1 Introduction

The removal of dangerous organic pollutants is of great importance and interest for environmental safety [1–5]. It is difficult to remove pollutants from fuel oils that contain sulfur-containing organic compounds [6]. One of the main compounds in oil pollutants is thiophene, which is very difficult to remove by a conventional oxidation process such as the desulfurization process. The low electron density on the sulfur atom and the aromaticity of the thiophene molecule make it difficult to oxidize. Therefore, researchers must develop an efficient photocatalyst to oxidize thiophene. The efficiency of the photocatalyst depends on its stability, particle size, surface area, band gap, and electron–hole recombination lifetime [7]. Many researchers have tried to develop photocatalysts by changing preparation methods, doping with metals, and oxide mixing [8–12]. The most famous photocatalyst is TiO$_2$, which has a band gap of approximately 3.2 eV, and many published papers have attempted to increase its photocatalytic activity and surface area and increase its e–h recombination lifetime and band gap [13–19]. The semiconductor silver sulfide has a narrow band gap with excellent optical properties and good chemical stability [20–24]. Silver sulfide has been prepared by many methods, such as using organometallic precursors [25], using gamma irradiation [26], sonochemical methods [27], templating methods [28], sol–gel and ion-implantation techniques [29], microemulsions [30], etc. To the best of our knowledge, there are no published papers about enhancement of photocatalytic activity of lead sulfide. In this work, PbS and Pt/PbS nanoparticles were prepared and characterized. The photocatalytic performance of PbS and Pt/PbS nanoparticles was studied for the oxidation of thiophene under visible light.

2 Experimental

2.1 Synthesis of PbS

All chemicals used are of analytical grade and are used without further purification. The PbS nanoparticles were prepared by the following procedure. 10 mM thioacetamide and 2.5 mM PbCl$_2$ were dissolved in deionized water (40 mL). The resulting mixture was placed into an autoclave for 24 h at 200°C. The material produced was separated by centrifugation and then washed several times by deionized water and absolute ethanol. Finally, the PbS nanoparticles were dried in a vacuum oven for 3 h at 80°C.

2.2 Synthesis of Pt/PbS

The Pt/PbS nanoparticles were prepared by the photo-assisted deposition (PAD) method according to the following procedure. A certain amount of PbS was dispersed in an aqueous solution of H$_2$PtCl$_6$, and then the resulting mixture was irradiated by UV light for 24 h. The material produced was dried for 24 h at 100°C. Using the PAD method, various wt% values of Pt (0.05, 0.10, 0.15, and 0.20 wt% of Pt metal) were deposited onto the PbS.

2.3 Characterization techniques

X-ray diffraction (XRD) analysis was performed at room temperature (Bruker AXS D8) using Cu Kα radiation (λ = 1.540 Å). The specific surface area was calculated from measurements of the N$_2$ adsorption using a Nova 2000-series Chromatech apparatus at
77 K. Prior to the measurements, all of the samples were held under vacuum at 250°C for 2 h. The band gap for each of the samples was identified by UV-Vis diffuse reflectance spectra. The measurements were taken in air at room temperature over the wavelength range of 200–800 nm using UV/Vis/near IR spectrophotometry (V-570, JASCO, Japan). The transmission electron microscopy (TEM) was recorded with a JEOL-JEM-1230 microscope. The samples were prepared by suspension in ethanol and ultrasonication for 30 min. Subsequently, a small amount of this solution was placed onto a carbon-coated copper grid before it was dried and loaded into the TEM. X-ray photoelectron spectroscopy (XPS) studies were performed (Thermo Scientific K-ALPHA, XPS, England) and photoluminescence (PL) emission spectra were recorded with a Shimadzu RF-5301 fluorescence spectrophotometer.

2.4 Photoreaction apparatus and procedure

The photocatalytic oxidation reactions of thiophene were performed in a Pyrex reaction cell with O₂ bubbled in a constant flow as the oxidant. The required amount of photocatalyst was dispersed in an acetonitrile solution containing thiophene ([sulfur content]_{initial} = 600 ppm). The suspension was stirred in the dark for 30 min to establish adsorption/desorption equilibrium between the solution and the photocatalyst, before being irradiated by a 500-W xenon lamp with a maximum emission at approximately 470 nm, used as a source of visible light. The wavelength of the visible light was controlled by a cut-off filter (λ > 420 nm). The temperature of the reaction solution was maintained at 12°C by a flow of cooling water. The products and by-products were analyzed by GC equipped with a flame photometric detector (Agilent 7890, FED column) and gas chromatography–mass spectrometry after the catalyst particles had been separated from the reaction system by centrifugation. The chromatographic conditions applied for the photocatalytic oxidation of thiophene are summarized in Tab. 1.

3 Results & Discussion

3.1 Morphological, structural and compositional characterization

Figure 1 shows the XRD patterns of the PbS and Pt/PbS nanoparticles. The results reveal that the structure of the PbS and Pt/PbS nanoparticles are mostly composed of PbS, which indicates that the deposition of Pt over the PbS has no significant effect on the structure of PbS. Additionally, no peaks for Pt or Pt₂O appeared for the Pt/PbS pattern, which indicates that Pt is well dispersed on the PbS. The deposition of Pt affects only the crystallization of PbS, which broadened the PbS peaks and decreased their intensity as the Pt wt% increased (Fig. 1). Therefore, as the wt% of Pt decreased, the particle size of PbS decreased.

XPS measurements were performed to determine the nature of the Pt introduced into the PbS suspension. XPS for 1.5 wt% Pt/PbS is shown in Fig. 2. The results reveal that the peaks assigned to Pt, which indicate the formation of nanoscale Pt metal, appeared at approximately 70.4 and 74 eV.

Figure 3 shows the TEM images of the Pt/PbS nanoparticles. The results revealed that the particle size of the PbS nanoparticles decreased as the wt% of Pt increased, whereas the particle size of the Pt on the PbS increased as the wt% of the Pt increased. Additionally, the increased wt% of Pt from 0.05 to 0.15 increased the homogeneity of the Pt on the PbS. However, above 0.15 wt% of Pt, the homogeneity of the Pt decreased, which means that the optimum value for the wt% of Pt is 0.15.

Table 1. Chromatographic conditions applied for the photocatalytic oxidation of thiophene

<table>
<thead>
<tr>
<th></th>
<th>Oxidation of thiophene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oven</td>
<td>50°C for 5 min → 200°C with 10°C/min</td>
</tr>
<tr>
<td>Detector</td>
<td>Type: FED</td>
</tr>
<tr>
<td></td>
<td>Heater: 300°C</td>
</tr>
<tr>
<td></td>
<td>H₂ flow: 150 mL/min</td>
</tr>
<tr>
<td></td>
<td>Air flow: 110 mL/min</td>
</tr>
<tr>
<td></td>
<td>Makeup flow: 25 mL/min</td>
</tr>
<tr>
<td>Injection</td>
<td>Heat: 250°C</td>
</tr>
<tr>
<td></td>
<td>Pressure: 13.762 psi</td>
</tr>
<tr>
<td></td>
<td>Total flow: 41.384 mL/min</td>
</tr>
<tr>
<td></td>
<td>Septum purge flow: 3 mL/min</td>
</tr>
<tr>
<td></td>
<td>Mode: split with ratio (10:1)</td>
</tr>
<tr>
<td>Column</td>
<td>(30 m × 0.32 μm × 0.25 μm)</td>
</tr>
</tbody>
</table>

Figure 1. XRD patterns of PbS and Pt/PbS nanoparticles.

Figure 2. XPS for Pt species of 1.5 wt% Pt/PbS nanoparticles.
3.2 Surface-area analysis

The Brunauer–Emmett–Teller (BET) specific surface areas of PbS and Pt/PbS nanoparticles were determined. The $S_{\text{BET}}$ values for PbS, 0.05 wt% Pt/PbS, 0.10 wt% Pt/PbS, 0.15 wt% Pt/PbS, and 0.20 wt% Pt/PbS were 19.00, 17.00, 15.00, 13.00, and 11.00 m$^2$/g, respectively. Table 2 shows the surface-area parameters and the data calculated from the $t$-plot for the PbS and Pt/PbS nanoparticles. The total pore volume of the Pt/PbS nanoparticles was lower than that of the PbS, due to the deposition of Pt onto the PbS surface causing the blockage of pores of the PbS nanoparticle.

3.3 Optical characterization

Figure 4 shows the UV–Vis diffuse reflectance spectra of the PbS and Pt/PbS nanoparticles. The results reveal that the deposition of

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Table 2. Texture parameters of the PbS and Pt/PbS nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$S_t$ (m$^2$/g)</th>
<th>$S_{\text{mic}}$ (cm$^2$/g)</th>
<th>$S_{\text{ext}}$ (cm$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_{\text{micro}}$ (cm$^3$/g)</th>
<th>$V_{\text{meso}}$ (cm$^3$/g)</th>
<th>$r$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS</td>
<td>19.00</td>
<td>20.00</td>
<td>9.00</td>
<td>10.00</td>
<td>0.112</td>
<td>0.081</td>
<td>0.031</td>
<td>38.00</td>
</tr>
<tr>
<td>0.05 wt % Pt/PbS</td>
<td>17.00</td>
<td>18.00</td>
<td>8.00</td>
<td>9.00</td>
<td>0.094</td>
<td>0.066</td>
<td>0.028</td>
<td>42.00</td>
</tr>
<tr>
<td>0.10 wt % Pt/PbS</td>
<td>15.00</td>
<td>16.00</td>
<td>7.00</td>
<td>8.00</td>
<td>0.086</td>
<td>0.060</td>
<td>0.026</td>
<td>46.00</td>
</tr>
<tr>
<td>0.15 wt % Pt/PbS</td>
<td>13.00</td>
<td>14.00</td>
<td>6.00</td>
<td>7.00</td>
<td>0.073</td>
<td>0.050</td>
<td>0.023</td>
<td>48.00</td>
</tr>
<tr>
<td>0.20 wt % Pt/PbS</td>
<td>11.00</td>
<td>13.00</td>
<td>5.00</td>
<td>6.00</td>
<td>0.068</td>
<td>0.047</td>
<td>0.021</td>
<td>52.00</td>
</tr>
</tbody>
</table>

$S_{\text{BET}}$, BET-surface area; $S_t$, surface area derived from $V_{\text{l-t}}$ plots; $S_{\text{mic}}$, surface area of micropores; $S_{\text{ext}}$, external surface area; $V_p$, total pore volume; $V_{\text{micro}}$, pore volume of micropores; $V_{\text{meso}}$, pore volume of mesopores; $r$, mean pore radius.
Pt onto PbS caused a red shift from 407 to 445 nm for the PbS and the 0.2 wt% Pt/PbS nanoparticles, respectively. Table 3 shows the direct band-gap energies for PbS and Pt/PbS, which are calculated from Fig. 4 by the method described in a previous work [18]. The results reveal that the band gap of PbS, 0.05 wt% Pt/PbS, 0.10 wt% Pt/PbS, 0.15 wt% Pt/PbS, and 0.20 wt% Pt/PbS were 3.05, 2.96, 2.85, 2.80, and 2.78 eV, respectively.

Figure 5 shows the PL spectra of the PbS and Pt/PbS nanoparticles. The results reveal that the increased wt% of Pt decreased the PL intensity of PbS, which means that Pt acts as a trapping site. Therefore, the deposition of Pt onto PbS lead to an increased e–h recombination lifetime and an increased photocatalytic activity.

### 3.4 Photocatalytic activity

#### 3.4.1 Effect of wt% of Pt on the photocatalytic activity of PbS for the oxidation of thiophene

Figure 6 shows the effect of the wt% of Pt on the photocatalytic activity of PbS for the oxidation of thiophene. The experiment was performed under the following conditions: 0.6 g of the photocatalyst, 600 ppm of thiophene, and 500 mL of the thiophene solution. The results reveal that the parent photocatalyst (PbS) has no photocatalytic activity under visible light because it absorbs in the UV region and the experiment is performed under visible light. Additionally, we noticed that the deposition of Pt onto PbS leads to increased photocatalytic activity in the following order: PbS < 0.05 wt% Pt/PbS < 0.1 wt% Pt/PbS < 0.20 wt% Pt/PbS < 0.15 wt% Pt/PbS. Therefore, the 0.15 wt% Pt/PbS has the highest photocatalytic activity.

To examine the photoproducts, the gas was introduced into a 0.2 M aqueous NaOH solution for further analysis. After the addition of a 0.2 M aqueous Ba(NO₃)₂ solution, a white precipitate was obtained and denoted as precipitate 1. The white precipitate BaCO₃ was produced as shown in Fig. 6b. This result indicates that CO₂ is one product of photocatalytic oxidation of thiophene. When an attempt was made to dissolve precipitate 1 in aqueous HNO₃, a portion of white precipitate could not be dissolved and was denoted as precipitate 2. The XRD pattern of precipitate 2 can be readily assigned to BaSO₄, as shown in Fig. 6c. This indicates that CO₂ and SO₃ are the main product of photocatalytic oxidation of thiophene as shown in the following equation:

\[
\text{Thiophene + photocatalyst} \rightarrow \text{CO}_2 + \text{SO}_3 + \text{H}_2\text{O}
\]
3.4.2 Kinetics of thiophene

The reaction order with respect to thiophene was determined by plotting reaction time versus log [thiophene] according to the following equation:

$$
\log C_t = -kt + \log C_{t0}
$$

where \([C]_t\) and \([C]_{t0}\) represent the concentration of the substrate in solution at time zero and time \(t\) of illumination, respectively, and \(k\) represents the apparent rate constant (min\(^{-1}\)). The findings are represented in Fig. 7. The results show that the reaction followed first order kinetics with respect to thiophene and the rate constants were found in the range of \(10^4\) to \(2 \times 10^4\) min\(^{-1}\). The first order rate equation for thiophene is given by

$$
R = k[C_{[\text{thiophene}]})
$$

3.4.3 Effect of photocatalyst quantity on the photocatalytic activity of PbS for the oxidation of thiophene

Another important factor in the photocatalytic oxidation of thiophene under visible light irradiation is the quantity of the photocatalyst. The quantity of 0.15 wt% Pt/PbS ranged from 0.2 to 1.6 g L\(^{-1}\) in 1000 mg L\(^{-1}\) of the selected solutions of thiophene, as shown in Fig. 8. The results reveal that increasing the amount of 0.15 wt% Pt/PbS from 0.2 to 0.9 g L\(^{-1}\) increases photocatalytic degradation efficiency of thiophene from 89 to 99%, respectively. The reaction time required for the oxidation of thiophene decreased from 60 to 40 min by increasing the amount of 0.15 wt% Pt/PbS from 0.9 to 1.2 g L\(^{-1}\), respectively. However, increasing the amount of catalyst to >1.2 decreased the photocatalytic degradation of thiophene. This is because increasing the amount of photocatalyst used increases the number of active sites, which increases the photocatalytic activity [31]. However, increasing the amount of photocatalyst above 1.2 g L\(^{-1}\) blocked the penetration of light to the photocatalyst, and therefore decreased the photocatalytic activity [31]. We found that our 0.15 wt% Pt/PbS photocatalyst has a more effective photocatalytic activity for the oxidation of thiophene than the photocatalyst Pt(RuO\(_2\))/TiO\(_2\) [32].

3.4.4 Recycling of the photocatalyst

One of important factors for the commercialization of a photocatalyst is the stability of the photocatalyst. Our 0.15 wt% Pt/PbS photocatalyst was examined for its photocatalytic stability by reusing it six times. The results reveal that after six uses of the 0.15 wt% Pt/PbS photocatalyst, the photocatalytic conversion of thiophene was 100%. Therefore, the photocatalyst was stable and effective for environmental remediation.

4 Conclusions

PbS and Pt/PbS nanoparticles were successfully prepared. The sample with 0.15 wt% Pt/PbS has a high photocatalytic activity for the oxidation of thiophene under visible light, and these results may lead to find potential applications for this material in related fields. UV–Vis spectra reveal that the deposition of Pt onto PbS led to a red shift to a higher wavelength. The use of 0.15 wt% Pt/PbS, 1000 mL of thiophene, and 1.2 g of the catalyst degrades 100% of thiophene under visible light after a reaction time of 40 min. The photocatalytic activity of 0.15 wt% Pt/PbS after use six times remains almost the same, which confirms the photostability of the 0.15 wt% Pt/PbS nanoparticles.

The authors have declared no conflict of interest.

References


