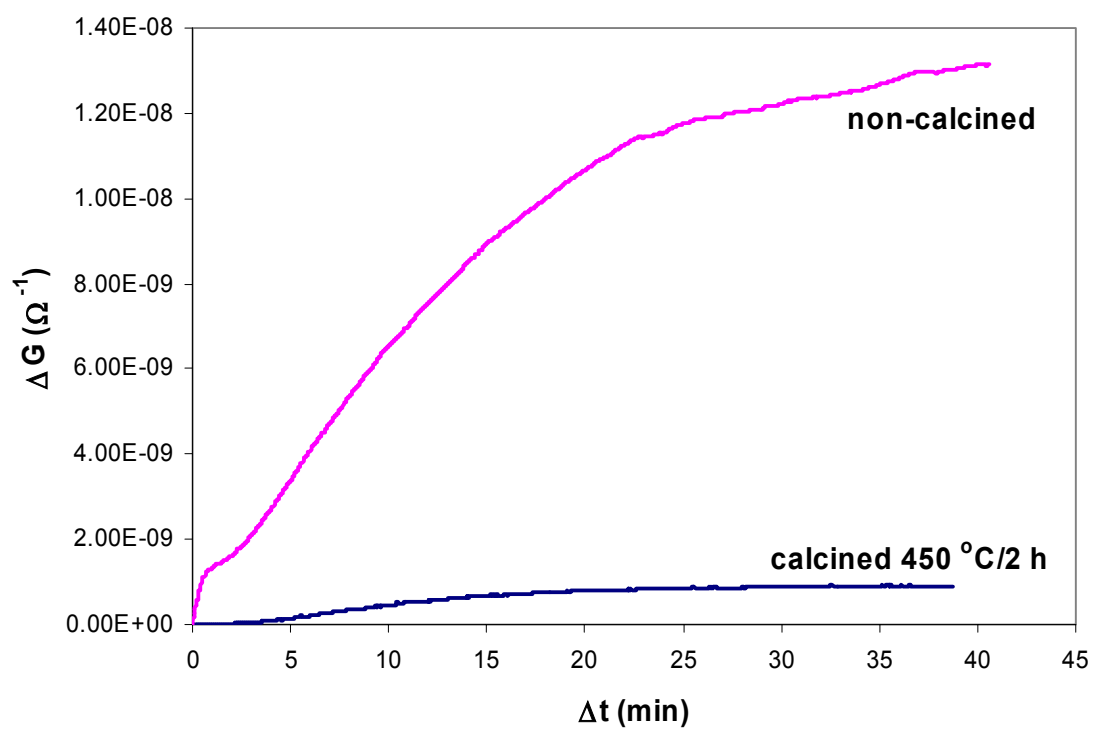
Figure 7: Change in conductance as a function of UV irradiation time for catalytic TiO_2 before and after calcination at 450 ^{o}C for 2 h.
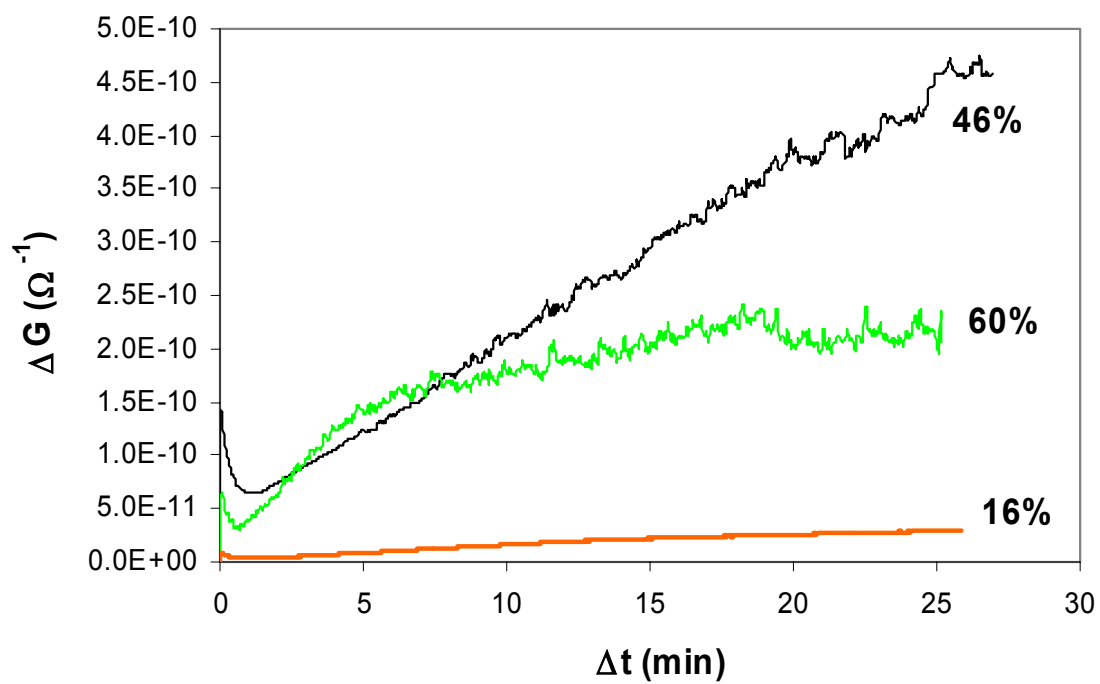
Figure 8: Change in conductance as a function of UV irradiation time for catalytic TiO_2 measured at 16 %, 46 % and 60 % RH.

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