

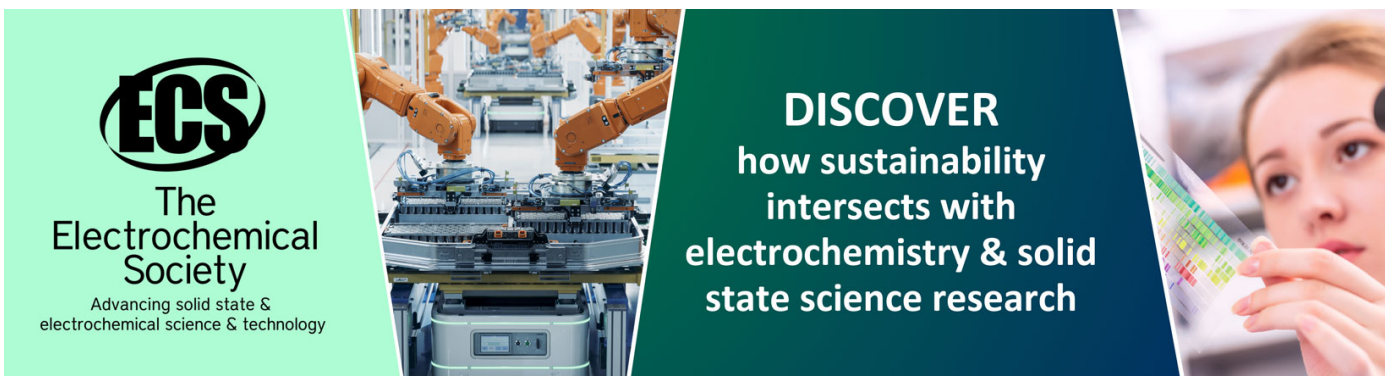
The photostability of dye-sensitized solid state photovoltaic cells: factors determining the stability of the pigment in a nanoporous n-TiO₂/cyanidin/p-CuI cell

To cite this article: K Tennakone *et al* 1997 *Semicond. Sci. Technol.* **12** 128

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The photostability of dye-sensitized solid state photovoltaic cells: factors determining the stability of the pigment in a nanoporous n-TiO₂/cyanidin/p-CuI cell

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Received 23 July 1996, accepted for publication 13 September 1996

Abstract. The factors determining the stability of the pigment in a dye-sensitized solid state photovoltaic nanoporous n-TiO₂/cyanidin/p-CuI cell was investigated by varying the gaseous environment around the cell and the sources of light used. It is found that photodegradation of the pigment cyanidin is almost completely suppressed provided oxygen, moisture and UV-light ($\lambda \leq 348$ nm) are excluded.

1. Introduction

Dye-sensitized solid state photovoltaic cells (DSSSPCs) that utilize pigments to trap light could turn out to be a promising alternative to the conventional photovoltaic devices [1–9]. The major problem with DSSSPCs has been their low quantum and energy conversion efficiency [3–5]. One of the present authors and co-workers have succeeded in developing a DSSSPC whose performance is impressive compared with previously reported DSSSPCs [1, 2]. This cell is based on nanocrystalline porous (nanoporous) films of TiO₂ deposited on conducting tin oxide (CTO) glass, coated with a monolayer of cyanidin (pigment extracted from flowers) [1]. The transparent p-type semiconductor cuprous iodide (CuI) is then deposited on the porous TiO₂ film, so as to fill the intercrystallite pores. The back-contact was made by evaporation of gold onto the outer surface of CuI (figure 1) [3]. Nanoporous n-TiO₂/cyanidin/p-CuI cells fabricated in the above manner generate photocurrents and photovoltages as high as 3.0 mA cm⁻² and 530 mV respectively (800 W m⁻² simulated sunlight).

Compared with conventional solid state solar cells (that are based entirely on photostable inorganic semiconductor materials) the photostability of DSSSPCs is questionable because of the presence of a pigment. The most important parameter determining the practical utility of DSSSPCs is the long-term photostability of the dye. In the cell we had reported earlier, the natural pigment cyanidin [10, 11] was used as the sensitizer. Cyanidin has the advantage of readily chelating with the surface of TiO₂, thereby affixing the pigment firmly to the TiO₂ surface [1]. However, *in vivo*

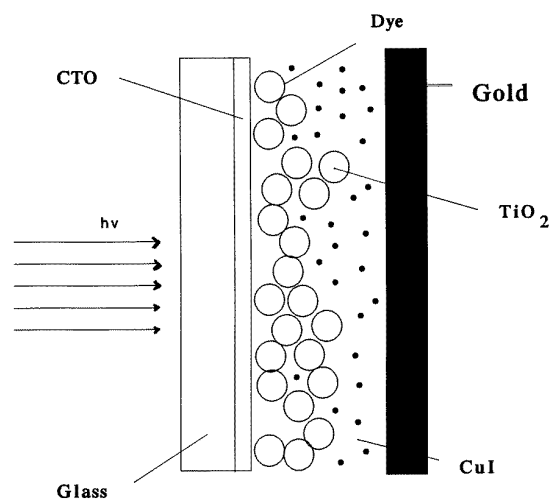


Figure 1. Construction of the nanoporous n-TiO₂/cyanidin/p-CuI photovoltaic cell.

cyanidin is not a highly photostable substance and studies on solid state photovoltaic cells sensitized with cyanidin will yield information necessary to determine the factors that affect the stability of such devices. In the present investigation, the factors determining the photodegradation of cyanidin in the nanoporous n-TiO₂/cyanidin/p-CuI cell were identified and it was found that in the absence of oxygen and moisture, the cell is amazingly photostable provided UV light ($\lambda \leq 348$ nm) is excluded.

2. Experiment

Nanoporous layers of TiO_2 were coated on CTO glass ($1 \times 2 \text{ cm}^2$, sheet resistance $15 \Omega \square^{-1}$) by the method described in [1], using a colloidal solution of TiO_2 . The flower pigment cyanidin was extracted from flowers of Anthurium and purified by chromatography [1]. Nanoporous films of TiO_2 deposited on CTO glass plates were coated with the pigment by warming the plates in a 15% acetic acid solution of the pigment [11–14]. Pigment adsorbed plates were washed with water, ethanol and dried in an argon atmosphere for 30 min. CuI was deposited on the dye-coated porous surface by dip and spray coating from a solution of CuI in acetonitrile [1]. A gold-plated CTO glass sheet firmly pressed against the outer CuI surface was used as the back-contact. A layer of gold evaporated onto the outer surface of CuI serves as a better back-contact [1], but to enhance the penetration of gases (in experiments where the cell is housed in a gaseous atmosphere) and removal of occluded gases (experiments conducted in vacuum) a loose contact was found to be preferable.

In one set of experiments, the cell was housed inside a double-walled, water-cooled (26°C) photochemical reactor which served as a thermostatic chamber. The chamber was kept slowly purged with moist air, dry air, dry argon (oxygen free), and moist argon (i.e. argon first bubbled through a wash bottle containing water) and illuminated with different sources of light (i.e. 200 W tungsten filament lamp, solar simulator with and without potassium nitrate filter that cuts off light of wavelength $\leq 348 \text{ nm}$). The time development of the short-circuit photocurrent under different conditions was recorded. In the other set of experiments, the cell was placed in an evacuated stainless steel cell ($3 \times 3 \times 3 \text{ cm}^3$) with a glass window and the time development of the short-circuit photocurrent was monitored using the different sources of illumination mentioned above.

To examine the degradation of the pigment coated on nanoporous films of TiO_2 (i.e. in the absence of the CuI deposit), these films deposited on CTO glass and coated with cyanidin were irradiated under experimental conditions identical to those used in the previous experiments and the optical absorbance of the film at 580 nm (the absorption peak of cyanidin coated on TiO_2 films) was measured at different intervals of time.

3. Results and discussion

The curves in figures 2 and 3 illustrate the time development of the photocurrent of the cell under conditions given in table 1. From the curves presented in figures 2 and 3 it is clear that stable photocurrents are observed only in cases a, b and f where oxygen, moisture and UV light ($\lambda \leq 348 \text{ nm}$) are excluded. Here the fading of the dye or any detectable decrease in the photocurrent was not observed even after 15 h of illumination, whereas in all the other cases except c and g, the decay of the photocurrent was accompanied by a noticeable fading of the dye adsorbed on the TiO_2 film. In case c (water saturated argon atmosphere) the decay of the photocurrent resulted from condensation of moisture

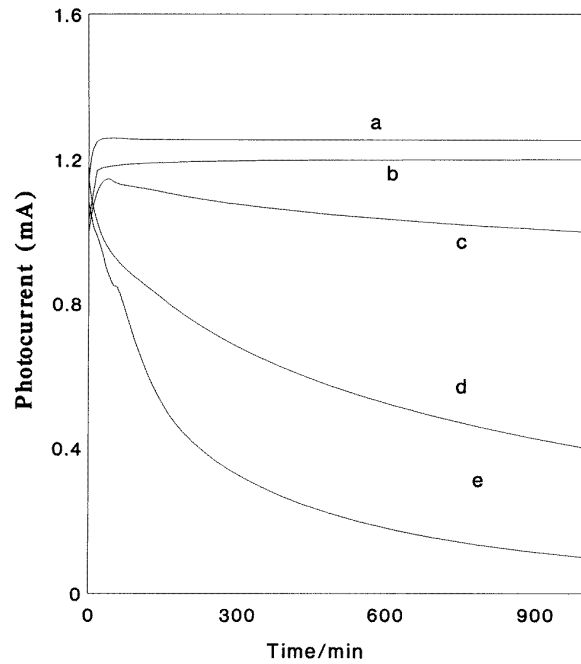


Figure 2. Time development of the photocurrent of the n- TiO_2 /cyanidin/p-CuI photovoltaic cell under conditions a, b, c, d and e given in table 1.

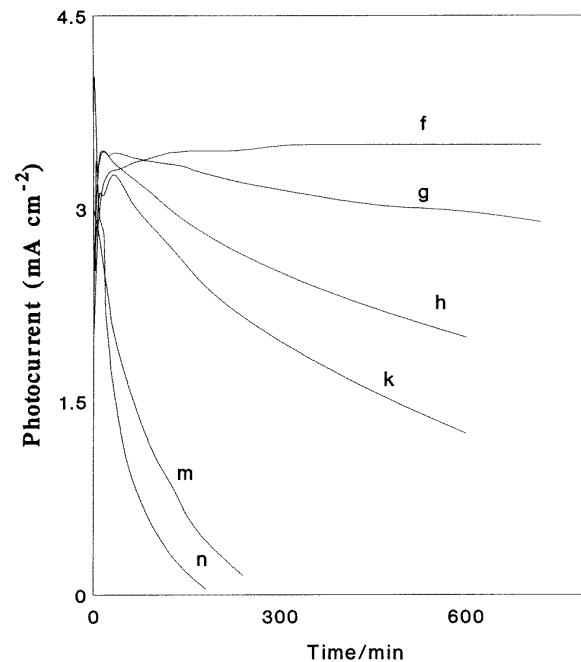
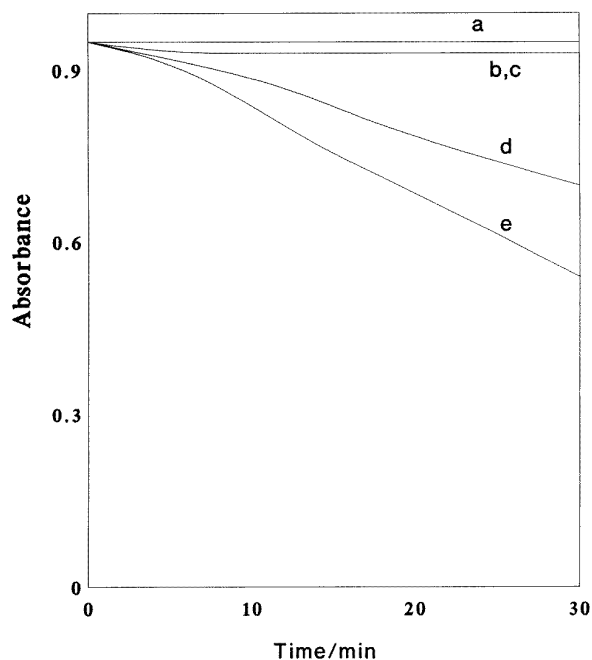
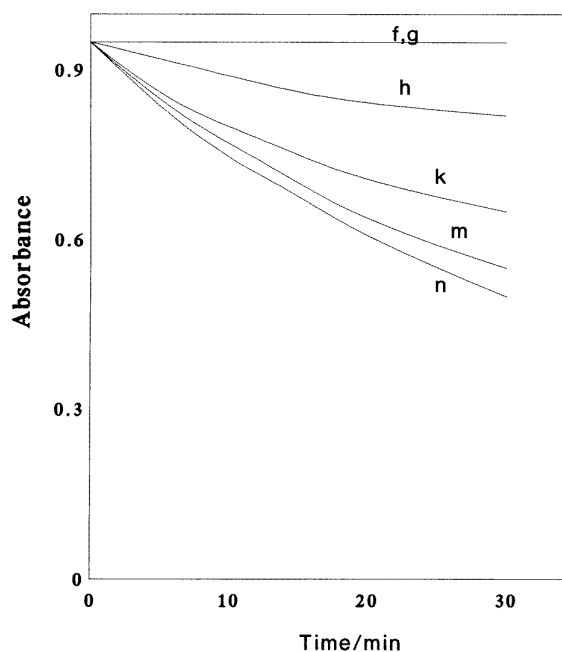


Figure 3. Time development of the photocurrent of the cell n- TiO_2 /cyanidin/p-CuI photovoltaic cell, under conditions f, g, h, k, m and n given in table 1.

in the CuI film and in g photocurrent decayed because of a progressive decrease in the electrical conductivity of the CuI film (p-type conductivity of CuI depends on the stoichiometric excess of iodine, vacuum conditions and warming of the cell from the light of the solar simulator

Table 1. Experimental conditions labelled as a, b, c, d, e, f, g, h, k, m and n in the curves of figures 2, 3, 4 and 5.

Label	Cell environment	Light source (intensity (W m^{-2}))
a	Vacuum	Tungsten filament lamp (430)
b	Dry Ar	Tungsten filament lamp (430)
c	Water saturated Ar	Tungsten filament lamp (430)
d	Dry air	Tungsten filament lamp (430)
e	Moist air	Tungsten filament lamp (430)
f	Dry Ar	Solar simulator intercepted by UV filter (600)
g	Vacuum	Solar simulator intercepted by UV filter (600)
h	Moist Ar	Solar simulator intercepted by UV filter (600)
k	Dry air	Solar simulator intercepted by UV filter (600)
m	Dry Ar	Solar simulator without UV filter (800)
n	Moist air	Solar simulator without UV filter (800)

**Figure 4.** The decrease in the optical absorbance at 580 nm (absorption peak of cyanidin) of a film of nanoporous n-TiO₂ coated with cyanidin during irradiation under conditions a, b, c, d and e given in table 1.**Figure 5.** The decrease in the optical absorbance at 580 nm (absorption peak of cyanidin) of a film of nanoporous n-TiO₂ coated with cyanidin during irradiation under conditions f, g, h, k, m and n given in table 1.

removes iodine from the CuI film).

The curves in figures 4 and 5 show the decrease in the absorbance of the dye-coated nanoporous TiO₂ film (i.e. in the absence of the CuI deposit) at 580 nm during the progress of irradiation under different conditions as given in the table 1. Again it is evident that cyanidin deposited on nanoporous TiO₂ does not undergo photodecomposition in the absence of oxygen and moisture provided UV light ($\lambda \leq 348$ nm) is excluded.

Several different mechanisms are operative in photo-degradation of the pigment coated on the nanoporous TiO₂ film. In addition to visible light, cyanidin also absorbs UV radiation intensely around 330 nm (the absorption spectrum of cyanidin is presented in figure 6) and photons in this region of the spectrum are sufficiently energetic to break bonds of the cyanidin molecule (figure 7 gives the structural formula of cyanidin). Clearly the decay of

the photocurrent in vacuum and dry argon when the cell is illuminated with a solar simulator (in the absence of the filter) originates via direct degradation of the pigment. When oxygen is present, UV light brings about very rapid TiO₂-sensitized degradation of the dye, which is further enhanced if moisture is also present. UV light ($\lambda \leq$ bandgap wavelength of TiO₂ nanocrystallites ~ 360 nm) generates electrons and holes in TiO₂ and electrons are readily accepted by oxygen to form the superoxide ion (O_2^-) whereas the dye molecules accept holes producing dye cations D^+ . (There is clear evidence that holes generated in TiO₂ by UV light are transferred to the dye molecules adsorbed at the surface of TiO₂. In the heterojunction n-TiO₂/p-CuI, the peak corresponding to the bandgap excitation of TiO₂ is barely detectable, but in n-TiO₂/cyanidin/p-CuI the same peak is much more pronounced, indicating that the minority carriers are rapidly

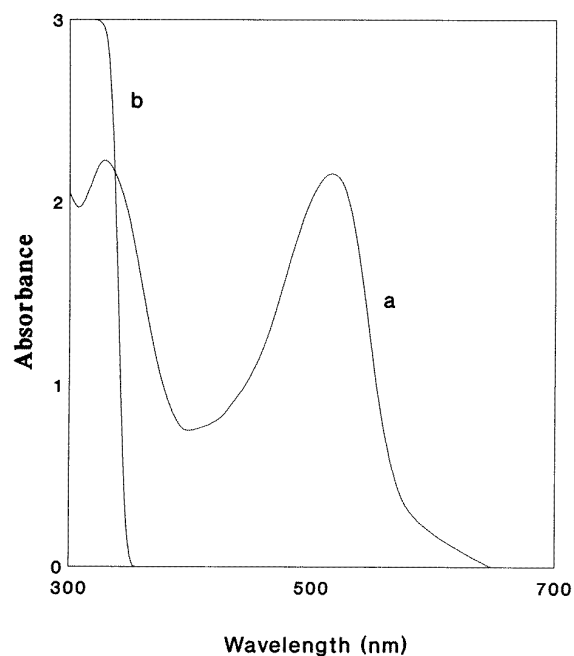


Figure 6. Absorption spectrum of an aqueous solution of (a) cyanidin and (b) potassium nitrate.

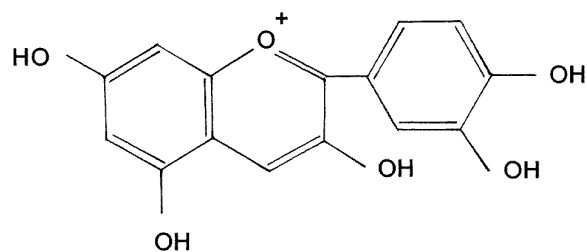
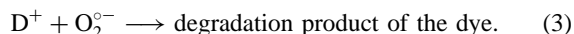
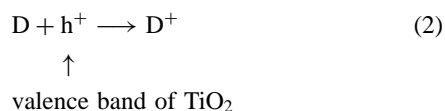
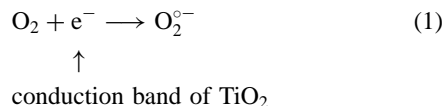


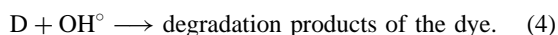
Figure 7. Structural formula of cyanidin.

transferred to the cyanidin molecules adsorbed at the surface of TiO_2 and then to CuI .) The reaction between the dye cation and the superoxide ion oxidizes the dye.

Reactions involved in sensitized degradation of the dye can be summarized as follows:



If moisture is also present, UV photodecomposition of the dye is further enhanced (compare curves m and n of figures 3 and 4). Here, holes are also scavenged by hydroxyl ions to form highly oxidative OH^\bullet free radicals that rapidly attack the dye [15], i.e.



It is interesting to note that in the experiment with the solar simulator under argon purging using the UV filter (that cuts off light of wavelength ≤ 348 nm), dye degradation occurs in the presence of moisture. The explanation is that the UV filter effectively cuts off light having wavelengths in the vicinity of the UV absorption peak of cyanidin which is located at ~ 330 nm (figure 6), while transmitting some light in the bandgap wavelength region of TiO_2 . The holes in TiO_2 created as a result oxidize dye via reaction (4). The charge transfer cycle is completed by participation of the electron, hydroxyl ion and an intermediate from (4) in other reactions.

When visible light is used photoreduction of the dye is seen only in the presence of oxygen. The reaction mechanism is presumably the following. The photoexcited dye molecules (D^*) inject electrons into the conduction band of n-TiO_2 forming the dye cation D^+ . Dye degradation results from reaction of D^+ with $\text{O}_2^{\bullet-}$ generated by scavenging of electrons by oxygen. The presence of water vapour enhances the rate of degradation of the dye (compare curves d and e of figure 4), because of the reaction of D^+ with OH^- ions. However, in the absence of O_2 , visible light illumination did not degrade the dye, even if water vapour was present. The reason for this is likely to be the absence of an efficient electron scavenger (in the former case, photogenerated electrons were readily accepted by O_2).

4. Conclusion

The above investigations clearly demonstrate that in the absence of oxygen and moisture the solid state nanoporous $\text{n-TiO}_2/\text{cyanidin}/\text{p-CuI}$ cell remains photostable provided UV light is filtered. The UV degradation of the pigment is mainly caused by direct attack of UV photons on cyanidin molecules. Rapid TiO_2 -sensitized UV degradation occurs when oxygen and/or moisture is present. Undoubtedly, cyanidin is not the pigment ideally suitable for future practical DSSSPCs (ruthenium complexes used as a sensitizer for wet cells [16, 17] are highly photostable, but they are not fully compatible with the deposition technique of CuI). Nevertheless the amazing stability of the cell under the conditions stated above is an indication of the feasibility of dye-sensitized solid state cells as practical devices. In a practical device, ensuring satisfactory UV filtration would be a technical problem. Direct UV degradation of the pigment can be suppressed by selecting a pigment that does not absorb light in the UV region of the spectrum. Sensitized UV degradation occurs only in the presence of oxygen and/or moisture; a suitable fabrication technique can avoid inclusion of moisture and oxygen.

Acknowledgment

This work is partly supported by the grant RG/95/P/04 of the Natural Resources, Energy and Science Authority of Sri Lanka.

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