SYNTHESIS AND PHOTOCATALYTIC ACTIVITY
OF THE MOS₂ AND WS₂ NANOPARTICLES
IN DEGRADATION OF ORGANIC COMPOUNDS

A THESIS
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Abstract

Nanoparticles of MoS$_2$ and WS$_2$ were synthesized by decomposing the appropriate metal hexacarbonyl in the presence of sulfur dissolved in decalin at $140^\circ$C. A significant fraction of the nanoparticles was $\leq 15$ nm in diameter as verified by Transmission Electron Microscopy. The process was repeated in the presence of silica and then titania to produce supported metal sulfides. The unsupported nanoparticles were found to exhibit a size-dependent shift in their threshold UV-visible absorption due to quantum confinement. Photocatalytic properties of each sulfide from synthesis in decalin were explored by using each as a catalyst in the photodegradation of methylene blue by visible light. These sulfides were also used to catalyze the photodegradation of acetone.

Unsupported MoS$_2$ and WS$_2$ nanoparticles catalyzed the photodegradation of acetone under visible light of $\geq 400$ nm wavelength. This is the first study reporting the photocatalytic properties of the unsupported WS$_2$ nanoparticles. Photodegradation of methylene blue under $\geq 435$ nm irradiation was detected using unsupported WS$_2$ but not unsupported MoS$_2$, likely because activity was masked by the likely photobleaching of the dye. When deposited on silica or titania, the nanosized MoS$_2$ and WS$_2$ could be uniformly distributed in aqueous solutions to maximize the photocatalytic efficiency. Correcting the absorbance measurements for light scattering by solids proved to be beneficial for extracting kinetic information. Both silica deposited sulfides were found to significantly increase the rate of methylene blue photodegradation, and deposited WS$_2$ increased this rate significantly more than deposited MoS$_2$. Similarly, both titania deposited sulfides significantly increased the rate of methylene blue photodegradation, and the deposited WS$_2$ increased this rate significantly more than the deposited MoS$_2$. 
Table of Contents

Chapter 1. Introduction .......................................................................................................1
  1.1. Semiconductor-Mediated Photocatalysis.................................................................1
  1.2. Studies of the Photocatalytic Behavior of MoS2 and WS2 .....................................4
  1.3. Carbonyl Based Synthesis of Nanosized MoS2 and WS2 .....................................7
  1.4. Goals of the Reported Research ...........................................................................9

Chapter 2. Synthesis of the Sulfide Photocatalysts .........................................................10
  2.1. Synthesis of Unsupported MoS2 and WS2 Nanoparticles in p-Xylene .................10
  2.2. Decomposition of W(CO)6 in the Absence of Sulfur ...........................................13
  2.3. Synthesis of Unsupported MoS2 and WS2 Nanoparticles in Decalin .................14
  2.4. Synthesis of Silica Deposited MoS2 and WS2 Nanoparticles ...............................16
  2.5. Synthesis of Titania Deposited MoS2 and WS2 Nanoparticles .............................18

Chapter 3. Characterization of Synthesized Nanoparticles ............................................20
  3.1. Imaging of Nanoparticles with Transmission Electron Microscopy ......................20
  3.2. UV-visible Spectra of the Nanoparticles .............................................................28
  3.3. Energy Dispersive X-Ray Analysis .......................................................................32

  4.1. Photocatalysis Setup ..............................................................................................36
  4.2. Photocatalytic Tests Protocols ...............................................................................38
    4.2.1. Methylene Blue Degradation by Unsupported MoS2 and WS2 .....................39
    4.2.2. Methylene Blue Degradation by MoS2 and WS2 Supported on SiO2 or TiO2- Anatase .................................................................40
    4.2.3. Accounting For Light Scattering by SiO2 and TiO2 .......................................41
    4.2.4. Acetone Methylene Blue Degradation By Unsupported MoS2 and WS2 .........45

Chapter 5. Photocatalytic Degradation Tests: Results ....................................................46
  5.1. Methylene blue degradation by unsupported MoS2 and WS2 .............................46
  5.2. Methylene blue degradation by MoS2 and WS2 supported on SiO2 .....................49
  5.3. Methylene blue degradation by MoS2 and WS2 supported on SiO2: Accounting For Light Scattering by SiO2 .................................................................51
  5.4. Methylene blue degradation by MoS2 and WS2 supported on TiO2-Anatase .......55
  5.5. Methylene blue degradation by MoS2 and WS2 supported on TiO2-Anatase: Accounting For Light Scattering by TiO2 .........................................................56
  5.6. Acetone Degradation By Unsupported MoS2 and WS2 .....................................60
  5.7. Conclusions .........................................................................................................63

References ....................................................................................................................65
List of Figures

Figure 1. Photocatalytic destabilization of an adsorbed molecule by TiO₂ ...............1
Figure 2. Strategies for optimization of the bandgap for photocatalysis ......................3
Figure 3. Increase of the photocatalytic efficiency of composite semiconductors due to improved charge separation across the interface. ..............................................................6
Figure 4. Dried products from the synthesis of unsupported MoS₂ and WS₂ ..............16
Figure 5. TEM Image of MoS₂ in p-xylene at 60,000x magnification .........................21
Figure 6. TEM image of the Catalase standard at 200,000x magnification .................22
Figure 7. TEM image of MoS₂ in p-xylene at 150,000x magnification ......................23
Figure 8. TEM image of WS₂ in p-xylene at 100,000x magnification .......................24
Figure 9. TEM image of MoS₂ in decalin at 200,000x magnification .......................25
Figure 10. TEM image of WS₂ in decalin at 200,000x magnification .......................26
Figure 11. TEM image of WS₂ in decalin at 200,000x magnification with high contrast added ........................................................................................................................27
Figure 12. TEM image of WS₂ in decalin at 100,000x magnification .......................28
Figure 13. UV-visible difference spectra determined from spectra obtained during the settling of MoS₂ in p-xylene .................................................................30
Figure 14. UV-visible difference spectra determined from spectra obtained during the settling of WS₂ in decalin .................................................................31
Figure 15. UV-visible difference spectra determined from spectra obtained during the settling of MoS₂ in decalin .................................................................32
Figure 16. Energy dispersive X-ray analysis of WS₂ synthesized in decalin ...............33
Figure 17. Energy dispersive X-ray analysis of MoS₂ synthesized in decalin ............34
Figure 18. Close-up view of the UV-visible light beam irradiating the beaker with a reaction mixture. Long-pass cut-off filter is visible in the upper left corner ...............37
Figure 19. The path of the light through the experiment setup ....................................37
Figure 20. (A) UV-visible spectrum of aqueous methylene blue. (B) UV-visible spectrum of aqueous methylene blue in the presence of WS₂/SiO₂ .........................42
Figure 21. An increase in scattering by the dispersing catalyst contributes an observable increase in the 665 nm absorbance measurement as the mixture stirs over time .......43
Figure 22. Relative UV-visible absorption at 665 nm plotted over time using unsupported MoS₂ and WS₂ as the catalysts .......................................................46
Figure 23. Methylene blue degradation by MoS₂/SiO₂, WS₂/SiO₂, and with the SiO₂ control ..............................................................................................................50
Figure 24. Linear correlation between light intensity losses at 665 nm and at 420 nm for aqueous suspensions of three solids: (A) MoS₂/SiO₂, (B) WS₂/SiO₂, (C) SiO₂ ......52
Figure 25. Methylene blue degradation by MoS₂/SiO₂, WS₂/SiO₂, and with the SiO₂ control adjusted for light scattering ..............................................................54
Figure 26. Relative UV-visible absorption at 665 nm plotted over time using titania and titania deposited MoS₂ and WS₂ as catalysts .............................................55
Figure 27. Linear correlation between light intensity losses due to scattering at 665 nm and at 375 nm for aqueous suspensions of three solids: (A) MoS₂/TiO₂, (B) WS₂/TiO₂, (C) TiO₂ .................................................................57
Figure 28. Methylene blue degradation by MoS₂/TiO₂, WS₂/TiO₂, and with the TiO₂ control ..............................................................................................................59
Figure 29. The 265 nm absorption peak in the baseline corrected spectrum of acetone decreases as the acetone/MoS₂ mixture is irradiated by light ≥ 400 nm.

Figure 30. Baseline corrected, relative UV-visible absorption at 265 nm plotted over time using unsupported MoS₂ and WS₂ as the catalysts.
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1</td>
<td>Reactant quantities for synthesis of unsupported metal sulfides in $p$-xylene</td>
<td>11</td>
</tr>
<tr>
<td>Table 2</td>
<td>Reactant quantities for control synthesis</td>
<td>13</td>
</tr>
<tr>
<td>Table 3</td>
<td>Reactant quantities for synthesis of unsupported metal sulfides in decalin</td>
<td>14</td>
</tr>
<tr>
<td>Table 4</td>
<td>Reactant quantities for synthesis of silica supported metal sulfides</td>
<td>17</td>
</tr>
<tr>
<td>Table 5</td>
<td>Reactant quantities for synthesis of titania supported metal sulfides</td>
<td>18</td>
</tr>
<tr>
<td>Table 6</td>
<td>Quantities of solid used as catalysts to test deposited sulfides</td>
<td>40</td>
</tr>
<tr>
<td>Table 7</td>
<td>Quantities of solid used in tests to determine proportionate scattering</td>
<td>44</td>
</tr>
<tr>
<td>Table 8</td>
<td>Analysis of the rates of the methylene blue degradation by unsupported MoS$_2$ and WS$_2$</td>
<td>48</td>
</tr>
<tr>
<td>Table 9</td>
<td>Analysis of the rates of the methylene blue degradation by MoS$_2$/SiO$_2$ and WS$_2$/SiO$_2$</td>
<td>51</td>
</tr>
<tr>
<td>Table 10</td>
<td>Functions relating the scatter at 665 nm and 420 nm for MoS$_2$/SiO$_2$, WS$_2$/SiO$_2$, and SiO$_2$</td>
<td>51</td>
</tr>
<tr>
<td>Table 11</td>
<td>Analysis of the rates of the methylene blue degradation by MoS$_2$/SiO$_2$ and WS$_2$/SiO$_2$</td>
<td>54</td>
</tr>
<tr>
<td>Table 12</td>
<td>Analysis of the rates of the methylene blue degradation by MoS$_2$/TiO$_2$ and WS$_2$/TiO$_2$</td>
<td>56</td>
</tr>
<tr>
<td>Table 13</td>
<td>Functions relating the scatter at 665 nm and 375 nm for MoS$_2$/TiO$_2$, WS$_2$/TiO$_2$, and TiO$_2$</td>
<td>58</td>
</tr>
<tr>
<td>Table 14</td>
<td>Error Analysis of the rates of the methylene blue degradation by MoS$_2$/TiO$_2$ and WS$_2$/TiO$_2$</td>
<td>59</td>
</tr>
<tr>
<td>Table 15</td>
<td>Analysis of the rates of the acetone degradation by unsupported MoS$_2$ and WS$_2$</td>
<td>63</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1. Semiconductor-Mediated Photocatalysis

The predominant photocatalyst for pollutant degradation is currently TiO₂. TiO₂, or titania, is a wide-band semiconductor. When it absorbs light, an electron is excited from the valence band to the conduction band as illustrated by the left-hand diagram in Figure 1.

![Figure 1. Photocatalytic destabilization of an adsorbed molecule by TiO₂.](image-url)
The photogenerated electron and hole often recombine. However, they can also migrate to the surface and appear in close proximity to an adsorbed species. The excited electron can then reduce an adsorbed species by transferring to an available orbital. This available orbital must be of lower energy compared to the energy of the conductance band. This is a transfer of the electron from a more negative redox potential towards zero.[1] The addition of an electron to the adsorbed species can convert the adsorbed molecule to radicals or radical ions. These may undergo rearrangements, fragmentations, and reactions with other molecules. Similarly, the adsorbed species can become oxidized by transferring an electron from one of its occupied orbitals to the hole, h+, in the semiconductor’s valence band. This is equivalent to the transfer of the hole to the occupied orbital of the adsorbed molecule.[1] For the hole to transfer, the valence band must be of lower energy than the occupied molecular orbital, i.e. the hole must have a highly positive redox potential.

In water, TiO2 will usually act as a photocatalyst by oxidizing the water resulting in a hydroxyl radical.[1] Water is oxidized when a hole in the valence band, h+, with sufficient redox potential accepts an electron from the highest filled orbital. An H+ is lost, and the resulting OH can diffuse in the water and react with other molecules. Organic contaminants in the water will eventually come into contact with a hydroxyl radical, resulting in oxidation. This process is capable of oxidizing a hydrocarbon to carbon dioxide, water, and H+. [2, 3]

In order to absorb light for photocatalysis, an electron from the upper edge of the valence band must absorb a photon with the energy of the bandgap. If the photon has more energy than is required, then the excited electron will quickly relax through thermal
states to the lower edge of the conduction band. For titania, the required energy is about 3 eV, which is why titania is only capable of using about 3% of the sunlight reaching Earth’s surface for photocatalysis.[4]

Two useful approaches to solve these problems are displayed in Figure 2. The first one is to dope titania with other elements, metals or nonmetals. This can result in an effective bandgap which is narrower than the original, thereby sensitizing titania to visible light.

**Strategy 1:** Doping TiO₂ to decrease the bandgap

**Strategy 2:** Nanodispersing of narrow-band semiconductors to widen the bandgap

Figure 2. Strategies for optimization of the bandgap for photocatalysis.

The second approach is to start with a completely different material, a narrow-band semiconductor. Narrow-band semiconductors are capable of absorbing light throughout the visible spectrum because they have much smaller bandgaps. However, these bandgaps do not produce holes with high enough redox potentials to oxidize water. Dispersing the narrow-band semiconductor on the nanoscale takes advantage of the
quantum size effect, resulting in a wider bandgap.[4,5] The quantum size effect arises in particles of a size comparable to quantum dots.[6] Comparing these nanoparticles to the bulk size, far fewer occupied and unoccupied orbitals contribute to the valence and conductance bands respectively.[6] This leads to smaller bands with a wider bandgap between them.

Exciting electrons across this wider bandgap results in a higher redox potential for the hole. The hole may then be capable of oxidizing water to generate a hydroxyl radical.

The electron’s ability to absorb a photon with more than enough energy to cross the bandgap results in a threshold frequency for absorbance. The increase in bandgap caused by the quantum size effect has been demonstrated for MoS$_2$.[4,5,7] It can be observed as a blue-shift in the threshold absorption frequency of the nanoparticles compared to the bulk metal sulfide. This blue-shift in the threshold absorbance of a sample of metal sulfide indicates the presence of these nanoparticles.

1.2. Studies of the Photocatalytic Behavior of MoS$_2$ and WS$_2$

Studies of heterogeneous photochemistry on MoS$_2$ have been pioneered by Tributsch and Bennett.[8] However, the bulk of the well controlled experiments were done by Wilcoxon et al.[4,5,7] Their work has shown that narrow-band semiconductors MoS$_2$ and WS$_2$ are capable of photodegradation of organic compounds using visible light. In order to function as photocatalysts, the sulfides were either dispersed on the nanoscale or used to sensitize TiO$_2$. Nanoparticles of MoS$_2$ 3.0-4.5 nm in diameter were found to catalyze the degradation of phenol, 4-chlorophenol, and pentachlorophenol under visible
light. The 8-10 nm size of MoS$_2$ nanoparticle was not able to photodegrade phenol; however, TiO$_2$ sensitized with it was able to do so under visible light. Both sizes of MoS$_2$ nanoparticle were noted to exhibit a blue-shift in absorbance due to quantum confinement of charge carriers. Wilcoxon et al. took great care to prepare size-selected MoS$_2$ nanoparticles to investigate size-dependent photochemistry. The laborious synthesis was performed using inverse micelles with long-chain polyalcohol surfactants. No purification was done to remove the surfactant afterwards. It is not clear if the presence of the surfactants affected the photocatalytic processes in solutions. Degradation of organics by unsupported, nanosized WS$_2$ was not studied by these authors. MoS$_2$ and WS$_2$ were also used to prepare composite photocatalysts by depositing them onto another photoactive semiconductor. The presence of two different semiconducting materials with mismatched bandgaps has a synergistic effect on the efficiency of photocatalytic processes. Electrons and holes photogenerated close to the interface tend to migrate to the opposite sides driven by the difference in energies of the valence and conduction bands (Figure 3). This decreases the chance of recombination and increases the chance of photochemistry taking place on the outer surfaces.
MoS$_2$ and WS$_2$ grown on TiO$_2$ were shown to sensitize it to visible light.[4,9] This sensitivity extended the wavelength of light absorbed by TiO$_2$ up to about 600 nm in the case of WS$_2$ or about 700 nm in the case of MoS$_2$.[9] The resulting cocatalyst pairs were able to catalyze the photodecomposition of methylene blue and 4-chlorophenol by visible light relative to TiO$_2$ alone.[9] The cocatalyst pair of MoS$_2$/TiO$_2$ was expected to catalyze the formation of hydroxyl radical in water by two sets of reactions[9]:

1a. $2\text{MoS}_2 \ (h^+) + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+$

1b. $\text{H}_2\text{O}_2 \rightarrow 2^\bullet \text{OH}$

2a. $\text{TiO}_2 \ (e^-) + \text{O}_2 \rightarrow \text{O}_2^-$

2b. $\text{O}_2^- + \text{H}_2\text{O} \rightarrow \ ^\bullet \text{O}_2\text{H} + \text{OH}^-$

2c. $^\bullet \text{O}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + ^\bullet \text{OH}$

2d. $\text{H}_2\text{O}_2 \rightarrow 2^\bullet \text{OH}$

Note that the hole, $h^+$, and the excited electron separated. The hole migrated to MoS$_2$ from the junction of the two semiconductors while the electron migrated to TiO$_2$. Each
reacts to produce hydroxyl radicals. In a sample of MoS₂, WS₂, or TiO₂ alone, there would be no junction between two semiconductors. So, the hole and the excited electron would exist inside the same nanoparticle. Recombination of the charges is more likely when h⁺ and e⁻ are proximal, and interfacial redox processes are inhibited.

In a different study, Zong et al. achieved redox production of H₂ from water by using MoS₂ particles deposited onto CdS.[10] Under irradiation with visible light (wavelength > 420 nm), individual sulfides were almost inactive compared to the composite material.

1.3. Carbonyl Based Synthesis of Nanosized MoS₂ and WS₂

Samples of nanosized MoS₂ and WS₂ can be prepared by precipitation in an organic solvent.[11] This is a fairly simple one-pot synthesis that requires thermally decomposing the metal carbonyl in the presence of dissolved sulfur. The precipitation is achieved by first dissolving sulfur in the solvent by warming, followed by adding Mo(CO)₆ or W(CO)₆ to the cooled solution and reheating it to 140°C.[11] p-Xylene has been used previously as an organic solvent which refluxes at about 140°C. This temperature is maintained for several hours to complete the reaction using molybdenum or for several days for the use of tungsten.[11]

Decalin was substituted for p-xylene to improve the yield of WS₂ because it had the additional characteristic of being an alkane. This characteristic was desired to avoid aromatic π-systems which might coordinate with tungsten. Coordination of the solvent with tungsten was to be avoided because the proposed synthesis produces elemental
tungsten as an intermediate by decomposing the W(CO)₆.[11] It was speculated that
trapping the tungsten in an intermediate stage by coordinating with the p-xylene solvent
may have been the cause of a lack of product for the first and second attempts at WS₂
synthesis described in Chapter 2. Such a coordination compound between W(CO)₃ and
p-xylene has been synthesized previously in the literature by heating W(CO)₆ and
p-xylene in an organic solvent.[12-15]

Using decalin, the synthesis was then repeated in the presence of silica and titania
separately to deposit products on the inert or photoactive substrates. These modifications
are alterations to the process described in the literature.[11] Neither deposited nor
unsupported products of the precipitation in organic solvent have been previously studied
in the photodegradation of organics. Determining the photocatalytic properties of these
sulfides in the degradation of organics is the central purpose of this work.
1.4. Goals of the Reported Research

The goals of this research were:


2. Synthesis of these sulfides in the presence of silica and titania by precipitation in an organic solvent to form silica and titania deposited sulfides.

3. Characterization of the unsupported sulfides in terms of elemental composition and size.

4. Verification of the presence of the quantum size effect for the unsupported sulfides.

5. Test the photocatalytic properties of each synthesized sulfide by use of the sulfide as a catalyst in the degradation of methylene blue by light $\geq 400$ nm.

6. Test unsupported sulfides for photocatalytic properties by use of the supported sulfide as a catalyst in the degradation of acetone by light $\geq 400$ nm.
Chapter 2. Synthesis of the Sulfide Photocatalysts

2.1. Synthesis of Unsupported MoS$_2$ and WS$_2$ Nanoparticles in $p$-Xylene

MoS$_2$ and WS$_2$ nanoparticles were synthesized similarly to the method described by Duphil, Bastide and their colleagues.[11] All synthesis steps were carried out in a reflux apparatus under argon purge to prevent reaction with oxygen. The reflux apparatus consisted of a two-necked round bottom flask equipped with a reflux condenser. Valves were inserted into the top of the reflux condenser and the second mouth through which argon flowed. This way, the solvent could be degassed by allowing argon to flow from the side mouth up and out through the top of the condenser with the condenser valve removed during reflux. Positive argon pressure was maintained while transferring solids to the flask through the side mouth by allowing argon to flow down the condenser from its valve.

Before each synthesis, the glassware for reflux apparatus and the large stir bar was washed each time, once already scrubbed visually clean, with wash grade acetone to remove any grease. Then it was soaked in \textit{aqua regia} for a minimum of two hours to remove traces of metals. Finally it was rinsed with deionized water and dried with acetone (Spectrum Chemical 99.5% pure). The exception was the synthesis of MoS$_2$ in $p$-xylene, which was rinsed with wash grade acetone. A sacrificial portion of reaction
solvent was refluxed inside the apparatus before each synthesis, cooled, and removed by
glass pipette as a final rinse.

Reactant amounts were often scaled up or down from the original paper, but the mole
to mole ratio of sulfur to metal carbonyl was kept at 2:1. For example, the reactant
quantities were often doubled resulting in a target of \(4.6 \times 10^{-4}\) moles of sulfur (Fisher
Scientific, sublimed) and \(2.3 \times 10^{-4}\) moles of metal carbonyl, Mo\(\text{(CO)}_6\) (Aldrich 98%) or
W\(\text{(CO)}_6\) (Strem Chemicals 99%), in 200 mL \(p\)-xylene (EM Science 98%) or decalin
(Aldrich 99%, anhydrous). Some synthesis runs were also scaled down. Additions of
solids to the reaction vessel were done under argon purge to prevent oxygenation of the
mixture and any grains of reactant stuck on the joint are rinsed down into the reaction
vessel by an aliquot of solvent from within. The actual measured amounts of reactants
and solvents for all sulfides synthesized alone can be found in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Product Synthesis & Metal Carbonyl Mass & Sulfur Mass & Solvent Volume (mL) \\
& (mg ± 0.1 mg) & (mg ± 0.1 mg) & \\
\hline
Mo\(\text{S}_2\) & 60.0 & 14.8 & 200 \\
WS\(\text{S}_2\) & 81.0 & 15.0 & 200 \\
& 40.0 & 7.2 & 100 \\
\hline
\end{tabular}
\caption{Reactant quantities for synthesis of unsupported metal sulfides in \(p\)-xylene.}
\end{table}

The sulfur was transferred to the \(p\)-xylene and warmed to reflux, 140-143°C, over
thirty minutes to both dissolve the sulfur and degas the solution. After being allowed to
cool to room temperature, the metal carbonyl is added, and the solution is heated again to
reflux. The reflux temperature is held for three hours for Mo\(\text{S}_2\) or over four days for WS\(\text{S}_2\),
and then the reaction vessel is allowed to cool to room temperature. The product mixture
is then distilled by heating to reflux under heavy argon purge to remove much of the
\(p\)-xylene. Finally the mixture is cooled under argon pressure and transferred into a brown
Several color changers were observed for both of these reactions. The $p$-xylene itself was clear, and remained clear after both the sulfur and metal carbonyl were dissolved. Both carbonyls were white in solid form. When the temperature reached about 120°C, the solution turned yellow. As the solution heated to 140°C, it became browner in color. The solution then quickly turned very dark purple, but still looked reddish or yellowish through thin portions of liquid. Solid is visible being stirred. After another half an hour, the mixture looks almost black with a slight purple tinge. This color remains throughout the rest of the synthesis, which appears thick with solid being stirred. When a sample of this mixture is taken in a test tube, it is purple with a tinge of red.

When using the tungsten carbonyl, a yellow color appeared as the temperature reached 140°C. The solution became darker yellow and slightly green in color over the next five minutes and continued growing darker over the next hour becoming and slightly brown. Overnight the solution developed a purple tinge. By the next day it was brownish purple and growing darker, finally turning a brownish black. When thin layers of the liquid are looked through, the solution looks red, yellow, or slightly orange depending on the angle of the light. After being left to settle, the solution is still very dark brown with red visible through slim portions of the liquid. There was no visible solid, even after centrifuging. The solution never cleared or decolorized, but it was of a dark orange color when viewed in a 1 cm cuvette. A slight film was noticed on the inside of the round bottom flask which was a translucent orange. Some of this was scraped in a $p$-xylene rinse with a glass stir rod and poured with the rest of the solution into a brown bottle for storage. The synthesis was repeated with the same color changes observed and
produced no visible solid except for the slight film, which seemed to dissolve when introduced to the rest of the solution.

### 2.2. Decomposition of W(CO)$_6$ in the Absence of Sulfur

The synthesis of WS$_2$ was repeated twice without the addition of sulfur for comparison as the first and second control experiments listed in Table 2. The control runs were also observed to turn from yellow, to greenish yellow soon after the carbonyl was heated to a temperature of 140°C.

<table>
<thead>
<tr>
<th>Product Synthesis</th>
<th>Metal Carbonyl Mass (mg ± 0.1 mg)</th>
<th>Sulfur Mass (mg ± 0.1 mg)</th>
<th>Solvent Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten Control</td>
<td>44.9</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>20.3</td>
<td>0</td>
<td>50</td>
</tr>
</tbody>
</table>

The solution stayed yellow for over an hour and was left overnight to reflux. The next morning a reddish brown was observed, which slowly developed into a brown color and finally a brownish black as before. At the meniscus the solution looked purple or orange depending on the angle of the light. In the 1 cm cuvette the solution looked orange like the synthesis of WS$_2$ solution. There was no solid visible, even after centrifuging. The control was repeated a second time with the same results, but there was also an orange film noticed on the inside of the flask. The fact that the bulk of the solution, which did not have sulfur added, developed the same color as the solution containing sulfur as a reagent, means that the color of the solution is not due to WS$_2$ formation. One explanation for the lack of formation of solid during the WS$_2$ synthesis in $p$-xylene would be that the tungsten was trapped by a side reaction. A likely candidate for this side
reaction is the formation of a π-complex such as a “piano stool” \( (\eta^6-\text{C}_8\text{H}_{10})\text{W(CO)}_3 \), which has been synthesized by heating \( \text{W(CO)}_6 \) to 135°C in the presence of \( \text{p-xylene} \) and by other methods.[12-15]

2.3. Synthesis of Unsupported MoS\textsubscript{2} and WS\textsubscript{2} Nanoparticles in Decalin

Decalin was chosen as a replacement for the solvent \( \text{p-xylene} \) because of its lack of the aromatic double bonds potentially used to form coordination bonds with tungsten or \( \text{W(CO)}_3 \). Synthesis was then repeated for both WS\textsubscript{2} and MoS\textsubscript{2} using decalin. It should be noted that temperature fluctuations of 140-155°C using decalin as a solvent were higher than those observed with \( \text{p-xylene} \), but no problems resulted. The exact reactant quantities are listed in Table 3.

<table>
<thead>
<tr>
<th>Product Synthesis</th>
<th>Metal Carbonyl Mass (mg ± 0.1 mg)</th>
<th>Sulfur Mass (mg ± 0.1 mg)</th>
<th>Solvent Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS\textsubscript{2}</td>
<td>15.5</td>
<td>3.6</td>
<td>50</td>
</tr>
<tr>
<td>WS\textsubscript{2}</td>
<td>40.5</td>
<td>7.4</td>
<td>100</td>
</tr>
</tbody>
</table>

During the synthesis of WS\textsubscript{2} in decalin, it was noticed that the decalin solution remained clear, even after the addition and dissolution of sulfur. Once the carbonyl was added and dissolved with the temperature reaching 150°C, the solution was a slight gold color. The metal carbonyl itself had been white. After about twenty minutes at this target temperature, the color has become more beige, and then it acquired a slightly red tinge. This color remained for several hours, and the reaction was allowed to continue over the weekend. After two days, solid had begun to settle to the bottom in spite of stirring and adhered to the inside of the flask. The mixture and the solid were a rusty
brown color.

Observations recorded during the synthesis of MoS$_2$ in decalin were that the decalin solution remained clear throughout the dissolution of sulfur until the carbonyl had been dissolved and the temperature reached 110\(^\circ\)C. At that point the solution turned from colorless to a brownish color. Over ten minutes the temperature was raised to 139\(^\circ\)C and the solution became redder and rust colored. The solution then quickly turned nearly black, but still looked brown through thin portions of the liquid. There are some dark flecks of solid being stirred. After half an hour since the solution reached 139\(^\circ\)C, the solvent looks almost green, and there is enough floating solid to see that it is a reddish brown color. After another ten minutes, it is more uniformly black, but fifteen minutes later the edges of the flask look more of a green or brown color. After yet another fifteen minutes the solution still looks black but with a purple tinge and stays that way throughout the last hour of heating. When a sample of this mixture is taken in a test tube, it looks purple with a red tinge. This is a similar appearance to the MoS$_2$ mixture synthesized in \(p\)-xylene.

After concentrating under argon purge, then cooling, synthesized sulfides were then isolated from their solvents. This required several steps. Each mixture was agitated and transferred to a polysulfone bottle. These were ultra centrifuged at 5000 rpm for fifteen minutes, and the clear, colorless supernatant was carefully removed by pipette. About 100 mL of cyclohexane was added. Nanoparticles were re-dispersed by shaking, then sonication for several seconds each. This cycle of ultracentrifuging and re-dispersion was repeated four more times. The samples were then dried in a rotary evaporator. The dry nanoparticles of MoS$_2$ and WS$_2$ which were synthesized in decalin are displayed in
Figure 4. Dried products from the synthesis of unsupported MoS$_2$ and WS$_2$.

Figure 4. Once dry, the nanoparticles were re-dispersed readily in chloroform and stored in brown bottles for future use.

2.4. Synthesis of Silica Deposited MoS$_2$ and WS$_2$ Nanoparticles

Synthesis of both metal sulfides was also carried out in the presence of silica (Aldrich, 99.5% 10-20 nm nanoparticles) to form deposited catalysts. For this purpose, several modifications were made to the procedure. First, a mixture of silica in decalin was heated to reflux, 170-180°C, over an hour’s time with argon purge to degas the decalin and drive off any moisture from the silica. Afterwards, it was cooled back to about 40°C before adding the sulfur and continuing the procedure as before. Table 4 lists the amounts of reactants used along with the expected mass ratio of silica to sulfide with the
metal carbonyl as the limiting reagent.

**Table 4.** Reactant quantities for synthesis of silica supported metal sulfides.

<table>
<thead>
<tr>
<th>Product Synthesis</th>
<th>Metal Carbonyl Mass (mg ± 0.1 mg)</th>
<th>Sulfur Mass (mg ± 0.1 mg)</th>
<th>Solvent Volume (mL)</th>
<th>Silica Mass (g)</th>
<th>Silica to Sulfide Mass Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS2 / SiO2</td>
<td>30.5</td>
<td>7.4</td>
<td>100</td>
<td>1.80</td>
<td>97.3 : 1</td>
</tr>
<tr>
<td>WS2 / SiO2</td>
<td>40.3</td>
<td>7.5</td>
<td>100</td>
<td>2.85</td>
<td>100. : 1</td>
</tr>
</tbody>
</table>

These reactions go through several color changes. The silica in hot decalin looks more like a sludge or gel than a powder, and this does not change after sulfur is dissolved. For MoS2 synthesis, the mixture turns brown once the carbonyl is dissolved and the temperature reaches about 120°C. Then it quickly takes on a greenish hue. After quickly increasing the temperature to 140°C over two minutes, the color has changed to a very dark brown and stays there. Once the mixture has cooled and the silica has settled, it appears that the silica itself is brown throughout while the solvent is clear. Even under light stirring, the brown color does not seem to spread into solution but sticks with silica.

During WS2 synthesis with silica, the mixture turns an amber or golden color after the carbonyl is dissolved and the temperature reaches about 125°C. Five minutes later the temperature had reached 150°C and the color was the same. After another thirty minutes, the color was slightly more brownish. Two hours later, the color is best described as butterscotch, which became slightly darker over the next hour. After heating overnight, the silica mixture looks uniformly rusty brown. This color remained throughout the day. By the third day, the color had changed to brown without any red tinge. Letting the silica settle to the bottom leaves the decalin clear and the silica uniformly tan colored.

Each silica deposited sulfide was then removed from decalin as described for the removal of free nanoparticles from their solvents. Then each was dried by rotary
evaporation. Instead of being re-dispersed in chloroform, the silica deposited sulfides were dried, kept in a bottle, and used as needed.

2.5. Synthesis of Titania Deposited MoS$_2$ and WS$_2$ Nanoparticles

Titania deposited metal sulfides were synthesized by replacing the silica in this procedure with titania (Aldrich, 99.7% pure anatase nanoparticles less than 25 nm diameter). The anatase form of TiO$_2$ which was used is one of the crystalline modifications along with rutile and brookite. For MoS$_2$, the synthesis was let to heat over the weekend as an additional modification to ensure the reaction completed. The exact amounts of reactants used are listed below in Table 5.

Table 5. Reactant quantities for synthesis of titania supported metal sulfides.

<table>
<thead>
<tr>
<th>Product Synthesis</th>
<th>Metal Carbonyl Mass (mg ± 0.1 mg)</th>
<th>Sulfur Mass (mg ± 0.1 mg)</th>
<th>Solvent Volume (mL)</th>
<th>Titania Mass (g)</th>
<th>Titania to Sulfide Mass Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/TiO$_2$</td>
<td>30.2 mg ± 0.1 mg</td>
<td>7.4 mg ± 0.1 mg</td>
<td>100 mL</td>
<td>1.84 g</td>
<td>100 : 1</td>
</tr>
<tr>
<td>WS$_2$/TiO$_2$</td>
<td>40.2 mg ± 0.1 mg</td>
<td>7.5 mg ± 0.1 mg</td>
<td>100 mL</td>
<td>2.85 g</td>
<td>100 : 1</td>
</tr>
</tbody>
</table>

During heating, titania suspension in decalin had the appearance of milk, however dissolving the sulfur gave it a tan or peach color that appeared homogeneous. This stands out because dissolving sulfur in solvent alone or solvent plus silica did not result in a color change. When using MoS$_2$, this color remained until the mixture reached 140°C. At that time, it was noticed that the mixture had become darker in color. The tan color shifted to a light brown through to the end of the synthesis. For WS$_2$ synthesized with titania, there was no noticeable change from the peach color over a period of several hours. Left overnight, the mixture became perceptively darker to a light brown. For both sulfides, the brown color appears to be from the solid and to be uniform, while the
solvent left behind is clear.

Each titania deposited sulfide was then removed from decalin and dried. This process consisted agitating each mixture and transferring about 20 mL of it into a polypropylene bottle. Using the smaller, polypropylene bottle was a change in procedure for convenience in isolating nanoparticles from small volumes of decalin. The mixture was agitated and then centrifuged for 10 minutes at 12,000 rpm. The clear supernatant was carefully removed by pipette. Then, about 20 mL of acetone (Spectrum Chemical 99.5%) were added and the bottle was shaken to re-disperse the pellet. Acetone could safely be used with these bottles, so it was used instead of hexane. This process of centrifuging and re-dispersing was repeated three more times. The nanoparticles were then dried in the rotary evaporator as before. Redispersion of silica and titania supported catalysts was accomplished by shaking rather than sonication to avoid the detachment of supported MoS$_2$ and WS$_2$. 
Chapter 3. Characterization of Synthesized Nanoparticles

3.1. Imaging of Nanoparticles with Transmission Electron Microscopy

In order to observe the nanoparticles and verify the size, images were taken of the product mixture from each synthesis with a transmission electron microscope (Electron Microscopy Sciences, part No. I400-Cu). The sample grid for the transmission electron microscope, TEM, was a carbon film supported by a copper grid. Sample grid preparation consisted of agitating the product mixture, removing less than a milliliter with a disposable glass pipette, and drying drops of product mixture on the sample grid. TEM images of the MoS$_2$ synthesized in $p$-xylene reveal nanoparticles ranging from about 5 nm to 30 nm in diameter (Figure 5).

The very small specs in the image alongside the larger, dark bodies illustrate the wide range of nanoparticle sizes formed. This collection of relatively small nanoparticles was located near a large agglomeration visible on the right and top side of the photo.
Collections of individual nanoparticles were often observed near larger agglomerations. It is not clear from the images whether these agglomerations consist of separate particles that are physically in contact with each other, or bound together by a lattice into a large contiguous structure.

The sizes of particles formed in either $p$-xylene or decalin were determined by comparing the TEM images of products with a scale derived from a TEM image of a catalase standard (Electron Microscopy Sciences, part No. 80014) (see Figure 6).
Two-dimensional packing of the catalase molecules results in a grid of lines 6.85 nm x 8.75 nm. The measured distance between the lines provides a scale. Figure 6 shows the negative image of the catalase standard with some of the lines accented in Powerpoint to make them clearer to see. The scale drawn from these regularly spaced lines can be adjusted depending on the magnification. The bright white specs are adventitious particles like lint, which the scanner commonly detects in TEM negatives. Any slight creases or bends in the film can also be seen, like the slight curve running from top to bottom near the center of this image.

Figure 7, another TEM image of the MoS$_2$ synthesized in $p$-xylene with a larger
magnification verifies the presence of nanoparticles with diameters of 5-25 nm.

Figure 7. TEM image of MoS$_2$ in $p$-xylene at 150,000x magnification.

There appear to be many nanoparticles in this photo with diameters of about 10 nm or less using the scale on the left side and several particle sizes have been labeled for comparison.

As noted earlier in the synthesis section, the WS$_2$ synthesis in $p$-xylene did not yield any visible product, even after use of the centrifuge. This was likely due to the formation of a side product with $p$-xylene.[12-15] TEM revealed that the solution did contain very few particles. These were shaped like tissues like the one in Figure 8, and did not resemble those documented by previous researchers.[11] The close-up image of one
tissue shows the folds in the structure.

![TEM image of WS$_2$ in $p$-xylene at 100,000x magnification.](image)

**Figure 8.** TEM image of WS$_2$ in $p$-xylene at 100,000x magnification.

This may be a thin layer of nanosized WS$_2$ which has begun to fold in on itself, or an unintended side product. The approximate size of the tissue in the folded form appears to be 300 nm $\times$ 750 nm, but the folds prevent the exact size of the sheet from being determined by TEM.

Decalin was chosen as a replacement for the solvent $p$-xylene because of its lack of double bonds or aromaticity. These properties were desired to avoid the potential formation of coordination compounds with tungsten or tungsten carbonyl. MoS$_2$ was synthesized in decalin to check if sulfide nanoparticles would form in this new solvent.
The new particles were imaged in Figure 9. Drying the sample on the TEM plate resulted in the particles grouping together, yet retaining their individual boundaries. The boundaries can be seen in Figure 9 where the particles form peninsulas off the main group because fewer particles overlap. Reoccurring particle diameters represented in this photo were about 15 nm, 8 nm, and 5 nm. It is unclear from the relatively low resolution of these TEM images whether the MoS$_2$ nanoparticles are amorphous or crystalline; however, Duphil et al. [11] found that the nanoparticles tend to be amorphous under similar reaction conditions.

**Figure 9.** TEM image of MoS$_2$ in decalin at 200,000x magnification.

TEM images of WS$_2$ in decalin reveal particles as small as about 5nm in diameter.
(Figure 10). Although a few particles as small as 5 nm in diameter were found in this image, most were about 10 nm in size. Individual particle sizes can best be seen near the edges of the group of particles, much like in the MoS₂ samples. Figure 11 displays an image of one such area from a WS₂ synthesis in decalin with greatly enhanced contrast.

![Figure 10. TEM image of WS₂ in decalin at 200,000x magnification.](image-url)
Figure 11. TEM image of WS$_2$ in decalin at 200,000x magnification with high contrast added.

In this image, nanoparticles about 5 nm in size were found surrounding a large peninsula of an agglomeration. This image confirms the formation of WS$_2$ nanoparticles under 10 nm in diameter.

The WS$_2$ nanoparticles synthesized in decalin are comparable in size and appearance to those found in the samples of MoS$_2$. In scanning across the sample, a majority of the nanoparticles with visible borders appear to be about 15 nm in diameter (Figure 12). There are also particles in the 20-30 nm diameter size similar to the particles observed for MoS$_2$. These results are too qualitative to determine if the WS$_2$ synthesis produced routinely smaller or larger particles than the MoS$_2$ syntheses.
3.2. UV-visible Spectra of the Nanoparticles

The UV-visible absorption threshold can allow estimation of the electronic bandgap in the sample. In addition, UV-visible spectra of particles of different sizes can verify if the quantum confinement of charge carriers takes place. Within the quantum confinement regime, as the particle size decreases, the bandgap value increases as fewer molecules contribute their d-orbitals to the valence and conductance bands.[6] This leads to a blue-shift in the absorption threshold of the nanoparticles.

Samples of MoS$_2$ synthesized in $p$-xylene and decalin as well as WS$_2$ synthesized in
decalin were tested for nanoparticles exhibiting a blue-shift in absorbance. The Agilent diode array UV-visible spectrometer model 8453 was used to record the UV-visible spectra of the synthesized samples. Each of the samples was agitated and then let to settle in a 1 cm quartz cuvette as spectra were taken over time. Large particles are expected to settle first, while smaller particles stay suspended for longer periods of time. A shift in the size distribution of suspended particles towards small sizes exhibiting quantum confinement would be expected to cause a shift in the resulting absorption spectrum. By subtracting a spectrum from another taken earlier, the spectrum of the particles which settled to the bottom in the meantime can be obtained as a difference spectrum.

Figure 13 displays difference spectra obtained during sedimentation of MoS$_2$ from the batch synthesized in $p$-xylene. Sedimentation is carried out in $p$-xylene and monitored by taking UV-visible spectra over time. The reference spectrum of $p$-xylene was taken before the start of sedimentation. For comparison, these difference spectra have been normalized to a peak absorbance of 1.
Figure 13. UV-visible difference spectra determined from spectra obtained during the settling of MoS$_2$ in $p$-xylene.

It is easy to see that particles settling out within 30-90 min. have an absorption peak around 600 to 700 nm. Compared to them, smaller particles which settled out within 90-300 min. exhibit a blue-shift in absorbance peaking at about 500 nm. Even smaller particles settling within 300-900 minutes exhibit an even stronger blue-shift in absorbance peaking at about 430 nm.

Their spectrum also begins to exhibit a sharper absorption threshold similar to the 4.5 nm particles studied by Wilcoxon.[4] This further indicates the presence of particles exhibiting quantum confinement. The long tail to this threshold could be due to the remainder of larger particles which had not settled until this time.

The blue-shift in absorbance is also observed for WS$_2$ synthesized in decalin (Figure 14). Particles settling out within the first twenty minutes are mostly large and absorb
throughout the visible spectrum. In the next forty minutes, the settling particles contributed more to the absorbance of light between 700-800 nm. The next set of particles favored even shorter wavelengths of light. During the following night, the distribution of particles settling had a peak absorbance at about 550nm. The centrifuge managed to remove nanoparticles with a peak absorbance around 500nm.

![Difference Spectra of Tungsten Sulfide Settling in Decalin](image)

**Figure 14.** UV-visible difference spectra determined from spectra obtained during the settling of WS$_2$ in decalin.

MoS$_2$ synthesized in decalin was allowed to settle in decalin and monitored to check if the size-dependent blue-shift was present (Figure 15).
The blue-shift is certainly evident when comparing the spectra of the particles settling out during these three time periods, the first twenty minutes, the next forty-three minutes, and then the final fifty-seven minutes. An absorption threshold seems to be forming. The spectra for the next sixty minutes became complex however, and even a fifteen point moving average still has many peaks instead of a threshold.

3.3. Energy Dispersive X-Ray Analysis

Energy dispersive X-ray (EDX) analysis is an elemental analysis method. This method is based on the emission of characteristic X-ray photons by an atom after it has been excited by an electron beam impact. The analysis is performed with a scanning
electron microscope (SEM JEOL 6300 with Noran EDX adapter). The presence of both tungsten and sulfur was determined in a sample of WS$_2$ which had been synthesized in decalin (Figure 16). This determination was done using an area of 1 µm × 1 µm, and so the results reflect the average composition of a group of nanoparticles.

Figure 16. Energy dispersive X-ray analysis of WS$_2$ synthesized in decalin.

The peaks at 0.3 keV, 1.4 keV, 1.9 keV, and 2.1 keV indicate the presence of tungsten and are labeled with a “W” in the figure. Peaks at 0.6 keV and 2.3 keV confirm the presence of sulfur and are appropriately labeled with an “S.” Copper peaks at 0.9 keV,
8.0 keV, and 8.9 keV marked with a “Cu” are from the sample grid. The first labeled peak corresponds to both carbon from the sample grid and tungsten, so it is also labeled with a “C.” Peaks attributable to tungsten and sulfur from the EDX analysis indicate that WS₂ was formed.

Performing EDX analysis on a sample from the MoS₂ synthesized in decalin detected a carbon peak from the grid at 0.3 keV, copper peaks at 0.9 keV and 8 keV, and a peak at 2.4 keV where both molybdenum and sulfur respond (Figure 17).

Figure 17. Energy dispersive X-ray analysis of MoS₂ synthesized in decalin.
Separate molybdenum and sulfur peaks at 2 keV and 0.6 keV respectively confirm the presence of both molybdenum and sulfur. This would indicate that MoS$_2$ was formed.
Chapter 4. Photocatalytic Degradation Tests: Setup and Protocols

4.1. Photocatalysis Setup

The light source is a 300 W xenon arc bulb in a fan-cooled, universal housing from Newport powered by the Newport power supply (model 69911) that is set to the maximum output of 300 W in constant power mode. Light from the source first passes through a focusing lens and a water-cooled water filter that removes infrared radiation. Then, it passes through a selected long-pass filter (Edmund Industrial Optics) that removes high energy UV light and only transmits UV-visible radiation with the wavelength above a certain threshold. Then a mirror reflects the beam straight down into a beaker containing the solution of a compound to be degraded and the catalyst (Figure 18). The path of the light can be traced through each attachment in Figure 19.
Figure 18. Close-up view of the UV-visible light beam irradiating the beaker with a reaction mixture. Long-pass cut-off filter is visible in the upper left corner.

Figure 19. The path of the light through the experiment setup.
The mixture is stirred rapidly throughout the experiment by a magnetic stirrer, and is covered by a watch glass to slow evaporation of the solution. Both watch glass and beaker are pyrex, which has an absorption cutoff around 310 nm. This cutoff is far lower in wavelength than any of the long-pass filters used and therefore does not affect the incident light spectrum. The lens, water filter, long-pass filter holder, and reflecting mirror are all attachments linked together to the lamp housing by screws, so the light path up to this point is constant in length. The beaker and watch glass are always re-centered under the beam after a sample is taken. The condenser is adjusted to narrow the beam as much as possible. Under these conditions, the light beam is slightly diverging and has a radius slightly larger than the 250 mL beaker. The beaker itself is placed inside of an evaporating dish covered in reflective foil to maximize the exposure of the beaker to the light. About 20 mL of Millipore water are added to the evaporating dish before each run to dampen any temperature fluctuations. This water did not warm above room temperature, indicating that the water filter was successful in removing the IR component of the lamp spectrum.

4.2. Photocatalytic Tests Protocols

Photodegradation of methylene blue was used to test the photocatalytic activity of six synthesized catalysts, namely, unsupported MoS$_2$ and WS$_2$ nanoparticles synthesized in decalin, MoS$_2$ and WS$_2$ supported on SiO$_2$, and MoS$_2$ and WS$_2$ supported on TiO$_2$ (anatase). Solutions of methylene blue were irradiated in the presence of each of the six synthesized catalysts with light of wavelength $\geq$ 400 nm (400 nm long-pass filter). The
absorbance peak at 665 nm was used to monitor the degradation of methylene blue with the Agilent 8453 UV-visible diode array spectrometer. Unsupported MoS\textsubscript{2} and WS\textsubscript{2} nanoparticles were also tested in degradation of acetone. Acetone solutions were irradiated using the 400 nm long-pass filter. The absorbance peak at 265 nm was used to monitor the degradation of acetone with the HP 8452A UV-visible diode array spectrometer. To account for autodegradation of methylene blue, acetone evaporation, and any other unforeseen effects, control experiments were performed, in which metal sulfide catalysts were absent.

4.2.1. Methylene Blue Degradation by Unsupported MoS\textsubscript{2} and WS\textsubscript{2}

In preparation for testing un-supported catalysts, the MoS\textsubscript{2} or WS\textsubscript{2} is first dispersed in chloroform and then dried in a clean, dry 250 mL beaker, coating the bottom with a visible layer. The beaker for the control trial is not coated. A 200 mL solution of methylene blue with is added to each beaker by graduated cylinder. The methylene blue solution is then stirred vigorously with a magnetic stir rod for at least half an hour prior to taking any samples for absorption measurements. The mixture is not irradiated during this period. Stirring continues throughout the trial. Spectra of three separate samples of the 200 mL reaction mixture are taken to determine an average original absorbance. The three absorptions are checked to ensure they are within a range of 0.02 abs units. Unsupported MoS\textsubscript{2} and WS\textsubscript{2} nanoparticles exhibit hydrophobic properties and do not disperse in aqueous solution. During the experiment, they remain attached to the bottom of the beaker or deposit onto a Teflon stirrer.

The standard operating procedure for taking a sample has several steps. A
background spectrum is obtained with Millipore water. Then the quartz cuvette is rinsed with less than half a milliliter of reaction mixture using a disposable glass pipette, and finally that pipette is used to deliver about 1 milliliter of reaction mixture to the cuvette. The spectrum is taken as soon as possible with an integration time of 5 seconds. When the cuvette is not in use, it is rinsed with and let to soak in Millipore water. The lamp is warmed up for at least 15 minutes with the shutter closed before it is used to irradiate the reaction mixture. Finally the shutter is opened. To monitor the absorbance of methylene blue, samples are taken throughout the next 6 to 9 hours and a UV-visible spectrum is taken of each sample. Absorption measurements taken from the beakers containing MoS$_2$, the control, and WS$_2$ are used as data for Trials 1, 2, and 3 respectively.

4.2.2. Methylene Blue Degradation by MoS$_2$ and WS$_2$ Supported on SiO$_2$ or TiO$_2$-Anatase

Methylene blue solutions for photocatalytic testing of deposited sulfides were prepared through a series of steps. First, a stock solution of $6.25 \times 10^{-5}$ M methylene blue in Millipore water was prepared using 95% pure methylene blue hydrate (MW = 319.85), 10. mg in a 500.0 mL volumetric flask. Then a clean, dry 100 mL beaker was used to mass the amount of solid listed in Table 6 for the sulfide or control being tested.

<table>
<thead>
<tr>
<th>Solid Tested</th>
<th>Mass (mg ± 2 mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS$_2$/SiO$_2$</td>
<td>16</td>
</tr>
<tr>
<td>MoS$_2$/SiO$_2$</td>
<td>14</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>14</td>
</tr>
<tr>
<td>WS$_2$/TiO$_2$</td>
<td>15</td>
</tr>
<tr>
<td>MoS$_2$/TiO$_2$</td>
<td>15</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>15</td>
</tr>
</tbody>
</table>

Of the stock solution, 25.0 mL was added along with 60.0 mL of Millipore water by graduated cylinder to the 100 mL beaker followed by a magnetic stir rod. The mixture
was then allowed to stir vigorously for two hours to disperse the solids. Three samples were taken shortly before the lamp shutter was opened. Samples were taken by standard operating procedure, with the exception that the cuvette was also sonicated while not in use. The lamp was again warmed up for at least fifteen minutes with the shutter closed before use. The lamp setting of 300 watts constant power remained but the filter was changed to a 400 nm long pass filter. Reaction mixtures were irradiated for about 8 hours for the silica-deposited sulfides and about 4 hours for the titania-deposited sulfides. Throughout this time, samples were taken for UV-spectroscopy as before.

4.2.3. Accounting For Light Scattering by SiO₂ and TiO₂

SiO₂ and TiO₂ have hydroxylated wettable surfaces. These powders easily disperse in aqueous solutions even if MoS₂ or WS₂ are deposited on them. Therefore, the catalysts in this case are not attached to the bottom of the beaker, as was in the case of unsupported MoS₂ or WS₂. The photocatalyst is expected to be more efficient if dispersed throughout the mixture.

Highly dispersed SiO₂ and TiO₂ cause sufficient light scattering that manifests as a sloping baseline in the UV-visible spectra. This sloping baseline is superimposed onto the absorption peak of methylene blue at 665 nm. This effect can be seen in the case of silica deposited WS₂, for example (Figure 20). A UV-visible spectrum of a 200 mL solution of methylene blue was taken before stirring in 29 mg of silica deposited WS₂ for 1.5 hours and taking another spectrum. The mixture has an absorption measurement between 360 nm and 440 nm due to scattering, and the absorption at 665 nm decreased substantially due to adsorption of methylene blue onto the silica.
Figure 20. (A) UV-visible spectrum of aqueous methylene blue. (B) UV-visible spectrum of aqueous methylene blue in the presence of WS₂/SiO₂. Light scattering by silica offsets the absorption peak of methylene blue. The offset can be estimated using the linear correlation with the light scattering contribution in a remote part of the spectrum far from the absorption peaks.
Taking further spectra over time, it was also observed that increases in the scattering due to more fully dispersing the silica are reflected in an increase in the 665 nm absorption measurement (Figure 21).

![The Changing Spectrum of Methylene Blue and Silica Deposited Tungsten Sulfide after Minutes of Stirring](image)

**Figure 21.** An increase in scattering by the dispersing catalyst contributes an observable increase in the 665 nm absorbance measurement as the mixture stirs over time.

As the time spent stirring increases, the catalyst becomes better dispersed, which results in an increase in scattering. This increase can be seen clearly in the range between 360 nm and 420 nm and coincides with an increase in the absorbance of the methylene blue spectrum.

In order to determine the absorbance due to methylene blue, the scatter contribution under the peak at 665 nm can be estimated and subtracted. For this, one can start with a solution that contains no methylene blue and only the scattering solid (SiO₂ or TiO₂). Then one can determine the scatter level at 665 nm and in the region far from the absorption signatures. As shown in the next chapter, for each solid photocatalyst, there is
an empirical proportionality between the two values and it can be conveniently exploited. By measuring the scatter level far from absorption peaks, one would use the proportionality to reconstruct the scatter contribution at 665 nm under the methylene blue absorption peak. This contribution will have to be subtracted from the peak absorbance to yield the correct methylene blue signal. Note that calculating and subtracting the scattering must be done individually for each spectrum.

The remote spectral region far from absorption peaks was chosen at 375 nm (for TiO$_2$-containing catalysts) or 420 nm (for SiO$_2$-containing catalysts). 15 mg of each deposited sulfide as well as titania and silica were each added to 85.0 mL of Millipore water in a 100 mL beaker. The measured masses are listed in Table 7 below.

<table>
<thead>
<tr>
<th>Solid Tested</th>
<th>Mass (mg ± 2 mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS$_2$/SiO$_2$</td>
<td>15</td>
</tr>
<tr>
<td>MoS$_2$/SiO$_2$</td>
<td>15</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>14</td>
</tr>
<tr>
<td>WS$_2$/TiO$_2$</td>
<td>15</td>
</tr>
<tr>
<td>MoS$_2$/TiO$_2$</td>
<td>15</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>15</td>
</tr>
</tbody>
</table>

The silica, titania, and deposited sulfide mixtures were stirred vigorously for over two hours before samples were taken for UV-spectroscopy. Samples were taken from each mixture over a period of several hours. The measured absorption at 665 nm was plotted versus absorption at 420 nm (for SiO$_2$ containing mixtures) or versus absorption at 375 nm (for TiO$_2$ containing mixtures). A satisfactory linear relationship was found in each case as shown in the next chapter.
4.2.4. Acetone Methylene Blue Degradation By Unsupported MoS$_2$ and WS$_2$

Rates of degradation of acetone with unsupported WS$_2$ or MoS$_2$ were determined. As a control, the degradation rate of acetone in absence of photocatalysts was determined as well. A 0.02 M solution of acetone in Millipore water was first prepared. Then, 50.0 mL of .02 M acetone was added to three 250 mL beakers. One was clean and dry for the control trial, the other two had WS$_2$ or MoS$_2$ dispersed in chloroform dried in them. The masses were 18 mg of WS$_2$ or 11 mg of MoS$_2$. Drying was done immediately before weighing and then adding the acetone solution followed by 150.0 mL of Millipore water. The mixture was then stirred for at least fifteen minutes. The same lamp setup was used as for the silica-deposited sulfide trials as well as the titania-deposited sulfide trials, and the sulfide appeared to adhere to the bottom of the beaker and stirrer as with the free nanoparticles. The magnetic stirrer in this case was set to two out of 10 to slowly stir the mixture. One sample was taken directly before opening the lamp shutter and the absorption of this at 265 nm was used as $A_0$. During 4 to 7 hours of irradiation, samples were taken as before for UV-visible spectroscopy to monitor the degradation of acetone by relative absorption.
Chapter 5. Photocatalytic Degradation Tests: Results

5.1. Methylene blue degradation by unsupported MoS$_2$ and WS$_2$

During the degradation of methylene blue by a photocatalyst, the reaction can be monitored by observing a prominent absorption peak of methylene blue at 665 nm. If the original absorbance at 665 nm is $A_0$, then it decreases to $A$ as methylene blue is degraded. Figure 22 shows the methylene blue photodegradation kinetics under visible light.

![Degradation of Methyene Blue with a Long-Pass 435 nm Filter by Metal Sulfide Catalysts](image)

**Figure 22.** Relative UV-visible absorption at 665 nm plotted over time using unsupported MoS$_2$ and WS$_2$ as the catalysts.
The relative absorption, \( A/A_0 \), provides a convenient measure of the extent of reaction. It has to be noted that the original absorbance, \( A_0 \), is usually an average of measured several measurements before the photoreaction is started.

Three separate trials were conducted: on unsupported nanoparticulate MoS\(_2\), WS\(_2\), and in the control experiment with no photocatalyst added. Methylene blue concentration decreases in all three cases. This means that in addition to the sulfide-catalyzed heterogeneous process, there is also a possible self-degradation of methylene blue due to the interaction of the optically excited dye with dissolved oxygen in the solution. The exact mathematical expression for the reaction kinetics is not known.

If the reaction rate is proportional to the concentration of methylene blue, the first-order kinetics would lead to an exponential decay curve. Zero-order kinetics could lead to linear decay plots if the reaction rate is independent of the concentration of methylene blue in the solution. This can be the case if the rate-limiting step is the diffusion of photoproduced electrons and holes to the surface or in the case of some adsorption-desorption equilibria.[16] Over the period of 6-8 hours, the curvature in the kinetic data is not apparent. On this time scale, each data set can be approximated with a line. First-order exponential curves did not produce significantly better fits as judged by r-squared values.

Regression analysis was performed in Microsoft Excel to find the best-fit line for each trial, and the obtained slopes and fitting errors are listed in Table 8. Comparisons of the reaction rates are made by comparing the slopes of the fits. Statistical analysis was carried out focusing on the slope for each trial to determine if the different slopes were a result of random error. The standard deviation of each slope was determined using the
LINEST function in Excel. The margin of error for each slope was calculated at the 90% confidence level ($\pm 1.645 \delta$, where $\delta$ is the standard deviation).

Table 8. Analysis of the rates of the methylene blue degradation by unsupported MoS$_2$ and WS$_2$. Slopes of the linear fits from Figure 22 are listed along with the error limits at the 90% confidence level.

<table>
<thead>
<tr>
<th></th>
<th>MoS$_2$</th>
<th>WS$_2$</th>
<th>Control (No Catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$ Value</td>
<td>0.9979</td>
<td>0.9926</td>
<td>0.9976</td>
</tr>
<tr>
<td>Slope ($x10^{-2}$ hr$^{-1}$)</td>
<td>-3.7 ± 0.1</td>
<td>-4.6 ± 0.296</td>
<td>-4.13 ± 0.15</td>
</tr>
<tr>
<td>Upper Limit ($x10^{-2}$ hr$^{-1}$)</td>
<td>-3.6</td>
<td>-4.4</td>
<td>-3.98</td>
</tr>
<tr>
<td>Lower Limit ($x10^{-2}$ hr$^{-1}$)</td>
<td>-3.8</td>
<td>-4.9</td>
<td>-4.28</td>
</tr>
</tbody>
</table>

In the presence of WS$_2$, the relative absorption at 665 nm decreases faster over time compared to the control. The slope of the plot is more negative, indicating that the degradation of methylene blue was catalyzed by WS$_2$ nanoparticles. At the same time, MoS$_2$ failed to catalyze the degradation of methylene blue under the reaction conditions.

Moreover, nanosized MoS$_2$ apparently exhibits a less negative slope than the control, which lacked any catalyst. This indicates the use of MoS$_2$ led to less photodegradation of methylene blue than the photobleaching observed without catalyst. This underscores the challenges of photocatalytic measurements under conditions when the photocatalyst is not uniformly dispersed in the solution but remains attached to the bottom of the reactor.

Some of these issues relate to the experiment design. Deposition of the photocatalysts by drying the chloroform suspensions is inherently not very reproducible. It can introduce variations of the solid layer thickness from experiment to experiment. In addition, when a Teflon stirring bar spins on the deposited nanoparticulate layer, the nanoparticles are capable of transferring from the glass onto the Teflon stirring bar over the course of an experiment. This introduces another variable into the kinetics. These issues can be overcome by “solubilizing” the photocatalyst in the reaction mixture by means of depositing it onto a highly dispersed hydrophilic substrate. This strategy is
explored by using highly dispersed SiO$_2$ and TiO$_2$ powders as described in the following sections.

Other considerations involve the choice of an organic compound for photodegradation. Since the MoS$_2$ and WS$_2$ nanoparticles are very hydrophobic, they likely undergo clustering in aqueous media, which decreases the sulfide-water interface area. Interfacial charge transfer of electrons and holes would be hindered and, logically, this would greatly diminish the photocatalytic efficiency. The overall kinetics might become dominated by side reactions, such as self-degradation of a dye due to electronic excitations and subsequent interactions with oxygen. Visible light irradiation at $\geq 435$ nm can excite the methylene blue electronic transition at 665 nm and initiate the homogeneous self-degradation. Such side reactions can be minimized if another organic compound is used, which does not have appreciable electronic transitions in the visible or near-UV region. Under these conditions, the heterogeneous catalytic processes can be detected more reliably. This strategy is explored by using acetone photodegradation as described in the last section.

5.2. Methylene blue degradation by MoS$_2$ and WS$_2$ supported on SiO$_2$

The relative absorption of methylene blue at 665 nm was plotted over time during photodegradation with MoS$_2$/SiO$_2$, WS$_2$/SiO$_2$, and with the SiO$_2$ control. Regression analysis by Excel yielded best-fit lines for each. Each data set in Figure 23 contains three data points at Time = 0 hours. However, not all of the symbols are visible due to overlap. These three data points effectively weight each fit line toward the y-intercept of 1.0.
Figure 23. Methylene blue degradation by MoS$_2$/SiO$_2$, WS$_2$/SiO$_2$, and with the SiO$_2$ control. Relative UV-visible absorption at 665 nm plotted vs. time.

From the initial examination of the plot, both MoS$_2$/SiO$_2$ and WS$_2$/SiO$_2$ seemed to catalyze the methylene blue photodegradation compared to the SiO$_2$ control. From the raw data, it appears that the silica-supported MoS$_2$ might be somewhat more active than the WS$_2$.

The standard deviations of the slopes were again calculated using the Linest function in Excel to give the margin of error at the 90% Confidence Level. These are listed in Table 9. The R-squared value of 0.6649 for the control plot suggests that there is much scatter in the data, so the error in the slope may be too large to statistically determine that the different slopes are not a result of random error. The error range for the control is nearly twice that of either of the other two trials.
Table 9. Analysis of the rates of the methylene blue degradation by MoS$_2$/SiO$_2$ and WS$_2$/SiO$_2$. Slopes of the linear fits from Figure 23 are listed along with the error limits at the 90% confidence level.

<table>
<thead>
<tr>
<th>Solid</th>
<th>MoS$_2$/SiO$_2$</th>
<th>WS$_2$/SiO$_2$</th>
<th>Control (SiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$ Value</td>
<td>0.9386</td>
<td>0.8873</td>
<td>0.6649</td>
</tr>
<tr>
<td>Slope ($\times 10^{-2}$ hr$^{-1}$)</td>
<td>-2.7 $\pm$ 0.4</td>
<td>-2.3 $\pm$ 0.45</td>
<td>-1.9 $\pm$ 0.8</td>
</tr>
<tr>
<td>Upper Limit ($\times 10^{-2}$ hr)</td>
<td>-2.3</td>
<td>-1.9</td>
<td>-1.1</td>
</tr>
<tr>
<td>Lower Limit ($\times 10^{-2}$ hr)</td>
<td>-3.2</td>
<td>-2.8</td>
<td>-2.7</td>
</tr>
</tbody>
</table>

Due to that, at the 90% Confidence Level, the slopes of the WS$_2$ and MoS$_2$ runs already fall within the error limits of the control. Therefore, without additional data processing, we cannot say that either MoS$_2$/SiO$_2$ or WS$_2$/SiO$_2$ catalyzes the degradation of methylene blue at the 90% confidence level.

5.3. Methylene blue degradation by MoS$_2$ and WS$_2$ supported on SiO$_2$: Accounting For Light Scattering by SiO$_2$

Data from MoS$_2$/SiO$_2$, WS$_2$/SiO$_2$, and the SiO$_2$ control were adjusted to account for the light scattering by the solids. In a separate experiment, light scattering was determined for MoS$_2$/SiO$_2$, WS$_2$/SiO$_2$, and SiO$_2$ aqueous suspensions (see Table 7). Absorbance at 665 nm was plotted against the absorbance at 420 nm for all three systems (Figure 24). 665 nm is where methylene blue normally absorbs. 420 nm is where methylene blue does not absorb and the only light losses here are due to scattering plus any absorption by the deposited sulfide.

Table 10. Functions relating the scatter at 665 nm and 420 nm for MoS$_2$/SiO$_2$, WS$_2$/SiO$_2$, and SiO$_2$.

<table>
<thead>
<tr>
<th>Solid</th>
<th>MoS$_2$/SiO$_2$</th>
<th>WS$_2$/SiO$_2$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Function</td>
<td>$y = 0.5518x + 0.0224$</td>
<td>$y = 0.5178x + 0.0208$</td>
<td>$y = 1.0113x + 0.1963$</td>
</tr>
<tr>
<td>$R^2$ Value</td>
<td>0.9977</td>
<td>0.9684</td>
<td>0.967</td>
</tr>
</tbody>
</table>
Figure 24. Linear correlation between light intensity losses at 665 nm and at 420 nm for aqueous suspensions of three solids: (A) MoS$_2$/SiO$_2$, (B) WS$_2$/SiO$_2$, (C) SiO$_2$. 
Regression analysis by Excel calculated best-fit lines for each. The solids, their equations, and the R-squared values along with the corresponding trials are listed in Table 10.

The linear correlations yield different slopes for each of the three solids, which is to be expected. Light scattering in a particular direction depends on the wavelength, the particle size, and the refraction index, which also depends on the absorption spectrum, according to Raleigh Theory.[17] As the MoS₂ or WS₂ nanoparticles attach to the SiO₂ nanoparticles, the resulting particle size is larger and there is a change in the absorption spectrum as well as the refraction index.

The found spectral correlations were then applied to the absorption measurements for the reaction mixtures containing methylene blue and MoS₂/SiO₂, or WS₂/SiO₂, or the SiO₂ control. Scatter contribution at 665 nm was calculated for each spectral measurement for each system. The calculated scatter contributions were then subtracted from their respective measurements yielding a more correct absorbance of methylene blue. Figure 25 displays these corrected kinetic data. Regression analysis was used to determine best-fit lines. The slopes all increase in magnitude because now the A₀ and A values have been reduced by subtracting the scattering contribution from each. While dividing by a smaller number, any change in the numerator will make a larger change in the quotient.
Using WS₂ as a catalyst now appears to degrade methylene blue even faster than using MoS₂, which still degrades methylene blue faster than the silica control.

Statistical analysis was performed with the excel function Linest to find the standard deviation for each slope and calculate the margin of error at the 90% Confidence Level.

Table 11. Analysis of the rates of the methylene blue degradation by MoS₂/SiO₂ and WS₂/SiO₂. Slopes of the linear fits from Figure 25 are listed along with the error limits at the 90% confidence level.

<table>
<thead>
<tr>
<th></th>
<th>MoS₂/SiO₂</th>
<th>WS₂/SiO₂</th>
<th>Control (SiO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R² Value</td>
<td>0.9725</td>
<td>0.9767</td>
<td>0.6394</td>
</tr>
<tr>
<td>Slope (x10⁻² hr⁻¹)</td>
<td>-4.4 ± 0.46</td>
<td>-5.14 ± 0.435</td>
<td>-2.7 ± 1.24</td>
</tr>
<tr>
<td>Upper Limit (x10⁻² hr⁻¹)</td>
<td>-3.9</td>
<td>-4.70</td>
<td>-1.4</td>
</tr>
<tr>
<td>Lower Limit (x10⁻² hr⁻¹)</td>
<td>-4.8</td>
<td>-5.57</td>
<td>-3.9</td>
</tr>
</tbody>
</table>

There is an overlap in the error limits for MoS₂/SiO₂ and the error limits for the control at the 90% Confidence Level. However, the slopes in the plots for the use of MoS₂/SiO₂...
and WS$_2$/SiO$_2$ as catalysts are significantly more negative than the slope of the control plot at the 90% Confidence Level. Further, the slope of the WS$_2$/SiO$_2$ plot is significantly more negative than that of the MoS$_2$/SiO$_2$ plot. These facts indicate that both sulfides successfully catalyzed the degradation of methylene blue under light ≥ 400 nm, but WS$_2$/SiO$_2$ worked significantly better as a catalyst than MoS$_2$/SiO$_2$.

5.4. Methylene blue degradation by MoS$_2$ and WS$_2$ supported on TiO$_2$-Anatase

The relative absorption of methylene blue at 665 nm was plotted over time during photodegradation with MoS$_2$/TiO$_2$, WS$_2$/TiO$_2$, and with the TiO$_2$ control.

![Degradation of Methylene Blue with a Long-Pass 400 nm Filter by Titania Deposited Catalyst](image)

**Figure 26.** Relative UV-visible absorption at 665 nm plotted over time using titania and titania deposited MoS$_2$ and WS$_2$ as catalysts.
Regression analysis by Excel yielded best-fit lines for each. The control run, TiO$_2$, had scattering that changed throughout the experiment, and this changing contribution to absorption is reflected in the R-squared value of only .4796. Although WS$_2$/TiO$_2$ has a visually more negative slope, it is still useful to analyze the error in each slope using the Linest function to determine if there is any statistical difference between the slopes of each run at the 90% Confidence Level.

Table 12. Analysis of the rates of the methylene blue degradation by MoS$_2$/TiO$_2$ and WS$_2$/TiO$_2$. Slopes of the linear fits from Figure 26 are listed along with the error limits at the 90% confidence level.

<table>
<thead>
<tr>
<th>R$^2$ Value</th>
<th>MoS$_2$/TiO$_2$</th>
<th>WS$_2$/TiO$_2$</th>
<th>Control (TiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (x10$^{-2}$ hr$^{-1}$)</td>
<td>-0.950 ± 0.3303</td>
<td>-2.4 ± 0.1</td>
<td>-0.959 ± 0.735</td>
</tr>
<tr>
<td>Upper Limit (x10$^{-2}$ hr)</td>
<td>-0.620</td>
<td>-2.3</td>
<td>-0.224</td>
</tr>
<tr>
<td>Lower Limit (x10$^{-2}$ hr)</td>
<td>-1.281</td>
<td>-2.5</td>
<td>-1.694</td>
</tr>
</tbody>
</table>

The MoS$_2$/TiO$_2$ and TiO$_2$ slopes are statistically identical because the slope of each falls into the error limits for the slope of the other. The slope of WS$_2$/TiO$_2$ is significantly more negative than that of the others, and its error limits do not overlap the error limits of the other two trials at this confidence level. So, this data indicates a significant increase in the rate of methylene blue degradation at the 90% Confidence Level when WS$_2$/TiO$_2$ is used in place of TiO$_2$.

5.5. Methylene blue degradation by MoS$_2$ and WS$_2$ supported on TiO$_2$-Anatase: Accounting For Light Scattering by TiO$_2$.

Data from MoS$_2$/TiO$_2$, WS$_2$/TiO$_2$, and the TiO$_2$ control were adjusted to account for the light scattering by the solids. In a separate experiment, light scattering was determined for MoS$_2$/TiO$_2$, WS$_2$/TiO$_2$, and TiO$_2$ aqueous suspensions (see Table 7).
Absorbance at 665 nm was plotted against the absorbance at 375 nm for all three systems (Figure 27). 665 nm is where methylene blue normally absorbs. 375 nm is where methylene blue does not absorb and the only light losses here are due to scattering plus any absorption by the deposited sulfide. The best-fit function for each trial was determined by regression analysis in Excel.

Figure 27. Linear correlation between light intensity losses due to scattering at 665 nm and at 375 nm for aqueous suspensions of three solids: (A) MoS$_2$/TiO$_2$, (B) WS$_2$/TiO$_2$, (C) TiO$_2$.

The line function and the R-squared value for each is displayed in Table 13 for easy reference. The disparity between the scatter caused by the same mass of these different solids reflects the need to adjust the titania-deposited sulfide trials for scattering. This difference is not simply due the higher molecular weight of the deposited sulfide since the mass ratio of sulfide to titania is only 1:100. It could be due to a difference in the
ability for the solid to disperse in a given amount of time spent stirring, particle size, or refraction index as pointed out in the case of SiO₂ scattering.

**Table 13.** Functions relating the scatter at 665 nm and 375 nm for MoS₂/TiO₂, WS₂/TiO₂, and TiO₂.

<table>
<thead>
<tr>
<th>Solid</th>
<th>MoS₂/TiO₂</th>
<th>WS₂/TiO₂</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Function</td>
<td>y = 0.8056x + 0.0021</td>
<td>y = 0.712x + 0.008</td>
<td>y = 0.8549x + 0.0481</td>
</tr>
<tr>
<td>R² Value</td>
<td>0.9982</td>
<td>0.9981</td>
<td>0.9971</td>
</tr>
</tbody>
</table>

The functions for MoS₂/TiO₂, WS₂/TiO₂, and TiO₂ scattering from Table 13 were then applied to the absorption measurements at 375 nm for MoS₂/TiO₂, WS₂/TiO₂, and TiO₂ respectively. This resulted in a calculated scatter contribution for each measurement of 665 nm absorption in these three degradation runs. The calculated scatter contributions were then subtracted from their respective measurements. For each trial, the last measurement of original absorption was used as the first data point and A₀ to avoid using an average of growing scatter. The MoS₂/TiO₂ and WS₂/TiO₂ have more negative slopes than the control, TiO₂. The best fit line for the control has a higher R-squared value now that the scatter has been subtracted. This data at 665 nm was plotted in Excel as Figure 28.
Figure 28. Methylene blue degradation by MoS$_2$/TiO$_2$, WS$_2$/TiO$_2$, and with the TiO$_2$ control. Relative UV-visible absorption at 665 nm has been corrected for the light scattering.

The MoS$_2$/TiO$_2$ and WS$_2$/TiO$_2$ have more negative slopes than the control, TiO$_2$. The most noticeable change is that the control data fits the function much better with an R-squared value of 0.8682 compared to an R-squared value of 0.4796 before the scatter was subtracted. Each slope has increased with the subtraction of the scatter from the $A_0$ of each trial, and so has the standard deviation of the slopes as calculated by the Linest function in Excel.

Table 14. Error Analysis of the rates of the methylene blue degradation by MoS$_2$/TiO$_2$ and WS$_2$/TiO$_2$. Slopes of the linear fits from Figure 28 are listed along with the error limits at the 90% confidence level.

<table>
<thead>
<tr>
<th></th>
<th>MoS$_2$/TiO$_2$</th>
<th>WS$_2$/TiO$_2$</th>
<th>Control (TiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$ Value</td>
<td>0.9976</td>
<td>0.9900</td>
<td>0.8682</td>
</tr>
<tr>
<td>Slope (x10$^{-2}$ hr$^{-1}$)</td>
<td>-4.8 ± 0.22</td>
<td>-5.80 ± 0.554</td>
<td>-3.0 ± 1.1</td>
</tr>
<tr>
<td>Upper Limit (x10$^{-2}$ hr)</td>
<td>-4.5</td>
<td>-5.25</td>
<td>-1.9</td>
</tr>
<tr>
<td>Lower Limit (x10$^{-2}$ hr)</td>
<td>-5.0</td>
<td>-6.36</td>
<td>-4.1</td>
</tr>
</tbody>
</table>
As Table 14 shows, the error limits at the 90% Confidence Level do not overlap, which means that these slopes are statistically different and the increase in the magnitude from one slope to the next is significant. So, to the 90% Confidence Level, both MoS$_2$/TiO$_2$ and WS$_2$/TiO$_2$ significantly increased the rate of degradation of methylene blue compared to the use of the TiO$_2$ control. They succeeded in sensitizing the titania to visible light for use as a catalyst. The increase in the magnitude of the slope for use of WS$_2$/TiO$_2$ compared to MoS$_2$/TiO$_2$ was also significant at this confidence level, meaning that WS$_2$/TiO$_2$ exhibited more photocatalytic activity than MoS$_2$/TiO$_2$.

A comparison between WS$_2$/SiO$_2$ and WS$_2$/TiO$_2$ can be made (Table 12 and Table 14). Titania-supported WS$_2$ exhibited 13% higher photocatalytic efficiency than its silica-supported counterpart. The effect is probably due to the semiconducting nature of TiO$_2$, which allows for charge separation at the TiO$_2$-WS$_2$ interface. With MoS$_2$, the comparison is not so definitive. At a first glance, MoS$_2$/TiO$_2$ indeed exhibits a steeper slope of the kinetic data than MoS$_2$/SiO$_2$, implying a higher photocatalytic activity. However, given the scatter in the MoS$_2$/SiO$_2$ photocatalysis data, the slope of the MoS$_2$/TiO$_2$ plot fits within the error limits of the slope for the MoS$_2$/SiO$_2$ plot at the 90% Confidence Level. So, the slope using MoS$_2$/TiO$_2$ was not significantly more negative than the slope using MoS$_2$/SiO$_2$ as a catalyst.

5.6. Acetone Degradation By Unsupported MoS$_2$ and WS$_2$

Unsupported MoS$_2$ and WS$_2$ catalyze photodegradation of acetone upon irradiation with visible light of $\geq$ 400 nm wavelength. The absorption peak of acetone at 265 nm progressively decreases (Figure 29).
Degradation of Acetone by Molybdenum Sulfide and Light $\geq$ 400 nm Over Time with Baseline Subtracted

![Graph showing absorbance over time with baseline subtraction](image)

**Figure 29.** The 265 nm absorption peak in the baseline corrected spectrum of acetone decreases as the acetone/MoS$_2$ mixture is irradiated by light $\geq$ 400 nm.

Since the unsupported sulfides do not disperse in the aqueous solution, there is no light scattering contribution to subtract from the spectra. Due to the UV source variations in the spectrometer, the acetone spectra are often slightly offset with respect to each other. The offset can be removed by subtracting the baseline as measured at 320 nm.

The spectrum at 390 minutes may or may not indicate non-isosbestic behavior. It is difficult to conclude if an isosbestic point is present in this short wavelength region because random variations in the source make this region unreliable.
For MoS$_2$, WS$_2$, and the catalyst-free control solution, the baseline corrected absorbance measurements were plotted in Excel and the best-fit lines were found by regression analysis (Figure 30).

![Degradation of Acetone with a Long-Pass 400 nm Filter by Metal Sulfide Catalysts](image)

**Figure 30.** Baseline corrected, relative UV-visible absorption at 265 nm plotted over time using unsupported MoS$_2$ and WS$_2$ as the catalysts.

From the plot, it is noticeable that the two metal sulfides successfully catalyze the acetone degradation compared to the control mixture because they exhibit more negative slopes than the control.

Using the Excel Linest function to calculate the standard deviation in the slope, the error limits at the 90% Confidence Level were calculated (Table 15).
Table 15. Analysis of the rates of the acetone degradation by unsupported MoS$_2$ and WS$_2$. Slopes of the linear fits from Figure 30 are listed along with the error limits at the 90% confidence level.

<table>
<thead>
<tr>
<th></th>
<th>MoS$_2$</th>
<th>WS$_2$</th>
<th>Control (No Catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$^2$ Value</td>
<td>0.9839</td>
<td>0.8514</td>
<td>0.7924</td>
</tr>
<tr>
<td>Slope (x10$^{-2}$ hr$^{-1}$)</td>
<td>-2.69 ± 0.28</td>
<td>-1.84 ± 0.634</td>
<td>-1.2 ± 0.6</td>
</tr>
<tr>
<td>Upper Limit (x10$^{-2}$ hr$^{-1}$)</td>
<td>-2.41</td>
<td>-1.21</td>
<td>-0.6</td>
</tr>
<tr>
<td>Lower Limit (x10$^{-2}$ hr$^{-1}$)</td>
<td>-2.97</td>
<td>-2.48</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

From these it can be seen that although error limits overlap, the slopes of the MoS$_2$ and WS$_2$ runs are significantly more negative than that of the control at the 90% Confidence Level. The slope of MoS$_2$ is also significantly more negative than that of WS$_2$. So, it would be correct to say at the 90% Confidence Level that the use of MoS$_2$ as a catalyst significantly increased the degradation rate of acetone with visible light compared to the use of WS$_2$ as a catalyst, and that both sulfides catalyzed the degradation of acetone relative to the use of visible light alone.

5.7. Conclusions

1. Pure MoS$_2$ and WS$_2$ nanoparticles are very hydrophobic, which presented a challenge in conducting the photocatalytic measurements in aqueous solutions. Inability to disperse in water likely lowers the sulfide-water interface area and lowers the overall efficiency of interfacial charge transfer. As a result, any side reactions and variations of experimental conditions can mask the photocatalytic reaction kinetics.

2. Tests of the degradation of methylene blue by the unsupported sulfides under visible light ($\lambda \geq 435$ nm) demonstrated the photocatalytic activity of WS$_2$ but not that of MoS$_2$, likely due to sufficient photo-bleaching rate of methylene blue under intense light. In experiments with acetone, which is less susceptible to photo-bleaching, photocatalytic activity was observed with MoS$_2$ and, to a lesser degree, with WS$_2$. 

63
3. Supporting the sulfide nanoparticles on SiO$_2$ or TiO$_2$ allowed dispersing them in the aqueous medium and increased the overall rates of photocatalytic degradation of methylene blue. Accounting for light scattering by solids was essential here.

4. When silica, an insulator, is used as a support, WS$_2$/SiO$_2$ exhibits higher photocatalytic activity than MoS$_2$/SiO$_2$. Both succeeded in catalyzing the degradation of methylene blue compared to the SiO$_2$ control at the 90% Confidence Level.

5. When titania, a semiconductor, is used as a support, WS$_2$/TiO$_2$ exhibits higher photocatalytic activity than MoS$_2$/TiO$_2$, and both of these composite catalysts were successful at increasing the degradation rate of methylene blue compared to TiO$_2$ at the 90% Confidence Level. The titania-supported WS$_2$ was significantly more photoactive than the silica-supported WS$_2$ at the 90% Confidence Level. This was probably due to the semiconducting nature of TiO$_2$, which allows for charge separation at the TiO$_2$-sulfide interface. Even though the titania-supported MoS$_2$ appeared at first glance to be more photoactive than the silica-supported MoS$_2$, the increase in the degradation rate of methylene blue was not significant at the 90% Confidence Level.
References

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