Synthesis, Structural, Spectroscopic, and Morphology of Metal-Organic Frameworks Based on La (III) and Ligand 2,6-Napthalenedicarboxylic acid (La-MOFs) for Hydrogen Production

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Abstract. Metal-organic frameworks (MOFs) based on lanthanum metal ions (La³⁺) and 2,6-napthalenedicarboxylic ligand (La-MOFs) have been synthesized by solvothermal method at 120 °C and 150 °C for 24 h using dimethylformamide and water (5:1) as a solvent. Furthermore, the chemical bonding and vibration spectroscopy, crystallographic structure, band gap, particle size and microscopic, and redox potential studies of La-MOFs were also investigated as well. FTIR results shown that there were no wave numbers at 1690-1730 cm⁻¹, which affirmed that the La-MOFs had formed. UV-VIS DRS characterization with solvent (DMF: Water) using (Ln³⁺) metal was confirmed at 492 nm (2.53 eV). SEM/EDX results shown that La-MOFs have an ultrahigh skeleton and the EDS revealed the composition of La, O, and C atoms that reside within La-MOFs, cyclic voltammetry results shown that LUMO level was -2.5 V vs. H⁺/H₂. Finally, the photocatalytic activity of La-MOFs was performed, which produced 24.99 µmol of H₂ after being measured for 4 hours.

1. Introduction
Metal-organic frameworks (MOFs) are one of the porous materials formed by the coordination bond [1]. MOFs are made from inorganic metal ions & organic ligand bridges with an unlimited network structure in three-dimension (3D) space [2]. Due to their exceptional design flexibility, vast surface to volume ratio, and adjustable pore channels, MOFs have become the centre of attention and have been utilized for several applications lately [3].

The analogous chemistry of the lanthanide metal ions remains largely unexplored, although high coordination number and flexible coordination geometry of lanthanide ions makes the rational design of lanthanide coordination polymers difficult, this feature of pliability or coordinative ambivalence can be exploited to engineer or discover exotic supramolecular networks with high connectivity topologies unprecedented in transition metal coordination polymers [4]. The 2,6-napthalenedicarboxylic acid ligand (2,6-NDC), as a fascinating ligand of aromatic dicarboxylic acids, has shown an excellent bridging ligand in constructing novel MOFs with attractive structural topologies and unique properties because of its various coordinating modes, high symmetry, and structural rigidity. Thus, in this research,
the 2,6-NDC and Ln (III) were used to construct 3D open-framework coordination polymers under ambient conditions [5,6].

As for today, fossil fuels reserves have been reduced significantly due to the enormous usage worldwide, and it causes several environmental problems, such as global warming. As such, nowadays hydrogen is considered as an ideal energy source, due to its gravimetric combustion heat that reaches almost three times that of gasoline ($H_2 = 120$ MJ/kg and gasoline = $44.5$ MJ/kg). Moreover, only water is released as the side-reaction of the combustion. However, industrial-scale hydrogen production continues to depend on fossil fuels for economic reasons. Although the natural gas and petroleum hydrocarbon still become the primary energy source worldwide nowadays, they will be eventually replaced with hydrogen, which provides clean, environmentally friendly energy sources rather than the former one [7].

Photocatalyst was first introduced by Fujishima Honda in 1970 with TiO$_2$ to separate water under UV light irradiation to produce H$_2$ and O$_2$ [8]. The photocatalyst band gap and the edge of the conduction band (CB) and valence band (VB) must meet the water separation requirements. The lower level of CB must be more negative than the redox potential of $H^+ / H_2$ (0.0 V vs. normal hydrogen electrode (NHE)), while the upper level of the VB must be more positive than the $O_2/H_2O$ redox potential (1.23 V vs. NHE) [9]. In addition, in terms of confirming the photocatalytic activity of Gd-MOFs for hydrogen in theory, UV-VIS absorption and electrochemical properties of Gd-MOF show the extent of absorption band as expected, with an edge above 530 nm, which is the perfect source for harvesting activity, when sunlight is absorbed by MOFs, electrons, and holes in HOMO are separated and electrons can be attracted to LUMO Therefore, the LUMO-HOMO gap is 2.35 eV based on $E_g = 1240 / \lambda$ relationship. Solid-state cyclic voltammetry results (CV) revealed that Gd-MOFs have a redox potential at 0.41 V vs. Ag / AgCl (0.61 V vs. NHE), associated with the HOMO level. It can be estimated that the LUMO of Gd MOFs is -1.74 V vs. NHE, which is more negative than potential redox tolerance of $H^+ / H_2$ so that it can reduce protons for hydrogen production [10].

2. Materials and Methods

All chemicals used in this study were obtained and purchased from commercial sources and used without further purification. Furthermore, several instruments such as FTIR spectroscopy (IR Prestige-21 Shimadzu) and UV-Vis DRS (Shimadzu 2450) were utilized for characterization purposes.

2.1. Synthesis of Lanthanum-MOFs (La-MOFs)

La-MOFs was synthesized with a solvothermal method by pouring a mixture of $La_2(NO_3)_3$:2H$_2$O (0.1083 g), and 2,6-NDC (0.054 g) into a Teflon autoclave, followed by the admixed of distilled water (1 mL) and dimethylformamide (DMF) (5 mL) at 120°C and 150°C. Then, the magnetic bar was put into the Teflon autoclave and stirred for 10 minutes before the mixture was heated into the oven for 24 hours. Finally, the mixture was filtered and dried at 60°C for 4 hours.

2.2. Characterization of Lanthanum MOFs (La-MOFs)

The synthesized La-MOFs was characterized using several instruments. To identify the functional groups that existed in La-MOFs, the FTIR spectroscopy (IR Prestige-21 Shimadzu), with KBr as the pellets, was utilized, while the band gap measurements were determined by UV-Vis DRS (Shimadzu 2450). The crystalline structure and phase La-MOFs were analyzed by XRD employing with Cu-Kα radiation ($\lambda = 1.5418$ Å). Finally, the morphology and particle size of La-MOFs were observed with SEM-EDS instrument.

2.3. Photocatalytic activity test of Lanthanum MOFs (La-MOFs)

The 8% w/v synthesized La-MOFs that has been characterized before was put into the reactor, followed by the irradiation process for 30 minutes before the hydrogen measurement was carried out using GC-TGD. The measurement lasted for 4 hours with sampling processes was occurred every 1 hour.
3. Results and Discussion

A light white crystal of La-MOFs was synthesized by using a solvothermal method in the presence of La$_2$(NO$_3$)$_3$ with DMF and H$_2$O in 1:1 molar ratio at 120 °C. DMF, as an aprotic solvent, was used to dissolve the metal and the ligand. In order to identify the functional group of La-MOFs, the FTIR spectroscopy was utilized throughout the region at wavenumbers of 400-4000 cm$^{-1}$ (mid-infrared). As shown in Figure 1, two strong peaks were observed at 1364 cm$^{-1}$ and 1401 cm$^{-1}$, which indicated the existence of both symmetry and asymmetric vibrations of C=O, respectively. Moreover, a strong peak at 1554 cm$^{-1}$ showed the complex interaction of the C=O with La$^{3+}$. The vibration C=O stretching mode of DMF shifted to the lower wavenumbers (1660 cm$^{-1}$) relative to the free amide value (1680 cm$^{-1}$) shows that the ligations of all DMF molecules with their carbonyl groups were successfully formed. Furthermore, the absence of the absorption band in the region of 1700 cm$^{-1}$ indicated that carboxylic groups in the dicarboxylic ligand were completely deprotonated. Finally, the O-H stretching vibrations, which emerged from water molecules, were also observed as well in the FTIR spectra (two peaks; sharp peak and broad peak, at 3450 cm$^{-1}$ and 3200 cm$^{-1}$, respectively).

![Figure 1. FTIR Spectra of La-MOFs 120 °C.](image)

The band gap value determination is one of the requirements factors for a material that can be utilized as a semiconductor in photocatalysis, which determines how much energy is needed by photocatalyst material for photocatalysis processes and identifies the wavelength of the light source, whether in the UV or visible light area. Determination of band gap using the Tauc plot method is illustrated in Figure 2, which then the measurement result of La-MOFs reflectance was converted into Kubelka-Munk function with curve F (R). In this research, the optical band gap value of La-MOFs was obtained at 3.10 eV.
Figure 2. Band Gap Determination of La-MOFs at 120 °C.

The XRD patterns of La-MOFs were also characterized as well in this study. The result of this characterization was compared to the La-MOFs patterns that have been studied previously [1]. As it depicts in Figure 3, The XRD result of La-MOFs shows at their characteristic peaks at 8.19; 11.20; 16.64; 22.61; and 33.29. This result implied that the La-MOFs was successfully synthesized with high crystallinity. Moreover, the surface particle and the composition of La-MOFs was determined using SEM-EDS instrument. According to the results, the surface particle of La-MOFs that has been synthesized had decent crystallinity with a huge skeleton structure even though few precursors have not been perfectly formed. The structure of surface particle and the composition of La-MOFs are displayed in Figure 4 and Figure 5, respectively.

Figure 3. XRD Pattern of La-MOFs at 120 °C.
Figure 4. SEM image with scale bar 200 µm

Figure 5. EDS Spectrum of La-MOFs at 120 °C.

Cyclic voltammetry was used to determine the redox potential of La-MOFs. From Figure 6, the HOMO level of La-MOFs was determined at 0.47 vs. Ag / AgCl (0.67 vs. H⁺/H₂), which means the LUMO level was -2.5 V or more negative than the reduction potential of H⁺/H₂. Therefore, according to this result, La-MOFs can be used to reduce H⁺/H₂ to produce hydrogen.

Figure 6. Potential Redox of La-MOFs 120°C by Voltammogram.
Finally, the photocatalytic activity test at La-MOFs was carried using GC-TCD. The photocatalytic reactor used in this study contained 90mL of water and 10mL of methanol. The La-MOFs concentration used was 8% w/v and measured for 4 hours. According to the result in Figure 7, the hydrogen produced from the photocatalytic activity of La-MOFs was generated at 24.99 µmol.

![Graph](image_url)

**Figure 7.** Photocatalytic H\(_2\) production of La-MOFs 120\(^\circ\) C.

4. Conclusions
In this study, the La-MOFs was successfully synthesized using the solvothermal method, while the characterization of La-MOFs was also investigated as well. According to the FTIR results, the dicarboxylic functional group in the 2,6-NDC were completely deprotonated due to the absence of the absorption band in the region of 1700 cm\(^{-1}\). Moreover, the characterization of La-MOFs using UV-Vis DRS, XRD, SEM, and EDS affirmed the formation of the La-MOFs in this research. Lastly, the photocatalytic activities of La-MOFs confirmed that this MOFs produced about 24.99 µmol of H\(_2\) when measured for 4 hours and the concentration La-MOFs used was 8 % w/v. Thus, to determine the optimum hydrogen concentration which generates higher hydrogen, the optimization of La-MOFs, particularly in the La-MOFs concentration, can be performed in the further investigation with an extended time of photocatalytic activity test.

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