1 / VOL. 3, NO. 2
THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
10.1007/s00897980187a

Laboratories and Demonstrations

Comparison of The Effectiveness of Sunscreen Lotions Using A TiO_2-based UVA/UVB Dosimeter

MINHUA WANG, JIANSHENG HUANG, AND YUZHUO LI*
[1]Department of Chemistry
Clarkson University,
Potsdam, NY 13699-5810

WILLIAM F. BARNARD
AREAL, US-EPA
Research Triangle Park, NC 20771
yuzhuoli@craft.clarkson.edu

When designed properly, this dosimeter can be used to evaluate the effectiveness of sunscreen lotions.

This paper describes a simple method for the evaluation of the effectiveness of a sunscreen product. It illustrates the basic principle of semiconductor (such as TiO_2) band gap, band-gap excitation, conduction-band electron trapping, and its application as an effective dosimeter in the UVB and UVA regions. The color change of the dosimeter, prepared from TiO_2 sol, can be quantitatively determined with a UV-vis spectrometer or qualitatively by visual inspection. The experiment can be used as a freshman-chemistry laboratory exercise or performed as a classroom demonstration for high school students or nonchemistry-major college students.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 02187-7

Introduction

The recent rapid growth of the sunscreen and sunscreen-containing cosmetic market indicates that people are quite conscious of the possible dangers of premature skin aging and skin cancer that occur as a result of excessive exposure to ultraviolet radiation (UV) [1]. A UV Index (UVI) developed and forecasted by the United States Environmental Protection Agency (EPA) and the National Weather Service (NWS), along with various other radiation indices, provides the general public with a daily reminder and guideline for the use of sunscreen products where outdoor activities are involved [2]. The EPA-NWS UV Index is determined from the forecasted sunlight spectrum and Diffey's erythemal curve; it is an action spectrum that specifies the relative erythemal response at different wavelengths [3]. Figure 1 shows both the erythemal-action spectrum and a typical sunlight spectrum in the UV region. Figure 2 shows the overlapping area between the erythemal-action spectrum and the sunlight spectrum [2]. When integrated over the range of 290–400 nm in Figure 2, the resulting erythemal irradiance (mW m^{-2}) or "dose rate" indicates the instantaneous amount of skin-damaging UV radiation. A "dosage" value may be obtained by integrating the dose rate over a period of time (i.e., minutes, hours, etc.). The UVI is then calculated based on the predicted dosage for a given location at noon for each day.

An effective sunscreen should absorb or reflect the wavelengths covered by the area shown in Figure 2. Since the first introduction of sunscreen lotion near the turn of this century, a wide range of organic and inorganic compounds have been studied for their sunscreen effectiveness and potential side effects [4–7]. The widely accepted sun-protection factor (SPF) provides a measure for the effectiveness of a particular formulation's ability to protect skin against wavelengths within the UVA/UVB region of the ultraviolet (290–400 nm) [8]. As a laboratory evaluation of the relative effectiveness of a sunscreen, a conventional actinometer, such as benzophenone or potassium ferrioxalate could be used [9]. The experimental procedure for ferrioxalate actinometry, however, tends to be time consuming and the actinometer is often *too* sensitive to the sunlight. A benzophenone-type actinometer, on the other hand, is often not sensitive enough to the sunlight. In addition, these actinometers involve no visible color change and hence are not suitable for classroom demonstration. The objective of this paper is to describe the use of a simple and unique UVA/UVB dosimeter for the evaluation of sunscreen products. The dosimeter is based on the photochemical

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 02187-7

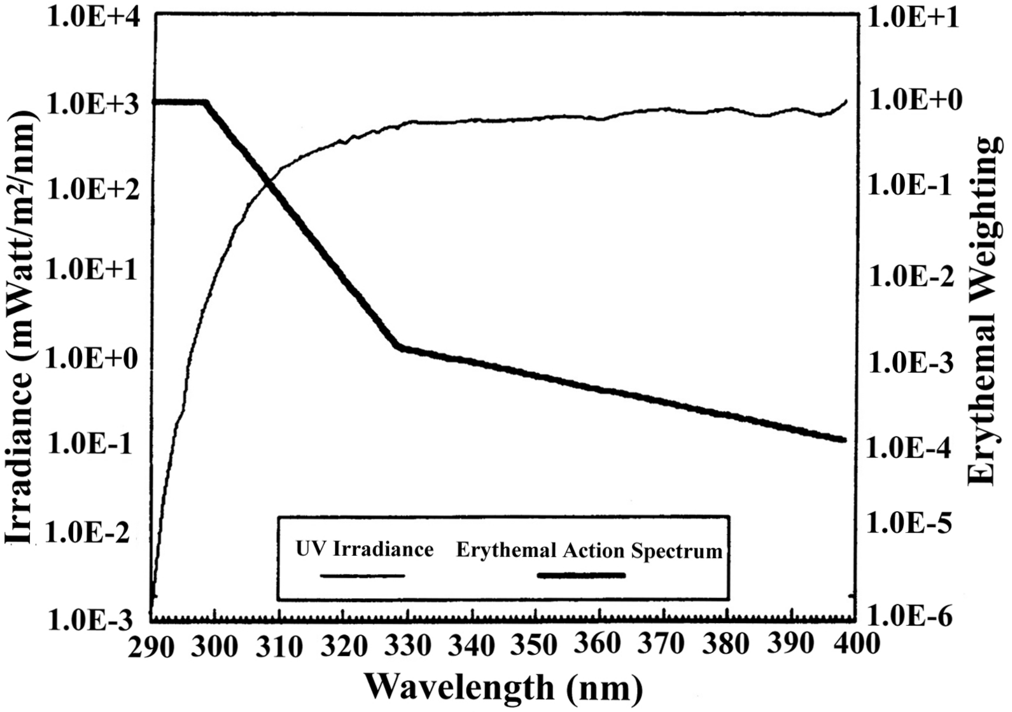

FIGURE 1. ERYTHEMAL-ACTION PROFILE AND SOLAR-ENERGY SPECTRUM. (REPRODUCED WITH PERMISSION OF THE AMERICAN METEOROLOGICAL SOCIETY.)

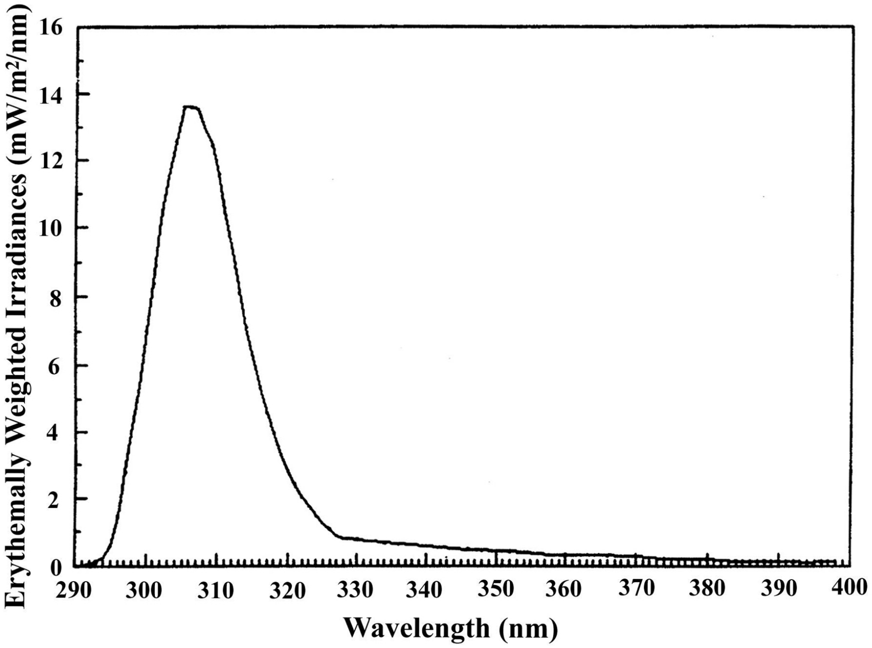

FIGURE 2. OVERLAPPED AREA BETWEEN THE ERYTHEMAL-ACTION CURVE AND A TYPICAL SUNLIGHT SPECTRUM. (REPRODUCED WITH PERMISSION OF THE AMERICAN METEOROLOGICAL SOCIETY.)

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 02187-7

behavior of a crystalline variant of rutile TiO_2 that is commonly used in sunscreen products [10].

We will first describe the photophysical and photochemical properties of TiO_2, followed by a brief discussion on their applications in sunscreen and photocatalysis. We will then present an experimental procedure to demonstrate the effectiveness of a set of sunscreen products with different SPF ratings.

Background

Ultraviolet (UV) Radiation

Ultraviolet radiation can be divided into three regions: UVA (320–400 nm), UVB (290–320 nm) and UVC (200–290 nm). Although UVC is the most damaging UV radiation, it is filtered out by the ozone layer in the stratosphere before reaching the earth’s surface. The radiation in the UVB region (partially filtered by ozone) can penetrate both the stratum corneum and the epidermis of human skin [11]. It has sufficient energy to cause damage, such as sunburn, to human skin. This is particularly true for fair-skinned individuals. The UVA radiation, which is unfiltered by ozone, has deeper penetration of human skin to the dermis; it, thereby, stimulates the formation of melanin and produces a tan, which acts as the first line of defense for the protection from sunburn. UVA radiation, therefore, is also called the “tanning region.” Although having considerably lower energy than UVB, UVA photons can cause delayed damages to the skin [12].

The fundamental function of a sunscreen is to serve as a filter that can prevent the penetration of ultraviolet radiation. The substances most commonly used in commercial sunscreen preparations include *p*-aminobenzoic acids (PABA), cinnamates, oxybenzone, salicylates, and metal oxides, such as TiO_2 and ZnO [13, 14]. In addition to their ability to scatter sunlight, inorganic particles, such as TiO_2, do absorb strongly in the UVA and UVB regions.

Rutile and Anatase TiO_2

In addition to its amorphous state, two of the most common crystalline forms of TiO_2 are rutile and anatase [15]. The two crystalline forms share many similarities, such as their physical appearance, refractive index, density, low toxicity, and high stability in the presence of strong acids and bases [16]. As a physical blocker for sunlight, both

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 02187-7

crystalline forms would serve the purpose well. Their photochemical properties, however, are very different. TiO_2 is a semiconductor. When a semiconductor particle absorbs light, it promotes an electron from its valence band to its conduction band, leading to a charge separation. When extra electrons are found in the conduction band and positive charges found in the valence band, the particle is denoted as TiO_2 (e^-, h^+) as shown in equation 1 [17]. In rutile TiO_2, the charge separation is quickly diminished through a charge recombination within the particle and the energy is released as heat. This translates to a low photoactivity and an effective conversion of UV light into heat. As a result, any photoinduced reactions that can pose damage to the skin are avoided. The low photoactivity and its desirable UV absorption spectrum, which cover the entire erythemal curve make rutile TiO_2 an ideal choice as UV blocker for sunscreen preparations [19].

$$\mathrm{TiO_2} \xrightarrow{h\upsilon} \mathrm{TiO_2}\left(e^-, h^+\right) \qquad (1)$$

For amorphous and anatase TiO_2, the lifetime of the charge separation is much longer than that on a rutile particle. The electron and electron hole, therefore, have greater opportunity to undergo redox reactions on the surface; therefore, anatase has been extensively used for applications involving such electron transfer processes as photocatalysis for environmental waste treatment and photovoltaic design for solar energy storage. Extensive reviews on these interesting topics are available [19–24]. Due to their photoactivity, amorphous and anatase TiO_2 are not suitable for sunscreen applications.

In addition to the redox reactions and charge recombination process, the electrons or electron holes on amorphous or anatase TiO_2 particles can be trapped (preserved). For example, in the presence of a good electron donor, such as alcohol, the electron holes can be easily filled by an electron donation from the alcohol. The conduction band electron, TiO_2 (e^-), therefore, will have a longer lifetime and thus can be more easily trapped in the crystal lattice. The net reaction for such process can be illustrated by equation 2 [25–27].

$$\mathrm{RCH_2OH + TiO_2\,(e^-, h^+) \rightarrow RCHO + H^+ + \tfrac{1}{2}\,H_2 + TiO_2(e^-)} \qquad (2)$$

The trapped electrons, $TiO_2(e^-)$, give a strong absorption in the visible range with a maximum at 546 nm. The sample, therefore, turns from colorless to dark blue. To a

S 1430-4171 (98) 02187-7

certain extent, the number of electrons trapped in the matrix is linearly proportional to the number of photons absorbed by TiO_2 and the number of effective band-gap excitations. The absorption spectrum of the trapped electrons, therefore, can be used for dosimetry [28]. The TiO_2 sol prepared for this experiment contains mainly amorphous and anatase TiO_2 and has the same absorption profile in the UVA/UVB region as those rutile TiO_2-based sunscreen preparations. By measuring the UV doses received by a TiO_2 sol with and without the protection of a sunscreen, the effectiveness of a particular sunscreen preparation can be evaluated.

Experimental Procedures

Precautions:

Direct contact of chemicals with skin should be avoided when handling concentrated hydrochloric acid. Protective gloves should be worn accordingly. Avoid direct eye contact with radiations from the sun and sunlamp. Protective sunglasses should be worn accordingly

General

Three sunscreen lotions used in this study, Coppertone (SPF 4, waterproof), Banana Boat (SPF 8, waterproof), and Vaseline Intensive Care (SPF 30), were purchased off the shelf from a local drug store. Glycerol and ethylene glycol (99%) were obtained from Alfa. Titanium isopropoxide (97%) was obtained from Aldrich. Hydrogen chloride (13 M) was obtained from Baker. All reagents were used as received without purification. UV-vis spectra were recorded on a Perkin Elmer Lambda 6 UV-vis Spectrophotometer. The color change of the dosimeter was inspected visually and monitored with a Milton Roy Spectronic 20D at 546 nm. Irradiation experiments were conducted with natural sunlight or a 300-watt sunlamp (GE, Underwriters Laboratories Inc.). The distance between the dosimeter samples and the sunlamp is ca. 0.5 m. *Caution:* Avoid direct eye contact with radiations from the sun and sunlamp. Protective sunglasses should be worn accordingly.

Preparation of TiO_2 Sol

TiO_2 sol is prepared by hydrolysis of titanium isopropoxide, $Ti(OC_3H_7)_4$ at room temperature [29, 30]. While stirring, concentrated HCl (0.40 mL, 13.0 M) is added dropwise into 40.0 mL of ethylene glycol (99%). To the acidic solution, 1.0 mL of

ISSN 1430-4171
THE CHEMICAL EDUCATOR
http://journals.springer-ny.com/chedr

S 1430-4171 (98) 02187-7

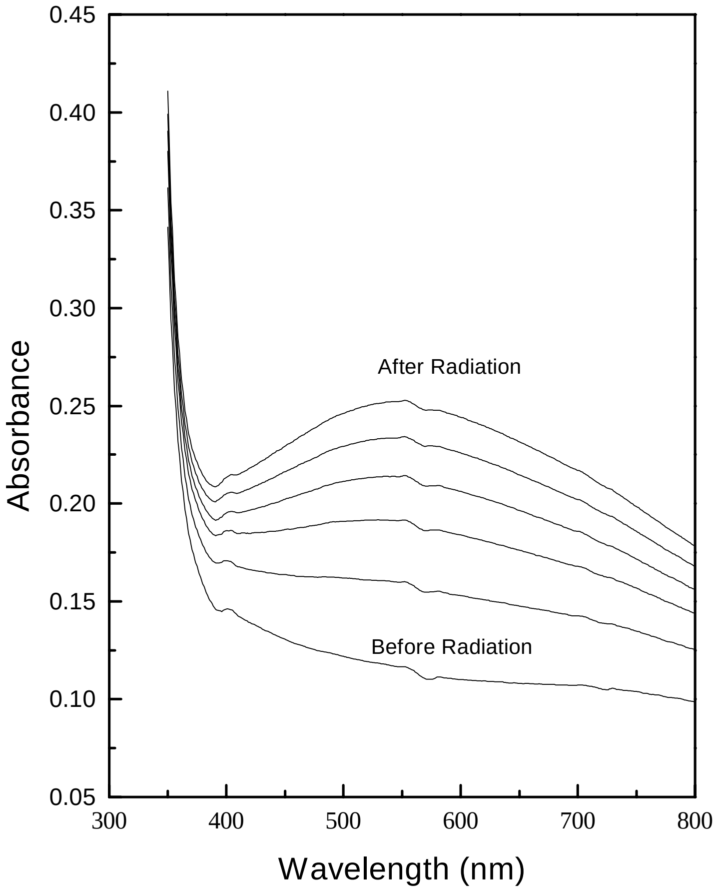

FIGURE 3. UV-vis ABSORPTION SPECTRA OF A TIO_2 SOL SAMPLE BEFORE AND AFTER UV RADIATION.

$Ti(OC_3H_7)_4$ is then added. The resulting solution is stirred for an additional 10 min. The prepared sol is colorless and stable in the dark at room temperature for months.

Photochemical Properties of TiO_2 Sol

To a standard Pyrex cuvette (10 × 10 × 40 mm) equipped with a round neck, 4.0 mL of prepared TiO_2 sol is added. The cuvette is then sealed with a rubber septum and inserted with two needles (a long one and a short one) through the septum. The long needle carrying a stream of nitrogen is extended to the bottom of the sol sample. A short needle that barely passes the septum serves as a vent. After the sample is purged with nitrogen for ca. 5 min, its UV-vis absorption spectrum is recorded. As shown in Figure 3, the TiO_2 sol absorbs strongly in the UV region, but not in the visible region. The cuvette is then placed in the front of the sunlamp and irradiated. Its UV-vis spectra are recorded again after radiation. As the TiO_2 sol does not absorb strongly in the visible region, room light or visible light does not have any significant effect on its color change.

Preparation of Sunscreen Samples

The sunscreen samples are prepared by mixing a known amount of (0–30 % w/w) sunscreen lotion and glycerol. The mixtures are stirred until transparent. The prepared samples are stable at room temperature for at least several days.

Evaluation of Sunscreen Samples

One method to examine the effectiveness of sunscreen lotion is to coat the sunscreen lotion directly onto a tube or sample cell that contains the TiO_2 sol. It is impractical, however, to measure the amount of sunscreen applied on the tube or cell. Furthermore, it is difficult to coat tubes or cells evenly. For this experiment we have developed a dual-tube method to overcome these difficulties. A Pyrex tube (Corning #9800-13, 12.4 mm o.d.; 11.1 mm i.d.; 100 mm long) was filled with TiO_2 sol (ca. 5.0 mL). This tube will be called the inner tube. In a slightly larger Pyrex tube (Corning #9800-16 with a original 160-mm length, 15.7 mm o.d.; 13.5 mm i.d.; cut to ca. 100 mm in length), a small amount of the prepared sunscreen sample (ca. 1.0 mL) was added. The latter tube will be called the outer tube. Prior to radiation, the inner tube was inserted into the outer tube. The sunscreen sample formed a thin layer of liquid in between the two Pyrex tubes. A rubber septum was then placed upon the inner tube and sealed over the outer tube. The TiO_2 sol in the inner tube was then purged with nitrogen for ca. 8 min using a method similar to that for the cuvettes.

The entire dual-tube assembly was placed in a Spectronic 20 and its absorbance at 546 nm was recorded. The sample was then irradiated with sunlight or in front of a sunlamp. The color change of the sample was monitored with a Spectronic 20 at 546 nm. There is no need to remove the outer tube prior each measurement as the absorption change due to sunscreen lotion at 546 nm is negligible.

Results and Discussions

General Considerations: Glassware, pH, Oxygen, and Disposal

The ozone layer in the stratosphere practically prevents the UVC photons from reaching the earth’s surface. Of concern for human skin damage, therefore, only UVB and UVA radiations are relevant. A dosimeter for sunscreen lotion evaluation should, therefore, exclude the interference from UVC radiation. In general, the cut-off wavelength for quartz glassware is as low as 180 nm, which allows all UV radiation to pass through. The cut-off wavelength is ca. 300 nm for Pyrex; this allows the passage of both UVA and UVB photons while preventing the UVC photons from exciting the TiO_2 sol. Pyrex glass, therefore, should be used for this experiment.

To accurately measure the numbers of incident photons and the trapped electrons, the titanium dioxide sols for the dosimeter should have minimum light scattering and preferably be transparent (with small particles). A key to prepare a transparent TiO_2 sol is control of the hydrolysis reaction (equation 3). The most effective method for controlling the reaction rate is to use low pH for the reaction solution and a limited amount of water as described in the experimental section.

$$Ti(OC_3H_7)_4 \quad + \quad 2\,H_2O \xrightarrow[HOC_2H_4OH]{HCl} TiO_2 \quad + \quad 4\,C_3H_7OH \tag{3}$$

Oxygen is known to react with the conduction band or trapped electrons, TiO_2 (e^-), to form oxygen radical anions (equation 4). Prior to irradiation, therefore, the sol should be purged with nitrogen to remove the influence of oxygen. If the sol sample contains an oxygen residue, the appearance of blue color upon radiation will be delayed. For the same reason, a TiO_2 sol after UV irradiation will regain its original colorlessness upon exposure to oxygen. The sol samples, therefore, can be reused.

$$O_2 + TiO_2(e^-) \rightarrow O_2^- \tag{4}$$

The dosimeter samples described for this experiment contain no toxic materials. They can be safely disposed of down the drain after dilution with water. It is desirable, however, to neutralize the solution prior to disposal.

Comparison Among Three Sunscreen Preparations

As a control experiment, a sample containing no sunscreen lotion was first used for the test. The absorbance changes confirm the linear relationship between the doses received by the dosimeter and its absorbance change at 546 nm (Figure 4). Three sunscreen samples were then prepared with 10, 20, and 30% (w/w) of Coppertone (SPF 4) in glycerol. The UV-vis absorption after the samples had been exposed to the sunlight or sunlamp was measured on a Spectronic 20D. The results shown in Figure 5

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 02187-7

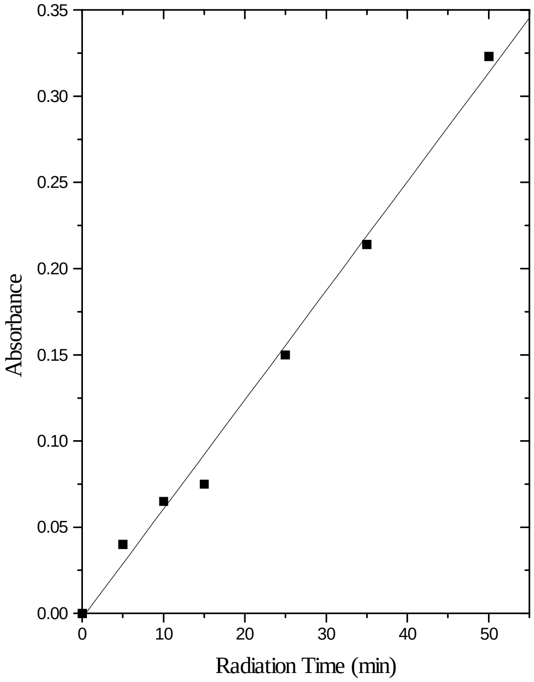

FIGURE 4. THE RELATIONSHIP BETWEEN THE RADIATION TIME WITH A SUNLAMP AND UV ABSORBANCE CHANGE OF A TIO_2 SOL IN A PYREX CUVETTE WITHOUT SUNSCREEN-LOTION PROTECTION.

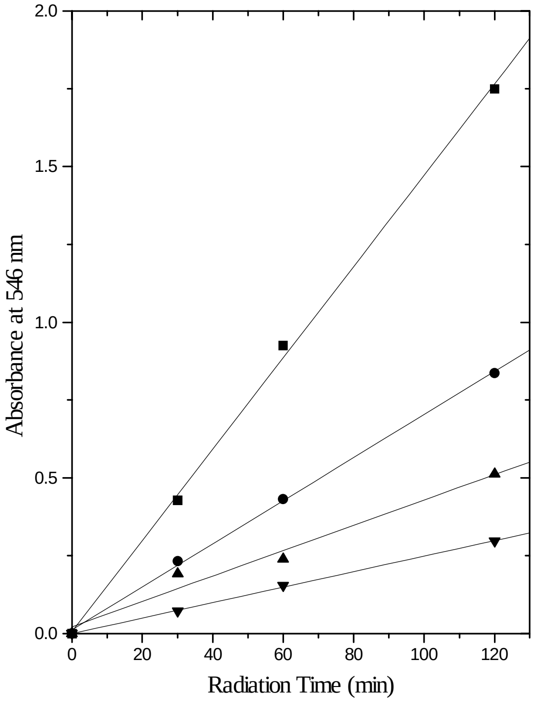

FIGURE 5. ABSORBANCE CHANGE (AT 546 NM) OF A TIO_2 SOL IN A PYREX TEST TUBE PROTECTED BY VARIOUS CONCENTRATIONS OF SUNSCREEN LOTION (■, 0%; ●, 10%; ▲, 20%; ▼, 30%) UPON EXPOSURE TO A SUNLAMP.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 02187-7

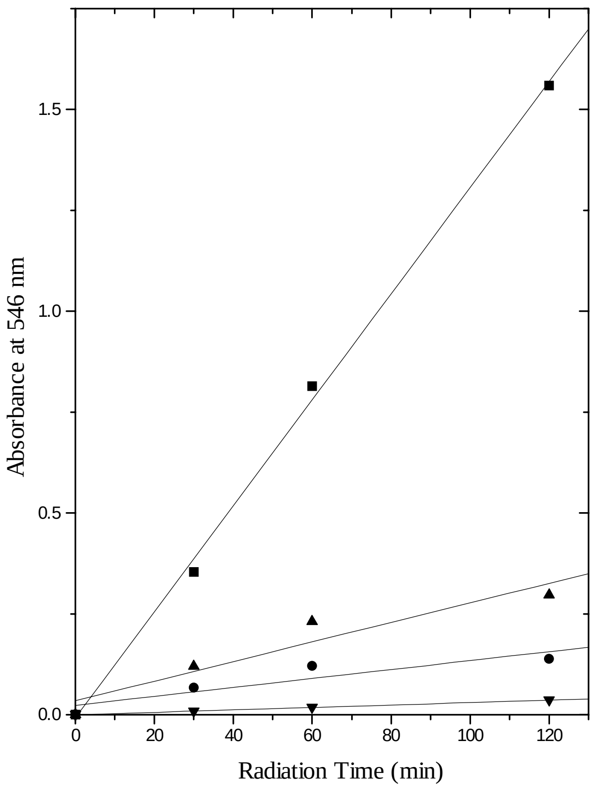

FIGURE. 6. ABSORBANCE CHANGE OF A TIO_2 SOL AT 546 NM IN A PYREX TEST TUBE PROTECTED BY VARIOUS SUNSCREEN LOTIONS [■, NO SUNSCREEN; ▲, COPPERTONE (SPF 4); ●, BANANA BOAT (SPF 8); ▼, INTENSIVE CARE (SPF 30)] UPON EXPOSURE TO A SUNLAMP.

---

clearly demonstrate that, as expected, the higher the sunscreen lotion concentration, the greater the protection it offers to the inner test tube. The absorbance at 546 nm, therefore, is lower with samples protected by a higher concentration of sunscreen lotion. This translates to a delayed color change.

A set of sunscreen samples made with three different types of sunscreen lotions was also prepared. They are 10% (w/w) solutions of Coppertone (SPF 4), Banana Boat (SPF 8), and Vaseline Intensive Care (SPF 30) in glycerol. In this set of experiments, the absorbance changes of TiO_2 sol at 546 nm were measured. The results are illustrated in Figure 6. The absorbance changes clearly agree with the SPF ratings, that is, the higher the rating, the higher the sunscreen's effectiveness for protecting the dosimeter in the inner tube.

ISSN 1430-4171
THE CHEMICAL EDUCATOR
http://journals.springer-ny.com/chedr

S 1430-4171 (98) 02187-7

Conclusion

The charge separation on amorphous and anatase TiO_2 particles caused by UV radiation leads to the trap or “preservation” of their conduction-band electrons in the presence of a good electron donor such as alcohol. The trapped electrons have a strong absorption in the visible region and thus can be used as a dosimeter for UV radiation. When designed properly, this dosimeter can be used to evaluate the effectiveness of sunscreen lotions. It is found that the dosimeter responded accordingly when sunscreen lotions with different SPF values are used, showing a quicker color change for a less effective sunscreen lotion. Due to its simplicity and relevance to daily life, this experiment can be used as a freshman-chemistry laboratory exercise or performed as a classroom demonstration for high school students or nonchemistry-major college students. For more advanced and interested readers, it is suggested that they explore the quantitative correlation between the slopes found in Figure 6 and their SPF values. Such a quantitative correlation could be obtained after a careful consideration of the spectral characteristics of each sunscreen lotion and the quantum yield of TiO_2 excitation [7].

REFERENCES

1. *Sunscreens: Development, Evaluation, and Regulatory Aspects*; Lowe, N. J.; Shaath, N. A.,. Eds.; Marcel Dekker: New York, 1990; Chapters 11–14.
2. Long, C. S.; Miller, A. J.; Lee, H. T.; Wild, J. D.; Przywarty, R. C.; Hufford, D. *Bull. Am. Meterorol. Soc.* **1995**, *77*(*4*), 729.
3. Wilson, L. J. *Canada’s UV Index—How It Is Computed and Disseminated*; Atmospheric Environment Service: Ontario, 1993.
4. Andrady, A.L. In UV-B Radiation and Ozone Depletion, Effects on Humans, Animals, Plants, Microorganisms, and Materials; Manfred, T., Ed.; Lewis Publishers: Boca Raton, FL, 1993.
5. *Human Exposure to Ultraviolet Radiation: Risks and Regulations*; Mcklilay, A. F.; Diffey, B. L., Eds.; Elsevier: New York, 1987; pp 83–87.
6. Shaath, N. A. In *Sunscreens: Development, Evaluation, and Regulatory Aspects*; Lowe, N. J.; Shaath, N. A., Eds.; Marcel Dekker: New York, 1990; Chapter 1.
7. Kimbrough, D. R. *J. Chem. Educ.* **1997**, *74*(*1*), 51.
8. Walters, C.; Keeney, A.; Wigal, C. T.; Johnston, Cornelius, R. D. *J. Chem. Educ.* **1997**, *74*(*1*), 99.

ISSN 1430-4171
http://journals.springer-ny.com/chedr

S 1430-4171 (98) 02187-7

9. Murov, S.L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993, 298.
10. Wahi, A.; Hoyer, P.; Konenkamp, R. *J. Non-cryst. Sol.* **1995**, 166, 869.
11. (a) Epstein, J. H. “Biological Effect of Sunlight” In *Sunscreens: Development, Evaluation, and Regulatory Aspects*; Lowe, N. J.; Shaath, N. A., Eds.; Marcel Dekker: New York, 1990; Chapter 3; (b) Kligman, L. H.; Kligman, A. M. “Ultraviolet Radiation-Induced Skin Aging” In *Sunscreens: Development, Evaluation, and Regulatory Aspects*; Lowe, N. J.; Shaath, N. A., Eds.; Marcel Dekker: New York, 1990; Chapter 4; (c) Pathak, M. A. “Intrinsic Photoprotection in Human Skin” In *Sunscreens: Development, Evaluation, and Regulatory Aspects*; Lowe, N. J.; Shaath, N. A., Eds.; Marcel Dekker: New York, 1990; Chapter 5.
12. Forbes, P. D. *Photochem. Photobio*. **1996**, *63*(*4*), 357.
13. Kuroda, A.; Ogino, K. *Fragrance J*. **1994**, *22*(*2*), 17.
14. Griese, A. C.; Christensen, E.; Jeppon, J. *J. Am. Pharm. Assoc.* **1950**, *39*, 30.
15. *The Merck Index*, 11th ed.; Budavari, S.; O’Neil, M. J.; Smith, A.; Heckelman, P. E., Eds.; Merck & Co.: New Jersey, 1989, 1492.
16. Goldhaber, S. Z. et al. *Lancet* **1988**, *1,* 842.
17. Surface Electron Transfer Processes; Miller, R. J. D.; Mclendon, G. L.; Nozik, A. J. Schmickler, W. Willing, F., Eds.; VCH: New York, 1995.
18. Liddell, P. V.; Boger, D. V. *Ind. Eng. Chem. Res.* 1994, *8*(*6*) 587.
19. Kamat, P.V. *Chem. Rev*. **1993**, *93*, 267.
20. Fox, M. A.; Duly, M. T. *Chem. Rev*. **1993**, 93, 341.
21. Purden, J. C.; Pross, J.; Li, Y. *J. Org. Chem.* **1992**, *57*, 5087.
22. Mahdavi, F.; Bruton, T.; Li, Y. *J. Org. Chem.,* **1993**, *58*, 744.
23. Li, Y.; Wang, L. In *Semiconductor Nanoclusters: Physical, Chemical, and Catalytic Aspects*; Kamat, P. V.; Meisel, D., Eds.; Elsevier: New York, 1997, 391.
24. Wang, H.; Partch, R.; Li, Y. *J. Org. Chem*. **1997**, *62,* 5222.
25. Bahnemann, D.; Henglein, A. and Spanel, L. *Faraday Discuss. Chem. Soc*. **1984**, *78*, 151.
26. Gratzel, M.; Pelizzetti, E.; Serpone, N. *Heterogen. Heterogen. Photocata.* **1986**, 91.
27. Vinodgopal, K.; Bedja, I.; Hotchandani, S.; Kamat, P.V. *Langmuir* **1994**, *14*, 1767.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 02187-7

28. Huang, J.; Ding , H.; Dodson, W. S.; Li, Y. *Ana. Chim. Acta* **1995**, *311*, 115.

29. Weller, H.; Eychmuller, A. In *Semiconductor Nanoclusters-Physical, Chemical, and Catalytic Aspects*; Kamat, P. V.; Meisel, D., Eds.; Elsevier: New York, 1997, 5.

30. Yoldas, B. E. *Appl. Opt.* **1982**, *21*, 2960.