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Synthesis and Characterization of Samarium-Perylene MOFs for Photocatalytic Applications

Yulian Syahputri[a,b], Agustino Zulys[a]*, Jarnuzi Gunlazuardi[a]

Abstract. Hydrogen is a renewable and environmentally friendly energy source that has significant potential as a substitute for fossil fuels. The energy contained in hydrogen per unit mass is greater than the energy of fossil fuels and other fuels. One of the methods that can be used to produce hydrogen is photocatalytic water splitting using semiconductors. One of the semiconductor materials used for photocatalysis is metal organic frameworks (MOFs). MOFs have been extensively studied as photocatalysts for hydrogen gas production from water. This research aims to synthesize MOFs materials using samarium metal and perylene-3,4,9,10-tetracarboxylate (PTC) ligand through a solvothermal method at varying temperatures (100, 120, and 170 °C) for 24 hours, then characterized using FTIR, XRD, DRS spectrophotometer and cyclic voltammetry, as well as its potential as a photocatalyst for hydrogen gas production. The synthesis results show that a temperature of 100 °C is the optimal reaction temperature. The FTIR analysis results show the presence of a bond between Sm and O at a wave number of 470-400 cm^{-1}. The XRD results indicate that MOFs (Sm-PTC) are crystals with an average crystal size of 43-58 nm. The band gap energy obtained ranges from 1.80-2.05 eV at a maximum wavelength of 689-605 nm. Cyclic voltammetry analysis shows that Sm-MOFs have the potential to be used as photocatalysts for hydrogen gas production.

Keywords : MOFs, Perylene, Photocatalyst, Samarium.

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Introduction

Hydrogen is a renewable and environmentally friendly energy source that has significant potential as a substitute for fossil fuels. The energy contained in hydrogen per unit mass is greater than the energy of fossil fuels and other fuels [1]. One of the methods that can be used to produce hydrogen is photocatalytic water splitting using semiconductors. One of the semiconductor materials used for photocatalysis is metal organic frameworks (MOFs) [2]. MOFs have been extensively studied as photocatalysts for hydrogen gas production from water. MOFs have several characteristics such as large surface area, homogeneous active sites, and tunable functionality, allowing MOFs to be applied in various fields such as gas storage, sensors, catalysts, and other applications [3]. The selection of lanthanide metals is due to their weak sensitivity to f-f transition absorption, but the use of organic chromophores through the antenna ligand effect makes lanthanides more effective at absorbing visible light. The use of organic ligands such as perylene that serve as photofunctional linkers makes MOFs have characteristics as semiconductors [4]. The most commonly used synthesis method for MOFs is the solvothermal method, as it allows the system to be operated without the need for special equipment and enables relatively fast crystal growth with high crystallinity, phase purity, and surface area [5].

There are several studies on the synthesis of lanthanide metal-based MOFs, one of which is Zulys et al (2019) who successfully synthesized and characterized La-MOF with the ligand perylene-3,4,9,10-tetracarboxylate using a solvothermal method (varying molar ratios and reaction times). The results obtained show that La-MOF with a molar ratio of 0.33:0.25 has a surface area of 72.445 m^2/g and a band gap value of 2.686 eV, while La-MOF with a molar ratio of 0.29:0.29 has a surface area of 102.565 m^2/g and a band gap value of 2.732 eV [6]. Another research was conducted by Yulianiza et al (2021) who successfully synthesized Sm-MOF and La-MOF with the ligand crysophenine using a solvothermal method with DMF and water as solvents. The XRD results showed that La-MOF has higher crystallinity compared to Sm-MOF, with a band gap value of Sm-MOF at 2.12 eV and La-MOF at 2.07 eV, indicating that both MOFs can be applied as photocatalysts for water splitting under visible light [7]. To the best of the author's knowledge, the potential of Sm-PTC MOFs as photocatalysts for hydrogen production under varying reaction temperatures (100, 120, and 170 °C) has not been extensively studied. The use of perylene ligand aims to enhance the visible light absorption of samarium metal. Based on the background described above, this study aims to synthesize MOFs materials using samarium metal and perylene-3,4,9,10-tetracarboxylate (PTC) ligand through a solvothermal method at varying temperatures (100, 120, and 170 °C) for 24 hours using a solvent DMF and water in ratio 4:1, then characterized using FTIR, XRD, and DRS spectrophotometer, as well as its potential as a photocatalyst for hydrogen gas production.

Experimental

This research was initiated by the synthesis of the PTC ligand from perylene 3,4,9,10-tetracarboxylic dianhydride (PTCDA) and NaOH, following the procedure previously reported in Ref. [6]. The synthesis of MOFs (Sm-PTC) was continued by reacting $Sm(NO_3)_3.6H_2O$ with the PTC ligand using the solvothermal method with temperature variations (100, 120, and 170 °C) for 24 hours, using a solvent of DMF and water in a 4:1 ratio, following the procedure previously reported in Ref [8].

A total of 0,29 mmol of PTC ligand and 0,33 mmol of $Sm(NO_3)_3.6H_2O$ were dissolved in 16 ml of DMF and 4 ml water in beakers. Next, the solutions were stirred using a magnetic stirrer for 1 hour at room temperature and pressure. The resulting solution are orange in color, then transfer to a teflon-autoclave to be heated at the reaction temperatures (100, 120, and 170°C) for a reaction time of 24 hours. After the reaction time is completed, cool down, then filter and wash with distilled water and DMF, and then dry in an oven at 60°C overnight. The obtained product is then weighed, ground, and placed in a vial. The resulting complexes were characterized by fourier transform infrared spectrophotometer (FTIR), DRS spectrophotometer, X-Ray Diffraction (XRD), and cyclic voltammetry (CV).

Result and Discussion

PTCDA (perylene-3,4,9,10-tetracarboxylic dianhydride) is made into its derivative, Na-PTC (tetrasodium; perylene-3,4,9,10-tetracarboxylic),

through a hydrolysis reaction of PTCDA. PTCDA has properties that are insoluble in water at neutral pH, so hydrolysis is necessary for it to dissolve in water and to facilitate the reaction with Sm3+ metal ions, forming Sm-MOFs [9]. The color change from red PTCDA to yellow Na-PTC indicates that Na-PTC has been successfully formed. The yield of Na-PTC obtained is 90.47%. The FTIR results of PTCDA and Na-PTC can be seen in Figure 1.

The FTIR analysis results for PTCDA and Na4PTC (Figure 1) indicate that at the wavenumber 1758 cm-1, identified as the stretching vibration of the C=O anhydride functional group from the closed chain (cyclic) in PTCDA, no longer appears in the FTIR spectrum of Na4PTC. The FTIR spectrum of Na4PTC shows absorptions at wavenumbers 1580 and 1402 cm-1 identified as the stretching vibrations of the (-COO-) group, confirming the presence of the conjugated carboxylate sodium group in the perylene ring [10]. The wavenumber 1026 cm-1 shows the stretching vibration (C-O) from the cyclic anhydride PTCDA [8]. In the Na4PTC spectrum, there is an absorption appearing at the wavenumber 3502 cm-1 identified as the broad stretching vibration (O-H), This is suspected to be due to the presence of an anhydride group from PTCDA that has been opened; however, part of it does not bind to Na+ cations but instead forms a carboxylate group (-COOH) that possibly originates from the washing of the material with ethanol to neutral pH [11]. In the FTIR spectrum of PTCDA and Na4PTC, an absorption appears at wavenumbers 799 and 798 cm-1, which is identified as the stretching vibration (C-H) of aromatic [12].

Optimization of the reaction temperature in the synthesis of Sm-MOFs (Sm-PTC) was

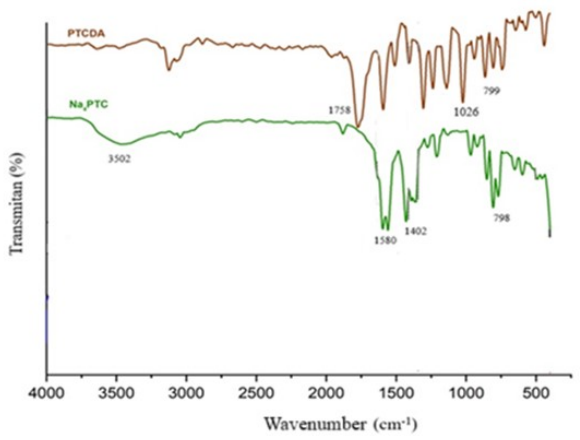

Figure 1. FTIR Spectrum of PTCDA and Na_4PTC

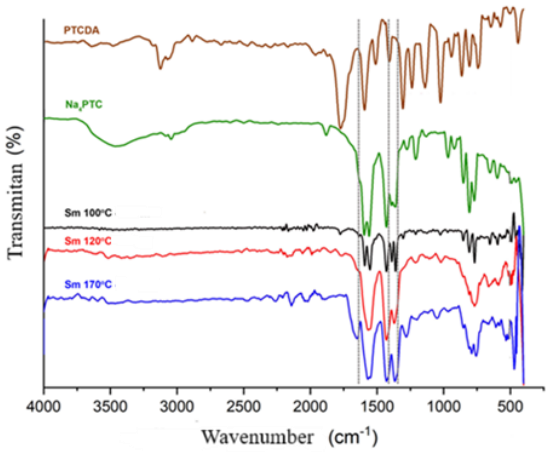

Figure 2. FTIR Spectrum of Sm-PTC on variations in reaction temperature

performed by varying the reaction temperatures of 100, 120, and 170°C for 24 hours, followed by characterization using FTIR, XRD, and UV-Vis DRS spectroscopy. The FTIR analysis results are shown in Figure 2.

The C=O carboxylate stretching vibration at wavenumbers 1725-1700 cm^{-1} does not appear in the Sm-PTC spectrum. This indicates that there has been a deformation of the ligand structure, marked by the emergence of asymmetric and symmetric stretching vibrations at wavenumbers 1551 and 1427 cm^{-1} for Sm-PTC 100 ^oC, 1566 and 1419 cm^{-1} for Sm-PTC 120oC, and 1566 and 1417 cm^{-1} for Sm-PTC 170oC [13-14]. In the FTIR spectrum of Sm-PTC, the absorption appearing at wavenumbers 777, 776, 765 cm^{-1} indicates aromatic alkene (C-H) stretching vibrations [12]. The absorption appearing at wavenumbers 469, 452, 411 cm-1 is indicated as (Sm-O) vibrations, confirming the existence of coordination bonds between lanthanide metal ions and oxygen in the range of 470-400 cm^{-1} [9]. The color change from yellow Na-PTC to MOFs (Sm-PTC) and the % yield obtained can be seen in Table 1. This color change serves as a visual indication of the formation of a specific MOF structure [15].

XRD characterization was performed to observe the crystallinity of MOFs. Metal Organic Frameworks are known as compounds that have high crystallinity. The crystallinity of the material is very important to know because it is closely related

Table 1. Results of wavenumber shift of ligands and La complex compounds

MOFs	Temperature (^oC)	Color	% Yield
Sm-PTC	100	Orange	84.98
	120	Red	82.86
	170	Red	80.73

to photocatalytic activity [9]. The XRD results of Sm-PTC at varying temperatures can be seen in Figure 3 and Table 2.

Based on Figure 3, the material shows no broad absorption peak, indicating its well-defined crystalline structure [14]. The sharpest peaks in the MOFs (Sm-PTC) spectrum are in the 2θ region around 5° to 15°, specifically at 6.36° and 6.39°. This is consistent with the XRD patterns of most MOFs consisting of lanthanide metals and other organic ligands in previous studies [14, 16-17]. The analysis of MOFs with XRD can also determine the degree of crystallinity and crystal size. The degree of crystallinity is obtained by comparing the area of the main diffraction peak with the total area of all peaks, while the crystal size is obtained using the Debye-Scherer equation. The results of the degree of crystallinity and crystal size of Sm-PTC at variations of temperature can be seen in Table 3.

The crystallinity of MOFs is known to be strongly influenced by reaction parameters such as temperature and reaction time, which can favor the thermodynamically preferred crystalline phase at

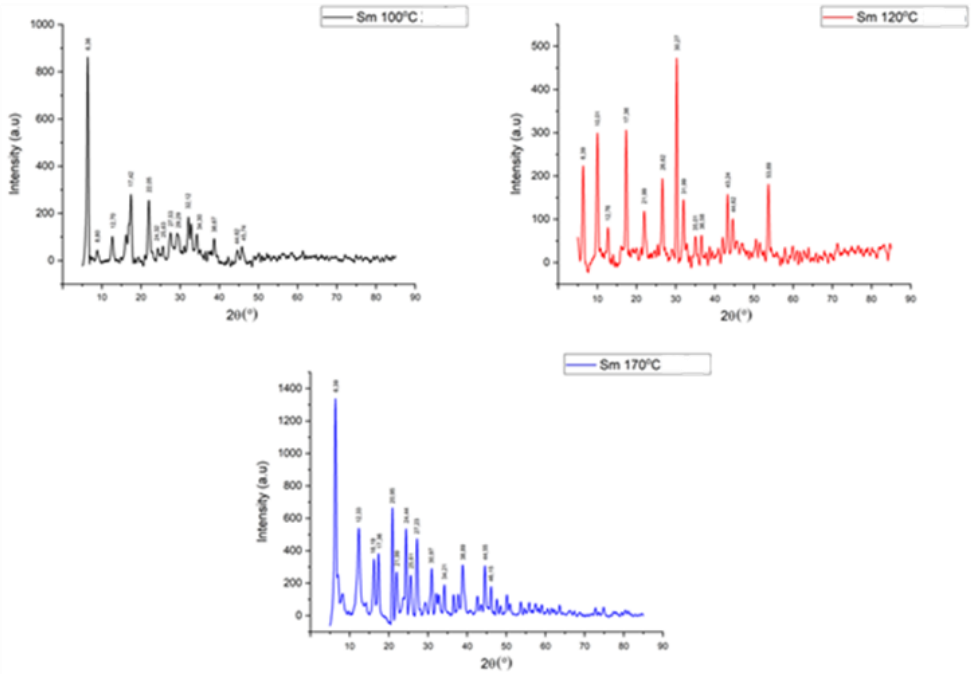

Figure 3. Diffraction pattern of Sm-PTC at varying reaction temperatures (100; 120; 170 °C) during a reaction time of 24 hours

Table 2. XRD results of Sm-PTC at 100°C (a); 120°C (b); 170°C (c) after a reaction time of 24 hours

2θ (°)	Intensity (a.u)	2θ (°)	Intensity (a.u)	2θ (°)	Intensity (a.u)
6,36	861,68	6,39	224,43	6,39	1337,07
8,80	45,73	10,01	299,53	12,33	539,54
12,70	102,05	12,76	81,13	16,19	349,17
17,42	280,28	17,36	306,96	17,36	382,47
22,05	255,21	21,99	118,77	20,95	665,11
24,32	53,16	26,62	194,38	21,99	270,40
25,63	60,90	30,27	473,03	24,44	535,49
27,53	119,07	31,99	145,27	25,61	249,25
29,29	116,28	35,01	60,71	27,23	473,83
32,12	184,97	36,58	63,58	30,97	292,91
34,30	112,26	43,24	157,59	34,21	189,84
38,67	92,15	44,62	101,22	38,89	312,26
44,62	45,42	53,69	181,22	44,55	307,76
45,74	59,97			46,15	180,39

Table 3. Crystal size and degree of crystallinity of Sm-PTC at varying reaction temperatures

Parameter	Sm-PTC		
	100 °C	120 °C	170 °C
Average Crystal size (nm)	46.07	43.03	58.89
% Crystallinity	99.53	99.27	99.80

elevated temperatures, whereas lower temperatures or shorter durations tend to yield amorphous products. Furthermore, the rigidity of the organic linker plays a crucial role: rigid ligands generally enhance MOF stability and crystallinity [18-20].

Diffuse reflectance spectroscopy (DRS) is one of the spectroscopic techniques used to analyze a solid material by utilizing the reflectivity of the sample against infrared or UV-visible light. The Kubelka-Munk equation and Tauc plot are used in advanced analysis to determine the band gap energy value of a material. The band gap energy refers to the distance between the valence band and the conduction band. The band gap energy is an important parameter to consider for a semiconductor material that will be applied as a photocatalyst, as it affects the activity of the semiconductor used as a photocatalyst [21].

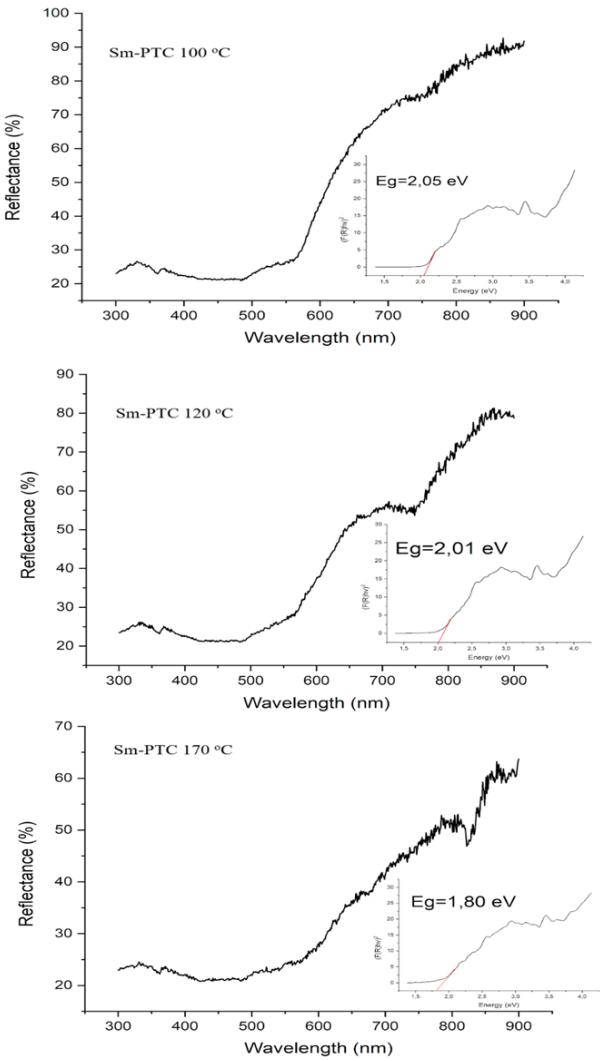

Figure 4. Reflectance spectrum and energy gap curve of Sm-PTC at varying temperatures

The band gap energy of MOFs Sm-PTC was obtained by correlating the E values (eV) against (FR)2 as shown in Figure 4. The band gap energy obtained for MOFs Sm-PTC at varying temperatures (100; 120; 170°C) were 2.05 eV (λmaks = 605 nm); 2.01 eV (λmaks = 617 nm); and 1.80 eV (λmaks = 689 nm), respectively. The results of the band gap energy obtained are still within the semiconductor range for photocatalysis applications under visible light, namely in the range of 3.0<E<1.6 [22].

The cyclic voltammetry (CV) results of Sm-PTC under optimal conditions are shown in Figure 5, with an onset oxidation potential at –0.580 V vs Ag/AgCl (–0.370 V vs NHE). This potential corresponds to the valence band (VB) level of the Sm-PTC MOF. Given the obtained band gap energy of 2.06 eV, the conduction band (CB) level is estimated to be –2.43 V vs NHE. Since the reduction potential of Sm-PTC is more negative than the H^+/H_2 standard reduction potential (0.00 V vs NHE), it can be concluded that Sm-PTC meets the thermodynamic requirement for H^+/H_2 reduction.

Based on the results of FTIR, XRD, and UV-Vis DRS spectrophotometry analyses, it can be concluded that the optimum reaction temperature for MOFs Sm-PTC is at 100°C for a reaction time of 24 hours, and that MOFs Sm-PTC have the potential to be used as a photocatalyst for hydrogen gas production.

Conclusion

The MOFs from Sm metal and PTC ligand has been successfully synthesized which can be seen from the characterization data. The synthesis

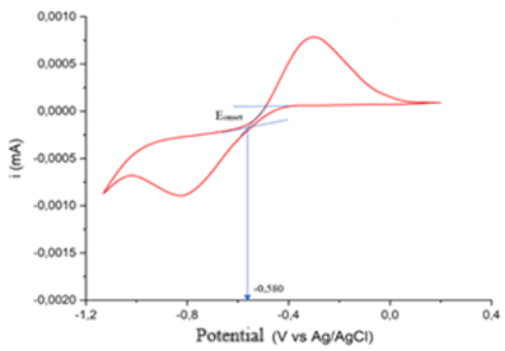

Figure 5. Sm-PTC voltammogram at optimum temperature reaction (100°C)

results show that a temperature of 100 °C is the optimal reaction temperature. The FTIR analysis results show the presence of a bond between Sm and O at a wave number of 470-400 cm-1. The XRD results indicate that MOFs (Sm-PTC) are crystals with an average crystal size of 43-58 nm. The band gap energy obtained ranges from 1.80-2.05 eV at a maximum wavelength of 689-605 nm. Based on the cyclic voltammetry results, Sm-MOFs have the potential to be used as photocatalysts for hydrogen gas production.

Author Contributions

All authors contributed to the researchand writing in this article. Agustino Zulys: validation, supervision, methodology, conceptualization, data curation, and review. Yulian Syahputri: writing-original draft, visualization, investigation, editing, and formal analysis. Jarnuzi Gunlazuardi: validation, supervision, methodology, data curation and review.

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