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*by* Sanaul Haque

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**Submission date:** 13-Oct-2025 11:21PM (UTC+0700)

**Submission ID:** 2779974068

**File name:** research\_proposal\_-\_Rayhanul\_Islam\_Lamun.pdf (107.56K)

**Word count:** 2852

**Character count:** 17131

**Research Proposal Title: Perovskite Based Materials for Sustainable Hydrogen Production: Opportunities and Challenges**

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**Submission Date:** 28 / 09 / 2025

## **Title: Perovskite Based Materials for Sustainable Hydrogen Production: Opportunities and Challenges**

**Introduction:** Energy drives modern development and supports essential human needs like health, food, and mobility. Currently, fossil fuels dominate global energy use, but growing demand is rapidly depleting these resources. Their continued use also causes air pollution, greenhouse gas emissions, climate change, and economic risks. Therefore, finding sustainable alternative energy sources is crucial[1]. There are several types of renewable energy that can serve as alternatives to fossil fuels. Among these, hydrogen has become a very promising option to replace fossil fuels because of ⑤ high energy content and does not emit toxic byproducts. In addition, hydrogen is considered one of the most energy dense sources of clean and sustainable energy, as it results in net zero carbon emissions after combustion[2].

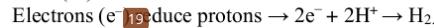
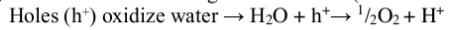
Right now, most hydrogen is made using a method called steam methane reforming, which relies on fossil fuels and leads to a lot of greenhouse gas emissions. Green hydrogen is produced from renewable resources through biomass utilization and water-splitting techniques[3]. Water splitting is a chemical process that requires multifunctional materials and an energy source, like electricity, light, or heat,③ to separate water ( $H_2O$ ) into its two main elements, hydrogen ( $H_2$ ) and oxygen ( $O_2$ )[4]. Solar energy is a clean and unlimited① source of energy, and various types of water splitting processes take place as a result of its use. Perovskite materials have become a promising option for sustainable hydrogen ( $H_2$ ) production because of their adjustable bandgaps, strong light absorption abilities, good charge movement characteristics, and effective catalytic performance. Perovskites are mainly classified into oxides and halides, where halide perovskites excel in visible light optoelectronic applications due to their strong and broad absorption characteristics, while perovskite oxides act as versatile, cost effective catalysts in electrocatalytic processes[5]. These features make them suitable for the three main methods of producing hydrogen: photocatalytic, thermochemical, and photoelectrochemical (PEC) water splitting[6]. This proposal explores the future possibilities of perovskite materials for hydrogen generation, focusing on their potential roles, current challenges, and experimental strategies to advance the field.

### **Research Question:**

1. How can perovskite materials be strategically designed by tailoring their composition, applying protective encapsulation, and integrating them into functional devices to deliver stable, high efficiency, and environmentally responsible hydrogen production through water splitting?
2. Among halide, oxide, and lead-free variants, which perovskite chemistries strike the most effective balance between catalytic activity and long-term structural stability?
3. What forms of interfacial modification or encapsulation (coating, oxide overlayers, hybrid heterostructures, or polymer barriers) are most successful in mitigating degradation of perovskite-based electrodes in aqueous environments?
4. What challenges and opportunities emerge when evaluating the techno-economic feasibility of scaling perovskite-based hydrogen generation technologies from laboratory prototypes to industrial applications?

**Literature Overview:** The ideal oxide perovskite chemical formula is  $\text{ABO}_3$ , and its crystal structure is cubic[7]. Where A can be both organic or inorganic (e.g.,  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{FA}^+$ ,  $\text{MA}^+$ ) larger cation with 12-fold coordination, B is a smaller divalent metal cation (e.g.,  $\text{Pb}^{2+}$ , and  $\text{Sn}^{2+}$ ) with octahedral, 6-fold coordination[8]. Metal halide perovskites have the formula  $\text{ABX}_3$ , where X is a halide anion (such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ )[9]. Perovskite oxides ( $\text{ABO}_3$ ) are easy to modify, and their band gaps can be tuned by doping or changing atoms. They are stable and common, but many still have wide band gaps. To improve visible-light activity, scientists use defects and heterostructures[10]. Halide perovskites absorb light well and have tunable band gaps, making them efficient for hydrogen production. However, they are unstable in water and oxygen, so scientists add protective coatings, composites, or encapsulate them to make them more stable[11].

Photocatalytic water splitting is a three-step energy process where sunlight and a special material called a photocatalyst are used to break water ( $\text{H}_2\text{O}$ ) into hydrogen ( $\text{H}_2$ ) and oxygen ( $\text{O}_2$ ). In this process of water splitting using a catalyst: energy from sunlight drives the reaction, the catalyst accelerates the process, and the outcome is hydrogen gas, which can be utilized as a clean fuel[12]. There are (i) Light absorption: Sunlight (UV/visible) strikes the surface of the perovskite. Energy of the light meets or exceeds the band gap, the material absorbs it. (ii) Charge excitation: The absorbed light energizes electrons, elevating them from the valence band (VB) to the conduction band (CB), formation of electron-hole ( $e^-/\text{h}^+$ ) pairs. (iii) Charge separation & transport: Energized electrons relocate to the CB while the holes remain in the VB. Maintain the separation of these charges and transport them to the catalyst surface to prevent recombination[6][13] (iv) Surface redox processes: Electrons ( $e^-$ ) in the CB reduce protons ( $\text{H}^+$ ) into hydrogen gas ( $\text{H}_2$ ). Holes ( $\text{h}^+$ ) in the VB oxidize water into oxygen ( $\text{O}_2$ ) and can also oxidize organic molecules (like alcohols)[6][13]



Photoelectrochemical water splitting uses semiconductor materials to absorb sunlight and directly split water into hydrogen ( $\text{H}_2$ ) and oxygen ( $\text{O}_2$ ) via the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively[5]. Three sequential phases are involved in solar-driven water splitting over a cocatalyst-assisted semiconductor. There are i) Light absorption: When sunlight strikes a semiconductor, high-energy photons cause electrons in the valence band to move into the conduction band ii) Charge movement: The excited electrons and remaining holes separate and migrate to the semiconductor's surface iii) Water splitting reactions: Water is split into hydrogen ( $\text{H}_2$ ) and oxygen ( $\text{O}_2$ ) by the electrons and holes participating in chemical reactions at the surface[14]. The Hydrogen evolution reaction (HER):



Despite being extremely effective at producing hydrogen, hybrid halide perovskite materials have serious stability and toxicity issues[15]. Their long-term operating performance is limited by their susceptibility to degradation under conditions of moisture, heat, light, and applied bias. Lead is also present in many high-efficiency perovskites, which poses major health and environmental risks[16]. Additionally, it is still very difficult to scale up perovskite-based hydrogen-generating systems from laboratory to large, industrial-scale devices[17]. Complex encapsulation techniques are needed to protect the fragile perovskite layers, which raises the cost and engineering

complexity. Furthermore, durability problems are frequently encountered by the catalysts that power the evolution reactions of hydrogen and oxygen. Despite their high efficiency, noble-metal catalysts can be costly and degrade over time[18]. While there are less expensive, earth-abundant alternatives, their performance is still inferior.

#### Methodology:

1. **Materials Design and Synthesis:** The design of perovskite materials for hydrogen production focuses on achieving both high efficiency and stability. This involves selecting suitable types, such as halide perovskites ( $\text{MAPbI}_3$ ,  $\text{FAPbBr}_3$ ), oxide perovskites ( $\text{BaTiO}_3$ ,  $\text{LaFeO}_3$ ), or lead-free options ( $\text{CsSnI}_3$ , Bi-based), and fine-tuning their composition through ion substitution and doping to improve conductivity and catalytic performance. Different synthesis methods like spin coating for halides, sol-gel for oxides, or hydrothermal routes for nanostructures are used based on material type. Finally, thorough characterization using XRD, SEM/TEM, UV-Vis, PL, and electrochemical techniques ensures the materials are optimized for stable and efficient water-splitting.
2. **Protective Encapsulation and Electrode Fabrication:** To improve the durability of perovskite materials in water-based environments, it is important to use protective coatings and precise methods for creating electrodes. Protective layers can be made from inorganic oxides such as titanium dioxide ( $\text{TiO}_2$ ) or aluminum oxide ( $\text{Al}_2\text{O}_3$ ), or from polymers like Nafion and poly(methyl methacrylate) (PMMA). Another approach involves combining perovskites with materials such as graphene or carbon nanotubes to enhance both their stability and electrical conductivity. When making electrodes, perovskite films are applied onto conductive surfaces such as fluorine-doped tin oxide (FTO), indium tin oxide (ITO), or carbon paper. The thickness and surface texture of these films are carefully adjusted to ensure maximum contact with the active material. After coating, the electrodes are tested for their performance in water solutions with varying acidity or alkalinity, and their coating quality is assessed using measurements like contact angle and adhesion strength.
3. **Electrochemical Evaluation:** To assess the catalytic activity, efficiency, and durability of perovskite electrodes [15] three-electrode electrochemical system is employed. In this setup, the perovskite serves as the working electrode, while a platinum counter electrode and an Ag/AgCl reference electrode are used. The electrodes are tested in acidic, neutral, and alkaline electrolyte environments. Important performance indicators include linear sweep voltammetry (LSV) to measure overpotential and current density, Tafel slope analysis for understanding reaction kinetics, chronoamperometry to evaluate long-term stability, and [24] Faradaic efficiency to quantify hydrogen evolution. Additional advanced techniques like electrochemical impedance spectroscopy (EIS) are used to examine charge transfer resistance. After electrolysis, the electrodes are analyzed using XRD and SEM to detect any structural or morphological changes.
4. **Techno-Economic Assessment:** The techno-economic assessment aims to evaluate the feasibility of scaling perovskite-based hydrogen production from laboratory prototypes to industrial applications. This involves collecting data on synthesis costs, including precursors and processing, electrode lifetime and efficiency, as well as energy input and hydrogen yield. The levelized cost of hydrogen (LCOH) will be estimated, alongside sensitivity analyses to assess how perovskite stability, efficiency, and material costs impact

overall economics. Potential scale-up challenges, such as material degradation, large scale encapsulation, and environmental concerns, will be identified, and strategies for industrial adaptation like continuous coating methods and modular electrolyzer designs will be proposed to ensure practical and sustainable deployment.

5. **Data analysis :** Data analysis will involve using statistical methods to compare the performance of different perovskite compositions, coatings, and electrode configurations. Structural and compositional features will be correlated with catalytic activity and stability to identify key factors influencing performance. Additionally, predictive models will be developed to forecast perovskite behavior under varied operational conditions, guiding optimization for both efficiency and durability.

**Expected Outcome:** The anticipated results of this research aim to identify perovskite materials that demonstrate strong catalytic performance and durability over extended periods for hydrogen production. Additionally, the study will focus on creating effective methods for protecting and improving the interfaces of these materials to reduce their deterioration. It will also examine the cost-effectiveness of producing hydrogen using perovskite technologies on a larger scale and suggest designs for systems that are both eco-friendly and suitable for industrial applications.

**Significance:** This research integrates materials science, renewable energy, and environmental engineering to advance hydrogen production. It aims to establish a pathway for low cost, high efficiency green hydrogen generation, provide environmentally safer alternatives to steam methane reforming, and develop practical strategies for the commercialization of perovskite based hydrogen technologies.

**Limitation:** This research has several limitations. Perovskite materials, especially those containing halides, are sensitive to moisture, heat, and light, which may affect their long term stability even when protected by encapsulation. Scaling up the laboratory synthesis and coating processes for industrial production might face difficulties in achieving uniformity, consistent results, and cost effectiveness. Environmental and safety issues, particularly with lead-based perovskites, could limit the range of materials that can be used. Additionally, the stability of these materials in extreme pH electrolytes might restrict their operational conditions. The estimated costs and predictive models may not accurately reflect real world performance or degradation when applied on a large scale.

**Conclusion:** Perovskite materials present a hopeful approach for creating hydrogen using solar energy through processes like photocatalytic and photoelectrochemical water splitting. This is because they have adjustable bandgaps, strong optoelectronic features, and the ability to absorb light effectively while transporting charges efficiently. These materials have shown great potential for producing large amounts of hydrogen and improving the efficiency of converting sunlight into hydrogen.<sup>10</sup> However, even though there has been a lot of progress in creating perovskite-based systems, there are still issues related to scaling up production, maintaining performance over time, and managing costs. These challenges are holding back the move from research in labs to real-world and commercial use. Overcoming these issues will be essential for making perovskite technologies more sustainable, efficient, and affordable for hydrogen production.

**Project Practicalities:** Over all the 12 month project, the first three months will be used to create perovskite materials and perform initial tests to understand their properties. The next three months will focus on testing different ways to protect these materials from damage and conducting accelerated aging tests to find better methods for improving their long-term stability. From month seven to nine, the work will involve making devices and testing their performance, including how efficiently they convert sunlight into hydrogen and how durable they are. Months ten and eleven will include reviewing the economic and environmental impacts of the technology, along with further testing for long-term durability. The last month will be spent analyzing all the collected data, writing reports, preparing scientific papers, and sharing the findings with others.

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**Post Program Plan:** Once the research is completed, research findings will be published through academic publications, industry presentations, journals, and relevant organizations to highlight progress in perovskite-based hydrogen technologies. Moreover, there will be active engagement with industry partners, and if possible, a hydrogen production company will be set up in Bangladesh to apply the technology in real world settings.

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