Samarium Complexes from 2,6-Naphtalenedicarboxylate: Synthesis, Photocatalytic Properties and Degradation of Methylene Blue

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Abstract. Coordination polymer have been attracting considerable attention and present a great potensial in photocatalytic water treatment, paving the way for building efficient and enviromentally friendly photocatalysts. In this work, samarium complexes constructed from 2,6-naphtalenedicarboxylate ligand was successfully synthesized using solvothermal methode. Samarium complexes are characterized by Powder X-ray Diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Uv-vis Diffuse Reflectance and Cyclic Voltametric. FTIR characterization results indicate peak absence of absorption band around 1700 cm⁻¹ further confirms that the carboxylate groups in dicarboxylate ligand are completely deprotonated. The value of the band gap obtained from the corresponding transition is 3.1 eV. The LUMO Level reduction potential O₂/O₂⁻ is obtained -2.1 volt, this value is more negative than the potential standard O₂/O₂⁻ reduction is -0.33 volt, so the ability to form O₂⁻ is greater. Based on the characteristics obtained, this material potential as a semiconductor for photocatalysts methylene blue degradation, where samarium complexes in 240 minutes can degradation methylene blue by 68.6 percent.

1. Introduction
Dyes play a vital role in various branches of the dyeing and textile industries. The total annual production of synthetic dye is more than 7×10⁵ tons. Annually, through textile waste effluents, around one thousand tons of these non-biodegradable textile dyes are discharged into natural streams and water bodies [1]. One of the most commonly used dyes is methylene blue (MB). Even though the methylene blue threshold is only around 5-10 ppm [2]. Methylene blue contamination can cause various health problems. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [3]. In general, these dyes have been found to be resistant to biological as well as physical treatment technologies. In this regard, heterogeneous advanced oxidation processes (AOPs), involving photocatalyzed degradation of dyes using semiconductor is considered as an efficient cure for dye pollution [1].

Recently, the utilization of samarium complexes as semiconductor catalysts for organic dye photocatalysts under ultraviolet radiation or visible light irradiation. Samarium complexes constructed...
from ligan 2,6-naphtalenedicarboxylic acid are a novel class of 3D crystalline micro-mesoporous hybrid materials constructed from metal cluster nodes interconnected with multitentacted organic linkers. Samarium complexes can be regarded as isolated inorganic semiconductor quantum entities, while the organic linkers can serve as antenna for light harvesting and activate these semiconductor quantum dots via the linker to metal charge transfer (LMCT) upon light excitation [4].

Lanthanide ions with high coordination number and versatile coordination modes are widely adopted for the construction of large complexes allow for facile tuning of their light absorption to ensure an efficient utilization of the solar energy, and the highly crystalline nature of material can ensure rapid charge transfer from the light-excited organic linker to metal cluster. 2,6-naphthalenedicarboxylic acid (NDC) is able to increase the sensitivity of certain lanthanide metals, this shows the efficient transfer of ligand energy to metal [5]. Samarium complexes are considered to be promising in variety photocatalytic field, include water reduction and oxidation, CO₂ reduction, organic transformation as well as enviromental reductions have been reported [4]. In addition, samarium complexes show high dye degradation performance compared to metal oxides and sulfides [6].

Herein, we report the synthesis of a series samarium complexes constructed from 2,6-naphthalendicarboxylate ligand, using a solvothermal method. The complexes are characterized by Powder X-ray Diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Uv-vis Diffuse Reflectance and Cyclic Voltammograms. Methylene blue concentration after degradation measured with spectrophotometer UV/Vis.

2. Experimental

2.1. Materials and Characterization
All chemicals were purchased from commercial suppliers in analytical grade and used without further purification. The Powder X-ray Diffraction (PXRD) experiment was carried out on Rigaku D-MAX 2550 (λ = 1.54184 nm) with 2θ ranging from 5° to 70° under ambient conditions. The Fourier Transform Infrared (FTIR) spectrum was recorded using KBr pellets on a Shimadzu IR 8400S Spectrometer over range of 400-4000 cm⁻¹. The UV-Vis spectrum for the solid state sample was obtained on a Shimadzu UV-2450 spectrophotometer, and (CV) Cyclic Voltammograms measured with a CHI760D workstation in a conventional three electrode system with a scanning rate of 50 mV/s.

2.2. Synthesis of samarium complexes using solvothermal method
Samarium (III) nitrate hexahydrate (0.25 mmol) and 2,6-naphthalenedicarboxylic acid (0.25 mmol) were suspended in 6 mL N,N-dimethylformamide and 2 mL H₂O. The mixture was transferred to a stainless autoclave with a teflon container and kept at 120 °C for 20 hours. The autoclave cooled down naturally to room temperature. Yellow powder were collected and analyzed by FTIR (KBr pellet over range of 400-4000 cm⁻¹).

3. Results and Discussion

3.1 Preparation of the catalyst
Samarium complexes have been synthesized by solvothermal. This method employs samarium (III) nitrate hexahydrate, aromatic ligands substituted with carboxylic group (2,6-naphthalenedicarboxylic acid) and a suitable solvent mixture (in this case DMF and H₂O) kept at 120 °C for 20 hours. Since the crystallinity, surface and structural characteristics of samarium complexes are affected by the presence of traces of water, extra-dry solvents (previously distilled) and fully controlled reaction conditions must be employed to obtain solids with reproducible results. The fact that samarium complexes are
coordination polymers that are insoluble in conventional solvents (organic) [7]. The yellow powder is synthesized, claimed to be polymer coordination samarium complexes.

3.2 Chemical Bonding and Vibration Spectroscopy

Figure 1. show the FTIR spectra recorded in the region 4000-400 cm\(^{-1}\). The presence of water molecules in the structures of the complexes was confirmed by the broad absorption bands in the range of 3600-3200 cm\(^{-1}\) assigned to the stretching vibration of \(v(O-H)\) groups from hydrogen bonded water molecules in the frameworks. In addition, the absence of absorption bands of around 1700 cm\(^{-1}\) further confirmed that the carboxylic groups in dicarboxylic ligands were completely deprotonated and samarium complexes was successfully formed. Coordination of lanthanide ion through the carboxylate groups resulted in appearance of the asymmetric and symmetric stretching vibrations of the COO groups in the spectra of the complexes in the regions 1557 cm\(^{-1}\) and 1489 - 1412.92 cm\(^{-1}\), respectively.

Figure 1. FTIR spectra of samarium complexes

3.3 Crystallographic studies

Figure 2. XRD pattern of samarium complexes
The framework structure is obtained between samarium metal bonds and oxygen from ligands. Samarium is a high oxophilicity metal or hard acid (more likely to bind to oxygen atoms), this advantage can be utilized in complexes design which uses organic ligands with oxygen atoms as metal links [8]. Hard acid metal will tend binds to hard base ligands to get stable complexes design [9]. The band due to the metal oxygen bond appear at 452,50 and 487,48 cm⁻¹ [10].

Figure 2. show the PXRD pattern of samarium complexes solid prepared by solvothermal method. The strong and sharp diffraction peak indicate good crystallinity of the sample. The XRD result of samarium complexes show at 2θ = 6,50°; 8,44°; 9,65°; 15,68°; 16,76°; 18,81°; 20,62° and 21,64°.

3.4 Diffuse Reflectance Studies
The band gap energies (Eg) of samarium complexes were calculate from diffuse reflectance UV-vis spectra according to the Kubelka-Munk theory. The Eg value for samarium complexes was 3,1 eV. This semiconductor can be activated under near visible light irradiating (400 nm) to initiate the photocatalytic process.

![Figure 3. Band gap of samarium complexes using Kubelka-Munk method](image)

3.5 Cyclic Voltammogram and Reduction-Oxidation Potential.
The reduction potential value of O₂ to O₂⁻ is -0.33 volts and oxidation potential OH⁻/OH⁺ is 2,38 volts [11]. Potential values OH⁻/OH⁺ and O₂/O₂⁻ must be fulfilled to produce radical species capable of degrading organic pollutants. In other words the oxidation potential possessed by a material must be more positive than the value of the OH⁻ to OH⁺ oxidation potential, while the O₂/O₂⁻ reduction potential must be negative. The cyclic results of samarium complexes voltammetry in Figure 4.a Where the oxidation potential value (HOMO) is obtained at 0.4 volts vs (Ag/AgCl 0.2 volts). The value of 0.4 volts is still against the Ag / AgCl comparative electrode, while the potential value for hydrogen Nerst is 0.58 volts ≈ - 5.3 eV. If the gap energy obtained is 3.1 eV, then the LUMO value of Sm-MOFs is obtained at -2.2 eV ≈ -2.1 volts.
From the data above, a potential energy diagram of samarium complexes are used as a semiconductor as shown in Figure 4.b. In the LUMO band the O$_2$/O$_2^-$ reduction potential value has been fulfilled and is obtained in the O$_2^-$ active species. Whereas the HOMO oxidation potential which is only 0.6 volts has not been able to produce OH$^-$ in the HOMO band, but OH$^-$ formation can also occur in the subsequent O$_2^-$ reaction which reacts with H$^+$ to form HOO$^-$ which is then converted to H$_2$O$_2$, this peroxide can react with water forming OH$^-$ [12]. So OH$^-$ might also be involved in the degradation mechanism using samarium complexes, as outlined in the following equation [13].

3.6 Degradation of Methylene Blue
The decrease in the intensity absorbance of methylene blue for 240 minutes as shown in Figure 5. While the inserted picture shows a percent degradation of methylene blue uses samarium complexes semiconductors, obtaining 68.6% for 240 minutes. Thus, samarium complexes can be used as a semiconductor in photocatalytic processes for the degradation of methylene blue in overcoming the problem of methylene blue dye waste.

Figure 4. (a). Cyclic voltammogram of samarium complexes, (b). Potential energy diagram

Figure 5. The degradation spectra of methylene blue from degradation using samarium complexes for 240 minutes, then the insertion image is a percent degradation of methylene blue.
4. Conclusions
A new coordination polymers based on 2,6-naphtalenedicarboxylic acid have been successfully synthesized and characterized. The value of the band gap obtained from the corresponding transition is 3.1 eV. The LUMO Level reduction potential $O_2/O_2^-$ is obtained -2.1 volt, this value is more negative than the potential standard $O_2/O_2^-$ reduction is -0.33 volt, so the ability to form $O_2^-$ is greater. Based on the characteristics obtained, this material potential as a semiconductor for photocatalysts methylene blue degradation, where samarium complexes in 240 minutes can degradation methylene blue by 68.6 percent.

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References
[1] A. Anila, M. Imran, M. Riffat, I. Hicham and N. Muhammad, in RSC Adv 4, 37003 (2014)
[2] Y. D. Lestari, S. Wardhani, M.M. Khunur, in Student Journal 1, 592 – 598 (2015)
[3] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad. Journal of Hazardous Materials 177. 70-80 (2010)
[4] D. Wang, Z. Li, in Res Chem Intermed 43, 5169-5186 (2017)
[5] Y. Lu, S. Jin, Z, Zhou, S. Zhang, & G. Lou, in Inorg Chem Comm 48,73-76 (2014)
[6] Q. Xia, X. Yu, H. Zhao, S. Wang, H. Wang, Z. Guo, H. Xing, in Cryst. Growth. 17, 4189–419 (2017)
[7] K. Olga, B. Wojciech, A.S. Amy, H.T. Joseph & F.K. Omar, in Journal of Visualized Experiments 91 (2014)
[8] J. Suhyun, K. Youngmee, K. Sung-Jin & P. Seongsoon, in Bull. Korean Chem. Soc vol 33, 4-1349 (2012)
[9] L. Renata & L. Agnieszka, in Microporous and Mesoporous Materials 168. 81–91 (2013)
[10] L. Renata, R. Zofia, K. Alina, and G. Agnieszka, in Journal of Analytical and Applied Pyrolysis 92 , 347–354 (2011)
[11] L. Ai, C. Zhang, L. Li, & J. Jiang, in Applied Catalysis B: Environmental 148–149. (2014)
[12] D. Ranjith, K.S. Rajith, & R. T. Rajendra, in Optik 154, 115–125. (2018)
[13] M.A. Rauf, & S.S. Ashraf, in Chemical Engineering Journal 151, 10-18. (2009)