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Synthesis of Biofuel Using Organic-Inorganic Perovskite Solar Cell Material Based on Nanocomposite

Priyanko Protim Gohain[1], Nageswara Rao Medikondu[2], Vinjamuri Venkata Kamesh[3], Mahua Gupta Choudhury[4], Kunal Chakraborty[1], Samrat Paul[1,*]

[1] *Advanced Materials Research and Energy Application Laboratory (AMREAL), Department of Energy Engineering, North-Eastern Hill University, Shillong-793022 Meghalaya, India*
[2] *Department of Mechanical Engineering, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Andhra Pradesh-533437, India*
[3] *Department of Mechanical Engineering, Aditya Engineering College (A), Surampalem, East Godavari District, Andhra Pradesh-533437, India*
[4] *Department of Animal Health and Fisheries Sciences, Indian Council for Agricultural Research, NEHRC, Umiam, Shillong-793103, India*

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To take precautionary measures for the environment to diminish the toxic gases emitted from fossil fuels; an alternative fuel has to replace fossil fuel. Biofuel an alternative fuel can replace the counterpart. In this work, biofuel is synthesized by using a novel organic-inorganic perovskite-based nanocomposite as a catalyst. The synthesized catalyst has been characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The transesterification method is used for biofuel synthesis. Researchers across the globe have mostly synthesized biofuel especially biodiesel by transesterification method where temperature plays a major role in the catalytic reaction. Most of the researchers reported the synthesis of biofuel by using heterogeneous catalysts at higher temperatures which is greater than 60 °C but in this study, the synthesis of biofuel at ambient temperature is attempted under the influence of UV light. The synthesized biofuel is characterized by Gas Chromatography Mass Spectrometry (GCMS). GCMS signifies the different fatty acid methyl ester compositions present in the biofuel which assured the presence of all the necessary compounds in a biofuel.

Keywords: Biofuel, Catalyst, Perovskite, Synthesis, Nanocomposite, Transesterification.

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1. INTRODUCTION

Due to the industrial revolution, a drastic rise in anthropogenic gases in the environment leads to serious concern across the globe [1]. Conventional fossil fuels are the main sources of transportation that result in the emission of toxic gases like CO_x, SO_x and NO_x [2]. It resulted in serious health issues. Renewable or non-conventional fuel has to be introduced to stop the calamities. Biofuel is a good alternative to fossil fuels. Biodiesel commonly known as Fatty acid Methyl Esters can be produced from plant oils, animal fats etc. [3]. The method used for the process is transesterification. The transesterification reaction takes place through the reaction of oil, alcohol and catalyst [4]. The catalysts that are used mostly are homogeneous and heterogeneous. The heterogeneous catalyst has various advantages over the homogeneous catalyst such as non-corrosive, easy separation and high thermal stability [5]. The heterogeneous catalyst has a wide range of varieties. But among them, metal oxide has gained more attention because of its superior physical and chemical properties [6]. The researchers have found it to be an efficient candidate for the synthesis of biofuel. Mixed metal oxide especially perovskite acquires thermal stability and high catalytic potential. Umar and his group synthesized solid catalysts by sol-gel method using citric acid as a chelating agent. The catalysts i.e., $CaSr_{0.2}Mn_{0.8}O_3$ and $CaSr_{0.2}Mn_{0.5}O_3$ were used for the synthesis of biofuel. The optimized reaction conditions for the transesterification method are a reaction temperature of 80 °C, a methanol-to-oil molar ratio of 12:1 and catalyst loading of 0.5 gm and a reaction time of 4 hours. $CaSr_{0.2}Mn_{0.8}O_3$ was found to be more effective than its counterpart. It achieves a biofuel yield of 100 % [7]. A high thermal stability catalyst consisting of bismuth and iron was used to produce biodiesel from palm cooking oil. The heterogeneous bismuth ferrite nanocatalysts ($BiFeO_3$) using Kappa-carrageenan polysaccharides showed outstanding catalytic activity. The catalyst was characterized by XRD and showed rhombohedral crystalline phases. The optimized reaction conditions for the transesterification reactions were oil to methanol ratio 1:15, catalyst dosage of 7 wt % and a reaction temperature of 2 h. Razuki and his group also reported that the synthesized heterogeneous catalyst was recycled for five consecutive cycles and found to be shown good catalytic activity [8].

The present work aims to synthesize a novel mixed metal oxide i.e., organic-inorganic heterogeneous perovskite-based nanocomposite catalyst for biofuel synthesis.

2. MATERIALS AND METHODS

2.1 Materials Used

Various precursors were used for the synthesis of organic-inorganic perovskite-based nanocomposite

* paulsamrat17@gmail.com

(Fe_2O_3-$FAPbI_3$-TiO_2). The precursors used without purification were Urea (CH_4N_2O, Emparta ACS-Merck Millipore, 99.0-100.5 %),Ferric nitrate nonahydrate ($Fe(NO_3)_3$,Fischer Scientific, 98.0 %), Hydroiodic acid (HI, Alfa Aesar, 55 %), Formamidiniumacetatepowder ($HN{=}CHNH_2.CH_3COOH$, Sigma-Aldrich, 99 %), Lead (II) iodide (PbI_2, Sigma-Aldrich, 99 %), Titanium dioxide (TiO_2, Sisco Research Laboratories Pvt. Ltd. India, 99.7 %), N,N-Dimethyl formamide (C_3H_7NO, Sisco Research Laboratory Pvt. Ltd., India, 99 %), Isopropanol (C_3H_8O, Fischer Scientific, 99.7 %), Diethyl ether ($(C_2H_5)_2O$, Qualigens, 98 %), Titanium (IV) isopropoxide ($C_{12}H_{28}O_4Ti$, Sigma Aldrich, 97.0 %), Nitric acid (HNO_3, Fisher Scientific, 69-71 %) and Methanol (CH_3OH, Emparta ACS-Merck Millipore, 99.8 %) respectively. The biofuel was synthesized using raw Karanja oil and alcohol. The raw Karanja oil was purchased from Green Leaf Industries, Surat, Gujrat. Methanol (CH_3OH, Emparta ACS-Merck Millipore, 99.8 %) was used as an alcohol.

2.2 Synthesis

Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite was synthesized in two steps. Initially, Fe_2O_3-TiO_2 nanocomposite was synthesized and finally, Fe_2O_3-TiO_2 was doped in $FAPbI_3$. Fe_2O_3-TiO_2 nanocomposite was synthesized by using 5 ml of Propan-2-ol mixed with 15 ml of Titanium (IV) isopropoxide. The mixture was stirred for approximately 5 minutes. Two drops of Nitric acid were added and stirred the mixture for 30 minutes at 40 °C. During stirring Fe_2O_3 was added. Distilled water was added dropwise, and a reddish-white precipitate was settled at the bottom. The precipitate was calcined at 600°C to obtain Fe_2O_3-TiO_2 nanocomposite. Finally, the Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite was synthesized by sol-gel method followed by the addition of Fe_2O_3-TiO_2 nanocomposite. Lead iodide and Formamidinium iodide were dissolved in N, N-Dimethyl Formamide in the molar ratio of 3:1. The mixture was stirred for two hours at room temperature. Fe_2O_3-TiO_2 was added to the solution during stirring. A reddish-yellow gel appeared which was dried in the oven at 85 °C to obtain Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite.

The biofuel was synthesized by using organic-inorganic perovskite-based nanocomposite i.e. Fe_2O_3-$FAPbI_3$-TiO_2 as a catalyst. Basically, the transesterification method was used for the synthesis of biofuel. The reaction takes place by using Karanja oil, Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite as catalyst and Methanol. A reactor was used which was equipped with a UV light with a light intensity of 8 μW/cm^2. The reaction was initiated by taking the molar ratio 10:1 (methanol: oil), 2wt. % catalyst loading and the reaction speed at 1000 rpm. The reaction was performed at room temperature for 3 hours. Two distinct layers were seen which consist of the top layer: biofuel and the bottom layer: glycerol and catalyst. The biofuel was separated by using a separating funnel and later it was centrifuged to remove the trace amount of catalyst if present.

3. RESULTS AND DISCUSSION

3.1 Characterization of Nanocomposite

3.1.1 XRD Analysis

Fig. 1 shows the XRD spectra of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite. The peaks observed at 11.79° and 25.93 correspond to the crystallographic planes (010) and (021) with *d*-spacing of 0.75 nm and 0.34 nm assigned to the δ-$FAPbI_3$. It possesses a hexagonal structure with lattice parameters as a = 8.70 A° and c = 7.88 A° which is analogous to the earlier reported data [9]. The α-$FAPbI_3$ peak appeared at 34.20° corresponding to the *hkl* plane (211) comprising d spacing as 0.26 nm. It acquires a cubic phase with the lattice parameters as a = 6.87 A°. A common peak that appeared at 26.23° is assigned for both δ and α phase of $FAPbI_3$ [10, 11]. The hematite Fe_2O_3 peaks appeared at 32.82° and 54.4° procure crystallographic planes at (110) and (116) comprising *d*-spacing 0.27 nm and 0.16 nm respectively. A hexagonal structure with the lattice constants as a = 5.3 A° and c = 13 A° was found and it is analogous to the previously reported data [12]. The anatase TiO_2 appears at two theta angles 26.23° and 38.66° attributed to the crystallographic planes at (101) and (004) respectively. It acquires lattice spacings of 0.33 nm and 0.23 nm. The lattice constants were found to be a = 3.60 A° and c = 9.37 A° which resemblance to a tetragonal structure [13]. Again, the peaks at 27.43° and 41.63° which correspond to crystallographic planes at (110) and (111) are attributed to the rutile TiO_2 possesses. interplanar spacings as 0.32 nm and 0.21 nm. The lattice constants were found to be a = 4.44 A° and c = 2.99 A° assigned to a tetragonal structure [14]. The PbI_2 peak appears at two theta angles of 12.68° [15]. The synthesized Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite acquires an average crystallite size of 62.85 nm.

3.1.2 TEM Analysis

Fig. 2 (a) shows the TEM image of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite. A clear picture of the nanocomposite is seen where the dark spots signify the Fe_2O_3-TiO_2 and the lighter section surrounding the darker spots signifies the $FAPbI_3$. Fig. 2(b) shows the HR TEM image of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite. The crystallinity of the nanocomposite is clearly seen from the fringes. GATAN micrograph software was used to calculate the d-spacing. The *d*-spacing of nanocomposite is found to be 0.18 nm, 0.21 nm and 0.16 nm assigned to the orientation plane at (222), (111) and (116) corresponds to cubic α $FAPbI_3$, rutile tetragonal TiO_2 and hexagonal hematite Fe_2O_3 respectively [10, 11, 14, 16]. Fig. 2 (c) shows the SAED image of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite. The bright dotted spot signifies the polycrystallinity. The orientation was observed at (104), (021), (222), (116) and (004) attributed to d-spacing 0.27 nm, 0.34 nm, 0.18 nm, 0.16 nm and 0.23 nm corresponds to hexagonal hematite Fe_2O_3, hexagonal δ-$FAPbI_3$, cubic α-$FAPbI_3$, hexagonal hematite Fe_2O_3 and tetragonal anatase TiO_2 respectively [9, 11-15, 17-18]. The orientation obtained from the SAED pattern is analogous to the XRD data.

3.2 Characterization of Biofuel

3.2.1 GCMS Analysis

Table 1 shows the fatty acid methyl esters (FAME) synthesized from raw Karanja oil using Fe_2O_3-$BaTiO_3$-

TiO_2 nanocomposite as a catalyst. All the necessary FAMEs were present in the synthesized biofuel and it matched with the earlier reported data [15, 17]. The maximum fatty acid methyl esters were acquired by lignoceric and α-linolenic acid methyl esters i.e., 31.25 and 23.10 % as shown in Table 1. The unsaturated fatty acid methyl ester and saturated fatty acid methyl ester present in the synthesized fatty acid methyl esters lead to longer premixed combustion/high peak pressure and excellent combustion properties [18, 19]. The GCMS results conclude that the synthesized biofuel is an outstanding candidate because of the presence of both saturated and unsaturated fatty acids.

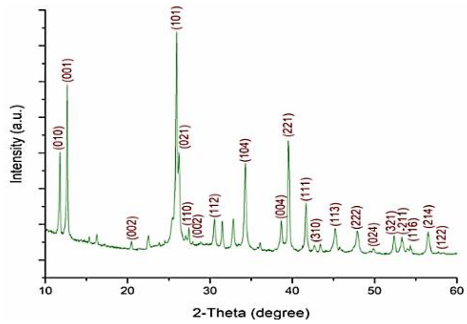
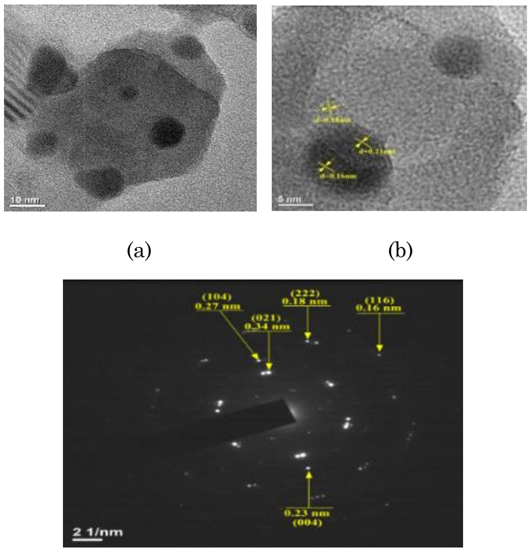


Fig. 1 – XRD of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite



(a) (b) (c)

Fig. 2 – (a) TEM image of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite (b) HRTEM image of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite (c) SAED image of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite

Table 2 shows the comparison of catalysts performance of various heterogeneous perovskite catalysts with the present work synthesized catalyst in the production of biofuel. The synthesized perovskite-based nanocomposite catalyst can be a potential catalyst in the future for the synthesis of biofuel. The biofuel yield of the present experimental data was compared with the biofuel yield of other reported data synthesized from perovskite catalysts and found that the biofuel yield of present experiment is quite lower than the biofuel yield of counterpart perovskite catalysts. Temperature plays a major role in the transesterification reaction. As compared to the data's reported by other researchers; the present work was performed at an ambient temperature which was less than 20 °C; but the other reported experiments were performed at temperature greater than 60 °C.

Table 1 – GC-MS chromatogram of biofuel from Karanja oil using Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite as a catalyst

Sl. No.	Retention time (min)	Fatty Acid Methyl Ester	Composition (%)
1	31.60	Linoleic Acid Methyl Ester	1.10
2	31.68	Linoleic Acid Methyl Ester	1.78
3	32.45	Linolenic Acid Methyl Ester	16.52
4	34.22	Behenic Acid Methyl Ester	1.28
5	37.61	Lignoceric Acid Methyl Ester	31.35
6	39.04	α-Linoleic Acid Methyl Ester	23.10
7	40.71	Eicosenoic Acid Methyl Ester	1.08

The lower temperature might be a parameter that affects the yield of biofuel. Further, an appropriate amount of catalyst loading and molar ratio might enhance the yield of biofuel. An inadequate amount of catalyst loading can lead to incomplete conversion, as the catalyst may not be able to efficiently promote the transesterification reaction. On the contrary excessive catalyst loading might not sufficiently improve the conversion rate; it can increase production costs. Finding the optimal catalyst loading is mandatory to achieve high conversion efficiency.

Table 2 – Comparison of various perovskite catalyst's performance in the transesterification process

Catalyst	**Molar ratio (Methanol to oil)**	**Reaction Temperature (°C)**	**Reaction time**	**Catalyst loading (wt%)**	**Yield (%)**	**Ref.**
$BaSnO_3$	16:1	65	25 min	2.5	98	15
$SrTiO_3$	15:1	170	3 h	6	86.50	16
$BaCeO_3$	19:1	65	100 min	1.2	98.4	17
Fe doped $SrTiO_3$	18:1	150	3 h	5	97.52	18
Strontium doped TiO_2-GO	10:1	120	3 h	10	96.5	19
Fe_2O_3-$FAPbI_3$-TiO_2	10:1	20	3 h	2 wt%	15-20	This experiment

Simultaneously, a higher molar ratio can improve the conversion rate and increase the yield of biofuel. Moreover, using an excessively high molar ratio can increase production costs. Therefore, it is vital to regulate the appropriate molar ratio based on the definite catalyst and reaction condition to ensure complete conversion while maintaining cost-effectiveness. So, to make it an industrially potential catalyst further optimization of the process parameters is a mandatory need for increasing the yield of biofuel.

4. CONCLUSION

The biofuel was successfully synthesized using a novel organic-inorganic perovskite-based nanocomposite as a catalyst. The nanocomposite was characterized by XRD and TEM. The XRD analysis clearly signifies the formation of Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite. The morphology of the nanocomposite was determined by TEM. The transesterification method with the reaction parameters as catalyst loading of 2wt. %, ambient reaction temperature and reaction speed 1000 rpm under UV light irradiation were used for the synthesis of biofuel from Karanja oil. The biofuel was characterized by GCMS. The GCMS signifies the different fatty acid methyl esters present in the biofuel. Among the fatty acid methyl esters lignoceric and α-linolenic acid methyl esters acquire 31.25 and 23.10 %. The corresponding fatty acid methyl esters are saturated and unsaturated fatty acid methyl esters. The presence of both the categorized methyl esters lead to excellent premixed combustion and results in better combustion properties. The maximum biofuel yield by using Fe_2O_3-$FAPbI_3$-TiO_2 nanocomposite as a catalyst was found to be in the range of 15-20 %. Increasing the yield of biofuel requires further optimization of the process parameters such as reaction temperature, reaction time, catalyst loading, reaction speed etc. Temperature is an important parameter for the synthesis of biofuel. The present work was performed at ambient temperature. So, raising the reaction temperature can potentially lead to a higher yield. Further, the nanocomposite will be used as a catalyst for the transesterification of various inedible oils. The synthesized biofuel can be further used in engines by blending with commercial diesel at various proportions. Hence, the synthesized organic-inorganic perovskite-based nanocomposite can be a potential candidate for synthesizing biofuel in the near future.

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Синтез біопалива з використанням органо-неорганічного перовскітного матеріалу сонячної батареї на основі нанокомпозиту

Priyanko Protim Gohain[1], Nageswara Rao Medikondu[2], Vinjamuri Venkata Kamesh[3], Mahua Gupta Choudhury[4], Kunal Chakraborty[1], Samrat Paul[1]

[1] *Advanced Materials Research and Energy Application Laboratory (AMREAL), Department of Energy Engineering, North-Eastern Hill University, Shillong-793022 Meghalaya, India*

[2] *Department of Mechanical Engineering, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Andhra Pradesh-533437, India*

[3] *Department of Mechanical Engineering, Aditya Engineering College (A), Surampalem, East Godavari District, Andhra Pradesh-533437, India*

[4] *Department of Animal Health and Fisheries Sciences, Indian Council for Agricultural Research, NEHRC, Umiam, Shillong-793103, India*

Альтернативне паливо повинно замінити викопне паливо. Це дозволить вжити запобіжних заходів для навколишнього середовища задля зменшення токсичних газів, що виділяються з викопного палива. У цій роботі біопаливо синтезується з використанням нового органо-неорганічного нанокомпозиту на основі перовскіту як каталізатора. Синтезований каталізатор досліджено методами рентгенівської порошкової дифракції (XRD) та просвічуючої електронної мікроскопії (TEM). Для синтезу біопалива використовується метод переетерифікації. Дослідники з усього світу здебільшого синтезували біопаливо, особливо біодизель, методом переетерифікації, де температура відіграє головну роль у каталітичній реакції. Більшість дослідників повідомили про синтез біопалива з використанням гетерогенних каталізаторів при вищих температурах, що перевищує 60 °C, але в цьому дослідженні спроба синтезу біопалива за температури навколишнього середовища здійснюється під впливом ультрафіолетового світла. Для дослідження параметрів синтезованого біопалива також використовується метод мас-спектрометрії газової хроматографії (GCMS).

Ключові слова: Біопаливо, Каталізатор, Перовскіт, Синтез, Нанокомпозит, Переетерифікація.