

The Basis for Photocatalytic Writing

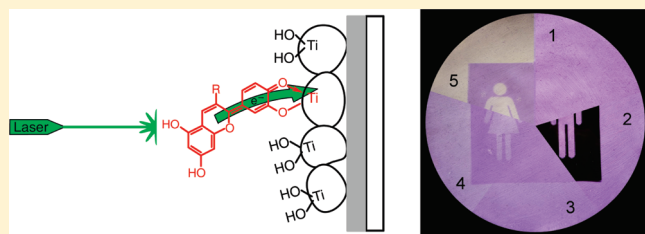
Jorge G. Ibanez,^{*,†} Michael W. Tausch,[‡] Claudia Bohrmann-Linde,[‡] Isabel Fernandez-Gallardo,[†] Ainocha Robles-Leyzaola,[†] Simone Krees,[‡] Nico Meuter,[‡] and Mathias Tennior[‡]

[†]Centro Mexicano de Química Verde y Microescala, Departamento de Ingeniería y Ciencias Químicas, Universidad Iberoamericana, Prolongación Reforma 880, 01219 DF Mexico

[‡]FBC Chemie und ihre Didaktik, Bergische Universität Wuppertal, Gausstrasse 20 D-42119 Wuppertal, Germany

ABSTRACT: We present a demonstration involving the oxidative photobleaching of a raspberry juice dye under visible laser light irradiation using the semiconductor titanium dioxide. A plausible interpretation of the phenomenon is discussed that aids in the understanding of semiconductor energetics and the nature of light.

KEYWORDS: First-Year Undergraduate/General, Demonstrations, Physical Chemistry, Public Understanding/Outreach, Lasers, Photochemistry, Semiconductors



Irradiation of a semiconductor with light of energy greater than its band gap (ΔE_g) results in the formation of photogenerated holes and electrons. These species are capable of respectively oxidizing or reducing (directly or indirectly) nearby species provided that the system energetics is adequate. Such a scheme is frequently utilized for the transformation of pollutants (e.g., oxidation of toxic organics, reduction of metal ions) into less dangerous species (e.g., carbon dioxide, metal deposits). The semiconductor facilitates these reactions by passing electrons from a donor to an acceptor. Because the semiconductor does not undergo any net change, the general process is called photocatalysis. There are a few processes that take advantage of both the reduction and the oxidation reactions,^{1–3} and we have developed educational experiments that demonstrate this effect.^{4,5}

Owing to its physical, chemical, toxicological, economical, and accessibility characteristics, the anatase phase of titanium dioxide (TiO_2) is typically the semiconductor of choice. Its worldwide market is in the vicinity of 4×10^9 kg per year.⁶ Unfortunately, its large band gap (3.2 eV, equivalent to ca. 380 nm) precludes visible light-initiated photoevents. However, this problem can be circumvented, for example, by adsorbing a dye on the semiconductor surface to function as an “antenna” that captures visible light and then transfers energized electrons to the excited-state conduction band of titanium dioxide to initiate photocatalytic activity. This is the principle of the “light-harvesting” dye-sensitized solar cells (Grätzel cells) or photogalvanic cells, whose key component is a semiconductor photoelectrode.^{7–9} Related applications based on this principle include erasure of writing produced with dyes by exposing them to sunlight or fluorescent light¹⁰ and testing photocatalytic activity by applying a redox ink that changes color upon oxidation or reduction.¹¹ For example, methylene blue becomes colorless upon irradiation due to its oxidation by dioxygen on a surface covered with a TiO_2 film, thus, indicating favorable photocatalytic activity.

On the basis of this last scheme, we present here a proof-of-concept for a novel application: the oxidation of a colored organic species under visible laser light irradiation to produce a photobleached product. The novelty of our proposal is that the discussed phenomenon can in principle be used for direct *photocatalytic writing* with commonly available green and red laser pointers, where the reading device is simply the naked eye. In this demonstration, titanium dioxide is sensitized by anthocyanin dyes from raspberry juices. Commercially available laser pointers are recommended as light sources, but students may perform analogous experiments using sunlight or other alternatives. In an undergraduate course, this demonstration can be used as a model experiment on photocatalysis. The instructor can discuss the positions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the sensitizing dye as related to the position of the conduction band of the semiconductor and can also explain electron transfer and photosensitization phenomena. Comparing the experimental results of photobleaching with a red versus a green laser enables students to reason how color, wavelength, and photon energy are related. On the basis of their experimental results, students can make predictions pertaining to the long-term stability of the “written” information, taking into account possible chemical reactions caused by ambient light or any surrounding substances. For a more advanced course, students can go a step further and combine the materials into an actual working solar cell.¹²

DEMONSTRATION

Preparation of a Sensitized Photocatalytic Titanium Dioxide Layer

Stir 1.5 g of nanocrystalline TiO_2 (anatase)¹³ with 5 mL of distilled water. Spread several portions of the resulting slurry with

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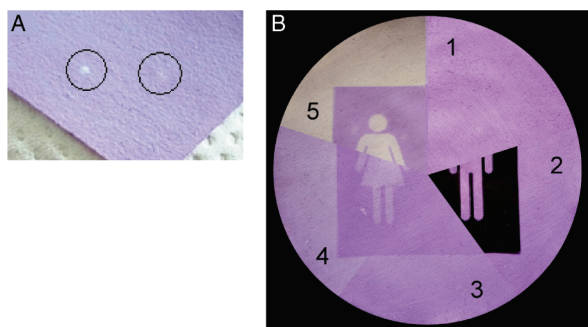


Figure 1. Photobleaching of raspberry anthocyanin on TiO_2 . (A) Spots generated after 60 s irradiation with a green laser pointer (left) and with a red laser pointer (right). (B) Collage of filter papers before and after irradiation with an Ultra-Vitalux lamp (300 W) at a distance of 30 cm: zone 1, sensitized filter paper before irradiation without a mask; zone 2, sensitized filter paper before irradiation with a mask (a picture printed in black on a photocopying transparency); zones 3–5, sensitized filter paper with a mask removed after 60 s irradiation (zone 3), after 120 s irradiation (zone 4), and after 300 s irradiation (zone 5). Note, the differences in color of the filter papers in (A) and (B) are due to the use of different cameras.

a brush on pieces of regular laboratory filter paper and dry the paper with a hair dryer.¹⁴

Sensitization

Mechanically mash several fresh or frozen raspberries, filter the resulting juice through a sieve, and place the juice in a Petri dish with a diameter greater than the size of the filter paper. Place the filter paper in the Petri dish (the titanium dioxide layer facing upward) and soak it in the juice for 2 min. Take the paper out, rinse it, first with distilled or deionized water and then with ethanol, and briefly dry with an air stream. This procedure can produce several pieces of “sensitized” paper. Even though the aqueous raspberry solution is red, the sensitized titanium dioxide surface looks violet. This is because the covalent binding of the anthocyanin dye to the titanium dioxide surface leads to a change in the structure of the chromophore. Extracts of other fruits, petals, or red leaves containing anthocyanins can be used as sources for sensitizers as well, provided that there are two vicinal OH groups at the benzene ring of their molecules. These OH groups are a precondition for the bonding of anthocyanin molecules to the TiO_2 particles.

Photobleaching

With a green laser pointer ($\lambda = 532$ nm, power peak <1 mW), irradiate the sensitized filter paper, fixing the laser pointer to a stand at a distance of ≤ 10 cm from the test sample for 60 s. Repeat the procedure with a red laser pointer ($\lambda = 640\text{--}660$ nm, power peak <1 mW) aimed at a different place of the filter paper. Selective color photochanges appear on the irradiated spots. Even if both laser pointers are tightly fixed to a stand, the bleached spot generated by the green laser pointer is sharp, whereas the bleached spot generated by the red laser pointer is diffuse (Figure 1A). For a better visibility of the results, we suggest the use of a camera. Photobleaching can even be observed when irradiating a sensitized filter paper across a lecture hall with a strong green laser pointer ($\lambda = 532$ nm, power peak <5 mW) from a distance of 9 m and an irradiation time of 4 min.¹⁵

Photobleaching of anthocyanin-sensitized TiO_2 can also be obtained using other light sources such as sunlight or a strong

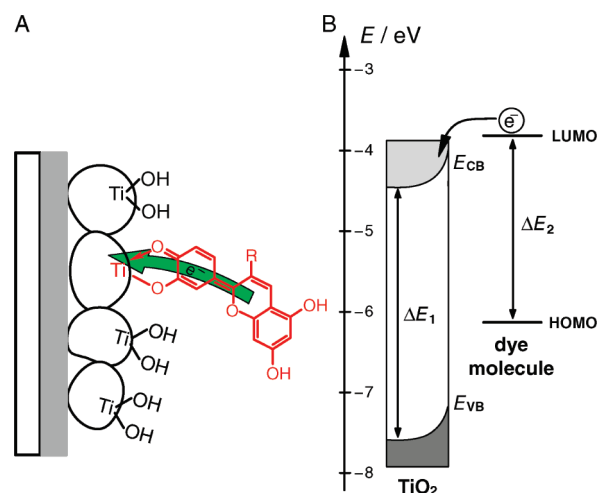


Figure 2. (A) Anthocyanin ($R = \text{glucose}$) bonded to the TiO_2 surface.¹⁶ (B) Energy levels of the TiO_2 semiconductor and of the selected anthocyanin. Note that $\Delta E_1 = \Delta E_g$, which is the band gap of the semiconductor. E_{VB} is the valence band energy and E_{CB} is the conduction band energy.

lamp (e.g., Ultra-Vitalux lamp, Osram 300 W). For example, a mask or a coin can be placed on the surface of the filter paper, which is then placed into direct sunlight. On a well-lit summer day, one can observe initial photobleaching in the exposed area after only 2 min. Very clear results can be obtained after 20–25 min. With an Ultra-Vitalux lamp, complete photobleaching of the exposed areas takes place within 5 min (Figure 1B). These light sources allow the creation of a large-area photobleached pattern, which is not possible with laser pointers within the same time scope. Control experiments with sensitized filter papers without titanium dioxide show significantly less photobleaching under similar conditions.

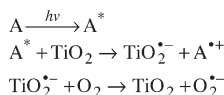
HAZARDS

Avoid eye exposure to direct as well as reflected light from the lasers. Note that much more powerful green lasers are commercially available that may produce faster and more obvious results. However, the instructor should also be aware of the concomitant increased hazards.

DISCUSSION

The bleaching of the photocatalytic layer depends on the wavelength and power of the light source as well as the distance and time of its exposure to light. In these demonstrations, anthocyanin serves both as a sensitizer and as the target species to be photodegraded. This occurs because of (i) the ability of the dye to covalently bind to the TiO_2 nanoparticles (Figure 2A), (ii) the relative magnitude of the energy gap, ΔE_2 between the HOMO and LUMO, and (iii) the position of the LUMO relative to the conduction band of the semiconductor (Figure 2B). Thus, the dye's excited electron is easily injected into the TiO_2 conduction band. Control experiments using thin-layer chromatographic foils coated with silica or aluminum oxide (i.e., electrical insulating oxides) do not show photobleaching owing to the magnitude of their energy gaps ($\Delta E_g > 4$ eV), which in fact are insulators rather than semiconductors.

Scheme 1. General Mechanism for the Photocatalytic Degradation of an Adsorbed Dye (A) in the Presence of O₂: A* Is the Excited Dye, A^{•+} Is the Dye Radical Cation, TiO₂^{•−} Is the Semiconductor after Electron Transfer



If the excited electron is transferred to an external acceptor (e.g., dioxygen), irreversible photodegradation (i.e., photo-oxidation) of the dye occurs, leading to the destruction of the chromophore. In the present reaction scheme, the excited dye typically injects an electron to the conduction band of the semiconductor, which then reacts with preadsorbed O₂ to form oxidizing species such as the superoxide anion radical (O₂^{•−}), peroxide (H₂O₂), and the hydroxyl radical (•OH).^{17,18} The general mechanism can be described by Scheme 1. Note that the photocatalyst (TiO₂) is regenerated. The superoxide anion radical O₂^{•−} is further reduced to H₂O₂ (and ultimately to H₂O) either by the process, A^{•+} → A²⁺ + e[−], or by a second TiO₂^{•−} → TiO₂ + e[−]. Dye A quickly becomes irreversibly photooxidized (i.e., bleached).¹⁹

From the results of the irradiation with green and red laser pointers, one can deduce that the energy of even the red laser photons is at least equivalent to ΔE₂ in Figure 2B, as photodegradation takes place in both cases. From the equation $E = hc/\lambda$, it becomes clear that the green light photons contain more energy than those of the red light. In both cases, this energy is larger than ΔE₂ in Figure 2B, but there is a greater energy excess when green light is used. This energy excess leads to higher vibronic states of the same electronically excited state of the dye molecule. For a more detailed understanding, the vibronic states may be included in the depicted energy level model, and Kasha's rule may be discussed,²⁰ but this would certainly be beyond the purview of a typical undergraduate course.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jorge.ibanez@uia.mx.

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(13) Examples of TiO₂ sources: P25 from Degussa (<http://corporate.evonik.de/de/Pages/default.aspx>) and Hombikat UV100 from Sachtleben Chemie GmbH (P.O.B. 17 04 54, D-47184 Duisburg, Germany. Tel. +49-2066-22-2326, Fax +49-2066-22-3326, e-mail Bproft@sachtleben.de).

(14) Alternatively, more stable and homogeneous surfaces can be obtained if a glass substrate is used instead of a filter paper. The preparation of a photosensitive layer on conductive glass is described in refs 9 and 21. Here, the sintering process causes the titanium dioxide particles to form a mesoporous network. This version is suggested if one chooses to use this demo as part of a larger series of experiments including photogalvanic and Grätzel cells.

(15) Source for the Ultra Bright Green Laser Pointer: Edmund Scientific Co. Stock no. NT55-789; available from: <http://www.edmundoptics.com/onlinecatalog/displayproduct.cfm?productID=2218> (accessed May 2011).

(16) As on all oxides, there are OH groups on the TiO₂ particles due to their production process.

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(19) In photogalvanic cells with dye-sensitized TiO₂ photoelectrodes,⁹ the fundamental step is also the electron injection from the LUMO of the dye to the conduction band of the semiconductor leading to a temporarily oxidized dye. This corresponds to A^{•+} in Scheme 1. Ideally, A^{•+} is reduced by a sacrificial donor. In fact, photodegradation takes place after some time. This can be well understood after having dealt with the proposed photocatalytic writing scheme.

(20) According to Kasha's rule, any process following excitation (e.g., fluorescence) starts from the lowest vibronic level of the electronically excited state.²²

(21) Web Site of the Chemistry and Didactics group, University of Wuppertal. <http://www.chemiedidaktik.uni-wuppertal.de/> → teaching photochemistry → experiments → W7a preparation of the photoelectrode (accessed Feb 2011).

(22) Web Site of the IUPAC Goldbook. <http://goldbook.iupac.org/K03370.html> (accessed Feb 2011).