Analysing Research Trends in Nanomaterials for Green Hydrogen Value Chain: "A Bibliometric approach"

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Abstract:

Nanomaterials can play a significant role in various stages of the hydrogen value chain, from production to storage and utilization. This paper is an overview of how nanomaterials are being explored in different aspects of the hydrogen value chain. The study aims to identify and elucidate emerging trends in catalyst development for hydrogen production. By leveraging the Web of Science's expansive repository, the research will not only reveal the current state of the field but also unveil patterns in research trajectories, highlighting key thematic areas, innovative methodologies, and transformative technologies. The identification of prolific authors, institutions, and leading countries will add a valuable dimension to understanding the global landscape of nanomaterial research in hydrogen catalysts. Overall, this study holds the promise of not only advancing our understanding of the current state of the field but also providing a roadmap for future endeavours, fostering innovation and contributing to the sustainable development of hydrogen technologies.

Keywords: *Titanium; Poly (3,4-ethylenedioxythiophene) (PEDOT); Gallium; Corrosion; Bioactivity; Orthopaedic*

1. Introduction

With the increase in population growth, the demand for energy has also increased in last few years and this is going to increase more in upcoming years. To meet the energy demands, there is a need to increase the use of clean energy and curb the use of conventional fossil-fuel based energy. Taking environmental constraints into consideration, green hydrogen has been considered as a good alternative of fossil – fuel based energy system. Green hydrogen can serve as a long – term and ideal solution for energy related environmental constraints as its heating value is three times more as compared to petroleum and it leads to zero harmful emissions as well [1], [2]. There are a variety of renewable as well as non-renewable methods to produce hydrogen. Non-renewable methods of hydrogen production include natural gas, coal gasification, heavy oil, methane decomposition etc. Renewable methods include water electrolysis, solar photochemical, photobiological water decomposition, biomass – conversion etc. Although these methods are highly efficient and eco-friendly but these are not cost-effective methods. Although hydrogen as a fuel has various advantages but it is a highly flammable gas with the range from 4% to 75% vol in air and can cause an explosion. Since it is colourless and odourless, it is very difficult to discover and configure it in case of leakages [3]. Another challenge is the lack of safe, easy and cost-effective storage method. To address these types of challenges associated with the production and storage of hydrogen, the role of nanomaterials has been increased tremendously. The physico-chemical properties of nanomaterials render its usage in catalysis, complex hydrides, metal organic frameworks etc. There are different types of nanomaterials that are used in hydrogen production and storage such as activated carbon, carbon nanotubes, metal-doped carbon-based nanomaterials, complex hydrides, clathrates, metal-

organic frameworks etc. The size of engineered nanomaterials ranges from 1 – 100 nm and designed in a specific manner to simulate the only properties for specific purpose or application. The storage of hydrogen depends upon two phenomenon i.e. physisorption and chemisorption. MOFs, Zeolites and carbonaceous materials fall in the former category whereas complex hydrides and metal hydrides fall in the later one. The use of nanomaterials has increased tremendously not just in the field of hydrogen production but in other fields also. This has gained a great momentum in water splitting such as photochemical, electrochemical and photoelectrochemical water splitting methods [4], [5].

The materials such as MnO_2 nanosheet is used for photocatalysis, electrocatalysis and electrochemical energy storage whereas TiO_2 is used as a photocatalytic semi-conductor. The TiO_2/ MnO_2 nanocomposites have great photocatalytic activity and can consume solar energy efficiently because of their small energy band gap, negatively charged surface property and large surface area. The scientists are trying to improve photocatalysis by switching to various carbon based nanomaterials [6].

According to the study conducted by researchers, if one introduces the nanomaterials impregnated biomass in SCW (Supercritical Water) gasification, the difficult operating conditions can be reduced and conversion efficiency into product can be enhanced [7]. Other important and prominent magnetic nanocatalysts with or without inherent magnetic properties are Fe_2O_3 and Fe_3O_4 which can be easily separated from the solution and can prove non-hazardous to the environment. According to the materials employed, their properties, efficiencies and applications, nanomaterials have been classified as Zero-Dimensional (0D), One-Dimensional (1D), and Two- Dimensional (2D). Zero-Dimensional (0D) consist of low efficiency materials that are highly corrosive and have high charge-recombination rates. These include carbon quantum dots, CdS and CdSe which are used for H_2 evolution in visible light. One-Dimensional (1D) nanomaterials have superior properties which makes them suitable for photocatalysis process of hydrogen production. These include nanotubes, nanowires, nanorods, and nanofibers. Example of One-Dimensional (1D) nanomaterial is Zn_2GeO_4 that has the highest rate of hydrogen production i.e. 0.6 mmol/h. Two- Dimensional (2D) nanomaterials have higher surface area comparable with that of 0- and 1-D nanomaterials and are in the form of thin films made for hydrogen evolution. Due to the advantageous properties of 2D nanomaterials, researchers explore thin film photocatalysts with novelties such as graphene oxide, g-C_3N_4, and transition metal dichalcogenides (TMDs). The pH range for hydrogen evolution reactions has been studied extensively in 1D, 2D and 3D MOFs (Metal Organic Frameworks) and among which the 2D metal organic frameworks with sheet like morphology have become the highly potential materials [8], [9].

Recently, another class of materials 'halide perovskite materials' has emerged for the photocatalytic applications due to their optical and electronic properties as well as suitable band position, high carrier mobility and great lengths of electron-hole [10]. So, a lot of materials and combinations thereof are used as photo- or electro- or photoelectrocatalysts to produce hydrogen in an efficient and effective manner.

By analysing the literature review, it can be concluded that the use of nanomaterials for hydrogen production is increasing nowadays which will be gaining more momentum in the upcoming years. The overall paper covers the bibliometric analysis using different keywords and operators, co-occurrence based keyword analysis, research trend of countries and institutes and review based analysis. This analysis would help us understand the current status of 'nanomaterials' in the hydrogen value chain.

2. Bibliometric Analysis

Bibliometric analysis is an established technique for assessing the state of the art in a particular field of study. Through the analysis of quantitative data and statistics, the approach can be used to

describe publication trends through time as well as across literature. As a result, information regarding the quantity of papers published by a country, research group, institute, or authors with the highest technological generation may be identified. To analyse the research trend in the use of nanomaterials in Green Hydrogen Production, Bibliometric analysis was done and the result presented in this paper are based on a bibliometric analysis of articles published between 2005 and 2022.

Methodology

Web of Science (WOS) has been chosen as the database for the study of research trend in this area. WOS is one of the most popular and commonly used database which covers various subjects. The search was initiated with the use of string performed in Web of Science which was based on 'topic'. Distinct search queries were developed to retrieve the relevant publications in the time span '2016-2023'. The number of papers retrieved is with respect to the 7 key strings which is given in Table-1. For removing the duplicate as well as ambiguity, manual cleaning of the .csv file extracted from WOS was done. For this authors have gone through the abstract and keywords to remove any ambiguous papers, resulting in 2902 papers, which have been finally screened for further literature analysis for indicators like publication analysis, top countries, and keyword co-occurrence analysis.

Table 1: Keyword Strings Search in Web of Science with total number of counts

Sl. No.	Keywords	Total Papers
1	"Hydrogen Production" and "Nanomaterials"	1076
2	"Hydrogen Evolution" and "Nanomaterials"	1896
3	"Hydrogen generation" and "Nanomaterials"	352
4	"Water splitting" and "Nanomaterials" and "Hydrogen Production"	304
5	"Photocatalysis" and "Nanomaterials" and "Hydrogen Production"	295
6	"Electrocatalyst" and "Nanomaterials" and "Hydrogen Production"	96
7	"Electrolysis" and "Nanomaterials" and "Hydrogen Production"	60
	Paper retrieved after removing duplicates	2902

2.1 Publication analysis

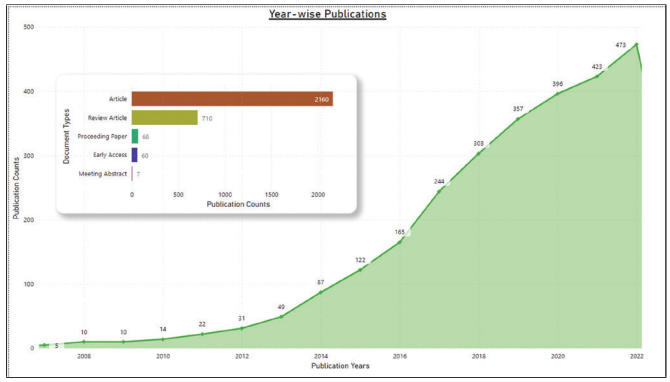


Figure 1: Year-wise publication trends globally

To find the year-wise publication trend and number of publications in different document type, Microsoft Excel and Microsoft Power BI is used. First the analysed data of 2902 papers was downloaded and sorted in excel according to the requirement. After the data was ready, we exported the data in Power BI [33] where we transformed the data in power query, filtered the repeatation and analysed the results till 2022. After creating the line graph it can be clearly seen in Figure 1 that with the year passes the number of publications increases, where the maximum contribution are in Article.

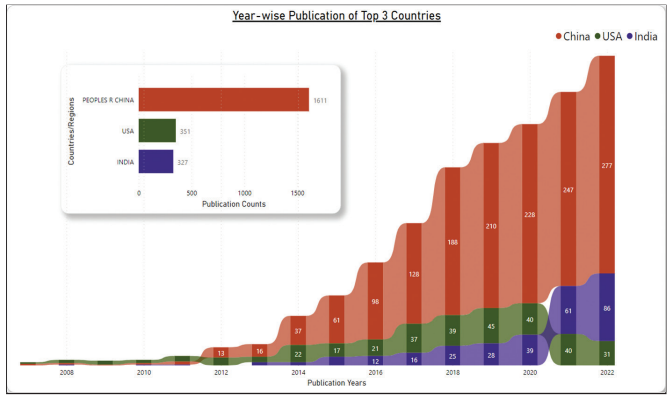


Figure 2: Year-wise publication trends of Top three countries

To analyse the top contributor countries, the same data set was analysed on yearly basis with the filter of top countries, and the result are shown in Figure 2, where China has been stably publishing around 55% of the total publication, USA contributes to around 12% and India shares around 11% of the total publications. The growth in India' publication shows exponentiality after 2020, leaving USA behind.

We also analysed the top Institutes that are countributing within these countries (Figure 3), and in India it shows that IIT and CSIR are the prominent institues contributing around 18.96% and 10% of the publications respectively, apart from this NITs, SRM Chennai and Jain University are a few other institutes and universities which join the top contributors in India. Top institutes of China are Chinese Academy of Sciences contributing around 16% and Jilin University contributes ~6% and in case of China, the contribution for publications are majorly from universities only. The top contribution in USA comes from mainly institutes and universities, the top two are US-DOE, contributing around 12% and University of California, contributing around 11%.

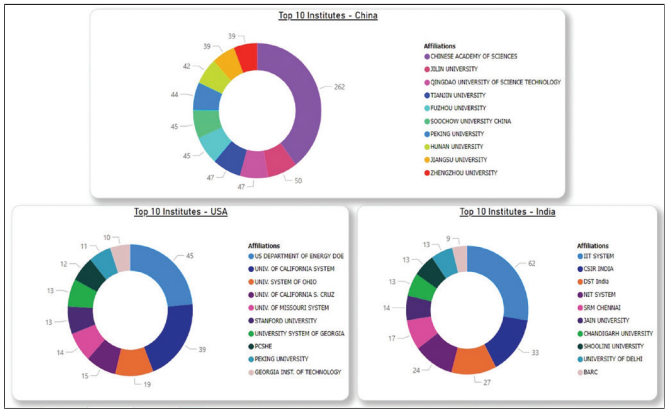


Figure 3: Top 10 institutions of the top three countries

2.2 Keyword Co-occurrence analysis

Keyword analysis plays a crucial role in research by revealing current trends and research topics within a particular field. By examining keyword co-occurrence, researchers can determine the direction of research and the main subjects of a field. In this case, keyword analysis was carried out using data extracted from the 'Web of Science' database [31]. The data was then visualized using 'VOSViewer' software [32] to create a keyword co-occurrence map, which helps identify research focus areas and emerging research trends. We analyzed top 3 countries data. In this network analysis the top cited papers, 10% of total results found i.e. 290 papers are analysed. By extracting the top cited data in text file, we did the network visualisation in VOS Viewer by taking Citation based analysis with unit Country. We took full counting method, where the maximum number of countries per document was 25, and the minimum number of a country was 5. Out of the total 35 countries 14 meet the threshold. From the analysis of top 10% papers of the result that came from the above query in Web of Science. 192 papers of China has 47552 citations, 54 USA papers has 29014 and India has 19 papers having 5878 citations went to 5th position in top 10% citation count where in publication count it was on 3rd position.

The keyword analysis of China (Figure 4) deciphered around 143 items, 11 clusters, 1147 links, and the most dominant group where the study trend is seen are 'Hydrogen', 'photocatalysis', 'evolution reaction', 'nanomaterials', 'hydrogen production' and other smaller clusters.

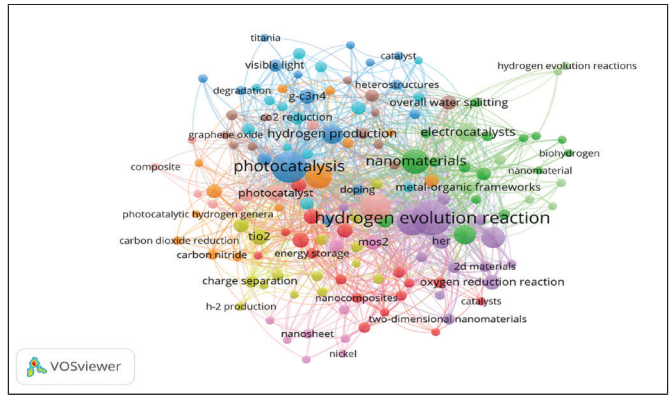


Figure 4: Co-occurrence based Keyword Analysis of China

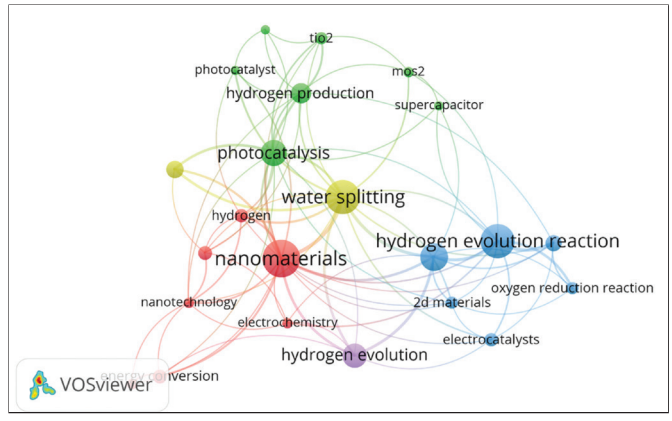


Figure 5: Co-occurrence based Keyword Analysis of USA

The keyword analysis of USA (Figure 5) deciphered around 23 items, 5 clusters, 87 links, and the most dominant group where the study trend is seen are 'nanomaterials', 'Hydrogen', 'photocatalysis',

'water splitting', 'hydrogen evolution', 'hydrogen production' and other smaller clusters.

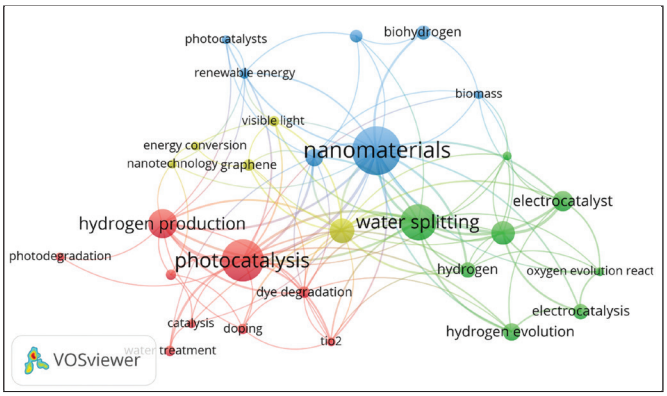


Figure 6: Co-occurrence based Keyword Analysis of India

The keyword analysis of India (Figure 6) deciphered around 29 items, 4 clusters, 111 links, and the most dominant group where the study trend is seen are 'nanomaterials', 'photocatalysis', 'water splitting', 'hydrogen production' 'electrocatalyst', and other smaller clusters.

These finding suggest the most prominent and recent approaches within the top countries scientific community. Keyword analysis provides valuable insights into research focus areas, emerging topics, and new research directions. By understanding the research landscape and areas of interest across different countries, researchers can broaden their research scope and explore new avenues for investigation.

Table 2: Country-wise total publication and citation with total link strength

Sl. No	Country	Documents	Citations	Total Link Strength
1	China	192	47552	511
2	USA	54	29014	307
3	Singapore	32	11431	235
4	Australia	25	8941	125
5	Japan	13	7429	48
6	India	19	5878	58
7	France	8	4717	36
8	South Korea	16	4684	83
9	Czech Republic	7	3480	41
10	England	8	2424	47
11	Saudi Arabia	6	2019	24
12	Germany	6	2004	36
13	Canada	5	1792	23
14	Spain	8	1637	16

In Figure 7, the bar graph is showing documents count and line graph is showing number of citations.

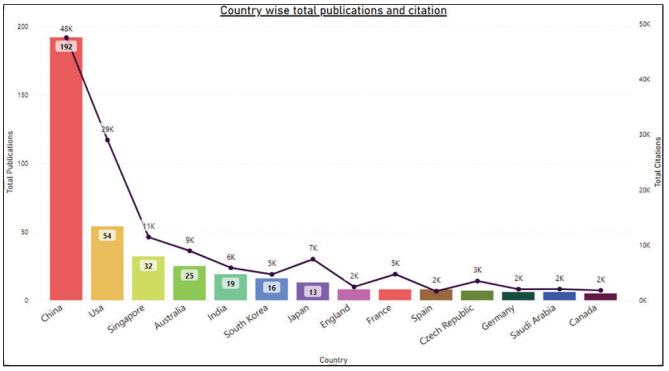
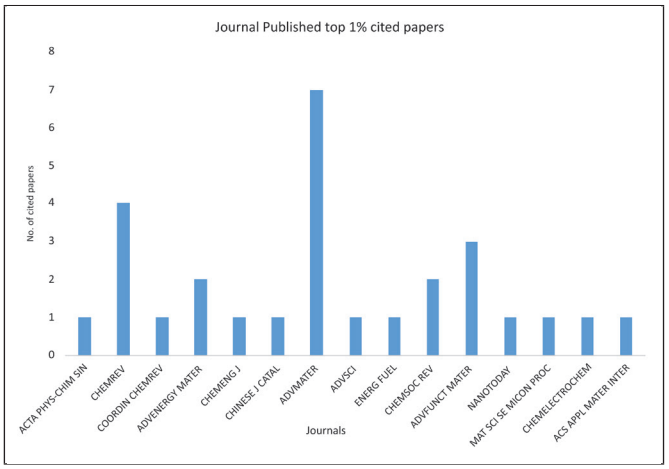


Figure 7: Country-wise total publications and citations



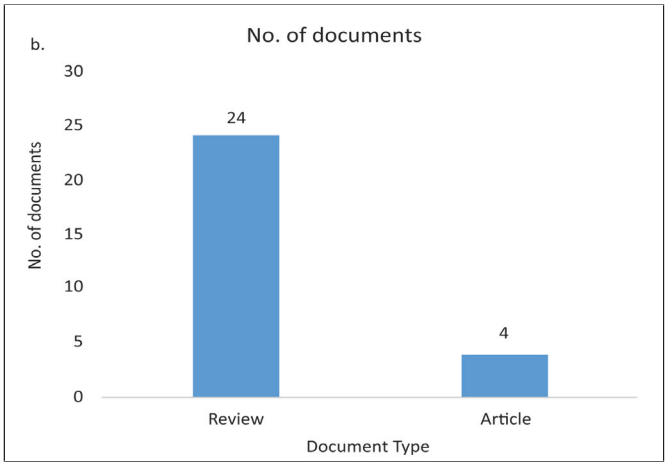


Figure 8 a: No. of Top 1 % cited papers in journals & b: No. of documents (Review and Article)

Figure 8 shows the number of top 1 % cited papers in different journals which clearly indicates the maximum papers in Journal 'Advanced Materials' and mostly the documents are of review type.

2.3 Research Trend analysis based on Top 1 % cited paper

The significance of Metal-Organic Frameworks (MOFs) in forming N- or P-doped graphite-based nanomaterials, enhancing catalysis for water splitting was highlighted [11]. These MOF catalysts, known for their stability and water-resistant properties, particularly excel in photo-degradation of organic pollutants. The controlled thermal transformation of MOFs into Single Atom Catalysts (SACs) adds another layer of complexity, offering potential breakthroughs in catalytic processes [12].

Transitioning to Metal-Nitrogen-doped Carbon (M-N-C) materials, [13] emphasize the importance of tuning metal ion centers and coordination for catalytic reactions, including Oxygen Evolution Reaction (OER), Hydrogen Evolution Reaction (HER), and more. The search for cost-effective and efficient alternatives to commercially used catalysts like Pt/C and IrO2/RuO2 is highlighted by [14].

The exploration of Transition Metal Sulfides (TMS) and Transition Metal Selenides emerges as a vital research focus for improving the performance of electrocatalysts in both HER and OER [15]. The unique properties of TMSs and their conductance, especially in multi-metal selenides, make them a hotspot for further investigation.

Novel approaches, such as sequential electrodeposition techniques for fabricating nanosheets and nanoparticles, showcase promising electrocatalytic properties for Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) [16]. Carbon dots, highlighted by [17], present an intriguing avenue for photocatalysis, though challenges remain in understanding their quantum yields and correlation with formation rates.

Localized Surface Plasmon Resonance (LSPR) emerges as a driving force in photocatalytic reactions, enhancing the activity and selectivity of HER and OER [18]. Structural defects in 2D photocatalysts, as discussed by [19], are identified as critical elements for improving photocatalytic activity, paving the way for future studies on structure-activity relationships.

The review by [20] delves into the progress of co-doping and mono-doping of nitrogen-doped carbon electrocatalysts, emphasizing the need for sustainable, metal-free catalysts. Band gap engineering in two-dimensional nano materials is thoroughly analyzed by [21], exploring materials like 2D MOFs, mxENES, 2D perovskites, and more for advancements in nanotechnology.

Cu-based nanoparticles and their applications in various catalytic processes [22], while [23] focus on semiconductor photocatalysis as a potential solution for environmental degradation and energy demands.

The comprehensive study by [24] proposes strain engineering as a novel route for enhancing the electrocatalytic performances of hydrogen evolution and oxygen evolution reactions, aligning with the growing interest in sustainable hydrogen fuel production.

Effective strategies were unravelled for molecular hydrogen production, concentrating on Transition Metal Phosphides (TMPs) [25]. The challenges in synthesizing TMPs with specific exposed facets are acknowledged, presenting avenues for further research [26].

Transition Metal Nitrides (TMNs) are explored by [27] for electrochemical energy applications, offering insights into nanostructuring as a successful approach to address inherent limitations. Delve into the optimization of catalytic activity through crystalline–amorphous heterojunctions, showcasing the potential for further advancements [28].

In the realm of 2D electrocatalysts, [29] advocate for specific compositions and functionalities, underscoring their significance in clean energy systems. The need for large-scale production of photocatalysts at the industrial level and the optimization of surface areas for increased efficiency are highlighted as future research focuses by [30].

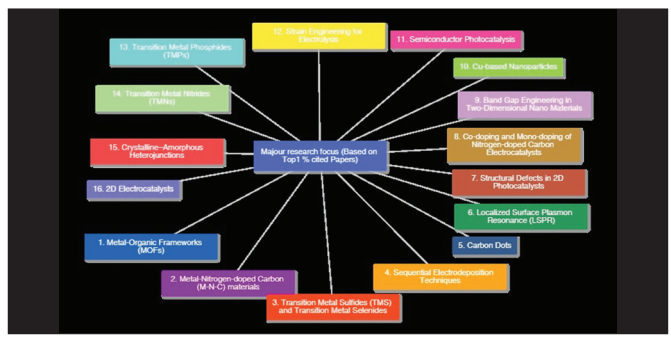


Figure 9: Major research focus (Based on Top1 % cited Papers)

This comprehensive review navigates through a myriad of nanomaterials and their applications in hydrogen production, offering valuable insights into the evolving landscape of this dynamic field. The diverse range of materials discussed, from MOFs to carbon dots and beyond, reflects the multi-faceted approach researchers are adopting to address the challenges in achieving sustainable and efficient hydrogen production.

3. Conclusion

The utilization of nanomaterials in the hydrogen value chain has been a topic of research and development in various countries.

Incorporating nanomaterials across the hydrogen value chain has the potential to enhance efficiency, reduce costs, and address some of the challenges associated with hydrogen production, storage, transportation, and utilization. However, it's important to note that the widespread implementation of these technologies may require further research, development, and consideration of safety and environmental aspects. By leveraging the unique properties of nanomaterials, researchers aim to address challenges, improve efficiency, and optimize various aspects of the hydrogen value chain.

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