Morphological Studies, Photocatalytic Activity, and Electrochemistry of Platinum Disulfide Nanoparticles from Bis(morpholinyl-4-carboxidithioato)-platinum(II)

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ABSTRACT: Bis(morpholinyl-4-carboxidithioato)-platinum(II) was synthesized and characterized using spectroscopic techniques and single-crystal X-ray crystallography. The Pt(II) complex crystallized in a monoclinic space group P2₁/n with a Pt(II) ion located on an inversion center coordinated two morpholinyl dithiocarbamate ligands that are coplanar to form a slightly distorted square planar geometry around the Pt(II) ion. The complex was thermolyzed at 120, 180, and 240 °C to prepare PtS₂ nanoparticles. Powder X-ray diffraction patterns confirmed the hexagonal crystalline phase for the as-prepared PtS₂ nanoparticles irrespective of thermolysis temperature. Bead-like shaped PtS₂−120 nanoparticles with a particle size in the range of 12.46–64.97 nm were formed at 120 °C, while PtS₂−180 prepared at 180 °C is quasi-spherical in shape with particles in the range of 24.30–46.87 nm. The PtS₂−240 obtained at 240 °C is spherical with particles in the range of 11.45–46.85 nm. The broad emission maxima of the as-prepared PtS₂ nanoparticles are ascribed to the particles’ broad size distributions. The photocatalytic degradation of methylene blue by the PtS₂ nanoparticles shows a maximum efficiency of 87% for PtS₂−240 after 360 min. The effects of photocatalytic dosage, irradiation time, pH medium, and scavengers were also evaluated. Cyclic voltammetry of the PtS₂ nanoparticles showed a reversible redox reaction, while the electrochemistry of the as-prepared PtS₂ indicates that the electron transfer process is diffusion-controlled.

INTRODUCTION

The industrialization of the 20th century lead to an increase and discharge of industrial pollutants to the aquatic water system and wastewater. ¹ Although several methods have been developed for the treatment of wastewater,²,³ the use of an advanced oxidation process (AOP) that utilizes semiconductor nanoparticles in the presence of sunlight to degrade harmful contaminants are being explored.⁴ The degradation in photocatalysis is ascribed to the promotion of an electron from the valence band of a semiconductor to the conduction band on photo-irradiation, which results in photogenerated holes with a high oxidative potential.⁵,⁶ Transition metal–semiconductor nanoparticles such as ZnS, NiS₂, CdS, ZnO, TiO₂, and GeO₂/Fe₂O₃ have been studied in photocatalytic hydrogen generation, photodegradation, and oxidation of organic contaminants.⁷–¹⁰ Metal sulfides are considered as efficient photocatalysts due to their ability to absorb light in the visible and ultraviolet region, electronic structure, and easier access to electron–hole pair on photoexcitation.¹¹ It has also been shown that metal sulfide can degrade toxic environmental contaminants to nonhazardous products.¹² Tavker and Sharma reported that bare MoS₂ has low photodegradation efficiency compared to cellulose-supported MoS₂, due to fast recombination of electron–hole pairs.¹² Nickel sulfide was also reported to degrade methylene blue by Marand et al.¹³ on exposure to visible light with an efficiency of ~56%.

Therefore, there is need for other metal sulfide semiconductors with improved photocatalytic efficiency to be developed. In recent years, there have been renewed interests in the applications of platinum chalcogenides in catalysis,¹⁴,¹⁵ photodetector,¹⁶ and photocatalysis.¹⁷ Ehsan et al.¹⁸ fabricated Pt thin films from platinum dialkyl dithiocarbamate with high efficiency as counter electrodes in dye-sensitized solar cells. PtS₂ and PtSe₂ are useful materials for electrocatalysis, nanoelectronics, and nano-optoelectronics because of their ultrastability, tunable band gap, high carrier mobility, and electrical conductivity.¹⁹ Platinum dichalcogenide has been evaluated as a photocatalyst due to its broad band gap and sustainable energy applications.²⁰ It has been shown that the morphology and porosity of metal dichalcogenide influence their electrochemical properties, and PtS₂ electrochemistry is dependent on the redox performance of the electroactive moiety in the presence of applied electrochemical potential.²¹
In view of the above, there is a need to investigate the photocatalytic efficiency, reusability, and recovery of platinum disulfide in the photocatalytic degradation of organic dyes as a means to reduce secondary pollution in the environment. Herein, we report the synthesis and crystal structure of bis(morpholinyl-4-carboxothioato)-platinum(II) and its use as a precursor to prepare PtS₂ nanoparticles at 120, 180, and 240 °C. The as-prepared PtS₂ nanoparticles were used as a photocatalyst for the degradation of methylene blue. The effects of parameters such as irradiation time, catalyst dosage, pH medium, and scavenging ability on the photocatalytic process were evaluated.

RESULTS AND DISCUSSION

Spectroscopic Studies. The overlay Fourier transform infrared (FTIR) spectra of the morpholinyl dithiocarbamate ligand and the Pt(II) complex (Figure S1) showed a single sharp band at 979 cm⁻¹ assigned to a ν(C–S) stretching vibration, which shifted to 1003 cm⁻¹ in the Pt(II) complex and indicate that the ligands bidentately coordinate the Pt(II) ion. The ν(C–N) stretching vibration that appeared as a single band at 1457 cm⁻¹ in the ligand shifted to 1498 cm⁻¹ in the complex. This band is an intermediated between ν(C–N) and ν(C≡N) and indicates a shift in electron density toward the metal center as a result of the coordination of the morpholinyl dithiocarbamate ligand to the Pt(II) ion. In the absorption spectra of the ligand, the bands at 263 and 287 nm are assigned to the intra-ligand transition due to the S–C, the (001) plane is favored, which results in the observed spherically shaped nanoparticles. The nanoparticles obtained at 240 °C are amorphous in nature due to the low intensity of most transitions of the ligand, while the band at 240 °C is ascribed to the delocalization of electron within the thioureide moiety of the dithiocarbamate ligand. In the Pt(II) complex, the absorption bands observed at 257 and 353 nm are assigned to intra-ligand charge transfer transitions and indicate the formation of charge transfer transitions and d→d transitions of the Pt(II) ion (Figure S2). These transitions are consistent with Pt(II) in a square planar environment, as confirmed by the crystal structure.

X-Ray Crystallography. The crystallographic data and relevant bond lengths and bond angles are listed in Tables 1 and 2. The Pt(II) complex crystallized in a monoclinic space group P2₁/n with the Pt(II) ion located on an inversion center bonded to two morpholinyl dithiocarbamate ligands that are coplanar to form a slightly distorted square planar geometry around the Pt(II) ion (Figure 1). The Pt–S bond lengths are approximately symmetrical with Pt1–S1 and Pt1–S1 bond lengths of 2.3141(8) Å, Pt1–S2 = 2.3166(15) Å, and Pt1–S2 = 2.3165(15) Å. The thioureido intermolecular C5–N1 bond length is 1.468(4) Å. The S1–C5 and S2–C5 (1.719(3) and 1.713(3) Å) bond lengths are shorter compared to typical S–C (1.815 Å) but longer than C=S (1.671 Å), which could be attributed to the delocalization of electron within the dithiocarbamate moiety. The S1–Pt1–S2 bite angle of 74.79° is lower than the 90° for the perfect bond angle of a square planar geometry, which indicates that the geometry around the Pt(II) ion is a distorted square planar geometry. Powder X-Ray Diffraction of PtS₂ Nanoparticles. The powder diffraction patterns of PtS₂ nanoparticles synthesized at 120, 180, and 240 °C are presented in Figure 2. PtS₂ synthesized at 120 and 180 °C favors the (100) plane, which can account for the bead-like shapes obtained, while at 240 °C, the (001) plane is favored, which results in the observed spherically shaped nanoparticles. The nanoparticles obtained at 240 °C are more crystalline in comparison with those obtained at 120 and 180 °C, which are amorphous in nature due to the low intensity of most planes (Figure 2, inset). This indicates that the formation of crystalline PtS₂ nanoparticles is favored at a higher temperature of 240 °C. The characteristic peaks of the nanoparticles are indexed to the 001, 100, 101, 002, 111, 200, 003, and 201 planes of the hexagonal phase of PtS₂ (JPCD: 01-070-1140).

| Table 1. Crystal Data and Structure Refinements of the Complex |
|---------------------------------------------------------------|
| [Pt(L)₂] |
| formula | C₁₀H₁₆N₂O₂Pt₀.₉₈S₄ |
| D_{obs} (g/cm³) | 2.385 |
| μ (μm⁻¹) | 10.153 |
| formula weight | 515.68 |
| T (K) | 100(2) |
| crystal system | monoclinic |
| space group | P2₁/n |
| a (Å) | 4.22070(10) |
| b (Å) | 20.3910(5) |
| c (Å) | 8.4414(2) |
| α (°) | 90 |
| β (°) | 98.7840(10) |
| γ (°) | 90 |
| V (Å³) | 718.21(3) |
| Z | 2 |
| Θ_{max} (°) | 28.209 |
| measured reflection | 6197 |
| independent reflection | 1752 |
| reflections used | 1587 |
| R_{int} | 0.0216 |
| parameters | 89 |
| restraints | 0 |
| largest peak | 2.795 |
| deepest hole | −2.560 |
| Goof | 1.179 |
| wR₂ (all data) | 0.0855 |
| wR₁ (all data) | 0.0822 |
| R₁ (all data) | 0.0321 |
| R₁ | 0.0299 |

| Table 2. Some Selected Bond Lengths (Å) for [Pt(L)₂] and Bond Angles (°) for [Pt(L)₂] |
|---------------------------------------------------------------|
| bond | length | atoms | angle |
| Pt1–S1 | 2.3141(8) | S1–Pt1–S1 | 180.00(4) |
| Pt1–S1 | 2.3141(8) | S1–Pt1–S2 | 74.79(3) |
| Pt1–S2 | 2.3165(15) | S2–Pt1–S2 | 180.0 |
| S1–C5 | 1.719(3) | C5–S1–Pt1 | 87.55(12) |
| S2–C5 | 1.713(3) | C5–S2–Pt1 | 87.62(12) |
| C1–N1 | 1.468(4) | C5–S2–C1 | 110.03(19) |
| C4–N1 | 1.462(5) | C5–N1–C1 | 122.3(3) |
The diffraction pattern of PtS$_2$-240 obtained at 240 °C shows a pure PtS$_2$ hexagonal phase. The lattice parameters “$a$” and “$c$” were calculated to be 3.549 and 4.978, respectively, which is close to those of the bulk ($a = 3.543$ and $c = 5.038$) using eq 1

\[
\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}
\]  

(1)

The Debye–Scherer equation $D = 0.94\lambda/\beta \cos \theta$ was used to calculate the average sizes of the synthesized PtS$_2$ nanoparticles. “$D$” is the average crystallite size, “$\lambda$” is the wavelength, and “$\beta$” and “$\theta$” are the full width at half-maximum (FWHM) and angle of the diffraction peak. Estimated average sizes were 37.88 nm for PtS$_2$-120, 48.76 nm for PtS$_2$-180, and 26.64 nm for PtS$_2$-240 along the 100 plane, which are relatively close to the sizes obtained from transmission electron microscopy (TEM) imaging.

**Morphological Studies of the PtS$_2$ Nanoparticles.** The TEM micrograph of PtS$_2$-120 prepared at 120 °C (Figure 3) revealed closely packed bead-like shaped nanoparticles with sizes in the range of 12.46–64.97 nm with a bit of aggregation. At 180 °C, the TEM micrograph of PtS$_2$-180 revealed agglomerated quasi-spherical-like shaped nanoparticles with particle size in the range of 38.44–59.31 nm. The TEM micrograph of PtS$_2$-240 prepared at 240 °C showed a spherical pattern.
particle with size ranges of 11.45–46.85 nm. As the temperature increases, the nanoparticles possess a large surface area due to van der Waals attractive forces, which has a tendency of minimizing the interfacial energy, consequently decreasing the sizes of the nanoparticles. The growth and nucleation of the nanoparticles are favored at low temperatures due to the use of molecular precursors, which favors the Ostwald ripening process until the organic bonds are broken by heat of reaction, allowing hexadecylamine to control PtS₂ nanoparticle growth, as seen in the TEM micrograph.

**Optical Properties of Platinum Disulfide Nanoparticles.** Absorption spectra of PtS₂ nanoparticles were recorded in the wavelength range of 230–800 nm. The spectra show that the different temperature results in a variation of absorption wavelengths, as shown in Figure 4a. The absorption band edge of PtS₂-120 nanoparticles is at 292 nm while that of PtS₂-180 appeared at 316 nm and PtS₂-240 at 321 nm. It has been shown that the particle size of nanoparticles affects their optical properties.\(^\text{31}\) The band gap of the synthesized PtS₂ nanoparticles was obtained by extrapolation of \((\alpha hv)^2\) versus \((hv)\) where \(\alpha\) and \(h v\) denote the absorption coefficient and the incident of light frequency. The band gap energy of platinum disulfide nanoparticles synthesized at 120 °C is 4.25 eV, while at 180 °C, it is 3.92 eV, and at 240 °C, it is 3.86 eV (Figure 4b). The band gap energy is higher than the bulk (1.53 eV),\(^\text{32}\) showing that the nanoparticles are blue-shifted from their bulk. The deviation from the bulk band gap is as a result of quantum confinement caused by photo-generated electron–hole pairs. The increase in the band gap is attributed to a decrease in the size of the nanoparticles. PtS₂ photoluminescence emission spectra at a 360 nm excitation wavelength are shown in Figure 4c. The emission maxima of the as-prepared platinum disulfide nanoparticles appeared at 488 nm for PtS₂-120, 449 nm for PtS₂-180, and 418 for PtS₂-240. These are red-shifted in comparison to absorption band edges. The broad emission curve of PtS₂ could be due to the distribution size of the particles\(^\text{31}\) and effective passivation of the surface trap by hexadecylamine. Furthermore, the rate of electron–hole recombination can be determined via the emission intensity as lower intensity corresponds to a lower recombination rate and vice versa.\(^\text{32}\) PtS₂-240 with lower emission peak intensity compared with the other two PtS₂ nanoparticles indicates lower electron–hole recombination rate. Thus, it might be an excellent photocatalyst for the degradation of methylene blue.

**Electrochemistry of the PtS₂ Nanoparticles.** The cyclic voltammetry of PtS₂ nanoparticles was measured in a potential window of −1.5 to +0.6 V using tetrabutylammonium hexafluorophosphate as an electrolyte. The cathodic peak at −0.99 V observed in all the PtS₂ nanoparticles is ascribed to the reduction of Pt from Pt⁴⁺ → Pt⁴⁻ → Pt⁰ (metal). The anodic peak detected at −0.8 V is ascribed to the dissociation of S²⁻ as it oxidized to HSO₄⁻ and SO₄²⁻, which has been reported to be thermodynamically stable.\(^\text{21,33}\) Also, during the five scan rates of PtS₂ nanoparticles, the curve shape shows no change, indicating the high stability of the nanoparticles.

The Randles–Sevcik equation \(I_{pa} = 0.4463nFAC(DV/RT)^{1/2}\) was used to investigate the electrochemical properties of the PtS₂ nanoparticles based on its reversible process. The plot of \(I_{pa}\) (cathodic peak current) versus \(v^{1/2}\) (scan rate square root) gave a linear relationship with an increment of scan rate showing diffusion control of the electron transfer process. This is an affirmation that the reaction temperature influences the electrochemical properties of the PtS₂ (Figure 5).

**Mott–Schottky Measurement.** To further confirm the semiconducting nature and band gap edge of the synthesized PtS₂ nanoparticles, Mott–Schottky measurement was done under electrochemical analysis. A p-type semiconductor is identified from the negative slope of the potential axis, while the positive slope indicates an n-type semiconducting material.\(^\text{35}\) Figure 6 indicates that PtS₂ is an n-type semiconductor. The estimated flat-band potential \(V_{fb}\) is obtained from the Mott–Schottky plot as values of −0.6S, −0.5S, and −0.75 V for PtS₂-120, PtS₂-180, and PtS₂-240, respectively. Based on the band gap potentials obtained from UV–vis absorption, the valence (VB) and conduction band (CB) of PtS₂ can be calculated using eqs 2 and 3 below:\(^\text{35}\)

\[
E_{\text{VB}} = X - E^e + (E_g/2) \tag{2}
\]

\[
E_{\text{CB}} = X - E^e - (E_g/2) \tag{3}
\]
where $E^e$ is the energy of free electrons on the hydrogen scale (4.5 eV), $E_g$ is the band gap energy, and $X$ (electronegativity) is estimated using eq 4 to be 5.99 eV. In our calculation, the electronegativity values for Pt and S were taken to be 5.55 and 6.22 eV, respectively.

$$X(PtS_2) = (X(Pt)X(S))^{1/3}$$ (4)

The VB and CB potentials are 3.62 and $-0.64$ V, respectively, for PtS$_2$-120, while for PtS$_2$-180, they are 3.45 and $-0.47$ V, and for PtS$_2$-240, they are 3.42 and $-0.44$ V. The potential at NHE (normal hydrogen electron) can be calculated using eq 5

$$V_{(NHE)} = V_{fb} + 0.059pH + 0.242$$ (5)

At pH 8, the corresponding $V_{(NHE)}$ values are 0.064, 0.164, and $-0.036$ for PtS$_2$-120, PtS$_2$-180, and PtS$_2$-240, respectively.

**Adsorption Evaluation of PtS$_2$ Nanoparticles.** The adsorption capacities of the samples were evaluated since adsorption has a great influence on the photocatalytic activity. The adsorption capacities of PtS$_2$-240 (0.79 mg/g) and PtS$_2$-180 (0.65 mg g$^{-1}$) were much higher than PtS$_2$-120, as shown in Figure 8a. It was also observed that the adsorption capacity increases drastically at 30 min and thereafter becomes stable until 60 min. Although the adsorption was more than 30 min in all the samples, it indicates that an adsorption—desorption—adsorption order was followed.$^{36}$ Therefore, the desired adsorption time was chosen to be 30 min.

**Photodegradation of Methylene Blue Using PtS$_2$ Nanoparticles as Catalyst.** Methylene blue is an organic pollutant model due to its toxicity to the environment. Evaluation of degradation efficiency of methylene blue using the synthesized PtS$_2$ was done in the presence of an 80 W mercury lamp. The absorption band at the 663 nm characteristic of methylene blue was used.

**Effect of Catalytic Dosage.** Figure 7 shows the effect of varying the dosage of the PtS$_2$ catalyst on the degradation of methylene blue. The degradation efficiency of the catalysts increases with the increase in the catalyst dosage from 0.2 to 1 mg/mL. The results showed that the degradation efficiencies of methylene blue using 0.2 mg of PtS$_2$-120, PtS$_2$-180, and PtS$_2$-240 are 27.89, 36.49, and 38.80%, respectively. The degradation...
Increasing the catalyst dosage might result in a decrease in the penetration of light. Therefore, a catalyst dosage of 1 catalyst, thereby increasing the production of active site numbers that are available on the surface of the catalyst. Consequently, the increase in catalytic dosage results in an increase in photodegradation efficiency due to their large surface area, which enhances their efficiency due to the increase in the active site and OH· scavengers on the PtS2 nanoparticle photocatalytic activity. In the presence of isopropanol, the degradation of methylene blue increased by 21.64, 14.31, and 26.03% for PtS2−120, PtS2−180, and PtS2−240, respectively. The order of efficiency was PtS2−120 < PtS2−180 < PtS2−240, and this degradation corresponds with their sizes. Nanoparticles with small sizes have been reported to have better degradation efficiency due to their large surface area, which enhances their absorption capability, thereby making them transfer an efficient electron charge in the oxidation—reduction process, which is in conformity with our results. The degradation efficiency observed with the synthesized nanoparticles is relatively close to that observed for the degradation of methylene blue using ZnS nanoparticles. This indicates that the as-synthesized PtS2 nanoparticles are good photocatalysts.

The degradation rate of methylene blue with respect to irradiation time in the presence of PtS2 nanoparticles as a catalyst was investigated using the Langmuir–Hinshelwood kinetic model. The natural logarithm of C/C0 versus irradiation time was plotted, showing a linear relationship (Figure 8c). The values of R² were 0.958, 0.9843, and 0.9948 for PtS2−120, PtS2−180, and PtS2−240, and their rate constants are 0.0029, 0.0048, and 0.0057 min⁻¹, respectively. PtS−120 has a lower photodegradation efficiency correlating with the degradation efficiency plot in Figure 8b.

The as-prepared platinum sulfide showed better degradation efficiency of methylene blue dye in comparison to other reports, as presented in Table 3. Most of the literature studies made use of high intensity and the watt light source, while we made use of low intensity and the watt light source.

**Photocatalyst Reusability.** It is important for the photo-stability of photocatalyst to be evaluated for practical purposes. Hence, PtS2−240 recyclability was evaluated for five cycles (Figure 8d). PtS2−240 was recovered after each degradation by washing with distilled water and centrifugation to remove the absorbed methylene blue. A slight decrease in the photocatalytic activity of PtS2−240 using methylene blue was observed after five cycles by retaining about 85% of its initial photocatalytic activity. The results show high stability of the photocatalyst and prove that the catalyst itself does not degrade but rather regenerate efficiently, making it a potential for practical application.

**Effect of Solution pH.** The pH of organic contaminants is very important in the photocatalytic degradation process. It helps in the generation of protons and hydroxyl radicals that play important roles in the oxidation and reduction process of holes and electrons, respectively. The effect of pH media on the degradation of methylene blue were evaluated at different pH values (3, 5, 6, 7, 9, and 11), and the results are shown in Figure 9. At pH 11, 1 mg/mL PtS2−120, PtS2−180, and PtS2−240 photocatalysts degraded 75.42, 88.88, and 99.55% of 10 mg/L methylene blue, respectively. The observed efficiency could be due to the increase in the active site and OH⁻ radical concentration. At pH 3, there was a reduction in photodegradation due to the increase of protons at low pH. The photodegradation can be explained using the mechanism below:

\[
PtS_2 + h\nu \rightarrow e^- + h^+ + PtS_2^-
\]

\[
h^+ + H_2O_{(aq)} \rightarrow OH_{(aq)}
\]

methylene blue_{(aq)} + OH → decolorization

**Scavengers Effect.** To explicate the degradation of methylene blue through PtS2 nanoparticles, isopropanol, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), and acrylamide (AC) were used respectively for hydroxyl radicals, holes, and superoxide radicals’ scavengers. Scavengers are compounds that inhibit free radicals’ activities during photodegradation, and this makes known the species actively involved in the process. Figure 10 shows the effects of different scavengers on the PtS2 nanoparticle photocatalytic activity. In the presence of isopropanol, the degradation of methylene blue

![Figure 6. Mott–Schottky spectra of PtS2 nanoparticles.](image-url)

Efficiencies increased to 63.79, 81.58, and 87.28% with 1 mg of PtS2−120, PtS2−180, and PtS2−240, respectively. This indicates that the increase in catalytic dosage results in an increase in active site numbers that are available on the surface of the catalyst, thereby increasing the production of OH⁻ and O₂⁻. Increasing the catalyst dosage might result in a decrease in efficiency due to the turbidity of the suspension, which reduces the penetration of light. Therefore, a catalyst dosage of 1 mg/mL was selected as the optimal value and used for further experiments.

**Effect of Irradiation Time.** The intensity of the peak was absorbed to decrease with an increase in irradiation time (Figure S4a–c) due to the photodegradation of methylene blue by the synthesized PtS2 nanoparticles. The graph in Figure 6a shows that the degradation efficiencies of methylene blue at 60 min were 21.64, 14.31, and 26.03% for PtS2−120, PtS2−180, and PtS2−240, respectively; increasing the irradiation time to 360 min, they became 63.80, 81.58, and 87.28%, respectively. The order of efficiency was PtS2−120 < PtS2−180 < PtS2−240, and this degradation corresponds with their sizes. Nanoparticles with small sizes have been reported to have better degradation efficiency due to their large surface area, which enhances their
was retarded; this indicates that the hydroxyl radicals (\( \cdot \text{OH} \)) play a significant role in the degradation of methylene blue. Introducing EDTA-2Na into methylene blue solution, the degradation was significantly reduced, suggesting that the hole (\( h^+ \)) has a role to play in the degradation process. The degradation could occur as a result of \( h^+ \) oxidizing the solution, consequently instigating the generation of \( \cdot \text{OH} \) through the reaction below:

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \cdot \text{OH}
\]

The addition of AC showed little effect in the degradation efficiency like other scavengers; this shows that \( \cdot \text{O}_2 \) plays an important role in the degradation of methylene blue during photocatalysis.

The results obtained from the scavenging activity shows that the participation of \( h^+ \), \( \cdot \text{O}_2 \), and \( \cdot \text{OH} \) dominates the degradation of methylene blue.

The photocatalytic degradation mechanism of methylene blue using synthesized PtS\(_2\) nanoparticles on exposure to visible light irradiation has been proposed on the basis of photocatalytic experiment and electrochemical measurement. The exposure of methylene blue solution containing PtS\(_2\) nanoparticles to light excites the conduction band, thereby generating electrons resulting in holes in the valence band:

\[
\text{PtS}_2 + h\nu \rightarrow e^- + h^+
\]

The resulting holes and electrons generated migrate to the PtS\(_2\) nanoparticle surface and react with the adsorbed reactant. The electrons react with surrounding oxygen to form a superoxide radical, while the hole reacts with hydrogen in water to form a hydroxyl radical. These radicals react with methylene blue, splitting them into carbon dioxide (CO\(_2\)) and water (H\(_2\)O) resulting from degradation:

\[
h^+ + \equiv\text{PtOH} \rightarrow \equiv\text{PtO} + \text{H}^+
\]

\[
e^- + \equiv\text{PtO} + \text{H}^+
\]

\[
e^- + \text{O}_2 \rightarrow \cdot \text{O}_2
\]

\[
\text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2
\]

\[
\text{methylene blue} + \text{O}_2^- + \cdot \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

Figure 7. Effect of PtS\(_2\) catalytic dosage and their corresponding plots of In(C\(_0\)/C) versus time.
CONCLUSIONS

Bis(morpholinyl-4-carbodithioato)-platinum(II) was synthesized and characterized by spectroscopic techniques and single-crystal X-ray crystallography. The molecular structure of the compounds revealed that the Pt(II) complex in a monoclinic space group $P2_1/n$ with the Pt(II) ion located on an inversion center coordinated to two morpholinyl dithiocarbamate ligands that are coplanar in a slightly distorted square planar geometry. The complex was thermolyzed at 120, 180, and 240 °C to prepare PtS$_2$ nanoparticles. Bead-like shaped nanoparticles were formed at 120 °C with a particle size of 12.46−64.97 nm, while at 180 °C, quasi-spherical particles with size in the range of 38.44−59.31 nm were obtained, and at 240 °C, spherically shaped nanoparticles were formed with particle size in the range of 11.45−46.85 nm. The optical band gap values of the as-prepared PtS$_2$ nanoparticles are 4.25, 3.91, and 3.58 eV. The reaction temperature was found to influence the size and band gap of the synthesized PtS$_2$ nanoparticles. The effect of photocatalytic dosage shows that the rate of photodegradation increases with an increase in the amount of PtS$_2$ photocatalyst dosage. The rate of photodegradation was found to be higher in the alkaline medium than the acidic medium. Holes (h$^+$), O$_2^-$, and OH radicals were found to be the active species in the photodegradation of methylene blue. Cyclic voltammetry of the PtS$_2$ nanoparticles showed a reversible redox reaction, while electrochemical studies show that the electron transfer process of the as-prepared PtS$_2$ nanoparticles is diffusion-controlled. Mott−Schottky showed that the PtS$_2$ nanoparticles are n-type in nature.

MATERIALS

The solvents and starting materials, potassium tetrachloroplatinate(II) (K$_2$PtCl$_4$), tri-octylphosphine (TOP), hexadecylamine (HDA), methanol, hexane, methylene blue, ethylenediaminetetraacetic acid disodium salt, acrylamide, isopropanol, hydrochloric acid, and sodium hydroxide were obtained from a commercial source and used without further purification. The sodium salt of morpholine dithiocarbamate was prepared, as reported previously.

EXPERIMENTAL SECTION

Synthesis of Pt(II) Complex. K$_2$PtCl$_4$ (0.25 mmol, 0.1038 g) aqueous solution was added slowly to sodium morpholine dithiocarbamate (0.5 mmol, 0.0926 g) aqueous solution and stirred for 6 h at room temperature. The resulting yellow precipitate was washed with distilled water several times, and dried over a silica gel. Rod-shaped crystals of the complex were obtained.
were obtained by slow evaporation of the dichloromethane solution of the complex.

Complex ([Pt(L)]). Yield 63%, yellow solid, m.p. 309–311 °C, Anal. Calcd for \([\text{Pt(S}_2\text{CNC}_4\text{H}_8\text{O})_2]\): C, 23.12; H, 3.10; N, 5.39; S, 24.68; Found: C, 23.43; H, 3.03; N, 5.38; S, 24.97. TOF MS: Anal. Calcd 518.9743, Anal. Found: 518.9747. Selected FTIR (solid state, cm\(^{-1}\)): 1498 \(\text{V}^-\text{N}\), 1003 \(\text{V}^-\text{S}, \text{U}^-\text{V}\) (CH\(_2\)Cl\(_2\)), \(\lambda_{\text{max}}\) nm); 257, 353, 419.

**Single-Crystal X-Ray Structure Determination.** Single crystal data of the complex were obtained on a Bruker SMART

Figure 9. Photocatalytic degradation of methylene blue using different pH solutions: (a) PtS\(_2\)-120 (b) PtS\(_2\)-180, and (c) PtS\(_2\)-240.

Figure 10. Effect of different scavengers on methylene blue photodegradation using PtS\(_2\) nanoparticles.
APEX2 area detector diffractometer using MoKα. The crystal temperature was maintained at 100(2)°K during data collection. Using Olex222 as a molecular graphical interface, the structure was solved with an SHELXS-201331 structure solution program using the direct solution method. The structure was refined with version 2016/6 of SHELXL54 using least squares minimization.

Preparation of Platinum Disulfide Nanoparticles. Hexadecylamine (4 g) was heated under nitrogen to 100 °C in a three-necked flask. The system was degassed and purged with nitrogen for 15 min. The temperature was then raised to 120 °C and stabilized. [Pt(L)2] (250 mg) was dissolved in 5 mL of tri-ocetylphosphine (TOP) and injected into hot HDA. The reaction was set for 1 h at 120 °C. Excess cold methanol was added to the solution at 70 °C. The ensuing flocculant was isolated from the supernatant by centrifugation and washed several with methanol. The procedure was repeated with the reaction temperature varied to 180 and 240 °C. The resulting nanoparticles were labeled as PtS2-120, PtS2-180, and PtS2-240.

Characterization Techniques. A Bruker Avance III NMR spectrometer (400 and 100.6 MHz) was used to obtain 1H and 13C NMR spectra using TMS as an internal reference. FTIR spectra were obtained on a PerkinElmer spectrum 100 FTIR spectrometer in the range of 4000–500 cm−1. Absorbance spectra were recorded on a PerkinElmer Lambda 25 UV–vis spectrophotometer. A Thermoscientific Flash 2000 was used for elemental analysis. A Philips PW1830 X-ray diffraction spectrometer was used for PtS2 phase identification. A JEOL 1400 transmission electron microscope was used to capture TEM images. Emission spectra of PtS2 were measured using a PerkinElmer LS 45 fluorescence spectrometer.

Adsorption Experiment. The adsorption capacity of the synthesized PtS2 nanoparticles was evaluated by dispersing 50 mg of each nanoparticle in 50 mL of methylene blue (10 mg/L). The resulting mixture was placed in a beaker, stirred in the dark for 60 min using a magnetic stirrer, and analyzed at regular time intervals. The adsorption capacity was calculated using eq 64

\[
Q_e = \frac{(C_0 - C_e)}{M} \times V
\]

where \(Q_e\) is the PtS2 adsorption capacity, \(C_0\) and \(C_e\) are the initial and residual dye concentration at time \(t\), \(M\) is the weight of the photocatalyst in grams, and \(V\) is the volume of the dye solution in liters.

Photocatalytic Activity of PtS2 Nanoparticles. The synthesized PtS2 nanoparticle photocatalytic activity was appraised through the degradation of methylene blue (as an organic pollutant) under visible light irradiation. Prior to the photocatalytic experiments, the adsorption of methylene blue on PtS2 nanoparticles was done by mixing 50 mL of aqueous solution (10 mg/L) with 50 mg of the nanoparticles. Adsorption–desorption equilibrium of the dye molecule on the nanoparticle surface was attained by stirring the mixture for 30 min in the dark. The solution was placed 10 cm away from the irradiation (80 W high-pressure mercury lamp). An aliquot was taken at intervals (60 min) for 360 min.55,56 The percentage of degradation was calculated using eq 7 below

\[
degradation(\%) = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) and \(C_t\) denote the methylene blue concentration at a time \(t\), 0 and for 360 min. The reaction rate constant of PtS2 as a photocatalyst was found using methylene blue degradation kinetics. To study the effect of pH solution on the photodegradation process, the initial solution was adjusted using 0.1 N HCl or 0.1 N NaOH.

Electrochemical Studies of PtS2 Nanoparticles. The electrochemical behavior of PtS2 nanoparticles was studied using an Autolab potentiostat equipped with three-electrode systems. The working electrode was glassy carbon, while the reference electrode is pseudo-Ag/AgCl, and the auxiliary platinum was used as a counter electrode. A fresh 2 mM solution of the nanoparticles alongside the supporting electrolyte (0.1 M tetrabutylammonium hexafluorophosphate) was prepared in dimethylsulfoxide (DMSO). The solutions were purged for about 20 min with nitrogen before each experiment.

ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03063.

FTIR spectra of ligand and complex (Figure S1); Electronic spectra of ligand and complex (Figure S2); TOF Mass Spectrum of complex (Figure S3) and photodegradation of methylene blue absorption spectra by the nanoparticle (Figure S4) (PDF)

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Notes

The authors declare no competing financial interest.

CCDC 1864307 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge crystallographic data centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44)-1223-336-033 or email: deposit@ccdc.cam.ac.uk.

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