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# Selective and efficient catalytic and photocatalytic oxidation of diphenyl sulphide to sulfoxide and sulfone: the role of hydrogen peroxide and TiO<sub>2</sub> polymorph†

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In this paper, we describe the role of anatase and rutile crystal phases on diphenyl sulphide (Ph<sub>2</sub>S) catalytic and photocatalytic oxidation. The highly selective and efficient synthesis of diphenyl sulfoxide (Ph<sub>2</sub>SO) and diphenyl sulfone (Ph<sub>2</sub>SO<sub>2</sub>) at titanium dioxide was demonstrated. Ph<sub>2</sub>S oxidation in the presence of hydrogen peroxide at anatase-TiO<sub>2</sub> can take place both as a catalytic and photocatalytic reaction, while at rutile-TiO<sub>2</sub> only photocatalytic oxidation is possible. The reaction at anatase leads mainly to Ph<sub>2</sub>SO<sub>2</sub>, whereas, in the presence of rutile a complete conversion to Ph<sub>2</sub>SO is achieved after only 15 min (nearly 100% selectivity). Studies on the mechanistic details revealed a dual role of H<sub>2</sub>O<sub>2</sub>. It acts as a substrate in the reaction catalysed only by anatase, but it also plays a key role in alternative photocatalytic oxidation pathways. The presented study shows the applicability of photocatalysis in efficient and selective sulfoxide and sulfone production.

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## Introduction

Conventional routes of synthesis of many important organic chemicals often require harsh operating conditions, such as high temperature and pressure. Moreover, sometimes the presence of toxic oxidation or reduction agents is required, far from the principles of green chemistry. The development of synthesis, which offers efficient organic compound production under mild reaction conditions, is highly desirable. Consequently, a photocatalytic organic synthesis, which utilizes economically sustainable and clean solar energy, has achieved tremendous attention in recent years.<sup>1</sup> However, photocatalysis has been mostly considered as a non-selective process, involving activation of small molecules to initiate a chemical reaction (especially in water). These types of photocatalytic reactions include mainly processes governed by reactive oxygen species such as oxidation of alcohols,<sup>2</sup> oxidation of aromatics<sup>3,4</sup> or oxidation of side chains.<sup>5,6</sup> Nevertheless, a carefully selected photocatalyst and synthesis conditions in a non-aqueous solvent can lead to highly selective photocatalytic fine product formation.

Oxidation of organic sulphides (diphenyl sulphide, dimethyl sulphide) is one of the most important processes in organic

chemistry. The organic sulfoxides and sulfones, which are the products of this reaction, were found to be very important substances for pharmacy, medicine, or substrates in drug synthesis. They can be used for the production of antibacterial, antifungal,<sup>7</sup> antihypertensive agents,<sup>8</sup> and vasodilators.<sup>9</sup> Many catalytic systems, containing, *e.g.*, V, Re, Ti, Mo, Te, W, Se, Fe elements, have been studied in a sulphide to sulfoxide oxidation.<sup>10–14</sup> Titanium dioxide is used as a catalyst due to its desired physicochemical properties, high chemical stability, low cost of production, and lack of toxicity. Additionally, TiO<sub>2</sub> doped with vanadium was found to be an active catalyst of Ph<sub>2</sub>S oxidation giving nearly 100% conversion of Ph<sub>2</sub>S with high selectivity to Ph<sub>2</sub>SO<sub>2</sub>.<sup>15</sup> SiO<sub>2</sub>-TiO<sub>2</sub> mesoporous xerogel catalyses oxidation to the final product, diphenyl sulfone, with the selectivity of 85%.<sup>16</sup> Furthermore, it was confirmed that titanosilicate zeolites (*inter alia*, Ti-beta,<sup>17</sup> Ti-MWW,<sup>18</sup> Ti-FER, MTS-1 (ref. 19) and Ti-ITQ-6 (ref. 20)) present a good catalytic activity in this process. NaIO<sub>4</sub>, trichloroisocyanuric acid, sodium perborate, KMnO<sub>4</sub>, can be successfully applied as oxidizing agents.<sup>21</sup> However, hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, seems to be the most suited oxidizer due to its low environmental impact (H<sub>2</sub>O is the only side product), nontoxicity, and high content of active oxygen.<sup>22–24</sup> Aromatic sulphides can also be transformed using photocatalysts such as wide bandgap oxide semiconductors (TiO<sub>2</sub>, ZnO, *etc.*). Although, they undergo deep oxidation in the aqueous media, sulfoxides, and sulfones are the main reaction products in the presence of organic solvents.<sup>25</sup> To the best of our knowledge, the air is the most common source of oxygen in the

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photocatalytic transformation of sulphides described in the literature. In this system, even when selectivity is high, the concentration of the final product is rather low. However, we showed recently that hydrogen peroxide is a crucial oxidation agent in the photocatalytic oxidation of Ph<sub>2</sub>S.<sup>26</sup> No Ph<sub>2</sub>S conversion after 3 hours of the reaction in both catalytic and photocatalytic tests conducted in the absence of H<sub>2</sub>O<sub>2</sub> over bare and doped TiO<sub>2</sub> materials (concentrations of Ph<sub>2</sub>S oxidation products below the detection limit) was observed. Nevertheless, in the presence of hydrogen peroxide, the reaction can occur at P25 (anatase and rutile mixture) both on the catalytic and photocatalytic way, with significantly higher conversion of Ph<sub>2</sub>S under irradiation compared to the dark process. In our previous paper, we studied the influence of TiO<sub>2</sub> modification (doping with vanadium, zinc, or tin) on the Ph<sub>2</sub>S oxidation. We suggested that the crystal phase composition has a higher influence on both catalytic and photocatalytic activity than the surface metal modifications.<sup>26</sup> The goal of this work is to understand the difference between anatase and rutile in catalytic and photocatalytic Ph<sub>2</sub>S oxidation, describe the role of particular reactive oxygen species in these reactions, and learn how to control the reaction selectivity to different products.

## Experimental

### Materials

Titanium dioxide materials containing anatase phase [Hombikat N100 (N100), Sachtleben Chemie; Tronox AK-1 (TRX\_A)], and rutile [Tronox TR (TRX\_R); (CR-EL), Ishihara Sangyo] were studied.

### Crystal structure, morphology and phase composition

The phase compositions of materials were studied by the powder X-ray diffraction (XRD) using a Rigaku MiniFlex 600 X-ray diffractometer (Cu K<sub>α</sub> radiation, 0.3 mm Ni filter) in 2θ range from 10 to 90°, at speed 3° min<sup>-1</sup> and 0.05° step. The crystal size was calculated based on the Scherrer equation. To calculate the crystal size the most intense peaks were used, *i.e.*, (101) and (110) for anatase and rutile, respectively.

Materials morphology was examined by scanning electron microscopy (SEM) Tescan VEGA 3 with an LaB<sub>6</sub> emitter. The measurements were performed on a carbon sheet.

The specific surface area (SSA) of studied materials was determined from nitrogen adsorption-desorption isotherms at 77 K using a Quantachrome Autosorb iQ-MP-AG-AG instrument. The Brunauer-Emmett-Teller model was applied.

### Studies on reaction conversion and product selectivity

Catalytic and photocatalytic oxidation of diphenyl sulphide (Ph<sub>2</sub>S, 98%, Sigma Aldrich) to diphenyl sulfoxide (Ph<sub>2</sub>SO, 96%, Sigma Aldrich) and sulfone (Ph<sub>2</sub>SO<sub>2</sub>, 97%, Sigma Aldrich), in the presence of hydrogen peroxide (30%, Sigma Aldrich) was investigated. The reaction mixture consisted of 0.4 mmol dm<sup>-3</sup> of diphenyl sulphide, 10 cm<sup>3</sup> of acetonitrile (99.9%, Sigma Aldrich) and 0.1 mmol dm<sup>-3</sup> of bromobenzene (≥99.5%, Sigma Aldrich) used as the internal standard. In a typical experiment,

5 mg of the tested material powder was sonicated for 2 min in 10 cm<sup>3</sup> of the reaction mixture, then 2 mmol dm<sup>-3</sup> of 30% hydrogen peroxide was added (suspension concentration of 0.5 g dm<sup>-3</sup>). The prepared suspension was placed in a round quartz cuvette (5 cm dia., 1 cm optical path) and irradiated for 3 hours with a xenon lamp (XBO-150, Instytut Fotonowy) equipped with 10 cm 0.1 mol dm<sup>-3</sup> CuSO<sub>4</sub> aqueous solution filter and a 320 nm cut-off filter. To determine the apparent quantum efficiency the photon flux in the range of 300 to 400 nm was measured with the StellarNet spectroradiometer. In the case of the catalytic studies, the reaction tests were performed in the dark in order to avoid a light-assisted conversion of Ph<sub>2</sub>S. The progress of the reactions was monitored by HPLC analysis of the reaction mixture using a mixture of acetonitrile/water in the volume ratio of 70 : 30 as the eluent. The samples of the reaction mixtures were filtered using a 0.22 μm nylon membrane filter and analysed by the PerkinElmer Flexar chromatograph equipped with the COL-Analytical C18 column (150 mm × 4.6 mm i.d., 5 μm pore size). The column was maintained at 25 °C during the analysis and the UV detector was set at 254 nm.

### Electrochemical measurements

The electrochemical measurements were carried out in a three-electrode system with Ag/Ag<sup>+</sup> electrode [AgNO<sub>3</sub> (10 mmol dm<sup>-3</sup>) in 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>NClO<sub>4</sub> in acetonitrile], platinum wire, and carbon electrode as the reference, counter, and working electrodes, respectively. As the electrolyte 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> solution in acetonitrile was used. The potential of the reference electrode relative to the standard hydrogen electrode (SHE) was set at +0.62 V based on the cyclic voltammetry measurement for ferrocene (scan speed 10 mV s<sup>-1</sup>) and the literature value for Fe<sup>+/0</sup> couple. The electrode potential was controlled by an electrochemical analyser (Bio-Logic, SP-150). The cyclic voltammetry (CV) was collected at room temperature, with a scan rate of 60 mV s<sup>-1</sup>, from -0.1 V to 2.0 V vs. Ag/Ag<sup>+</sup>.

### Hydroxyl radicals generation

The hydroxyl radicals generation by studied materials was examined in the reaction of terephthalic acid (TA) hydroxylation. TiO<sub>2</sub> (0.5 g dm<sup>-3</sup>) suspended in 16 cm<sup>3</sup> of the TA solution (Aldrich, 98%; 3 × 10<sup>-3</sup> mol dm<sup>-3</sup> dissolved in 0.01 mol dm<sup>-3</sup> NaOH, pH = 7.6) was irradiated with a xenon lamp (XBO-150, Instytut Fotonowy). To avoid excitation of TA a 320 nm cut-off filter was used as well as a near infra-red and IR filter (10 cm optical path, 0.1 mol dm<sup>-3</sup> solution of CuSO<sub>4</sub>). Samples of 1.5 cm<sup>3</sup> were collected during irradiation, then centrifuged to separate the photocatalyst powder. In the reaction of non-fluorescent TA with hydroxyl radicals, hydroxyterephthalic acid (TAOH) is formed. TAOH was monitored by emission spectroscopy. TAOH shows a broad emission band at λ<sub>max</sub> = 425 nm (when excited at λ<sub>exc</sub> = 315 nm). Moreover, TAOH generation in the presence of hydrogen peroxide (2 mmol dm<sup>-3</sup>) was investigated.



## Results and discussion

### Morphology and phase composition

Materials in the form of white powders were used for the catalytic tests. Scanning electron microscopy revealed that anatase and rutile materials form aggregates in size *ca.* 1  $\mu\text{m}$  and below 0.5  $\mu\text{m}$ , respectively (Fig. 1). The crystal structure of the materials was confirmed using X-ray diffraction (XRD) (Fig. S1†). The crystal size of anatase and rutile materials is *ca.* 20 and 50 nm, respectively. In XRD of all samples only one polymorph is present, only CR-EL material contains a small admixture of anatase, up to 1%.<sup>27</sup> Porosimetry measurements showed that the anatase samples have a much higher specific surface area than the rutile materials (Table 1).

$\text{Ph}_2\text{SO}_2$  was the main product of the photocatalytic  $\text{Ph}_2\text{S}$  oxidation at anatase materials. In the case of N100 material 100% conversion of  $\text{Ph}_2\text{S}$  was achieved after 45 minutes of irradiation (Fig. 2a). In the case of the reaction conducted at TRX\_A material, total  $\text{Ph}_2\text{S}$  oxidation was reached after 1 hour of irradiation (Fig. 2b). A slightly better selectivity to  $\text{Ph}_2\text{SO}_2$  was observed in the case of N100 (100% after 90 minutes of irradiation) than for TRX\_A material. Diphenyl sulphide oxidation at anatase materials in the dark was tested as well. The reaction progress was observed for both anatase samples. Additionally, the reaction products were not observed in the absence of  $\text{TiO}_2$  in the reaction mixture, even when the mixture was heated to 40  $^\circ\text{C}$ . Nevertheless, after 3 hours of irradiation in the same reaction mixture (without  $\text{TiO}_2$ , with  $\text{H}_2\text{O}_2$ ) a slight conversion (*ca.* 7%) of  $\text{Ph}_2\text{S}$  to  $\text{Ph}_2\text{SO}$  as the final product took place (Fig. S2a†). We suggest that the residual oxidation of diphenyl sulphide is possible due to  $\text{H}_2\text{O}_2$  photolysis, although 320 nm cut-off filter was used. The absorbance of the initial reaction mixture is negligible above 320 nm (Fig. S2b†), however, direct

Table 1 Phase, specific surface area, and crystal size of studied materials<sup>a</sup>

Material	Phase	Specific surface area/ $\text{m}^2 \text{g}^{-1}$	Crystal size/nm $\pm 0.1$
N100	Anatase	$97 \pm 2$	18.1
TRX_A	Anatase	$90 \pm 2$	17.3
TRX_R	Rutile	$5.5 \pm 0.1$	48.2
CR-EL	Rutile	$8 \pm 0.1$	46.9

<sup>a</sup> (Photo)catalytic conversion of diphenyl sulphide in the presence of anatase and rutile.

photolysis of  $\text{H}_2\text{O}_2$  initiated at any wavelength lower than 380 nm was reported by Cataldo.<sup>28</sup>

These results clearly show that the oxidation of  $\text{Ph}_2\text{S}$  in the presence of anatase materials is possible both as catalytic and photocatalytic processes. However, a significantly higher conversion of  $\text{Ph}_2\text{S}$  for photocatalytic conditions compared to the dark processes was observed (Fig. S3a and b†). A similar positive effect of light was observed when  $\text{Ph}_2\text{SO}$  as a substrate was used (Fig. S10†). Both photocatalytic and catalytic oxidation of  $\text{Ph}_2\text{S}$  at anatase materials leads mainly to  $\text{Ph}_2\text{SO}_2$  production with the selectivity of almost 100% after 3 h of tests (Fig. 2a, b and S3c, d†). Nevertheless, for both anatase materials, during the first hour more sulfoxide is formed upon irradiation than under purely catalytic conditions.

Results of photocatalytic oxidation of  $\text{Ph}_2\text{S}$  at rutile materials are depicted in Fig. 2c and d. Photocatalytic conversion of  $\text{Ph}_2\text{S}$  at rutile materials was significantly faster compared to both photocatalytic and catalytic conditions applied to anatase materials. The total conversion of  $\text{Ph}_2\text{S}$  was observed after 15 and 30 min of irradiation for TRX\_R and CR-EL, respectively (Fig. 2c and d). Based on these data and the measured photon flux the apparent quantum efficiency of  $\text{Ph}_2\text{S}$  to  $\text{Ph}_2\text{SO}$  conversion within the first 15 min of irradiation was  $\geq 2\%$ . Oxidation of  $\text{Ph}_2\text{S}$  at rutile materials led to  $\text{Ph}_2\text{SO}$  as the main product. High selectivity to  $\text{Ph}_2\text{SO}$  at the beginning of the photocatalytic reaction was noticed (*ca.* 100%). During the reaction course the selectivity to  $\text{Ph}_2\text{SO}$  was decreasing, while the production of  $\text{Ph}_2\text{SO}_2$  became the dominant process. However, upon further irradiation, the production of  $\text{Ph}_2\text{SO}$  increased again, hence diphenyl sulfoxide was the main product of the long term photocatalytic oxidation at rutile (Fig. 2c and d). Contrary to anatase, rutile induced no conversion in the absence of light, neither for  $\text{Ph}_2\text{S}$  nor  $\text{Ph}_2\text{SO}$  used as a substrate (Fig. S4 and S11a†).

Interestingly, the total concentration of analyzed reactants ( $\text{Ph}_2\text{S}$ ,  $\text{Ph}_2\text{SO}$ ,  $\text{Ph}_2\text{SO}_2$ ) decreased by *ca.* 5% during the experiments with rutile material under illumination. Moreover, in the case of photocatalytic reaction over CR-EL material, at chromatograms the appearance of low amounts of a new compound, not detected for any other material described above was observed. To elucidate the role of  $\text{H}_2\text{O}_2$  in this reaction a new portion of  $\text{H}_2\text{O}_2$  was added after 90 min of irradiation (Fig. S5†). No increase of the selectivity to  $\text{Ph}_2\text{SO}_2$  was observed. Furthermore, in our previous work we showed that after almost

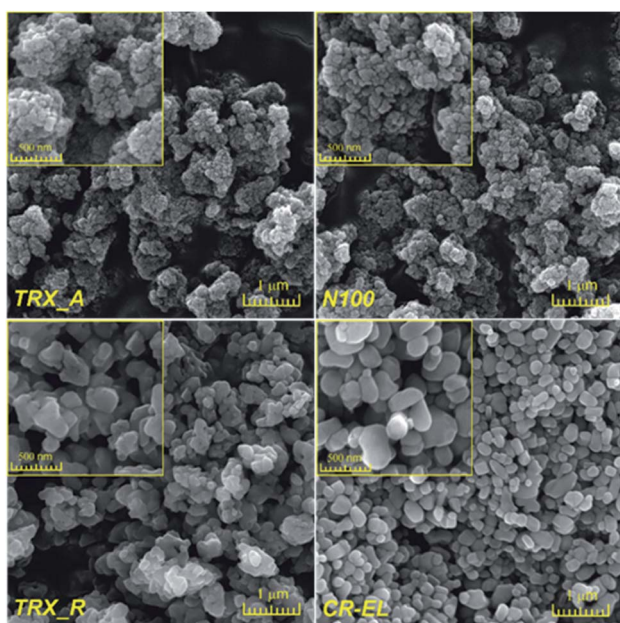


Fig. 1 SEM images of studied materials.



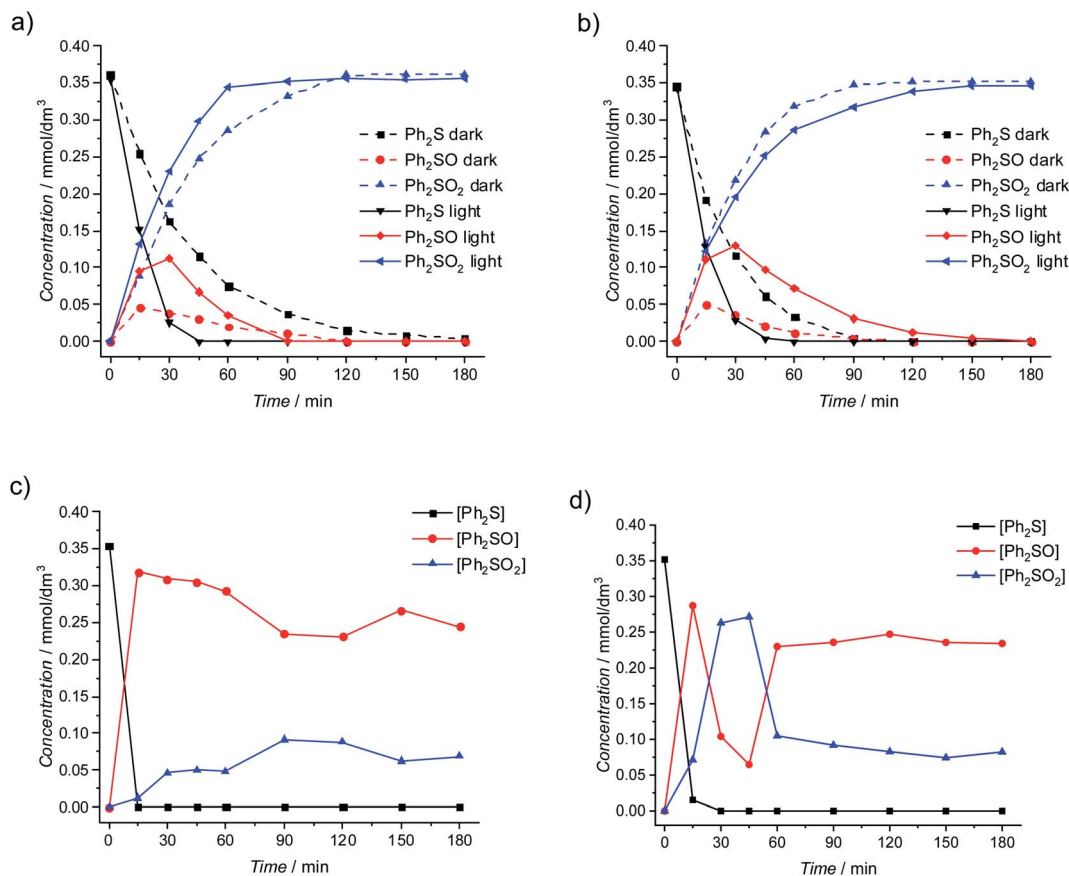


Fig. 2 Concentration of reactants during  $\text{Ph}_2\text{S}$  oxidation: at anatase materials (a) N100, (b) TRX\_A upon irradiation  $\lambda > 320$  nm (solid lines) and in the dark (dotted lines); at rutile material (c) TRX\_R, (d) CR-EL upon irradiation.

complete conversion of  $\text{Ph}_2\text{S}$  into both  $\text{Ph}_2\text{SO}$  and  $\text{Ph}_2\text{SO}_2$ , hydrogen peroxide was not totally consumed,<sup>20</sup> pointing at a sufficient amount of  $\text{H}_2\text{O}_2$  used in the reaction. As the  $\text{Ph}_2\text{SO}_2$  concentration decreases after prolonged irradiation (Fig. 2c), either its reduction to  $\text{Ph}_2\text{SO}$  or transformation to other products could be considered. A photocatalytic reduction of  $\text{Ph}_2\text{SO}_2$  directly by electrons from the conduction band does not seem plausible, since 3 hours of irradiation of  $\text{Ph}_2\text{SO}_2$  in the presence of  $\text{H}_2\text{O}_2$  and CR-EL did not result in any  $\text{Ph}_2\text{SO}$  formation (data not shown). Moreover, the initial concentration of  $\text{Ph}_2\text{SO}_2$  remained unchanged, what excludes a possibility of  $\text{Ph}_2\text{SO}_2$  transformation to any other product. Taking these observations into account it was postulated that a decrease in  $\text{Ph}_2\text{SO}_2$  and increase in  $\text{Ph}_2\text{SO}$  concentrations, observed after 45 min of the test, are possibly the result of  $\text{Ph}_2\text{SO}_2$  disproportionation resulting a new unidentified compound. A detailed analysis of this product is still needed, however, we suggest that it could be one of many products identified by Vosoooghian *et al.* in their meticulous analysis.<sup>29</sup>

It is worth comparing the presented results with our earlier work where we tested the activity of doped titanium dioxide. Here we conclude, that rutile is not acting as a catalyst (*i.e.*, it is not active in the dark), however, we previously reported that materials with higher amounts of this polymorph show a higher activity in the oxidation of  $\text{Ph}_2\text{S}$ . Therefore, it can be concluded

that the presence of rutile has an indirect effect on the catalytic process – the material itself is not active, but the coexistence of rutile and anatase enhances the catalytic activity of the materials. Such anatase/rutile composites appeared also very active in photocatalytic transformations, both of  $\text{Ph}_2\text{S}$  and  $\text{Ph}_2\text{SO}$ , due to a synergistic effect of these phases reported in numerous publications on P25 and similar materials.<sup>30–34</sup> N100 and TRX\_A appear more active catalytically, therefore, in a similar time window the second oxidation product,  $\text{Ph}_2\text{SO}_2$ , becomes the main product both in the dark and upon irradiation. The pure rutile phase, despite of its catalytic inactivity, appears the most active photomaterial. In this case a mixture of  $\text{Ph}_2\text{SO}$  and  $\text{Ph}_2\text{SO}_2$  is obtained.

### Reaction mechanism

Research studies on sulphides oxidation describe both catalytic and photocatalytic processes. The mechanism of catalytic oxidation involves  $\text{H}_2\text{O}_2$  activation on the catalyst surface. Al-Maksound *et al.* studied catalytic oxidation of various sulphides using  $\text{H}_2\text{O}_2$  and self-synthesized  $\text{TiO}_2$  (75–80% of anatase).<sup>22</sup> The authors showed high selectivity to sulfones. Rodríguez-Padrón *et al.* studied microwave-assisted catalytic oxidation of sulphides using  $\text{H}_2\text{O}_2$  and commercial anatase, as well as self-synthesized protein-templated anatase  $\text{TiO}_2$  in



ethanol solution.<sup>35</sup> The authors showed that Ph<sub>2</sub>S oxidation over reference anatase leads to sulfone production, while at protein-templated TiO<sub>2</sub> mainly sulfoxide was produced. Radko *et al.* studied catalytic oxidation of sulphides in the presence of titanosilicates and found that the dimethyl sulphide and diphenyl sulphide conversion increased with the increasing titanium content in the zeolite structure.<sup>20</sup> In our current study catalytic Ph<sub>2</sub>S oxidation with H<sub>2</sub>O<sub>2</sub> at anatase TiO<sub>2</sub> to Ph<sub>2</sub>SO<sub>2</sub> was observed. Contrary to that, no catalytic oxidation of Ph<sub>2</sub>S at rutile materials was observed. We suggest that the opposite results can be attributed to the various activation paths of hydrogen peroxide (and maybe Ph<sub>2</sub>S) on the anatase/rutile surfaces. However, the differences can also originate from a low specific surface area of rutile materials, and therefore a low number of active sites. In order to elucidate the effect of specific surface area, the catalytic test with self-synthesized rutile material (SSA of ca. 25 m<sup>2</sup> g<sup>-1</sup>) was performed. Although the specific surface area was 3–5 times higher in this case, no catalytic oxidation of Ph<sub>2</sub>S was observed as well.

Published articles describing photocatalytic oxidation of sulphides postulate that the photocatalytic oxidation is initiated by the formation of a surface bound radical cation generated as a result of oxidation with the photogenerated hole.<sup>29</sup> Also, superoxide radical anion (O<sub>2</sub><sup>•-</sup>) plays a key role in the reaction.<sup>36–38</sup> Zhang *et al.* suggested that O<sub>2</sub><sup>•-</sup> reacts with generated organosulfur radical.<sup>39</sup> Lang *et al.* studied Ph<sub>2</sub>S visible light induced oxidation in the presence of a dye (alizarin red S) and TEMPO as the redox mediator to increase the dye stability.<sup>40–44</sup> The authors reported Ph<sub>2</sub>S conversion to Ph<sub>2</sub>SO, pointing at O<sub>2</sub><sup>•-</sup> importance in the reaction mechanism. Li *et al.* confirmed significance of superoxide radical anions and sulphide cation radicals by experiments involving radical scavengers and <sup>18</sup>O<sub>2</sub>.<sup>45</sup> Vosoughian *et al.* showed that oxidation of diphenyl sulphide was effective only in the oxygen rich atmosphere (detectable amounts of products were neither observed in the presence of atmospheric oxygen nor under argon flux).<sup>29</sup> In the presence of photosensitizers able to produce singlet oxygen, it is postulated that <sup>1</sup>O<sub>2</sub> may participate in the Ph<sub>2</sub>S oxidation.<sup>46–49</sup> The mechanism described in the literature (illustrated in Fig. 3, blue color) cannot fully explain our results, which show that no oxidation products are formed in the absence of hydrogen peroxide. In other words, the mechanism involving Ph<sub>2</sub>S<sup>•+</sup> formation and its reaction with either O<sub>2</sub><sup>•-</sup> or <sup>1</sup>O<sub>2</sub> should lead to the products (Ph<sub>2</sub>SO, Ph<sub>2</sub>SO<sub>2</sub>), which have not been detected.

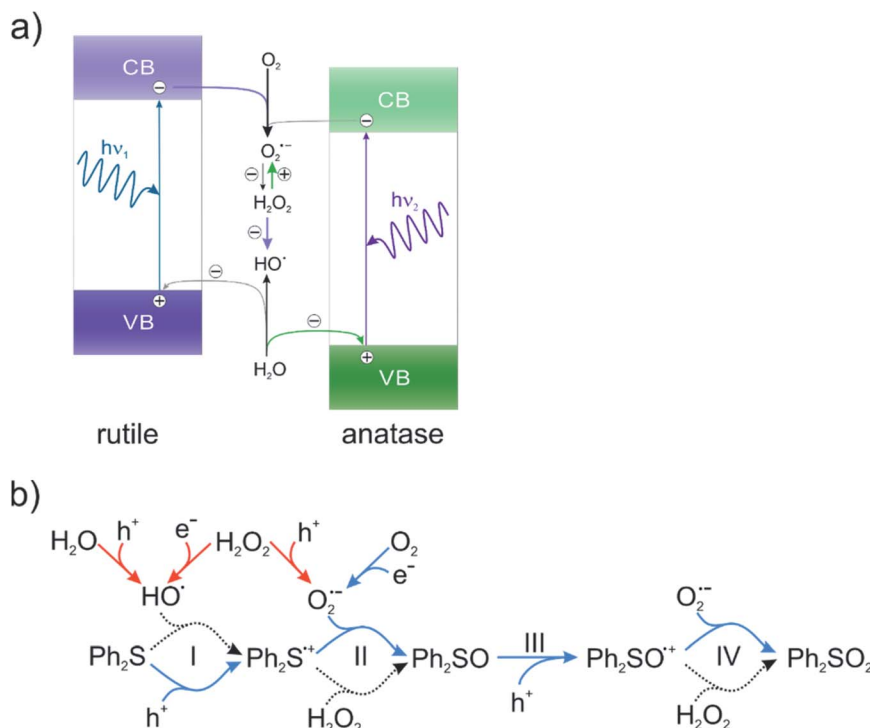
According to our knowledge the role of H<sub>2</sub>O<sub>2</sub> in the mechanism and its influence on the efficiency of photocatalytic Ph<sub>2</sub>S oxidation have not been reported in the literature. The presence of H<sub>2</sub>O<sub>2</sub> dramatically influences the generation of HO<sup>•</sup> and O<sub>2</sub><sup>•-</sup>, both at rutile and anatase material (Fig. 3, red color). Photocatalytic production of hydroxyl radicals at rutile is inefficient, however, the generation of this reactive species is strongly enhanced in the presence of H<sub>2</sub>O<sub>2</sub>, as the result of its reduction. On the other hand, a similar effect of H<sub>2</sub>O<sub>2</sub> on anatase photoactivity is not observed. Addition of H<sub>2</sub>O<sub>2</sub> leads to increasing O<sub>2</sub><sup>•-</sup> production at anatase, as the result of H<sub>2</sub>O<sub>2</sub> oxidation with holes.<sup>50</sup> Generally, rutile has better reduction properties compared to anatase, meanwhile, anatase is a better

oxidant.<sup>31</sup> Using various TiO<sub>2</sub> phase compositions in the combination with H<sub>2</sub>O<sub>2</sub> can be an effective way to control the selectivity of the reaction in the system, in which a fine product formation is highly dependent on the generated ROS type. The HO<sup>•</sup> generation was monitored in the reaction of terephthalic acid oxidation. Hydroxyl radicals are generated as the result of a hole reaction with surface hydroxyl groups or adsorbed water molecules. In the reaction of TA with hydroxyl radicals, highly-fluorescent hydroxyterephthalic acid (TAOH) is formed. TAOH generation in the presence of hydrogen peroxide (2 mmol dm<sup>-3</sup>) was also investigated. The TAOH formation is depicted in Fig. S6.† In the absence of hydrogen peroxide anatase shows a more efficient HO<sup>•</sup> generation compared to the rutile (TAOH concentration amounted 57 μmol dm<sup>-3</sup> and 29 μmol dm<sup>-3</sup> respectively). However, after addition of H<sub>2</sub>O<sub>2</sub> to the system containing anatase, TAOH generation decreased (10 μmol dm<sup>-3</sup>), while it significantly increased for rutile material (452 μmol dm<sup>-3</sup>). Undoubtedly, combination of hydrogen peroxide and rutile significantly enhances HO<sup>•</sup> generation.

The presence of hydrogen peroxide can lead to the increased concentration of photogenerated O<sub>2</sub><sup>•-</sup> and/or HO<sup>•</sup> radicals, whereas only the influence of O<sub>2</sub><sup>•-</sup> on the oxidation of Ph<sub>2</sub>S is known. In order to determine the possible role of hydroxyl radicals in the reaction, the Fenton process was induced in the presence of Ph<sub>2</sub>S. In the Fenton reaction (production of HO<sup>•</sup> in the reaction of H<sub>2</sub>O<sub>2</sub> with iron(II) cations) the conversion of Ph<sub>2</sub>S and efficient production of Ph<sub>2</sub>SO were observed (Fig. 4a). Slight oxidation of Ph<sub>2</sub>SO (Ph<sub>2</sub>SO<sub>2</sub> formation) in the Fenton process was also noticed. However, an inefficient Ph<sub>2</sub>SO<sub>2</sub> generation might originate from the transformation of other species that contaminate the original Ph<sub>2</sub>SO sample (Fig. 4b). This shows that the hydroxyl radical and/or hydrogen peroxide (the reactant in this reaction) is able to oxidize Ph<sub>2</sub>S to Ph<sub>2</sub>SO. Recently, we described that the addition of *tert*-butyl alcohol (hydroxyl radical scavenger) significantly diminishes the Ph<sub>2</sub>S conversion.<sup>26</sup> Furthermore, isotopic oxygen (H<sub>2</sub><sup>18</sup>O) experiments, reported by Li *et al.* revealed that the oxygen atoms of sulfoxide (obtained photocatalytically from phenyl sulphide in water containing mixture, in the absence of H<sub>2</sub>O<sub>2</sub>) originated mainly from water.<sup>51</sup> We concluded that hydroxyl radicals play a significant role in the first step of diphenyl sulphide oxidation, yielding Ph<sub>2</sub>SO. Similarly, in our actual system HO<sup>•</sup> is involved in the oxidation of Ph<sub>2</sub>S to Ph<sub>2</sub>SO, but the further oxidation to Ph<sub>2</sub>SO<sub>2</sub> is not possible.

In order to explain why the Fenton reaction leads only to Ph<sub>2</sub>SO generation, cyclic voltammetry measurements were performed (Fig. 5). In the case of Ph<sub>2</sub>S, two oxidation peaks ( $E'_{a,Ph_2S} = 1.83$  V vs. SHE;  $E''_{a,Ph_2S} = 2.07$  V vs. SHE) and one reduction peak ( $E'_{c,Ph_2S} = 2.01$  V vs. SHE) were observed in the cyclic voltammogram. In the case of Ph<sub>2</sub>SO only one oxidation peak was detected ( $E'_{a,Ph_2SO} = 2.43$  V vs. SHE). Finally, the CV of Ph<sub>2</sub>SO<sub>2</sub> has shown neither oxidation nor reduction peaks in the explored potential range. In the case of Ph<sub>2</sub>S cyclic voltammogram, the first oxidation at 1.83 V vs. SHE can presumably be attributed to Ph<sub>2</sub>S<sup>•+</sup> formation. Furthermore, based on the CV measurements the formation of Ph<sub>2</sub>SO as an irreversible process was found. The second oxidation process at 2.07 V vs.

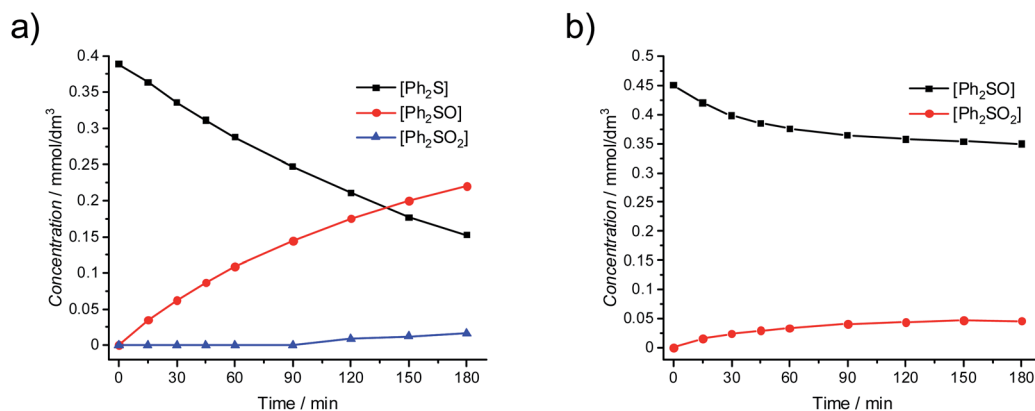




**Fig. 3** (a) Main reactive oxygen species generation pathway in the presence of rutile and anatase photocatalysts, based on ref. 31. Violet and green arrows depict main processes characteristic for rutile and anatase, respectively. (b) Plausible pathway of  $\text{Ph}_2\text{S}$  oxidation at  $\text{TiO}_2$ . Blue color shows the paths described in the literature so far. Red color shows pathways of  $\text{H}_2\text{O}_2$  oxidation and reduction. Dotted black lines show discussed processes, which complete the mechanism of  $\text{Ph}_2\text{S}$  oxidation at  $\text{TiO}_2$  in the presence of  $\text{H}_2\text{O}_2$ .

SHE is a partially reversible reaction ( $E'_{\text{c,Ph}_2\text{S}} = 2.01 \text{ V vs. SHE}$ ) with oxidation and reduction halfwaves separated by 0.06 V, pointing at one electron reversible process. Based on these considerations we conclude that oxidation of  $\text{Ph}_2\text{S}$  to  $\text{Ph}_2\text{SO}$  can be achieved by  $\text{HO}^\bullet$  ( $\text{HO}^\bullet/\text{H}_2\text{O} = 2.27 \text{ V vs. SHE, pH} = 7$  (ref. 52)). CV of  $\text{Ph}_2\text{SO}$  reveals that the potential of sulfoxide oxidation is too high to enable its oxidation by hydroxyl radicals. Nevertheless,  $\text{Ph}_2\text{SO}$  can be still directly oxidized to  $\text{Ph}_2\text{SO}^{\bullet+}$  by  $\text{TiO}_2$  VB holes (step III, Fig. 3).<sup>53</sup>

To summarize, the electrochemical and Fenton experiments showed that  $\text{Ph}_2\text{S}$  can be easily oxidized by  $\text{HO}^\bullet$  to  $\text{Ph}_2\text{S}^{\bullet+}$ . However, holes are required for further oxidation of  $\text{Ph}_2\text{SO}$  to the  $\text{Ph}_2\text{SO}^{\bullet+}$  radical, which explains why the Fenton reaction led only to  $\text{Ph}_2\text{SO}$ . The Fenton process does not generate  $\text{O}_2^{\bullet-}$ , however,  $\text{Ph}_2\text{SO}$  as a product of the Fenton reaction was effortlessly detected. It is noteworthy that in the Fenton reaction the concentration of hydrogen peroxide was the same that in the photocatalytic system. The results suggest that  $\text{H}_2\text{O}_2$  is involved in the  $\text{Ph}_2\text{S}^{\bullet+}$  to  $\text{Ph}_2\text{SO}$  conversion (Fig. 3). Our



**Fig. 4** Oxidation of (a)  $\text{Ph}_2\text{S}$  by the Fenton reagent ( $0.4 \text{ mmol dm}^{-3} \text{ Ph}_2\text{S}$ ,  $2 \text{ mmol dm}^{-3} \text{ H}_2\text{O}_2$ ,  $0.2 \text{ mmol dm}^{-3} \text{ Fe}^{2+}$ ); (b)  $\text{Ph}_2\text{SO}$  by the Fenton reagent ( $0.4 \text{ mmol dm}^{-3} \text{ Ph}_2\text{SO}$ ).



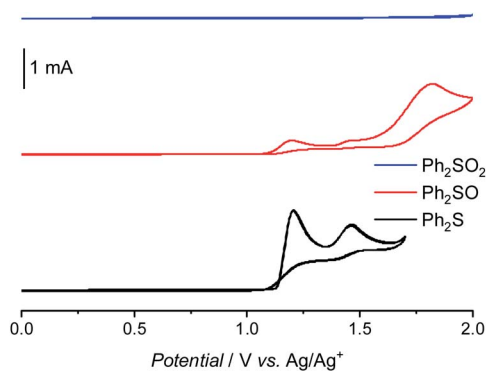


Fig. 5 Cyclic voltammograms of diphenyl sulphide, sulfoxide, and sulfone in acetonitrile.

hypothesized mechanism explains the results of photocatalytic oxidation of  $\text{Ph}_2\text{S}$  at anatase and rutile materials. In the case of rutile, a very fast conversion of  $\text{Ph}_2\text{S}$  was observed, due to a highly efficient  $\text{H}_2\text{O}_2$  reduction, and thus effective  $\text{HO}^\bullet$  formation (Fig. S6†). These radicals oxidize  $\text{Ph}_2\text{S}$  within first few minutes of the reaction. Our study on  $\text{HO}^\bullet$  generation shows that in the presence of rutile and  $\text{H}_2\text{O}_2$  ca.  $400 \mu\text{mol dm}^{-3}$  of TAOH is generated after 15 min of irradiation (in aqueous solution). This concentration of hydroxyl radicals trapped as TAOH is equal to the initial concentration of  $\text{Ph}_2\text{S}$  in the tested reaction. These results clearly show that a fast conversion of  $\text{Ph}_2\text{S}$  at rutile CR-EL is a purely photocatalytic process, being a result of an efficient  $\text{H}_2\text{O}_2$  reduction. At anatase, which preferably oxidizes  $\text{H}_2\text{O}_2$ ,  $\text{HO}^\bullet$  generation is much less effective, therefore, the oxidation rate is lower.

The presented results indicate that hydrogen peroxide and superoxide radical anion play a similar role, oxidizing the radical cations,  $\text{Ph}_2\text{S}^{\bullet+}$  and  $\text{Ph}_2\text{SO}^{\bullet+}$ , to sulfoxide and sulfone, respectively. However, to unequivocally confirm these conclusions, the influence of oxygen on the reaction was tested. The studied reaction mixtures were purged with argon or oxygen before (15 min) and during the experiments. For the dark reaction at TRX\_A, the observed conversion and selectivity were independent on the presence of oxygen (Fig. S7†). This result suggests that catalytic oxidation of  $\text{Ph}_2\text{S}$  involves only the activation of hydrogen peroxide activation, without any contribution of  $\text{O}_2$  (alternatively, the contribution of oxygen is low, with a negligible influence on the products formation). However, when TRX\_A was used as a photocatalyst (under irradiation), the influence of  $\text{O}_2$  on the reaction progress was significant. A decrease of the  $\text{Ph}_2\text{S}$  conversion from ca. 60% under ambient conditions to ca. 35% under argon atmosphere and increased conversion to ca. 75% under the oxygen rich atmosphere was observed (Fig. S8a†). Under the oxygen free conditions, the  $\text{Ph}_2\text{S}$  conversion decreased, but photocatalytic oxidation of  $\text{Ph}_2\text{S}$  to  $\text{Ph}_2\text{SO}$  was still observed. Moreover, changes in the selectivity to  $\text{Ph}_2\text{SO}_2$  at TRX\_A were observed. The selectivity to  $\text{Ph}_2\text{SO}_2$  increased in the following order: under argon, ambient, and oxygen-rich conditions (Fig. S8b†). In the case of the photocatalytic reaction at CR-EL, no significant changes in the  $\text{Ph}_2\text{S}$  conversion under various conditions were observed (Fig. S9a†).

Nevertheless, remarkable changes in the selectivity to  $\text{Ph}_2\text{SO}_2$  were observed. Under oxygen-rich conditions a decrease in the production of  $\text{Ph}_2\text{SO}$ , and an increase in the  $\text{Ph}_2\text{SO}_2$  production after first 15 min of the reaction, were observed (Fig. S9b†). Moreover, the point of the second increase of the  $\text{Ph}_2\text{SO}$  production appeared earlier (after 30 min of irradiation) for oxygen-rich conditions.

The first stable oxidation product,  $\text{Ph}_2\text{SO}$ , can be further oxidized by holes from the valence band of  $\text{TiO}_2$  to  $\text{Ph}_2\text{SO}^{\bullet+}$ . This intermediate is further transformed to  $\text{Ph}_2\text{SO}_2$  in the reaction with superoxide radical ( $\text{O}_2^{\bullet-}$ ) formed as the result of either oxygen reduction or  $\text{H}_2\text{O}_2$  oxidation. To confirm this path a possibility of  $\text{Ph}_2\text{SO}$  oxidation, both in the dark and upon irradiation in the presence of hydrogen peroxide and  $\text{TiO}_2$ , was studied. In the case of anatase material, an efficient conversion of  $\text{Ph}_2\text{SO}$  to  $\text{Ph}_2\text{SO}_2$  under both catalytic and photocatalytic conditions was observed, with a much better efficiency upon irradiation (Fig. S10†). In the case of rutile, no conversion was observed in the dark, however, irradiation induced this reaction (Fig. S11†). Clearly, the higher rate of the photocatalytic reaction in the case of anatase material is the result of a more efficient  $\text{O}_2^{\bullet-}$  production at anatase than on the rutile in the presence of  $\text{H}_2\text{O}_2$ . Furthermore, the possibility of  $\text{Ph}_2\text{SO}$  oxidation upon irradiation in the presence of  $\text{TiO}_2$ , but in the absence of  $\text{H}_2\text{O}_2$ , was tested (Fig. S12†). Low conversion of  $\text{Ph}_2\text{SO}$  under such conditions was observed – ca. 13% and 9% after 3 hours of irradiation in the presence of anatase and rutile, respectively. In a similar test, performed under anaerobic conditions (Ar-saturated solution and addition of  $\text{Fe}^{3+}$  as an electron acceptor), the conversion of  $\text{Ph}_2\text{SO}$  to  $\text{Ph}_2\text{SO}_2$  was not observed. Abovementioned results clearly show that  $\text{O}_2^{\bullet-}$  radicals can easily react with  $\text{Ph}_2\text{SO}^{\bullet+}$ , yielding  $\text{Ph}_2\text{SO}_2$ . We suggest that the formation of  $\text{Ph}_2\text{SO}_2$  is possible in the presence of  $\text{O}_2^{\bullet-}$  and  $\text{Ph}_2\text{SO}^{\bullet+}$  (hole oxidized  $\text{Ph}_2\text{SO}$ ), however, such reaction has a low effectivity. In order to enhance the production of  $\text{Ph}_2\text{SO}_2$ , the presence of hydrogen peroxide is necessary. The full mechanism of the photocatalytic  $\text{Ph}_2\text{S}$  oxidation in the presence of hydrogen peroxide is shown in Fig. 3.

## Conclusions

In summary, we demonstrated that  $\text{Ph}_2\text{S}$  oxidation in the presence of hydrogen peroxide at anatase- $\text{TiO}_2$  can take place both as a catalytic and photocatalytic reaction. In contrast, at rutile materials only photocatalytic oxidation is possible, and no reaction progress was observed in the dark. The reaction at anatase leads mainly to  $\text{Ph}_2\text{SO}_2$  as the product, whereas, the same reaction in the presence of rutile leads mainly to  $\text{Ph}_2\text{SO}$  formation. In the case of rutile the total conversion of  $\text{Ph}_2\text{S}$  was observed already after 15 min (compared to at least 1 h required for a catalytic conversion) with nearly 100% selectivity towards  $\text{Ph}_2\text{SO}$ . It is the first reported photocatalytic conversion of  $\text{Ph}_2\text{S}$  using  $\text{H}_2\text{O}_2$  in the presence of pure rutile. Moreover, the efficiency of this reaction under the tested conditions is also much higher compared to the systems described in literature so far (apparent quantum yield of ca. 2%, concentration of products in the absence of  $\text{H}_2\text{O}_2$  below the detection limit). The conversion



level and the reaction selectivity can be controlled by the choice between rutile and anatase polymorphs, as well as by irradiation time (in the case of rutile).

Catalytic oxidation of Ph<sub>2</sub>S involves only the activation of hydrogen peroxide at the catalyst surface, without any contribution of dioxygen. Whereas, the presence of O<sub>2</sub> in the photocatalytic reaction increases the Ph<sub>2</sub>S conversion due to generation of O<sub>2</sub><sup>•−</sup>. Studies on the mechanistic details revealed the dual role of H<sub>2</sub>O<sub>2</sub> (Fig. 3). At the same time, it plays the role of a substrate in the reaction catalysed only by anatase, but it also plays a key role in alternative oxidation pathways available through photocatalysis. Hydrogen peroxide can be either oxidized or reduced photocatalytically, resulting in the generation of O<sub>2</sub><sup>•−</sup> and HO<sup>•</sup> radicals, respectively. Hydroxyl and superoxide radicals play an important role in various reaction steps. Hydroxyl radicals can oxidize Ph<sub>2</sub>S to Ph<sub>2</sub>S<sup>•+</sup>, however, Ph<sub>2</sub>SO oxidation to Ph<sub>2</sub>SO<sup>•+</sup> requires a stronger oxidant, *i.e.* holes. The cation radical intermediates, Ph<sub>2</sub>S<sup>•+</sup> and Ph<sub>2</sub>SO<sup>•+</sup>, react with superoxide anions or directly with H<sub>2</sub>O<sub>2</sub> yielding stable sulfoxide (Ph<sub>2</sub>SO) and sulfone (Ph<sub>2</sub>SO<sub>2</sub>).

The presented studies prove the applicability of photocatalysis in an efficient and selective synthesis of sulfoxide and sulfone through oxidation of organic sulphides.

## Author contributions

Conceptualization P. M., M. K.; methodology P. M., M. K.; formal analysis P. M., M. K., A. Ś.; investigation P. M., M. K., A. Ś.; resources, L. C., W. M.; data curation P. M., M. K.; writing P. M., M. K., A. Ś., L. C. and W. M.; visualization P. M., M. K.; supervision M. K., W. M.; project administration W. M.; funding acquisition W. M.

## Conflicts of interest

There are no conflicts to declare.

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