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Abstract
The preparation of a visible light-absorbing, very thin (2.5 µm), flexible CdS nanoparticle coated polystyrene (PS) film, CdS-PS, with a 3D-printed backing is described. Scanning electron microscopy confirms that the CdS-PS film comprise a thin layer of CdS nanoparticles (26 ± 4 nm) on just one side of the PS film, with no nanoparticles on the other side. When irradiated with 420 nm or 365 nm radiation, in air-saturated water, the CdS film is photobleached, and dissolved O$_2$ consumed, due to the photoinduced oxidative corrosion of the CdS by O$_2$. In contrast, under the same aerobic conditions, the CdS-PS film is very stable, when a sacrificial electron donor (SED) is present, such as EDTA or ascorbate/ascorbic acid, with the latter appearing the most effective. In the presence of an SED, the CdS-PS film photocatalyses the reduction of the dyes, methyl orange and crystal violet, and the electron-relay, methyl viologen, by different SEDs, using visible and UV light. In the photocatalysed reduction of methyl viologen by EDTA, colloidal Pt reacts with the highly coloured blue methyl viologen radicals generated to produce H$_2$. Visible light irradiation of the CdS-PS/MV$^2+/$/EDTA/colloidal Pt system promotes the reduction of water to H$_2$ by the SED, EDTA, mediated by methyl viologen. A colourless, TiO$_2$-PS film, made using P25 TiO$_2$, is used to effect the same photocatalytic reduction reactions as the CdS-PS film, but only when irradiated with UV (365 nm) radiation. In both cases the films are used repeatedly with no evidence of deterioration in activity or film stability. This is the first example of the preparation and testing of a visible-light absorbing photocatalytic, i.e. CdS, thin plastic film, the preparation of which is very simple and inexpensive and may prove invaluable for the production of thin, flexible plastic photocatalytic films for solar research.

1. Introduction
CdS is a well-known semiconductor photocatalyst, due to its ability to absorb visible light (bandgap: 2.4 eV [1]) and, in theory at least, to photodissociate water into H$_2$ and O$_2$, given the highly reducing nature of its photogenerated conductance band electrons ($E_{CB}(e^-) = -0.93$ V vs NHE at pH 7 [2]) and the highly oxidising nature of its photogenerated valence band holes ($E_{CB}(h^+) = 1.47$ V vs NHE at pH 7 [2]). However, like most visible-light absorbing photocatalysts, it is prone to photoanodic corrosion, which in the case of CdS can be summarised as follows [3]:

$$2h^+ + \text{CdS} \rightarrow \text{Cd}^{2+} + S \downarrow.$$ (1)

This is particularly true in aerobic aqueous solution, as the dissolved O$_2$ is usually a very effective scavenger of photogenerated conductance band electrons, i.e.,

$$e^- + \text{O}_2 \rightarrow \text{O}_2^-$$ (2)

where, the product, superoxide, O$_2^-$, is eventually reduced to water [4–6]. The above photocorrosion process, i.e. reactions (1) and (2), quickly causes CdS to stop working as a photocatalyst, due to the accumulation of sulfur on its surface and the dissolution of the semiconductor [7]. CdS can, however, act as a photocatalyst...
for driving a variety of different reduction reactions, provided a suitable sacrificial electron donor (SED), such as: sodium sulfide [8] EDTA [9] or cysteine [10, 11], is used as the reductant. The role of the SED is to react rapidly and irreversibly with the photogenerated holes, before they are able to oxidise the CdS itself, i.e.,

$$h^+ + \text{SED} \rightarrow \text{SED}^+ \quad (3)$$

where SED$^+$ is an oxidised form of the SED, which readily and irreversibly decomposes. The remaining photogenerated conductance band electrons are then able to effect the reduction of an electron acceptor, A, i.e.,

$$n e^- + A \rightarrow A^{n^-} \quad (4)$$

where A$^-$ is a stable, reduced form of A. The electron acceptor, A, may be for example, a metal ion, such as PtCl$_6^{2-}$, water or a dye, such as methyl orange, MO. The SED does not react directly with the electron acceptor. In such cases, the overall photocatalytic process can be summarised as follows:

$$A + \text{SED} \rightarrow h\nu \geq 2.4 \text{ eV} \rightarrow A^- + \text{SED}^+ \quad (5)$$

Reaction (5) is a general redox reaction which describes the reduction of A by an SED, photocatalysed by CdS.

Of these photocatalysed reduction reactions, possibly the most well studied is that of water by CdS, i.e., where A = H$^+$, and SED = EDTA, Na$_2$S or cysteine. However, this reaction is only very effective if a suitable water reduction catalyst, such as Pt, is deposited onto the surface of the CdS particles [8, 12, 13]; such particles are usually referred to as Pt/CdS particles [14–16]. This type of photocatalysis has been referred to as ‘reductive photocatalysis’—in that the focus of the reaction is the reduction of A, i.e. reaction (4), even though the overall photosensitised reaction is, of course, a redox reaction [17], i.e. reaction (5), in which the SED is also oxidised. Conversely, the popular study of the photocatalysed oxidation of organics (by oxygen) is, as the name suggests, an example of ‘oxidative photocatalysis’ [17]. Due to the efficacy of various SEDs, CdS continues to be used as a visible light photocatalyst, and notable recent reductants include: nitrophenol [18–20], MO [21] and water [22].

Most studies of CdS photocatalysis utilise dispersions of the semiconductor photocatalyst, in powder or colloid form, which have the advantage of high surface area, and thus high rates, but also the inherent disadvantage that they cannot be readily extracted/separated from the reaction solution. This is a particular problem with colloids. This problem is avoided if the photocatalyst is used in the form of a film, however, very little photocatalytic work has been carried out on CdS films, especially on flexible substrates. The advantages of such films, over colloids and powder dispersions include: easy to extract, recyclable/reusable, compatible with use in batch and flow photoreactors and can be used in gas phase, as well as liquid phase, photocatalytic reactions.

There is a continued interest in CdS photocatalysis, especially in the presence of an SED, and a move, away from powder or colloid based photocatalysis, to that of films, especially inexpensive, flexible films. As a result, there is a need to develop simple, inexpensive methods for making a CdS coating on a flexible substrate, such as plastic. In this paper, a method for making nanoparticulate metal-based films on polystyrene (PS), from a metal colloid [23], has been modified to allow the production of a visible light-absorbing, very thin (2.5 $\mu$m), flexible CdS nanoparticle coated PS film, CdS-PS. The characteristics and activity of this CdS-PS photocatalytic film, and a TiO$_2$-PS film for comparison, are reported here.

2. Materials and methods

2.1. Materials

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used as received. P25 TiO$_2$ powder was supplied by Evonik, and comprised aggregated particles, with a fundamental particle size of ca. 25–30 nm, which were a mixture of anatase and rutile phases (typically 80% anatase), with a surface area of ca. 50 m$^2$ g$^{-1}$ [24].

2.2. Cadmium sulfide colloid

The cadmium sulfide (CdS) colloid was made using a method described previously by Kuznetsova et al [25]. Briefly, 150 ml solutions of CdCl$_2$ (8 mM) and Na$_2$EDTA (16 mM) were mixed together and then quickly added to a 150 ml solution of Na$_2$S (8 mM). The colourless solution turned rapidly a bright yellow colour and was then left to stir for an hour. The CdS colloidal solution, a photograph of which can be found in figure S1.
2.3. TiO$_2$ dispersion

A slightly opalescent, colloidal dispersion of P25 TiO$_2$, a photograph of which is illustrated in figure S1, was made using a sonication-centrifugation process reported previously [27]. As can be seen in figure S1, the final dispersion is slightly translucent with a pale brown/yellow colour; other work revealed the concentration of TiO$_2$ in the colloid was 67 mg l$^{-1}$. Analysis of the XRD of the precipitated colloid confirmed that the XRD pattern was the same as the bulk P25 powder and had an 80:20 ratio of anatase and rutile TiO$_2$. A TEM image of this dispersion is shown in figure 1(b) and reveals an average particle diameter of 24 ± 2 nm. The pzc of P25 TiO$_2$ is approximately 5.9, and so at pH 2, the particles are positively charged [28].

2.4. Platinum colloid

A Pt-citrate colloidal solution was synthesised using a method previously reported by Mills et al [29]. TEM images of the Pt colloid are illustrated in figure 1(c) from which an average particle size of 1.9 ± 0.3 nm was calculated. UV–vis spectra of the three colloids/dispersions, i.e. CdS, TiO$_2$ and Pt, without dilution are illustrated in figure 1(d).

2.5. CdS- and TiO$_2$-PS film production

As noted earlier, the CdS-PS film was made using a modified method for making nanoparticulate metal-based films on PS, from a metal colloid [23]. In the preparation of the CdS-PS film, the CdS colloidal particles are negatively charged and so able to ion-pair with a cationic phase transfer agent (PTA), tetrabutylammonium nitrate, i.e. TBAN. Thus, 5 ml of the CdS colloid were mixed with 1.2 ml of a 0.1 mM solution of TBAN and then 3 ml of a 0.05 g ml$^{-1}$ solution of PS (MW 192 k) in DCM. This biphasic solution was then shaken vigorously for a few seconds and the resulting emulsion transferred to a 50 mm diameter polypropylene (PP) Petri dish, where the DCM was allowed to slowly evaporate at room temperature. As the DCM evaporated, the CdS-TBA ion-paired colloidal particles, which had gathered at the DCM/water interface, partially embedded themselves into the slowly forming film of PS on the DCM side. The complete evaporation of the DCM was complete after ca. 2 h, following which the remaining CdS-PS film was removed from the aqueous solution and left to dry in air for at least 1 h before being used. The preparation of the TiO$_2$-PS film followed the same procedure, using the the TiO$_2$ colloid and sodium tetraphenylborate as the PTA.

The CdS-PS film was transparent with a yellow colour, while the TiO$_2$-PS film was transparent and colourless; both films had an average thickness of ca. 2.5 μm. The CdS and TiO$_2$ loadings on the PS films were estimated (by scanning electron microscopy (SEM) and particle counting) to be 1.04 and 5.20 μg cm$^{-2}$ respectively. Photographs of the two films are illustrated in figure S3, ESI.
2.6. 3D-printed backing for photocatalyst-PS (PC-PS) films
The very thin CdS- and TiO$_2$-PS films described above can be used as is—but their robustness and ease of use were improved markedly by 3D printing a thin layer of PP (200 µm) onto the back of the film, using a 3D printer (Ultimaker 3). Thus, all the photocatalyst-PS films reported below had a 200 µm PP support substrate to aid handling. A schematic illustration of how these films were printed along with photographs of the final CdS-PS-PP films are illustrated in figure S4, ESI.

2.7. Photocatalysed reduction of O$_2$
In a typical experiment, an 8 mm × 12.5 mm (1 cm$^2$ area) strip of a CdS- or TiO$_2$-PS film was cut out and stuck to the inside wall of a 1 cm cuvette using double-sided tape. Next to this film was placed an O$_2$xyDot® (OxySense [30]), secured with Blu Tack, which was used to measure the level of dissolved O$_2$, i.e. the %O$_2$, in the non-stirred, initially air-saturated, aqueous solution, with and without a variety of different SEDs. Thus, the cuvette—with the photocatalyst-PS, i.e. PC-PS, film and O$_2$xyDot® in place—was filled with either 3 ml of water, or 3 ml of a 50 mM solution of either Na$_2$EDTA, cysteine, or 1:1 molar ratio sodium ascorbate and ascorbic acid (NaA/AA). A schematic illustration of the irradiation set-up is given in figure S5, ESI. Note that the same irradiation set-up was used in the studies of the photocatalysed reduction of the dyes reported below. The solution was then sparged with air for 10 min before being sealed in the cell with no headspace. The film was then irradiated through the back of the photocatalyst film using either a violet LED (420 nm) or a UV LED (365 nm), each with an irradiance of 15 mW cm$^{-2}$, for CdS and TiO$_2$, respectively. The O$_2$xyDot® probe allowed the variation in the dissolved %O$_2$ to be monitored as a function of irradiation time, with readings taken every 15 s over a 1 h irradiation period.

2.8. Photocatalysed reduction of dyes
In a typical experiment, an 8 mm × 12.5 mm strip of CdS- or TiO$_2$-PS film was cut out and stuck to the inside wall of a 1 cm cuvette using double-sided tape. The cuvette was equipped with a crown-shaped stirrer from VWR and 3 ml of a well-mixed aqueous solution, containing either: (i) MO (25 µM) with AA (5 mM) and sodium ascorbate (5 mM) as the SED, or (ii) crystal violet, CV, (9 µM) with sodium ascorbate (10 mM) as the SED, were added. The reaction solution was then sparged with argon for 10 min, sealed, and the cuvette placed on a magnetic stirrer inside the UV–vis spectrometer. A bright LED (365, 420 or 595 nm, each with irradiance 10 mW cm$^{-2}$) was then used to irradiate the film through its back, perpendicular to the monitoring beam of the spectrophotometer. This arrangement allowed the UV–vis absorption spectrum of the continuously stirred dye-containing reaction solution to be monitored as the PC-PS film was irradiated. In this work, the typical irradiation time was 3 h and the UV–vis spectrum of the solution was recorded every 5 min.

2.9. Photocatalysed reduction of methyl viologen (MV) and hydrogen generation in solution
A 2 cm × 3 cm strip of CdS- or TiO$_2$-PS film was cut out and stuck to the inside wall of a cylindrical cell by its vertical edges using double sided tape. A small magnetic stirrer flea and a 25 ml aqueous solution, containing MV$^{2+}$ (5 mM) and disodium EDTA dihydrate, Na$_2$EDTA, (50 mM), were then added to the cell, which was then sealed with a silicone suba seal cap, but also allowed gas samples to be taken using a gas-tight syringe. The cell was sparged with argon for at least 30 min before irradiation. After sparging, the system was sealed and the PC-PS film under test was then irradiated with the required bright LED light source (irradiance = 85 mW cm$^{-2}$) whilst being stirred continuously. For every irradiation, the UV–vis spectrum of the reaction solution was recorded every 5 min and a 100 µl sample of the headspace taken for gas chromatography (GC) analysis every 30 min. After 90 min of irradiation, 200 µl of the argon-sparged Pt colloid was injected into the system and the headspace composition monitored using GC, along with the UV–vis spectrum of the reaction solution, for another 3 h irradiation. Note that the Pt colloid was NOT deposited on the CdS, rather it was dispersed in solution.

2.10. Instrumentation
All UV–vis spectrophotometry was performed using an Agilent Cary 60 UV–vis spectrophotometer. Digital images were taken using a Canon 1200D. SEM was carried out using an FEI Quanta FEG 250 on samples that were first sputter-coated with gold using a Q150R S sputter coater (Quorum Technologies). Irradiations were carried out using either a 420 nm LED (RS Components, ILH-XQ01-S410-SC211-WIR200), a 365 nm LED (RS Components, LZ1-10UV00), or a 595 nm LED (Thorlabs, M595L3). The distance between LED and film, as well as the applied current to the LED, were adjusted so that the irradiances of each LED incident on the PC-PS films were 15, 10 and 85 mW cm$^{-2}$ for the photocatalysed reduction of O$_2$, dye and MV$^{2+}$/water (H$_2$ generation) experiments, respectively. These irradiances were measured using an OL 756 spectroradiometer from Gooch & Housego. XRD was performed on the precipitated colloidal CdS and TiO$_2$.
using a Bruker D8 ADVANCE Eco with a Cu Kα source, scanned between 5° and 100°. GC was carried out using a Shimadzu GC-2014 with an Alltech CTR I column installed with a thermal conductivity detector and argon as a carrier gas. The Alltech CTR I column consisted of two 6 ft stainless steel columns; an inner column of 1/8” OD and an outer column of 1/4” OD, which had been packed with a porous polymer mixture and an activated molecular sieve, respectively.

3. Results and discussion

3.1. CdS-PS film characterisation

The CdS-PS film was pale yellow-coloured, as shown by its photograph illustrated in figure S3 and its UV–vis spectrum illustrated in figure 2(a). The latter reveals a rise in the background absorbance at ca. 520 nm which reflects the typical band gap of CdS (2.4 eV). The TiO₂-PS film on the other hand, as illustrated by the UV–vis spectrum in figure 2(a), starts to absorb just below 380 nm, while the blank PS film does not absorb above ~280 nm. The emission spectra of the three different LEDs used in this work, with λ<sub>max</sub> values of 365, 420 and 595 nm, are also illustrated in figure 2(a) and show that while the 365 nm LED’s emission spectrum overlaps with absorption spectra of the CdS- and TiO₂-PS films, that of the 420 nm LED only overlaps with the CdS-PS absorption spectrum. The emission spectrum of the 595 nm LED does not overlap with the absorption spectra of either PC-PS film, but, as illustrated in figure S6, does overlap strongly with the absorption spectra of the CV dye.

SEM of the CdS-PS film, illustrated by the images in figure 2(b), show the CdS nanoparticles, ca. 26 ± 4 nm, are embeded in the surface of the PS plastic film on one face only. A similar analysis of the SEMs for the TiO₂-PS film, reveal the same feature, but with a particle size of ca. 25 ± 5 nm.

3.2. Photocatalysed reduction of O₂

As noted earlier, one of the major limitations of most visible light-absorbing photocatalysts is their tendency to undergo photoanodic corrosion under aerobic conditions, summarised by the combination of reactions (1) and (2). This corrosion process can be largely prevented by the addition of a SED, of which there are
many, although not all are equally effective for different semiconductor photocatalysts. It is possible to demonstrate the effectiveness of different SEDs, and identify which is best to use for the semiconductor photocatalysts under study, by monitoring the rate of the photocatalysed reduction of oxygen by the SED, i.e. the rate of the following reaction,

\[
\text{SED} + \text{O}_2 \xrightarrow{h\nu \geq E_{\text{bg}}} \text{O}_2^- + \text{SED}^+. \tag{6}
\]

Here, the study of reaction (6), by the CdS- or TiO\textsubscript{2}-PS films was carried out by placing a dissolved oxygen-measuring sensor, an O\textsubscript{2}xyDot\textsuperscript{®} [30], in the cell, next to the photocatalytic film under test, as described in section 2.7 and illustrated in figure S5, ESI. The resulting recorded plots of dissolved O\textsubscript{2} concentration (measured in units of %O\textsubscript{2} saturation, where 100% = 1.3 x 10\textsuperscript{-4} M O\textsubscript{2}) versus irradiation time, for the CdS- and TiO\textsubscript{2}-PS films, immersed in an aqueous solution containing different SEDs, are illustrated in figure 3. These results show that for both the CdS- and TiO\textsubscript{2}-PS films the most effective SED was the ascorbate/ascorbic acid mixture, i.e. NaA/AA, followed by cysteine and then Na\textsubscript{2}EDTA. When no SED is present, little or no change is seen in the appearance of the TiO\textsubscript{2}-PS film or the level of dissolved O\textsubscript{2} in the reaction solution as a function of irradiation time. This feature is expected, given that TiO\textsubscript{2} is not prone to anodic corrosion and so no overall photocatalytic reaction occurs in a TiO\textsubscript{2}/dissolved O\textsubscript{2} system with no SED present. In contrast, under the same conditions the %O\textsubscript{2} vs irradiation time profile recorded for CdS-PS film with no SED present (black line) reveals an initial small degree of O\textsubscript{2} consumption, and then, after ca. 10 min, a slow recovery in %O\textsubscript{2} to its initial value of 21%. This apparently unusual profile is readily explained by reviewing the simultaneous change in the absorption spectrum of the CdS-PS film, as a function of irradiation time which is illustrated in figure S7. The latter profile shows that upon irradiation, the CdS-PS film rapidly loses its pale yellow colour, indicating a high degree of photoanodic corrosion, i.e. reaction (1), so that within 10 min it is colourless. Thus, the initial drop in %O\textsubscript{2} observed for the CdS-PS film in water, see figure 3, is due to the photocatalysed reduction of O\textsubscript{2}, via reaction (2), coupled with the oxidative corrosion of the CdS, i.e. reaction (1), and once complete, the level of %O\textsubscript{2} dissolved in solution is able to slowly return to its initial value of 21% as the O\textsubscript{2} depleted zone around the O\textsubscript{2} sensor and CdS-PS film slowly equilibrates with the rest of the aqueous air-saturated solution. In contrast, the absorption spectrum of an identical CdS-PS film remains unchanged upon irradiation in the presence of an SED, such as NaA/AA, as also illustrated in figure S7, which shows that the photoanodic corrosion of CdS, i.e. reaction (2) is replaced by the photocatalysed oxidation of the SED, reaction (3), so that the overall photocatalysed reaction is summarised by reaction (6).

The %O\textsubscript{2} vs irradiation time profiles illustrated in figure 3 highlight the importance of having an SED, especially when using a visible-light absorbing photocatalyst like CdS, and the fact that the best of the SEDs tested was NaA/AA for both PC-PS films.

3.3. Photocatalysed reductive bleaching of MO and CV

A commonly studied system used to test the photocatalytic activities of many different semiconductor photocatalysts, including CdS [21, 31], is the photocatalysed reduction of MO by an SED [9, 32–35] in anaerobic aqueous solution, i.e. reaction (5), where A = MO. In this work, the pH of the reaction solution was adjusted to 4.7 using a mixture of AA and NaA so that the MO (pK\textsubscript{a} = 3.4) was in its anionic, deprotonated form, and so did not readily adsorb onto the surface of the negatively charged CdS particles, given CdS’s pzc = 2 [26]. From previous work on CdS photocatalyst powders [9] it was expected that the MO will be photocatalytically reduced at its azo group to form the colourless hydrazine derivative of the dye, by the CdS-PS film when irradiated with light of energy ≥ E\textsubscript{bg}, i.e. 2.4 eV, while the SED, NaA/AA, will be oxidised to dehydroascorbic acid or its deprotonated form. The overall photocatalytic process is summarised by reaction (5), with A = MO and SED = NaA/AA.

In this work the photocatalysed reduction of MO by the CdS-PS film, irradiated with either the 365, 420 or 595 nm LED, was monitored \textit{in situ} using UV–vis spectrophotometry. The results of this work are illustrated in figure 4(a), and show the photocatalysed bleaching of MO is effected by the CdS-PS film, when irradiated by either the 365 or 420 nm LEDs, but not when irradiated with the 595 nm LED, as the latter does not overlap with the absorption spectrum of the CdS-PS film as noted previously, see figure 2(a).

The same CdS-PS film was used in a series of repeat irradiations of the same MO/NaA/AA/420 nm LED system and showed little loss in photocatalytic activity, as illustrated by the plot of the absorbance due to MO, at 470 nm, vs irradiation time profiles illustrated in figure 4(b). These results suggest the CdS-PS film is stable as a photocatalyst when an effective SED, such as the mixture of NaA/AA used here, is present. The flexibility of the CdS-PS film after this repeated irradiation was unchanged and SEM analysis of the films before and after the irradiation showed no change in surface morphology. Similar results were found using
Figure 3. Plots of %O₂ (measured using the O₂xyDot®) against irradiation time recording using a CdS-PS film (top figure), or a TiO₂-PS film (bottom), photocatalyst film irradiated with a 420 nm, or 365 nm, LED, respectively, in a 3 ml aqueous solution containing 50 mM of the following SED: Na₂EDTA (green), cysteine (blue), NaA/AA (red) or none (black). The incident irradiance of each LED was set to be 15 mW cm⁻².

the TiO₂-PS film and FT-IR studies of the latter showed no change in the polymer fingerprint spectrum with repeated irradiation, i.e. no evidence of oxidation. These findings suggest that, for the CdS or TiO₂ films, the PS support substrate is not significantly degraded with prolonged, > 12 h, irradiation.

When a CdS colloid, with the same loading of CdS, 1.04 µg, but per cm³ rather then cm², as used above in the CdS-PS film was used for the photocatalysed reduction of MO, the rate of MO reduction was 1.7 x’s higher than that measured using the CdS-PS film. This observation is not too surprising as all the surface of the CdS particles would be available for photocatalysis when the colloid was used, whereas only ca. 50% would be available to the CdS particles in the PS film.

Not surprisingly, under the same conditions the TiO₂-PS film was also found to be photocatalytically active. However, the TiO₂-PS film was only able to photocatalyse the bleaching of MO at an appreciable rate when irradiated with the 365 nm LED, and even then, the rate was not as striking as that observed for the CdS-PS film. This difference is most likely due to the modest overlap of the emission spectrum of the 365 nm LED with that of the absorption spectrum of the TiO₂-PS film, see figure 2(a). As with the CdS-PS film, the photocatalytic activity and the stability of the PS substrate appeared unchanged with repeated use.

In the study of the TiO₂-PS film/MO/NaA/AA photocatalytic system, the low/negligible rate of reduction of MO observed using the 420 nm LED as a light source, illustrated in figure S8 of the ESI is particularly relevant since, at this wavelength the TiO₂ does not absorb the incident light, whereas the MO does, as shown by the significant overlap of the emission spectrum of the 420 nm LED with the MO absorption spectrum, both of which are illustrated in figure S6 in the ESI. The lack of dye photobleaching observed for the anaerobic TiO₂-PS/MO/NaA/AA/420 nm system, see figure S8, suggests that dye photosensitised bleaching is unlikely, which is not surprising, given that this type of bleaching, involving semiconductors such as TiO₂, is usually attributed to their oxidation in the presence of a sacrificial electron acceptor, such as O₂ via a photosensitised reaction, i.e.,

\[
D \rightarrow D^+ + PC \rightarrow D^+ + PC (e^-) \rightarrow D^{\cdot +} + O_2^-(7)
\]

where hν’ is the energy of the photons absorbed by the dye, PC is the semiconductor photocatalyst under test (usually TiO₂), and D^{\cdot +} is an oxidised radical of the dye that is unstable and usually able to react further to produce colourless degradation products [36].

In order to confirm, by inference at least, that the bleaching of MO photocatalysed by the CdS-PS is not an example of dye photosensitisation, another dye, CV, which absorbs strongly at 595 nm was used in its place, using just sodium ascorbate as the SED, so that the pH was 7.4. In this case, the overall photocatalytic process is summarised by reaction (5), with A = CV and SED = NaA.
Figure 4. (a): Typical UV-vis spectra of the reduction of 3 ml of an anaerobic aqueous solution of 25 µM MO, by 5 mM ascorbic acid and 5 mM sodium ascorbate photocatalysed by a CdS-PS film irradiated with 420 nm light over 3 h recorded every 5 min, with an inset diagram showing the measured absorbance due to MO at 470 nm, Abs(470 nm) in the presence of a CdS-PS film irradiated with 365 nm, 420 nm or 595 nm light (black, violet and orange lines respectively) in the same reaction solution, as a function of irradiation time; (b) measured variation in Abs(470 nm) for the same CdS-PS film, in the MO/NaA/AA reaction solution described in (a) across four cycles of reduction. Incident irradiance of all LEDs was set at 10 mW cm$^{-2}$.

Figure 5. Typical UV–vis spectra of the reduction of an anaerobic aqueous solution of 9 µM crystal violet, CV, by 10 mM sodium ascorbate photocatalysed by a CdS-PS film irradiated with 420 nm light over 3 h in 5 min intervals. The inset diagram shows the measured absorbance due to CV at 590 nm, in the presence of a CdS-PS film irradiated with: 365 nm, 420 nm or 595 nm light (black, violet and orange lines respectively), as a function of irradiation time. Incident irradiance of all LEDs was adjusted to 10 mW cm$^{-2}$.

The results of the irradiation of the anaerobic CdS-PS/CV/NaA system, with 365, 420 or 595 nm radiation, are illustrated in figure 5 and confirms that, as with MO, the CdS-PS film is only able to effect the photocatalysed bleaching of the dye by the SED, NaA, using radiation the CdS film is able to absorb, i.e. that from the 365 or 420 nm LEDs, but not that from the 595 nm LED.

The negligible rate of dye bleaching observed for this system using the latter LED shows that in this system, the observed bleaching of CV, using either 365 or 420 nm radiation, is NOT due to dye photosensitisation, i.e. reaction (7), but rather the photocatalysed reduction of the dye by the SED.

3.4. Reduction of MV$^{2+}$ and H$_2$ generation in solution with Pt

Previous work has established that, in the presence of a suitable SED, such as EDTA, colourless methyl viologen, MV$^{2+}$, is readily reduced photocatalytically using visible light, to its bright blue-coloured radical cation, MV$^{+•}$, ($\lambda_{max} = 605$ nm, $E^0(MV^{2+}/MV^{+•}) = -0.446$ V vs. NHE for [37]) by a powder or colloidal dispersion of CdS [14, 38–41]. The overall reaction, which is the reduction of methyl viologen by EDTA,
Figure 6. (a) Photographs of the anaerobic reaction solution (3 ml, 5 mM MV and 50 mM Na\(_2\)EDTA), in the presence of a 6 cm\(^2\) area CdS-PS film irradiated before and after 90 min of irradiation (420 nm LED); (b) typical UV–vis spectra of the solution in the reaction system in (a) recorded over 90 min in 5 min intervals. The inset graph shows the measured change of the absorbance due to the MV\(^{+•}\) radical (605 nm), when a CdS-PS film (solid lines), or TiO\(_2\)-PS film (dashed lines) was irradiated with either 365 nm (black lines) or 420 nm (violet lines) LED radiation. The incident irradiance for all irradiations was 85 mW cm\(^{-2}\).

photocatalysed by CdS, can be summarised as follows:

\[
\text{MV}^{2+} + \text{EDTA} \xrightarrow{\text{CdS, } h\nu \geq 2.4 \text{ eV}} \text{MV}^{+•} + \text{EDTA}^{+}. \tag{8}
\]

In this work, when a CdS-PS film was placed in 25 ml of an argon-sparged MV\(^{2+}\) (5 mM) solution, with an SED (Na\(_2\)EDTA; 50 mM) present, and irradiated with a 420 nm LED (85 mW cm\(^{-2}\)), the blue radical of reduced methyl viologen, MV\(^{+•}\), forms, as shown by the photographs of the irradiation solution before and after (90 min) irradiation in figure 6(a).

The change in UV–vis absorption spectrum of the reaction solution was monitored as a function of irradiation time and the results are illustrated in figure 6(b); the latter reveal that MV\(^{2+}\) absorbs little between 320 and 800 nm, while the radical MV\(^{+•}\) has characteristic peaks at 398 nm and 605 nm \([42, 43]\). The light-induced variation in the absorbance of the reaction solution at 605 nm, due to reaction (8) and the formation of MV\(^{+•}\), i.e. \(\Delta \text{Abs}(605)\), was monitored as a function of time for both the CdS- and TiO\(_2\)-PS photocatalytic films, when irradiated with 365, or 420 nm radiation, respectively, and the results are illustrated in the insert diagram in figure 6(b). These results show that the kinetics of reaction (7), photosensitised by the CdS-PS film, are approximately the same when irradiated with either the 365 nm or 420 nm LED, whereas when a TiO\(_2\)-PS photocatalytic film is used, reaction (8) is only effected by radiation from the 365 nm LED. These findings are very similar to those reported earlier in this paper for the photocatalysed reduction of MO, or CV, by the same PC-PS films, and largely reflect the degree of overlap between the UV–vis absorption spectra of the PC-PS films and the LEDs used. Other work showed that both films were able to effect the photocatalysed reduction of MV\(^{2+}\) numerous times, without showing evidence of any significant deterioration in activity (see figure S9 in ESI).

If a noble metal such as platinum is added to the above system, the MV\(^{+•}\) radical should be able to reduce water to H\(_2\) \([41, 44–46]\), i.e.

\[
2\text{MV}^{+•} + 2\text{H}_2\text{O} \xrightarrow{\text{Pt}} 2\text{MV}^{2+} + \text{H}_2 + 2\text{OH}^{-} \tag{9}
\]

Note that the Pt colloidal particles are NOT adsorbed onto the surface of the CdS film, but rather simply mediate reaction (9) in the bulk solution. Thus, not surprisingly, when even a small amount of argon-sparged Pt colloid (200 \(\mu\)l) was added to either of the PC-PS/MV\(^{2+}\)/EDTA systems post-irradiation, the blue-coloured photocatalytically reduced solution immediately turned colourless and H\(_2\) was detected in
Figure 7. Plots of the amount of H\(_2\) generated by the MV\(^{2+}/\text{Na}_2\text{EDTA/Pt}\) system when either a CdS-PS film (crosses) or an TiO\(_2\)-PS film (triangles) are irradiated with either 365 nm (black) or 420 nm (violet) LED radiation. The incident irradiance for all irradiations was 85 mW cm\(^{-2}\).

the headspace of the cell. In order to confirm the H\(_2\) generating ability of the CdS- and TiO\(_2\)-based PC-PS/MV\(^{2+}/\text{EDTA/Pt}\) colloid systems, another set of experiments was carried out using the same set up as in figure 6, using a CdS- or TiO\(_2\)-PS film, but with 200 µl of colloidal Pt added to the reaction solution. This Pt- colloid particles containing photosystem was then irradiated with radiation from either the 365, or 420 nm LED, and the variation in the [H\(_2\)] in the gas phase monitored as function of irradiation time. The results of this work are illustrated in figure 7 and show that, once again, 420 nm radiation is not able to utilise the TiO\(_2\)-PS as a photocatalyst, whereas radiation from the 365 nm LED is able to promote the overall reduction of water by Na\(_2\)EDTA, via reactions (8) and (9), photocatalysed by the TiO\(_2\)-PS film. In contrast, radiation from either the 420 and 365 nm LED is effective in photosensitising the same reactions by the CdS-PS film. Note that in the absence of MV\(^{2+}\), irradiation of the CdS-PS film with the Pt colloid produced little, if any, H\(_2\). This finding is in keeping with the results reported by Henglein in his study of the same CdS/MV\(^{2+}\) system, but using a CdS colloid [41], and was attributed to the ability of the Pt colloid to short-circuit the electron transfer process, effectively promoting electron-hole recombination, in the absence of MV\(^{2+}\).

4. Conclusion

A visible light-absorbing, very thin (2.5 µm), flexible CdS nanoparticle coated PS film, CdS-PS, was made using a CdS colloid, and then given a transparent PP backing layer using 3D-printing to increase robustness. SEM confirms that the CdS-PS films comprise a thin layer of aggregated nanoparticles (26 ± 4 nm) on just one side of the PS film, with no nanoparticles on the other side. When irradiated with 420 nm or 365 nm radiation, in air-saturated water, the CdS-PS on PP film is photobleached, and some O\(_2\) consumed, due to its photoinduced oxidative corrosion by O\(_2\), i.e. reactions (1) and (2). However, under the same conditions, the CdS-PS film is very stable when a SED is added. In the presence of an SED, the CdS-PS film effects the visible light (i.e. 420 nm radiation) photocatalysed reduction of MO, CV and methyl viologen by the SED, and in so doing produces a number of different, striking changes in the colour of the reaction solution. When colloidal Pt is added to the methyl viologen/SED containing reaction solution, the CdS-PS film is able to sensitise the photocatalysed reduction of water to H\(_2\) by the SED. A colourless, TiO\(_2\)-PS film is used to effect the same photocatalytic reduction reactions as the CdS-PS film, but only when irradiated with UV (365 nm) radiation.

This paper is the first report of the physical and photocatalytic characteristics of a visible light absorbing thin plastic film coated with semiconductor photocatalyst nanoparticles of CdS, the preparation of which is very simple and inexpensive and may prove an invaluable generic route to the production of thin, flexible plastic photocatalytic films for a wide number of applications.

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