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Photocatalytic organic synthesis in an NMR tube: C—C coupling of phenoxyacetic acid and acrylamide☆

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ABSTRACT

NMR was used to study the semiconductor photocatalytic (SPC) C—C coupling of phenoxyacetic acid (PAA) with acrylamide (ACM) in an NMR tube photoreactor. Using an NMR tube with a sol–gel titania inner coating as a photoreactor, this reaction is relatively clean, forming only 1 product, 4-phenoxybutanamide (4-PB), in yields up to 78%. This SPC reaction is used to assess the activity of the sol–gel titania coating as a function of their annealing temperature, which alters the surface area and phase of the titania, and the general reusability of the TiO$_2$ coated NMR tubes. The optimum temperature range for annealing the sol–gel titania films is between 450 °C and 800 °C, with the maximum yield and rate attained at 450 °C. Despite a decrease in the initial rates of formation of 4-PB above an annealing temperature of 450 °C, the final product yields remained similar, giving maximum yields within 60 min of irradiation. The reusability study reveals that the activity of the sol–gel titania can quickly deteriorate with repeated use due to the adsorption of yellow/brown coloured, insoluble, most likely organic polymeric, material and its screening effect on the underlying photocatalyst. The titania can, however, be restored to its original activity by a simple heat treatment at 450 °C for 30 min.

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1. Introduction

The generally low environmental impact associated with using semiconductor photocatalysis (SPC) to promote desired organic reactions makes it an increasingly attractive route in the design of more 'green' organic synthetic routes. SPC has been used for many useful organic transitions such as: carbon–heteroatom bond formation [1], cyclisation [2], reduction [3], and oxidation [4], and has been the subject of numerous reviews, e.g. [5–7]. The advantages of SPC over conventional synthetic routes include: a high-level control (i.e. the reaction can be stopped at the flick of a switch), and often, high degree of selectivity, and the feature to perform usually demanding reactions under ambient conditions, using light, rather than heat, as the promoting energy.

SPC has also proven to be useful in a range of carbon–carbon coupling reactions. An early example of a SPC mediated carbon–carbon coupling reaction is the reported photo-Kolbe reaction [8,9], which generates a carbon-centred radical via the decarboxylation of an unactivated carboxylic acid. In the case of acetic acid, methane and carbon dioxide are formed upon UV irradiation in the presence of a semiconductor photocatalyst [9], Eq. (1), but, most relevant to

this study, also acid dimers are formed, via the termination of two carbon-centred radicals, Eq. (2).

$$CH_3CO_2H \rightarrow CH_4 + CO_2 \qquad (1)$$

$$2CH_3CO_2H \rightarrow C_2H_6 + H_2 + 2CO_2 \qquad (2)$$
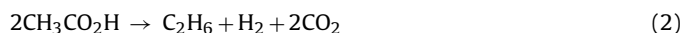
Manley et al. [10] have reported recently a range of SPC-mediated carbon–carbon coupling reactions involving a number of different carboxylic acids and alkenes, using a modified version of the photo-Kolbe reaction, to generate a carbon centred radical, which then attacks the alkene, generating a new carbon–carbon bond. A large part of their study looked at the coupling of phenoxyacetic acid (PAA) with maleic anhydride and N-substituted maleimides, however, they also reported briefly the SPC mediated carbon–carbon coupling of PAA with acrylamide (ACM) (see Scheme 1) which gave rise to only one major product, namely; 4-phenoxybutanamide (4-PB) in a respectable 82% yield, although it did require a 5-fold excess of PAA (42 mM acid:8 mM alkene) and irradiation for over 2.5 days!

Mills and O'Rourke have recently demonstrated a number of advantages of performing semiconductor photocatalysed organic reactions in an NMR tube and using NMR to monitor their progress [11]. For example, in the oxidation of toluene, a small scale (1.5 mL) reaction performed in an NMR tube using a P25 TiO$_2$ dispersion was found to be much faster (8×) than the same reaction performed on a 100 mL scale in a Dreschel bottle using a powder dispersion of the same ubiquitous P25 titania (0.5 mg mL^{-1}). The use of a sol–gel
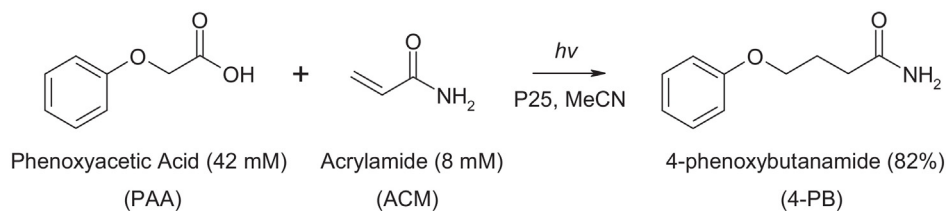
Scheme 1. SPC C—C coupling of PAA (42 mM) and ACM (8 mM) using P25 (1 mg mL^{-1}) in a 80 mL reaction solution [10].

titania coating in an NMR tube also provided a further improvement on the reaction time (1.3×'s) over the use of a P25 dispersion in a tube, and eliminated the need to maintain a dispersion of the semiconductor photocatalyst.

The aim of this work is to study the titania photocatalysed carbon–carbon coupling of PAA with ACM in further detail, using a sol–gel coated NMR tube to serve simultaneously as both the photoreactor and analytical solution sample holder. This photocatalysed reaction is then used to probe the efficacy of the titania coating as a function of annealing temperature, as well as the reusability of the coated tubes.

2. Experimental

Unless otherwise stated, all chemicals used in this project were purchased from Sigma–Aldrich and were used as supplied. The P25 titania was provided by Evonik Degussa Corporation. P25 has a surface area of *ca.* 50 m^2 g^{-1} and is 80% anatase and 20% rutile [12].

2.1. Preparation of TiO$_2$ coated NMR tubes

A paste of titania nanoparticles was prepared using the sol–gel method described by Mills et al. [13]. Briefly, the precursor, titanium(IV) isopropoxide (20 mL), was modified by the addition of glacial acetic acid (4.65 g) under argon. The titania was then synthesised *via* the sol–gel process by the addition to the solution of 120 mL of deionised water containing 1.08 g of nitric acid, thus initiating the hydrolysis reaction, which leads to a condensation reaction, that produces the hydrous oxide. The colloidal titania particles were then grown *via* Ostwald ripening using an autoclave (220 °C for 720 min). The resulting precipitated particles were dispersed using an ultrasonic probe and the solution was rotary evaporated until a weight percent of titania of 10–12% was achieved. At this stage 50 wt% of polyethylene glycol was added as a binder to help prevent the formation of cracks in the cast films.

A few drops of the titania paste were pipetted into a NMR tube and shaken with the cap in place until the paste covered completely the inside of the tube. The cap was then removed and the NMR tube placed in the chuck of an overhead stirrer turned on its side, and rotated horizontal to the floor at 1000 rpm for 5 min. This created an even thickness of the paste film on the sides of the NMR tube, before placing it under vacuum using a rotary evaporator to remove all the solvent. The use of vacuum ensured no bubbles were present in the paste, which could lead to poor adhesion on the sides of the tube and result in flaking when dry. The tube was then placed in a furnace and heated to 450 °C for 90 min with a ramp rate of 10 °C min^{-1}. The tube was then left overnight to cool slowly inside the furnace to create a final robust, clear coating of anatase titania (*ca.* 1.4 mg cm^{-2}, thickness ~4 μm, so that 1 mL of reaction solution is typically exposed to ~11 cm^2 of titania photocatalyst) on the inside of an otherwise conventional Pyrex®/quartz NMR tube (5 mm o.d., length = 20.3 cm). XRD reveals the annealed TiO$_2$ film is in its anatase crystal form [13].

2.2. NMR tube irradiations

In-situ NMR tube irradiations were carried out using a titania sol–gel coated NMR tube. A photoreactor, consisting of two lots of 6 × 8 W black light blue (BLB) UV lamps (λ_{max} (emission) 365 nm), each arranged in a hemispherical cylinder with an aluminium reflector, were used to irradiate the contents of the NMR tube. The two photoreactor hemispheres were brought together to surround the NMR tube as shown in Fig. 1. Unless otherwise stated, the UV irradiance of each hemisphere of the photoreactor was 3.5 mW cm^{-2}. For a typical reaction, a 5 mL stock reaction solution was prepared comprising: the reactant(s) i.e. 10 mM of the PAA and/or 20 mM of the ACM, dissolved in deuterated acetonitrile. This reaction solution was then purged with argon for 5 min, to remove any dissolved oxygen, and then 1 mL was pipetted into an argon flushed sol–gel coated NMR tube. The cap was then quickly replaced on the tube and sealed with Parafilm. The loaded NMR tube was then placed in an overhead stirrer (turned on its side), which was then spun at 250 rpm. The tube was held at a slight angle to horizontal in the 'chuck' of the overhead stirrer so that, when rotated, it described a small (ca. 2 cm) circle at its non-chuck-held end (see Fig. 1(b)) so as to agitate the reaction solution. Once the NMR tube, filled with reaction solution, was in place, the irradiation was started and, periodically, the tube was removed from the chuck and placed in the NMR instrument for analysis, before being returned for further irradiation.

All NMR analyses were performed using a Bruker AVIII 400 Spectrometer fitted with a 5 mm PABBO BB-1H/D Z-GRD Z108618/0146 probe and equipped with TopSpin 1.3 software. Unless otherwise stated, all experiments were performed in deuterated solvents. Analyses of the data were carried out using ACD/NMR Processor software (version 12.01) by ACD/Labs.

3. Results and discussion

3.1. Photocatalysis: phenoxyacetic acid (PAA)

Phenoxyacetic acid (PAA) (λ_{max} = 270 nm) does not absorb in the UVA region and therefore, it is not surprising that irradiation with UVA of a 1 mL CD$_3$CN solution containing 10 mM of PAA, in the absence of titania, in an NMR tube over a 240 min period shows no reaction/degradation. However, in the presence of a sol–gel coating on the inside of the NMR tube, irradiation does give rise to the formation of anisole and 1,2-diphenoxyethane in yields of 45% and 30% respectively, after 90 min. Fig. 2 shows the overall reaction and the observed change in the NMR spectra as a function of irradiation time. The latter shows the disappearance of the PAA ((i), δ 4.65), accompanied by the appearance of both anisole ((ii), δ 4.31) and 1,2-diphenoxyethane ((iii), δ 3.78).

A likely mechanism for the SPC formation of anisole and 1,2-diphenoxyethane from PAA is illustrated in Scheme 2 . Thus, initial oxidation of the PAA on the surface of the titania by photogenerated holes, h^+, gives rise to the formation of a cationic radical, which then

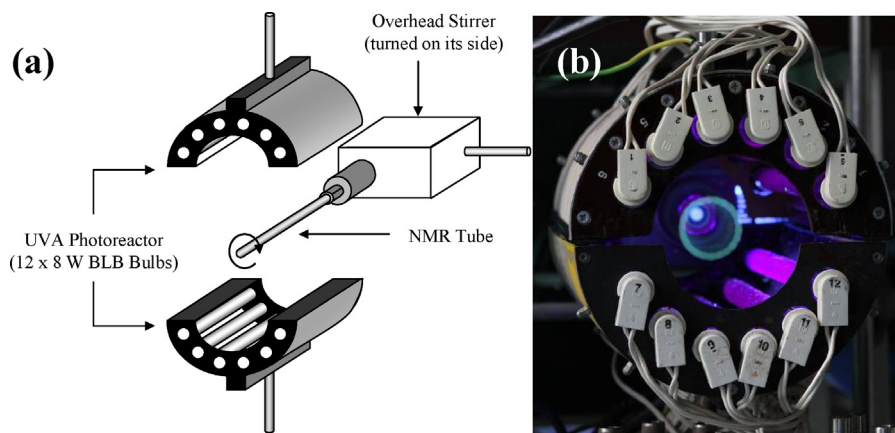**Fig. 1.** (a) Schematic of the NMR tube irradiation setup [11]. (b) Long exposure photograph showing the conical rotation of the NMR tube.
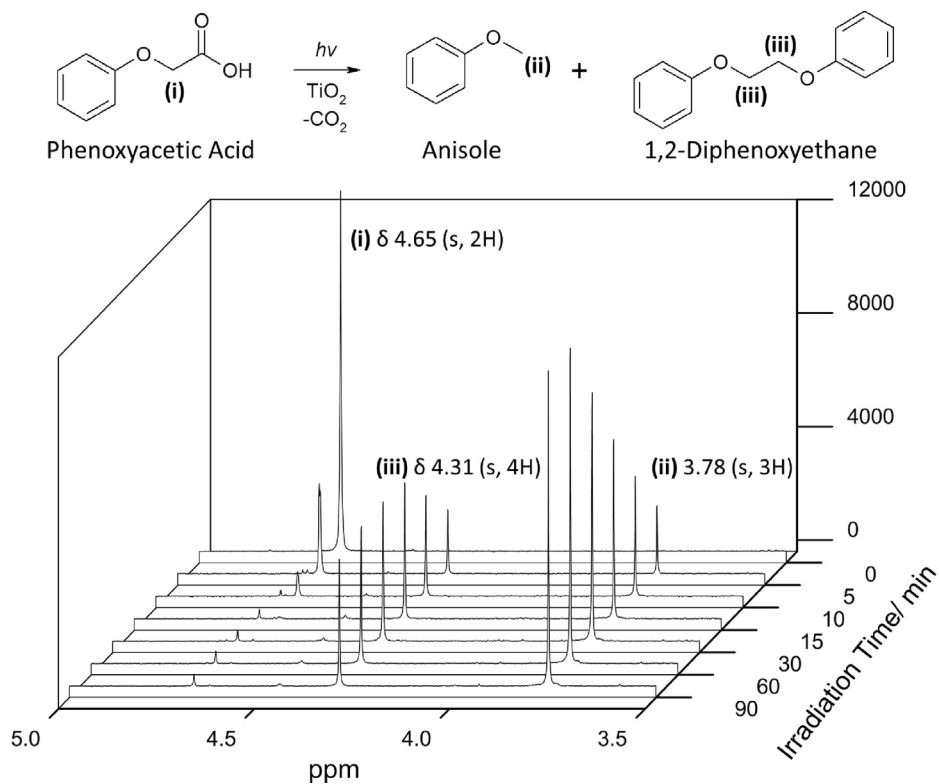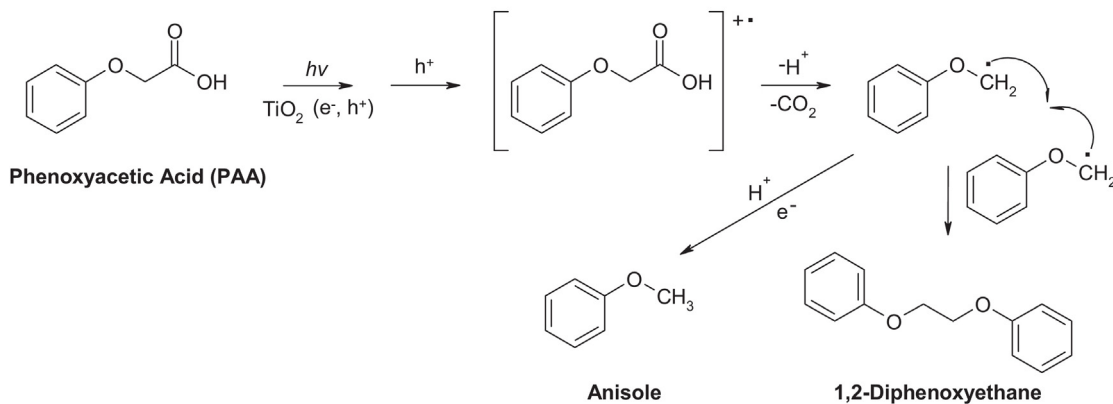

Fig. 2. General reaction scheme for the SPC irradiation of 1 mL of PAA (10 mM in CD_3CN) in a sol–gel coated NMR tube and the change in NMR spectra as a function of irradiation time.

Scheme 2. Proposed SPC mechanism for the formation of anisole and 1,2-diphenoxyethane from PAA.

subsequently loses a proton and carbon dioxide to form the neutral PhOCH$_2$$^{\bullet}$ radical. The later species then either gains a proton and an electron from the surface of the titania to form the anisole, or couples in a termination step with a second PhOCH$_2$$^{\bullet}$ radical to form 1,2-diphenoxyethane.

3.2. Photocatalysis: acrylamide (ACM)

Acrylamide (ACM) (λ_{max} = 190 nm), like PAA, also does not absorb in the UVA region, therefore, similar to PAA, irradiation of a 1 mL CD$_3$CN solution containing 20 mM of ACM, in the absence of titania, in an NMR tube over a 240 min period shows no reaction/degradation.

In contrast, when the same solution is irradiated in a sol–gel titania coated NMR tube, the formation of propionamide (see Scheme 3) is observed, however, the yield is low (1.3%) even with a 38% consumption of the ACM over 120 min of irradiation. It appears likely that most of the ACM that is lost during this irradiation process goes to form insoluble polymeric species on the surface of the titania, via oxidative polymerisation, initiated by photogenerated holes, which would help to account for the latter turning brown with prolonged irradiation (vide infra).

3.3. Photocatalysis: C—C coupling of phenoxyacetic acid (PAA) and acrylamide (ACM)

Fig. 3 shows the general reaction scheme and the measured change in the NMR spectra for the SPC C—C coupling of 10 mM PAA with 20 mM ACM in 1 mL CD$_3$CN using a sol–gel titania coated NMR tube. 4-phenoxybutanamide (4-PB) is produced in an impressive yield of 78% after only 30 min, along with a 12% yield of anisole. Fig. 4 shows the progress of the concentrations of the starting materials, the main adduct product, 4-PB, and anisole as a function of irradiation time, as measured by NMR (data from Fig. 3).

In another set of experiments, the initial ratio of ACM/PAA was varied from 1:1 to 3:1 and the results are given in Table 1 for the SPC C—C coupling of PAA and ACM using a sol–gel coated NMR tube. These results reveal that the optimum conditions to produce the maximum yield of the adduct product are with a 2:1 (ACM/PAA) ratio. As might be expected, increasing the ACM ratio to 3:1 reduced the yield of the anisole, formed in the single component SPC background reaction, from 12% to 5% but, the adduct product yield (74%) was slightly lower than for the 2:1 ratio.

A dispersion of P25 titania was also used as the semiconductor photocatalyst to assess the coupling reaction using a 2:1 ratio of
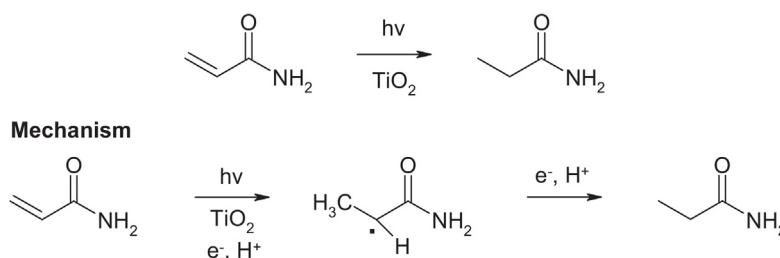
Scheme 3. General reaction scheme/proposed mechanism for the SPC irradiation of 1 mL of ACM (20 mM in CD$_3$CN) in a sol–gel coated NMR tube, forming propionamide.
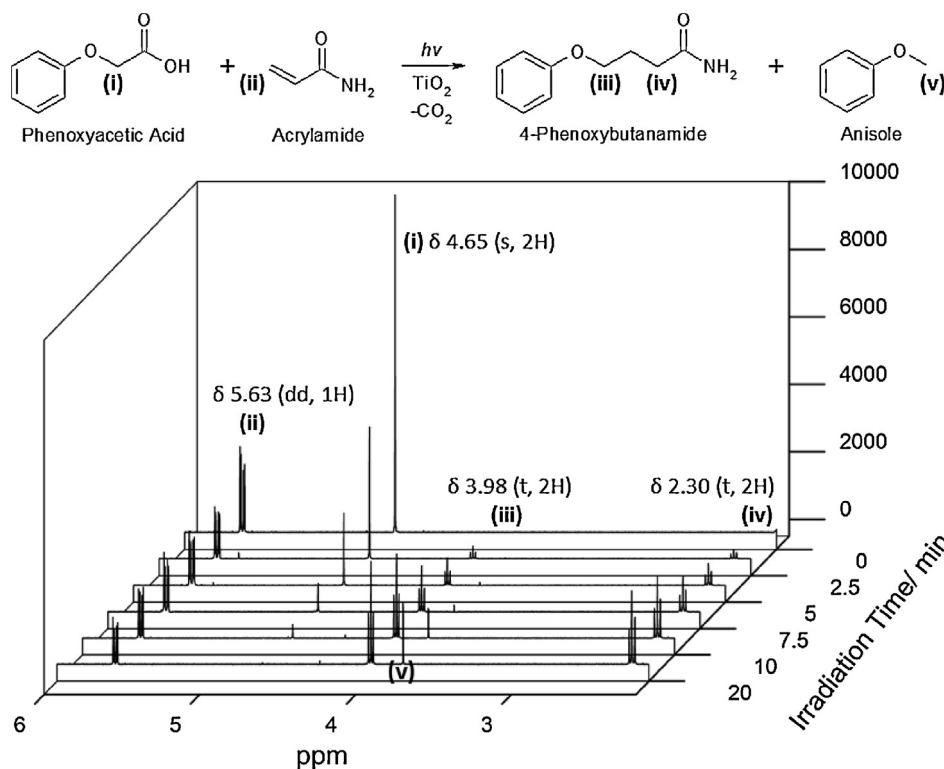
Fig. 3. General reaction scheme for the SPC carbon–carbon coupling of PAA and ACM (1 mL, 10 mM acid: 20 mM alkene, in CD$_3$CN) in a sol–gel coated NMR tube, and the change in NMR spectra as a function of irradiation.

Table 1
SPC C—C coupling of PAA with ACM to form 4-PB, monitored over 120 min using sol–gel titania coated NMR tubes, and 700 min for the P25 titania dispersion in an NMR tube.

SC	Starting materials				Products	
	Phenoxyacetic Acid		Acrylamide		4-Phenoxybutanamide	Anisole
	mM	% Conversion	mM	% Conversion	% Yield[a]	% Yield[a]
Sol–gel[a]	10	100%	30	48%	74% (60 min)	5%
Sol–gel[a]	10	100%	20	59%	78% (30 min)	12%
Sol–gel[a]	10	100%	10	49%	32% (40 min)	1%
P25[b]	10	87%	20	60%	40% (>700 min)	5%

[a] Sol–gel coated NMR tube: sol–gel mass = $1.4 \pm 0.2 \, \text{mg cm}^{-2}$, 1 mL solution is exposed to ~11 cm^2.
[b] P25 dispersion in an NMR tube: $0.5 \, \text{mg mL}^{-1}$. Reaction solution = 1 mL.
% Conversions are quoted at the time the maximum yield of 4-PB is attained.

starting materials. Initial results using a dispersion in an NMR tube gave rise to only a 40% yield of the adduct product after >700 min irradiation, although it was noted that the dispersion of P25 was difficult to maintain inside the NMR tube, as it readily aggregated and settled at the bottom of the tube. Even in a scaled up photoreactor (100 mL Dreschel bottle), using P25, where the solution was vigorously stirred and the dispersion was well maintained, the yield of 4-PB was 44% after 1200 min, i.e. 3×'s faster than that reported by Manley et al. [10], using a 5:1 PAA/ACM but, in turn, 40×'s slower than when using a sol–gel titania film in an NMR tube. These results highlight the more rapid nature of SPC films when carried out in a TiO$_2$ paste coated NMR tube, compared with P25 in a scaled up photoreactor and, therefore, the more appropriateness as a rapid screening photoreactor in SPC organic reactions at least.

The proposed mechanism for the SPC C—C coupling reaction between PAA and ACM is shown in Scheme 4. Thus, the PAA is initially oxidised by a hole, h^+, on the titania to produce a radical cation. This radical then undergoes decarboxylation to produce a PhOCH$_2$• radical, which then attacks the double bond of the ACM to produce a radical adduct. Formation of 4-PB is then achieved by reduction of the radical adduct by a photo-generated electron from the titania, followed by the addition of a proton. Scheme 4 also shows an alternative route for the PhOCH$_2$• radical to be reduced and so form anisole, as previously shown in Scheme 2 for the single component SPC irradiation of PAA.

3.4. Photocatalyst film: an annealing temperature study

The durability of the sol–gel paste is an important factor if it is to be reused and increasing the annealing temperature of the sol–gel coating creates a more robust film on the inside of the tube, making it less susceptible to flaking with continued use. The SPC C—C coupling reaction between PAA and ACM (see Scheme 4) was used to probe the effect of annealing temperature on the photocatalytic activity of the sol–gel titania used to coat the inside of quartz NMR tubes.

The range of annealing temperatures used for this study (350 - 1000 °C) exceeded the limits of standard Pyrex® NMR tubes, therefore quartz NMR tubes were used instead. Seven quartz tubes were coated with the sol–gel titania and annealed for 90 min at temperatures spanning the range: 350–1000 °C. The effect of the annealing temperature on the appearance of the sol–gel films in the NMR tubes is shown in Fig. 5(a). To each of these tubes, 1 mL of an argon saturated solution, containing 10 mM PAA and 20 mM ACM in CD$_3$CN, were added. Each tube was then irradiated and the photocatalysed C—C coupling reaction monitored by NMR over a 60 min period. Table 2 lists, for each of the annealed films, the initial rate, r_i, of formation of the main adduct product, 4-PB, over the first 10 min, along with the maximum yield of the adduct product. Table 2 also lists the relative robustness of the sol–gel titania films as a function of annealing temperature, as measured using a simple 3 M Scotch® tape test [14] on the sol–gel titania films when cast on quartz disks,

see Fig. 5(a). Briefly, in this test, a strip of the Scotch® tape was placed on top of each coated disk and a paperweight was placed on top to apply equal force on each to ensure an equal pressure to adhere. The tape was then removed at a 180° angle and photographs were taken before and after the removal of the Scotch® tape. Photoshop was then used to determine from the two pictures, the area of the sol–gel remaining on each quartz disk, and the relative robustness of a film was calculated as the ratio of final to initial photocatalyst areas remaining after tape removal from the film. Complete removal of the titania was observed for the 350 °C and 450 °C films, whereas, no titania was removed from the sol–gel film annealed at 1000 °C. Fig. 5(b) shows a plot of the initial rate and relative robustness as a function of annealing temperature. The initial rate steadily decreases from its maximum at 450 °C up to 900 °C, after which the rate becomes negligible. Despite the decrease in rate with increasing annealing temperature, the final yields of adduct product are fairly similar up to an annealing temperature of 800 °C.

It was noted that prior to irradiation of the reaction solutions in the sol–gel titania coated NMR tubes, an initial decrease of the PAA occurred due to adsorption on the titania surface. The amount of PAA initially adsorbed on each titania film annealed at different temperatures was measured by NMR and is listed in Table 2. No adsorption of ACM was evident from the NMR spectra. The sol–gel titania used in this work has previously been characterised by Mills et al. [15] and Table 3 lists some relevant reported properties of the titania films, namely: % anatase and particle size.

The plot in Fig. 6(a) reveals a linear relationship between the initial rate of formation, r_i, of the adduct product, 4-PB, and the amount of PAA initially adsorbed, [PAA]$_{ads}$, on the surface of the sol–gel titania. In addition, a plot of [PAA]$_{ads}$ vs. 1/particle size (proportional to surface area if we assume the titania film to comprise approx-
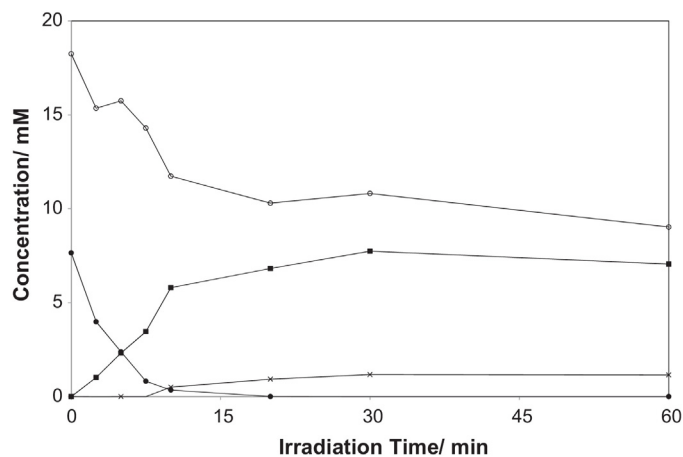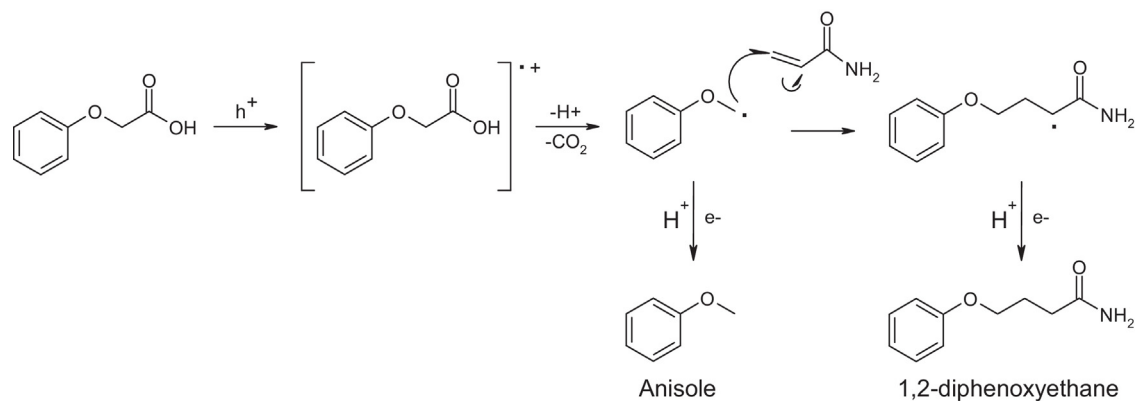

Fig. 4. Change in concentration of PAA (●), ACM (○), 4-PB (■), and anisole (×), upon irradiation of 10 mM PAA with 20 mM ACM in a sol–gel titania coated NMR tube, using a 12 × 8 W BLB photoreactor (λ_{max} = 365 nm).

Scheme 4. Proposed mechanism for the photocatalytic C—C coupling of PAA and ACM.

Table 2
Initial rate, r_i, of formation of 4-PB over the first 10 min of the SPC irradiation of a 1 mL solution of 10 mM PAA and 20 mM ACM in CD_3CN. The maximum yields achieved at, t_{max}, are also listed, as well as the initial amount of PAA adsorbed on the titania prior to irradiation, and the relative robustness of each of the films.

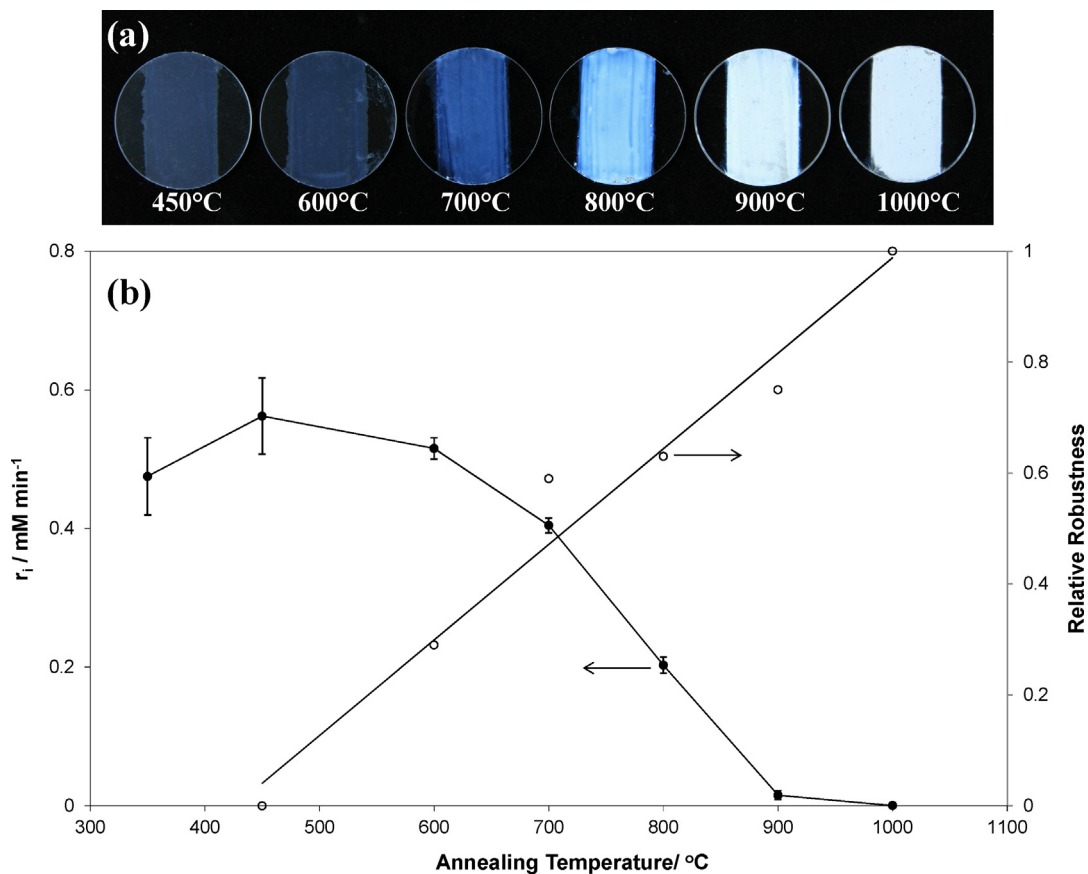| Annealing temp. (°C)	4-Phenoxybutanamide			Initial $[PAA]_{ads}$ (mM)	Relative robustness
	r_i (mM min^{-1})	t_{max} (min)	Yield		
350	0.48	20	38%	5.71	0
450	0.56	30	78%	2.35	0
600	0.52	30	70%	2.21	0.29
700	0.40	60	74%	1.94	0.59
800	0.20	60	68%	1.04	0.63
900	0.02	>60	12%	1.44	0.75
1000	–	>60	1%	0.30	1.00

Fig. 5. (a) Photograph showing the change in relative robustness of the sol–gel coating as a function of annealing temperature. (b) Initial rate, r_i, of formation of the adduct product (4-PB) over the first 10 min as a function of annealing temperature.
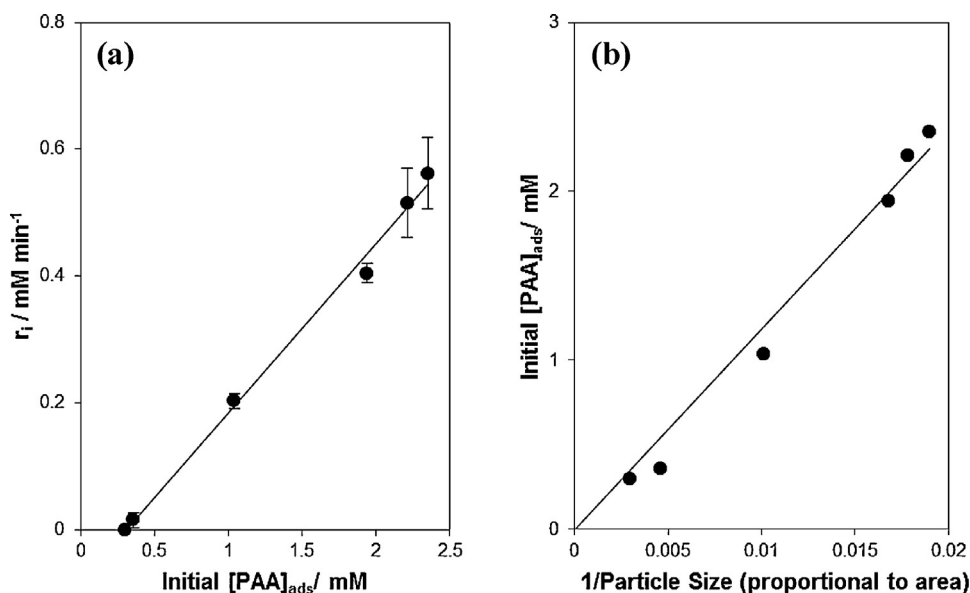
Fig. 6. (a) Plot of initial rate, r_i, of formation of 4-PB, r_i, vs. the initial concentration of PAA adsorbed, $[PAA]_{ads}$, also showing a linear relationship. (b) Plot of the initial concentration of PAA adsorbed, $[PAA]_{ads}$, vs. 1/particle size (proportional to area), showing a linear relationship.

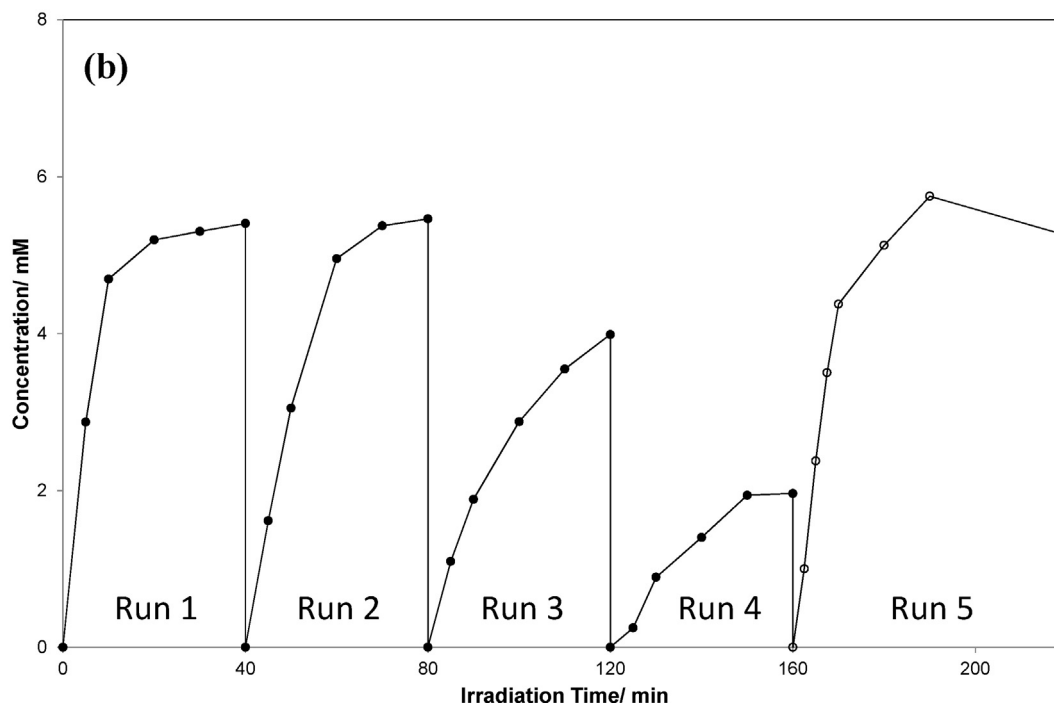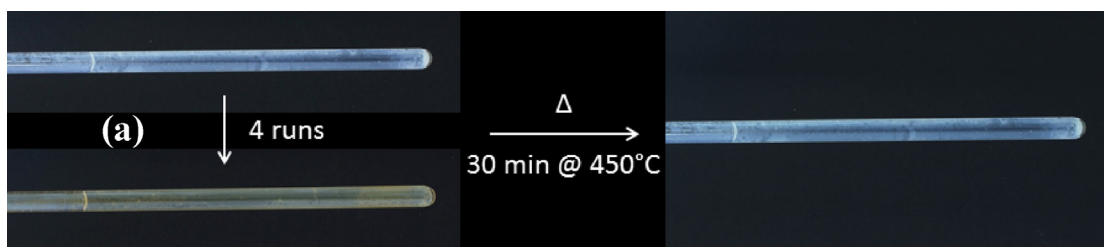**Fig. 7.** (a) Photograph showing the change in colour of the sol–gel film after 4 runs. (b) Reusability experiment showing the formation of 4-PB from the SPC C—C coupling of PAA and ACM in the same sol–gel coated NMR tube irradiated using the 12 × 8 W BLB photoreactor. Runs 1–4 show the change in activity with repeated use, and run 5 shows the regeneration of the sol–gel activity after heat treatment at 450 °C for 30 min.

Table 3
Key physical properties of the sol–gel titania films annealed at various temperatures as determined by Mills et al. [15].

Annealing temperature (°C)	% Anatase	Particle size (nm)
350	100	50
450	100	53
600	100	56
700	100	60
800	75	99
900	0	217
1000	0	336

imately spherical particles, which a previous TEM study suggests [15]), shown in Fig. 6(b) shows, not too surprisingly, the amount of PAA initially adsorbed is dependent upon the surface area of the titania. The system is, however, complicated by the fact that, above 700 °C anatase begins to convert to its rutile form. This could account for the fact the straight line shown in Fig. 6(a) does not cut through the origin as the rate is negligible when a not insignificant amount of PAA is still adsorbed. This suggests that the (PAA plus ACM) C—C coupling photocatalysed reaction does not readily occur when rutile TiO_2 is the photocatalyst. In support of this, work using a high surface area (130–190 $m^2 g^{-1}$) dispersion of rutile titania on a scaled-up reaction revealed no reaction over a 900 min period. The decrease in initial rate as the annealing temperature increases as illustrated in Fig. 5, is most probably due to a combination of surface area and phase of the titania.

3.5. Reusability study of the sol–gel titania coated NMR tubes

As noted earlier, the prolonged use of the sol–gel titania in the C—C coupling reaction, results in the colouration of the film (it turns brown), most likely due to the photocatalytic production and adsorption of insoluble polymeric material. Similar observations and conclusions have been reported previously for the SPC oxidation of benzene by TiO_2 powder (P25) [16,17]. The detrimental effects of this adsorbed coloured material on the activity of the sol–gel titania film and an assessment of just how 'reusable' the films are, was carried out using the clean, high yielding SPC C—C coupling of PAA and ACM.

Thus, using a 1:2 ratio of starting materials, the SPC C—C coupling reaction was performed using a sol–gel coated NMR tube. After 40 min of irradiation, with periodic monitoring by NMR, the solution was removed and the tube was rinsed with fresh acetonitrile to remove any traces of products from the previous irradiation. 1 mL of fresh reaction solution was then added to the tube and irradiated; the whole process was repeated four times in total. The titania became increasingly yellow/brown in colour with subsequent reactions as shown in Fig. 7(a). A plot of the formation of the major product, 4-PB vs. irradiation time, shown in Fig. 7(b), demonstrates that the adsorption of an insoluble, brown-coloured, material has a significant impact on the reusability of the sol–gel paste. Thus, the first two irradiations/runs produced almost identical conversions of 55% and 54% after only 30 min, although, the initial rate of the second irradiation was approximately 1.6×'s slower. Subsequent irradiations showed a significant drop in the percentage conversion to 41% for the third repeat and only 20% for the fourth. After the 4th run, the sol–gel coated tube was emptied and the tube was placed in a furnace at 450 °C for 30 min. This was sufficient to remove all traces of organics and return the sol–gel titania film back to its original photoactivity and colour, as demonstrated by the 5th run shown in Fig. 7(b), which gave rise to a 57% yield of the adduct product, showing that such a thermal treatment was sufficient to regenerate the original photocatalyst film. Work is currently ongoing to further assess the reusability of the sol–gel titania over many more thermal treatment cycles.

4. Conclusions

As neither PAA nor ACM absorb in the UVA region, the SPC carbon–carbon coupling reaction is not complicated by the possibility of background homogeneous photochemistry. In the presence of titania, however, irradiation of PAA (10 mM in CD_3CN) produced high yields of anisole (45%) and acid dimer (30%) after 90 min. In contrast, irradiation of ACM in the presence of a sol–gel titania coating gave rise to only a 1.3% yield of propionamide after 240 min, indicating a comparatively inefficient SPC process.

Using a 2:1 ratio (20 mM ACM:10 mM PAA) of starting materials, the SPC C—C coupling of PAA and ACM using a sol–gel coated NMR tube gave rise to the formation of the main adduct product, namely; 4-phenoxybutanamide in a respectable yield of 78%, with a 12% yield of anisole.

The use of a dispersion of P25 as an alternative photocatalyst on in an NMR tube provided a much lower yield of the main adduct product of 40% after 700 min irradiation, c.f. a 78% yield after only 30 min using a sol–gel titania coated NMR tube. This decreased efficiency could be attributed to the difficulty in maintaining a good dispersion of the semiconductor.

A study of the effect of the annealing temperature on the activity of the sol–gel titania films using the SPC C—C coupling reaction of PAA and ACM, demonstrated that the optimum annealing temperature, giving rise to the highest rate of formation, and the highest yield, of the adduct product, is ca. 450 °C. As the annealing temperature is increased above this temperature, a steady decrease of the initial rate of formation of the adduct product is observed up to 900 °C, after which the initial rate becomes negligible. A linear relationship is observed between the initial rate of formation of the adduct product and the amount of PAA initially adsorbed on the surface of the titania, indicating that the rate of photocatalysed reaction is dependent directly upon photocatalyst surface area. However, there is also an increasing change in phase at temperatures above 700 °C and so the rate is probably also intimately dependent upon the phase of the titania.

The activity/performance of the sol–gel titania coating quickly diminishes with repeated use due to the adsorption of insoluble material on the surface of the titania, evident by the increasing yellow/brown colour of the titania film. The activity of titania can however be regenerated by heat treatment at 450 °C for 30 min in a furnace, which removes all traces of organics and restores the original white colour of the titania.

This work suggests that titania-coated NMR tubes are ideal for rapid screening and optimisation studies of SPC driven organic reactions such as the C—C coupling of PAA and ACM.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2013.10.083.

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