

Large Enhancement in Photocurrent Efficiency Caused by UV Illumination of the Dye-Sensitized Heterojunction TiO₂/RuLL'NCS/CuSCN: Initiation and Potential Mechanisms

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Wide-band-gap, dye-sensitized, heterojunctions of the composition n-TiO₂/Ru-dye/p-CuSCN undergo large increases in efficiency when subjected to low-power UV illumination (<40 mW/cm²) for periods between 10 and 30 min. Ru-dye refers to any of several ruthenium polypyridyl dyes. The UV illumination increases the incident-photon-to-current-efficiency for light absorbed by the dye by a factor of 5–10 and increases the open circuit voltage by 100–300 mV. This beneficial effect is stable for months after the UV illumination is terminated. Investigation of the effects of varying the UV wavelength and the applied bias show that the reaction(s) responsible for the increase in efficiency begin with the oxidation of some interface species by a photoexcited hole in the TiO₂ valence band. Treatment of the TiO₂/dye/CuSCN cells with oxidized thiocyanate in solution causes a similar increase in the efficiency of dye sensitization. Results from TiO₂ and CuSCN photoelectrochemical cells are also presented. The combined results indicate that the UV illumination creates an interfacial layer of (SCN)₃⁻, and/or its polymerization product (SCN)_x, between the TiO₂ and the CuSCN. The data are consistent with the hypothesis that the (SCN)_x⁻ layer increases the rate at which the oxidized dye is regenerated after electron injection into the TiO₂.

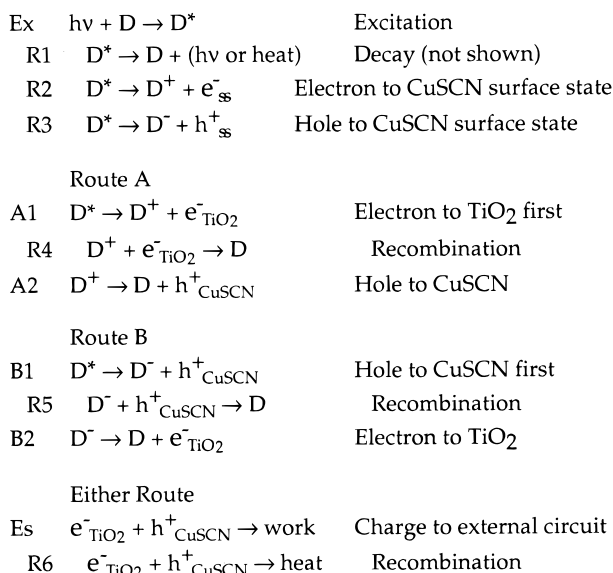
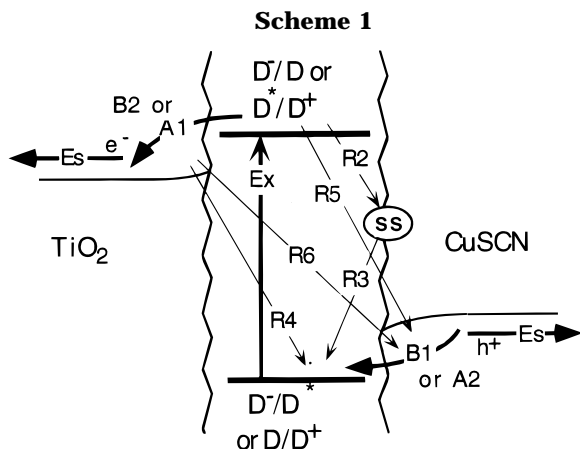
Introduction

Electron injection from excited dyes into wide-band-gap n-type semiconductors is receiving increasing attention due to recent developments that presage commercial applications in photovoltaics and smart windows.^{1–13} In these devices a dye monolayer is adsorbed on the surface of a nanoporous n-type semiconductor, usually TiO₂. For solar applications, the

TiO₂/dye electrode is incorporated into a regenerative photoelectrochemical cell for which the active interface can be written TiO₂/dye/electrolyte. An ohmic contact to the TiO₂, connected via an external circuit to a counter electrode in the electrolyte, completes the device. Hole injection from excited dyes into wide-band-gap p-type semiconductors has received far less attention but has also been demonstrated in photoelectrochemical cells. A range of substrates have been the subject of preliminary studies,^{14–18} whereas slightly more work has been done on silver halides,^{19–21} molecular crystals,^{22–24} copper iodide, and copper thiocyanate.^{25–27}

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Recently we have demonstrated that it is possible to generate both efficient electron injection and efficient hole injection from a monolayer of dye confined to the interface between an n-type and p-type semiconductor.^{28,29} The active interface in our studies can be written n-TiO₂/dye/p-CuSCN. We refer to this structure as a dye-sensitized heterojunction (DSH). In our format, a flat TiO₂ film is deposited on conductive (SnO₂:F) glass, a monolayer of dye is adsorbed to the TiO₂, and a CuSCN film is electrodeposited on top of the dye. Pressed graphite powder forms an ohmic contact to the CuSCN. A more complete description of the device has been published elsewhere.²⁸

Neither TiO₂ nor CuSCN (band gap ~ 3.6 eV)³⁰ absorbs visible light. Expected reactions at the interface, under visible light illumination, are shown in Scheme 1. In Scheme 1, desired (forward) reactions have thick lines and are left justified, and undesired reactions (those that do not lead to current in the external circuit) are indented. Arrows in the diagram

show electron movement except for hole transport in CuSCN. After excitation (Ex), either electron injection (route A) or hole injection (route B) can occur from the excited state or the excited state can decay by various routes (R1–3). Route A assumes that electron injection into TiO₂ occurs first (A1), after which, barring recombination (R4), a hole is injected into CuSCN from the oxidized dye (A2). Route B assumes that hole injection to CuSCN occurs from the excited state (B1), after which the reduced dye may inject an electron into TiO₂ (B2). If both charges are injected they can recombine across the interface (R6) or escape from the interface across the semiconductors to the external circuit (Es).

Although the excited dye cannot transfer an electron to the CuSCN conduction band, that reaction is ~ 1.5 eV uphill,³¹ the excited dye could transfer an electron to a trap state on the CuSCN surface, if such a state exists. This reaction (R2) will not lead to observed current unless the electron is then injected into TiO₂, which is unlikely. It is also possible for the excited state to transfer a hole to a trap state on the CuSCN surface (R3). If the trapped hole cannot escape thermally to the CuSCN valence band, it will eventually recombine with an electron and no external current will result. We have assumed in Scheme 1 that no holes are transferred to the surface of TiO₂ and that electrons do not become trapped at TiO₂ surface sites. Neither of these last mentioned reactions is found to occur significantly in TiO₂ dye-sensitized photoelectrochemical cells.

In other papers on TiO₂/dye/CuSCN DSHs, we have shown that the "as-fabricated" devices are inefficient, but that after certain posttreatments, the charge injection and collection processes can become quite efficient.^{28,29} The necessary posttreatment is different for two different classes of dyes. DSHs with organic dyes, such as rhodamine and fast green, respond best to mild heating, whereas DSHs containing ruthenium polypyridyl dyes respond best to exposure to UV light. The effect of the posttreatment on the overall efficiency of dye sensitization is large. Usually a 5- to 10-fold increase in the incident-photon-to-current-efficiency (IPCE) is observed for wavelengths absorbed by the dye.^{28,29}

In this paper we examine in detail the response of the TiO₂/dye/CuSCN interface to UV irradiation. We have investigated the sensitivity of the increase in dye-sensitized IPCE to several parameters and have found that a chemical posttreatment can mimic the effects of UV illumination. The results identify an important intermediate formed by the absorbed UV photons, and we discuss the possible mechanisms by which this intermediate causes the increase in efficiency.

Experimental Section

Nonporous TiO₂ electrodes were fabricated by spray pyrolysis. The thin (50–100 nm) TiO₂ films were deposited on commercial SnO₂-coated glass (Libby Owens Ford) at temperatures of about 500 °C.²⁸ The resultant films had a surface roughness between 1.5 and 2 as determined by dye adsorption. The dye Z105 (Ru(II)LL'(NCS)), where L is 2,2',6,2''-terpyridyl

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(31) The band gap of CuSCN is ~ 3.6 eV. We have measured the valence band edge to be around 0.4–0.7 V vs SCE; these data place the conduction band edge at least as negative as -2.8 V SCE, which is ~ 1.7 V negative of the reduction potential of Z105.

dine-4'-phosphonic acid and L' is 4,4'-dimethyl-2,2'-bipyridine) was a gift from the laboratory of Prof. Michael Grätzel.³³ Z105 was adsorbed from ethanol solution (10^{-5} M) by placing the TiO₂ electrode in the solution overnight. The amount of dye adsorbed was typically $\sim 3 \times 10^{-10}$ mol/cm², which corresponds to an absorbance of 0.7% of the incident light at 480 nm.²⁹ CuSCN was usually deposited from ethanol solutions of KSCN and Cu(BF₄)₂·xH₂O ($x \approx 4$) as previously described.³⁴ Morphologically similar CuSCN films were produced when CuSCN was deposited using other salts of Cu(II) and SCN⁻, or from acetone. Deposition was carried out between -0.1 and -0.2 V vs SCE, following a -0.4 V initial pulse that improved nucleation. Salts were purchased from Aldrich and used as delivered. Ohmic contact was made to the CuSCN by pressing finely powdered graphite onto the surface. All DSHs reported here had an active surface of ~ 1 cm².

Photocurrent action spectra were obtained using a 150 W xenon lamp (Oriel) focused through glass optics, a 10 cm water filter, and a Jobin/Yvon 0.20 M monochromator (grating blaze 450 nm). Currents were measured with a commercial potentiostat (Omni 90, Cypress Systems). Illumination containing UV was provided by the focused output of the same xenon lamp; for UV alone the lamp output was filtered through a UG2 (UV pass) filter. The integrated intensity for wavelengths <400 nm was varied from <1 to 30 mW/cm². The "action spectrum" for the effect of UV illumination on the dye-sensitized efficiency was measured by illuminating the DSH for 1 min with monochromatic UV and measuring the increase in dye-sensitized photocurrent generated by an additional light source containing only wavelengths > 520 nm. The increase in the visible photocurrent was divided by the incident UV photon flux at the UV wavelength. Scanning the UV region available (340–410 nm) produced the action spectrum. Photoelectrochemical measurements were carried out using the same lamp and monochromator and various custom built cells. The absorption spectra of Z105 adsorbed to TiO₂ was taken using transparent high surface area TiO₂ films made according to previously published recipes.^{1,35}

Dye-sensitized heterojunctions were exposed to solutions of oxidized thiocyanate by removing the graphite and placing the DSH in a sealed vial containing 5 mL of the solution. To make oxidized thiocyanate, we oxidized KSCN in ethanol in a three-compartment electrolysis cell. The compartments were separated by glass frits, and each compartment contained 5 mL of 0.025 M KSCN in ethanol. During electrolysis the liquid in the anode compartment remained clear until approximately $\frac{2}{3}$ of the SCN⁻ present had been oxidized. With further oxidation, the solution turned yellow and a yellow precipitate formed on the anode and in the bulk. Cessation of electrolysis at an approximate concentration of 5 mM (SCN)₃⁻ resulted in a clear to light yellow solution that developed a yellow precipitate over several days. The redox potential of the solution was 0.25 V vs SCE and moved slowly negative with storage. The results are consistent with previous reports of (SCN)₃⁻ formation.^{36–39} Both (SCN)₂ and (SCN)₃⁻ are unstable in solution at room temperature. Polymerization leads to the yellow product, which is reported to be a mixture of two polymorphs, ((SCN)₃)_x or (SCN)_x, depending on the electrolysis conditions.³⁹

Results and Discussion

For the results presented below, we have used the ruthenium dye Z105 which has a relatively sharp peak in the visible spectrum. This peak facilitates the measurement of the dye-sensitized photocurrent above the intrinsic response of the TiO₂/CuSCN heterojunction and also allows detection of spectral peak shifts. All of the results presented below have been duplicated several to many times. For example, the rate of increase in dye-sensitized efficiency with UV illumination has been measured over 50 times under varying conditions. Most of the results have also been duplicated with other ruthenium dyes such as Ru(II)L₂(NCS)₂, where L is 4,4'-dicarboxy-2,2'-bipyridine, and Ru(II)LL'(NCS)₂, where L is 4,4'-dicarboxy-2,2'-bipyridine and L' is 4-methyl-4'-phosphono-2,2'-bipyridine. The first is a common TiO₂ sensitizing dye,² and the second is a modification that contains a phosphonate group. Phosphonate binds more strongly than carbonate to TiO₂.³³ The results with these ruthenium dyes have been identical from the point of view of the effect of UV illumination.

Effect of UV Exposure on DSH Characteristics.

Figure 1a shows a typical photocurrent action spectrum for a TiO₂/Z105/CuSCN DSH in the initial state (solid line marked "0"). We use "initial state" to refer to the condition just after the deposition of the CuSCN and before any UV illumination or other postdeposition treatments. In the initial state, the efficiency of the dye sensitization is quite low. At the peak absorbance of Z105, 480 nm, the initial IPCE is usually between 0.15 and 0.25%. The initial IPCE is much larger for wavelengths less than 400 nm. This photocurrent is generated by UV photons absorbed by the TiO₂, as we will show later.

Illumination of an initial state DSH with UV light, or white light containing UV, causes a steady increase in the efficiency of dye sensitization. A typical series of action spectra, taken after increasing amounts of UV exposure, is shown in Figure 1a. Figure 1b shows the dye-sensitized IPCE (at 480 nm) and the intrinsic IPCE (at 360 nm) as a function of cumulative UV exposure. The initial rise of the dye-sensitized IPCE is well modeled by a single exponential, indicating a first-order process. For Z105 DSHs the dye-sensitized IPCE plateaus near 1.5%. Once the UV illumination has continued for some minutes beyond the point where the visible IPCE has reached the plateau, the increased efficiency becomes semipermanent. DSHs which have been exposed to UV and then stored in the dark for 6 months show less than a 5% decrease in the dye-sensitized IPCE at 480 nm. In contrast, the decrease in the intrinsic IPCE, at 360 nm, is transient. After several weeks of storage in the dark, the IPCE at 360 nm has usually recovered from a minimum of 3% back to 10–12%.

Once the plateau efficiency has been reached, continued UV exposure causes a decline in the dye-sensitized photocurrent (Figure 1b); however, removal of UV from the incident light decreases the decay rate dramatically. For Z105 the rate of decrease is typically 5% per day; however, we have exposed DSHs with other ruthenium dyes to over 500 h of illumination ($\lambda > 400$ nm) without loss of efficiency.²⁹

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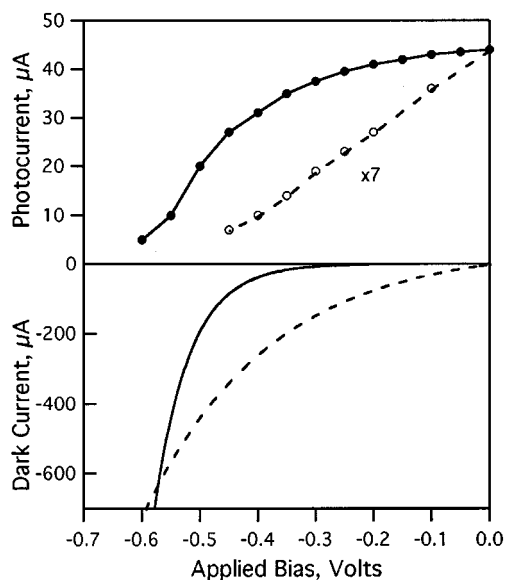


Figure 3. Current/voltage and photocurrent/voltage characteristics of a Z105 DSH before and after UV illumination with bias as applied to TiO₂. Upper: net photocurrent before (dashed) and after (solid) UV illumination. Values shown are the current under illumination minus that in the dark. Illumination: white light ($\lambda > 520$ nm), ~ 100 mW/cm². Lower: dark current before (dashed) and after (solid). Scan rate: 10 mV/s.

in no case did these changes produce a DSH that had a high efficiency before UV illumination or that failed to reach a high efficiency (for absorbed photons) after UV illumination.

The UV illumination also causes large changes in the current voltage response of the DSH. Before the UV illumination, the current voltage curve is that of a diode with a J_0 (exchange current) of 10–50 μ A and a quality factor of >5 (>300 mV/decade). A typical example is shown in Figure 3 (lower dashed line). The first effect of the UV illumination is to decrease J_0 to <1 μ A. The reduction in J_0 occurs simultaneously with the increase in the visible IPCE. There is no direct correlation, however, between the magnitude of the initial J_0 and the initial visible IPCE. Continued UV illumination (to the plateau IPCE) causes a further small decrease in J_0 and a significant decrease in the quality factor, to ~ 2.5 (~ 140 mV/decade). A typical I vs V curve at the end of the UV illumination is shown in Figure 3 (lower, solid line).

Figure 3 (upper) shows the changes in the photocurrent vs voltage curve with UV illumination. The value displayed is the net photocurrent ($I_{\text{illum}} - I_{\text{dark}}$). The photocurrent vs voltage relation undergoes a similar transformation as the dark current. In the initial state the photocurrent drops linearly with voltage to a photocurrent onset of ~ -500 mV. After the UV illumination, the photocurrent shows a distinct onset and plateau region but the photocurrent onset moves only slightly, to ~ -600 mV. The change in the shape of the photocurrent vs voltage curve is not due to the increase in the short circuit photocurrent. The data in Figure 3 were taken with the same light intensity before and after the UV treatment, however, the relative shapes are the same if the light intensities are adjusted to create the same short circuit photocurrent in the two states.

Initiation by UV-Excited Holes in TiO₂. All three materials in the DSH (TiO₂, the dye, and CuSCN) absorb UV light. To determine which materials were responsible for the UV effect, we measured the photocurrent action spectra of the various components separately and in pairs. We also measured the "action spectrum" of the UV effect and compared that to the action spectra of the three components.

Figure 4a compares the photocurrent action spectra of a TiO₂/CuSCN heterojunction, a TiO₂ film in a photoelectrochemical cell, and a CuSCN film in a photoelectrochemical cell, all without dye. The photocurrent onset for the TiO₂ alone and for the TiO₂/CuSCN rises steeply below 400 nm, consistent with the band gap of anatase (3.2 eV; 388 nm) or rutile (3.0 eV, 414 nm). The CuSCN photocurrent rises much more slowly in the region 350–400 nm, consistent with the reported band gap of ~ 3.6 eV.³⁰ The magnitude of the photocurrent of CuSCN is small compared to that of the TiO₂. Comparing the action spectra, it is evident that the photocurrent in the TiO₂/CuSCN structure comes almost entirely from photons absorbed by the TiO₂. Comparing the TiO₂ action spectrum with that of TiO₂/Z105/CuSCN (Figure 1a), it is clear that the UV photocurrent in the DSH is also due primarily to photons absorbed by TiO₂.

Figure 4b compares the "action spectrum" of the UV effect to the photocurrent action spectrum of TiO₂ and to the absorption spectrum of the dye. From the similarity of the first two spectra, it appears that the initial excitation responsible for the UV effect is a UV photon absorbed in the TiO₂ film. Consistent with that conclusion, the rate of the UV effect is higher for thicker TiO₂ films, which absorb more UV photons, and is not directly dependent on the thickness of the CuSCN layer.

Figure 4c shows the effect of bias applied to the DSH during UV exposure. Positive bias applied to the TiO₂ during UV exposure increases the rate at which the dye-sensitized IPCE improves, whereas negative bias applied to the TiO₂, or negative bias created by open circuit conditions, both decrease the UV effect rate. A positive bias of 2 V, applied without UV illumination, causes a slow increase in the dye-sensitized IPCE. Unfortunately the 2 V bias generally causes serious short circuits to develop as well. Positive bias on the TiO₂ will pull photogenerated electrons away from the interface and drive photogenerated holes toward the interface. Taken together, the data from the previous three paragraphs strongly suggest that the UV effect is caused by photogenerated holes arriving at the TiO₂ surface.

Interfacial Reactions Caused by UV Illumination. Valence band holes arriving at the TiO₂ surface in the DSH can oxidize most species present at the interface. Since SCN⁻ is known to adsorb to TiO₂ from solution,⁴⁰ it is likely that the TiO₂ surface in the DSH also has adsorbed SCN⁻ and that some of the UV excited holes result in the formation of thiocyanate radical, SCN[•], as the initial product. The thiocyanate radical is known to dimerize and to form (SCN)₂ in the presence of SCN⁻.³⁶ Both (SCN)₂ and (SCN)₃⁻ readily polymerize to form (SCN)_x, a conductive polymer also known as parathiocyanogen.³⁷

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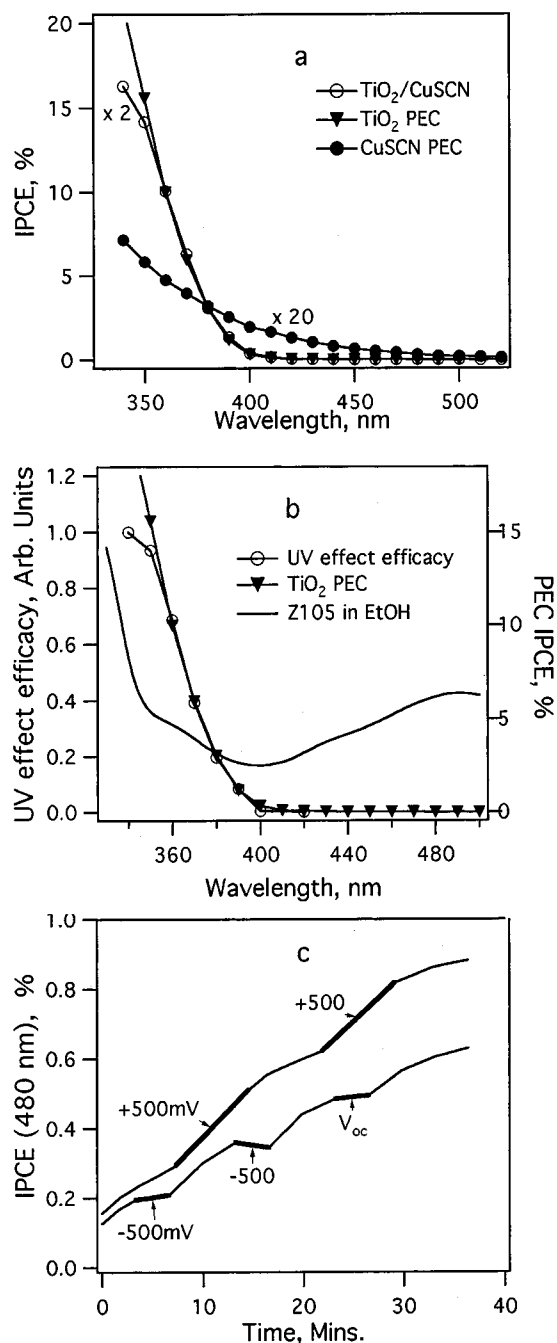


Figure 4. (a) Comparison of the photocurrent action spectra of a TiO₂/CuSCN heterojunction, TiO₂ photoelectrochemistry, and CuSCN photoelectrochemistry, all without dye. Electrolyte for TiO₂: ethanol/0.4 M KSCN. Electrolyte for CuSCN: ethanol/0.1 M tetrabutylammonium tetrafluoroborate. (b) Comparison of the "action spectrum" of the UV effect (see Experimental Section) to the action spectrum of the TiO₂ photoelectrochemical cell and to the absorption spectrum of Z105 (in ethanol, arbitrary units). (c) Effect of the bias potential applied to a Z105 DSH (bias as applied to TiO₂) on the rate of increase in the dye-sensitized IPCE with UV exposure. Thick lines represent the duration of the applied potential indicated by the label. Thin lines represent periods of zero bias (short circuit).

To test the involvement of thiocyanate oxidation in the UV effect we exposed several DSHs to an ethanol solution containing KSCN, K(SCN)₃, and soluble oligomers of (SCN)_x. The solution was created by partial anodic electrolysis of 0.025 M KSCN in ethanol (see the

Experimental Section). With a DSH having the standard 1 μm CuSCN layer, a 6-fold increase in the dye-sensitized IPCE occurs after 8 min of immersion in the oxidized thiocyanate solution (Table 1, line A1). The initial and final action spectra match closely those in Figure 1c, except that the intrinsic response (<400 nm) decreases by only 20%. Using a thicker, 5 μm, CuSCN layer, the response to oxidized thiocyanate is much slower (Table 1, line A2). Figure 5 shows the increase in the dye sensitization efficiency as a function of immersion time for the thicker CuSCN layer. The following two control experiments confirm that it is the oxidized thiocyanate that is responsible for the increase in efficiency. Exposure of a DSH to a KSCN solution that had not been electrolyzed did not cause an increase in efficiency, and exposure to an ethanol solution of LiClO₄ that had been electrolyzed by the same charge as the oxidized thiocyanate solution caused a slight decrease in the efficiency (Table 1, lines B1 and B2).

During treatment of the DSH with oxidized thiocyanate, the CuSCN layers remain translucent white. This indicates that the (SCN)₃⁻ does not oxidize the CuSCN to Cu(SCN)₂, as Cu(SCN)₂ is black.⁴¹ Scanning electron micrographs of the DSH show that the electrodeposited CuSCN is microcrystalline with crystallites ≤500 nm diameter. The films have a high density of grain boundaries, which may allow small molecules to diffuse from the CuSCN surface to the TiO₂/CuSCN interface. Evidence for the access of small molecules to the TiO₂ surface is found by immersion of the DSHs in water. Water immersion for 30 min causes a large decrease in the dye-sensitized IPCE, as expected for water at the TiO₂ surface. The Ru-dyes used do not sensitize TiO₂ efficiently when used with water electrolytes.

The sensitization of TiO₂ by Z105 in liquid junction cells is also sensitive to the presence of (SCN)₃⁻. When a spray pyrolysis TiO₂ electrode, with adsorbed Z105, is illuminated in an ethanol solution of KSCN, the initial IPCE is <0.3%. The addition of 1 mM K(SCN)₃ to the electrolyte causes a severalfold increase (Table 1, line P1). These experiments were done in a three electrode cell, so the increase in efficiency is not due to changes in the efficiency at the counter electrode.

UV illumination also causes changes in the action spectra of TiO₂/CuSCN heterojunctions without dye. Figure 6 (inset) shows the evolution of the UV IPCE and visible IPCE of a TiO₂/CuSCN heterojunction with increasing UV exposure. Similar to the dye-sensitized heterojunctions, the UV IPCE decreases and the visible IPCE increases. The maximum visible IPCE (at 480 nm) without dye is only 0.07%, 1/20 of that when dye is present. Figure 6 shows the action spectra for the same device before and after the UV illumination. The UV illumination causes the growth of a tail of photocurrent that extends into the blue and green part of the spectrum. An analogous tail appears in the action spectrum when a TiO₂ electrode, without dye, is UV-illuminated in an ethanol solution of KSCN (Figure 6). A similar change in the action spectrum has been observed during the oxidation of molten KSCN at a platinum electrode.³⁹ The authors of that work ascribe the photocurrent to an electrochemically formed layer of parathiocyanogen, (SCN)_x.

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Table 1. Effect of Exposure to UV or Oxidized Thiocyanate in Solution on Dye-Sensitized Heterojunctions and Photoelectrochemical Cells

Dye-Sensitized Heterojunctions							
label	substrate	CuSCN thickness, μm	initial IPCE, % ^a	treatment ^b	treatment time, min	final IPCE, %	increase
A0	TiO ₂	0.8	0.25	UV	5	1.6	$\times 6.4$
A1	TiO ₂	0.8	0.14	K(SCN) ₃	8	0.83	$\times 6$
A2	TiO ₂	4.2	0.29	K(SCN) ₃	143	2.1	$\times 7.2$
B1	TiO ₂	0.8	0.14	KSCN	8	0.14	
B2	TiO ₂	0.7	0.18	LiClO ₄	14	0.17	
Photoelectrochemical Cells							
label	substrate	electrolyte ^c	initial IPCE, %	treatment	treatment time, min	final IPCE, %	increase
P1	TiO ₂	KSCN	0.2	K(SCN) ₃ *	0 ^e	0.7	$\times 3.5$
P2	CuSCN ^d	TBABF ₄	0.23	UV	18	0.11	

^a IPCE of dye sensitization, 480 nm. ^b Treatments: K(SCN)₃ \equiv soaked in oxidized thiocyanate solution (5 mL of 25 mM KSCN in ethanol electrolyzed by 5 C anodic current). KSCN \equiv soaked in 5 mL of 25 mM KSCN in ethanol not electrolyzed. LiClO₄ \equiv soaked in 5 mL of 25 mM LiClO₄ in ethanol electrolyzed by 5 C anodic current. UV \equiv illuminated xenon arc lamp; intensity, 340 nm $< \lambda <$ 400 nm, ~ 30 mW/cm². K(SCN)₃* \equiv addition of oxidized thiocyanate to the electrolyte to ~ 1 mM K(SCN)₃. ^c Electrolytes: KSCN \equiv 0.2 M KSCN in ethanol. TBABF₄ \equiv 0.1 M tetrabutylammonium tetrafluoroborate in ethanol. ^d Electrodeposited CuSCN layer on conductive SnO₂ substrate. See ref 43 for details. ^e The increase appears within 30 s.

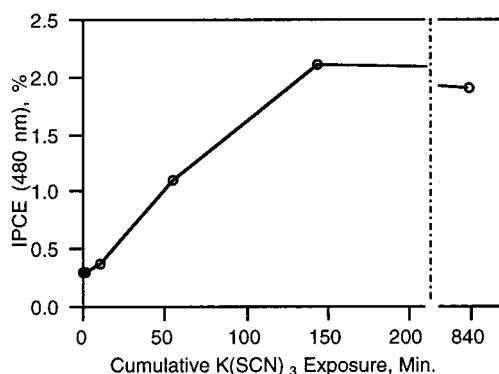


Figure 5. Increase in dye-sensitized IPCE for a TiO₂/Z105/CuSCN DSH vs immersion time in an oxidized thiocyanate solution. Solution: ethanol, 10 mM SCN⁻, 5 mM combined K(SCN)₃ and oligomeric (SCN)_x.

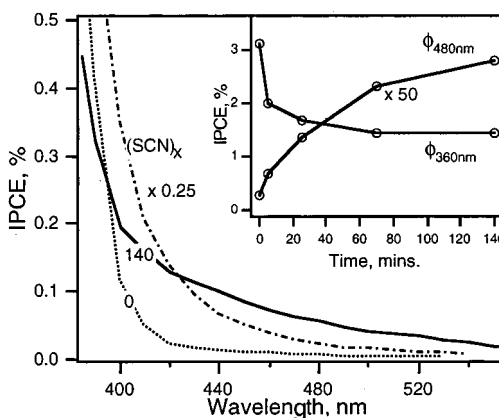


Figure 6. Effect of UV illumination on TiO₂/CuSCN heterojunctions without dye and on TiO₂ photoelectrochemistry in KSCN solution. Dotted and solid lines: photocurrent action spectra of TiO₂/CuSCN after 0 and 140 min of UV illumination, respectively. Dash-dot line: action spectrum of a spray pyrolysis TiO₂ film after 14 min UV illumination in saturated KSCN. Inset: time evolution of the intrinsic and visible part of the action spectrum of a TiO₂/CuSCN heterojunction under UV illumination.

The above results suggest strongly that the oxidation of SCN⁻ to (SCN)₃⁻ and/or (SCN)_x at the TiO₂/CuSCN interface, is responsible for the increase in dye sensitization efficiency observed during the UV illumination. The formation of (SCN)_x, as well as (SCN)₃⁻, is sug-

gested by the increase in the visible part of the action spectra of the DSH without dye, as (SCN)₃⁻ does not absorb in the visible.³⁶ The action spectra of the DSH and of the photoelectrochemically derived (SCN)_x are not identical; however, the absorption spectrum for (SCN)_x is dependent on the degree of polymerization and solvent.^{39,42}

The interaction of Z105 and CuSCN can also be examined in the absence of TiO₂ in an electrolyte/Z105/CuSCN photoelectrochemical cell. Z105 adsorbs weakly to CuSCN from ethanol solution. Electrodeposited CuSCN electrodes, sensitized with Z105, show a sensitized hole injection current in an electrolyte of 0.1 M tetrabutylammonium tetrafluoroborate in ethanol. The initial IPCE is $\sim 0.2\%$ whereas the fraction of the incident photons absorbed is $\sim 1\%$. UV illumination of the CuSCN in such a photoelectrochemical cell does not increase the efficiency of dye sensitization (Table 1, line P2). In contrast, CuSCN electrodes sensitized with cyanine dyes show photoelectrochemical absorbed-photon-to-current-efficiencies near one.⁴³ This indicates that some part of the charge injection and separation process is inefficient at the CuSCN/Z105 interface.

Interpretation

We now turn to the mechanism by which (SCN)₃⁻ or (SCN)_x improves the dye-sensitized efficiency in both the DSH and in PEC cells. Since the amount of dye is fixed, improvements in the dye-sensitized IPCE must result from improvement in the relative rates of the forward and back reactions in Scheme 1 or from an increase in the absorption coefficient of the dye molecules at the interface. It is unlikely that a 10-fold increase in the absorption coefficient of the dye could occur without large changes in the absorption spectrum. Because the initial and final action spectra of the DSH both match the absorption spectrum of the dye adsorbed to TiO₂ (Figure 1c), it is clear no large changes in the absorption spectrum of the dye have occurred during the UV treatment or the treatment with oxidized thiocyanate. We will focus our discussion of the possible mechanism on changes in relative reaction rates.

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In the photoelectrochemical cells, where no CuSCN is present, the mechanism of the increase in IPCE caused by $(\text{SCN})_3^-$ is likely to involve the relative rates of regeneration of the dye by $(\text{SCN})_3^-$ vs SCN^- . Data in ref 39 show that in molten KSCN the oxidation of $(\text{SCN})_3^-$ has better kinetics than the oxidation of SCN^- . We propose that the UV effect in the DSH can be explained as follows. In the initial state, electron injection from the excited dye to the TiO_2 is fast (Scheme 1, reaction A1), but the regeneration of the oxidized dye by CuSCN (A2) is too slow to compete with the recombination of the injected electron with the dye cation (R4). After UV illumination, which creates a layer of $(\text{SCN})_3^-$ and/or $(\text{SCN})_x$ at the interface, the oxidized dye is regenerated more quickly by oxidation of $(\text{SCN})_3^-$ or $(\text{SCN})_x$, which then passes the hole to the CuSCN valence band. Oxidation of $(\text{SCN})_x$ by the dye is shown by our recent observation of dye-sensitized photoconductivity in an $\text{TiO}_2/\text{dye}/(\text{SCN})_x$ structure.⁴⁴

In the initial state, the dye-sensitized IPCE is not zero, which shows that the oxidized dyes can inject holes into the CuSCN; however, the dye-sensitized photocurrent does not increase with time, showing that oxidized dye cannot carry out the reaction responsible for the UV effect. The explanation for this fact lies in the nature of the valence band in CuSCN. Although there are no published band structures for CuSCN, calculations and measurements on CuBr, which has a similar band gap to CuSCN, indicate a high contribution of Cu d-orbitals to the top of the valence band.^{45,46} The fact that $\text{Cu}(\text{II})(\text{SCN})_2$ is a stable solid is also strong evidence that copper-centered orbitals form the HOMO in CuSCN. This means that the mobile hole in CuSCN will be centered on copper, and that "hole injection" is effectively the oxidation of Cu(I) to Cu(II). Dye-sensitized photocurrent can flow through the cell without creation of oxidized thiocyanate. However, SCN^- at the interface can be oxidized by the hole in TiO_2 , which is a much more powerful oxidant than the oxidized dye.

The relatively high IPCE for the UV photocurrent shows that a large fraction of the UV-induced holes in the TiO_2 end up as mobile holes in CuSCN. Some of the UV-induced holes in TiO_2 will oxidize the dye. As described in the previous paragraph, this pathway can result in photocurrent, or in recombination, but not in the UV effect. Only a small fraction of the UV-induced holes need oxidize SCN^- to $(\text{SCN})_3^-$ for the UV effect to occur. The integrated UV-induced photocurrent necessary to reach the maximum dye-sensitized efficiency is typically 100 mC. Net oxidation of SCN^- by only 0.1% of this charge would be sufficient to create a monolayer of $(\text{SCN})_3^-$ at the interface.

It is also likely that band edge shifts of the TiO_2 are occurring during the UV illumination of the DSH. UV-induced band edge shifts have been used to explain the increase in dye-sensitized efficiency shown by a TiO_2 electrode in ethanol.⁴⁷ In the DSH, the persistence of the increase in efficiency, the effects of exposure to

$(\text{SCN})_3^-$, and the shifts in the current/voltage relations all argue against a band edge shift as the sole explanation of the changes caused by the UV exposure.

A full description of the UV effect must explain the maintenance of local charge balance. When the $(\text{SCN})_3^-$ is applied from solution, charge balance can be accomplished by simultaneous intercalation of K^+ ions. However, conversion of the near interface layers of SCN^- to $(\text{SCN})_x$ by holes from TiO_2 will result in an excess of positive charge at the interface. In the solid state, it is the electron of the UV-excited electron hole pair that supplies the balancing charge. Since the UV effect can occur with the DSH at open circuit, electron transit through the external circuit is not required. One intriguing possibility is that surface Cu(I) ions are reduced to Cu(0) at the interface. The UV effect could then be described as "TiO₂ photocatalyzed disproportionation of CuSCN". Reactions involving both the electron and the hole are well known in TiO_2 photodegradation.⁴⁸ As mentioned in the Results, the presence of Cu islands does not impair the charge separation at the interface. Further work will be required to resolve this question.

The model proposed does not explain the shift in the I vs V response or the changes in the UV IPCE of the DSH. As mentioned in the Results, neither of these changes are directly correlated with the increase in the dye-sensitized IPCE.

Conclusions

We have found that UV illumination causes a dramatic improvement in the efficiency of dye-sensitized heterojunctions of TiO_2 and CuSCN. We have demonstrated that the initial step in this effect is the reaction of photoexcited holes from the TiO_2 valence band with one or more species present at the $\text{TiO}_2/\text{CuSCN}$ interface. The data indicate that the key result of the hole reaction is a layer of oxidized thiocyanate at the interface. We have proposed that the oxidized thiocyanate, in the form of $(\text{SCN})_3^-$ or $(\text{SCN})_x$, increases the IPCE by increasing the regeneration rate of the oxidized dye. This hypothesis can be tested via the following experiments. To determine if oxidized Z105 can inject holes into $(\text{SCN})_x$, we plan to fabricate $\text{TiO}_2/\text{dye}/(\text{SCN})_x$ heterojunctions. To determine if oxidized $(\text{SCN})_x$ can inject holes into CuSCN, we will attempt to fabricate $\text{SnO}_2/(\text{SCN})_x/\text{CuSCN}$ heterojunctions or $\text{CuSCN}/(\text{SCN})_x/\text{dye}/\text{electrolyte}$ cells. It will also be of interest to establish, using laser flash photolysis, the relative rates of SCN^- vs $(\text{SCN})_3^-$ regeneration of the oxidized dye in photoelectrochemical cells. Use of thiocyanate as a redox couple might provide an increase in voltage in such cells, relative to the iodine couple presently in use.

The next step in the development of useful dye-sensitized heterojunctions is the demonstration of high surface area heterojunctions that contain enough dye to absorb a large fraction of the incident light. We have made considerable progress on this front, and our data show that the UV effect is even more important for high surface area devices.⁴⁹ Unfortunately, the UV effect does not seem to work on films with very small

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particles and very high surface areas. Incorporation of the alternative treatment using oxidized thiocyanate solutions will hopefully result in overcoming this barrier.

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