Review


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Abstract: Using hydrogen energy as an alternative renewable source of fuel is no longer an unrealized dream, it now has real-world application. The influence of nanomaterials on various aspects of hydrogen energy, such as hydrogen production, storage, and safety, is considerable. In this review, we present a brief overview of the nanomaterials that have been used as photocatalysts during hydrogen production. The use of nanomaterials and nanomaterial composites for hydrogen storage is also reviewed. The specific use of graphene and its associated nanocomposites, as well as the milestones reached through its application are elaborated. The need to widen the applicability of graphene and its allied forms for hydrogen energy applications is stressed in the future perspectives. Hydrogen energy is our future hope as an alternative renewable fuel, and graphene has the potential to become the future of hydrogen energy generation.

Keywords: hydrogen energy; storage; nanomaterials; renewable energy; graphene; nanocomposites

1. Introduction

Based on current consumption statistics, it is estimated that energy supplies from fossil fuels, such as coal, natural gas, and oil, will last up to 50, 53, and 114 years, respectively [1]. Nevertheless, the continuous exploitation of fossil fuels will bring about a negative environmental impact through enormous CO₂ emissions, which in turn can worsen global warming and have other human health-related impacts [2]. The demand for oil, and concerns about the rising levels of atmospheric CO₂ affecting climatic conditions, have resulted in a pressing need to transition from fossil fuels to hydrogen (H₂) fuels. Hydrogen energy is an alternate clean energy acquired from renewable resources. Non-depleting energy resources with self-replenishing capacities will positively aid our chances of creating a sustainable future [3,4]. Renewable energy is obtained from tidal/wave energy, biomass energy, geothermal energy, wind energy, solar energy, hydropower, and other natural sources. Though much emphasis has been placed on adapting renewable resources for clean energy production, their availability is subject to regional and seasonal factors [5].

Hydrogen, which is an alternative energy carrier to generate electricity, is obtained by splitting water, a renewable resource, through a simple and straightforward process called electrolysis. This being the case, the production of hydrogen will directly depend on the availability of water on earth. It is a simple and clean technology that does not generate any toxic pollutants other than pure water as a byproduct. Moreover, the fact that hydrogen has a comparatively higher specific energy density than other hydrocarbons is a key advantage [6,7]. Furthermore, hydrogen production can also be enabled by a wide variety of raw materials, including oil, gas, biofuels and sewage sludge [8], which make it easy to be locally produced without depending on external energy suppliers to ensure continuous production.

Hydrogen is produced using various techniques, such as steam methane reformation, hydrocarbon oxidation, coal gasification, and water–gas shift reaction, as well as from...
Nanotechnology is the fundamental understanding of physics, chemistry, biology, and technology of nanometer-scale objects. Nanotechnology is devoted to manipulating atoms and molecules at nanoscale dimensions, for designing, producing, and innovating structures, devices, and systems. Nanomaterials are those with dimensions of the order of 100 nanometers (100 millionth of a millimeter or less). Nanotechnology has successfully manipulated the molecular structure of materials, changing their intrinsic properties and obtaining others with revolutionary applications. Unique material reinforcements have been enabled based on nanotechnological inputs. Transparent graphene-modified carbon harder renewable sources, such as biomass and water, and water splitting techniques such as electrolysis, thermolysis, and photoelectrolysis via photocatalytic splitting are also being utilized. Figure 1 illustrates the process of the photocatalytic splitting of water for hydrogen production. However, for the hydrogen economy to be realized, many technical issues need to be resolved, of which discovering an ideal energy-efficient method for H₂ storage within limited space is the most important [9].

![Figure 1. An illustration of the process of photocatalytic water splitting for hydrogen production.](image)

Hydrogen storage promotes hydrogen production and applications, which make it very important for initiating the hydrogen economy [10–13]. In order to serve the requirements of fuel cell cars, onboard hydrogen storage is very important [14,15]. The optimal attributes that are prerequisites for hydrogen storage materials used in automobile applications include: (i) lightweight, (ii) cost-effective and readily available, (iii) high volumetric/gravimetric hydrogen density, (iv) rapid kinetics, (v) easily available for activation, (vi) low dissociation or decomposition temperature, (vii) ideal thermodynamic properties, (viii) extended cycling, and (ix) optimal degree of reversibility. These traits aid in understanding the fundamental mechanisms behind hydrogen catalysts and their physicochemical interactions with hydrogen at atomic or molecular scales.

Currently, metal, complex and chemical hydrides, adsorbents, nanospheres, nanotubes, nanofibers, nanohorns, nanoparticles, polymer nanocomposites, metal–organic frameworks, clathrate hydrates, and other materials [16–21] have been considered as candidate materials for hydrogen storage. However, none of these are able to deliver the adequate requirements, which include: (1) high hydrogen content (>6.0 wt.%), (2) favorable or tunable thermodynamics (30–55 kJ/mol H₂), (3) operation below 100 °C for H₂ delivery, (4) onboard refueling, and (5) cyclic reversibility (~1000 cycles) at moderate temperatures.

Nanotechnology is the fundamental understanding of physics, chemistry, biology, and technology of nanometer-scale objects. Nanotechnology is devoted to manipulating atoms and molecules at nanoscale dimensions, for designing, producing, and innovating structures, devices, and systems. Nanomaterials are those with dimensions of the order of 100 nanometers (100 millionth of a millimeter or less). Nanotechnology has successfully manipulated the molecular structure of materials, changing their intrinsic properties and obtaining others with revolutionary applications. Unique material reinforcements have been enabled based on nanotechnological inputs. Transparent graphene-modified carbon harder
than steel, lighter than aluminum, has been fabricated. Various other technological marvels have been enabled using nanotechnology, enriching electronics, energy, biomedicine, and defense applications [22,23].

In the following review, we survey the various nanomaterials that have been used for hydrogen production and hydrogen storage. The novel next-generation nanocomposites that have been used for hydrogen production, especially as photocatalysts, are discussed, and those aspects of carbon nanomaterials which have been less explored are identified as future projections.

2. Nanomaterials Used in Hydrogen Production

Hydrogen production involves four different methods: (1) photoelectrochemical (PEC) water splitting, (2) solid-state hydrogen storage, (3) photocatalytic hydrogen production, and (4) proton exchange membrane fuel cells (PEMFCs). Photocatalysis involves the following reaction: photogenerated electrons and holes at the conduction and valence bands lead to the redox reaction, resulting in hydrogen and oxygen production. Efficient photocatalysts are expected to possess: (1) suitable band gaps and structures to absorb sunlight/UV light, leading to hydrogen- and oxygen-evolution half-reactions; (2) good charge transfer ability for electrons and holes, with low recombination rates; and (3) high surface area for catalytic activity. Fujishima and Honda first reported the successful use of TiO$_2$ anode and Pt cathode for solar-driven water splitting for hydrogen production [24]. In 1979, Bard designed a water splitting system that operates photocatalytically, using particles/powders as semiconductor photocatalysts [25]. PEC water splitting is considered the primary approach and TiO$_2$ is the best choice of semiconductor for PEC water splitting [26,27]. TiO$_2$ band gap is 3.2 eV, hence it is difficult to absorb visible and infrared light for solar water splitting, this is why metal or non-metal ion doping has been involved in narrowing down the band gap of TiO$_2$, so that TiO$_2$ is also functional under visible light [26,28]. C-doped TiO$_2$ nanocristalline films possess high water splitting performance with enhanced conversion efficiency (11%) and photoconversion efficiency (8.35%), besides these credentials, they were active under visible light, which was an added advantage [29]. Grimes et al. demonstrated TiO$_2$ nanotube arrays for PEC water splitting yielding a photoconversion efficiency of 16.5% under UV light. The nanotube system owing to its nanotubular architecture, achieves superior electron lifetime and enhanced charge separation [30–36]. TiO$_2$ and fluorine-doped tin dioxide (SnO$_2$:F, and FTO), which is commonly used for preparing transparent conductive oxides (TCO), has been reported for their contribution in PEC cells [37]. ZnO is yet another popular wide band gap semiconductor, predominantly used for PEC water splitting applications [38,39]. Ion doping [40–42] and visible light sensitization with narrow band gap semiconductors [43–45] have expanded the light absorption range and improved the performance of PEC. ZnO nanostructures were doped with shallow Al donor levels, with added Ni for improved optical absorption [46]. Oval core/shell α-Fe$_2$O$_3$ nanorod nanoarrays, modified with thin WO$_3$/TiO$_2$ overlayers, have been reported to result in enhanced photo efficacy [47]. Other authors controllably tuned the ZnIn$_2$S$_4$ microstructure for enhanced visible light-mediated hydrogen evolution [48–50]. In the past decades, innumerable reports have addressed the critical requirements of photocatalysts [28,51–55].

Nanomaterials such as CdS, SiC, CuInSe$_2$, and TiO$_2$ have been used for photocatalytic hydrogen production [27,56–58] and demonstrated for their enhanced photocatalytic properties. Currently, Nb$_2$O$_5$ [59], Ta$_2$O$_5$ [60], α-Fe$_2$O$_3$ [61,62], ZnO [38,39], TaON [63], BiVO$_4$ [64,65], and WO$_3$ nanomaterials have been explored [66]. In most of these, band gap limitation can lower H$_2$ production [67]. To resolve this issue, noble metal/ion doping, sensitization and metal ion implantation techniques have been attempted. In noble metal doping, Pt is the best; but it is extremely expensive, so Ag, Ru, Pd, Ni, Cu, and Ir have been explored in parallel [68–76]. Incorporation of co-catalysts with photocatalyst nanomaterials for photocatalytic hydrogen production has also been attempted.

Loading cocatalysts onto photocatalysts to lead to hydrogen or oxygen evolution sites has enhanced photocatalytic splitting of water. In the past, transition metals, metal
oxides, metal sulfides and noble metals, such as Pt, Ru, Au, and metal oxides, such as NiO, Rh/CrO _3_ , etc., were well utilized as water reduction cocatalysts by entrapping electrons [28,52]. IrO _2_, RuO _2_, RhO _3_, CoO _4_, and MnO _4_ metal oxides have been able to function as effective oxidation cocatalysts by entrapping the holes [51]. Researchers have loaded noble metals and metal sulfides as dual cocatalysts (Pt–Ag _2_ S and Pt–CuS), which could result in efficient separation of photogenerated electrons and holes for enhanced hydrogen evolution [77,78].

3. Nanomaterials Used in Hydrogen Storage

Various hydrogen storage systems have been explored for hydrogen storage applications [16–21,79–81]. These include metal hydrides, complex hydrides, chemical hydrides, adsorbents and nanomaterials (nanotubes, nanofibers nanohorns, nanospheres, and nanoparticles), clathrate hydrates, polymer nanocomposites, metal organic frameworks, and others [9,16–21,81–83]. However, as mentioned earlier, none of the currently available materials meet all these requirements, and the hydrogen content, release temperature and reversibility requirements are especially hard to meet. The other major option is solid-state hydrogen storage in light metal hydrides [10,12–14,84–86] and complex hydrides such as alanates [87,88], amides [89,90], borohydrides [90–92] and their combinations [93,94]. An offset of light metal hydrides are the alkali/alkali earth metal hydrides NaH, LiH, and MgH _2_. Interstitial, or metallic, hydrides such as PdH x are formed by transition and rare earth elements. Covalently bound hydrides such as AlH _3_ and NH _3_ BH _3_ are also used, but have their own limitations. Recently, the focus has been more on boron hydrides such as LiBH _4_, alanates such as NaAlH _4_, and even systems containing multiple phases, such as LiBH _4_+MgH _2_. Yet, most of these store 5 wt.% hydrogen and face kinetics and reversibility issues because of its complex nature and the presence of multiple phases after dehydrogenation. This being the case, the other alternative method of increasing the hydrogen sorption kinetics is nanostructuring. Stable crystallites of 5–10 nm were reported in a MgH _2_ TiH _2_ system [95], smaller particles with sizes less than 10 nm have also been used. In 2005, the breakthrough pioneering work on nanoconfined borane in mesoporous silica enabled major changes in their hydrogen desorption properties, paving the way for a new beginning [96]. Additional effects have been identified, such as better mechanical stability and thermal management during cycling via incorporating carbon materials [97–99].

Carbonaceous materials are an attractive option for hydrogen storage owing to its adsorption ability, high specific surface area, pore microstructure, and low mass density. Despite numerous reports on hydrogen uptake by carbon materials, the actual mechanism of storage remains a mystery. The interaction is possibly based on van der Waals attractive forces (physisorption) or by chemisorption. The physisorption of hydrogen, limits the hydrogen-to-carbon ratio restricted to less than one hydrogen atom per two carbon atoms (i.e., 4.2 mass %). In chemisorption, this is realized as in the case of polyethylene [100–102]. Dillon et al. presented the first report on hydrogen storage in carbon nanotubes [103], which activated ripples worldwide in carbonaceous materials research. Now, it is known that hydrogen can be physically adsorbed on activated carbon and be “packed” more densely on the surface and inside the structure of carbon, as if it is compressed. The best results using carbon nanotubes, are verified to correspond to a hydrogen storage density of about 10% of the nanotube weight [104].

Fullerenes are currently one of the most popular carbon allotropes with a close-caged molecular structure [105]. They are able to react with hydrogen via the hydrogenation of carbon–carbon double bonds and so have been used for hydrogen storage. A maximum number of nearly 60 hydrogen atoms can be attached inside (endothedraly) and outside (exothermally) the spherical fullerene surfaces. Thus, a stable C _60_ H _60_ isomer is obtained with a theoretical hydrogen content of ~7.7 wt.%. It seems that the fullerene hydride reaction is reversible at high temperatures. The 100% conversion of C _60_ H _60_ indicates that 30 moles of H _2_ gas will be released from each mole of fullerene hydride compound, but this reaction requires high temperatures ranging from 823–873 K [106,107].
Hydrogen can also be stored in glass microspheres of approximately 50 µm diameter. These microspheres can be loaded with H$_2$ through heating these glass microspheres to increase their permeability to hydrogen. A pressure of approximately 25 MPa, resulting in a storage density of 14% mass fraction and 10 kg H$_2$/m$^3$ is reported [106]. At 62 MPa, a bed of glass microspheres can store 20 kg H$_2$/m$^3$. The release of hydrogen is through re-heating the spheres, which increases the permeability of hydrogen. Carbon-based sorbents, synthesized from various organic precursors, can be structured into various carbon forms, such as carbon nanotubes [108–110], fibers [108,110], fullerenes [110,111], and activated carbons [112,113]. These structurally diverse forms can be tuned for hydrogen gas storage. Metal–organic frameworks (MOFs) are highly porous, crystalline solids consisting of a periodic array of metal clusters linked through multi-topic organic struts [114,115]. Other highly porous, crystalline materials include zeolitic imidazolate frameworks (ZIFs) [116] and covalent organic frameworks (COFs) [117], which have also been considered as an option for hydrogen storage.

Nanocomposites consist of a polyaniline matrix that can be functionalized by catalytic doping or incorporation of a nanovariant. It has been reported that polyaniline can store 6–8 wt.% of hydrogen [118] and a recent study revealed a successful hydrogen uptake of 1.4–1.7 wt.% [119]. With all this in mind, there is still an urgent need for the development of new reversible materials. Clathrates are a new class of materials for hydrogen storage [18], which are primarily hydrogen-bonded H$_2$O frameworks, where hydrogen molecules can be incorporated, making it useful for off-board storage of hydrogen.

4. Graphene-Based Nanocomposites for Hydrogen Energy Applications

Carbon materials such as carbon nanodots, fullerenes, graphene, CQDs, (C60), and carbon nanotubes (CNTs) have been applied for surface modification of photocatalysts for hydrogen production [120]. Carbon materials have been used for enhancing hydrogen production at all ranges of the optical spectra. The results have shown that the use of carbon materials has extended the visible-light absorption range and enabled higher charge transfer. Graphene exhibits higher charge carrier mobility, larger surface area, excellent electrical and thermal conductivity, as well as good physical and chemical stability; moreover, it is synthesized easily [121–125]. Zhang et al. reported enhanced photocatalytic H$_2$ evolution from water splitting using graphene/Ti nanocomposites [126]. Li et al. prepared S and N co-doped graphene quantum dots/ TiO$_2$ (S,N-GQD/TiO$_2$) composites for enabling efficient photocatalytic H$_2$ evolution, it was also observed that these graphene-based nanocomposites exhibited higher photocatalytic activity than pure TiO$_2$. This is owing to enhanced absorption of visible light and efficient separation and migration of electrons and holes [127]. Fan et al. reported TiO$_2$/RGO nanocomposites [128], while Hao et al. anchored TiO$_2$ with graphene quantum dots and reported enhanced photocatalytic H$_2$ evolution [129], which is due to the credentials of graphene quantum dots that can act as efficient electron reservoirs and photosensitizers when associated with TiO$_2$.

Of the carbon materials, graphene is most suitable hydrogen storage material because of its active surface area and superior chemical properties. It is used as a free metal catalyst owing to its favorable electrochemical and chemical properties. Its physico-chemical properties include high carrier mobility, elasticity and generous thermal conductivity [130]. The hybridization of graphene is sp$^2$, its honeycomb-like structure accommodates the hydrogen atoms [131]. The adsorption is through either physisorption or chemisorption. Masjedi-Arani et al. [132] reported the synthesis and use of novel Cd$_2$SiO$_4$/graphene nanocomposites. Cd$_2$SiO$_4$ nanoparticles were blended into a graphene sheet to form Cd$_2$SiO$_4$/graphene nanocomposites. The electrochemical hydrogen storage capacity of Cd nanoparticles was found to be 1300 mA h$^{-1}$, which is nearly half of the storage capacity of Cd$_2$SiO$_4$/graphene nanocomposites (3300 mA h$^{-1}$). This is because of their ideal electrical properties and high surface area, which makes them more suitable for electrochemical hydrogen storage than graphene. Graphene is a highly lightweight material, so it is highly attractive for H-storage applications. Ngqalakwezi et al. prepared graphene
nanocomposites through a modified Tours method [133]. Hydrogen uptake improved by 2% in graphene to 4.98 wt.% and 3.99 wt.% in calcium/graphene nanocomposites, respectively. The addition of ammonia increases hydrogen storage in graphene. Their group reported that the addition of magnesium onto reduced graphene oxide resulted in reduced graphene oxide–Mg composites [134] suitable for electrochemical hydrogen storage. These magnesium nanocrystals reinforced with fine and reduced graphene oxide sheets have been applied successfully for hydrogen storage (6.5 wt.% and 0.105 kg hydrogen per liter in the total composite). Ravi and Grace fabricated novel MnFe$_2$O$_4$/graphene and ZnFe$_2$O$_4$/graphene nanocomposites for hydrogen evolution [135].

Metal decorated Ni/graphene-like materials (GLM) are another class of nanocomposites [136] that have been reported for hydrogen applications. ZnAl$_2$O$_4$/graphene nanocomposites [137] were prepared by green synthesis using green tea and olive leaf extracts and applied for electrochemical hydrogen storage. ZnAl$_2$O$_4$/graphene and ZnAl$_2$O$_4$ nanocomposites yielded the highest coulombic efficiency (67.5%) and discharge capacity (3100 mAh g$^{-1}$), respectively. Hierarchically prepared porous 3D-graphene materials were doped with TiO$_2$ through the electrostatic assembly method and tested for hydrogen adsorption efficiency [138]. Porous graphene–TiO$_2$ nanocomposites with greater pore volume (0.41 cm$^3$ g$^{-1}$) and high surface area (705 m$^2$ g$^{-1}$) and maximum storage capacity exhibited enhanced storage properties. In another study, vanadium-supported reduced graphene oxide nanocomposites combined with Mg$_{85}$Al$_{15}$ alloy were reported for hydrogen storage applications. Pd/graphene nanocomposites (8.67 wt.% in the 1% Pd/graphene nanocomposite with a pressure of 60 bar, and 7.16 wt.% uptake capacity) were also reported for enhanced H$_2$ storage [139]. These are a few selective examples of nanocomposites contributing towards hydrogen storage. Jain and Kandasubramanian have recently reviewed the role of functionalized graphene in hydrogen energy storage [140]. Table 1 presents a consolidated list of the graphene/graphene composites that have been engaged in hydrogen storage applications.

### Table 1. Graphene nanomaterial and its nanocomposites for hydrogen storage applications.

<table>
<thead>
<tr>
<th>Graphene Type</th>
<th>Material Composition</th>
<th>Hydrogen Storage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene nanocomposite</td>
<td>Graphene/Li</td>
<td>12.8 (maximum gravimetric density, wt.%)</td>
<td>[141]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Graphene/Ca</td>
<td>8.4 (maximum gravimetric density, wt.%)</td>
<td>[142]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Graphene oxide/Ti</td>
<td>4.9 (maximum gravimetric density, wt.%)</td>
<td>[143]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Graphene/Al</td>
<td>5.13 (maximum gravimetric density, wt.%)</td>
<td>[144]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Graphene/Li/B</td>
<td>10.7 (maximum gravimetric density, wt.%)</td>
<td>[145]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Be adsorbed on B-doped graphene</td>
<td>15.1 (maximum gravimetric density, wt.%)</td>
<td>[146]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Reduced graphene oxide/Mg</td>
<td>6.5 (maximum gravimetric density, wt.%)</td>
<td>[134]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>N doped graphene</td>
<td>7.23 (maximum gravimetric density, wt.%)</td>
<td>[147]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Lithium-doped fullerene/graphene</td>
<td>5</td>
<td>[148]</td>
</tr>
<tr>
<td>Graphene nanosheets</td>
<td>Graphene nanosheets</td>
<td>1.2 wt.% 77 K</td>
<td>[149]</td>
</tr>
<tr>
<td>Graphene</td>
<td>Hierarchical graphene</td>
<td>4.01 wt.% 77 K</td>
<td>[150]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Graphene oxide MWCNT</td>
<td>2.6 wt.% 298 K/50 bar</td>
<td>[151]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Pt/Pd/Graphene</td>
<td>0.156 303 K/57 bar</td>
<td>[152]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>N-doped palladium-decorated graphene</td>
<td>2.10 wt.% 298 K/20 bar</td>
<td>[153]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Ni (0.83 wt.% and B (1.09 wt.%) doped graphene</td>
<td>4.4 wt.% 77 K/1.06 bar</td>
<td>[154]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Cu-BTC with 9 wt.% graphene</td>
<td>3.58 wt.% 77 K/43 atm</td>
<td>[155]</td>
</tr>
<tr>
<td>Graphene nanocomposite</td>
<td>Cd$_2$SiO$_4$/graphene</td>
<td>Not specified</td>
<td>[132]</td>
</tr>
</tbody>
</table>
5. Future Perspectives

With developing concerns regarding atmospheric changes and the consumption of non-sustainable power sources, a visualized hydrogen economy is a definite option. In this review, different solid-state H₂ storage carbon-based nanomaterials were discussed. To accomplish H₂ economy, storage is the crucial factor, as traditional storage systems cannot perform adequately on several onboard applications. To address the concerns for future fuel needs, hydrogen must be utilized correctly and efficient storage systems must be planned.

This article discussed numerous nanomaterials and their nanocomposites as potential options for hydrogen storage. The limitations of the existing options have been addressed, and it is anticipated that additions of the new-generation nanomaterials for solid-state H₂ storage will be required to add to the future hydrogen vision.

We evaluated the current standing of hydrogen-energy-related nanomaterial research through a PubMed search. Nanomaterial contributions towards hydrogen production yielded a PubMed search result of 4264 hits (Figure 2a). Of these 4264 hits, 1161 hits (Figure 2b) resulted from the keywords ‘carbon nanomaterials and hydrogen production’, and 1468 hits from a keyword search for ‘hydrogen production and graphene’ (Figure 2c). Figure 3 clearly portrays the fact that, with respect to hydrogen storage, the PubMed search on ‘hydrogen storage and nanomaterials’ yielded 893 hits (Figure 3a), while, ‘hydrogen storage and carbon nanomaterials’ yielded 335 results (Figure 3b), and ‘hydrogen storage and graphene’ yielded 489 hits (Figure 3c). This PubMed based survey clearly reveals that in the current standing, carbon materials play a major role in hydrogen energy applications, be it hydrogen production or hydrogen storage. Furthermore, within the carbon nanomaterial itself, graphene and its nanocomposites hold a high reputation for their inputs towards hydrogen production and storage applications.

Hydrogen will apparently become the synthetic fuel for a hydrogen-based environmentally clean energy economy. Hydrogen storage needs to be planned to meet mobile or stationary storage requirements. Today, we know of several efficient and safe ways to produce and store hydrogen; we have reviewed the various nanomaterial options that have been applied towards hydrogen production and storage. The material science challenge is to develop a clearer understanding of the electronic behavior during the interaction between hydrogen and other elements, especially metals. Nanotechnology has been the source of numerous technical breakthroughs, the inputs of nanomaterials when put to use as photocatalysts and as storage materials have indeed helped overcome various barriers, however, there are many other new potential nanomaterials. Complex nanocomposite materials need to be explored for hydrogen production and storage options. Complex compounds such as Al(BH₄)₃ have to be investigated and new compounds from the lightweight metals need to be discovered. Particularly with respect to automobile applications, lightweight carriers are optimal. In this direction, energy conversion devices more efficient than the internal combustion engine, e.g., fuel cells, will be developed and will reduce the amount of hydrogen necessary on board and therefore also the weight of the storage system. In terms of light weight and utility, graphene is a prospective material. “Pristine” graphene is only one atomic layer thick, a material that has 10 atomic layers of carbon or fewer is referred to as graphene. Graphene is typically categorized based on its layers, as very-few-layered graphene (vFLG, 1–3 layers of carbon), few-layered graphene (FLG, 2–5 layers), multi-layer graphene (MLG, 2–10 layers), or graphene nanoplatelets (GNP, stacks of graphene sheets that consist of multiple layers and lateral dimensions ranging from 100 nanometers to 100 microns). Besides these, graphene is available commercially as graphene oxide (GO) and reduced graphene oxide (rGO), graphene powder, solution or paste and functionalized graphene. In this review, we presented scattered applications of graphene, mostly related to graphene nanocomposites, and we found that little has been done to test the utility of the other forms of graphene/GO, reduced GOs and their allies. Pristine and functionalized graphene have proven their unique applicability in numerous applications, but there is definitely more to offer.
Figure 2. Results of a PubMed search showing hits pertaining to the keyword search on (a) hydrogen storage and nanomaterials, (b) hydrogen storage and carbon nanomaterials, and (c) hydrogen storage and graphene.
Figure 3. Results of a PubMed search showing hits pertaining to the keyword search on (a) hydrogen production and nanomaterials, (b) hydrogen production and carbon nanomaterials, and (c) hydrogen production and graphene.
Moreover, a clear understanding of the mechanism of hydrogen adsorption is very important in order to plan for designing the most appropriate nanocomposites that will cater to the storage mandate. It is known that the adsorption energy for the hydrogen molecule in a given material depends not only on the material nature but also on the hydrogen molecule’s interaction with the adsorption sites. Given this fact, Reguera (2009) [156] has elaborately discussed the five different interactions that contribute to the adsorption of H\textsubscript{2}, which include: quadrupole moment interaction with the local electric field gradient; electron cloud polarization by a charge center; dispersive forces (van der Waals); quadrupole moment versus quadrupole moment between neighboring H\textsubscript{2} molecules, and H\textsubscript{2} coordination to a metal center [157–159]. The relative importance of these five interactions in hydrogen storage has been comprehensively discussed in that review, to yield a clear understanding of designing the right material and combining the right materials for hydrogen storage. In most of the reports that design nanocomposites for hydrogen storage, this aspect is not addressed, but this review emphasizes that a clear understanding of this subject will lead to more promising and applicable nanocomposites.

Hydrogen storage has been well researched and widely supported by various publication records [160,161], the use of nanomaterials for hydrogen production and storage is also substantiated by various research records, however, this review highlighted the fact that there are many nanomaterials that have not been attempted. Specifically in terms of carbonaceous nanomaterials, there is a lot to be tapped. Graphene in particular has a lot to offer, and while there are reports, there is more to exploit. Additionally, the combination of materials, such as nanocomposites, has been a fruitful field, and nanocomposites have been utilized in terms of hydrogen systems, but more diverse nanocomposites, specifically combining carbon materials with other metallic nanomaterials, could also have a lot to offer. These are a few aspects that can take things forward more smoothly and rapidly, which this review highlights as prospects for future directions.

Although the demand for hydrogen fuel is increasing rapidly for automated application, the safety of high-capacity hydrogen storage remains a scientific challenge [134]. Safety is an important aspect that needs to be assessed and enhanced. Every technology has its pros and cons, working on the cons is a crucial direction. Safe hydrogen storage is an aspect to which nanomaterials have a lot to contribute, this is something that has not been prevalently worked on and disclosed. This is a future direction that could plausibly add to the knowledge and practical implications in this research area.

6. Concluding Remarks

The use of nanomaterials for hydrogen production and hydrogen storage applications were briefly reviewed. The use of carbonaceous nanomaterials for hydrogen energy applications were also reviewed, specifically the use of graphene and its allied forms for hydrogen energy applications. The dearth in widespread use of graphene and its associated forms for hydrogen storage applications have been discussed and its future prospects have been presented.

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**References**


