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Heat-transfer ('iron-on') photocatalytic films

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Abstract

The simple preparation of nanoparticulate CdS and TiO₂ photocatalytic (PC) films embedded in a thin (2.5 µm) layer of polystyrene (PS), i.e. PC-PS films, is described. These CdS-PS, or TiO₂-PS, films are then readily and easily transferred onto a range of different common flexible materials, such as many different plastics and fabrics, using the heat from an iron. In all cases the heat-transfer PC-PS films appear physically robust, as demonstrated by the 3M Scotch Tape test, and, for the same PC, exhibit a similar photocatalytic activity, regardless of the material it is ironed onto. The photocatalytic activities of these iron-on films are demonstrated using cotton as the material support. Thus, the CdS-PS-Cot film is used to photo-reductively bleach methyl orange, methyl viologen and water using visible light (415 nm) and a sacrificial electron donor (ascorbate or EDTA). The TiO₂-PS-Cot film is used effect the same reduction reactions, but using UVA light (365 nm). The TiO₂-PS-Cot film is also able to photocatalyse the oxidation of methylene blue and NO by air. In most cases there is little or no loss of activity with repeated use. Encouragingly, the non-optimised TiO₂ PS-Cot film appears more active than the commercial flexible polymeric photocatalytic film Purify Mesh 30 (Taiyo Europe GmbH).

Key words: titanium dioxide; cadmium sulfide; colloidal, polystyrene; cotton; iron-on

1. Introduction

Semiconductor photocatalysis underpins a wide range of commercial products, such as: self-cleaning and/or air-purifying glass (such as Activ™ [1]), concrete (ItalCementi [2]), tiles (Hydrotech™, Deutsche Steinzeug [3]) and paint (STO Colour Climasan, STO [4]). In almost all cases, the semiconductor photocatalyst is TiO₂ because of its low cost, high activity and chemical and biological inertness. Currently, there are few *flexible*, especially very flexible, commercial photocatalytic products, due in part to the difficulty in making flexible, active, stable coatings. For example, the photocatalyst-coated plastic films that have been produced by magnetron sputtering tend to crack if bent completely backwards and so are usually deposited onto relatively thick (typically, $\geq 100\ \mu\text{m}$) plastic substrates [5,6]. Similarly, most reports of photocatalyst-coated fabrics involve soaking the fabric in a colloid or sol-gel of the photocatalyst [7-9], and so are not particularly stable physically, in that the photocatalyst particles are easily dislodged with handling. These problems appear to have been surmounted by the Taiyo Kogyo Corporation, which produces, amongst other things, Purify Mesh 30, the world's first PVC mesh membrane to incorporate a TiO₂ photocatalyst coating for building façade applications [10]. Possible applications of flexible photocatalytic materials include: plastic and fabric light-covers, curtains, awnings, tent materials and clothes. In almost all reports of photocatalyst-coated, flexible materials, the photocatalyst is TiO₂; there are no reports of any visible light-absorbing flexible photocatalyst films. In this short paper we report a simple, facile and versatile method for producing nanoparticulate UV-absorbing (e.g. TiO₂) and visible light-absorbing (e.g. CdS) photocatalyst coatings on a thin (ca. $2.5\ \mu\text{m}$) polystyrene (PS) film supporting substrate. The resulting photocatalytic films have the novel feature that they are heat-transferrable, i.e. easily and effectively adhered to a wide variety of highly flexible substrates, including different plastics and fabrics (natural and synthetic), using heat from an iron. To our knowledge, this is the first report of a facile method for making UV and visible light-absorbing, heat-transferrable (i.e. 'iron-on') photocatalytic films.

2. Experimental

2.1. Materials

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used as received. All gases were purchased from the British Oxygen Company (BOC) and all aqueous solutions were made up using doubly-distilled, deionised water. The samples of Activ™ self-cleaning glass and the Purify Mesh 30 were gifts from Pilkington Glass-NSG and Taiyo Europe GmbH, respectively.

2.2 TiO₂ and CdS nanoparticulate polystyrene films

The nanoparticulate photocatalyst films on a thin layer of PS, i.e. PC-PS films, were produced using a modified version of the method for making nanoparticulate metal-based films on PS, reported by Bell *et al.* [11], in which an aqueous solution of negatively charged colloidal Ag particles was added to a solution of polystyrene (PS) dissolved in dichloromethane (DCM), in which was also present the cationic phase transfer agent (PTA), tetrabutylammonium nitrate (TBAN). After shaking the resulting biphasic mixture the colloidal Ag particles form a film at the H₂O/DCM interface which, as the DCM is allowed to evaporate, slowly embeds itself into the PS to form a nanoparticulate Ag metal film on a thin layer of PS (i.e. a Ag-PS film).

In the preparation of the CdS-PS film in this work, a CdS colloid was first prepared using the method described by Kuznetsova *et al.* [12] and the final colloidal solution had a Cd concentration of 2.7 mM and CdS in its hexagonal crystal phase, comprising ca. 11x20 nm nanorod-like particles. The CdS colloid also had pH of 4.7 and, given the point of zero charge (pzc) of CdS is 2 [13], the CdS colloidal particles were negatively charged and so able to ion-pair with a cationic PTA, like TBAN. Thus, 5 mL of the CdS colloid were mixed with 1.2 mL of a 0.1 mM solution of TBAN followed by 3 mL of a 0.05 g mL⁻¹ solution of PS (MW 192k) in DCM. This biphasic solution was then shaken vigorously for a few seconds and the resulting emulsion transferred to a 50 mm diameter polypropylene Petri dish and the DCM allowed to evaporate at room temperature. This process was complete after ca. 2 h, after which the resulting CdS-PS film was removed from the aqueous solution and left to dry in air for at least 1 h before being used.

In the preparation of the TiO₂-PS film, the TiO₂ colloid was made from TiO₂ P25 powder using the method reported by Salinaro *et al.* [14], in which the dispersion was sonicated and centrifuged in HCl solution (pH 2) to remove any large aggregates. The TiO₂ colloid was ca. 80:20 mixture of anatase and rutile phases, with an average particle size of ca. 24 nm. The high acidity of the TiO₂ colloid (i.e. pH 2) renders the particles positively charged, given the pzc of TiO₂ is ca. 5.9 [13], and so able to ion-pair with an anionic PTA, such as sodium tetraphenylborate. The subsequent preparation of the TiO₂-PS film from the TiO₂ colloid followed the same procedure as outlined above for the CdS-PS film, but using sodium tetraphenylborate as the PTA.

The CdS-PS films were transparent and yellow coloured, while the TiO₂-PS films were transparent and colourless; both films had an average thickness of *ca.* 2.5 μm . The CdS and TiO₂ film loadings were *ca.* 1.04 and 5.20 $\mu\text{g cm}^{-2}$ respectively, and photographs of the two films are illustrated in the Fig. S1 of the electronic supplementary information (ESI), along with scanning electron micrographs of the CdS, TiO₂ and non-coated surfaces of the PS film. A brief inspection of the latter reveals that both comprise a layer of colloidal particles, with sizes similar to those noted above for the colloids, although the TiO₂ film appeared to be slightly less well ordered as a layer of particles, with some additional TiO₂ particles on top of the embedded particles.

Work showed that each PC-PS film was readily attached to flexible materials, such as plastics (polyethylene terephthalate (PET), polypropylene (PP) and polyethylene) and fabrics (cotton, polyester, nylon and silk) through the application of heat (*ca.* 200 °C) from an iron (Philips Affinia) for 10 s through silicone release paper to prevent it sticking to the iron, i.e. each film could be readily ironed onto a wide variety of flexible substrates. For example, Figure 1 presents photographs of the cotton (Cot) support substrate with, and without, the ironed-on CdS-PS film; the latter we shall refer to as the CdS-PS-Cot film. Not surprisingly, a TiO₂-PS-Cot film could be readily produced by ironing-on TiO₂-PS onto the same cotton fabric. In all cases the heat-transferred film appeared physically robust and was not removed, or rendered less active photocatalytically, using the 3M Scotch Tape test **or when submerged or rinsed with water.**

Figure 1: Photographs showing (left to right) a cotton fabric with and without an ironed-on CdS-PS film.

For brevity, most of the results on these PC-PS-flexible materials are illustrated using cotton as the flexible substrate, but it should be noted that other work showed that, for the same photocatalyst, all PC-PS films exhibited a similar activity, regardless of the flexible support substrate, be it polymer or fabric. This feature is perhaps not too surprising as in all cases the photocatalytic surface is the nanoparticulate PC-PS film, melted onto the flexible support polymer sheet or finely weaved (and

therefore not very rough) fabric. Note: although not demonstrated here, using the same method as outlined above it should be possible to make other PC-polymer films, using a polymer other than PS, such as nitrocellulose, PMMA and PVC, and an appropriate water immiscible solvent to dissolve the polymer.

2.3 Methods

All UV-Vis spectrophotometry was performed using an Agilent Cary 60 UV-Vis spectrophotometer. Digital images were taken using a Canon 1200D. Scanning Electron Microscopy was carried out using a 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 415 nm LED (RS Components, ILH-XQ01-S410-SC211-WIR200) or a 365 nm LED (RS Components, LZ1-10UV00). The irradiances reported here were measured using an OL 756 spectroradiometer from Gooch & Housego. XRD was performed on the precipitated colloidal CdS and TiO₂ using a Bruker D8 ADVANCE Eco with a Cu K α source, scanned between 5° and 100°. Gas chromatography 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.

3. Results and Discussion

3.1 Photocatalysed reduction of methyl orange (MO), methyl viologen and water

A common system used to test the photocatalytic activities of many different semiconductor photocatalysts, including CdS [15,16], is the photoreduction of methyl orange (MO) in the presence of a sacrificial electron donor (SED) [17-21] in anaerobic solution. In this system when a photocatalytically active sample is tested, the MO is usually photoreduced at its azo functional group by the photogenerated conductance band electrons to form the colourless hydrazine derivative of the dye [15], while the SED, here ascorbic acid (AA), is oxidised irreversibly by photogenerated holes, to form dehydroascorbic acid [22]. Thus, using this test system, an 8 mm x 12.5 mm (1 cm² area) strip of the CdS-PS-Cot material was stuck to the inside wall of a 1 cm cuvette using double-sided tape. 3 mL of a well-mixed aqueous solution containing MO, (25 μ M), with ascorbic acid (5 mM) and sodium ascorbate (5 mM), were then added, the solution sparged with argon for 10 min and then sealed. The cuvette containing the reaction solution was placed inside a UV/Vis spectrophotometer, with the sample film parallel to the monitoring beam since this allowed the UV/Vis absorption spectrum of the continuously stirred, dye-containing reaction solution to be monitored as the CdS-PS-Cot film was irradiated with visible light from a bright LED (415 nm, 10 mW cm⁻²). The variation in absorbance spectrum of the MO solution was then recorded as a function of irradiation time and the results are illustrated in Figure 2.

Figure 2: Change in UV/Vis absorption spectrum of a 25 μ M MO aqueous, anaerobic solution, with ascorbic acid (5 mM) and sodium ascorbate (5 mM), recorded every 10 min, as the CdS-PS-Cot photocatalytic film was irradiated with visible light (415 nm, 10 mW cm⁻²). The insert diagram show the variation in the absorbance due to MO, Abs(470), with irradiation time, when the same CdS-PS-Cot film was irradiated over 4 cycles.

The results illustrated in Figure 2 show that the CdS-PS-Cot film is able to efficiently photocatalyse the reductive bleaching of MO, repeatedly. Although, the repeat irradiation profiles illustrated in the insert plot in Figure 2 show a loss of apparent activity with time, this is not due to a loss of CdS nanoparticles from the film – which is quite robust physically, as noted above – but rather a slow, dark, dye-adsorption process, which screens the film from the incident visible light. **Note: in this and all other repeat irradiation studies reported here, after each irradiation the used reaction solution was simply replaced by an identical fresh one.**

The TiO₂-PS-Cot and the Purify Mesh 30 (Taiyo Kogyo) films were tested in the same way and, not surprisingly, both were able to effect the same reduction reaction, when irradiated with 365 nm radiation from a UV LED (10 mW cm⁻²), but not when irradiated 415 nm light. Perhaps most importantly, the easy to produce, inexpensive TiO₂-PS-Cot film was found to be of comparable activity to the commercial Purify Mesh 30 film, as illustrated by the Abs(470) due to MO vs. irradiation time decay profiles in Fig. S2, in the ESI.

Other work showed that both the CdS and TiO₂ films were able to effect the photoreduction of: (i) methyl viologen, MV²⁺, using Na₂EDTA as the SED and (ii) water to produce H₂, by adding colloidal Pt to the MV²⁺/Na₂EDTA solution in (i). A typical set of absorbance (due to methyl viologen radical, MV^{•+}, production, with $\lambda(\text{max}) = 605 \text{ nm}$, and [H₂] vs. time profiles arising from this work are illustrated in Fig. S3 in ESI for the CdS-PS film.

3.2 Photocatalysed oxidation of methylene blue and NO

The results described in the previous section illustrate the ability of both CdS- and TiO₂-Cot films to photocatalyse a number of different reduction reactions. The examples given are those of *reductive* photocatalysis; although, of course, all such heterogeneous photocatalysed reactions are redox reactions [23]. However, in most commercial applications of photocatalysis, the focus is on *oxidation* reactions, such as that of inorganic or organic pollutants in solution or air, using oxygen as an electron acceptor to react with the photogenerated electrons. Unfortunately, most visible light-absorbing semiconductor photocatalysts, like CdS, are prone to photoanodic corrosion when used in this way and, as a consequence, most commercial photocatalytic products utilise the very photostable, inexpensive, chemically inert, but UV-only absorbing semiconductor, TiO₂. It follows that in this work examples of photo-*oxidative* catalysis are illustrated using the TiO₂-PS-Cot and commercial Purify Mesh 30 films.

A popular reaction for assessing the photo-*oxidative* (self-cleaning) activity of a photocatalytic material is the bleaching of methylene blue (MB, $\lambda(\text{max}) = 665 \text{ nm}$) in aqueous solution, by dissolved oxygen. Indeed, it is the basis of an ISO for assessing the self-cleaning ability of a photocatalytic films [24,25]. In this work, the same experimental arrangement as used to generate the data illustrated in

Figure 2 was used to monitor the oxidative bleaching of MB (10 μ M) by dissolved O_2 , photocatalysed by the TiO_2 -PS-Cot film, but with a higher irradiance (80 $mW\ cm^{-2}$) because, as is often the case, the kinetics of oxidation were much slower than for reduction. The results of this work are illustrated in Figure 3 and show that the TiO_2 -PS-Cot film is able to photocatalyse the oxidative bleaching of MB repeatedly, with no evidence of loss of activity. A similar set of results were generated using the commercial Purify Mesh 30 film, although the latter proved slightly less active ($\sim 15\%$ less), as illustrated by the Abs(665) vs. time profiles illustrated in Fig. S4 in the ESI.

Figure 3: Change in UV/Vis absorption spectrum of a 10 μ M MB aerated, aqueous solution, recorded every 5 min, as the TiO_2 -PS-Cot photocatalytic film was irradiated with UVA light (365 nm, 80 $mW\ cm^{-2}$). The insert diagram show the variation in the absorbance due to MB, Abs(665), when the same TiO_2 -PS-Cot photocatalytic film was over 4 cycles.

Another common method for testing the photo-oxidative activity of a photocatalytic material is the photocatalysed oxidation of NO by air. Thus, the TiO_2 -PS-Cot film, the Purify Mesh 30 film and Activ™ self-cleaning glass were tested for NO removal capability using a modified version of the NO removal ISO photocatalyst test in a standard ISO test reactor [26,27]. In the standard NO removal ISO protocol, a flow rate of 3 $L\ min^{-1}$ of a 1000 ppm NO (with 50% relative humidity) in air is flowed over a 10x5 cm sample of the photocatalyst sample under test, and the sample irradiated with UVA radiation (1 $mW\ cm^{-2}$) for 5 h. The overall reaction is usually summarised as follows [26]:

In this work, the sample size was reduced to 5x5 cm^2 , the flow rate decreased to 0.25 $L\ min^{-1}$ and the irradiation time set to 1 h; the UV irradiance of 1 $mW\ cm^{-2}$ as provided by two 8 W black light blue lamps with a peak emission wavelength of 352 nm. The recorded variation in [NO] vs. time profiles

for the three samples are illustrated in Figure 4 and show that, in terms of NO removal activity, the TiO₂-PS-Cot film >> Activ™ > Purify Mesh 30 film with the %NO removed is *ca.* 5.3, 1.2 and 1.1 %, respectively. Thus, once again, the very simple to produce, non-optimised TiO₂-PS-Cot film is found to be more active than the commercial, much less flexible, awning-type TiO₂ photocatalytic film, Purify Mesh 30, as well as Activ™ self-cleaning glass.

Figure 4: [NO] vs time profiles recorded for the TiO₂-PS-Cot film (black line), the Purify Mesh 30 film (green line) and Activ™ self-cleaning glass (red line), using the ISO NO_x reactor, run at 0.25 L min⁻¹ for 1 h, with all other conditions as set in the NO_x ISO, i.e. [NO]_{in} = 1000 ppb, I = 1 mW cm⁻² 352 nm BLB. The broken horizontal line is the typical level of NO that flowed into the reactor (*ca.* 1017 ppm).

Note: the decrease in NO removal with irradiation time exhibited by all three photocatalytic films, and illustrated in Fig. 4, is typical of most photocatalytic films and is due to the accumulation of nitric acid on the surface of the photocatalyst which lowers the rate of reaction (1) and the overall ability of the photocatalyst to remove NO_x [26,28].

Conclusions

This work describes a new, simple, versatile method for depositing visible and UV-light absorbing nanoparticulate photocatalytic films, partially embedded in a thin polymer layer, onto a wide range of flexible materials such as polymers and fabric. These films are able to effect both reductive and oxidative photocatalytic reactions and, in all the test reactions tried, the TiO₂-PS film exhibited comparable, and usually superior, photocatalytic activity when compare to a popular, commercial flexible polymer film, Purify Mesh 30. Although only CdS- and TiO₂-PS films have been produced here, there appears no major barrier to depositing other semiconductor photocatalysts, like Fe₂O₃ or CeO₂,

onto PS and other polymers, like PMMA, nitrocellulose and PVC. To our knowledge, this is the first report of a heat transfer, i.e. 'iron-on', thin plastic photocatalytic film and, because of its novel and yet generic nature, simplicity, and ease of production of very effective photocatalytic films, which can compete with those currently in the market, it should attract significant interest and find widespread application.

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