Selective and efficient catalytic and photocatalytic oxidation of diphenyl sulphide to sulfoxide and sulfone: the role of hydrogen peroxide and TiO₂ polymorph†

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In this paper, we describe the role of anatase and rutile crystal phases on diphenyl sulphide (Ph₂S) catalytic and photocatalytic oxidation. The highly selective and efficient synthesis of diphenyl sulfoxide (Ph₂SO) and diphenyl sulfone (Ph₂SO₂) at titanium dioxide was demonstrated. Ph₂S oxidation in the presence of hydrogen peroxide at anatase-TiO₂ can take place both as a catalytic and photocatalytic reaction, while at rutile-TiO₂ only photocatalytic oxidation is possible. The reaction at anatase leads mainly to Ph₂SO₂, whereas, in the presence of rutile a complete conversion to Ph₂SO is achieved after only 15 min (nearly 100% selectivity). Studies on the mechanistic details revealed a dual role of H₂O₂. 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.

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.† 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, oxidation of aromatics or oxidation of side chains. 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, antihypertensive agents and vasodilators. Many catalytic systems, containing, e.g., V, Re, Ti, Mo, Te, W, Se, Fe elements, have been studied in a sulphide to sulfoxide oxidation. 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, TiO₂ doped with vanadium was found to be an active catalyst of Ph₂S oxidation giving nearly 100% conversion of Ph₂S with high selectivity to Ph₂SO₂.

In this study, we report on the catalytic and photocatalytic oxidation of diphenyl sulphide (Ph₂S) (1) to diphenyl sulfone (Ph₂SO₂) (2) and diphenyl sulfoxide (Ph₂SO) (3) at rutile (R) and anatase (A) phases of TiO₂. We demonstrate that rutile-TiO₂ is a suitable catalyst for the oxidation of Ph₂S to Ph₂SO₂ (100% selectivity), whereas, for the formation of Ph₂SO, only anatase-TiO₂ is highly efficient. In this paper, we describe the role of anatase and rutile crystal phases on diphenyl sulphide (Ph₂S) catalytic and photocatalytic oxidation. The highly selective and efficient synthesis of diphenyl sulfoxide (Ph₂SO) and diphenyl sulfone (Ph₂SO₂) at titanium dioxide was demonstrated.

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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 Ph₂S.²⁶ No Ph₂S conversion after 3 hours of reaction in both catalytic and photocatalytic tests conducted in the absence of H₂O₂ over bare and doped TiO₂ materials (concentrations of Ph₂S 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 Ph₂S under irradiation compared to the dark process. In our previous paper, we studied the influence of TiO₂ modification (doping with vanadium, zinc, or tin) on the Ph₂S oxidation. We suggested that the crystal phase composition has a higher influence on both catalytic and photocatalytic activity than the surface metal modifications.²⁶ The goal of this work is to understand the difference between anatase and rutile in catalytic and photocatalytic Ph₂S 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 Kα2 radiation, 0.3 mm Ni filter) in 2θ range from 10 to 90°, at speed 3° min⁻¹ 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 LaB₆ 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 (Ph₂S, 98%, Sigma Aldrich) to diphenyl sulfoxide (Ph₂SO, 96%, Sigma Aldrich) and sulfone (Ph₂SO₂, 97%, Sigma Aldrich), in the presence of hydrogen peroxide (30%, Sigma Aldrich) was investigated. The reaction mixture consisted of 0.4 mmol dm⁻³ of diphenyl sulphide, 10 cm³ of acetonitrile (99.9%, Sigma Aldrich) and 0.1 mmol dm⁻³ 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 cm³ of the reaction mixture, then 2 mmol dm⁻³ of 30% hydrogen peroxide was added (suspension concentration of 0.5 g dm⁻³). 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⁻³ CuSO₄ 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 Ph₂S. 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⁺ electrode [AgNO₃ (10 mmol dm⁻³) in 0.1 mol dm⁻³ Bu₄NCIO₄ in acetonitrile], platinum wire, and carbon electrode as the reference, counter, and working electrodes, respectively. As the electrolyte 0.1 mol dm⁻³ LiClO₄ 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⁻¹) and the literature value for Fe³⁺/Fe²⁺ couple. The electrode potential was controlled by an electrochemical analyser (Bio-Logie, SP-150). The cyclic voltammetry (CV) was collected at room temperature, with a scan rate of 60 mV s⁻¹, from −0.1 V to 2.0 V vs. Ag/Ag⁺.

**Hydroxyl radicals generation**

The hydroxyl radicals generation by studied materials was examined in the reaction of terephthalic acid (TA) hydroxylation. TiO₂ (0.5 g dm⁻³) suspended in 16 cm³ of the TA solution (Aldrich, 98%; 3 × 10⁻³ mol dm⁻³ dissolved in 0.01 mol dm⁻³ 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⁻³ solution of CuSO₄). Samples of 1.5 cm³ 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_max = 425 nm (when excited at λ_exc = 315 nm). Moreover, TAOH generation in the presence of hydrogen peroxide (2 mmol dm⁻³) 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 μm and below 0.5 μm, 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%.\(^{27}\) Porosimetry measurements showed that the anatase samples have a much higher specific surface area than the rutile materials (Table 1).

Ph\(_2\)SO\(_2\) was the main product of the photocatalytic Ph\(_2\)S oxidation at anatase materials. In the case of N100 material 100% conversion of Ph\(_2\)S was achieved after 45 minutes of irradiation (Fig. 2a). In the case of the reaction conducted at TRX_A material, total Ph\(_2\)S oxidation was reached after 1 hour of irradiation (Fig. 2b). A slightly better selectivity to Ph\(_2\)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 TiO\(_2\) in the reaction mixture, even when the mixture was heated to 40 °C. Nevertheless, after 3 hours of irradiation in the same reaction mixture (without TiO\(_2\), with H\(_2\)O\(_2\)) a slight conversion (ca. 7%) of Ph\(_2\)S to Ph\(_2\)SO\(_2\) as the final product took place (Fig. S2a†). We suggest that the residual oxidation of diphenyl sulphide is possible due to H\(_2\)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 photolysis of H\(_2\)O\(_2\) initiated at any wavelength lower than 380 nm was reported by Cataldo.\(^{28}\)

These results clearly show that the oxidation of Ph\(_2\)S in the presence of anatase materials is possible both as catalytic and photocatalytic processes. However, a significantly higher conversion of Ph\(_2\)S for photocatalytic conditions compared to the dark processes was observed (Fig. S3a and b†). A similar positive effect of light was observed when Ph\(_2\)SO as a substrate was used (Fig. S10†). Both photocatalytic and catalytic oxidation of Ph\(_2\)S at anatase materials leads mainly to Ph\(_2\)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.

![Table 1](https://example.com/table1.png)

| Material | Phase     | Specific surface area/m\(^2\) g\(^{-1}\) | Crystal size/nm |
|----------|-----------|---------------------------------|-----------------|
| N100     | Anatase   | 97 ± 2                          | 18.1            |
| TRX_A    | Anatase   | 90 ± 2                          | 17.3            |
| TRX_R    | Rutile    | 5.3 ± 0.1                       | 48.2            |
| CR-EL    | Rutile    | 8 ± 0.1                         | 46.9            |

\(^{a}\) (Photo)catalytic conversion of diphenyl sulphide in the presence of anatase and rutile.

Results of photocatalytic oxidation of Ph\(_2\)S at rutile materials are depicted in Fig. 2c and d. Photocatalytic conversion of Ph\(_2\)S at rutile materials was significantly faster compared to both photocatalytic and catalytic conditions applied to anatase materials. The total conversion of Ph\(_2\)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 Ph\(_2\)S to Ph\(_2\)SO conversion within the first 15 min of irradiation was ≥2%. Oxidation of Ph\(_2\)S at rutile materials led to Ph\(_2\)SO as the main product. High selectivity to Ph\(_2\)SO at the beginning of the photocatalytic reaction was noticed (ca. 100%). During the reaction course the selectivity to Ph\(_2\)SO was decreasing, while the production of Ph\(_2\)SO\(_2\) became the dominant process. However, upon further irradiation, the production of Ph\(_2\)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 Ph\(_2\)S nor Ph\(_2\)SO used as a substrate (Fig. S4 and S11a†).

Interestingly, the total concentration of analyzed reactants (Ph\(_2\)S, Ph\(_2\)SO, Ph\(_2\)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 H\(_2\)O\(_2\) in this reaction a new portion of H\(_2\)O\(_2\) was added after 90 min of irradiation (Fig. S7†). No increase of the selectivity to Ph\(_2\)SO\(_2\) was observed. Furthermore, in our previous work we showed that after almost...
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,\(^{20}\) 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 \( \text{CR-EL} \) 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 Vosooghian et al. in their meticulous analysis.\(^{29}\)

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 (\( \text{i.e.} \), 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 \( \text{Ph}_2\text{SO}_2 \) due to a synergistic effect of these phases reported in numerous publications on P25 and similar materials.\(^{28-34}\) 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).\(^{22}\) The authors showed high selectivity to sulfones. Rodriguez-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.\textsuperscript{35} The authors showed that \( \text{Ph}_2\text{S} \) oxidation over reference anatase leads to sulfone production, while at protein-templated \( \text{TiO}_2 \) mainly sulfoxide was produced. Radko et al. studied catalytic oxidation of sulfides 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.\textsuperscript{28} In our current study catalytic \( \text{Ph}_2\text{S} \) oxidation with \( \text{H}_2\text{O}_2 \) at anatase \( \text{TiO}_2 \) to \( \text{Ph}_2\text{SO}_2 \) was observed. Contrary to that, no catalytic oxidation of \( \text{Ph}_2\text{S} \) at rutile materials was observe. We suggest that the opposite results can be attributed to the various activation paths of hydrogen peroxide (and maybe \( \text{Ph}_2\text{S} \)) 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 \( \text{m}^2\text{ g}^{-1} \)) was performed. Although the specific surface area was 3-5 times higher in this case, no catalytic oxidation of \( \text{Ph}_2\text{S} \) was observed as well.

Published articles describing photocatalytic oxidation of sulfides 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.\textsuperscript{29} Also, superoxide radical anion \( \text{O}_2^{-} \) plays a key role in the reaction.\textsuperscript{30}\textsuperscript{–}\textsuperscript{32} Zhang et al. suggested that \( \text{O}_2^{-} \) reacts with generated organosulfur radical.\textsuperscript{33} Lang et al. studied \( \text{Ph}_2\text{S} \) visible light induced oxidation in the presence of a dye (alizarin red S) and TEMPO as the redox mediator to increase the dye stability.\textsuperscript{34}\textsuperscript{–}\textsuperscript{38} The authors reported \( \text{Ph}_2\text{S} \) conversion to \( \text{Ph}_2\text{SO}_2 \) pointing at \( \text{O}_2^{-} \) importance in the reaction mechanism. Li et al. confirmed significance of superoxide radical anions and sulphide cation radicals by experiments involving radical scavengers and \( ^{18}\text{O}_2 \).	extsuperscript{39} Vosooghian 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).\textsuperscript{39} In the presence of photosensitizers able to produce singlet oxygen, it is postulated that \( ^1\text{O}_2 \) may participate in the \( \text{Ph}_2\text{S} \) oxidation.\textsuperscript{40}\textsuperscript{–}\textsuperscript{44} 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 \( \text{Ph}_2\text{S}^{2+} \) formation and its reaction with either \( \text{O}_2^{-} \) or \( \text{O}_2 \) should lead to the products (\( \text{Ph}_2\text{SO} \), \( \text{Ph}_2\text{SO}_2 \)), which have not been detected.

According to our knowledge the role of \( \text{H}_2\text{O}_2 \) in the mechanism and its influence on the efficiency of photocatalytic \( \text{Ph}_2\text{S} \) oxidation have not been reported in the literature. The presence of \( \text{H}_2\text{O}_2 \) dramatically influences the generation of \( \text{HO}^+ \) and \( \text{O}_2^{-} \) at rutile and anatase material (Fig. 3, red color). Photocatalytic production of hydroxyl radicals at rutile is insufficient, however, the generation of this reactive species is strongly enhanced in the presence of \( \text{H}_2\text{O}_2 \), as the result of its reduction. On the other hand, a similar effect of \( \text{H}_2\text{O}_2 \) on anatase photoactivity is not observed. Addition of \( \text{H}_2\text{O}_2 \) leads to increasing \( \text{O}_2^{-} \) production at anatase, as the result of \( \text{H}_2\text{O}_2 \) oxidation with holes.\textsuperscript{28} Generally, rutile has better reduction properties compared to anatase, meanwhile, anatase is a better oxidant.\textsuperscript{34} Using various \( \text{TiO}_2 \) phase compositions in the combination with \( \text{H}_2\text{O}_2 \) 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 \( \text{HO}^+ \) 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 hydroxysterterephthalic acid (TAOH) is formed. TAOH generation in the presence of hydrogen peroxide (2 mmol dm\textsuperscript{-3}) was also investigated. The TAOH formation is depicted in Fig. S6.\textsuperscript{†} In the absence of hydrogen peroxide anatase shows a more efficient \( \text{HO}^+ \) generation compared to the rutile (TAOH concentration amounted 57 \( \mu\text{mol dm}^{-3} \) and 29 \( \mu\text{mol dm}^{-3} \) respectively). However, after addition of \( \text{H}_2\text{O}_2 \) to the system containing anatase, TAOH generation decreased (10 \( \mu\text{mol dm}^{-3} \)), while it significantly increased for rutile material (452 \( \mu\text{mol dm}^{-3} \)). Undoubtedly, combination of hydrogen peroxide and rutile significantly enhances \( \text{HO}^+ \) generation.

The presence of hydrogen peroxide can lead to the increased concentration of photogenerated \( \text{O}_2^{-} \) and/or \( \text{HO}^+ \) radicals, whereas only the influence of \( \text{O}_2^{-} \) on the oxidation of \( \text{Ph}_2\text{S} \) is known. In order to determine the possible role of hydroxyl radicals in the reaction, the Fenton process was induced in the presence of \( \text{Ph}_2\text{S} \). In the Fenton reaction (production of \( \text{HO}^+ \) in the reaction of \( \text{H}_2\text{O}_2 \) with iron(II) cations) the conversion of \( \text{Ph}_2\text{S} \) and efficient production of \( \text{Ph}_2\text{SO}_2 \) were observed (Fig. 4a). Slight oxidation of \( \text{Ph}_2\text{SO} \) (\( \text{Ph}_2\text{SO}_2 \) formation) in the Fenton process was also noticed. However, an inefficient \( \text{Ph}_2\text{SO}_2 \) generation might originate from the transformation of other species that contaminate the original \( \text{Ph}_2\text{SO} \) sample (Fig. 4b). This shows that the hydroxyl radical and/or hydrogen peroxide (the reagent in this reaction) is able to oxidize \( \text{Ph}_2\text{S} \) to \( \text{Ph}_2\text{SO}_2 \). Recently, we described that the addition of tert-butyl alcohol (hydroxyl radical scavenger) significantly diminishes the \( \text{Ph}_2\text{S} \) conversion.\textsuperscript{45} Furthermore, isotopic oxygen (\( ^{18}\text{H}_2 \text{O} \)) 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 \( \text{H}_2\text{O}_2 \)) originated mainly from water.\textsuperscript{34} We concluded that hydroxyl radicals play a significant role in the first step of diphenyl sulphide oxidation, yielding \( \text{Ph}_2\text{SO}_2 \). Similarly, in our actual system \( \text{HO}^+ \) is involved in the oxidation of \( \text{Ph}_2\text{S} \) to \( \text{Ph}_2\text{SO} \), but the further oxidation to \( \text{Ph}_2\text{SO}_2 \) is not possible.

In order to explain why the Fenton reaction leads only to \( \text{Ph}_2\text{SO}_2 \) generation, cyclic voltammetry measurements were performed (Fig. 5). In the case of \( \text{Ph}_2\text{S} \), two oxidation peaks (\( E_{\text{F}_{\text{Ph}_2\text{S}}} = 1.83 \text{ V vs SHE} \); \( E_{\text{F}_{\text{Ph}_2\text{S}}} = 2.07 \text{ V vs SHE} \)) and one reduction peak (\( E_{\text{C}_{\text{Ph}_2\text{S}}} = 2.01 \text{ V vs SHE} \)) were observed in the cyclic voltammogram. In the case of \( \text{Ph}_2\text{SO}_2 \) only one oxidation peak was detected (\( E_{\text{F}_{\text{Ph}_2\text{SO}_2}} = 2.43 \text{ V vs SHE} \)). Finally, the CV of \( \text{Ph}_2\text{SO}_2 \) has shown neither oxidation nor reduction peaks in the explored potential range. In the case of \( \text{Ph}_2\text{S} \) cyclic voltammogram, the first oxidation at 1.83 V vs. SHE can presumably be attributed to \( \text{Ph}_2\text{S}^{2+} \) formation. Furthermore, based on the CV measurements the formation of \( \text{Ph}_2\text{SO} \) as an irreversible process was found. The second oxidation process at 2.07 V vs.
SHE is a partially reversible reaction ($E_{c,Ph_{2}S}^0 = 2.01 \text{ V vs. SHE}$) 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 Ph$_2$S to Ph$_2$SO can be achieved by HO$^\cdot$ ($\text{HO}^\cdot$/H$_2$O $= 2.27 \text{ V vs. SHE}, \text{pH} = 7$ (ref. 52)). CV of Ph$_2$SO reveals that the potential of sulfoxide oxidation is too high to enable its oxidation by hydroxyl radicals. Nevertheless, Ph$_2$SO can be still directly oxidized to Ph$_2$SO$^+$ by TiO$_2$ VB holes (step III, Fig. 3). To summarize, the electrochemical and Fenton experiments showed that Ph$_2$S can be easily oxidized by HO$^\cdot$ to Ph$_2$S$^{3+}$. However, holes are required for further oxidation of Ph$_2$SO to the Ph$_2$SO$^{4+}$ radical, which explains why the Fenton reaction led only to Ph$_2$SO. The Fenton process does not generate O$_2$$^{2-}$, however, Ph$_2$SO as a product of the Fenton reaction was effortlessly detected. It is noteworthy that in the Fenton reaction the concentration of hydrogen peroxide was the same that in the photocatalytic system. The results suggest that H$_2$O$_2$ is involved in the Ph$_2$S$^{3+}$ to Ph$_2$SO conversion (Fig. 3). Our

![Diagram of oxidative processes](image-url)
The presented results indicate that hydrogen peroxide and superoxide radical anion play a similar role, oxidizing the radical cations, Ph2S+ and Ph2SO2+, 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 Ph2S involves only the activation of hydrogen peroxide reduction, without any contribution of O2 (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 O2 on the reaction progress was significant. A decrease of the Ph2S 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 Ph2S conversion decreased, but photocatalytic oxidation of Ph2S to Ph2SO was still observed. Moreover, changes in the selectivity to Ph2SO2 at TRX_A were observed. The selectivity to Ph2SO2 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 Ph2S conversion under various conditions were observed (Fig. S9a†).

Nevertheless, remarkable changes in the selectivity to Ph2SO were observed. Under oxygen-rich conditions a decrease in the production of Ph2SO, and an increase in the Ph2SO2 production after first 15 min of the reaction, were observed (Fig. S9b†). Moreover, the point of the second increase of the Ph2SO production appeared earlier (after 30 min of irradiation) for oxygen-rich conditions.

The first stable oxidation product, Ph2SO, can be further oxidized by holes from the valence band of TiO2 to Ph2SO2+. This intermediate is further transformed to Ph2SO2 in the reaction with superoxide radical (O2−) as the result of either oxygen reduction or H2O2 oxidation. To confirm this path a possibility of Ph2SO oxidation, both in the dark and upon irradiation in the presence of hydrogen peroxide and TiO2, was studied. In the case of anatase material, an efficient conversion of Ph2SO to Ph2SO2 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 O2− production at anatase than on the rutile in the presence of H2O2. Furthermore, the possibility of Ph2SO oxidation upon irradiation in the presence of TiO2, but in the absence of H2O2, was tested (Fig. S12†). Low conversion of Ph2SO 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 Fe3+ as an electron acceptor), the conversion of Ph2SO to Ph2SO2 was not observed.

Abovementioned results clearly show that O2− radicals can easily react with Ph2SO2+, yielding Ph2SO2. We suggest that the formation of Ph2SO2 is possible in the presence of O2− and Ph2SO (hole oxidized Ph2SO), however, such reaction has a low effectiveness. In order to enhance the production of Ph2SO2, the presence of hydrogen peroxide is necessary. The full mechanism of the photocatalytic Ph2S oxidation in the presence of hydrogen peroxide is shown in Fig. 3.

Conclusions

In summary, we demonstrated that Ph2S oxidation in the presence of hydrogen peroxide at anatase-TiO2 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 Ph2SO2 as the product, whereas, the same reaction in the presence of rutile leads mainly to Ph2SO2 formation. In the case of rutile the total conversion of Ph2S was observed already after 15 min (compared to at least 1 h required for a catalytic conversion) with nearly 100% selectivity towards Ph2SO2. It is the first reported photocatalytic conversion of Ph2S using H2O2 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 H2O2 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 Ph₂S involves only the activation of hydrogen peroxide at the catalyst surface, without any contribution of dioxygen. Whereas, the presence of O₂ in the photocatalytic reaction increases the Ph₂S conversion due to generation of O₂⁻⁻. Studies on the mechanistic details revealed the dual role of H₂O₂ (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 O₂⁻⁻ and HO⁻ radicals, respectively. Hydroxyl and superoxide radicals play an important role in various reaction steps. Hydroxyl radicals can oxidize Ph₂S to Ph₂S₂⁺⁺, however, Ph₂SO oxidation to Ph₂SO⁺⁺ requires a stronger oxidant, i.e. holes. The cation radical intermediates, Ph₂S⁺⁺ and Ph₂SO⁺⁺, react with superoxide anions or directly with H₂O₂ yielding stable sulfoxide (Ph₂SO) and sulfone (Ph₂SO₃).

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 Ph2SO oxidation to Ph2SO stable sulfoxide (Ph2SO) and sulfone (Ph2SO2).

Hydrogen peroxide at the catalyst surface, without any contri-


cation of O2

catalytic reaction increases the Ph 2S conversion due to


generation of O2

oxidized or reduced photocatalytically, resulting in the genera-


tion of O2⁻⁻ and HO⁻ radicals, respectively. Hydroxyl and


superoxide radicals play an important role in various reaction


steps. Hydroxyl radicals can oxidize Ph₂S to Ph₂S⁺⁺, however,


Ph₂SO oxidation to Ph₂SO⁺⁺ requires a stronger oxidant, i.e.


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

Conflicts of interest
There are no conflicts to declare.

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