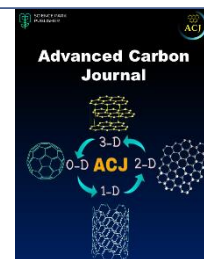


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Carbon Based Supports for Metal Nanoparticles for Hydrogen Generation Reactions Review

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Abstract

Hydrogen represents a highly promising alternative to fossil fuels due to its exceptional attributes. As the most abundant element in the universe, it holds the potential to revolutionize the energy landscape. When combusted, it generates energy, and the byproduct of this process is simply water, making it an environmentally friendly choice. The adoption of hydrogen as a fuel source has faced constraints primarily related to hydrogen storage technology. Nevertheless, innovative solutions are emerging, such as hydrogen feedstock materials like sodium borohydride (NaBH_4), which could offer effective storage capabilities. NaBH_4 is particularly noteworthy for containing 10.8% hydrogen by weight and for its ability to release hydrogen gas when reacting with water. Although this release occurs at a relatively slow rate, the introduction of a catalyst could enhance the efficiency of hydrogen production. This comprehensive review endeavors to evaluate the catalytic efficacy of metal nanoparticles when paired with environmentally sustainable catalyst support materials derived from fused carbon microspheres and graphene-like materials. These support materials, sourced from renewable origins, will be intricately combined with a spectrum of metal nanoparticles, encompassing gold, silver, platinum, palladium, and copper nanoparticles. The overarching objective is to investigate how these synergistic combinations can catalyze the expedited release of hydrogen from sodium borohydride, thereby contributing to the streamlined and efficient production of this clean and abundant energy source.

Keywords: Metal Nanoparticles , Carbon spheres, Graphene, Catalysis, Hydrogen

Introduction

The undeniable reality of Earth's finite resources underscores the pressing need for a paradigm shift in our approach to global energy consumption. With the current global population standing at approximately 8.1 billion and projections indicating an increase to 8.5 billion by 2030 and a further surge to 9.7 billion by 2050 [1], the impending challenges related to resource scarcity become increasingly apparent.

This population expansion is poised to trigger a substantial surge

in global energy demand, creating a formidable obstacle to sustainability. What amplifies this concern is the stark fact that a staggering 83.4% of the world's energy supply still heavily depends on fossil fuels, as graphically depicted in Figure 1. This heavy reliance on non-renewable energy sources raises critical environmental concerns, urging a reevaluation of our energy infrastructure and a compelling call to transition toward cleaner, more sustainable alternatives.

The consequences of maintaining such a significant dependence

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on fossil fuels are manifold, encompassing environmental degradation, climate change, and geopolitical tensions. As we grapple with these challenges, there arises an urgent need to explore and adopt alternative energy sources that can mitigate the environmental impact and contribute to a more resilient and sustainable energy future.

This juncture underscores the importance of a concerted effort to invest in and transition towards renewable energy technologies, such as solar, wind, hydro, and geothermal power. By diversifying our energy portfolio and reducing reliance on fossil fuels, we can pave the way for a more sustainable, environmentally friendly future. This shift is not just a technological imperative but a moral obligation to safeguard the well-being of our planet for future generations.

Therefore, the intersection of a growing global population, escalating energy demands, and the predominant reliance on fossil fuels necessitates a decisive shift towards sustainable and cleaner energy sources. The urgency of this transition cannot be overstated, and concerted global efforts are paramount to address the imminent challenges posed by resource limitations and environmental degradation.

these reserves will be exhausted remains a subject of debate, some models suggest that oil, gas, and coal may be depleted in as little as 35, 37, and 105 years, respectively [3]. This impending scarcity underscores the urgency of transitioning to alternative energy sources.

Greenhouse Gas Emissions



Figure 2. Smoke produced during industrial activity. †

The second, and perhaps more pressing, issue is the detrimental impact of fossil fuels on our environment. The burning of fossil fuels is a primary source of greenhouse gas emissions, including carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) [4]. Since 1751, it's estimated that the combustion of fossil fuels has released a staggering 337 billion metric tonnes of CO₂ into the atmosphere [5]. This trend is poised to continue, with global greenhouse gas emissions, measured in gigatons of equivalent CO₂ (GtCO₂e), projected to surge to 63.1 GtCO₂e in 2030 and a worrisome 73.6 GtCO₂e by 2050 [6]. Such a trajectory could lead to a substantial temperature increase of 3-4 °C, with catastrophic consequences for our environment [7].

Therefore, finding a sustainable alternative to fossil fuels is not merely a choice but an imperative for the health of our planet.

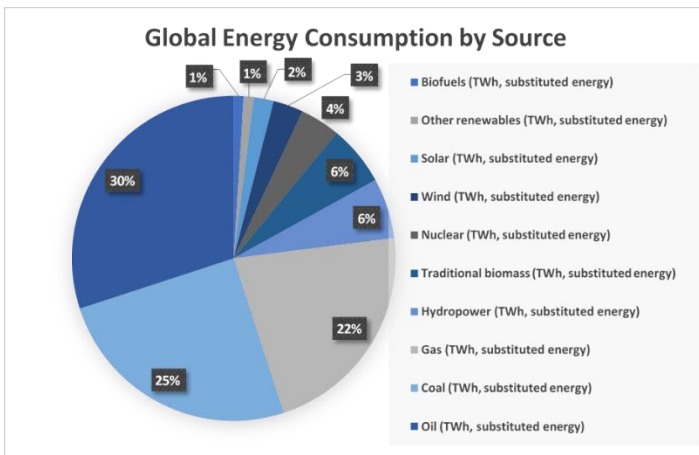


Figure 1. Global energy consumption by source [2].

Fossil Fuels

Our reliance on fossil fuels as a primary energy source presents two critical challenges. First and foremost, fossil fuels, formed over millions of years, are depleting rapidly due to our current consumption rates. While the exact timeline of when

Renewable Energy



Figure 3. A photovoltaic cell and a wind turbine. †

Renewable energy sources have emerged as a promising solution to address these challenges. Solar energy, harnessed from the sun, is particularly abundant, with approximately 1.08×10^{14} kilowatts of energy reaching the Earth's surface each year [8]. Much research has been dedicated to developing photovoltaic technology, which can convert sunlight into usable electricity [9].

However, photovoltaic cells, commonly found in solar panels, face several drawbacks, including high initial costs, relatively low efficiency, and intermittent energy output due to geographic conditions [10-11].

Wind Energy



Figure 4. A group of offshore wind turbines.

Wind energy, another promising renewable source, reached a record production of 651 GW in 2019 [12]. Advances in wind turbine technology have contributed to a reduction in their initial cost, making wind energy more accessible [13]. Yet, wind

energy has encountered resistance due to potential environmental issues, including noise pollution and disruptions to migratory patterns for birds [14-15].

Geothermal Energy



Figure 5. Pipes used during the transport of water in a geothermal power plant. ‡

Geothermal power, which harnesses Earth's natural heat, is another viable option, with a heat output equivalent to about 13,000 nuclear power plants [16]. Nevertheless, geothermal energy faces its unique set of environmental challenges, such as the leakage of heavy metals into the surrounding soils and an increase in seismic activity [17].

Hydrogen Fuel



Figure 6. A hydrogen powered car.

Among these renewable sources, hydrogen stands out as one of the most promising alternatives. Hydrogen, as the lightest element with a molecular weight of 1.008 amu, is the most abundant element in the universe, often existing as diatomic H_2 molecules. As a fuel, hydrogen offers nearly three times the energy potential of gasoline, with an energy density of 141.9

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MJ/kg compared to gasoline's 47.4 MJ/kg [18]. Notably, hydrogen's combustion produces only water as a byproduct (as shown in Equation 1), making it exceptionally clean and environmentally friendly.



One of the principal challenges hindering the widespread adoption of hydrogen as a fuel is its storage. Given that hydrogen primarily exists as a gas, it is typically stored in compressed tanks, however, the safety concerns associated with storing explosive gas in vehicles in the event of a collision have raised concerns. Storing hydrogen as a compressed liquid is a potential solution, as it can mimic the characteristics of a dense gas, making it suitable for use in vehicles [19], however, this method necessitates heavy refrigeration to maintain hydrogen in a 10K to 20K temperature range.

A third approach to hydrogen storage involves using solid materials. Various solid storage materials have been explored, including carbon nanotubes [20], metal hydrides [21], and borohydrides [22]. Among these, sodium borohydride (NaBH_4) has garnered significant attention for its high hydrogen weight percentage of 10.8% w/w. Researchers have been investigating its potential for hydrogen gas production through a water-splitting reaction (as depicted in Equation 2) since the work of Schlesinger et al. in 1953 [23]. Although this reaction is straightforward and operates under mild conditions, it occurs relatively slowly. Therefore, to make NaBH_4 a viable storage material for hydrogen energy, the need for a catalyst to optimize the hydrogen generation rate is evident:



Transition Metal Catalysts

Transition metals are commonly employed as catalysts due to their unfilled valence shells, enabling electron transfer. Various metals, including cobalt, nickel, zinc, platinum, and palladium, have been explored as catalysts for the hydrolysis of NaBH_4 [24-28]. While bulk metals can be efficient catalysts on their own [29], reducing them to the nanoscale has a remarkable effect on their catalytic activity. Nanomaterials, defined as

materials with at least one dimension ranging from 1 nm to 100 nm, offer increased catalytic potential due to their expanded surface area [29-33].

21	22	23	24	25	26	27	28	★ 29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
39	40	41	42	43	44	45	★ 46	★ 47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
57	72	73	74	75	76	77	★ 78	★ 79	80
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Figure 7. Transition metals in the period table. † Starred elements are elements discussed in this review.

Nanoparticles

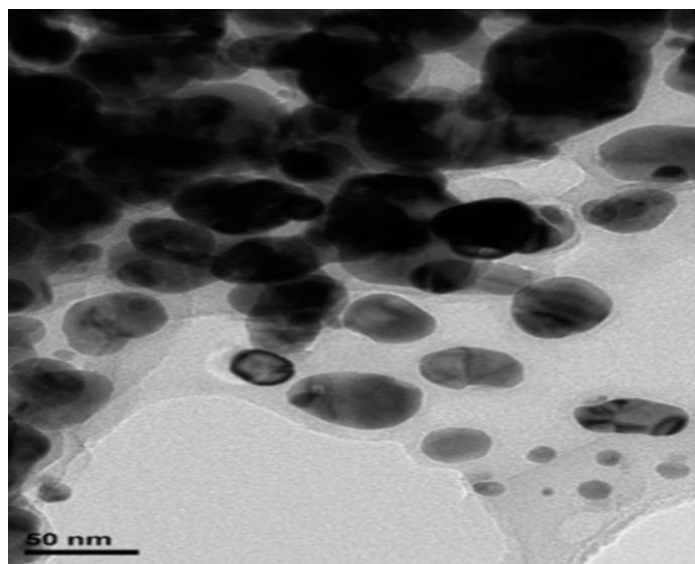


Figure 8. Silver Nanoparticles synthesized by this team [34].

Silver nanoparticles (AgNPs) have been extensively studied and found useful in medical applications [35], antimicrobial properties [36], and catalytic reactions [37-40]. Gold nanoparticles (AuNPs) have demonstrated efficacy in drug delivery [41], sensory materials [42], biomedical applications [43], and various catalytic processes [44-46]. Platinum, often used in its bulk state as a catalyst [47-49], also shines as platinum nanoparticles (PtNPs) in applications such as hydrogenation [50], fuel cells [51], and hydrogen generation reactions [33, 52]. Palladium nanoparticles (PdNPs) serve as catalysts in diverse reactions, including Suzuki Coupling [53, 54], Heck reactions

[55], NO oxidation [56], and hydrogen generation [57, 58]. Copper nanoparticles (CuNPs) have found utility in sensing materials [59], antimicrobial applications [60], and as catalysts in certain reactions [61-63].

Carbon-based Supports

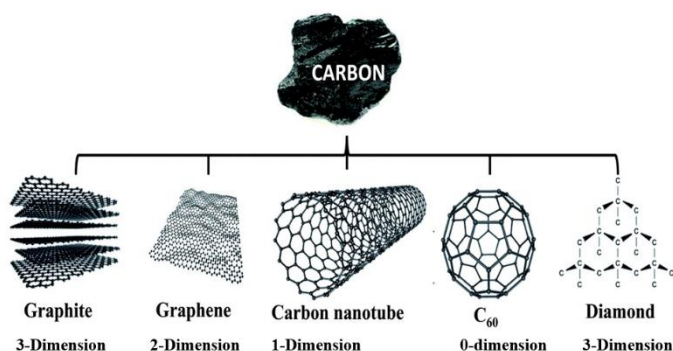


Figure 9. Different examples of carbon allotropes. ‡

One challenge with nanoparticles is their tendency to agglomerate into larger particles, which diminishes their catalytic efficiency [64, 65]. Recent research within our team has sought to mitigate this issue by incorporating support materials to facilitate nanoparticle dispersion.

Composite materials, which combine silver, gold, platinum, palladium, and copper nanoparticles with carbon nanotubes, have demonstrated competitive catalytic activity in the hydrolysis of NaBH_4 [40, 42, 52, 57]. One class of materials that has promise as a support for nanoparticles is graphene-like materials (GLM) [66]. A major difference between GLM and graphene itself is that graphene is a 2-D material that is made of only carbon atoms; a GLM material can incorporate other elements into its structure as long as it retains a 2-D structure with a somewhat similar hexagonal structure [66]. Since GLM includes such a variety of different materials they have a multitude of different applications [67]. Carbon Microspheres (CMS) are another material that could make a promising support for nanoparticles. CMS, as the name implies, are 3-D spherical objects made entirely out of carbon that can be solid [68], porous [69], or hollow [70]. These CMS materials have already been explored as a support for nanomaterials [71, 72] and have been

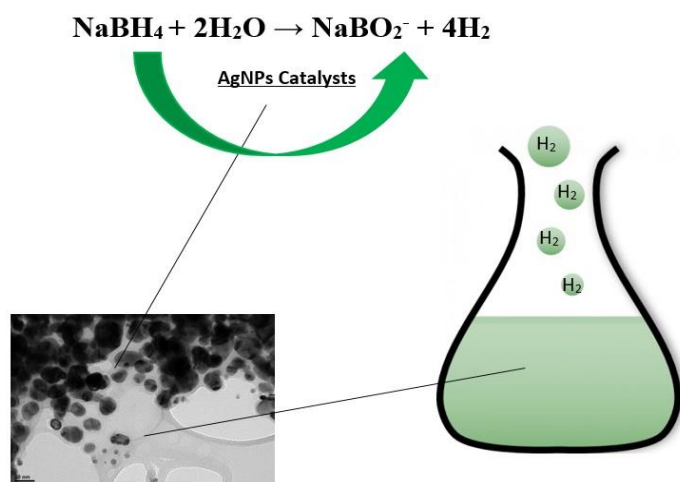
used in different applications from capacitors [69-71], to flame retardants [73], and even in catalysis [74].

Hydrogen Generation from Solid Precursors

To further enhance the sustainability and practicality of the nanoparticle composites, this review proposes the integration of NaBH_4 as a solid hydrogen source. By utilizing NaBH_4 into the suitable energy process, we aim to facilitate controlled reduction reactions for the formation of metal nanoparticles on the carbon-based support matrix. NaBH_4 , a well-established solid hydrogen storage material, offers several advantages in nanoparticle synthesis, including ease of handling, stability, and environmentally benign byproducts as in Equation 2. Sodium borohydride (NaBH_4) undergoes hydrolysis to liberate hydrogen gas, providing a reliable solid-state hydrogen storage solution. This release mechanism not only ensures safety by eliminating hazardous reagents but also promotes sustainability by minimizing environmental impact.

Furthermore, the utilization of NaBH_4 as a solid hydrogen source aligns with the overarching goal of developing greener synthesis methods for advanced materials. By minimizing the environmental footprint associated with traditional liquid-phase reduction processes, this approach contributes to the sustainable production of nanoparticle composites with reduced energy consumption and waste generation.

Therefore, integrating NaBH_4 as a solid hydrogen source holds promise for enhancing the environmental sustainability via utilization of nanoparticle composites anchored on carbon-based supports to speed the hydrogen production. This approach opens new avenues for the development of functional materials with diverse applications in catalysis, sensing, energy storage, and beyond.



Ag Nanoparticles (AgNPs) Catalysts

Figure 10. Silver nanoparticles used to catalyze a hydrogen generation reaction [34].

Also, this review endeavors to advance the existing body of research by harnessing the potential of nanoparticle composites anchored on an innovative, eco-friendly carbon-based substrate. Leveraging the inherent sustainability of dextrose, we aim to synthesize carbon microspheres (CMS) and graphene-like materials (GLMs) as robust support matrices. These support structures, derived from renewable sources, possess exceptional structural integrity and surface characteristics conducive to efficient nanoparticle immobilization.

In this review, we focused on functionalization of CMS and GLMs with a spectrum of noble and transition metal nanoparticles, including gold, silver, platinum, palladium, and copper. By employing these diverse metal constituents, we aim to explore the broad scope of applications enabled by the resulting composite materials as catalysts. Furthermore, the utilization of sustainable precursors not only underscores our commitment to eco-conscious practices but also opens avenues for scalable production processes that minimize environmental impact.

Through a comprehensive analysis of the morphologies via TEM and high-resolution TEM images, and performance in terms of activation energies attributes of these nanoparticle composites, this review seeks to provide valuable insights into their potential as multifunctional materials for hydrogen generation. By

elucidating the synergistic interactions between the carbon-based support and metal nanoparticles, we aim to illuminate mechanisms underlying their enhanced performance and durability. Moreover, we endeavor to identify avenues for further research and development, with a focus on optimizing synthesis techniques, tailoring material properties, and exploring novel applications in emerging domains.

In summary, this review aims to contribute to the advancement of nanoparticle composite technology by harnessing the versatility of carbon-based supports derived from sustainable sources. Through a holistic exploration of material morphologies, and application prospects, we aspire to pave the way for the development of next-generation functional materials that are not only efficient and durable but also environmentally responsible.

Copper Nanoparticles as Catalyst

In Figure 11, a striking visual narrative unfolds as copper nanoparticles exhibit a scattered distribution over the textured landscape of fused graphene-like material. The interplay of these nanoparticles across the substrate unveils a captivating scenario, providing crucial insights into the nanomaterial's architecture. Remarkably, the material appears stratified, with darker regions indicative of a multilayered composition, adding an additional layer of complexity to its structural intricacies.

This complex distribution between copper nanoparticles and the fused graphene-like material becomes evident under closer inspection. The dispersion of nanoparticles, characterized by varying sizes and spatial arrangements, highlights the precision achieved in crafting this composite material. The darker regions, signifying multiple layers, introduce a fascinating dimension, potentially influencing the material's electronic and mechanical properties.

Beyond its aesthetic allure, the layered nature of the material has profound implications for its functionality, particularly in catalytic or electronic applications. Understanding the nuanced layering and the spatial distribution of copper nanoparticles

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provides a foundation for unraveling the composite's potential in diverse fields. This visual representation acts as a pivotal starting point for further investigations, opening avenues for optimizing the material's performance and tailoring its properties to specific applications. Figure 11 encapsulates more than a mere snapshot of copper nanoparticles dispersed on fused graphene-like

material; it serves as a visual gateway to the elaboration of nanomaterial engineering. The observed layering enriches our comprehension of the material's complexity, inviting researchers to delve deeper into its applications and unlock the full spectrum of possibilities inherent in this finely tuned composite.

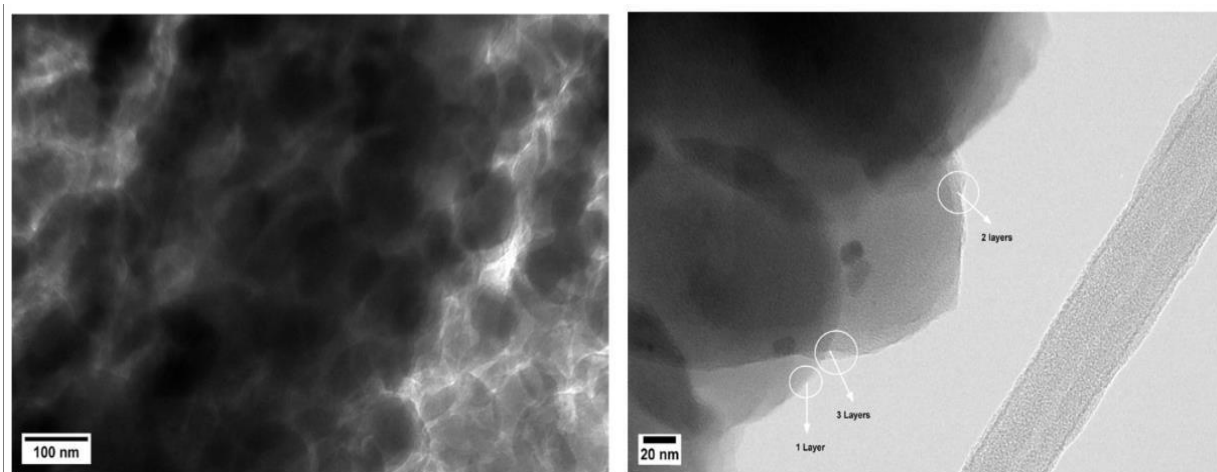


Figure 11. TEM images of the novel CuGLM material at a scale of 100 nm and 20 nm [80].

Palladium Nanoparticles as Catalyst

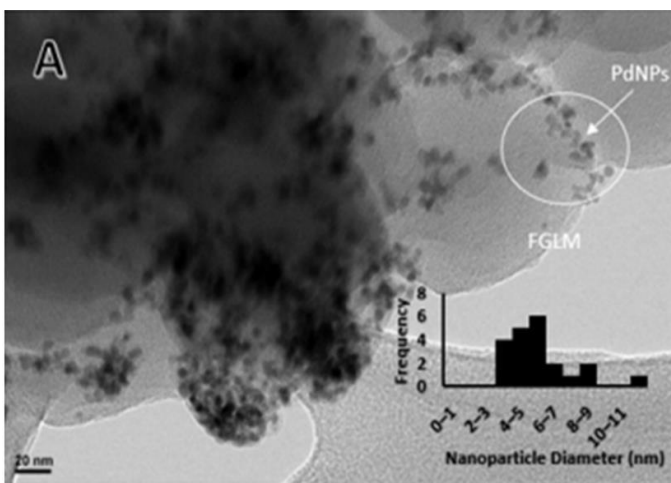


Figure 12. TEM images of the novel PdFGLM material at a scale of 20 nm [76].

In Figure 12, Transmission Electron Microscopy (TEM) provides insightful imagery of the PdFGLM composite, revealing a captivating interplay of materials at the nanoscale. Fused Graphene-Like Material (FGLM) takes center stage, forming a distinctive substrate visibly adorned with platinum

nanoparticles characterized by diameters spanning the range of 3 to 11 nanometers. The precision of TEM imaging allows for a detailed examination of the nanomaterial architecture, bringing to light the intricate distribution of these nanoparticles in dispersed clusters across the graphene-like matrix.

The captivating visual representation underscores the meticulous synthesis and integration of palladium nanoparticles onto the FGLM surface. The discernible clustering pattern hints at potential synergies between the platinum nanoparticles and the graphene-like material, offering valuable insights into the composite's structural characteristics. This detailed depiction serves as a visual testament to the precision and controlled synthesis achieved in crafting the PdFGLM composite.

Beyond the TEM images, the observed nanoscale arrangement holds profound significance for catalytic applications. The specific sizes and distribution patterns of the palladium nanoparticles are pivotal factors influencing the catalytic behavior of the composite. Understanding the spatial arrangement of these nanoparticles on the FGLM substrate is

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essential for deciphering the catalytic mechanisms and optimizing the performance of the composite in hydrogen generation or other relevant applications.

In essence, the TEM images encapsulate not just a visual representation of the PdFGLM composite but also serve as a window into the complex world of nanomaterial interactions. These insights contribute to advancing our understanding of the composite's potential applications in catalysis, paving the way for further exploration and optimization of nanomaterial-based technologies.

Gold Nanoparticles as Catalyst

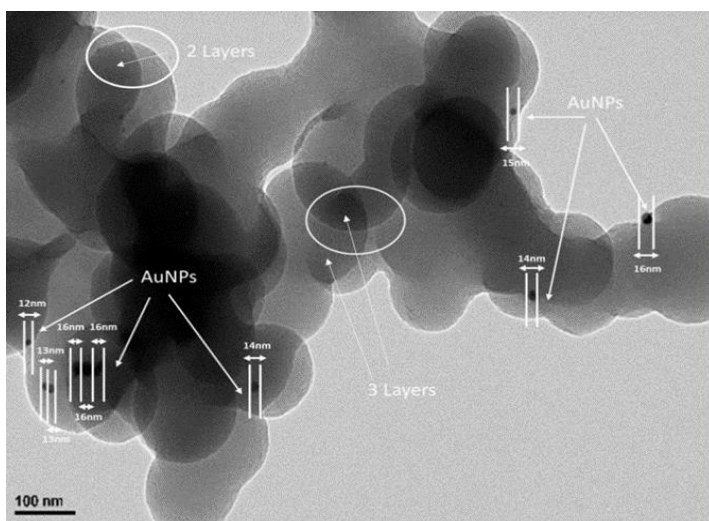


Figure 13. TEM images of the novel AuFGLM material at a scale of 100 nm [81].

In Figure 13, a resonant theme persists as a layered material unfolds, echoing the nuanced architecture observed in the previous images. This visual revelation showcases nanoparticles intricately distributed across the stratified layers, creating a compelling tapestry of nanoscale interactions. Notably, the layers exhibit a consistent pattern, providing visual cues to the material's underlying structure, while the nanoparticles, with an average diameter of approximately 16 nm, contribute to the overall complexity of the composite.

The recurring presence of layered structures prompts a deeper exploration into the material's inherent properties and potential applications. Each layer, distinct yet interconnected, becomes a

focal point for understanding how the nanoparticles engage with the layered matrix. This visual insight sparks curiosity about the role of layering in influencing the material's mechanical, electronic, or catalytic behaviors.

The well-dispersed nanoparticles, meticulously distributed across the layers, add an additional layer of sophistication to the composite. The uniformity in nanoparticle size and dispersion pattern suggests a controlled synthesis process, emphasizing the precision in crafting this layered material. Such precision holds promise for applications where homogeneity and consistency are paramount, underscoring the material's potential across various technological domains.

Beyond its visual appeal, the insight derived from Figure 13 becomes a steppingstone for in-depth investigations. Researchers can now embark on a journey to unravel the intricate relationships between layered structures and well-dispersed nanoparticles, seeking to optimize and tailor the material for specific functions. This visual representation, therefore, serves as a visual compass, guiding further research into the versatile realms of nanomaterial engineering and its myriad potential applications.

Platinum Nanoparticles as Catalyst

In Figure 14, a captivating visual unfolds, showcasing predominantly spherical fused carbon structures with diameters spanning around 200 nm. These fused carbon spheres, with their well-defined and mostly round morphology, provide a striking visual representation of the composite material under scrutiny.

However, the intricacies of this nanomaterial become even more apparent upon closer examination, revealing the presence of platinum nanoparticles dispersed meticulously across the surfaces of these carbon spheres, each with a diminutive diameter of approximately 3 nm.

The collocate fused carbon spheres and the platinum nanoparticles introduce a captivating dynamic to the composite. The uniformity in the spherical morphology attests to the precision achieved in synthesizing these carbon

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structures, while the dispersed platinum nanoparticles add a layer of complexity, suggesting a controlled and deliberate integration process.

The deliberate placement of platinum nanoparticles on the fused carbon spheres holds significant implications for the material's potential applications. The observed dispersion pattern, indicative of a well-engineered synthesis, raises questions about the catalytic or electronic properties that may arise from this specific arrangement. The synergy between the macroscopic carbon spheres and the nanoscopic platinum particles offers a unique combination of structural robustness and catalytic reactivity, opening avenues for exploration in

various technological domains.

Figure 14, therefore, serves not just as a visual presentation of the composite's morphology but as a portal to a realm of possibilities in nanomaterial engineering. The interplay between the macro and micro components prompts further inquiry, inviting researchers to unravel the synergies and harness the inherent properties for tailored applications. This visual revelation acts as a catalyst for deeper investigations, laying the foundation for a more profound understanding of the composite's potential in catalysis, sensing, or other cutting-edge technological applications.

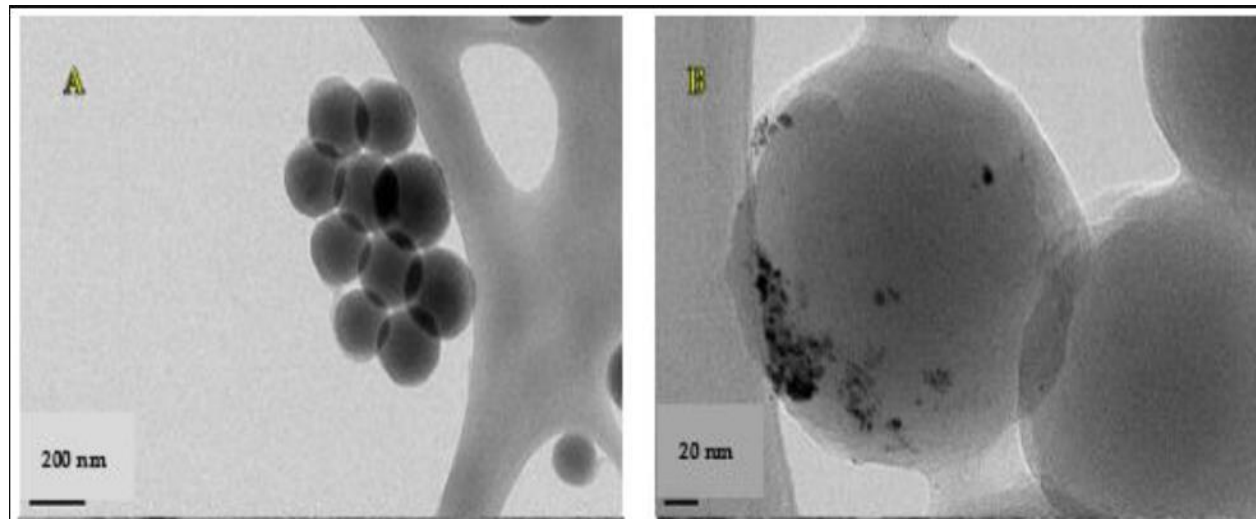


Figure 14. TEM images of the novel PtFCS material at a scale of 200 nm (A) and 20 nm (B) [82].

Silver Nanoparticles as Catalyst

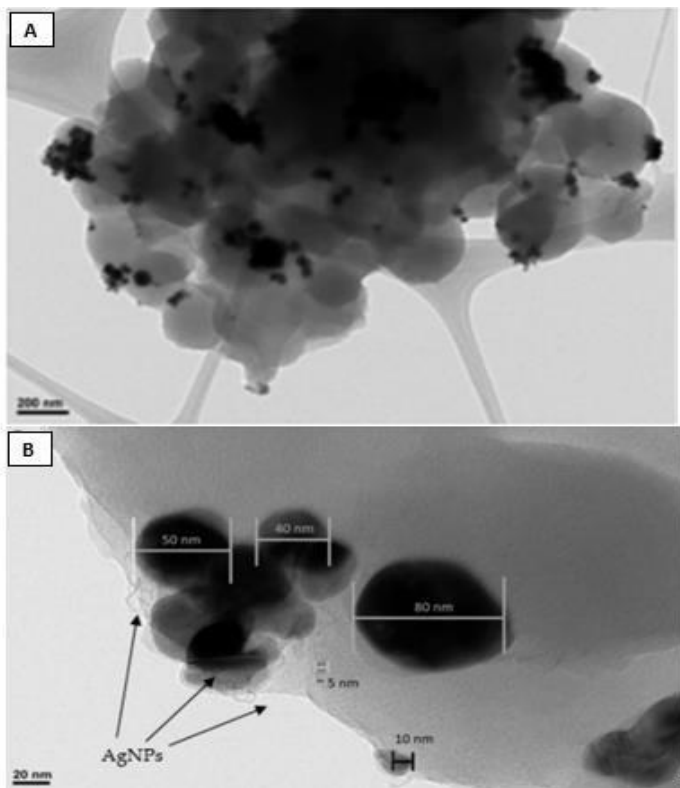


Figure 15. TEM images of the novel AgFCS material at a scale of 200 nm (A) and 20 nm (B) [75].

In Figure 15, a captivating spectacle unfolds as silver nanoparticles find their anchorage on the supportive structure of fused carbon 200 nm spheres. This visual depiction provides a nuanced glimpse into the intricate interplay between the macroscopic carbon spheres and the varying sizes of silver nanoparticles, showcasing a dynamic synergy within the composite material. Upon closer inspection, a spectrum of nanoparticle sizes becomes apparent, with some presenting small diameters ranging between 5 and 10 nanometers, while others command larger dimensions, reaching up to 80 nanometers.

The amalgamation of silver nanoparticles and fused carbon spheres introduces a captivating heterogeneity into the material's composition. The smaller nanoparticles, delicately distributed across the carbon spheres, contribute to the fine detailing of the composite, while the presence of larger nanoparticles adds a

layer of complexity, creating a visually compelling landscape of nanoscale interactions.

This variation in nanoparticle sizes raises intriguing questions about the synthesis methodology and the potential implications for the material's functionality. The deliberate selection of silver as the nanoparticle material and its diverse size range suggests a deliberate effort to engineer a composite with tailored properties. Understanding the role of nanoparticle size in influencing catalytic, electronic, or optical characteristics becomes paramount, as it opens avenues for fine-tuning the material for specific applications.

Figure 15 not only serves as a visual testament to the composite's morphological diversity but also acts as a catalyst for informed inquiries into the material's properties. Researchers may delve into the nuanced relationships between nanoparticle size, distribution, and the supportive carbon matrix, unlocking the material's potential in catalysis, sensing, or other technologically relevant domains. This visual revelation thus stands as a gateway to a deeper understanding of the composite's intricate dynamics and its potential in pushing the boundaries of nanomaterial applications.

Comparison of Reaction Activation Energies by Catalyst

Table 1 meticulously scrutinizes and compares the activation energies of diverse materials employed in catalyzing the hydrolysis of NaBH_4 . The investigation encompasses a spectrum of typical transition metal catalysts, including revered precious metals like gold, silver, platinum, palladium, and ruthenium. In addition, the analysis extends to several non-precious metals such as copper, cobalt, and nickel. Each material undergoes rigorous testing in solution, spanning temperatures from 273 K up to 358 K, contingent upon the specific nature of the material. Some metals find support on carbon-based structures, while others stand unsupported in the catalytic process.

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Broad patterns emerge from the comparative analysis, indicating that unsupported materials tend to exhibit higher activation energies than their counterparts supported on carbon-based materials. Among these, bulk cobalt, nickel, and Raney-nickel emerge with the highest activation energies overall.

Table 1. Comparison of activation energies.

Catalyst	Ea (kJ mol ⁻¹)	Temperature (K)	Reference
Pt/MWCNTs	46.2	273–303	52
Pd/MWCNTs	62.7	273–303	57
Ag/MWCNTs	44.5	273–303	40
Au/MWCNTs	21.1	273–303	44
AgNP-FCS	37.0	283-303	75
PdFGLM	45.1	283–303	76
Pt–Pd/CNTs	19	302–332	77
Pd/C	28	298–328	28
Ru/Graphite	61.1	398–318	78
PdNPs	58.9	273–303	79
PtNPs	39.2	283–303	33
CuGLM	46.8	283–303	80
AuFGLM	45.5	283–303	81
PtFCS	53.0	283–303	82
BCD-AuNP	54.7	283–303	32
Ru/C	67	298–358	83
Co	75	273–308	29
Raney-Nickel	63	273–308	29
Ni	71	273–308	29

An intriguing material noted in PtNPs, boasts an activation energy of 39.2 kJ mol⁻¹, surpassing eight of the supported materials. However, when scrutinizing activation energies

among materials supported on carbon-based structures, a clear pattern is elusive, although a subtle inclination towards lower activation energies is observed in catalysts supported on carbon nanotubes. This subtle trend warrants further exploration to substantiate its significance. Additionally, a noteworthy observation surfaces when comparing precious and non-precious metals, with precious metal materials generally exhibiting lower activation energies than their non-precious counterparts. This insight hints at the possibility that the choice of metal may supersede the selection of support structure in influencing catalytic performance. Intriguingly, Pt-Pd/CNTs stands out as a remarkable outlier with the lowest overall activation energy at 19 kJ mol⁻¹, emphasizing the potential synergy between the choice of metal and the carbon nanotube support structure.

These findings prompt contemplation on the intricate relationships between metal choices, support structures, and activation energies, encouraging further in-depth investigations. The nuanced dynamics uncovered in this comparative analysis lay the groundwork for future studies, allowing researchers to unravel the subtleties influencing catalytic efficiency. Ultimately, the quest for optimal catalysts in hydrogen generation processes gains valuable insights, steering the research community towards more effective and sustainable energy solutions.

Beyond activation energies, the study delved into the reusability of the catalysts, revealing a remarkable phenomenon. Many of the catalysts displayed an increase in catalytic activity with each successive trial, attributed to the gradual hydrolysis of bonds between BH₄⁻ and H⁺ ions. This process led to enhanced electrostatic stabilization of nanoparticle surfaces, ultimately amplifying the catalysts' activity. This revelation not only speaks to the stability and longevity of these materials but also emphasizes their potential utility in sustainable hydrogen generation processes.

The implications of this study extend beyond the laboratory, hinting at substantial promise for practical hydrogen generation applications. Future research endeavors can build upon these

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findings by exploring additional conditions to further optimize the catalytic efficiency of these materials. This may include investigating non-precious transition metals like cobalt and manganese, broadening the range of potential catalyst materials. Additionally, a deeper exploration of the reusability of these materials can yield valuable insights into their long-term performance, laying the groundwork for more sustainable and cost-effective hydrogen generation processes. In essence, this research represents a significant stride in the pursuit of clean and efficient energy sources, offering a myriad of possibilities awaiting exploration and harnessing.

Mechanism for Hydrogen Generation

The elucidation of the catalytic mechanism driving the hydrolysis of NaBH_4 is outlined in Scheme 1. This proposed mechanism provides a conceptual framework for understanding how the catalysts operate within the composite structure. At the heart of this mechanism lies the strategic positioning of metal nanoparticles on the surface of the carbon support material.

Scheme 1 offers a visual representation of the dynamic interactions occurring within the composite structure during the hydrolysis process. The metal nanoparticles, carefully situated atop the carbon support, act as catalytic sites, facilitating the initiation and progression of the hydrolytic reaction. This spatial arrangement is pivotal, as it allows the metal catalysts to engage with the reactants at the interface, enabling efficient catalytic activity.

In general, the proximity of metal nanoparticles to the carbon support material in this composite structure serves a dual purpose. Firstly, the carbon support provides a stable and conductive platform for the metal nanoparticles, ensuring their structural integrity and facilitating electron transfer during the catalytic process. Secondly, the spatial relationship between the metal catalysts and the carbon support creates an environment conducive to synergistic interactions, potentially enhancing catalytic performance.

Furthermore, this proposed mechanism underscores the importance of the composite architecture in dictating catalytic efficiency. The specific arrangement of metal nanoparticles on the carbon support material plays a critical role in optimizing the interactions with reactant molecules, ultimately influencing the overall effectiveness of the catalyst.

As research progresses, Scheme 1 provides a foundational understanding of the catalyst's operational dynamics, paving the way for further exploration and refinement. Subsequent investigations can build upon this conceptual framework, delving into the intricate details of the catalytic mechanism and exploring potential avenues for enhancing the efficiency of these composite catalysts in the hydrolysis of NaBH_4 .

The hydrolysis process of NaBH_4 unfolds as follows: NaBH_4 , when introduced into the solution, undergoes dissociation, giving rise to free BH_4^- ions. These BH_4^- ions, bearing a high affinity for catalytic metal nanoparticles, swiftly bind with any available nanoparticle on the composite's surface.

As this chemical ballet progresses, a pivotal moment occurs when a water molecule enters the scenario. This water molecule initiates an attack on the boron atom within the BH_4^- ion. This attack leads to the cleavage of a hydrogen atom from the BH_4^- ion, which then swiftly pairs with another hydrogen atom derived from the attacking water molecule. This harmonious collaboration culminates in the release of a diatomic hydrogen gas molecule into the surrounding medium, leaving in its wake a hydroxyl group firmly attached to the boron atom.

This process exhibits a remarkable capacity for repetition. For each of the remaining hydrogen atoms still associated with the boron atom in the BH_4^- ion, the same sequence can be iteratively reproduced. The hydroxyl group remains affixed to the boron atom after each hydrogen atom is cleaved and converted into diatomic hydrogen gas.

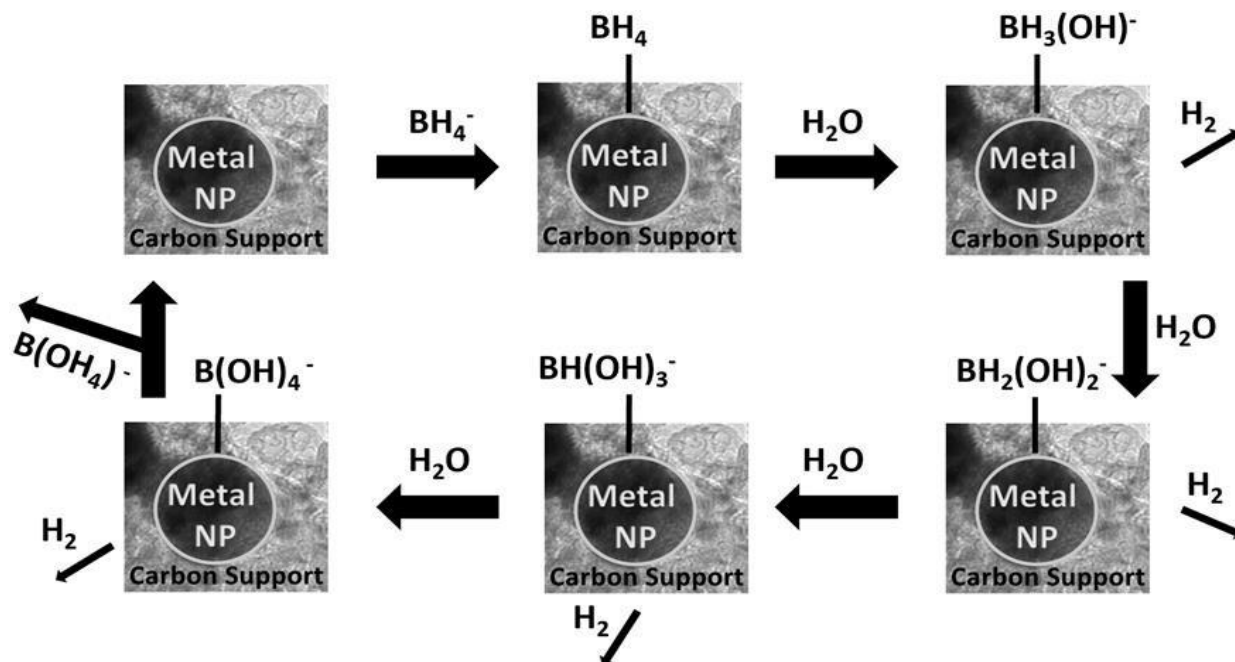
Once all the hydrogen atoms on the boron atom have been sequentially removed and converted into hydrogen gas, the $\text{B}(\text{OH}_4)^-$ species separates from the metal nanoparticle. This

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crucial step opens the door for the arrival of another BH_4^- ion, setting the stage for the cycle to commence anew.

This intricate and dynamic mechanism serves as a testament to the catalytic prowess of the metal nanoparticles in promoting the

hydrolysis of NaBH_4 . Through their orchestrated efforts, these catalysts effectively facilitate the release of hydrogen gas, contributing to the advancement of hydrogen-based energy technology.



Scheme 1. Proposed mechanism for the catalyzed hydrolysis of NaBH_4 .

Conclusions

This comprehensive review investigates various catalytic nanoparticle materials supported on carbon for hydrogen generation, specifically focusing on their efficacy in the hydrolysis of NaBH_4 . The investigation reveals a notable trend wherein precious metal nanoparticles, when supported on carbon-based materials, emerge as the most effective catalysts, demonstrating the lowest activation energies for the hydrolysis process. However, it is crucial to underscore the economic considerations associated with these catalysts. While the precious metal nanoparticles and carbon nanotube support materials showcase superior catalytic performance; their production costs are relatively high. This economic factor raises a pertinent concern about whether the potential benefits derived from their lower activation energies might be offset by the associated production expenses. Contrastingly, catalysts

supported on graphene-like materials (GLM) and carbon microspheres (CMS) present a more cost-effective alternative. The affordability of these support materials could potentially outweigh the advantages of lower activation energies seen with the more expensive counterparts. This observation underscores the need for a comprehensive cost-benefit analysis in the selection of catalysts for hydrogen generation, ensuring that economic viability aligns with catalytic efficiency. Furthermore, the review advocates for continued exploration and research into alternative support structures for catalysts. The implication is that there might be untapped potential in support materials like GLM and CMS, with the possibility of further reducing activation energies. This avenue of investigation holds promise for optimizing catalytic performance while simultaneously mitigating production costs.

This review contributes valuable insights into the hydrolysis of NaBH_4 by systematically comparing various factors influencing

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catalysis. The comparison of precious metal nanoparticles on GLM and CMS facilitates a nuanced understanding of the trade-offs involved in selecting catalysts for hydrogen generation. As research progresses based on the findings presented in this review, the field of green chemistry stands to advance, paving the way for a more sustainable future and inching society closer to a hydrogen economy that can supplant traditional fossil fuels.

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Conflicts of Interest

The authors declare no conflict of interest.

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References

- [1] Kitous, A., Keramida, K., Vandyck, T. and Saveyn, B. (2016). Global energy and climate outlook (GECO 2016) road from paris, JRC Research Report JRC101899, Joint Research Centre (Seville site). <https://doi.org/10.2790/89230>
- [2] Smil, V. (2017). Energy - our world in data [Online]. <https://ourworldindata.org/energy> (accessed November 25, 2023).
- [3] Shafiee, S. and Topal, E. (2009). When will fossil fuel reserves be diminished? *Energy Policy*, 37, 181. <https://doi.org/10.1016/j.enpol.2008.08.016>.
- [4] Rodhe, H. (1990). A. Comparison of the contribution of various gases to the greenhouse effect. *Science*, 248, 1217. <https://doi.org/10.1126/science.248.4960.1217>.
- [5] Boden, T.A., Marland, G. and Andres, R.J. (2010). Global, regional, and national fossil-fuel CO₂ emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. https://doi.org/10.3334/CDIAC/00001_V2010.
- [6] Platzer, M. F. and Sarigul-Klijn, N. (2021). The green energy ship concept: Renewable energy from wind over water. *Springer Briefs in Appl. Sci. & Technol. Series*, Springer: Cham, Switzerland, 3. <https://doi.org/10.1007/978-3-030-58244-9>.
- [7] Hansen, J., Kharecha, P., Sato, M., Masson-Delmotte, V., Ackerman, F., et al. (2013). Assessing “dangerous climate change”: Required reduction of carbon emissions to protect young people, future generations and nature. *PLOS ONE*, 8, e81648. <https://doi.org/10.1371/journal.pone.0081648>.
- [8] Thirugnanasambandam, M, Iniyan, S and Goic. R (2010). A review of solar thermal technologies. *Renewable and Sustainable Energy Rev.*, 14, 312. <https://doi.org/10.1016/j.rser.2009.07.014>.
- [9] Sampaio, P. G. V. and González, M. O. A. (2017). Photovoltaic solar energy: Conceptual framework. *Renewable and Sustainable Energy Rev.*, 74, 590. <https://doi.org/10.1016/j.rser.2017.02.081>.
- [10] Rehman, S., Bader, M. A. and Al-Moallem, S. A. (2007). Cost of solar energy generated using PV panels. *Renewable and Sustainable Energy Rev.*, 11, 1843. <https://doi.org/10.1016/j.rser.2006.03.005>.
- [11] Ferroni, F. and Hopkirk, R. J. (2016). Energy return on energy invested (ERoEI) for photovoltaic solar systems in

Review Article

- regions of moderate insolation. *Energy Policy*, 94, 336. <https://doi.org/10.1016/j.enpol.2016.03.034>.
- [12] Lee, J. and Zhao, F. (2019). Global wind report 2019 [Online], Global Wind Energy Council: Brussels, Belgium. <https://gwec.net/wp-content/uploads/2020/08/Annual-Wind-Report-2019-digital-final-2r.pdf>.
- [13] Wisler, R., Bolinger, M., Hoen, B., Millstein, D., Rand, J., et al. (2020). Wind energy technology data update: 2020 edition [Online], Lawrence Berkeley National Laboratory: Berkeley, CA. https://emp.lbl.gov/sites/default/files/2020_wind_energy_technology_data_update.pdf.
- [14] Wang, S. and Wang, S. (2015). Impacts of wind energy on environment: A review. *Renewable and Sustainable Energy Rev.* 49, 437. <https://doi.org/10.1016/j.rser.2015.04.137>.
- [15] U.S. Government Accountability Office (GOA). (2005). Wind power: Impacts on wildlife and government responsibilities for regulating development and protecting wildlife. GAO 05-906. U.S. Government Accountability Office: Washington, D.C., USA. <https://www.gao.gov/assets/gao-05-906.pdf>.
- [16] Bayer, P., Rybach, L., Blum, P. and Brauchler, R. (2013). Review on life cycle environmental effects of geothermal power generation. *Renewable and Sustainable Energy Rev.*, 26, 446. <https://doi.org/10.1016/j.rser.2013.05.039>.
- [17] Dhar, A., Naeth, M. A., Jennings, P. D. and Gamal El-Din, M. (2020). Geothermal Energy Resources: Potential Environmental Impact and Land Reclamation. *Environ. Rev.*, 28, 415. <https://doi.org/10.1139/er-2019-0069>.
- [18] Veziroglu, T. N. (2007). 21st Century's Energy: Hydrogen energy system. assessment of hydrogen energy for sustainable development. in assessment of hydrogen energy for sustainable development; Sheffield J.W., Sheffield Ç., Eds.; NATO Science for Peace and Security Series C: Environmental Security. Springer: Dordrecht., 9. https://doi.org/10.1007/978-1-4020-6442-5_2.
- [19] Hansen, O.R. (2020). Liquid hydrogen releases show dense gas behavior. *Int. J. Hydrogen Energy*, 45, 1343. <https://doi.org/10.1016/j.ijhydene.2019.09.060>.
- [20] Lyu, J., Kudiiarov, V. and Lider, A. (2020). An overview of the recent progress in modifications of carbon nanotubes for hydrogen adsorption. *Nanomaterials*, 10, 255. <https://doi.org/10.3390/nano10020255>.
- [21] Tarasov, B. P., Fursikov, P. V., Volodin, A. A., Bocharnikov, M. S., Shimkus, Y. Y. et al. (2021). Metal hydride hydrogen storage and compression systems for energy storage technologies. *Int. J. Hydrogen Energy.*, 46, 13647. <https://doi.org/10.1016/j.ijhydene.2020.07.085>.
- [22] Bannenberg, L. J., Heere, M.; Benzidi, H., Montero, J., Dematteis, E.M., et al (2020). Metal (Boro-) Hydrides for high energy density storage and relevant emerging technologies. *Int. J. Hydrogen Energy*, 45, 33687. <https://doi.org/10.1016/j.ijhydene.2020.08.119>.
- [23] Schlesinger, H. I., Brown, H. C., Finholt, E., Gilbreath, J. R., Hoekstra, H. R., et al. (1953). Sodium borohydride, its hydrolysis and its use as a reducing agent and in the generation of hydrogen. *J. Am. Chem. Soc.*, 75, 215. <https://doi.org/10.1021/ja01097a057>.
- [24] Zhang, X., Zhang, Q., Xu, B., Liu, X., Zhang, K., Fan, G. and Jiang, W. (2020). Efficient hydrogen generation from the NaBH₄ hydrolysis by cobalt-based catalysts: positive roles of sulfur-containing salts. *ACS Appl. Mater. Interfaces.*, 2, 9376. <https://doi.org/10.1021/acsami.9b22645>.
- [25] Netskina, O. V., Tayban, E. S., Rogov, V. A., Ozerova, A. M., Mukha, S. A. et al. (2021). Solid-state NaBH₄ composites for hydrogen generation: catalytic activity of nickel and cobalt catalysts. *Int. J. Hydrogen Energy*, 46, 5459. <https://doi.org/10.1016/j.ijhydene.2020.11.078>.
- [26] Kılınc, D. and Şahin, Ö. (2020). Performance of Zn-schiff base complex catalyst in nabh₄ hydrolysis reaction. *Int. J. Hydrogen Energy*, 45, 34783. <https://doi.org/10.1016/j.ijhydene.2020.07.156>.
- [27] Boran, A., Erkan, S., Ozkar, S. and Eroglu, I. (2013).

Review Article

- Kinetics of hydrogen generation from hydrolysis of sodium borohydride on pt/c catalyst in a flow reactor. *Int. J. Energy Res.*, 37, 443. <https://doi.org/10.1002/er.3007>.
- [28] Patel, N., Patton, B., Zanchetta, C., Fernandes, R., Guella, G. et al. (2008). Pd-C power and thin film catalysts for hydrogen production by hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy*, 33, 287. <https://doi.org/10.1016/j.ijhydene.2007.07.018>.
- [29] Kaufman, C.M. and Sen, B. (2014). Hydrogen generation by hydrolysis of sodium tetrahydroborate: effects of acids and transition metals and their salts. *J. Chem. Soc., Dalton Trans*, 1985, 307. <https://doi.org/10.1039/DT9850000307>
- [30] Abdel-Fattah, T. M. and Wixtrom, A. (2014). Catalytic reduction of 4-Nitrophenol using gold nanoparticles supported on carbon nanotubes. *ECS J. Solid State Sci. Technol.*, 3, M18-M20. <https://doi.org/10.1149/2.023404jss>.
- [31] Dushatinski, T., Huff, C. and Abdel-Fattah, T. M. (2016). Characterization of electrochemically deposited films from aqueous and ionic liquid cobalt precursors toward hydrogen evolution reactions. *Appl. Surf. Sci.*, 385, 282. <https://doi.org/10.1016/j.apsusc.2016.05.103>.
- [32] Quach, Q., Biehler, E., Elzamazami, A., Huff, C., Long, J.M. and Abdel-Fattah, T.M. (2021). Catalytic activity of beta-cyclodextrin-gold nanoparticles network in hydrogen evolution reaction. *Catalysts*, 11, 110. <https://doi.org/10.3390/catal11010118>.
- [33] Huff, C., Biehler, E., Quach, Q., Long, J. M. and Abdel-Fattah, T. M. (2021). Synthesis of highly dispersive platinum nanoparticles and their application in a hydrogen generation reaction. *Colloids Surf., A.*, 610, 125734. <https://doi.org/10.1016/j.colsurfa.2020.125734>.
- [34] Huff, C., Long, J.M. and Abdel-Fattah, T.M. (2020). Beta-cyclodextrin-assisted synthesis of silver nanoparticle network and its application in a hydrogen generation reaction. *Catalysts*, 10, 1014. <https://doi.org/10.3390/catal10091014>.
- [35] Prabhu, S. and Poulouse, E.K. (2012). Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. *Int. Nano Lett.*, 2, 32. <https://doi.org/10.1186/2228-5326-2-32>.
- [36] Nam, G., Purushothaman, B., Rangasamy, S. and Song, J. M. (2015). Investigating the versatility of multifunctional silver nanoparticles: preparation and inspection of their potential as wound treatment agents. *Int. Nano Lett.*, 6, 51. <http://doi:10.1007/s40089-015-0168-1>.
- [37] Sudrik, S. G., Chaki, N. K., Chavan, V. B., Chavan, S. P., Chavan, S. P. et al. (2006). Silver nanocluster redox-couple-promoted nonclassical electron transfer: an efficient electrochemical wolff rearrangement of α -diazoketones. *Chem. - Eur. J.*, 12(3), 859. <http://doi:10.1002/chem.200500696>.
- [38] Mitsudome, T., Mikami, Y., Mori, H.; Arita, S., Mizugaki, T. et al. (2009). Supported silver nanoparticle catalyst for selective hydration of nitriles to amides in water. *Chem. Commun.*, 22, 3258. <http://doi:10.1039/B902469G>.
- [39] Mitsudome, T., Mikami, Y., Funai, H., Mizugaki, T., Jitsukawa, K. et al. (2008). Oxidant-free alcohol dehydrogenation using a reusable hydrotalcite-supported silver nanoparticle catalyst. *Angew. Chem., Int. Ed.*, 47(1), 138. <http://doi:10.1002/anie.200703161>.
- [40] Huff, C., Long, J. M., Aboulatta, A., Heyman, A., Abdel-Fattah, T. M. (2017). Silver nanoparticle/multi-walled carbon nanotube composite as catalyst for hydrogen production. *ECS J. Solid State Sci. Technol.*, 6(10), M115. <http://doi:10.1149/2.0051710jss>.
- [41] Sengani, M., Grumezescu, A. M. and Rajeswari, V. D. (2017). Recent trends and methodologies in gold nanoparticle synthesis – a prospective review on drug delivery aspect. *Open Nano*, 2, 37. <http://doi:10.1016/j.onano.2017.07.001>.
- [42] Upadhyayula, V. K. K. (2012). Functionalized gold nanoparticle supported sensory mechanisms applied

Review Article

- in detection of chemical and biological threat agents: a review. *Anal. Chim. Acta*, 715, 1. <http://doi:10.1016/j.aca.2011.12.008>.
- [43] Elahi, N.; Kamali, M.; Baghersad, M. H. (2018). Recent biomedical applications of gold nanoparticles: a review. *Talanta*, 184, 537. <http://doi:10.1016/j.talanta.2018.02.088>.
- [44] Huff, C., Dushatinski, T. and Abdel-Fattah, T. M. (2017). Gold nanoparticle/multi-walled carbon nanotube composite as novel catalyst for hydrogen evolution reactions. *Int. J. Hydrogen Energy*, 42(30), 18985. <http://doi:10.1016/j.ijhydene.2017.05.226>
- [45] Osborne J., Horton M. R. and Abdel-Fattah, T. M. (2020). Gold nanoparticles supported over low- cost supports for hydrogen generation from a hydrogen feedstock material. *ECS J. Solid State Sci. Technol.*, 9(7), 071004. <http://doi:10.1149/2162-8777/abb036>.
- [46] Mitsudome, T. and Kaneda, K. (2013). Gold nanoparticle Catalysts for Selective Hydrogenations. *Green Chem.*, 15(10), 2636-2654. <http://doi:10.1039/c3gc41360h>.
- [47] Periana, R. A., Taube, D. J., Gamble, S., Taube, H., Satoh, T. et al. (1998). Platinum catalysts for the high-yield oxidation of methane to a methanol derivative. *Science*, 280(5363), 560. <http://doi:10.1126/science.280.5363.560>
- [48] Sabourault, N.; Mignani, G.; Wagner, A. and Mioskowski, C. (2002). Platinum oxide (PtO₂): a potent hydrosilylation catalyst. *Org. Lett.*, 4(13), 2117. <http://doi:10.1021/ol025658r>
- [49] Ely, J. C.; Neal, C. R.; Kulpa, C. F.; Schneegurt, M. A.; Seidler, J. A. and Jain, J. C. (2001). Implications of platinum-group element accumulation along U.S. roads from catalytic- converter attrition. *Envir. Sci. Technol.*, 35(19), 3816. <http://doi:10.1021/es001989s>.
- [50] Abu-Reziq, R., Wang, D., Post, M. and Alper, H. (2007). Platinum nanoparticles supported on ionic liquid-modified magnetic nanoparticles: selective hydrogenation catalysts. *Adv. Synth. Catal.*, 349, 2145. <https://doi.org/10.1002/adsc.200700129>.
- [51] Fang, B., Chaudhari, N. K., Kim, M.-S., Kim, J. H. and Yu, J.-S. (2009). Homogeneous deposition of platinum nanoparticles on carbon black for proton exchange membrane fuel cell. *J. Am. Chem. Soc.*, 131, 15330. <https://doi.org/10.1021/ja905749e>.
- [52] Huff, C., Quach, Q., Long, J.M. and Abdel-Fattah, T.M. (2020). Nanocomposite catalyst derived from ultrafine platinum nanoparticles and carbon nanotubes for hydrogen generation. *ECS J. Solid State Sci. Technol.*, 9, 101008. <https://doi.org/10.1149/2162-8777/abbe6d>.
- [53] Wolfe, J. P., Singer, R. A., Yang, B. H. and Buchwald, S. L. (1999). Highly active palladium catalysts for suzuki coupling reactions. *J. Am. Chem. Soc.*, 121, 9550. <https://doi.org/10.1021/ja992130h>.
- [54] Li, Y., Hong, X. M., Collard, D. M. and El-Sayed, M. A. (2000). Suzuki cross-coupling reactions catalyzed by palladium nanoparticles in aqueous solution. *Org. Lett.*, 2, 2385. <https://doi.org/10.1021/ol0061687>.
- [55] De Vries, A. H. M., Parlevliet, F. J., Schmieder-van de Vondervoort, L., Mommers, J. H. et al. (2002). A Practical recycle of a ligand-free palladium catalyst for heck reactions. *Adv. Synth. Catal.*, 344, 996. [https://doi.org/10.1002/1615-4169\(200210\)344:9<996::AID-ADSC996>3.0.CO;2-J](https://doi.org/10.1002/1615-4169(200210)344:9<996::AID-ADSC996>3.0.CO;2-J).
- [56] Weiss, B. M. and Iglesia, E. (2010). Mechanism and site requirements for NO oxidation on Pd catalysts. *J. Catal.*, 272, 74. <https://doi.org/10.1016/j.jcat.2010.03.010>.
- [57] Huff, C., Long, J. M., Heyman, A. and Abdel-Fattah, T. M. (2018). Palladium nanoparticle multiwalled carbon nanotube composite as catalyst for hydrogen production by the hydrolysis of sodium borohydride. *ACS Appl. Energy Mater.*, 1, 4635. <https://doi.org/10.1021/acsaem.8b00748>.
- [58] Şahin, Ö., Kılınç, D. and Saka, C. (2016). Hydrogen generation from hydrolysis of sodium borohydride with a novel palladium metal complex catalyst. *J. Energy Inst.*, 89, 182. <https://doi.org/10.1016/j.joei.2015.02.005>.
- [59] Athanassiou, E. K., Grass, R. N. and Stark, W. J. (2006).

Review Article

- Large-scale production of carbon-coated copper nanoparticles for sensor applications. *Nanotechnology*, 17, 1668. <https://doi.org/10.1088/0957-4484/17/6/022>.
- [60] Ramyadevi, J., Jeyasubramanian, K., Marikani, A., Rajakumar, G. and Rahuman, A. A (2012). Synthesis and antimicrobial activity of copper nanoparticles. *Mater. Lett.*, 71, 114. <https://doi.org/10.1016/j.matlet.2011.12.055>.
- [61] Huang, Z., Cui, F., Kang, H., Chen, J., Zhang, X. and Xia, C (2008). Highly dispersed silica-supported copper nanoparticles prepared by precipitation–gel method: A simple but efficient and stable catalyst for glycerol hydrogenolysis. *Chem. Mater.*, 20, 5090. <https://doi.org/10.1021/cm8006233>.
- [62] Ojha, N. K., Zyryanov, G. V., Majee, A., Charushin, V. N., Chupakhin, O. N. et al. (2017). Copper nanoparticles as inexpensive and efficient catalyst: A valuable contribution in organic synthesis. *Coord. Chem. Rev.*, 353, 1. <https://doi.org/10.1016/j.ccr.2017.10.004>.
- [63] Sarkar, A., Mukherjee, T. and Kapoor, S (2008). PVP-stabilized copper nanoparticles: A reusable catalyst for “Click” reaction between terminal alkynes and azides in nonaqueous solvents. *J. Phys. Chem. C.*, 112, 3334. <https://doi.org/10.1021/jp077603i>.
- [64] Antolini, E (2003). Formation, microstructural characteristics and stability of carbon supported platinum catalysts for low temperature fuel cells. *J. Mater. Sci.*, 38, 2995. <https://doi.org/10.1023/A:1024771618027>.
- [65] Liu, J., Zhou, Z., Zhao, X., Xin, Q., Sun, G. and Yi, B (2004). Studies on performance degradation of a direct methanol fuel cell (DMFC) in life test. *Phys. Chem. Chem. Phys.*, 6, 134. <https://doi.org/10.1039/b313478d>.
- [66] Ivanovskii, A. L (2012). Graphene-based and graphene-like materials. *Russ. Chem. Rev.*, 81, 571. <https://doi.org/10.1070/RC2012v081n07ABEH004302>.
- [67] Xu, M., Liang, T., Shi, M and Chen, H. (2013). Graphene-like two-dimensional materials. *Chem. Rev.*, 113, 3766. <https://doi.org/10.1021/cr300263a>.
- [68] Pol, V. G. (2010). Upcycling: Converting waste plastics into paramagnetic, conducting, solid, pure carbon microspheres. *Environ. Sci. Technol.*, 44, 4753. <https://doi.org/10.1021/es100243u>.
- [69] Xiong, W., Liu, M., Gan, L., Lv, Y., Li, Y. et al. (2011). Novel synthesis of mesoporous carbon microspheres for supercapacitor electrodes. *J. Power Sources*, 196, 10461. <https://doi.org/10.1016/j.jpowsour.2011.07.083>.
- [70] Jiang, J., Yuan, J., Nie, P., Zhu, Q., Chen, C. et al. (2020). Hierarchical N-doped hollow carbon microspheres as advanced materials for high-performance lithium-ion capacitors. *J. Mater. Chem. A*, 8, 3956. <https://doi.org/10.1039/c9ta08676e>.
- [71] Ko, Y. N., and Kang, Y. C. (2014). Electrochemical properties of ultrafine Sb nanocrystals embedded in carbon microspheres for use as Na-ion battery anode materials. *Chem. Commun.*, 50, 12322. <https://doi.org/10.1039/c4cc05275g>.
- [72] Nakhate, A. V. and Yadav, G. D (2018)..Cu₂O nanoparticles supported hydrothermal carbon microspheres as catalyst for propargylamine synthesis. *Mol. Catal.*, 451, 209. <https://doi.org/10.1016/j.mcat.2018.01.013>
- [73] Chen, Z., Yu, Y., Zhang, Q., Chen, Z., Chen, T. and Jiang, J. (2019). Preparation of phosphorylated chitosan-coated carbon microspheres as flame retardant and its application in unsaturated polyester resin. *Polym. Adv. Technol.* 2019, 30(8), 1933-1942. <https://doi.org/10.1002/pat.4625>.
- [74] Zhao, K., Liu, S., Li, K., Hu, Z., Yuan, Y. et al. (2017). Fabrication of –SO₃H functionalized aromatic carbon microspheres directly from waste camellia oleifera shells and their application on heterogeneous acid catalysis. *Mol. Catal.*, 433, 193. <https://doi.org/10.1016/j.mcat.2017.02.032>.
- [75] Biehler, E., Quach, Q. and Abdel-Fattah, T.M. (2023). Silver-nanoparticle-decorated fused carbon Sphere composite as a catalyst for hydrogen generation. *Energies*, 16, 5053. <https://doi.org/10.3390/en16135053>.

Review Article

- [76] Quach, Q., Biehler, E. and Abdel-Fattah, T.M. (2023). Synthesis of palladium nanoparticles supported over fused graphene-like material for hydrogen evolution reaction. *Catalysts*, 13, 1117. <https://doi.org/10.3390/catal13071117>.
- [77] Peña-Alonso, R., Sicurelli, A., Callone, E., Carturan, G. and Raj, R. A. (2007). Picoscale catalyst for hydrogen generation from NaBH₄ for fuel cells. *J. Power Sources*, 165, 315. <https://doi.org/10.1016/j.jpowsour.2006.12.043>.
- [78] Liang, Y., Dai, H.-B., Ma, L.-P., Wang, P. and Cheng, H.-M. (2010). Hydrogen generation from sodium borohydride solution using a ruthenium supported graphite catalyst. *Int. J. Hydrogen Energy* 2010, 35, 3023. <https://doi.org/10.1016/j.ijhydene.2009.07.008>.
- [79] Biehler, E., Quach, Q., Huff, C., and Abdel-Fattah, T.M. (2022). Organo-nanocups assist the formation of ultra-small palladium nanoparticle catalysts for hydrogen evolution reaction. *Materials*, 15, 2692. <https://doi.org/10.3390/ma15072692>.
- [80] Quach, Q.; Biehler, E. and Abdel-Fattah, T.M. (2023). Synthesis of copper nanoparticles supported over graphene-like material composite as a catalyst for hydrogen evolution. *J. Compos. Sci.*, 7, 279. <https://doi.org/10.3390/jcs7070279>.
- [81] Biehler, E., Quach, Q., and Abdel-Fattah, T.M. (2023). Gold nanoparticles AuNP decorated on fused graphene-like materials for application in a hydrogen generation. *materials*, 16, 4779. <https://doi.org/10.3390/ma16134779B>.
- [82] Biehler, E., Quach, Q. and Abdel-Fattah, T.M. (2023). Synthesis of platinum nanoparticles supported on fused nanosized carbon spheres derived from sustainable source for application in a hydrogen generation reaction. *Nanomaterials*, 13, 1994. <https://doi.org/10.3390/ma16134779B>.
- [83] Zhang, J.S., Delgass, W.N., Fisher, T.S. and Gore, J.P. (2007). Kinetics of Ru-catalyzed sodium borohydride hydrolysis. *J. Power Sources*, 164, 772. <https://doi.org/10.1016/j.jpowsour.2006.11.002>