Full Length Article

Effect of carbon-interaction on structure-photoactivity of Cu doped amorphous TiO₂ catalysts for visible-light-oriented oxidative desulphurization of dibenzothiophene


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GRAPHICAL ABSTRACT

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ABSTRACT

Amorphous TiO₂ (AT) was successfully prepared via the sol-gel technique, using different titanium sources followed by incorporation of copper via the electrochemical method to give CuO/TiO₂ (CAT) catalysts. The catalysts were characterized via XRD, N₂ physisorption, FTIR, TEM, EDX, XPS, ESR and UV–Vis DRS. The results verified that the use of different titanium precursors have profound effect on the physicochemical properties of the AT catalysts. Further one-pot self-doping carbon from titanium precursor during the addition of copper could greatly enhanced the photocatalytic activity of CAT on the oxidative desulphurization of dibenzothiophene (DBT). 15 CATTBOT exhibited the best performance mainly due to the narrowest band gap and higher numbers of O–Ti-C and Ti–O–C bonds, as well as appropriate amount of Ti³⁺ surface defects (TSD). These abovementioned properties offered good mobility of electron-hole pairs and/or trap the electrons for enhancement of photoactivity under irradiation of visible light. Kinetic studies showed that the photocatalytic oxidative desulphurization of DBT followed the pseudo-first order Langmuir-Hinshelwood model, where the adsorption was the
1. Introduction

The release of SOx which mainly formed via the burning of sulphur-containing compounds in fuel oils is one of the most serious worldwide environmental concerns [1]. In order to minimize its harmful influence on human health and the environment, the reduction of sulphur content in fuel is urgently required [2–4]. Photocatalytic degradation process using heterogeneous catalysts is fascinating and prominent for environmental protection as an environmental friendly, low cost, and sustainable technology [5]. Among photocatalytic materials, TiO2 is widely used for degradation of dyes and organic pollutants, as well as for the removal of inorganic materials due to its excellent photoactivity [6]. However, TiO2 only responds to ultraviolet radiation due to its large band gap (3.2 eV) and fast electron-hole recombination rate, which causes difficulties with respect to its practical application [7]. As a result, great effort has been expended toward the improvement of new visible-light-responsive photocatalysts.

Among the various types of TiO2 catalysts, amorphous TiO2 nanoparticles have experienced intensive advances, and a growing number of studies have started to challenge the belief that the amorphous TiO2 is not photoactive [8]. As compared to crystalline TiO2, amorphous TiO2 is easily prepared, owing to its lower demand of substrate [9]. It also does not require heat treatment processes, and may allow the use of a much wider range of dopants. Amorphous TiO2 has been used for various photocatalytic reactions such as hydrogen evolution from water, decolorization of methylene blue and disinfection of algae blooms, as well as oxidative desulphurization of dibenzothiophene [10–12].

Previous study showed that the use of different titanium precursor to synthesize amorphous TiO2 has contributed to dissimilar pore size distribution and surface area [13]. The presence of long chain carbon might reduce hydrolysis and condensation rate and restrict the particle nucleation, thus yields aggregated bigger particles with small surface area and high pore volume. During hydrolysis, Ti-alkoxide react with water to form Ti(OH)4 and alcohol, which subsequently polymerized to a three-dimensional oxide network [14]. The alcohol group that formed after hydrolysis process are determined by the carbon chain of alkoxide and subsequent drying or calcination might remove these species.

Recently, it has been reported that band gap modification via non-metal doping such as C, N, S, F and B can produce highly active TiO2 photocatalysts [15]. Non-metal doping is a promising way to enhance the photoabsorption properties of TiO2 by lowering the band gap and shift the absorption edge to the visible light region [16]. It is believed that bulk doping or matrix substitution can introduce interior electron states within the band gap and thus shift the response and harvest visible light for applications in photocatalysis [17]. In addition, the combination of TiO2 with other semiconductors with narrow band gaps is also an efficient pathway to extend the visible light response of TiO2-based catalysts. For coupling with TiO2, nanosized CuO is an ideal candidate due to its proper band edge, low cost, low toxicity, and abundant supply [18].

In recent years, numerous nanosized particles of ZnO, α-FeOOH and NiO supported on mesostructured silica nanoparticles (MSN), Ag supported on mesoporous TiO2 nanoparticles (MTN) and also CuO supported on carbon nanotubes (CNT) were successfully prepared via a facile electrochemical technique [19–22]. Their excellent performances in the photocatalytic degradation of dyes and organic pollutants, along with CO2 reforming of CH4, would encourage additional modification. In previous work, the electrochemical method provided a stronger interaction between the dopant and support, and consequently lessened the agglomeration of dopant, thus forming uniform and smaller dopant particles [23]. Therefore, herein we report new findings on (i) self-doped C via the electrochemical method for synthesis of CuO loaded onto AT catalysts, and (ii) their enhanced performance towards photocatalytic oxidative desulphurization of DBT under visible light irradiation. The physicochemical properties of the catalysts were well characterized by X-ray diffraction (XRD), N2 physisorption, Transmission electron microscopy (TEM), energy dispersive X-ray (EDX), Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), and ultraviolet-visible diffuse reflectance spectroscopy (UV–Vis DRS). The proposed structure of the catalyst, kinetic studies, and the proposed mechanism of photo-oxidative desulphurization are also discussed. We believe that this study could contribute to future design approaches for numerous organic pollutants and other reactions.

2. Experimental

2.1. Materials

Titanium tetrabutoxide (TBOT) was purchased from Merck Sdn. Bhd., Malaysia. Other chemicals used were similar with those used and prepared by earlier reported studies [24,25].

2.2. Synthesis of catalyst

The amorphous TiO2 was synthesized by sol-gel technique using TTIP or TBOT as titanium precursor and denoted as AT_{TTIP} and AT_{TBOT}, respectively [25]. The CuO/TiO2 amorphous were synthesized via electrolys method using AT_{TBOT} as support, based on previous reported study with some modification [25–27].

2.3. Characterization of the catalyst

The structural properties of the catalysts were determined with X-ray diffraction (XRD) recorded on powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Ka radiation source. Beckman Coulter SA 3100 surface area analyzer was used in N2 physisorption analysis to study the textural properties which is conducted at 77 K. Prior to measurement, the samples were degassed at 373 K for 1 h. The Brunauer-Emmett-Teller (BET) method was used to calculate surface area from the N2 adsorption isotherms. FTIR was performed by the KBr method using PerkinElmer Spectrum GX FTIR spectrometer in the range of 400–4000 cm$^{-1}$. Transmission electron microscopy (TEM) was used to examine the morphological properties using JEOL JEM-2100F while energy dispersive X-ray (EDX) was carried out to identify the chemical composition of the catalysts. The X-ray photoelectron spectroscopy (XPS) was conducted on a Shimadzu Axis Ultra DLD spectrometer, using Al X-ray source over binding energies of 0–800 eV to determine the chemical oxidation of the catalyst. The electron spinning resonance (ESR) analysis was performed using JEOL JESFA100 ESR spectrometer at room temperature. UV–Vis diffuse reflectance spectra (UV–Vis DRS) using a PIKE Technologies DiffuseIR in the range of 300 to 800 nm was conducted at room temperature to examine the band gap of the catalysts.

2.4. Photocatalytic oxidative desulphurization reaction

The photocatalytic oxidative desulphurization of dibenzothiophene (DBT) were carried out in a batch reactor as reported in our previous...
study [25].

3. Results and discussion

3.1. Characterisation of the catalyst

Two types of amorphous TiO₂ catalysts were used for photocatalytic oxidative desulphurization of dibenzothiophene (DBT), which were prepared from two different titanium sources; titanium tetraisopropoxide (TTIP) and titanium tetrabutoxide (TBOT), denoted as ATₜₜ and ATₜₜ respectively. The pore width distribution of both catalysts were calculated by Barrett-Joyner-Halenda (BJH) method as shown in Fig. 1. The ATₜₜ consists of mainly bimodal pore structure, in the range of 20–100 nm, as compared to ATₜₜ with bimodal pore structure in the range of 3–50 nm. The existence of longer carbon chains in TBOT might lead to a lower hydrolysis and condensation rate, which limits particle nucleation and produces aggregated larger particles with lower surface area and higher pore volume (Table 1) [28,29]. The higher pore volume of ATₜₜ could provide more sites for DBT molecules to be adsorbed, which subsequently enhance photooxidation [30]. Although it was reported that the larger pore size could only weaken the attraction toward adsorbate via dispersive forces, its important role in enhancing the adsorption capacity of the desired reaction could not be ruled out [31]. Similar phenomenon was reported previously on the adsorption of DBT by activated carbon, where the adsorption capacity might lead to a lower hydrolysis and condensation rate, which limits particle nucleation and produces aggregated larger particles with lower surface area [32].

3.1.1. Structural studies

Due to the higher performance of the ATₜₜ, it was chosen as a model catalyst and supported with the lower band gap of CuO via electrochemical method and denoted as CATₜₜ [25]. Two different loading of CuO, 5 and 15 wt% were investigated, and Fig. S1 shows the XRD pattern of ATₜₜ and both CATₜₜ. As can be seen, only a broad peak between 20 = 20–30° is found in ATₜₜ, with no distinct peak of TiO₂, signifying the presence of an amorphous structure [33]. A similar characteristic peaks to ATₜₜ were observed for CATₜₜ, proving the amorphous nature of the catalyst, which is in agreement with the XRD result [8]. Meanwhile, the presence of CuO nanoparticles on the 15 CATₜₜ was confirmed by its interplanar distance of 0.2720 nm as shown in inset figure of Fig. 3D. To further identify the elemental compositions and dispersion state of the dopants on 15 CATₜₜ, EDX analysis equipped with elemental mapping was performed and the results were shown in Figs. S2 and 3E–G, respectively. The EDX spectrum (Fig. S2) further confirmed the presence of Cu, C and N in the ATₜₜ support. In addition, the dispersion of all dopants was noticeably observed by EDX mapping as shown in the Fig. 3E–G.

3.1.4. Vibrational spectroscopy

The FTIR analysis was then performed between the region of 1600 and 400 cm⁻¹ and the spectra are presented in Fig. 4A. Comparing with ATₜₜ (Fig. 4A/a), the ATₜₜ (Fig. 4A/b) displays an obvious peak at 1460 cm⁻¹, attributed to a CH₂ scissoring, which is supposed to originate from the diffusion of carbon chain of butoxide after hydrolysis [19]. This may give significant effect on the higher performance of the ATₜₜ rather than ATₜₜ. Meanwhile, the aforementioned peak for both 5 CATₜₜ (Fig. 4A/c) and 15 CATₜₜ (Fig. 4A/d) catalysts became stronger after electrolysis process, and strong triplet bands corresponding to C–N stretching appeared at 1083–1141 cm⁻¹, signifying the probable contribution of the supporting electrolyte TEAP on the ATₜₜ support [25,36]. A small peak was also detected at 1005 cm⁻¹ after the electrolysis, which could be attributed to C–O and/or Ti–O–C bond that might also originate from the TEAP or trace butanol in the ATₜₜ [37]. In order to further confirm the presence of the above-mentioned non-metal species, 15 CATₜₜ was calcined at 873 K and denoted as 15 CATₜₜ(Teal) (Fig. 4A/e). It can be seen that the related species were totally removed after calcination process, confirming the fact of the postulation above. Next, the broad band at 800–400 cm⁻¹ was investigated via Gaussian curve-fitting. As presented in Fig. S3, four strong bands were detected at 735–475 cm⁻¹, which were attributed to Ti–O–Ti vibration modes [38]. For better view, the intensities of the mentioned bands are summarized in Fig. 4B. It can be seen that the Ti–O–Ti vibration mode decreased with the increasing CuO loading to produce the Ti–O–C bonds, elucidating the involvement of carbon sourced from TEAP in the interaction with the ATₜₜ support [39].

For further investigation on the hydroxyl groups of the catalysts, the catalysts were evacuated for 1 h at 623 K to eliminate the physisorbed water and the spectra are presented in Fig. 4C. Three leading bands

![Fig. 1. Pore distribution of ATₜₜ and ATₜₜ.](Fig. 1. Pore distribution of ATₜₜ and ATₜₜ.)
The introduction of dopants noticeably decreased the amount of Ti\(^{3+}\), indicating the loss of Vo, possibly due to the in-perturbation of titania framework by the presence of carbon dopant [5]. Moreover, the electrolyzed Cu ions are also supposed to interact with the germinal hydroxyl groups of ATTBOT to form Ti–C or/and Ti–C bonds, as reported in our previous study [25]. Thus, it could be dictated that besides C- and N-, the C- also interacted with the ATTBOT support.

### 3.1.5. Chemical oxidation state determination

In order to clarify the exact structure of the catalysts, 5 CAT\(_{\text{TBOT}}\) and 15 CAT\(_{\text{TBOT}}\) were then subjected to XPS analysis, and the results were compared with the parent ATTBOT. The XPS spectra of Ti 2p in the region of 470–450 eV was displayed in Fig. 5A. An obvious peak set corresponding to the Ti\(^{4+}\) state (Ti 2p\(_{1/2}\) and 2p\(_{3/2}\)) was detected for ATTBOT (Fig. 5A/a). The introduction of dopants noticeably decreased the intensity and split to two peak sets of Ti\(^{4+}\) and Ti\(^{3+}\) states (Fig. 5A/b and A/c). It was observed that after electrolysis, the Ti\(^{4+}\) ions were reduced to Ti\(^{3+}\) state to allow the generation of oxygen vacancies (Vo) [18]. However, the increasing in electrolysis time seems to decrease the amount of Ti\(^{3+}\), indicating the loss of Vo, possibly due to the incorporation of C atom into Vo to form O–Ti–C bond. Fig. 5B presents the deconvolution results of C 1 s in the region of 280–280 eV. The peak at 283.5 eV corresponded to C–C bond which might originate from butanol residues and ethyl groups derived from TEAP [42]. The other peak at around 285.7 eV is attributed to C–H bond, while the O–Ti–C, Ti–O–C and C–N stretching peaks for CAT\(_{\text{TBOT}}\) were detected at 282.3, 286.6 and 287.4 eV, respectively [43,44]. The formation of carbon atoms in the interstitial positions of the TiO\(_2\) lattice can occur by replacing titanium atoms in the form of Ti–O–C, while O–Ti–C bonds result from the substitution of Vo by a carbon atom [45]. From overall spectra, it can be summarized that the longer the electrolysis time, the higher amount of O–Ti–C or/and Ti–O–C bonds was formed, which contribute to the decreasing in Ti\(^{3+}\) species. These results verified the possible interaction of C that is originated from butanol residues and/or TEAP with ATTBOT, which is in line with the FTIR data.

Next, the ESR analysis were performed to study the electronic structure of the catalysts and the results are shown in Fig. 6A. A strong signal was observed for CAT\(_{\text{TBOT}}\) at g = 1.94, corresponding to the high amount of Ti\(^{3+}\) surface defects (TSD), which is in accordance with the XPS data (Fig. 5A). The decrease in TSD signal with increasing electrolysis time also verified the reduction of Vo due to the formation of O–Ti–C bonds (Fig. 6B) [46]. This was in parallel with the consumption of TEAP, as confirmed by the FTIR and further supported by the XPS analysis.

The band gap energy (E\(_g\)) of the catalysts were calculated by equation E\(_g\) = 1240/\(\alpha\) – 5, based on the UV–vis DRS spectra as shown in Fig. 7A. The observed E\(_g\) were then tabulated in Table 1. ATTBOT with a band gap of 3.26 eV, shows a red shift in absorption edge by the incorporation of dopants, demonstrating a significant improvement of the catalysts toward visible light absorption. In order to further confirm that the narrow band gap of the catalyst was also influenced by C, not by the Cu dopant only, the band gap of 15 CAT\(_{\text{TBOT}}\) was compared with 15 CAT\(_{\text{TBOT-TB}}\). It can be noted that the band gap of 15 CAT\(_{\text{TBOT-TB}}\) was higher, further supporting the contribution of non-metal elements in lowering the band gap of catalysts [47]. The presence of O–Ti–N bond that creating N-induced mid-gap was reported in our previous study [25]. However, in this study, the O–Ti–C bond also produces a new impurity level between the conduction and valence band of TiO\(_2\) [17]. The existence of those impurity level was then confirmed by Tauc’s plot of (αE\(^{1/2}\)) versus E (eV) for 15 CAT\(_{\text{TBOT}}\) as shown in Fig. 7B. It can be seen that, there are two band gap energies detected in the catalyst, in which the lower value (1.60 eV) might attributed to E\(_g\) between valence band and interbands, and 2.56 eV represents the E\(_g\) between the valence and conduction band [42]. It has been previously reported that impurity level could provide much easier electron excitation under visible light irradiation, thus more photogenerated electron-hole pairs might be produced for a better photoactivity [48].

### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m(^2)g(^{-1}))</th>
<th>Total pore volume (x10(^{-1}) cm(^3)g(^{-1}))</th>
<th>Band gap, E(_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATTBOT</td>
<td>402</td>
<td>4.51</td>
<td>3.16</td>
</tr>
<tr>
<td>CAT(_{\text{TBOT}})</td>
<td>355</td>
<td>5.14</td>
<td>3.26</td>
</tr>
<tr>
<td>5 CAT(_{\text{TBOT}})</td>
<td>198</td>
<td>2.80</td>
<td>2.95</td>
</tr>
<tr>
<td>15 CAT(_{\text{TBOT}})</td>
<td>181</td>
<td>2.58</td>
<td>2.56</td>
</tr>
<tr>
<td>15 CAT(_{\text{TBOT-TB}})</td>
<td>–</td>
<td>–</td>
<td>2.70</td>
</tr>
</tbody>
</table>

* Band gap derived from 1240/\(\alpha\) – 5, based on the UV–vis DRS spectra as shown in Fig. 7A. The observed E\(_g\) were then tabulated in Table 1. ATTBOT with a band gap of 3.26 eV, shows a red shift in absorption edge by the incorporation of dopants, demonstrating a significant improvement of the catalysts toward visible light absorption. In order to further confirm that the narrow band gap of the catalyst was also influenced by C, not by the Cu dopant only, the band gap of 15 CAT\(_{\text{TBOT}}\) was compared with 15 CAT\(_{\text{TBOT-TB}}\). It can be noted that the band gap of 15 CAT\(_{\text{TBOT-TB}}\) was higher, further supporting the contribution of non-metal elements in lowering the band gap of catalysts [47]. The presence of O–Ti–N bond that creating N-induced mid-gap was reported in our previous study [25]. However, in this study, the O–Ti–C bond also produces a new impurity level between the conduction and valence band of TiO\(_2\) [17]. The existence of those impurity level was then confirmed by Tauc’s plot of (αE\(^{1/2}\)) versus E (eV) for 15 CAT\(_{\text{TBOT}}\) as shown in Fig. 7B. It can be seen that, there are two band gap energies detected in the catalyst, in which the lower value (1.60 eV) might attributed to E\(_g\) between valence band and interbands, and 2.56 eV represents the E\(_g\) between the valence and conduction band [42]. It has been previously reported that impurity level could provide much easier electron excitation under visible light irradiation, thus more photogenerated electron-hole pairs might be produced for a better photoactivity [48].

![Fig. 2](image-url) (A) Nitrogen adsorption-desorption isotherm of a) ATTBOT, b) 5 CAT\(_{\text{TBOT}}\) and c) 15 CAT\(_{\text{TBOT}}\) and (B) Pore distribution of catalysts, and (inset figure) ATTBOT.
3.2. Proposed structure of the catalysts

A probable structure of the ATTBOT and CATTBOT are then illustrated in Fig. 8 according to the above characterization results. In the presence of water, alkoxides (TBOT) were hydrolyzed, forming butanol and Ti (OH)₄, which then polymerized to form a three-dimensional ATTBOT oxide network [49,28]. Electrolysis of the ATTBOT in the presence of the weak base TEAP then led to the introduction of C and Cu to form Ti–O–C, O–Ti–C and Ti–O–Cu(I) bonds into the ATTBOT network, as verified by the FTIR and XPS data [37,21,50]. Noticeably, oven dried ATTBOT at 383 K allowed self-doped C into the ATTBOT network, which originated from butanol residue in the system [51]. Based on the FTIR and XPS data, the O–Ti–C and Ti–O–C bonds seemed to dominate prior to the Ti–O–Cu(I) bond, and these occurrences also resulted in the decline of TSD and Vₐ, as confirmed by the ESR analysis. During electrolysis, Cu is considered as the last element that entered the TiO₂ network after C. The C might be originated from trace of butanol and TEAP supporting electrolyte. It is reported previously that the structure of support can be affected by sequence of dopants introduction, in which C might dispersed homogenously on ATTBOT support and hindered a possible inclusion of Cu [5]. Furthermore, due to the smaller atomic radii of C (70 pm) as compared to Cu (128 pm), as well as its higher electronegativity, led to easy formation of Ti–O–C than Ti–O–Cu(I) bond, as a consequence of removal of Ti⁴⁺ during electrolysis.

3.3. Photocatalytic oxidative desulphurization performance and proposed mechanism

As shown in Fig. 9A, the ATTBOT performed better in both extraction and photooxidation than the ATTTIP with the rates of 7.32 × 10⁻³ and 1.29 × 10⁻³ mM min⁻¹, respectively. These could be generally explained by the pore width distribution displayed in Fig. 1, in which the higher pore volume of ATTBOT provided more adsorption sites for DBT molecules, thus enhanced photooxidation. Overall, 15 CATTBOT...
demonstrated the best performance compared to other catalysts with the extraction and photooxidation rate of $8.14 \times 10^{-3}$ and $2.13 \times 10^{-3}$ mM min$^{-1}$, respectively. The adsorption capacity of 15 CATTBOT towards DBT molecules might be lower than other catalysts due to its lowest surface area and pore volume (Table 1). However, the higher rate shown by 15 CATTBOT may be due to the existence of the narrowest band gap, good interactions between C with ATTBOT support, and physical properties, which enhanced its photoactivity under visible light. Its larger number of O–Ti–C and Ti–O–C bonds, as well as an appropriate surface area and pore volume, increased the number of active sites and offered good surface contact with light to transport and/or trap electrons for enhancement of photoactivity. From the figure, it also could be clearly observed that 20 CATTBOT showed a lower extraction and photooxidation rates than 15 CATTBOT. This is most probably due to the agglomeration of Cu when excess of Cu was loaded onto ATTBOT, which further blocked the light penetration, thus decreased the activity \[52]\.

Fig. 9B shows the linear plot of ln ($C_0/C_t$) vs. irradiation time of

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Fig. 4. (A) FTIR spectra of a) ATTBOT, b) 5 CAT$_{\text{TROT}}$, c) 15 CAT$_{\text{TROT}}$ and d) 15 CAT$_{\text{TROT-cal}}$. (B) Intensity of the peaks in the 1600-400 cm$^{-1}$ region and (C) In evacuated system for region 3770-3700 cm$^{-1}$ of a) ATTBOT, b) 5 CAT$_{\text{TROT}}$ and c) 15 CAT$_{\text{TROT}}$.

Fig. 5. XPS spectra of (A) Ti 2p a) ATTBOT, b) 5 CAT$_{\text{TROT}}$ and c) 15 CAT$_{\text{TROT}}$ and (B) C 1s a) ATTBOT, b) 5 CAT$_{\text{TROT}}$ and c) 15 CAT$_{\text{TROT}}$.

Fig. 6. (A) ESR signals of the catalysts, (B) Intensity of TSD and CuO signals.

Fig. 7. Tauc plot of the catalysts.
photooxidation of DBT for initial concentrations in the range of 100 to 300 mg L\(^{-1}\) using 0.8 g L\(^{-1}\) of 15 CAT\(_{\text{TBOT}}\). The obtained straight line confirmed that the reaction followed the pseudo-first order kinetic of the Langmuir-Hinshelwood model [53]. A noteworthy effect of 15 CAT\(_{\text{TBOT}}\) on the photooxidation of DBT was shown by the \(k_{\text{app}}\) values listed in Table 2. It can be seen that the \(k_{\text{app}}\) value decreased inversely proportional with initial concentration, signifying that the DBT was saturated on the catalyst surface thus reduced the photooxidation effectiveness, and the system was less favourable at high concentrations [54]. The values of \(k_r\) (reaction rate constant) and \(k_{\text{LH}}\) (adsorption coefficient of the reactant) were 0.296 mg L\(^{-1}\) min\(^{-1}\) and 0.036 L mg\(^{-1}\), respectively (figure not shown), demonstrating that adsorption of DBT was the controlling step [55].

In order to examine the mechanism of photocatalytic oxidative
desulphurization of DBT, four important scavenging agents were used: potassium peroxodisulphate (PP), triethanolamine (TEOA), sodium hydrogen carbonate (SHC) and isopropanol (IP) as scavengers for electrons (e−), holes (h+), surface hydroxyl groups (•OHads) and hydroxyl groups in the bulk solution (•OHbulk), respectively. From Fig. 10A, it can be seen that h+ played a main role in photooxidation, assisted by •OHads, e− and •OHbulk. Consequently, it is proposed that, the electrons were excited from the valence band (VB) of TiO2 to the existing impurity level (C 1s) under visible light irradiation (Fig. 10B), before migrating to the conduction band (CB), leaving h+ at VB and impurity level [21, 56]. h+ could directly oxidize DBT, or produce •OHads when reacted with H2O or adsorbed OH− groups on the surface of TiO2 and oxidize DBT. In parallel, the excited e− reduced oxygen to superoxide anion radicals (•O2−), that is capable to oxidize DBT to DBTO2 or react with H+ to form •OHbulk. A similar phenomenon was reported previously for the photodegradation of 2-chlorophenol using IS-FeOOH/MSN [57].

The detailed photooxidation path of DBT is proposed as in Fig. 11, which was confirmed using GC-MSD (Figs. S4–S6), and in line with the other previous works. As shown in the figure, the DBT (1) was first oxidized to dibenzothiophene 5-oxide (DBTO) (2) and then to dibenzothiophene 5,5-dioxide (DBTO2) (3) [42]. A highly reactive 1,5-biradical intermediate may be formed when DBTO2 (3) was photo-excited by visible light irradiation, before being hydrogenated by OH groups of the catalyst and decomposed to biphenyl (4) [58]. At the same time, it is assumed that the sulphur species escaped as a gas from the solution. Further irradiated biphenyl may lead to the formation of biphenyl radical, which then reacted with O2 and degraded to benzoic acid (9) was produced from oxidation of the benzaldehyde [60]. At the same time, biphenyl radical may also being hydrolyzed to form hydroxybiphenyl (8) [59], that could fragmented into phenol compound (10), which finally hydrogenated into cyclohexen-1-one and 1-cyclohexen-1-ol [61].

3.4. Application on other S-containing compounds

The potential of 15 CATBOT catalyst was also examined on photocatalytic oxidative desulphurization of other S-containing compounds; thiophene (T), benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDDBT), and their performance rates were compared with DBT. As can be observed in Fig. 12, the photocatalytic performance decreased in the following order: 4,6-DMDDBT > DBT > BT > T. This is most probably due to their difference in electron densities which are 5.760, 5.758, 5.739 and 5.696, respectively [62]. It has been reported previously that the higher electron density of a sulphur atom has led to a higher reaction rate of a sulphur-containing compound [63]. This might generally explained a slightly higher performance rate of the catalyst towards 4,6-DMDDBT molecule than DBT [64].

4. Conclusion

In conclusion, amorphous TiO2 was successfully synthesized using different titanium precursors by the sol-gel method, and was self-doped with carbon by the electrochemical technique with different electrolysis time. This was then used as a catalyst in the photooxidative desulphurization of DBT under visible light irradiation. The physicochemical properties of the catalysts were examined by XRD, N2 physisorption, FTIR, TEM, EDX, XPS, ESR and UV–Vis DRS. XRD analysis identified the amorphous phase of the catalysts which are not affected by the presence of dopants. The N2 physisorption analysis verified the presence of larger bimodal pore structures in the range of 20–100 nm for ATBOT, as compared to ATTiP with bimodal pore structures in the range of 3–50 nm. The existence of larger pores was beneficial for greater adsorption of DBT molecules, which consequently enhanced photocatalytic activity. FTIR and XPS analyses revealed that the use of longer chain TBOT to synthesize ATBOT and electrolysis process in the presence of weak base TEAP led to the introduction of C to form 0–Ti–C and Ti–O–C bonds into the ATBOT network. The highest performance of 15 CATBOT was promoted by the presence of a narrow band gap, good absorption of light, and efficient charge separation. Further, the catalyst was also tested for the desulphurization of thio compounds such as thiophene, benzothiophene, and 4,6-dimethyldibenzothiophene, and the results showed that the catalyst was highly effective in removing sulphur from these compounds.
interactions between C with ATTBOT support, as well as its physical
properties, which enhanced photoactivity under visible light. The
higher numbers of Ti–O–C and O–Ti–C, bonds, as well as an appropriate
surface area and pore volume, increased the number of active sites and
offered good surface contact with light for transporting and/or cap-
turing electrons for enhancement of photocatalytic activity. The kinetic
studies revealed that the photocatalytic oxidative desulphurization of
DBT using 15 CAT TBOT followed a pseudo-first order Langmuir-
Hinshelwood model where the adsorption was the controlling step.
Therefore, the synthesized catalyst could be a promising candidate for
its practical applications in environmental puri-
fication and may also aid
in the improvement of visible-light-oriented catalysts for photo-
degradation of various pollutants specifically in the sulphur removal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the
References


