



**QUEEN'S
UNIVERSITY
BELFAST**

Action Spectra in Semiconductor Photocatalysis

Lee, S.-K., Mills, A., & O'Rourke, C. (2017). Action Spectra in Semiconductor Photocatalysis. *Chemical Society Reviews*, 46, 4877-4984. <https://doi.org/10.1039/c7cs00136c>

Published in:
Chemical Society Reviews

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

© The Royal Society of Chemistry 2017

This work is made available online in accordance with the publisher's policies. Please refer to any applicable terms of use of the publisher.

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access

This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: <http://go.qub.ac.uk/oa-feedback>

Action Spectra in Semiconductor Photocatalysis

Soo-Keun Lee^a, Andrew Mills^{*b} and Christopher O'Rourke^b

a: DGIST, 333, Techno Jungang Daero, Hyeonpung-Myeon, Dalseong-Gun, Daegu, 42988, Korea; b: School of Chemistry & Chemical Engineering, Queen's University Belfast, Stranmillis Road BT9 5AG, Belfast, United Kingdom.

E-mail addresses: andrew.mills@qub.ac.uk

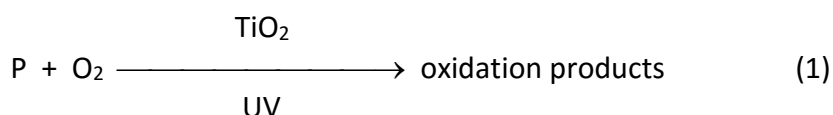
Abstract

Action spectra are an increasingly important part of semiconductor photocatalyst research, and comprise a plot of photonic efficiency, η , versus excitation wavelength, λ . The features and theory behind an ideal photocatalytic system are discussed, and used to identify: (i) the key aspect of an ideal action spectrum, namely: it is a plot of η vs λ which has the same shape as that of the fraction of radiation absorbed by the semiconductor photocatalyst, f , versus λ and (ii) the key requirement when running an action spectrum, namely, that the initial rate of the photocatalytic process is directly proportional to incident photo flux, ρ , at wavelengths where $\eta > 0$. The Pt/TiO₂/MeOH system is highlighted as an example of a photosystem that yields an ideal action spectrum. Most photocatalytic systems exhibit non-ideal action spectra, mostly due to one or more of the following: light intensity effects, crystal phase effects, dye-sensitisation, dye photolysis, charge transfer complex, CTC, formation and localized surface plasmon radiation, LSPR, absorption by a deposited noble metal catalyst. Each of these effects is illustrated using examples taken from the literatures and discussed. A suggested typical protocol for recording the action spectrum and absorption/diffuse reflectance spectrum of a photocatalytic system is described. The dangers of using a dye to probe the activity of a photocatalysts are also discussed, and a possible way to avoid this, *via* reductive photocatalysis, is suggested.

Key words: photocatalysis; action spectrum, titanium dioxide; photosensitisation; photolysis; spectral sensitisation

1. Introduction

Semiconductor photocatalysis continues to be an area of significant growth both in terms of research and commercial products¹. The latter are largely dominated by architectural materials, usually accompanied by the sobriquet 'self-cleaning', such as self-cleaning glass, tiles, paint and concrete¹. In their 'self-cleaning' role, most commercial photocatalytic materials use, as the semiconductor photocatalyst, TiO₂, usually in anatase form, to mediate the oxidation of pollutants, P, usually organic in nature, by ambient oxygen, i.e.



Note: the absorption of UV radiation is necessary to activate the TiO₂, since it has a bandgap of 3.0 eV.

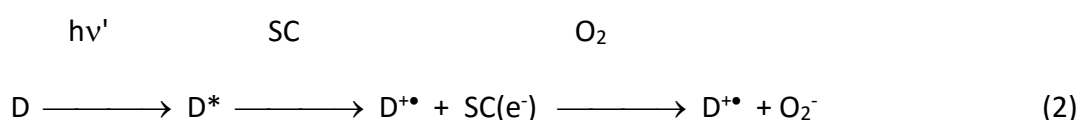
Most commercial photocatalytic materials are slow to act, not least because only about 4% of solar light is UV radiation, and most internal light sources have only a small UV component, if at all. It is no surprise, therefore, to note that many research groups are focused on developing a robust, visible light-absorbing semiconductor photocatalyst. Indeed, a brief inspection of the literature¹ reveals such a plethora of visible-light absorbing photocatalysts, not least those based on anion-doping (N, S and P) of TiO₂, that it is surprising that, to date, that most major commercial photocatalytic products, such as self-cleaning glass or tiles, remain TiO₂-based and so only UV absorbing.

There are many possible reasons why current visible-light promoted photocatalysts reported in the research literature have not made a significant impact on the major commercial, self-cleaning product scene, including: the cost of scaled-up production, low photostability and low activity, both in the visible and UV. However, another possible reason is that the original claim of visible light photocatalysis has been made in error, particularly if it was based on the photobleaching of a dye, as the test pollutant, so that some or all of the observed photobleaching may have been due to dye photosensitisation and/or dye photolysis, rather than photocatalysis^{2,3}. Alternatively, if the pollutant forms a visible-light absorbing ligand-to-metal charge transfer complex, i.e. LMCTC, or CTC for short, with the semiconductor, then the visible light induced disappearance of the organic pollutant may be due to a dye-photosensitisation mechanism, involving the electronically

excited state of the CTC, and, once again, not photocatalysis⁴. Given this range of possible routes to the destruction of 'P' in reaction (1), it is obviously, essential to establish the identity of the light-absorbing species (e.g. semiconductor, dye or CTC?) before any claim of visible light photocatalysis can be made with confidence; and, as we shall see, this is usually made possible by recording the action spectrum of the system.

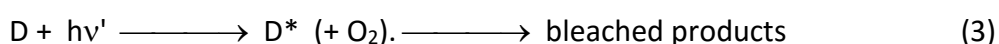
2. Dye-sensitisation and photolysis

Dye (photo)sensitisation usually involves the initial electronic excitation of the dye, D, to D*, by light of sufficient energy, $h\nu'$, so that D* is able to then inject an electron into the conduction band of the semiconductor, SC, which in turn then reacts with ambient O₂ present in the system^{4,5}. The process can be summarized as follows:



where $h\nu'$ is the energy of the photons absorbed by the dye, SC is the semiconductor under test (usually TiO₂), and D^{+•} is an oxidized radical of the dye that is unstable and able to react further to produce colourless degradation products. An example of a deliberate study of dye sensitization is provided the work of Wu *et al.*⁵, in their work on the photosensitized bleaching of Rhodamine B under visible light in an aqueous dispersion of TiO₂, and numerous reviews^{2,3} provide many more such examples. As noted above, a slightly modified version of the dye-sensitisation process can also operate if the non-visible light absorbing pollutant, P, forms a visible-light absorbing CTC between the SC and the substrate⁶.

Dye photolysis involves the electronically excited state of the dye which is either simply unstable and/or quenched by ambient O₂ to produce singlet oxygen – which then oxidises the dye, i.e.



Whatever the underlying mechanism, in dye photolysis the dye is bleached under irradiation, often at a rate that is largely independent of the presence of the semiconductor. In practice, in most photocatalytic studies the process of dye photolysis is usually quickly discounted by observing no dye photobleaching in the absence of the semiconductor

photocatalyst; although, as rightly noted by others, this latter 'blank' experiment doesn't eliminate the possibility of dye-sensitisation³.

A typical example of dye photolysis is the reported irreversible photobleaching of resazurin, Rz, in an anaerobic aqueous solution containing P25 TiO₂ and glycerol⁶. Rz absorb little in the UVA region (320-400 nm) and so UVA irradiation of the Rz/TiO₂/glycerol system results in the rapid (half-life, $t_{1/2}$, = ca. 1 min; 5 mW cm⁻²) photocatalysed reduction of Rz (blue colour) to resorufin (pink), and concomitant oxidation of glycerol. In contrast, when irradiated with 617 nm light (the $\lambda(\text{max})$ of Rz = 658 nm), where Rz does absorb, no Rf is produced, but the blue coloured dye slowly bleaches ($t_{1/2}$, = ca. 30 min; 10 mW cm⁻²) due to dye photolysis; as might be expected, the rate of the latter process is independent of the presence of glycerol and TiO₂.

3. Action spectrum and photonic efficiency

In semiconductor photocatalysis an action spectrum is a plot of photonic efficiency, not quantum yield⁷, versus excitation wavelength, λ , where photonic efficiency, η , is defined as the ratio between the number of molecules formed or degraded in a photocatalytic system per unit time, and the number of photons incident on the system per unit time, at a given wavelength, λ ⁸. In most cases, initial rate, r_i (units: moles s⁻¹) is taken as the numerator of this ratio and the incident photon flux, ρ (units: moles of photons of wavelength, λ , or Einsteins s⁻¹) as the denominator, i.e.

$$\eta = r_i/\rho \quad (4)$$

In most photocatalytic studies the irradiance, E (units of mW cm⁻²), rather than ρ is reported, where, for example, 1 mW cm⁻² of 365 nm UVA light is equivalent to 1.84×10^{15} photons cm⁻² s⁻¹, or 3.05×10^{-9} Einsteins cm⁻² s⁻¹. If polychromatic radiation is used, then the ratio of initial rate to incident photon flux has been defined^{8,9} as the formal (or apparent) quantum efficiency, FQE, although many use the two terms, η and FQE, interchangeably⁹. In contrast to photonic efficiency, quantum yield, QY, measurements are notoriously difficult to make¹⁰, as they require the accurate measurement of the *absorbed*, rather than *incident*, light flux. Thus, the measurement of QY, and the much less common reports of QY vs λ are outside the scope of this *tutorial* review, except where such plots appear wrongly named, and are really η vs λ plots, *vide infra*.

It is worth deviating slightly at this point to ask what – in the context of eqn (4) – is monochromatic (rather than polychromatic) radiation. A brief perusal of the literature associated with action spectra, and the measurement of η , suggests that it is not unusual for an excitation emission band with a full-width at half-maximum intensity (FWHM) of ca. 20 nm, to be considered sufficiently monochromatic to allow the calculation of η ; although FWHM values nearer 10 nm are more common, *vide infra*. In order to achieve this level of monochromaticity when recording an action spectrum, i.e. a plot of η vs λ , usually a polychromatic light source, such as a Xe lamp, is coupled to a monochromator (MC). Alternatively, interference-type optical filters maybe used, instead of a monochromator, to provide different wavelengths of 'monochromatic' radiation. However, optical cut-off filters, instead of interference filters, are not so useful, since they provide an integrated version of the action spectrum, i.e. a 'pseudo-action spectrum'¹³, and although it is possible to simply differentiate a pseudo action spectrum, to obtain the real action spectrum, it is not recommended, since the latter may be significantly distorted due to a variation in the sharpness of the filters and light intensity effects (*vide infra*).

Interestingly, the standard Black Light Blue lamp, BLB, with a phosphor which emits at 368 nm, and which is in general use in semiconductor photocatalyst research, has, typically, a FWHM of ca. 18 nm. In contrast, the other main type of BLB, with a phosphor that emits at 352 nm, has, a FWHM of ca. 40 nm. The narrow band BLB is of little use with regard to recording an action spectrum, but can provide a useful guide to the intensity dependence of the photocatalytic system at 365 nm, and so be used to test the validity of the often made assumption that the rate of the photocatalytic reaction is proportional to ρ (*vide infra*). For reasons that will become clear later, ideally, whatever the irradiation system, the irradiance should, ideally, be adjusted, using neutral density filters or by altering the distance, so that the number of photons incident to the reaction cell is the same at all wavelengths. In practice, this is a tedious process and so rarely carried out.

Obviously, if either dye photolysis or dye-sensitisation occurs, then a photocatalyst can appear to exhibit visible light photocatalytic activity, whereas in fact the observed photobleaching of the dye is NOT associated with semiconductor photocatalysis, i.e. NOT due to reaction (1), but instead is due to a dye-sensitisation and/or dye photolysis processes, i.e. reactions (2) or (3). As a consequence, in order to support any claim of

photocatalysis, especially visible light photocatalysis, there is a real need to identify the absorbing species and this can be achieved by recording the action spectrum of the system, which is usually a plot of photonic efficiency (or apparent quantum efficiency), η , of the system versus wavelength of the incident irradiation^{3,11}. If the action spectrum has a similar spectral profile to the photoabsorption spectrum of the semiconductor alone, then this can be taken as strong evidence that the reaction is indeed photocatalytic. If, on the other hand, there are striking discrepancies between the two then this suggests a non-photocatalytic mechanism is in operation.

4. Examples of action spectra

A list of some of the action spectra reported to date for both UV and visible light absorbing photocatalysts is given in table 1^{8,12-39}, a brief examination of which reveals that most involve the semiconductor photocatalyst TiO₂ for UV-absorbing photocatalysts. Action spectra for visible light absorbing photocatalysts include: CdS, WO₃ and non-metal-doped TiO₂. Most action spectra can be identified as being a member of one of the following two groups: (i) ideal (rare) or (ii) distorted (common) action spectra. An ideal action spectrum is one in which the initial rate of the reaction is proportional to ρ at all λ , and the semiconductor photocatalyst is the only absorbing species, so that the resulting action spectrum has the same spectral profile as the plot of the fraction of light absorbed by the semiconductor photocatalyst, f , versus λ . All photocatalyst action spectra that do not satisfy the definition of the ideal action spectrum, fall under the heading of distorted action spectra. Further discussion of ideal action spectra and the different types of distorted action spectra is provided in the following sections.

Table 1 Examples of reported photocatalyst action spectra

Semiconductor	Reaction	Comments (FWHM/nm)*	Ref
UV photocatalysis			
TiO ₂	Stearic acid	Similar action spectrum to that reported for acetic acid (7.5)	12
P25	Phenol, 4CP	Xe/Hg lamp (10)	8
TiO ₂	H ₂ evol. and Ag dep.	5 different types of TiO ₂ used for the 3 different photocatalytic reactions (23)	13
P25	Phenol, 4CP	Intermediate analysis, Xe/Hg lamp (10)	14
P25	4CP	Xe lamp	15
10% NaOH coated Rh-TiO ₂	H ₂ O splitting	Relative quantum efficiency gradually increases with decreasing wavelength	16
Pt-TiO ₂	H ₂ O splitting	Platinised anatase TiO ₂ (BDH) used for the reduction of H ₂ O. rate vs wavelength	17
TiO ₂ sol	Salicylate	Quantum yield vs excess photon energy	18
Visible photocatalysis			
P25, Pt-WO ₃	Acetic acid	Action spectrum similar to abs. spectrum	19
S-TiO ₂	Acetic acid	P25<S-TiO ₂ <1wt% Fe ₂ O ₃ S-TiO ₂	20
N-TiO ₂	Phenol, 4CP	Xe/Hg lamp (10)	21
Au-TiO ₂	2-propanol	Action spectrum similar to DRS (15)	22
C ₃ N ₄	H ₂ O splitting	band path filter (± 20 nm)	23
TiO ₂ , S-TiO ₂	MB, acetic acid	Dye sensitised reaction was found with MB degradation (17)	24
CdS	MB	N-demethylation of MB accelerated only by the excitation of CdS in aqueous solution.(10)	25
Pt-CdS	H ₂ O splitting	Only light of λ< 560 nm produces H ₂ and yields increased sharply close to the semiconductor band edge (2.4 eV, 510 nm)	26

*unless stated otherwise, a Xe-lamp with monochromator was used as the excitation source.

5. Ideal action spectra

In an 'ideal' heterogeneous semiconductor photocatalytic system, it is assumed that the initial rate of a photoreaction is proportional to the rate of absorption of the exciting light, so that eqn (4) transforms into:

$$\eta = (kf\rho)/\rho = kf \quad (5)$$

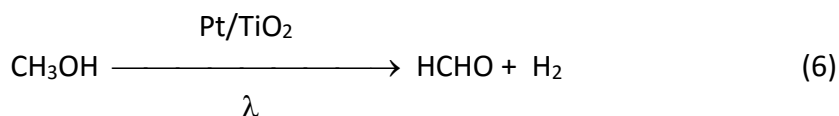
Where k is a proportionality constant, which, amongst other things, depends upon how efficient the photocatalyst is at promoting the photocatalytic reaction. The term, f , represents the fraction of exciting radiation of wavelength, λ , absorbed by the semiconductor photocatalyst. The conventional band theory view used to rationalize semiconductor photocatalysis suggests that the excess energy of any photons with energy $>$ the bandgap of the semiconductor is thermalized and, as a result, k should be largely independent of λ ⁸. If k is independent of λ , then a plot of η vs λ , i.e. an action spectrum of the photocatalytic system, should simply reflect the extent to which the semiconductor absorbs the light and so should have the same spectral profile as f vs λ . A rough approximation of the shape of the latter profile is provided by the absorption spectrum, or diffuse reflectance spectrum, i.e. DRS, of the photocatalyst^{3,9}.

Diffuse Reflectance Spectroscopy, DRS, is used routinely to identify wavelength the region where a solid material absorbs by measuring the reflectance, R_∞ , as a function of excitation wavelength, λ . This data is usually presented as either the absorbance ($\log(1/R_\infty)$) or the Kubelka-Munk, K-M function, i.e. $F(R_\infty) = (1 - R_\infty)^2/2 R_\infty$, which can be used 'as a proxy for the typical absorption spectrum'²⁷. DRS is often used to probe the absorption spectra of semiconductor photocatalysts,^{27,28} and when combined with an action spectrum can help identify the light-absorbing species^{3,29}.

Note also that the action spectrum for an ideal photocatalytic system should be independent of photo flux/irradiance. Thus, if the action spectrum for an ideal photocatalytic system is recorded at several different average irradiance values, then the resulting plots of η vs λ will superimpose on one another.

An ideal photocatalytic system is defined here as one in which: (i) the initial rate is proportional to ρ at all λ and (ii) the test pollutant does not form a charge transfer complex, CTC, nor does it absorb any of the wavelengths of excitation used in the study. A very nice

illustration of such an ideal system is provided by the work on Torimoto *et al*⁹, in their study of the photocatalysed dehydrogenation of methanol (MeOH; 50 vol%) in water using photoplatinized (2 wt%) anatase TiO₂ (10 mg cm⁻³) from Merck (BET surface area: 13 m² g⁻¹). In this case, the photocatalytic reaction can be summarized as:



The rate of hydrogen evolution was measured as a function of excitation wavelength, using a Xe/MC irradiation system (FWHM ca. 17 nm at all λ) at three different average irradiances (0.1, 1.4 and 7.5 mW cm⁻²)⁹. The resulting kinetic data were used to generate the plot of (normalized) photonic efficiency vs λ illustrated in figure 1. As expected for an ideal photocatalytic system, the three action spectra for reaction (6), corresponding to the three different average irradiances (i.e. 0.1, 1.4 and 7.5 mW cm⁻²), superimpose on one another and give a very approximate fit to the DRS of the TiO₂ powder (broken line in figure 1). The ca. 15 nm red shift in the action spectrum compared to the DRS is attributed by the authors¹⁰ to the relative large FWHM of the monochromatic light used in this work, when compared to the high resolution of the DRS.

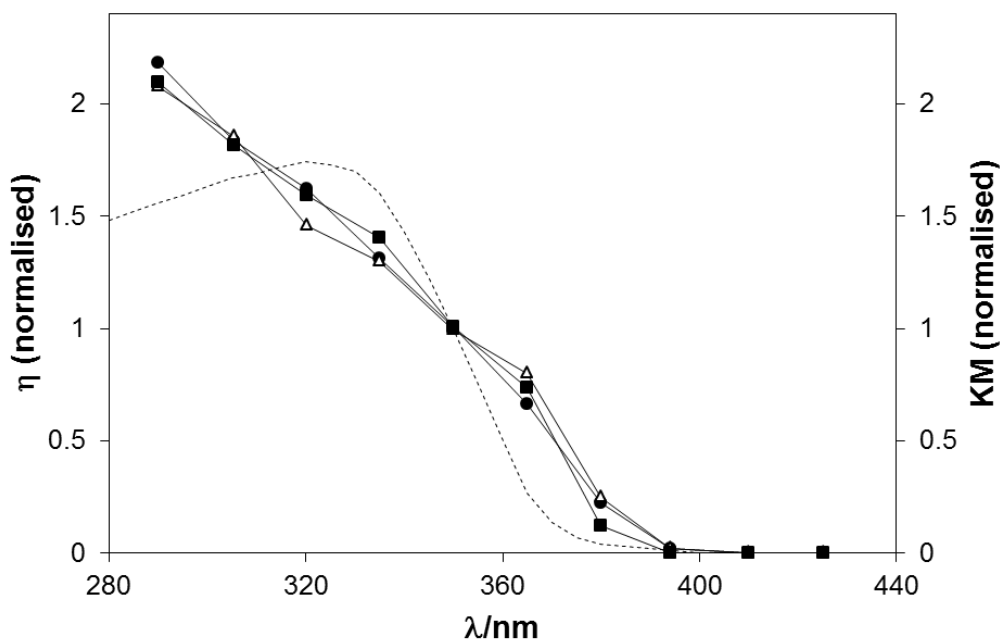


Figure 1: Plot of normalized (at 350 nm) photonic efficiency, η , for reaction (6), [MeOH] = 50 vol%; [TiO₂] = 0.010 g cm³, as a function of excitation wavelength, λ , measured using the following three different average irradiances: 0.1 (■), 1.4(Δ) and 7.5 (●) mW cm⁻². The broken line is the normalised (at 350 nm) Kubelka-Munk data from the DRS of the Pt/TiO₂ semiconductor photocatalyst powder. A Xe lamp/monochromator, i.e. Xe/MC, with FWHM = 17 nm was used as the light source. Data taken from reference 9.

Although the fit of the DRS to the action spectra illustrated in figure 1 is not very good, it does indicate that the semiconductor photocatalyst is most likely the light absorbing species in this system and, therefore, the reaction is probably a true example of photocatalysis. In contrast, most photocatalytic systems, such as many of those listed in table 1, are non-ideal.

6. Simulation and testing ideal action spectra

Recently, the optical properties of dispersions of TiO₂, from several different suppliers, have been characterised^{30,31} in sufficient detail that a value for f can be calculated at a number of different wavelengths for a particular dispersion of a relevant sample of TiO₂ using the expression:

$$f = 1 - 10^{-\text{Abs}(\lambda)} \quad (7)$$

Where $Abs(\lambda)$ is the effective absorbance of the TiO_2 dispersion at wavelength λ , and given by:

$$Abs(\lambda) = 0.434 \cdot \kappa(\lambda) \cdot [TiO_2] \cdot b \quad (8)$$

Where $\kappa(\lambda)$, units: cm^2g^{-1} , is the specific absorption coefficient at λ , $[TiO_2]$ is the concentration of the TiO_2 dispersion (units: $g\ cm^{-3}$) and b , units: cm , is the penetration depth of the excitation light of wavelength λ , assuming its less than the pathlength of the reaction cell. A value for b at each wavelength, λ , can be estimated by assuming that at b , 99% of the light has either been lost by scattering or absorption, i.e. at b , $Abs(\lambda) = 2$, thus:

$$b = 2 / (0.434 \cdot \beta(\lambda) \cdot [TiO_2]) \quad (9)$$

where, β is the Extinction (i.e. absorption plus scattering) coefficient. This calculation is appropriate only if the photoreactor has an optical path length that is $> b$; which – as we shall see – is likely in all cases considered here. The variations of β and κ as a function of λ for P25 TiO_2 , as reported by Satuf *et al.*³¹, are illustrated in figure 2(a). The variation of b as a function of λ can be calculated using this data, for example by assuming $[TiO_2] = 0.010\ g\ cm^{-3}$ and using eqn (8), so as to yield the plot of b vs λ in illustrated in figure 2(b). These results show that, for $[TiO_2] = 0.010\ g\ cm^{-3}$, b varies from ca. 0.007 to 0.011 cm as λ increases from 295 to 405 nm ; this being the case, it is reasonable to assume that in most photocatalytic studies in which $[P25\ TiO_2] = 0.010\ g\ cm^{-3}$, the photoreactor's optical pathlength is $> b$ at all λ , i.e. all light is either scattered (and lost), or absorbed within the photoreactor, and none is lost *via* transmission through the photoreactor.

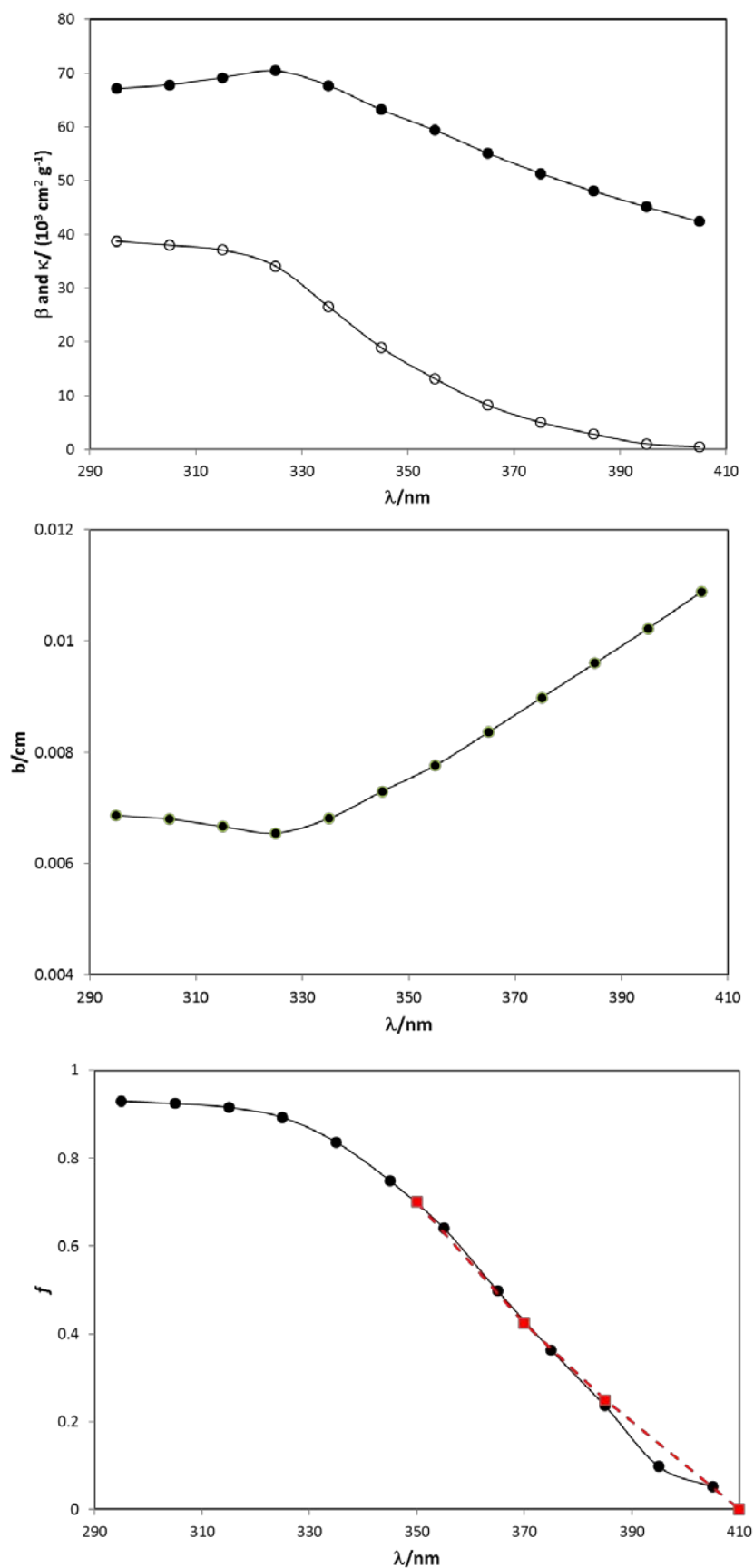


Figure 2: Plots, as a function of λ , of (a) reported values of β and κ , and calculated values of (b) penetration depth, b , and (c) fraction of light absorbed, f , by a 0.010 g cm^{-3} dispersion of P25 TiO_2 . The red broken line in (c) corresponds to the action spectrum (η vs λ) for Pt/ TiO_2 (P25) for reaction (6), normalized here to provide the best fit, reported by Torimoto *et al*¹³.

Given the calculated variation of b vs λ , for $[P25\ TiO_2] = 0.010\ g\ cm^{-3}$, illustrated in figure 2(b), it is then possible to calculate how f varies as a function of λ , using eqns (8) and (7), respectively, and the results of this work are illustrated in figure 2(c).

As noted above, in an ideal photocatalytic system the action spectrum should have the same spectral profile as f vs λ , which in turn should be similar in shape to the DRS of the semiconductor photocatalyst dispersion. Encouragingly, the measured action spectrum for reaction (6) using platinized P25 TiO_2 , using $[TiO_2] = 0.010\ g\ cm^{-3}$; $[MeOH] = 50\ vol\%$; FWHM = ca. 23 nm, reported by Torimoto *et al*¹³, red broken line in figure 2(c), provides an excellent fit to that of f vs λ predicted using the spectral data of Satuf *et al*. also illustrated in figure 2(c).

In practice, a feature of an 'ideal' photocatalytic system appears to be one in which at least one part of the overall photo-induced redox reaction, i.e. the reduction or oxidation, is facile. For example, in reaction (6), the sacrificial electron donor, MeOH, is in vast excess (50 vol% \equiv 12.4 M) and easily oxidized so that its reaction with the photogenerated holes on a semiconductor such as TiO_2 , would be expected to be very fast.

As noted earlier, an important characteristic of an ideal photocatalytic reaction is that the initial rate is proportional to ρ , or E , even at high levels, at all λ used to generate the action spectrum. Although it is impractical to check the latter feature at all λ , **a sample of wavelengths should be tested**. For example, in a study of reaction (6), Torimoto *et al*⁹ reported the initial rate to be largely independent of E over the range ca (0.05-0.1) – (5-10) $mW\ cm^{-2}$, when probed using 290, 350 and 380 nm light.

For all photocatalytic systems, even for an ideal one, as ρ is increased, a photon flux level will eventually be reached, the threshold flux, $\rho(\text{threshold})$, much above which the initial rate is no longer proportional to ρ , but rather ρ^θ , where θ is < 1 and typically tending towards 0.5 ³². Note that $\rho(\text{threshold})$ is used here as a mathematical construct, to help identify the regions: (i) $\rho \ll \rho(\text{threshold})$, over which rate is proportional to ρ and (ii) $\rho \gg \rho(\text{threshold})$, where rate is proportional to $\rho^{1/2}$.

In practice, this feature has been demonstrated in many different photocatalytic systems^{9,33,34}. A nice illustration of the $\rho(\text{threshold})$ region is provided by the work of by Egerton and King³³, in their study of the photocatalytic oxidation of 2-propanol to acetone,

by rutile TiO₂, in which the initial rate was determined as a function of ρ over an impressively wide range (ca. $(0.002 \text{ to } 103) \times 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}$) using a 250 W medium pressure Hg lamp (unfiltered) as the light source. A plot of these results is illustrated in figure 3, along with broken red lines to highlight the regions in which the initial rate is proportional to ρ (for low values of ρ) and proportional to $\rho^{0.5}$. In this system $\rho(\text{threshold})$ is ca. $4.7 \times 10^{15} \text{ photons s}^{-1}$, and, if we assume all photons are 365 nm, and an irradiation area = 2 cm^2 , this translates to an irradiance of ca. 1.3 mW cm^{-2} , which would be considered a moderate irradiance in most photocatalytic studies. The latter point is made to highlight the fact that it would be wrong to assume for any photocatalytic system the values of $\rho(\text{threshold})$ and $E(\text{threshold})$ are always exceptionally high, i.e. $\gg 10 \text{ mW cm}^{-2}$ at 365 nm say; whereas, in practice the threshold irradiance can be $< 1.5 \text{ mW cm}^{-2}$.

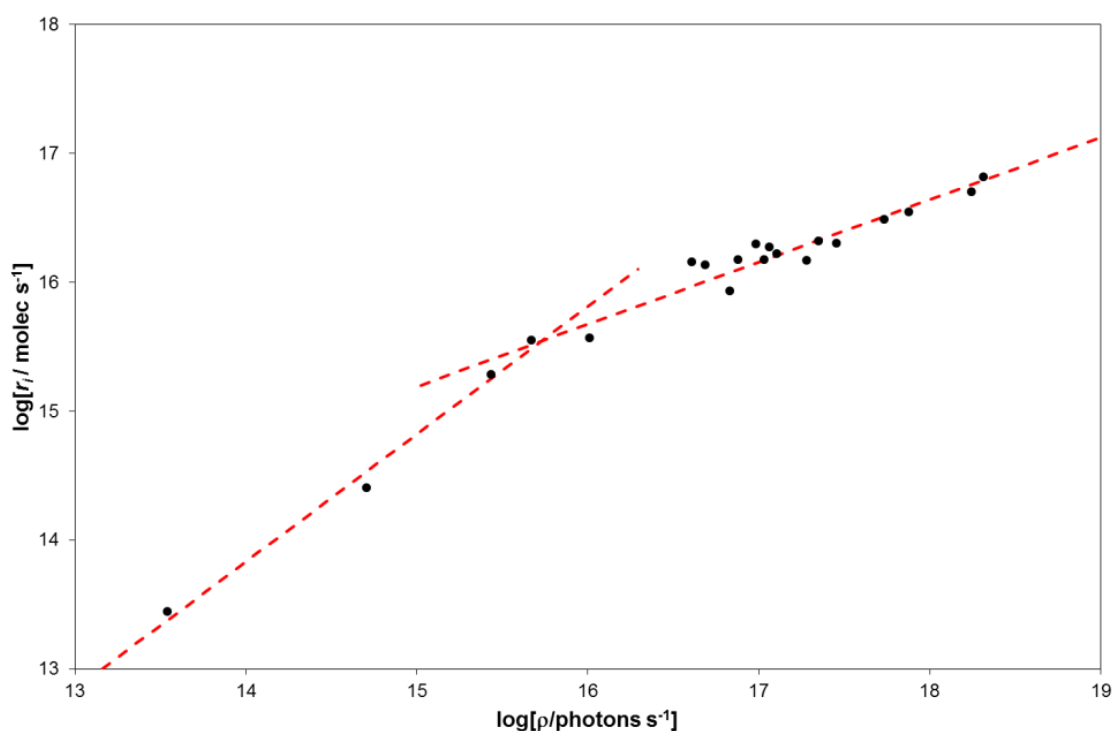


Figure 3: Plot of $\log(r_i)$ vs $\log(\rho)$, reported by Egerton and King³³ in their study of the photocatalytic reaction (1), using rutile TiO₂ and P = 2-propanol. The broken lines are the lines of best fit when the initial rate is initially (at low ρ) proportional to ρ and (at higher ρ) then proportional to $\rho^{0.5}$. The threshold photon flux for this system appears to be ca. $4.7 \times 10^{15} \text{ photons s}^{-1}$ (i.e. ca. 1.3 mW cm^{-2} , assuming all photons are 365 nm and an irradiation area of ca. 2 cm^2 ; Hg (med. pressure lamp)).

The often made argument³² for the change of dependence of initial rate upon ρ is that at low ρ the overall photocatalytic reaction is dependent directly upon the rate of generation of electron-hole pairs and, therefore, ρ , because direct electron-hole pair recombination is a minor process, but at high irradiances, electron-hole pair recombination dominates and the overall rate tends to be dependent upon $\rho^{0.5}$. In practice^{10,35}, at the moderate irradiances commonly employed in semiconductor photocatalysis (ca. 0.5-3 mW cm⁻²) it is not uncommon for the rate to be depend directly upon ρ^θ , where $0.5 < \theta < 1$.

So far we have considered the features of an ideal action spectrum, i.e. one in which $\theta = 1$ and so eqn (5) is obeyed at all λ . Any deviation from this ideal spectral profile can be considered a distortion (from the ideal), the cause of which may be due to one, or more effects which include: (i) variation in emission irradiance/intensity, (ii) crystal phase and (iii) pollutant, absorption; and, each of these effects is discussed below.

7. Intensity distorted action spectra

The intensity distortion effect is readily demonstrated by considering what the action spectrum of a simple photocatalytic system would look like if the initial rate is proportional to ρ^θ rather than ρ , where $0.5 < \theta < 1$.

It follows from eqn (5) that, at any excitation wavelength, the measured photonic efficiency, η , will be given by the expression:

$$\eta(\theta) = k_\theta(\alpha f \rho)^\theta / \rho \quad (10)$$

Where k_θ is a proportionality constant (units: moles/s) which depends upon: (i) the initial concentration of P: $[P]_0$ and (ii) the intrinsic activity of the photocatalyst, *i.e.* the probability that an absorbed ultra-bandgap photon leads to a reaction; α is a proportionality constant of convenience, with a value of unity, but with units: s einsteins⁻¹, so that it renders the collection of terms, $\alpha f \rho$, unitless and simplifies the units of k_θ and any subsequent mathematical manipulations of eqn (10). If we assume that at $\rho(\text{threshold})$, $\eta(\theta = 1) = \eta(\theta = 0.5)$, it follows that:

$$k_{0.5}/k_1 = (\alpha f \rho(\text{threshold}))^{0.5} \quad (11)$$

so that

$$\eta(\theta=0.5)/\eta(\theta=1) = \{\rho(\text{threshold})/\rho\}^{0.5} \quad (12)$$

And so in all cases where $\rho > \rho(\text{threshold})$, then the greater the value of ρ , compared to $\rho(\text{threshold})$, the lower the value of η , i.e. when $\theta = 0.5$ (and, in fact, more generally when $\theta < 1$). Thus, when $\theta < 1$, η will be dependent upon ρ , at any excitation wavelength, which is in striking contrast to an ideal system, where $\theta = 1$ and η is independent upon ρ . As a result, for any photocatalytic system under study in which $\theta < 1$, the resulting action spectrum will appear distorted from that of the true, i.e. 'ideal', action spectrum (for which $\theta = 1$).

In order to gain an insight into the extent of this distortion effect, consider a TiO_2 photocatalytic system in which the fraction of light absorbed, f , as a function of λ absorbed is as illustrated in figure 2. If the photon flux used was sufficiently low that it never exceeded $\rho(\text{threshold})$, it follows from eqn (5) that $\eta(\theta = 1) = k_1 f$ and the action spectrum would have the same spectral profile as that in figure 2(c), as illustrated in figure 4(a) – solid red line, assuming $k_1 = 1$; i.e. the system would generate an ideal action spectrum.

Now let us consider the case where the photon flux used was sufficiently high that at all λ , it always exceeded $\rho(\text{threshold})$. The combination of eqns (5) and (12) yields the following relationship between $\eta(\theta = 0.5)$ and ρ :

$$\eta(\theta=0.5) = k_1 f \cdot \{\rho(\text{threshold})/\rho\}^{0.5} \quad (13)$$

Note: this expression only holds provided $\rho > \rho(\text{threshold})$. In order to make these calculations more pertinent, we require a typical lamp profile and figure 4(b) illustrates some extreme lamp profiles, namely, those for: (i) a lamp with a photon flux density (i.e. ρ/A , where A = irradiation area, that is independent of λ (set at 10^{14} photons $\text{nm}^{-1} \text{cm}^{-2}$ ($\equiv 0.054 \text{ mW nm}^{-1} \text{cm}^{-2}$ at 365 nm), and the typical emission spectra of (ii) a Xe and (ii) Xe/Hg 1000W lamp. For simplicity we shall set $\rho(\text{threshold})$ to be ca. 3.5×10^{13} photon $\text{nm}^{-1} \text{cm}^{-2}$ ($\equiv 0.019 \text{ mW nm}^{-1} \text{cm}^{-2}$ at 365 nm), so that at all λ , $\rho > \rho(\text{threshold})$, and eqn (13) can be used to calculate the resulting action spectra, which are illustrated in figure 4(a). These calculated action spectra show that only if ρ is constant at all λ will the action spectrum (broken line in figure 4(a), have the same spectral profile as that of the ideal action spectrum, i.e. the action spectrum of same system, but carried out at $\rho < \rho(\text{threshold})$).

In contrast, in the two other cases, using emission profiles for real lamps, the calculated action spectra are distorted versions of the ideal action spectrum, and the distortion is due to the emission profile of the lamp. The most dramatic of these distortions is the action spectrum associated Xe/Hg lamp, i.e. the blue spikey line in figure 4(a), which highlights the striking effect a markedly variable lamp emission spectrum has on an the action spectrum for a photocatalytic system in which rate is proportional to ρ^θ , where $0.5 < \theta < 1$; in this example $\theta = 0.5$. A quick comparison between the action spectrum one might expect for a Xe/Hg lamp and the emission of that lamp (illustrated in figures 4(a) and 4(b), respectively) reveals that the action spectrum is a composite of the f vs λ spectrum of the semiconductor photocatalyst and the 'negative' of the lamp emission spectra, exhibiting peaks and troughs in the action spectrum where there are troughs and peaks in the emission spectrum. Clearly, this simulation suggests that it would be very unwise to run an action spectrum using a Xe/Hg lamp, since it is very possible that at the emission peaks in the spectrum the condition $\rho > \rho(\text{threshold})$ will be met, so that $\theta < 1$ and the resulting action spectrum will exhibit a series of peaks and troughs.

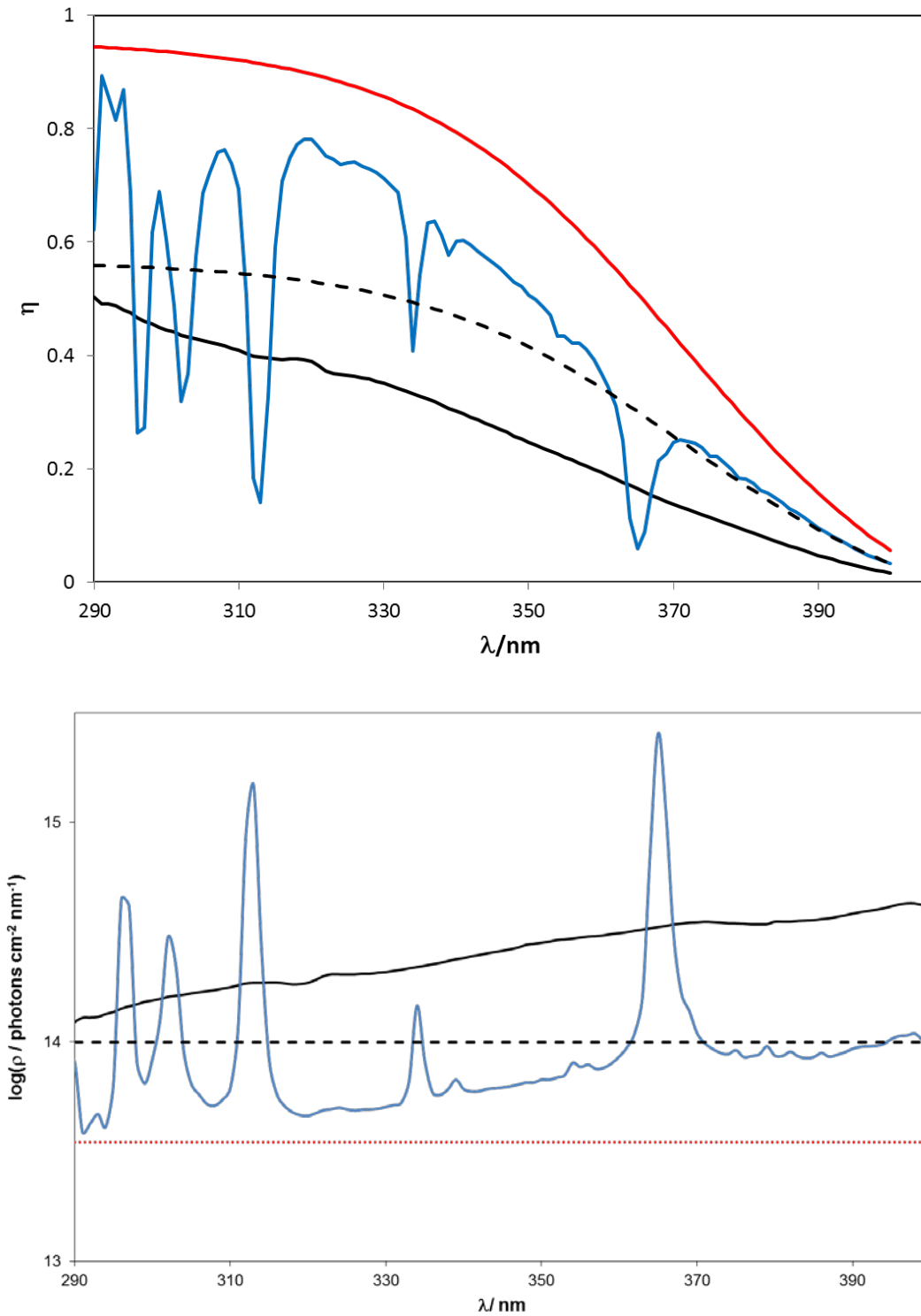
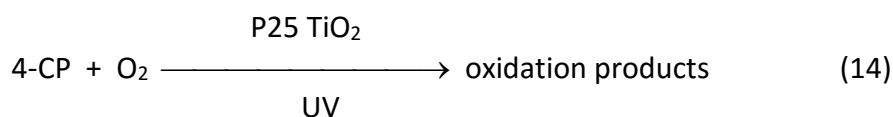


Figure 4: (a) Action spectra for a P25 dispersion calculated using eqn(13) and the variation of f vs λ illustrated in figure 2(c) combined with the emission spectra illustrated in (b). The solid red line corresponds to the action spectrum of the system which will be observed using any light source, provided $\rho < \rho(\text{threshold})$, i.e. $\theta = 1$ at all λ . The other action spectra have been calculated assuming $\rho > \rho(\text{threshold})$ and $\theta = 0.5$ at all λ , using either: (i) a constant ρ at all λ light source (broken black line), (ii) a Xe lamp (solid black line) and (iii) a Xe/Hg lamp (a solid blue line).

In fact, the mistaken use of a Xe/Hg lamp to record an action spectrum appears to be at the heart of the claim of spectral sensitivity reported by Emeline *et al.*⁸. in their study of the photocatalysed oxidation of 4-chlorophenol by P25 TiO₂. i.e.



Thus, Emeline *et al.*⁸ reported the action spectrum illustrated in figure 5(a) for reaction (14), using [4-CP]₀ = 0.2 mM, [TiO₂] = 0.3 g dm⁻³ and pH = 3 and a 1000W Xe/Hg lamp coupled to a monochromator (FWHM = 10 nm). A brief inspection of this η vs $\lambda(\text{ex})$ action spectrum reveals that it comprises a series of peaks and troughs (see figure 5(a), black line) which, the authors claim⁸, demonstrates that the photocatalysed oxidation of 4-CP by oxygen, photosensitised by P25, i.e. reaction (1), under the conditions described above, is spectrally dependent. Note that such spectral sensitivity is counter to the classical band model of semiconductor photocatalysis, in which the photogenerated charge carriers are thermalized before reacting⁸. However, when the photon fluxes used to calculate the different values of the various wavelengths are superimposed onto the action spectrum, as illustrated in figure 5(a), it is obvious that the troughs in the action spectra occur at the peaks in the emission spectrum and that the reported action spectrum for reaction (14) illustrated in figure 5(a) is the 'negative' of the sampled emission spectrum of the Xe/Hg lamp, with FWHM = 10 nm. This feature is as predicted above, assuming that, at the peaks in the emission spectrum at least, the initial rate is **not** proportional to ρ . This finding clearly calls into question any claim of spectral sensitivity for this system, or any system studied by any group using a Xe/Hg lamp in which the peaks and troughs in the action spectrum are matched by the troughs and peaks in the emission spectrum of the excitation lamp.

It should be noted at this point that in the same paper⁸ the authors reported that at 334, 365 and 380 nm, they found, for this system, that the initial rate of reaction (13) was proportional to ρ ; which – if true – would rule out the suggestion that the peaks and troughs in the action spectrum were due θ being < 1 at the Xe/Hg lamps' emission peak wavelengths at least, if not at the other λ . However, the irradiance at 365 nm at least (ca. 12.3 mW cm⁻²) is very high and others^{15,35,36}, studying the same system have reported $\theta < 1$, with typically $\theta = 0.5$, at much less levels (2-6.4 mW cm⁻²).

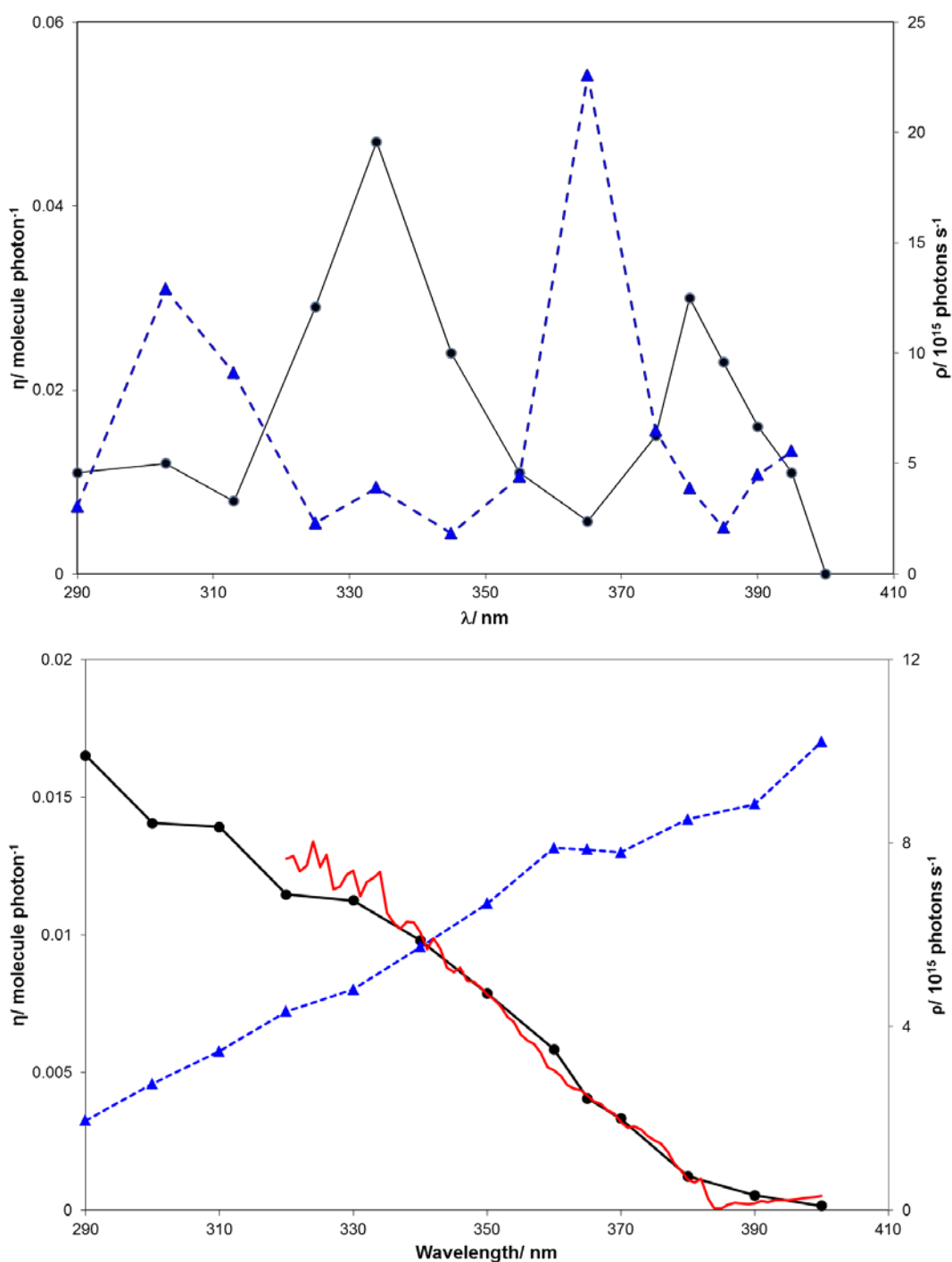
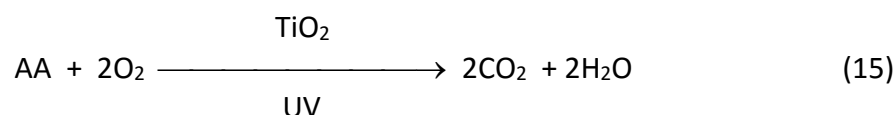


Figure 5: Action spectrum (black line, ● data points) for reaction (1), [P25 TiO₂] (0.3 mg cm⁻³), [4-CP]₀ = 0.2 mM and pH (pH 3), (a) as reported by Emeline *et al.*⁸, generated using the photon fluxes illustrated by the blue, broken line and ▲ data points for a 1000W Xe/Hg lamp/MC (FWHM = 10 nm) and (b) as reported by this group using the irradiances illustrated by the blue, broken line and ▲ data points for a 1000W Xe lamp. The red line corresponds to the diffuse reflectance absorbance spectrum of the photocatalytic reaction solution.

In order to test the claim of spectral sensitivity for this system the Mills group³⁶ recently reported the action spectrum for reaction (14) under identical conditions to those reported by Emeline *et al*⁸, but using a 1000W Xe lamp, and the results of this work are illustrated in figure 5(b). A brief inspection of the action spectrum for the 4-CP/P25 TiO₂/O₂ system, recorded using a Xe lamp/MC as the excitation light source illustrated in figure 5(b) reveals no evidence of spectral sensitivity, *i.e.* no peaks and troughs, but a striking similarity to the diffuse reflectance spectrum (absorbance) spectrum of the P25 dispersion in the photocatalytic system, also illustrated in figure 5(b) (red line). These results provide strong support for the proposition that the peaks and troughs in the action spectrum of the 4-CP/P25 TiO₂/O₂ system, recorded using a Xe/Hg lamp/monochromator are due to the lamp profile, *i.e.* there are a lamp artefact, and so do not provide evidence for spectral sensitivity in this system³⁶.

The distortion of an action spectrum due to the emission spectral profile of the lamp, provided that $\theta < 1$ at one or more wavelengths, is most apparent using a lamps with very spikey emission spectra, such as a Xe/Hg or Hg (medium or high pressure) lamp, however, researchers should be aware of the fact that even a Xe lamp can distort an 'ideal' action spectrum somewhat, as illustrated in figure 4(b), although, not very dramatically. A possible illustration of this distortion is the action spectrum reported by Torimoto *et al.*¹³ for the photocatalytic oxidation of acetic acid (AA), *i.e.*



In this work, amongst other commercial forms, P25 TiO₂ was used with [TiO₂] = 10 mg cm⁻³ and [AA] = 5 vol%. Previous work by the same group⁹, using Merck TiO₂, had established at sample wavelengths: 290, 350 and 380 nm, that the initial rate was proportional to $\rho^{0.5}$, over the irradiance range: 0.1 – 5 mW cm⁻², and so it will be assumed $\theta = 0.5$ in this same system using P25 as the photocatalyst. In their subsequent study¹³ of the action spectrum for P25 the intensities used were: 1.4, 2.1, 2.7 and 3.6 mW at 350, 370, 385 and 410 nm, respectively, using a Xe lamp/MC system with a FWHM of ca. 23 nm. The normalized action spectrum reported for this system is illustrated in figure 6, which matches quite well that of the normalized (at 350 nm) simulated action spectrum, (broken red line in figure 6) once the distortion by the Xe lamp emission spectrum has been included. The later simulated

spectrum was generated using the spectral data of Satuf *et al.*³¹ for P25 TiO₂, see figure 2(a), and the same method as used to generate the action spectra in figure 4. For comparison, the solid red line in figure 5 is the predicted shape of the action spectrum for the same system with no such distortion, *i.e.* if $\theta = 1$, so that the action spectrum is independent of the emission spectrum of the excitation light. A comparison between the solid and broken red lines reveals the predicted degree of distortion the action spectrum undergoes when $\theta = 0.5$ and a Xe lamp/MC (for which ρ is not constant at all λ s) is used as the excitation source and P25 TiO₂ is the photocatalyst. From this it is clear that the distortion is not very great from 400-350 nm at least, since over this range the Xe lamp emission spectrum is fairly flat, see figure 4(b). This would suggest that the Xe lamp is the best light source for recording the action spectrum of UV-absorbing photocatalysts, even if efforts are not made to make ρ the same at all wavelengths when recording the action spectrum.

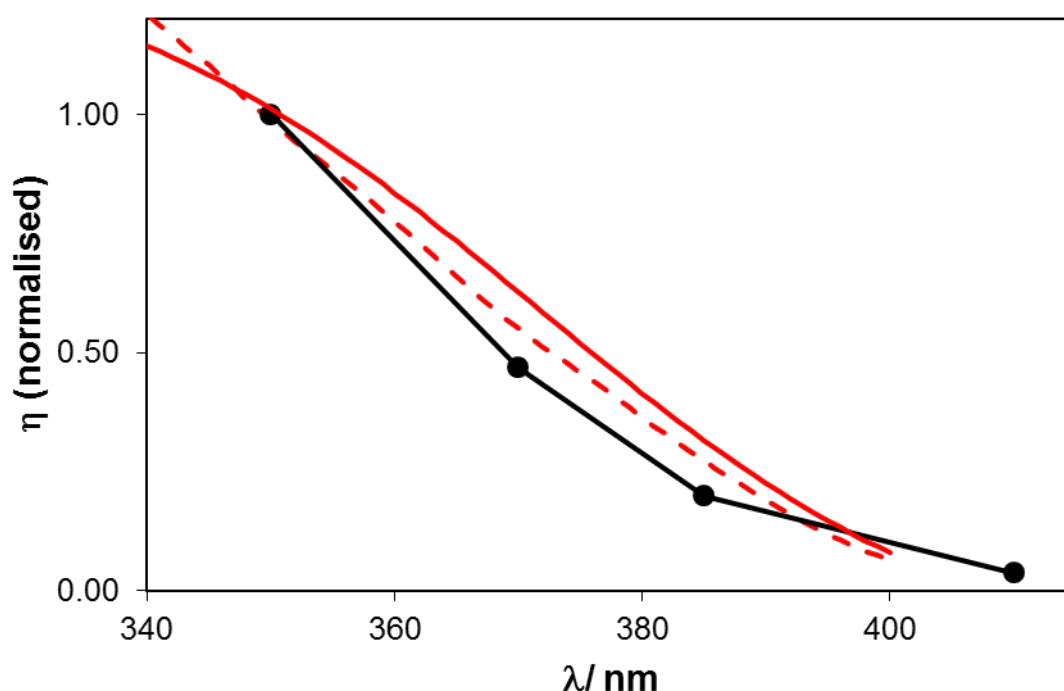
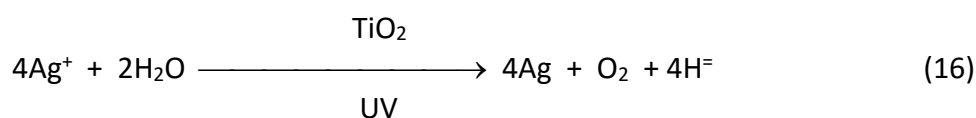


Figure 6: Action spectrum plot, normalized at 350 nm, for reaction (14), [AA] =5 vol%; [P25 TiO₂] = 0.010 g cm³, using a Xe lamp/MC with FWHM = 23 nm¹³. The broken red line is the normalized (at 350 nm) action spectrum predicted using the same process as used in figure 2, and assuming distortion by the Xe lamp spectral profile because $\theta = 0.5$. The solid red line is that predicted assuming no distortion, since $\theta = 1$.

Mixed crystalline phase distorted action spectra

In semiconductor photocatalysis the most important two crystalline phases of any semiconductor material tested to date are the anatase and rutile forms of TiO₂, with bandgaps 3.2 and 3.0 eV, respectively. This difference in bandgap is reflected in a difference in the conduction band potentials of: -0.20 and 0.01 V vs NHE at pH 0, for anatase and rutile TiO₂ respectively³⁷. Evidence has been found that these two different phases exhibit different activities depending upon the photocatalytic reaction that is under test. For example, it has been found¹³ that in the photo-oxidation of organic compounds, such as acetic acid, AA, in reaction (15), the anatase crystalline phase of TiO₂ is more reactive than rutile, whereas in the photocatalysed reduction of silver nitrate by water, i.e.



it appears that rutile is the more active phase. This should not affect the shape of the action spectra recorded using any pure phase, such as pure anatase or pure rutile TiO₂. However, it can lead to striking differences when a mixed phase, as a P25 TiO₂ is used (80:20 anatase:rutile³⁸) and this has been very well illustrated by the work of Torimoto *et al.*¹³ in their study of the action spectra of a wide variety of pure and mixed forms of TiO₂ when used to promote reactions (6), (15) and (16). Figure 7 illustrates their findings for P25 TiO₂, which shows that the action spectrum for the photodeposition of Ag from AgNO₃ is what might be expected for the narrow bandgap rutile form of TiO₂, whereas that for the oxidation of AA corresponds to that for the larger bandgap crystalline phase of this semiconductor, anatase. Interestingly, from the profile in figure 7, and as noted by the authors, it appears that when platinized P25 is used to photocatalyse reaction (6), the dehydrogenation of MeOH, neither phase is dominant, which helps justify its earlier use here as an example of an ideal photocatalytic system, see figure 1. The results in figure 7 show that in a mixed crystalline phase oxide such as P25 TiO₂, the shape of the action spectrum may depend on the selectivities of the two crystalline phases for the reaction under study and, under such circumstances the overall action spectrum may appear a distortion from the ideal, in which both phases are equally active.

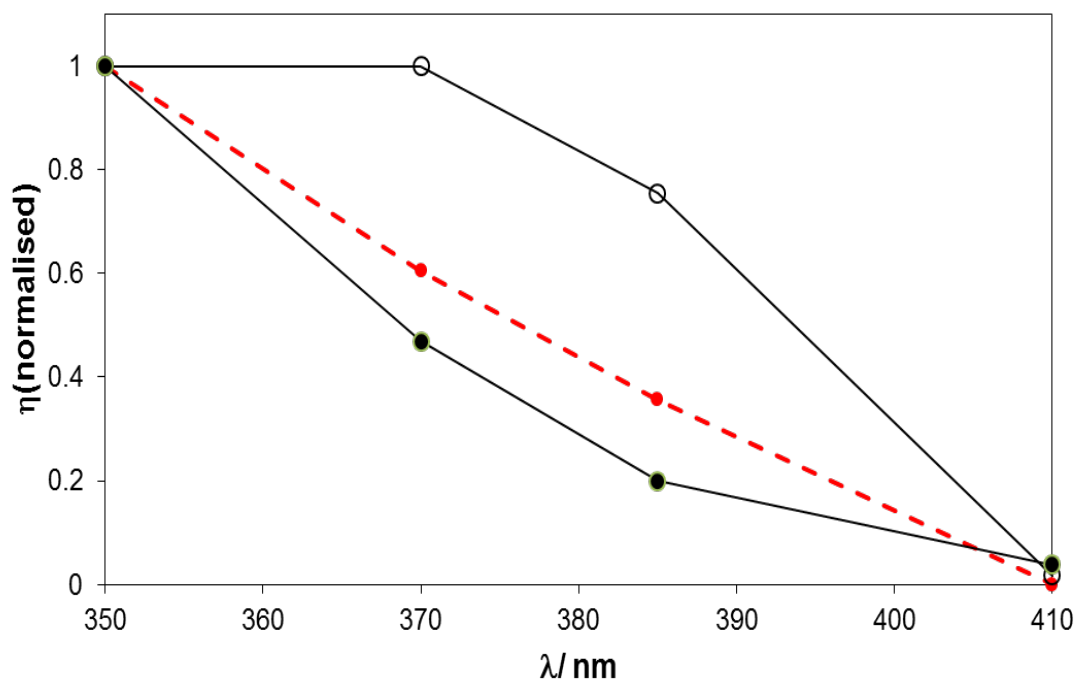


Figure7: Reported normalised action spectra for reactions: (6), open circles red broken line; [MeOH] = 50 vol%, (13), ●; [AA] = 5 vol%, and (14), ○; [AgNO₃] = 25 mM. In all cases: [TiO₂] = 10 mg cm⁻³ and irradiation source: Xe lamp/MC; FWHM = 23 nm¹³.

Pollutant distorted action spectra: Dyes

The process of dye photosensitization is probably the most well-known and established of the processes associated with pollutant distorted action spectra. A classic example of this process is the N-deethylation of Rhodamine B (RhB) adsorbed onto CdS in aerated aqueous solution reported by Watanabe *et al.* in 1977³⁹. This process is readily monitored by UV/Vis absorption spectroscopy since it is associated with a hypsochromic shift in the absorption maximum for the dye from 555 nm, see figure 8(b), to 498 nm. A typical action spectrum reported for this system is illustrated in figure 8(a), where [RhB] = 1 mM and [CdS] = 20 mg cm⁻³, and reveals significant activity at excitation wavelength > 540 nm, above which the CdS does not absorb, although it does scatter, as illustrated by its reported absorption spectrum illustrated in figure 8(b) (broken and dotted line). The action spectrum for the RhB/CdS system has a peak at ca. 600 nm, which is not too dissimilar to that of RhB adsorbed onto CdS ($\lambda(\text{max}) = 577 \text{ nm}$), since the former forms multimers when adsorbed on the powder,

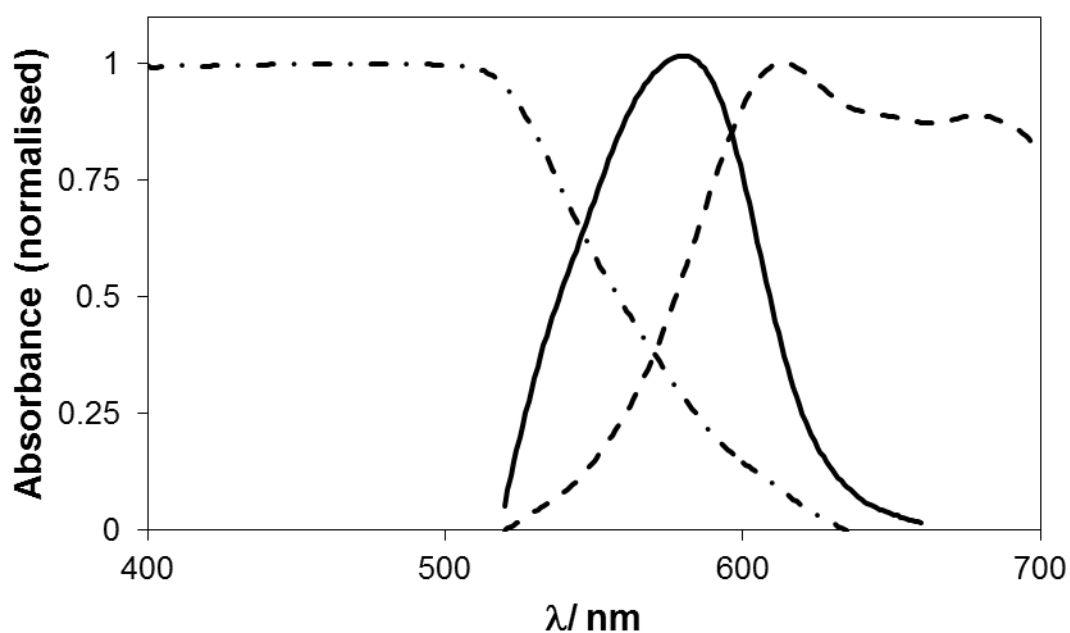
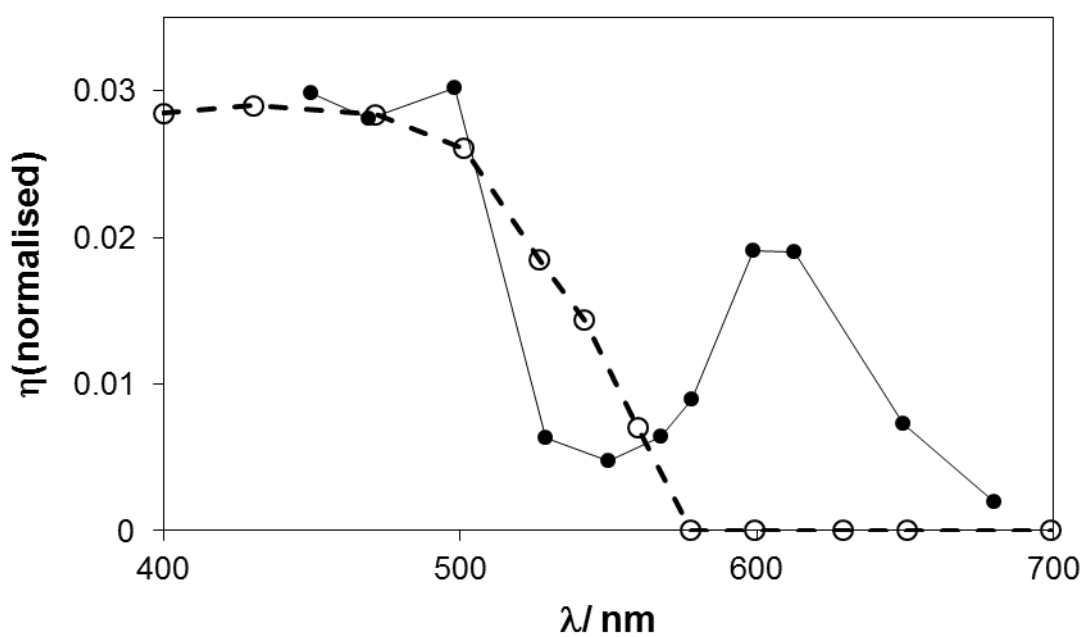


Figure 8: (a) Action spectra for dye de-alkylation: (i) CdS (20 mg cm^{-3}) /RhB (1 mM)/O₂ (air sat.), solid line; ●³⁹, and (ii) CdS (6 mg cm^{-3}) /MB (0.5 mM)/O₂ (air sat.), broken line, ○²⁵; (b) absorption spectra of RhB (solid line), MB (broken line) adsorbed on CdS (measured via the reflectance spectrum of the dyed powder and CdS powder alone (solid line); Xe lamp/MC, FWHM = ca. 20 nm.

see figure 8(b). This action spectrum is interesting in that at wavelengths < 540 nm, the value of η is approximately constant and equal to 0.03; further work shows that the latter value is independent of [RhB]. This feature is consistent with the suggestion of the authors³⁹ that at $\lambda < 540$ nm the deethylation of RhB is photocatalytic, with $\eta = \text{ca. } 0.03$, whereas above 540 nm it is a dye-sensitised process, with $\eta = \text{ca. } 0.46$ when $[\text{CdS}] = 200 \text{ mg cm}^{-3}$. These same group also studied²⁵ the demethylation of Methylene Blue (MB) by CdS and found that the action spectrum, illustrated in figure 8(a) (broken line, open circles) exhibited no evidence of a dye-sensitisation process, because the electronically excited state of MB is not sufficiently reducing to inject an electron into the conduction band of the CdS. As a result, the recorded action spectrum resembles that of the absorption spectrum of CdS alone, illustrated in figure 8(b), thereby indicating that the demethylation of MB reaction is, in striking contrast to RhB, solely a photocatalytic process²⁵. The absorption spectrum of MB adsorbed on the CdS, illustrated in figure 8(b), reveals that it too, like RhB, forms multimeric species when adsorbed on CdS powder ($\lambda(\text{max}) = 612 \text{ nm}$).

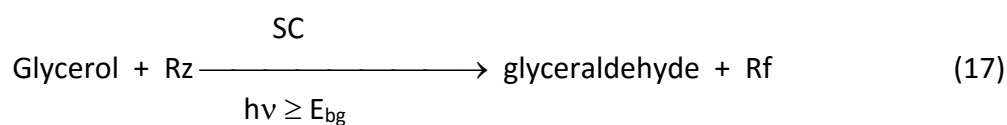
As illustrated by the data in figure 8(b), the CdS/RhB and CdS/MB systems are ones in which the adsorbed dye absorption spectrum overlaps with that of the semiconductor and so, as a consequence, it is essential to record an action spectrum in order to identify whether the semiconductor (in the case of photocatalysis), or dye (in the case of dye sensitisation or photolysis), is responsible for the observed photo-induced spectral changes in the absorption spectra of the reaction solutions. However, in cases where the dye absorption spectrum clearly doesn't overlap with that of the photocatalyst, as we shall see below, then it may be unnecessary to run an action spectrum to substantiate the photocatalytic nature of the reaction under test, provided the excitation light used is of a wavelength which the photocatalysts absorbs, but the adsorbed dye does not.

It is clear from the UV/Vis absorption spectra that of RhB and MB, and probably most other dyes, illustrated in figure 8(b), that when they are absorbed strongly onto the surface of the photocatalyst, the normally narrow visible bands of the monomeric forms of the dyes (typically FWHM = 40 nm), are significantly broadened, so much so that overlap with the absorption spectrum of the photocatalyst is possible. This broadening can render the system inappropriate for the unambiguous assessment of the photocatalytic activity of the semiconductor in the system. However, such significant absorption often depends both on

the dye concentration and, more importantly, the pH of the system⁴⁰⁻⁴². For example most cationic dyes, such as MB, do not absorb on TiO₂ when the pH is much more acidic (e.g. pH 2) than the pzc of TiO₂ (pH = 6.6), since the surface of the titania is then very positively charged^{61,63} under such conditions; whereas, in contrast, in alkali (pH 11) MB is very strongly absorbed onto TiO₂. Similarly, the anionic dye, AO7^{41,42}, does not absorb strongly on TiO₂ at pH 11, but does at pH 2. Thus, if a dye is to be used to test the photocatalytic activity of a new material, and if an action spectrum is not run, because the dye used has an absorption spectrum that appears very well separated from that of the photocatalyst, then it is important to note that the absorption spectrum that needs to be considered is that for the dye adsorbed on the photocatalyst under the conditions of the experiment and not the dye alone in aqueous solution. The latter is best determined by recording the diffuse reflectance spectrum of the reaction solution, rather than that of a dried form of the powder plus dye.

In spite of the significant potential pitfalls of using dyes⁷ to probe the photo-oxidation capability of a photocatalyst, via reaction (1), the use of dyes, especially MB and acid orange 7, AO7, as the test pollutant continues to be a very popular approach to the assessment of the photocatalytic activity of any new photocatalyst, *via* the photo-oxidised mineralization of the dye by dissolved oxygen. Its popularity lies in the striking nature of the reaction (highly colored – to colourless) and the ease with which it can be performed, as it requires only a UV/Vis spectrophotometer. However, in such work, unless an action spectrum of the system is run⁷, in order to demonstrate that it is exclusively a photocatalytic process, there will always be a doubt as to whether the observed dye bleaching process was due in part, or wholly, to dye-sensitisation *via* reaction (2), or dye photolysis. This confirmatory step is particularly important when the novelty of the claim is visible light photocatalysis for systems in which the only test pollutant tested was a dye, usually MB. Obviously, in such cases, in the absence of an action spectrum, the claim of visible light photocatalytic activity should be considered ambiguous at the very least. Indeed, there have been calls⁵ for the use of dyes as test pollutants in monitoring photocatalytic reactions to be abandoned, unless both the action spectrum and absorption spectrum have both been run for the system under study, to prove, as in the case of the demethylation of MB by CdS²⁵, that the reaction is truly photocatalytic (see figure 8).

One possible way in which a dye may be used to test photocatalytic activity and avoid the accompanying concern regarding dye photosensitization is to study the photocatalysed *reduction* of a dye, such as resazurin, Rz (blue coloured; $\lambda(\text{max}) = 605 \text{ nm}$), by a sacrificial electron acceptor, such as glycerol, in **anaerobic** solution, i.e.



where Rf is resorufin (pink coloured; $\lambda(\text{max}) = 585 \text{ nm}$)⁴³. This is in striking contrast to the usual use of dyes in photocatalysis in which the photo-*oxidation* of the dye is studied in the presence of a sacrificial electron acceptor, such as O₂, as in reaction (2). In the absence of O₂, as in reaction (17), the photo-bleaching of the dye *via* the traditional dye sensitisation route, i.e. reaction (2), is not possible. As a consequence, provided the excited state of the dye is not quenched by glycerol, as in the case of Rz, then reaction (17) can only occur *via* a photocatalytic process⁴⁴. A simple demonstration of this was reported recently by this group using a variety of different semiconductors, including CdS⁶. The photocatalysed reduction of Rz to Rf was monitored spectrophotometrically, and a typical set of results for CdS are illustrated in figure 9(a), which reveal that the blue to pink colour change is rapid when ultra-bandgap light is used ($\lambda(\text{excit}) = 455 \text{ nm}$; 20 mW cm^{-2}). A brief inspection of the absorption spectra of the Rz, $\lambda(\text{max}) = 608 \text{ nm}$, and Rf, $\lambda(\text{max}) = 585 \text{ nm}$, see figure 9(a), reveals little or no absorption at 455 nm by either Rz or Rf, but significant absorption by CdS, see figure 8(b). When the CdS/Rz system is irradiated with light which Rz does absorb and CdS doesn't, e.g. $\lambda(\text{excit}) = 617 \text{ nm}$; 15 mW cm^{-2} , the observed photobleaching is negligible over the 5 min time period required to complete reaction (17), using 455 nm light (see figures 9(a) and 9(b))⁶. However, prolonged irradiation at 617 nm of the CdS/Rz system does reveal that a very slow dye photobleaching process occurs, but at a rate that is unchanged in the absence of CdS and/or glycerol, thereby indicating that it is due to dye photolysis. These findings suggest that a dye, like Rz, could be used to assess the photocatalytic activity of UV and visible light absorbing semiconductors, via a *reductive* photocatalytic reaction, such as reaction (17), using 365 or 455 nm radiation, provided the photocatalysed reaction was much faster than the slow photolysis of the dye.

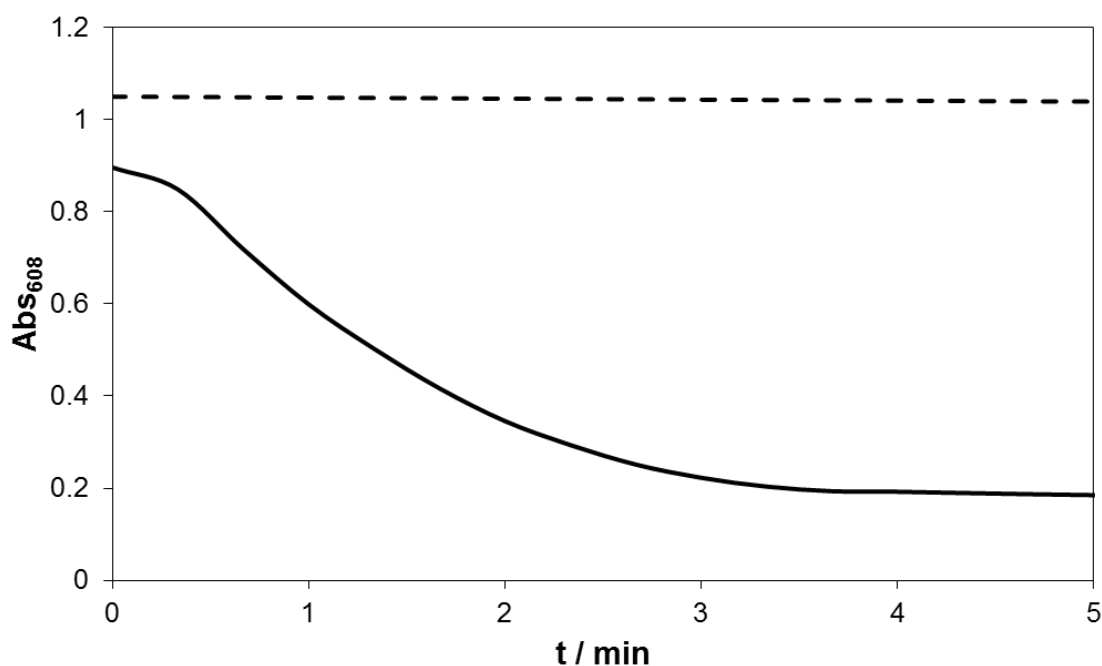
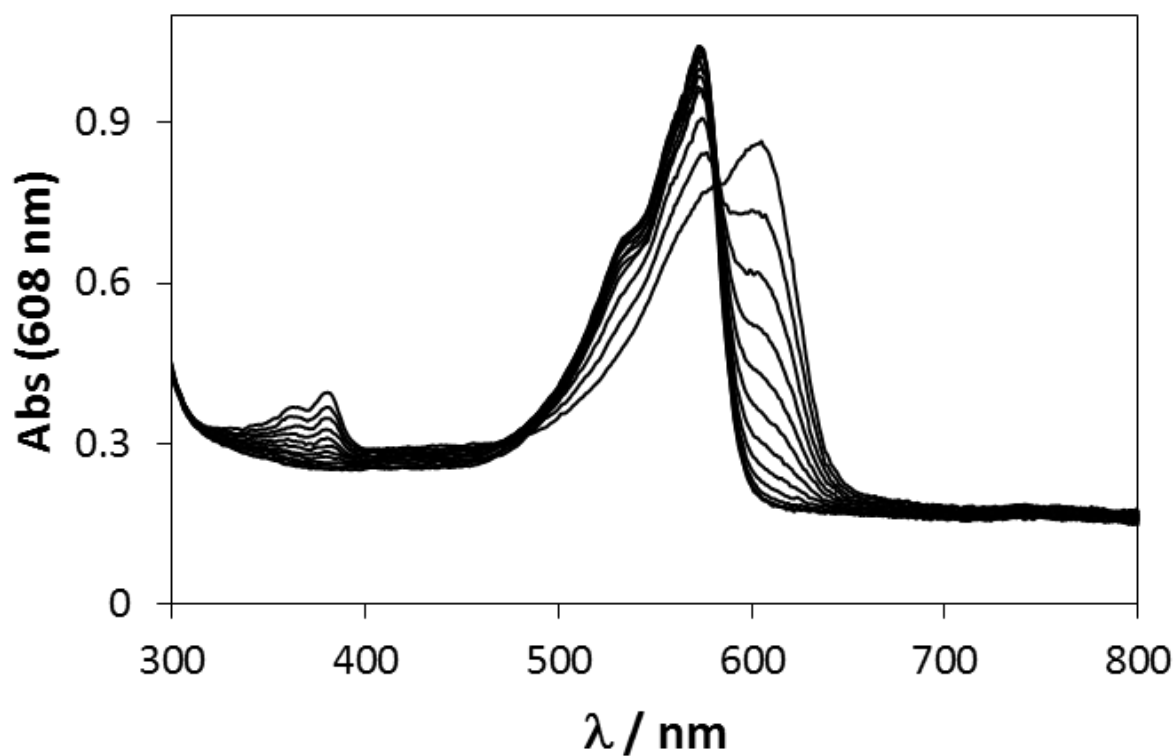


Figure 9: (a) Recorded spectral changes for the photocatalytic reaction (16), mediated by CdS in aqueous solution ($[\text{CdS}] = 0.5 \text{ wt\%}$; $[\text{glycerol}] = 10 \text{ wt \%}$)⁶, carried out in a 1 cm cuvette, using a 455 nm LED (20 mW cm⁻²). The spectra were recorded every 20 s; (b) Recorded absorbance at 608 nm ($\lambda(\text{max})$ Rz) as a function of irradiation time, t , for the same solution in (a) when irradiated with 455 nm light (20 mW cm⁻²), solid line, or 617 nm light (15 mW cm⁻²), broken line.

However, the most obvious way to avoid concerns of dye-sensitisation is to use simple organic test pollutants that will not absorb significantly the excitation light, such as MeOH, *via* reaction (6), although, in this case, this will require the semiconductor to be platinized beforehand, since photocatalysts most have high overpotentials for water reduction¹⁷. Alternatively, acetic acid, AA, *via* reaction (15), can be used as the test pollutant, as has been demonstrated by Nishijima and co-workers⁴⁴ in a study of the photocatalytic activity of a sulfur-doped TiO₂ visible light absorbing photocatalyst, the action spectrum for which, and that of an undoped, UV-only absorbing sample of P25 TiO₂ for comparison, are illustrated in figure 10.

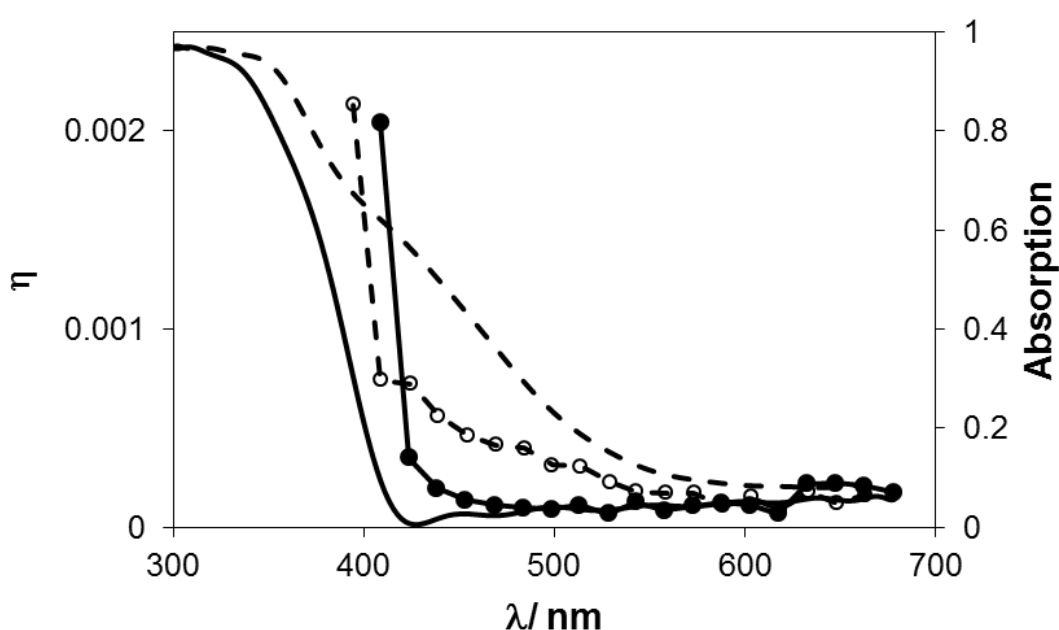


Figure 10 Diffuse reflectance and action spectra for the photocatalysed oxidation of AA by dissolved O₂, i.e. reaction (14) using either P25 (●, solid line) or S-doped TiO₂ (○, broken line) as the photocatalyst; [TiO₂] = 10 mg cm⁻³, [AA] = 0.05 mM; Xe lamp/MC, ca. FWHM = 17 nm⁴⁴.

The fits of the action spectra for reaction (15) to the DRS absorption spectra of the semiconductor photocatalysts are reasonable, although not great, as illustrated in figure 10; these less than perfect fits are attributed by the authors⁴⁴ to the large FWHM (17 nm) used to generate the action spectrum. However, it is clear from the action spectra illustrated in figure 10 that the S-doped photocatalyst action spectrum does show clear evidence of

visible light photoactivity, and that this feature is absent from that of P25 TiO₂. However, even with this apparently simple system, using TiO₂ alone, the reaction mechanism is complex, since below an irradiance of ca. 5 mW cm² the rate depends upon $\rho^{0.5}$, but depends upon ca. ρ^{-1} above this threshold. These two features, the authors⁹ tentatively suggest reflect the radical chain nature of mechanism, which probably involves peroxy radicals.

Pollutant distorted action spectra: Charge Transfer Complexes (CTCs)

If the pollutant doesn't absorb visible light itself but instead forms a visible-light absorbing (ligand to metal) charge transfer complex, i.e. CTC, with the semiconductor, then it is possible that the visible light induced disappearance of the organic pollutant observed upon irradiation may be due to electronic excitation of the CTC and not photocatalysis⁶. In the former case, the electron is photoexcited directly from the ground state of the adsorbate to the semiconductor, which is invariably TiO₂⁴. As in the dye sensitisation process, the oxidised form of the adsorbate may be sufficiently unstable so as to degrade, although complete oxidative mineralisation is not usually achieved *via* this process. Numerous groups have been reported cases of organics forming CTC's with TiO₂, including ones that can be described as: phenolic (such as catechol, salicylic acid and phenol), hydroxyl (e.g. cyclodextrin) and carboxylic (e.g. EDTA, oxalic, formic and citric acid and aromatic carboxylic acids)⁴.

In many cases, the CTC is unstable when exposed to visible light and thus the latter promotes the overall oxidative degradation of the original (non-complexed) organic with irradiation time. Clearly, this photochemical feature could be easily misinterpreted as an example of visible photocatalysis, whereas in fact it is a version of dye-sensitisation; where the CTC is the light-absorbing species. These CT complexes are usually identified *via* the appearance of additional absorption bands, often in the visible, in the DRS. As a consequence, it appears that before any unambiguous claim of visible light photocatalysis can be made, it is also essential to record the absorption spectrum, usually the DRS, of the photocatalytic system in order to identify where the various components absorb, *i.e.* the substrate and semiconductor, both alone and when combined to create the overall photocatalytic system under investigation.

Probably the most well-known of the CTC's is that formed between TiO₂ and 4-CP⁴. Choi and his co-workers have reported that 4-CP weakly absorbs onto TiO₂, most notably ST1 (Ishihara Co.) with a specific surface area ca. 340 m² g⁻¹, and as such can be degraded, to form CO₂ and Cl⁻, under visible light, and that the rate can be correlated with oxide specific surface area⁴. These same workers also reported that the combination of 4-CP and P25 TiO₂ form a weak CTC⁹, although others, looking at the same system report that such complexation is negligible⁴⁵. Choi *et al.*⁴ also note that: 'the LMCT induced degradation of phenolic compounds under visible light is much slower than that of bandgap-excited photocatalysis under UV-irradiation'.

An interesting example CTC photochemistry is that reported by Higashimoto *et al.*⁴⁶ in their study of the photocatalysed oxidation of benzyl alcohol (BA) to benzaldehyde by dissolved oxygen using TiO₂ in acetonitrile. This work is notable, not so much for the process, but rather the form⁴⁶ of the quantum yield, ϕ , versus λ , as illustrated in figure 11. As noted earlier, ϕ vs. λ plots are not common in heterogenous photocatalysis, and a brief inspection of the data reveals that the ϕ , vs λ plot matches quite well that of the absorption spectrum of the BA/TiO₂ CTC. However, theoretically this should not be the case, since for an ideal photocatalytic system, by definition:

$$\phi = \eta/f = k \quad (18)$$

i.e. unlike η , ϕ should be independent of the fraction of light absorbed, f , and most likely a constant at all wavelengths.

Any attempt to measure the ϕ vs. λ profile of a photocatalytic system requires details of how the f vs λ spectrum was determined in the first place, since without which the values of η cannot be converted to ϕ at each λ . In the case of Higashimoto *et al.*⁴⁶ and their study of the BA/TiO₂ system, no such details are given, suggesting that the researchers did not actually determine f vs λ for the BA/TiO₂ system. This observation, along with the fact that the action spectrum plot illustrated in figure 11 matches quite well with that of the absorption spectrum of the system, strongly suggests that the plot of ϕ vs λ in figure 11, is in fact a plot of η vs. λ , and that the researchers¹⁸ have mistakenly assumed that all the incident light is absorbed by the system, i.e. none is lost via scattering or transmission, so that $f = 1$ at all wavelengths, whereas in practice such losses are usually significant^{30,31}.

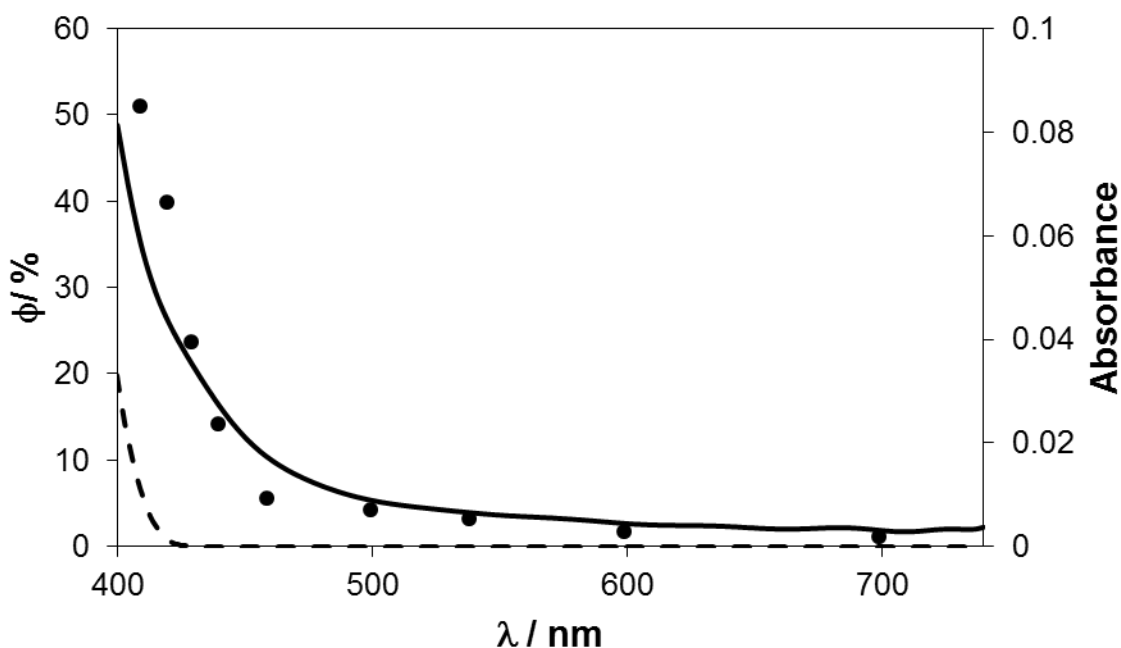


Figure 11: UV/Visible absorption (solid line) and action spectrum, ●, of the BA ($5\mu\text{mol cm}^{-3}$) /TiO₂ (5 mg cm^{-3}) system in MeCN (10 cm^3). 500 W Xe lamp/MC; FWHM = 13.6 nm^{46} . The dotted line is the absorption spectrum of TiO₂ alone.

Catalyst-distorted action spectra:

It is well known that deposits of noble metals, such as Pt, can greatly enhance the rate of a photocatalytic process, most notably that of the reduction of water for which the overpotential is so high for the semiconductor alone, that the rate is negligible in the absence of such deposits⁴⁷. Thus, the photocatalysed reduction of water, and concomitant oxidation of a sacrificial electron donor, SED, such as MeOH, see reaction (6), requires a platinumized photocatalyst, or at least one with a noble metal deposit, since all have low overpotentials for water reduction⁹. Similarly, the photo-oxidation of organics by oxygen, i.e. reaction (1), is often enhanced by the presence of deposits of noble metals, such as Pt, since this appears to facilitate the reduction of the oxygen by the photogenerated conduction band electrons^{47,48}.

In the case of Pt, nanodeposits on TiO₂ usually produce a grey powder which exhibits an action spectrum that is of the semiconductor alone, for example see figure 1, and which shows no evidence of any unexpected visible light activity⁹. In contrast, recent work on gold-modified titania (Au/TiO₂), reveals evidence of visible light activity, which has been attributed to photoexcitation of the localized surface plasmon resonance (LSPR) of the gold particles, in a process not too dissimilar to dye-sensitisation, i.e. reaction (2)^{22,48,49}. Thus, the latter is an example of a case where catalyst deposits can distort the expected action spectrum of a photocatalytic system, if they are LSPR photoactive, in much the same way a dye can, *via* a sensitization process.

A very good example of the above is provided by the work of Kowalska *et al.*²², in their study of the action spectrum for reaction (1), using Au (2 wt%)/TiO₂ and P = 2-propanol, the results of which are illustrated in figure 12. The match between the action spectrum and the DRS of the Au/TiO₂ (Aldrich-rutile) photocatalyst provides compelling evidence that over this wavelength range the Au particles (ca. 80 nm) are excited *via* their LSPR and that most likely this results in the injection of an electron from the Au particles to the TiO₂, which is then able to reduce adsorbed O₂, whilst the electron-deficient Au oxidises the 2-propanol to acetone²². Although, to date, most reported photocatalyst-related SPR processes are not every efficient, it is worth noting their existence at least, especially when considering cases of apparent visible light photocatalytic activity, in which nanoparticles of a metal are often used to enhance the efficacy of the photocatalytic process.

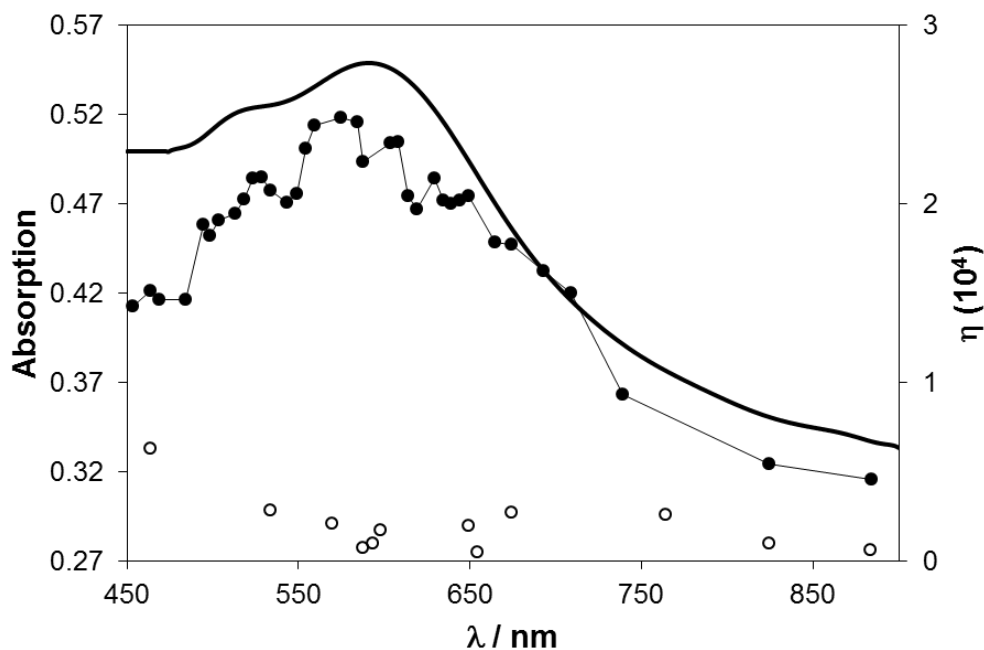


Figure 12: Action spectrum for the oxidation of 2-propanol by Au/TiO₂ (Aldrich: rutile), ●, and bare TiO₂, ○, and DRS (thick solid line) of the Au/TiO₂²².

General guide to running an action spectrum

An action spectrum is a plot of η vs λ which, in an ideal classical photocatalytic system, should have the same shape as the plot of f vs λ , which, in turn, should be similar in shape to the DRS/absorption spectrum of the system. Obviously, for any photocatalytic measurement the system should be as well-defined as possible, so that others might be able to reproduce it. Thus, all the usual experimental parameters should be defined, such as nature and source of the reactant(s), their concentrations, the nature and source of the semiconductor photocatalyst and its concentration, pH, temperature, ionic strength, solvent, light source, irradiation set up, photoreactor design and construction, method and degree of agitation (especially for powder dispersions), nature and method of gas (usually air) saturation. However, more particularly, when recording an action spectrum efforts should be made to:

(1) Use a light source devoid of spikes in its emission spectrum; e.g. use a Xe lamp but never a Hg/Xe or Hg lamp

(2) Use a monochromator with (1) to create light at each wavelength with a low FWHM, preferably ca. 10 nm

(3) Ensure that the %variation of ρ across the wavelength range under investigation is as small as possible, typically < 30%, but, ideally, 0%

(4) Before running the action spectrum, determine the variation in the initial rate of the light-induced reaction as a function of ρ at 3 different wavelengths that span the active wavelength range under investigation, so as to determine if it is reasonable to assume $\theta = 1$, i.e. that the system is 'ideal' and will not be prone to intensity distortion effects.

(5) Before running the action spectrum, record the DRS/absorption spectrum of the individual components of the photocatalytic system, *i.e.* the semiconductor and substrate, as well as the photosystem as a whole. Study these spectra for evidence of: (i) substrate aggregation/adsorption, P_{ads} , on the semiconductor photocatalyst and/or (ii) CTC formation. Evidence of (i) and/or (ii) will undermine any claim of pure photocatalytic activity. Any significant overlap of the absorbance due to P, P_{ads} , or CTC with that of the semiconductor photocatalyst alone will undermine any claim that the process under study is purely photocatalytic.

(6) Determine the action spectrum of the system based on initial rates and using equation (4) and compare the spectral profile of the action spectrum with that of the DRS/absorption of the photocatalytic system in order to identify the light absorbing species and help support any claim that the reaction is purely photocatalytic.

Note that even for a well-defined photocatalytic system, reproduction of the exact values of η may prove difficult from laboratory to laboratory, since the absolute value of the rate depends upon so many different parameters, including the light flux in the photoreactor, which depends amongst other things, the degree of scattering and reflection of the incident light, the beam size and shape and the reactor design . As a consequence, some have suggested that individual values of η 'have little, if any, meaning'⁵⁰. Thus, in recording the action spectrum, *i.e.* η vs. λ , of a photocatalytic system, it is not the absolute values of η that are of interest *per se*, but rather the spectral profile they reveal, which shows whether the system is photocatalytic or not.

Conclusions

The recording of an action spectrum, as well as the absorption or DRS spectrum, of a photocatalytic system is an increasingly important part of any study of photocatalytic systems, especially ones in which it is claimed that the photocatalyst is visible light absorbing. The ideal action spectrum of a classical photocatalytic system will have the same spectral profile as the fraction of light absorbed by the semiconductor as a function of λ , with an initial rate that is proportional to ρ at all wavelengths; unfortunately, most photocatalytic systems exhibit non-ideal action spectra. There are several major possible causes for non-ideal action spectra, including: light intensity effects, crystal phase effects, dye-sensitisation photolysis, CTC formation and LSPR absorption by a deposited noble metal catalyst. Such non-ideal behavior could lead to mistaken claims of visible light photocatalysis. Indeed, it has been suggested³ that it is unwise to use dyes to probe the activity of a photocatalyst, especially visible-light absorbing photocatalysts. In the latter case the photocatalyst is used to promote the *oxidation* of the dye by O₂, or another sacrificial electron acceptor. Recent results indicate⁶ that dyes may be appropriate for assessing photocatalytic activity when they are *reduced*, and a sacrificial electron donor is oxidized, i.e. *via* reductive photocatalysis. Whatever the assessment method, the recording of an action spectrum, as well as its DRS/absorption spectrum for the photocatalytic system under test, is essential in order to identify if it is truly photocatalytic in nature.

Acknowledgements:

SKL wishes to thank the DGIST R&D Program of Ministry of Science, ICT and Future Planning of Korea (17-NT-02) for supporting this work.

References

- (1) P. Pichat, Photocatalysis and water purification from fundamentals to recent applications, 1st edn, Wiley-VCH, Germany, 2013 and references therein.
- (2) K. Rajeshwar, M. E. Osugi, W. Chanmanee, C. R. Chenthamarakshan, M.V. B. Zanoni, P. Kajitvichyanukul and R. Krishnan-Ayer, *J. Photochem. Photobiol., C*, 2008, 9, 171–192.
- (3) B. Ohtani, *J. Photochem. Photobiol. C.*, 2010, 11, 157-178 and references therein.
- (4) G. Zhang, G. Kima and W. Choi, *Energy Environ. Sci.*, 2014, 7, 954–966, and references therein.
- (5) T. Wu, G. Liu, J. Zhao, H. Hidaka and N. Serpone, *J. Phys. Chem. B*, 1998, 102, 5845–5851.
- (6) A. Mills, N. Wells and C. O'Rourke, *J. Photochem. Photobiol., A*, 2017, 338, 123–133.
- (7) B. Ohtani, *Chem. Lett.*, 2008, 37(3), 216–229.
- (8) A.V. Emeline, A. Salinaro and N. Serpone, *J. Phys. Chem. B*, 2000, 104, 11202–11210 and references therein
- (9) T. Torimoto, Y. Aburakawa, Y. Kawahara, S. Ikeda and B. Ohtani, *Chem. Phys. Lett.*, 2004, 392, 220–224.
- (10) A.V. Emerline, X. Zhang, M. Jin, T. Murakami and A. Fujisima, *J. Phys. Chem. B*, 2006, 110, 7409-7413 and references therein.
- (11) X.L. Yan, T. Ohno, K. Nishijima, R. Abe and B. Ohtani, *Chem. Phys. Lett.* 2006, 429, 606–610.
- (12) R. Quesada-Cabrera, A. Mills and C. O'Rourke, *Appl. Catal. B*, 2014, 150–151, 338–344.
- (13) T. Torimoto, N. Nakamura, S. Ikedaab and B. Ohtani, *Phys. Chem. Chem. Phys.*, 2002, 4, 5910–5914.
- (14) A.V. Emeline and N. Serpone, *J. Phys. Chem. B*, 2002, 106, 12221–12226.
- (15) U. Stafford, K.A Gray, P.V. Kamat, *J. Catal.*, 1997, 167, 25–32.
- (16) K. Yamaguti and S. Sato, *J. Chem. Soc., Faraday Trans. 1*, 1985, 81, 1237–1246.
- (17) A. Mills and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 1982, 78, 3659–3669.
- (18) M.A. Grela, M.A. Brusa and A.J. Colussi, *J. Phys. Chem. B*, 1997, 101, 10986–10989.
- (19) R. Abe, H. Takami, N. Murakami and B. Ohtani, *J. Am. Chem. Soc.*, 2008, 130(25), 7780–7781.
- (20) K. Nishijima, B. Ohtani, X. Yan, T. Kamai, T. Chiyoya, T. Tsubota, N. Murakami and T. Ohno, *Chem. Phys.*, 2007, 339, 64–72.
- (21) A.V. Emeline, X. Zhang, M. Jin, T. Murakami and A. Fujishima, *J. Photochem. Photobiol., A*, 2009, 207, 13-19.

- (22) E. Kowalska, R. Abe and B. Ohtani, *Chem. Commun.*, 2009, 241–243.
- (23) J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S-T. Lee, J. Zhong and Z. Kang, *Science*, 2015, 347, 970–974.
- (24) X. Yan, T. Ohno, K. Nishijima, R. Abe and B. Ohtani, *Chem. Phys. Lett.*, 2006, 429, 606–610.
- (25) T. Takizawa, T. Watanabe and K. Honda, *J. Phys. Chem.*, 1978, 82, 1391–1396.
- (26) J.R. Darwent, *J. Chem. Soc., Faraday Trans. 2*, 1981, 77, 1703–1709.
- (27) J. Torrent, V. Barron, *Diffuse Reflectance Spectroscopy*. In *Methods of Soil Analysis Part 5—Mineralogical Methods*, A.L. Ulery, L.R. Drees, Eds.; Soil Science Society of America, Inc., Wisconsin, 2008, ch. 13, 367–385.
- (28) A.V. Emeline, G.N. Kuzmin, D. Purevdorj, V.K. Ryabchuk and N. Serpone, *J. Phys. Chem. B*, 2000, 104, 2989–2999.
- (29) X. Yan, T. Ohno, K. Nishijima, R. Abe and B. Ohtani, *Chem. Phys. Letts.*, 2006, 429, 606–610.
- (30) M.I. Cabrera, O.M. Alfano and A.E. Cassano, *J. Phys. Chem.*, 1996, 100(51), 20043–20050.
- (31) M.L. Satuf, R.J. Brandi, A.E. Cassano and O.M. Alfano, *Ind. Eng. Chem. Res.*, 2005, 44(17), 6643–6649.
- (32) A. Mills, C. O'Rourke and K. Moore, *J. Photochem. Photobiol., A*, 2015, 310, 66–105, and references therein.
- (33) T.A. Egerton, C.J. King, *J. Oil Col. Chem. Assoc.*, 1979, 62, 386–391.
- (34) K.Y. Okamoto, H. Yanamoto and H. Teneka and A. Itaya, *Bull. Chem. Soc. Jpn.* 1985, 58, 2023–2028.
- (35) G. Al-Sayyed, J-C. D'Oliveira, P. Pichat, *J. Photochem. Photobiol., A*, 1991, 58(1), 99–114.
- (36) S.K. Lee, A. Mills and C. O'Rourke, *J. Photochem. Photobiol., A*, accepted for publication, ref no.: JPC 10645. <http://dx.doi.org/10.1016/j.jphotochem.2017.05.018>.
- (37) A. Fijishima, X. Zhang and D.A. Tryk, *Surf. Sci. Reports*, 2008, 63, 515–582.
- (38) Degussa Technical Bulletin Fine Particles, No. 80, 'Titanium Dioxide p25, Manufacture – properties – Applications, 1998, Degussa AG, Frankfurt.
- (39) T. Watanabe, T. Takizawa and K. Honda, *J. Phys. Chem.*, 1977, 81, 1845-1851.
- (40) A. Mills and C. O'Rourke, *Green*, 2011, 1, 105–113.
- (41) C. O'Rourke and A. Mills, *J. Photochem. Photobiol., A*, 2010, 216, 261–267.
- (42) A. Mills, M. Sheik, C. O'Rourke and M. McFarlane, *Appl. Catal., B*, 2009, 89, 189–195.
- (43) A. Mills and N. Wells, *Chem. Soc. Rev.* 2015, 44, 2849–2864.

- (44) K. Nishijima, B. Ohtani, X. Yan, T. Kamaia, T. Chiyoyaa, T. Tsubotaa, N. Murakamia and T. Ohnoa, *Chem. Phys.*, 2007, 339(1–3), 64–72.
- (45) A.G. Agrios, K.A. Gray and E. Weitz, *Langmuir*, 2004, 20(14), 5911–5917.
- (46) S. Higashimoto, T. Nishi, M. Yasukawa, M. Azuma, Y. Sakata and H. Kobayashi, *J. Catal.*, 2015, 329, 286–290.
- (47) S-K. Lee and A. Mills, *Platinum Metals Rev.*, 2003, 47(2), 61–72.
- (48) Y. Tian and T. Tatsuma, *J. Am. Chem. Soc.*, 2005, 127(20), 7632–7637.
- (49) R.S. Sonawane and M.K. Dongare, *J. Mol. Catal. A*, 2006, 243(1–2), 68–76.
- (50) N. Serpone and A. Salerno, *Pure & Applied Chem.*, 1999, 71, 303–320.