

# Photocatalytic degradation of dye sulforhodamine B: a comparative study of photocatalysis with photosensitization

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The direct photocatalytic degradation of dye pollutant sulforhodamine B (SRB) in aqueous TiO<sub>2</sub> dispersions has been examined and compared to the photosensitization process. The mineralization extent of SRB degradation, the formation of intermediates and final products were monitored to assess the degradation pathways caused by direct photocatalysis. In the initial stage of the direct photocatalysis, SRB is mainly oxidized by a positive hole upon band-gap excitation of TiO<sub>2</sub> by UV light (330 nm < λ < 380 nm) and subsequently undergoes the similar degradation pathways as occur in the photosensitization under visible irradiation (λ > 420 nm). Diethylamine, *N,N*-diethylacetamide, *N*-ethylformamide, *N,N*-diethylformamide, formic acid and acetic acid were identified as intermediate species; SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, CO<sub>2</sub> and H<sub>2</sub>O are final mineralized products produced in the direct photocatalytic process.

Elimination of dyes and other commercial colorants from continual wastewater effluents of textile and paper mills and other colorant manufactures is now the subject of considerable concern of environmental remediation. Because most of the dyes are resistant to biodegradation, they are not easily removed in biological wastewater treatment plants. In addition, many N-containing dyes undergo natural reductive anaerobic degradation to potentially carcinogenic aromatic amines.<sup>1,2</sup> These chemicals, when discharged to environment, are hazardous for aquatic species, have significant impact on the aquatic environment and human health, and could result in serious consequence to the surrounding ecosystem.<sup>3</sup>

Direct photocatalytic reaction by using semiconductor powders has been shown to effectively degrade many kinds of pollutants including dye pollutants and in many cases even completely mineralize the compounds.<sup>4,5</sup> But it requires ultra-violet light to cause charge separation on the semiconductor particles. The pollutants can be oxidized by the photogenerated holes either directly or indirectly *via* hydroxide radical generation. Sensitized photocatalysis has been successfully applied to degrade dye pollutants.<sup>6–10</sup> With visible light excitation of adsorbed dyes, electron transfer from the excited dye to the conduction band of the semiconductor occurs and subsequent transformation of dye cation radical is possible. These photochemical transformations may enhance the biodegradability of dye pollutants by producing low molecular weight oxygenated species, suggesting that sensitized photocatalysis has a potential to be used as a pretreatment process in combination with biological treatment.

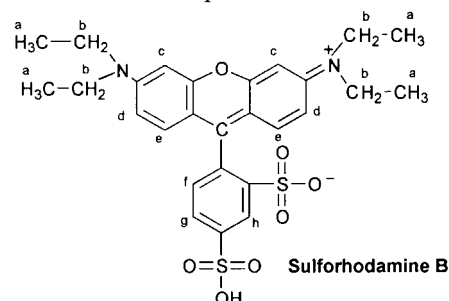
The mechanism of TiO<sub>2</sub> photocatalyzed reactions under UV irradiation has been extensively investigated, however, the photocatalytic degradation mechanisms of dye pollutants with larger and more complicated molecular structure, particularly, the nature of the intermediates and the reaction pathways, have not been clarified yet. The aim of our investigation is to increase our understanding on the pathway of SRB degradation by comparing the experimental results of direct photo-

catalysis with these of sensitized photocatalysis of SRB in TiO<sub>2</sub> aqueous dispersions. Major intermediates and final products were identified and it appears to involve similar primary oxidative steps in the initial photodegradation stage for both types of photoreactions, however further decomposing the degraded fragments to result in the complete mineralization of the dye can only be obtained in the direct photocatalysis. A possible mechanism of photodegradation is proposed on the basis of the experimental results of IR, <sup>1</sup>HNMR and GC-MS. The primary experimental results suggest that the TiO<sub>2</sub>/UV-Vis photocatalytic process has promising applications in the elimination of dye pollutants, especially under sunlight irradiation.

## Experimental

### Materials

P-25 TiO<sub>2</sub> (ca. 80% anatase, 20% rutile; BET area ca. 50 m<sup>2</sup> g<sup>-1</sup>) was kindly supplied by Degussa Co. Horseradish peroxidase (POD) was purchased from Huamei Biologic Engineering Co. (China), whereas the *N,N*-dimethyl-*p*-phenylenediamine (DPD) reagent was obtained from Merck (p.a.). The dye Sulforhodamine-B (SRB) was of laser grade quality (Across Co.); and all other chemicals were of analytical reagent grade quality and were employed without further purification. Deionized and doubly distilled water was used throughout. The pH of the solution was adjusted with either dilute HCl or NaOH (the original pH of the dye solution was ca. 4.2). The structure of SRB molecule is illustrated below; the small letters indicate the protons for NMR identification.



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## Photoreactor and light source

The UV resource is a 100 W Hg lamp ( $\lambda > 330$  nm, Toshiba SHLS-1002 A). To prevent direct excitation of the dye SRB, a cutoff filter was introduced between the irradiation source and the photoreaction vessel to eliminate radiation above 380 nm, thus only  $330 \text{ nm} < \lambda < 380 \text{ nm}$  UV light from the Hg lamp was available to cause band-gap excitation of  $\text{TiO}_2$ . The visible light source was a 500-Watt halogen lamp (Institute of Electric Light Source, Beijing) positioned inside a cylindrical Pyrex vessel and surrounded by a circulating water jacket (Pyrex) to cool the lamp. A cutoff filter was also placed outside the Pyrex jacket to ensure complete removal of radiation below 420 nm and to ensure that irradiation of the SRB/ $\text{TiO}_2$  system occurred only by visible light wavelengths.

## Procedures and analyses

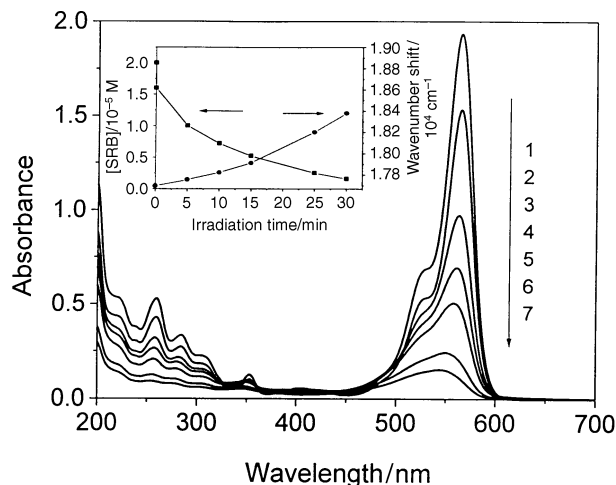
Aqueous suspensions of SRB (usually 50 mL,  $2 \times 10^{-5}$  M) and 100 mg of  $\text{TiO}_2$  particulates were placed in a Pyrex vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for *ca.* 30 min to establish an adsorption-desorption equilibrium between the dye and the  $\text{TiO}_2$  surface. At given intervals of illumination, a sample of the  $\text{TiO}_2$  dispersion was collected, centrifuged and then filtered through a Millipore filter (pore size 0.22  $\mu\text{m}$ ). The filtrates were analyzed by UV-Vis spectroscopy using a Lambda Bio 20 spectrophotometer (P.E. Co.). The chemical oxygen demand (COD) of the suspensions (50 mL of  $5 \times 10^{-5}$  M SRB,  $\text{TiO}_2$  loading 100 mg) was measured directly, without removal of the  $\text{TiO}_2$  particles, after various irradiation time intervals using the potassium dichromate titration method.<sup>11</sup>  $\text{NH}_4^+$  ions were analyzed with an ion chromatograph (Shimadzu LC-10AS) equipped with a CD-5 conductivity detector using a Y-521 cationic column with a  $\text{HNO}_3$  solution (4 mM) as the eluent and  $\text{SO}_4^{2-}$  ions were monitored by ion chromatography with an I-524 anionic column using an eluent of phthalic acid (2 mM). Total organic carbon (TOC) analyzer (Shimadzu TOC-5000) was used to assay the changes in TOC during the course of photodegradation of the dye.

Proton NMR spectra were obtained with a Varian 300 nuclear magnetic resonance spectrometer. Samples were prepared as follows: several dispersions containing 200 mL of the SRB dye ( $1 \times 10^{-4}$  M) and 400 mg of  $\text{TiO}_2$  were irradiated at different time intervals, following which the  $\text{TiO}_2$  particles were removed by centrifugation and filtration as described above. Subsequently, the solvent of the filtrate was removed under reduced pressure (below 323 K). The remaining residue was dissolved in 0.5 mL  $\text{D}_2\text{O}$ . Samples for infrared (IR) spectra (FTS-165 spectrophotometer) were prepared by a method similar to that for proton NMR, except that the residue was used directly. The intermediate and final products generated during the photocatalytic degradation process were analyzed by gas chromatography/mass spectrometric methods (GC/MS, Trio-2000, equipped with a BPX 70 column, size 28 m  $\times$  0.25 mm). The preparation of samples was similar as above but the residue was dissolved in methanol to be applied to the GC-MS analyses.

## Results and discussion

### UV-Vis spectroscopy

The absorption spectra of an aqueous solution of SRB recorded following the UV irradiation ( $330 \text{ nm} < \lambda < 380 \text{ nm}$ ) are shown in Fig. 1. In order to prevent the excitation of the dye by UV light, *i.e.* a charge transfer from excited SRB to  $\text{TiO}_2$ , a well-known sensitization phenomenon in semiconductor photochemistry that functions as another primary step oper-



**Fig. 1** UV-visible spectral changes of SRB ( $2 \times 10^{-5}$  M, 50 mL, pH 4.2) in  $\text{TiO}_2$  (100 mg) dispersions under UV irradiation ( $330 \text{ nm} < \lambda < 380 \text{ nm}$ ). Spectra 2–7 denote the irradiation times 0, 5, 10, 15, 25 and 30 min, respectively. Spectrum 1 is the UV-visible spectrum of SRB before addition of  $\text{TiO}_2$  to the solution. Inset: SRB concentration changes and wavenumber shifts of the absorption maximum as a function of irradiation time under the same conditions.

ating in the photodegradation of the dye, the wavelength of UV irradiation is limited at  $330 \text{ nm} < \lambda < 380 \text{ nm}$ . Although a very small absorption band of the dye appeared at 353 nm, the excitation of the dye is negligible compared with the excitation of  $\text{TiO}_2$  under the present conditions. The extent of adsorption of the dye ( $2 \times 10^{-5}$  M) on  $\text{TiO}_2$  (100 mg) particles was *ca.* 20% (see spectrum 2 in Fig. 1). The absorption peaks corresponding to the dye disappeared under UV light irradiation, indicating degradation of the dye. More interestingly, the characteristic absorption band of SRB at *ca.* 565 nm decreased rapidly, accompanied by a slight hypsochromic shift, indicating the occurrence of some *N*-de-ethylation during the photocatalytic oxidation of SRB, and similar observations have already been confirmed in the Rhodamine-B/CdS system.<sup>12</sup>

An aqueous dispersion (50 mL,  $2 \times 10^{-5}$  M) of the dye containing  $\text{TiO}_2$  (100 mg) was degraded (92.0%) within 30 min of irradiation, giving a pseudo-first-order rate constant  $k$  of  $7.43 \times 10^{-2} \text{ min}^{-1}$  (inset of Fig. 1). The blue shift of the SRB maximal absorption (expressed in wavenumber, *i.e.* reciprocal of the wavelength of the maximal absorption peak in inset of Fig. 1) indicates that the dye SRB is de-ethylated one by one. Two competitive processes, namely *N*-de-ethylation and cleavage of the SRB chromophore ring structure, occur concurrently during photocatalytic oxidation with the latter process predominating. Blank experiments indicated that the disappearance of SRB was negligible without UV irradiation or in the absence of  $\text{TiO}_2$ .

Comparing with our previous study of the sensitized photocatalysis,<sup>13</sup>  $2 \times 10^{-5}$  M SRB solution (50 mL, pH 4.2) can also be degraded with first-order kinetics ( $k = 8.8 \times 10^{-2} \text{ min}^{-1}$ ) in the presence of  $\text{TiO}_2$  (100 mg) under the visible light ( $\lambda > 420 \text{ nm}$ ) irradiation. Under otherwise identical conditions, we obtained that the photoefficiency ( $\xi = 0.012$ ) for the degradation induced by UV irradiation was *ca.* 5 times greater than that ( $\xi = 0.002$ ) by visible irradiation as we noted below. The absorption band of the dye disappeared irreversibly, indicating that at least the chromophoric structure of the dye was destroyed under visible irradiation. Control experiments established that SRB did not degrade in  $\text{TiO}_2$  suspensions in the dark or when illuminated with visible light in the absence of  $\text{TiO}_2$ . Under visible light irradiation, it is intriguing that a slight hypsochromic shift of the maximal absorption band was also observed in the degradation process, indicating the

occurrence of *N*-de-ethylation during the photosensitized oxidation of SRB as occurred under UV irradiation.

### Photoefficiencies

In this work, photoefficiencies  $\xi$  of the photodegradation of the dye SRB under both visible and UV irradiation were determined at 560 nm (using a Japan Optical Co. Interference filter to cutoff wavelengths below 550 nm and above 570 nm) and at 365 nm (using a similar filter to cutoff wavelengths below 355 nm and above 375 nm), respectively. The photon flux of the 500 W halogen lamp at 560 nm was  $3.4 \times 10^{-8}$  einstein  $s^{-1}$  determined by Reineckate actinometry ( $\xi = 0.27^{14}$ ) and the photon flux of the 100 W Hg lamp at 365 nm was  $5.4 \times 10^{-9}$  einstein  $s^{-1}$  also assessed by Reineckate actinometry ( $\xi = 0.29^{14}$ ). For the degradation of SRB under visible or UV irradiation, photoefficiencies were measured by observation of the amount of SRB degraded per photon (within 20 min of irradiation) using a 50 mL dispersion containing  $2 \times 10^{-5}$  M SRB and 100 mg of  $TiO_2$  under the same conditions as those employed for the photon flow measurements. The photoefficiency for SRB degradation *via* direct photocatalysis was 0.012, which falls within the reported quantum yields for the direct photocatalytic degradation of organic compounds ranging from 0.005 to 0.06.<sup>15</sup> The photoefficiency for the sensitized photocatalysis of SRB was 0.002, significantly lower than that for direct photocatalysis. Although the photoefficiencies for the SRB sensitized photocatalytic degradation are smaller than those for the direct photocatalytic degradation, the sensitized photocatalytic degradation of dye pollutant SRB may play the main role in the overall degradation by sunlight because the quantity of photons available for sensitized photocatalysis with sunlight is much higher than that for direct photocatalysis (<5% of total photons).

### Production of inorganic nitrogen, sulfur species ( $NH_4^+$ , $SO_4^{2-}$ ) and mineralization ( $CO_2$ )

The destruction of SRB conjugated chromophore ring structure, decreasing of total organic carbon (TOC), and formation of ammonium and sulfate ions in the direct photocatalytic degradation of a 50 mL of SRB solution ( $2 \times 10^{-4}$  M, pH 4.2) in the presence of  $TiO_2$  (100 mg) are illustrated in Fig. 2. The complete degradation of the dye required 10 h of irradiation with pseudo-zero-order rate constant  $k = 2.22 \times 10^{-7}$  M  $min^{-1}$ . The decreasing rate of TOC exhibited two different behaviors before and after 7 h of irradiation, respectively, indicating that the mineralization of the dye goes through two different stages: the ring cleavage in the initial photocatalytic degradation stage and subsequent oxidation of the fragments in the latter stage (see discussion below). The rate of TOC

reduction was slower than that of the degradation of the dye, 43.1% of TOC still remained in the dispersion at 10 h of irradiation after the dye solution was totally discolored. After 16 h of irradiation, the mineralization yield reached a value of 97.5%.  $NH_4^+$  ions began to form after a 6 h induction period at a rate slower than that of formation of  $SO_4^{2-}$ . This time-lag may be attributed to the repulsive interactions between the positively charged nitrogen moiety in the SRB structure and the positive surface of the illuminated  $TiO_2$  particulates under the conditions used (pH = 4.2;  $pI_{TiO_2} = 6.8$ ).<sup>16</sup> However, another more important reason that formation of  $NH_4^+$  was not observed before 6 h of irradiation is most probably because the cleavage of the conjugated chromophore ring structure is predominant in the initial stage as we noted above. Subsequently, ammonium ions arose from further oxidation of the nitrogen-containing fragments and increased with irradiation time to reach 72.0% ( $2.88 \times 10^{-4}$  M) of the theoretical quantity ( $4.00 \times 10^{-4}$  M) after 16 h of irradiation, while nitrate ion formation from the photooxidative step was negligible. It can be explained by the chemical structure of the substrate, which influences the production and relative quantities of  $NH_4^+$  and/or  $NO_3^-$  ions during the photocatalyzed oxidation of nitrogen-containing substances at the  $TiO_2$ -H<sub>2</sub>O interface.<sup>17-19</sup> In the formation of sulfate ions, electrostatic adsorption of the substrate *via* its most electronegative atom to the  $TiO_2$  surface is one of the important factors that influence the photooxidation pathway. AM1 (Austin model 1) molecular orbital calculations carried out semi-empirically using the MOPAC system<sup>20</sup> indicated that the O atoms of the sulfonate groups in the dye molecule bear the largest negative charge and therefore interact with the positively charged  $TiO_2$  surface. Thus, the sulfur atom or the  $\alpha$ -carbon adjacent to the sulfur atom are readily attacked by the electrophilic  $\cdot OH$  radicals formed on the  $TiO_2$  surface to produce  $SO_4^{2-}$  concomitant with the destruction of the chromophore ring structure. As depicted in Fig. 2, the amount of sulfate ions increased with irradiation time during the photocatalytic degradation process, and reached 72.6% ( $2.90 \times 10^{-4}$  M) of the theoretical value.

According to the previous results of photosensitization,<sup>13</sup> the degradation of the dye ( $2 \times 10^{-4}$  M, 50 mL) suspensions containing  $TiO_2$  (100 mg) under visible irradiation follows first-order kinetics with rate constant  $k = 1.73 \times 10^{-3}$   $min^{-1}$ . The TOC of the solution changed from the initial value of 52.4 ppm before irradiation to 24.0 ppm after 38 h of irradiation, indicating that only partial mineralization (54.2%) of the SRB occurred in aqueous  $TiO_2$  dispersion under visible irradiation, no more mineralization was observed with further irradiation after the dispersion was discolored completely. Meanwhile, the concentration of  $SO_4^{2-}$  ions formed increased with the irradiation time, reaching a constant value of 5.2 ppm after 38 h of irradiation, only 13.5% of the theoretically expected value (38.4 ppm). Formation of ammonium and nitrate ions could not be observed in the system, indicating no further mineralization of the nitrogen-containing fragments. All the above data indicate that the degraded fragments, especially the nitrogen-containing fragments, did not undergo further mineralization after the chromophore ring structure of the dye molecule was destroyed, which is different from that of direct photocatalysis.

### COD and $H_2O_2$ measurements

Fig. 3 shows the temporal changes of chemical oxygen demand (COD) in the direct photocatalytic degradation of the dye SRB, which reflect the mineralization extent of the organics in the total dispersions (both in the bulk and on the  $TiO_2$  surface). Under UV irradiation, the decrease in COD values of  $5 \times 10^{-5}$  M of SRB dispersions (50 mL, pH 4.2) containing  $TiO_2$  (100 mg) also shows two different stages similar to the

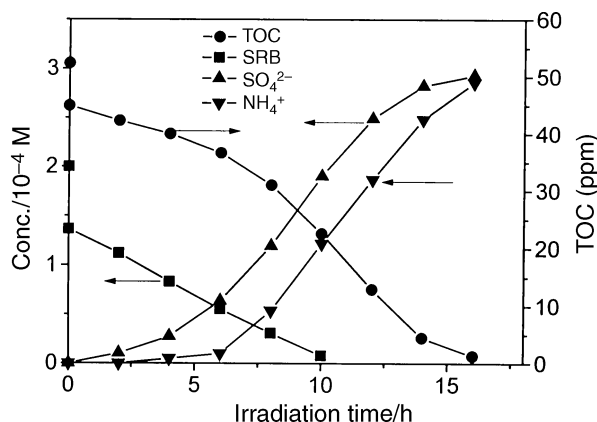
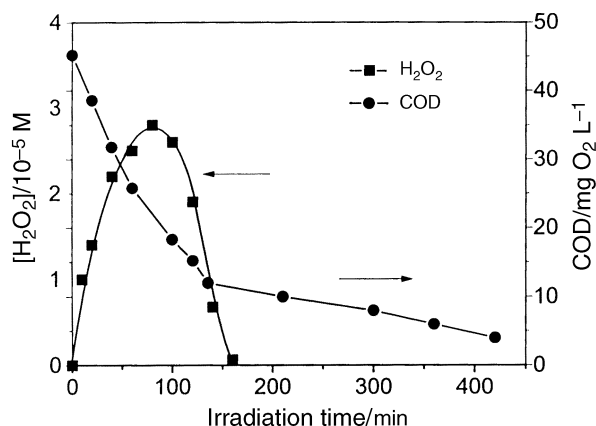


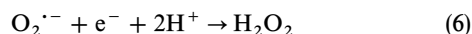
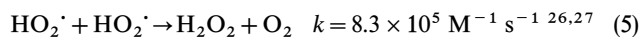
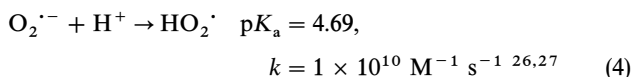
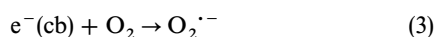
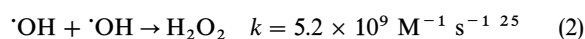
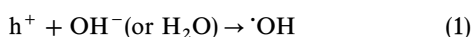
Fig. 2 The changes in SRB concentration and TOC, and the formation of  $SO_4^{2-}$  and  $NH_4^+$  during the course of direct photocatalytic degradation of SRB ( $2 \times 10^{-4}$  M, 50 mL) in the presence of  $TiO_2$  (100 mg) at pH 4.2.



**Fig. 3** Variation in COD and formation of H<sub>2</sub>O<sub>2</sub> during the course of direct photocatalytic degradation of SRB ( $5 \times 10^{-5}$  M, 50 mL, TiO<sub>2</sub>: 100 mg) at pH 4.2.

variation tendency of TOC, before and after 135 min of irradiation. 91.2% of total COD ( $45.2 \text{ mg O}_2 \text{ L}^{-1}$ ) was reduced after 420 min of UV irradiation; while under visible irradiation,<sup>13</sup> only 74.3% of the total COD was decreased after 780 min of irradiation and no change was observed with further irradiation after the dispersion was totally discolored. Of more importance is that the COD value ( $12 \text{ mg O}_2 \text{ L}^{-1}$ ) of the dispersion at 135 min of UV irradiation is almost the same as that ( $11.6 \text{ mg O}_2 \text{ L}^{-1}$ ) of the discolored dispersion under visible irradiation, indicating that the dye SRB mainly underwent the destruction of the chromophore structure before 135 min of UV irradiation (similar as occurred in the photosensitized degradation process) and subsequent mineralization of the fragments occurred after 135 min of UV irradiation as noted above.

Formation of H<sub>2</sub>O<sub>2</sub> as one of main intermediates in the direct photocatalysis was detected by the spectrophotometric DPD and catalase enzyme methods.<sup>21–24</sup> As shown in Fig. 3, the quantities of H<sub>2</sub>O<sub>2</sub> formation (a maximum value of  $2.8 \times 10^{-5} \text{ M}$ ) at pH 4.2 increased with the irradiation time with second-order rate constant  $k_p = 1.76 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$  in the initial stage (before 40 min of irradiation), indicating that the formation of H<sub>2</sub>O<sub>2</sub> is a radical-radical reaction under the present conditions. H<sub>2</sub>O<sub>2</sub> can be formed as following reactions (1)–(6) in the direct photocatalysis:



In the photosensitization H<sub>2</sub>O<sub>2</sub> can only be formed *via* reactions (3)–(6), where the conduction band electrons come from the excited dye rather than band-gap excitation of TiO<sub>2</sub>. Because little amounts of H<sub>2</sub>O<sub>2</sub> can be observed at pH 4.2 in the photosensitized degradation of the dye,<sup>13</sup> the amount of H<sub>2</sub>O<sub>2</sub> formed in the direct photocatalysis mainly comes from reactions (1)–(2) under the similar conditions, which is consistent with the notion that formation of H<sub>2</sub>O<sub>2</sub> is a radical-radical reaction under the present conditions. And moreover, H<sub>2</sub>O<sub>2</sub> was mainly produced before 135 min of UV irradiation during the process of destruction of the dye chromophore structure as depicted in Fig. 3, indicating that the hydroxyl radicals ( $\cdot\text{OH}$ ) are used mainly to produce H<sub>2</sub>O<sub>2</sub>. It is mainly the positive holes ( $h^+$ ), but not  $\cdot\text{OH}$  that participate in the

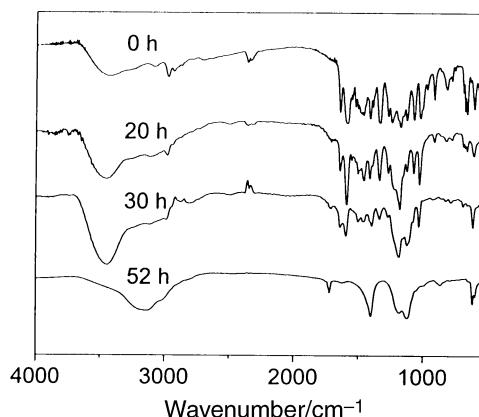
initial oxidation of the dye, resulting in the destruction of the dye chromophore structure, as will be further demonstrated in the following.

### IR and <sup>1</sup>HNMR measurements

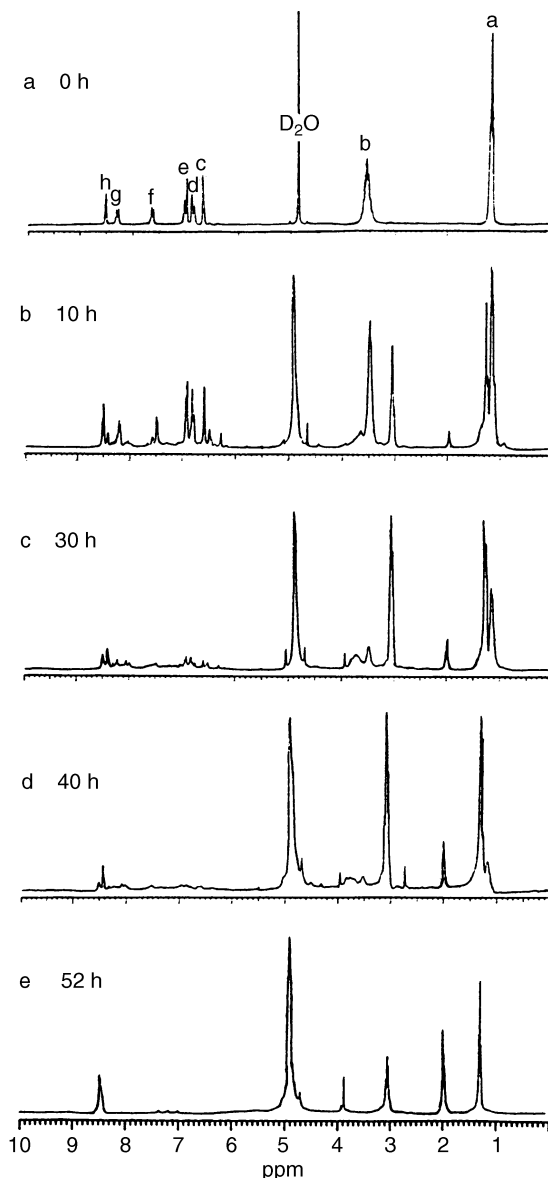
In order to probe the nature of surface photochemical events of the dye SRB adsorbed on the TiO<sub>2</sub> particles and to identify the intermediates and final products arising from direct photocatalytic degradation of the dye, a series of IR and <sup>1</sup>HNMR spectra were carried out at various irradiation times. The temporal variation of the IR spectra during the course of the photocatalytic degradation of SRB by UV irradiation is illustrated in Fig. 4.

The assignments for the principal bands in the IR spectra of SRB (before irradiation):<sup>28</sup> 1590, 1558, 1530, 1510, 1490 and 1470 cm<sup>-1</sup> correspond to aromatic ring vibrations; 1344 cm<sup>-1</sup> is due to C–aryl bond vibrations; 1120–1145 cm<sup>-1</sup> and 668–625 cm<sup>-1</sup> are caused by vibrations in the –SO<sub>3</sub><sup>-</sup> group; the band at 1649 cm<sup>-1</sup> is attributed to vibrations of the carbon–nitrogen bond; and the heterocycle vibrations are the origins of the absorption band at 1530–1558 cm<sup>-1</sup>. During the direct photocatalytic process, bands of vibrations characteristic of the carbon–nitrogen bond, the C–aryl bond, and nearly all of the aromatic skeletal and heterocycle vibrations decreased with irradiation time and disappeared after about 52 h of irradiation. Meanwhile, some new IR absorption bands appeared at 1720 cm<sup>-1</sup> (attributable to >C=O groups), 1400 cm<sup>-1</sup> (attribute to vibrations of –CH<sub>3</sub> or –CH<sub>2</sub>– of diethylamine), and 857 cm<sup>-1</sup>. The IR spectra of SRB in the photosensitization<sup>13</sup> also show the similar variation tendency except that the final products are more complicated than those in the direct photocatalysis; almost all the new absorption bands that appeared in the direct photocatalysis were found in the photosensitized process. The IR results indicate that the large conjugated chromophore structure of SRB is destroyed under both UV and visible light irradiation in aqueous TiO<sub>2</sub> dispersions, and the dye molecule undergoes irreversible chemical changes and degrades to smaller organic species containing >C=O groups. In the photosensitization, the degraded products remained unchanged with further irradiation after the dispersion was totally discolored. In the direct photocatalysis, the degraded small species (diethylamine, *N*-ethylformamide, *N,N*-diethylacetamide, *N,N*-diethylformamide, CH<sub>3</sub>COOH and HCOOH, as confirmed below by the <sup>1</sup>HNMR and GC-MS) can be further decomposed to inorganic species (CO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, H<sub>2</sub>O, *etc.*).

To further identify the species produced in the photooxidation of SRB and compare the photodegradation pathways under the two different photocatalytic mechanisms, the temporal proton NMR profiles of the dye, intermediates and final products were monitored. Spectrum *a* in Fig. 5 shows the



**Fig. 4** Temporal changes of the IR spectra in the direct photocatalytic degradation of SRB.



**Fig. 5** Temporal variation of the  $^1\text{H}$ NMR spectra during the course of direct photocatalytic degradation of SRB.

typical proton NMR signals of pure SRB and their assignments to the various protons in the structure of SRB (see above). The NMR signals of the aromatic hydrogens  $\text{H}_c$ ,  $\text{H}_d$ ,  $\text{H}_e$ ,  $\text{H}_f$ ,  $\text{H}_g$  and  $\text{H}_h$  were located at  $\delta$  6.66, 6.83–6.86, 6.96–6.99, 7.62–7.65, 8.25–8.28 and 8.52 ppm, respectively; those of  $\text{H}_a$  and  $\text{H}_b$  of the *N*-diethyl group appeared at  $\delta$  1.18–1.23 and 3.40–3.60 ppm, respectively. During the course of the direct photocatalytic oxidation of SRB (spectra *a* to *e* in Fig. 5), a series of new signals appeared at  $\delta$  1.23–1.40 ppm (hydrogens from  $\text{CH}_3$  and analogous groups), 1.98, 3.00–3.20, and 8.46, whereas the characteristic signals of SRB at  $\delta$  1.18–1.23 ( $\text{CH}_3$ ), 3.40–3.60 ( $\text{CH}_2$ ), and 6.60–8.60 (aromatic protons) disappeared. The new signal at  $\delta$  8.46 is attributed to the CH proton of formic acid and the signal of  $\delta$  1.98 to the methyl protons of  $\text{CH}_3\text{COOH}$  by comparison with  $^1\text{H}$ NMR signals of the standards, both of them increased with increasing illumination time. The intensities of the two new signals at  $\delta$  1.23–1.40 and 3.00–3.20 increased with the irradiation time whereas the methyl ( $\text{CH}_3$ ) protons at  $\delta$  1.18–1.23 ppm and the methylene ( $\text{CH}_2$ ) protons at  $\delta$  3.40–3.60 ppm of SRB decreased in intensity with irradiation time. More interesting is the ratio of the integrated area of the first two peaks which remained constant at 3 : 2 during the photooxidation, the same as the ratio of the latter two signals. This observation

demonstrates that the ethyl group ( $\text{CH}_2\text{CH}_3$ ) of SRB is not destroyed in the initial direct photocatalytic oxidation process, but remains in the diethylamine photooxidation products (also see the results of GC-MS below).

On the basis of the signal intensities from proton NMR spectra (spectrum *d* of Fig. 5), we establish that diethylamine is a major photooxidation product in the direct photocatalytic degradation of the dye. Additional evidence of the formation of diethylamine,  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  can be obtained in the following experiments. It is expected that distillation of an irradiated aqueous SRB/ $\text{TiO}_2$  sample under alkaline conditions (pH 10.5) would lead to removal of diethylamine while distillation under acidic conditions (pH 2.5) would lead to removal of  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$ . It was indeed the case evidenced by loss of the corresponding proton NMR signals at  $\delta$  1.23–1.40 and 3.00–3.20 [ $\text{HN}(\text{CH}_2\text{CH}_3)_2$ ] or  $\delta$  1.98 ( $\text{CH}_3\text{COOH}$ ) and  $\delta$  8.46 ( $\text{HCOOH}$ ) in the  $^1\text{H}$ NMR spectra under alkaline or acidic conditions, respectively.

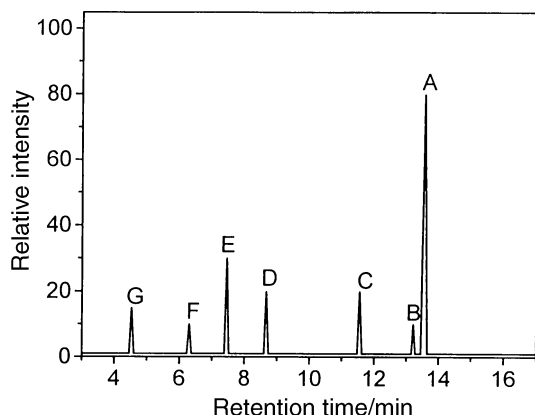
Surprisingly, the temporal proton NMR spectroscopy profiles of the dye, intermediates and final products in the photosensitized degradation<sup>13</sup> were exactly similar to that observed in the direct photocatalytic degradation, which indicates that the dye SRB probably underwent the same photodegradation pathway at least in the initial stages for the two different degradation mechanisms. The exclusive difference is that the degraded species (such as diethylamine) can be further decomposed to inorganic species ( $\text{CO}_2$ ,  $\text{NH}_4^+$ ,  $\text{H}_2\text{O}$ ) (as in Fig. 5 spectra *e*) under UV irradiation while under visible irradiation, no degradation can be observed after the dispersion was totally discolored.

The above NMR findings together with the results of IR support the notion that the same degradation pathway occurs, that is the breakup of the chromophoric structure of SRB and dominates during the initial irradiation stage in both the direct and sensitized degradation of the dye (formation of a large quantity of diethylamine) with only a small extent of de-ethylation taking place, as depicted in Fig. 1. The degraded fragments can be further decomposed to mineralized products in the direct photocatalysis while they remain unchanged in the photosensitization.

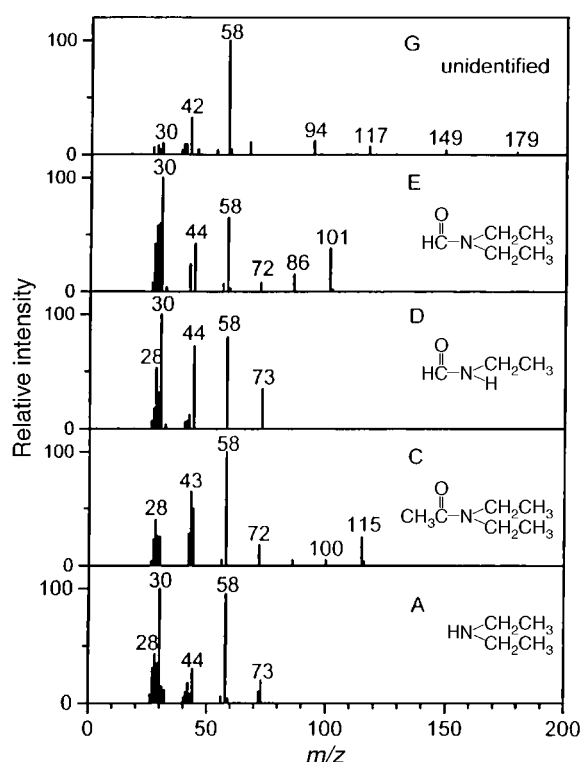
#### Identification of intermediates by GC-MS measurements

GC-MS was used to analyze the degraded intermediates and final products formed in the direct photocatalytic degradation of the dye SRB. Fig. 6 shows the gas chromatogram of the degraded SRB dispersion obtained after 30 h of UV irradiation. Seven peaks, marked with A–G, appeared in the chromatogram. Mass spectra of main peaks (A, C, D, E, G) are shown in Fig. 7. The compounds corresponding to the GC spectral peaks were determined to be as follows: (A) diethylamine ( $t_r = 13.6$  min), (C) *N,N*-diethylacetamide ( $t_r = 11.6$  min), (D) *N*-ethylformamide ( $t_r = 8.7$  min), (E) *N,N*-diethylformamide ( $t_r = 7.5$  min). The mass spectra revealed that the main peak (A) had a fragmentation pattern consistent with diethylamine, gave  $m/z$  73 [ $\text{M}]^+$  (the molecular ion peak), 58 [ $\text{M}-\text{CH}_3$ ] $^+$ , 44 [ $\text{M}-\text{CH}_2\text{CH}_3$ ] $^+$ , 30 [ $\text{M}-\text{NCH}_2\text{CH}_3$ ] $^+$  (the base peak). The chromatogram peaks C and E contained an ion peak at  $m/z$  72, which is assignable to a fragment of dehydrogenated diethylamine ion. The peak D (*N*-ethylformamide) has the same molecular mass and similar fragmentation pattern as peak A (diethylamine), they were separated from each other according to the different retention times in the column and were identified by comparison with retention times of standards. A species having the largest molecular mass of 179 of all the compounds observed in the GC was detected as chromatogram peak G, precise identification has not yet been done.

In addition to the intermediates shown in Fig. 7, two lower intensity intermediates having the molecular mass of 96 and 164 were also detected (peaks F and B appeared in Fig. 6).



**Fig. 6** GC chromatogram obtained by GC-MS analysis from the direct photocatalytic degradation of SRB after 30 h of irradiation.



**Fig. 7** Mass spectra of the species observed in the GC chromatogram shown in Fig. 6.

The latter species gave a mass spectrum showing a base peak at  $m/z$  133, some ion peaks at  $m/z$  39, 51, 77, indicating that the intermediate contains a benzene ring, which was produced in the initial stages as a result of destruction of the conjugated chromophoric structure of the dye. Their precise assignments were not made in this study. Some other kinds of intermediates having smaller molecular weights (such as formic acid and acetic acid confirmed in the  $^1\text{H}$ NMR section) should have been produced during the course of the mineralization of SRB to  $\text{CO}_2$ , but they are difficult to detect by GC-MS if intermediates having a high boiling point such as carboxylate salts were produced in the suspension, they were not easy to gasify in the GC-MS measurement; or if intermediates with too low boiling point were produced, they would be removed from the sample before it was used for GC-MS analysis because rotary evaporation had to be used to concentrate the samples.

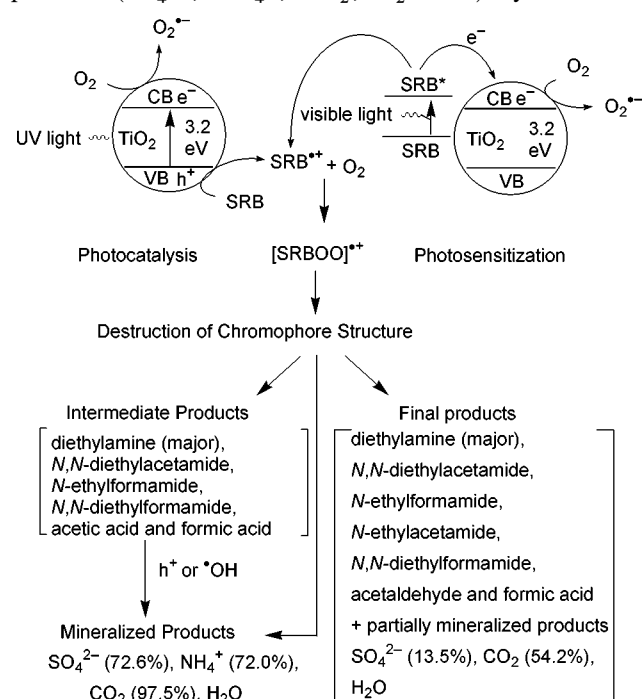
In the photosensitized degradation of the dye SRB, similar degraded products such as diethylamine, *N*-ethylacetamide, *N*-ethylformamide, *N,N*-diethylacetamide, *N,N*-diethyl-

formamide,  $\text{HCOOH}$  and  $\text{CH}_3\text{CHO}$  were also confirmed by the  $^1\text{H}$ NMR and GC/MS results as the end products.<sup>13</sup>

### Photocatalytic degradation pathways

In the direct photocatalysis, both positive holes and hydroxyl radicals have been proposed as the oxidizing species responsible for initiating the degradation of organic substrates. Some researchers proposed that when photocatalytic oxidation is conducted in the presence of water, indirect hole transfer, which involves water molecules and surfacial hydroxyl radicals, is a more efficient hole-scavenging pathway.<sup>29,30</sup> While others argued that substrates with the proper oxidation potentials can undergo direct oxidation, generating radical species,<sup>31,32</sup> in fact, a number of species, especially among organic compounds strongly adsorbed on the  $\text{TiO}_2$  surface, and appear able to compete efficiently for positive holes with OH groups adsorbed at the  $\text{TiO}_2$  surface.<sup>33</sup> In this system, we have confirmed that the degradation pathway of the dye SRB in the initial stages of the direct photocatalysis is exactly the same as that in the photosensitization on the basis of UV-Vis spectra, IR,  $^1\text{H}$ NMR and GC-MS experimental results. It is well known that in photosensitization the dye is excited by visible light and the excited dye injects an electron to the conduction band of  $\text{TiO}_2$  to form a cation radical, subsequent transformation of the cation radical results in the degradation of the dye.

In Scheme 1, we show a proposed mechanism with the reaction paths for positive holes in the direct photocatalysis, the  $\text{TiO}_2$  particles absorb UV photons to produce electron-hole pairs, which may be competitively trapped by adsorbed  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{O}_2$  and dye molecules. The dye SRB adsorbed on  $\text{TiO}_2$  is mainly oxidized by a photogenerated hole localized at the surface of the irradiated semiconductor  $\text{TiO}_2$ , generating an adsorbed cation radical, but not attacked by hydroxyl radicals to produce hydroxylated intermediates. The dye cation radicals formed combine with molecular oxygen adsorbed and result in the destruction of the dye chromophore structure to form small species (such as diethylamine, *N,N*-diethylacetamide, *N*-ethylformamide, *N,N*-diethylformamide, formic acid and acetic acid), these degraded fragments can be further decomposed to give mineralized products ( $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  etc.) by the direct



**Scheme 1** Proposed photodegradation pathways of the dye SRB in the direct photocatalysis and in the photosensitization processes.

oxidation of positive holes or the attack of hydroxyl radicals. On the contrary, in the photosensitization, the transformation of dye cation radicals produces the final degraded products (e.g. diethylamine, *N*-ethylacetamide, *N*-ethylformamide, *N,N*-diethylacetamide, *N,N*-diethylformamide, HCOOH and CH<sub>3</sub>CHO), which would not be further mineralized under visible light irradiation, the mechanism of their degradation is probably related to the active oxygen radicals produced in the photosensitization process, while independent of the mediation of the positive holes as occurs in the direct photocatalysis.

## Conclusions

The dye SRB can be effectively degraded by both the direct and sensitized photocatalysis. Similar intermediates (such as diethylamine, *N,N*-diethylacetamide, *N*-ethylformamide, *N,N*-diethylformamide, formic acid) and final products (SO<sub>4</sub><sup>2-</sup>, CO<sub>2</sub>) were identified by UV-Vis spectra, TOC, COD, IR, <sup>1</sup>HNMR and GC-MS techniques in the two different degradation processes, but their distribution is dependent on the photocatalytic mechanism. Direct and sensitized photocatalyses appear to involve similar photodegradation pathways in the initial stages, leading to a rapid destruction of SRB chromophore structure to form smaller organic species except that direct photocatalysis is capable of achieving complete mineralization with further irradiation. Ammonium is the exclusive primary inorganic nitrogen species produced in the direct photocatalysis, which is not found in the sensitization. The application of direct and sensitized photocatalysis has the potential for the treatment of dye pollutants because it can fully utilize solar radiation.

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## References

- 1 D. Brown and P. Laboureur, *Chemosphere*, 1983, **12**, 397.
- 2 J. McCann and B. N. Ames, *Proc. Natl. Acad. Sci. USA*, 1975, **73**, 950.
- 3 W. C. Tincher, *Text. Chem. Color.*, 1989, **21**, 33.
- 4 D. F. Ollis, E. Pelizzetti and N. Serpone, *Environ. Sci. Technol.*, 1991, **25**, 1522.
- 5 R. W. Matthews, *J. Catal.*, 1988, **111**, 264.
- 6 (a) K. Vinodgopal, D. Wynkoop and P. V. Kamat, *Environ. Sci. Technol.*, 1996, **30**, 1660; (b) C. Nasr, K. Vinodgopal, L. Fisher, S. Hotchandani, A. K. Chattopadhyaya and P. V. Kamat, *J. Phys. Chem.*, 1996, **100**, 8436.
- 7 H. Ross, J. Bendig and S. Hecht, *Sol. Energy Mater. Sol. Cells*, 1994, **33**, 475.
- 8 (a) F. Zhang, J. Zhao, L. Zang, T. Shen, H. Hidaka, E. Pelizzetti and N. Serpone, *J. Mol. Catal. A: Chem.*, 1997, **120**, 173; (b) F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti and N. Serpone, *Applied Catal. B: Environ.*, 1998, **15**, 147; (c) J. Zhao, K. Wu, T. Wu, H. Hidaka and N. Serpone, *J. Chem. Soc. Faraday Trans.*, 1998, **94**, 673.
- 9 (a) T. Wu, G. Liu, J. Zhao, H. Hidaka and N. Serpone, *J. Phys. Chem. B*, 1998, **102**, 5845; (b) J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, 1998, **32**, 2394.
- 10 (a) T. Wu, T. Lin, J. Zhao, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, 1999, **33**, 1379; (b) G. Liu, T. Wu, J. Zhao, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, 1999, **33**, 2081.
- 11 Chinese National Standard: GB 11914-89, 1989.
- 12 T. Watanabe, T. Takizawa and K. Honda, *J. Phys. Chem.*, 1977, **81**, 1845.
- 13 G. Liu, X. Li, J. Zhao, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, submitted. "In this paper, the photooxidation of sulforhodamine B has been examined under visible light illumination, two different oxidation pathways are described to account for differences in the final photooxidation products whose nature depends on the different modes of adsorption of the dye sulforhodamine B on the metal-oxide mediator (TiO<sub>2</sub>)."
- 14 E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, 1966, **88**, 394.
- 15 U. Stafford, K. A. Gray and P. V. Kamat, *J. Phys. Chem.*, 1994, **98**, 6343.
- 16 J. Zhao, H. Hidaka, A. Takamura, E. Pelizzetti and N. Serpone, *Langmuir*, 1993, **9**, 1646.
- 17 K. Nohara, H. Hidaka, E. Pelizzetti and N. Serpone, *Catal. Lett.*, 1996, **36**, 115.
- 18 K. Nohara, H. Hidaka, E. Pelizzetti and N. Serpone, *J. Photochem. Photobiol. A*, 1997, **102**, 265.
- 19 H. Hidaka, K. Nohara, J. Zhao, K. Takashima, E. Pelizzetti and N. Serpone, *New J. Chem.*, 1994, **18**, 541.
- 20 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
- 21 H. Bader, V. Sturzenegger and J. Hoigne, *Water Res.*, 1988, **22**, 1109.
- 22 Y. Zuo and J. Hoigne, *Science*, 1993, **260**, 71.
- 23 E. R. Carraway, A. J. Hoffmann and R. Hoffmann, *Environ. Sci. Technol.*, 1994, **28**, 786.
- 24 T. Wu, G. Liu, J. Zhao, H. Hidaka and N. Serpone, *J. Phys. Chem. B*, 1999, **103**, 4862.
- 25 K. Sehested, O. L. Rasmussen and H. Fricke, *J. Phys. Chem.*, 1968, **72**, 626.
- 26 B. H. J. Bielski, D. E. Cabelli, R. L. Arudi and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1985, **14**, 1041.
- 27 D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, 1981, **14**, 393.
- 28 P. N. O. Mchedlov, S. A. Shapovalov, S. I. Egorova, V. N. Kleshchevnikova and E. A. Cordova, *Dyes Pigm.*, 1995, **28**, 7.
- 29 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
- 30 W. Choi and M. R. Hoffmann, *J. Phys. Chem.*, 1996, **100**, 2161.
- 31 (a) P. V. Kamat, *Chem. Rev.*, 1993, **93**, 267; (b) M. A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, **93**, 341.
- 32 M. A. Fox, R. B. Draper, K. E. O'Shea, in *Photochemical Conversion and Storage of Solar Energy*, eds. E. Pelizzetti, and M. Schiavello, Kluwer, Dordrecht, 1991, p. 323.
- 33 A. Wahl, M. Ulmann, A. Carroy, B. Jermann, M. Dolata, P. Kedzierzawski, C. Chatelain, A. Monnier and J. Augustynski, *J. Electroanal. Chem.*, 1995, **396**, 41.