Nanoparticles for hydrogen generation

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In this Highlight article, we review recent progress in the application to nanoparticles for hydrogen generation. We focus primarily on reactive nanoparticles that produce hydrogen through chemical reaction and nanoparticle catalysts that promote hydrogen release from high hydrogen content materials. The area of nanoparticle photocatalysts is briefly mentioned for completeness. To facilitate comparison of the various approaches, we report mass normalized hydrogen generation rates for the papers reviewed. These values are determined using the reported experimental data.

Introduction

The scientific research community has been exploring the nanoscale for some time, noting that materials at the nanoscale exhibit unique and exciting properties, different from the bulk. The unique properties of nanoparticles can be attributed to the very small sizes which result in extremely large surface areas and quantum confinement effects. Numerous examples of the benefits of exploring the nanoscale have been published; tunable semiconductor band gaps, catalytic gold, and fluorescent carbon nanoparticles to name just a few. In the field of hydrogen generation, nanoparticles have been studied as reactive materials and catalysts. Part of this work is focused on near-term solutions to hydrogen as a useful energy carrier (reviewed here), while a far larger effort is focused on developing the fundamental science of photocatalytic hydrogen generation (not reviewed, but mentioned for completeness).

Hydrogen (as an energy carrier) has been suggested as an alternative to traditional fuels (oil, coal, and natural gas). One of the main selling points appears to be its potential as renewable energy; although, much of today’s hydrogen is obtained by steam reforming of natural gas or other hydrocarbon fuels. Hydrogen is an interesting material, possessing a dual personality with both good and bad characteristics. Hydrogen is very abundant, but it can only be found in other compounds and thus must be recovered. Hydrogen has a very high heat of reaction (142 kJ g⁻¹), but because of its very low density (0.0898 g L⁻¹) it either takes a tremendous volume or requires significant compression to compare with the energy density of common liquid fuels (Table 1). Finally, when hydrogen reacts to release its stored chemical potential, it forms the most benign reaction product possible (eqn (1)):

$$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$$  (1)

however, because it requires energy to produce, the gains from this environmentally friendly reaction can be easily lost. Much of the scientific research into nanoparticles for hydrogen generation has been focused on mitigating the negatives mentioned above. Important parameters such as yield, efficiency, release rates, and cost have all seen benefits from the application of nanoparticles. In this Highlight article, we review the latest advances in nanoparticles for hydrogen generation, focusing on reactive nanoparticles that produce hydrogen as part of a chemical reaction and catalysts that promote hydrogen release from suitable hydrogen containing compounds, and very briefly mention photocatalysts for water splitting. The goal of this article is to provide the reader with a comparison of the different approaches and examine current achievable rates within a common frame of reference.

Reactive nanoparticles: the aluminium–water reaction

It is well-known that aluminium can react with water to generate hydrogen:

$$2\text{Al}(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Al(OH)}_3(aq) + 3\text{H}_2(g)$$  (2)

$$2\text{Al}(s) + 4\text{H}_2\text{O}(l) \rightarrow 2\text{AlO(OH)}(s) + 3\text{H}_2(g)$$  (3)

$$2\text{Al}(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{H}_2(g)$$  (4)

A fundamental understanding of the mechanisms for these reactions has been gained using ultra-high vacuum (UHV) surface science techniques and, more recently, atomic cluster methods. Castleman and Khanna have studied a series of aluminium anion clusters (Alₙ⁻), where $n = 7–18$ for their reactivity with water molecules. Not all clusters were found to produce hydrogen. Those that did demonstrated a pair of active sites on the surface of the aluminium cluster, where a Lewis acid site first binds the water molecule through an Al–O bond, then a complimentary Lewis base site accepts...
the hydrogen, breaking the O–H bond (Fig. 1). Hydrogen release occurs after the binding of successive water molecules leads to hydrogen atoms on adjacent sites. Other researchers have identified similar pathways using purely computational techniques. These more recent studies are in good agreement with past UHV investigations.

While these efforts provide interesting insight into the reaction of pristine aluminium with water, they do not account for the thin (~3 nm), but highly protective aluminium oxide layer that coats aluminium metal under ambient conditions. This oxide layer hinders oxygen and water from accessing the underlying aluminium metal. Recently, Bunker et al. examined the role of the passivating oxide film in aluminium corrosion using secondary ion mass spectrometry (SIMS). Under the conditions of exposure to hot water, the authors found that hydroxide ions accounted for the largest defect component in the Al2O3 film, that the Al2O3 film was highly dynamic, undergoing repeated reversible hydrolysis reactions (Al–O to Al–OH, then back), and that hydration of the Al2O3 layer is likely due to the high mobility of the hydroxide ions. With respect to film failure and aluminium metal reaction with water, it was noted that Al–OH is not stable in the presence of aluminium metal, reacting to produce hydrogen and Al2O3. It is hypothesized that once the hydration layer reaches the aluminium metal surface, Al–OH reacts to generate hydrogen which then ruptures the passivating oxide film. Breaches in the oxide film would then allow exposure of the aluminium metal to bulk water resulting in hydrogen generation via eqn (2)–(4).

Dreizin et al. have examined the oxidation of aluminium nanoparticles at high temperatures where the application is combustion. These studies have shown a strong temperature dependence for the behavior of the passivating oxide (Fig. 2). For the case of oxidation in dry air, at relatively low temperatures (T < 823 K) oxidation is slow and apparently driven by the outwardly migrating Al cations. At higher temperatures (823 K > T > 923 K) the aluminium oxide changes from amorphous to γ-Al2O3, creating platelets and grain boundaries that can expose the underlying aluminium metal leading to rapid oxidation. When studies are conducted in the presence of water (steam), there is a significant change in the oxidation behavior at high temperatures (T > 873 K); the overall oxidation rate increases resulting in complete oxidation at a much lower temperature, and there is a region of rapid oxidation that correlates with the aluminium melting point. In discussing these results, the authors note the importance of the hydroxide ion; it possess great mobility through certain phases of the aluminium oxides, it may stabilize the γ-Al2O3 form at higher temperatures, and it might make the passivating oxide layer easier to disrupt when the aluminium particle melts and exerts outward pressure.

Both of these investigations point to the importance of the hydroxide ion in breaching the aluminium oxide layer. Not surprisingly, NaOH has been utilized in numerous studies for its ability to promote the aluminium–water reaction. In the presence of the hydroxide ion, eqn (2) becomes:

\[ 2\text{Al}(s) + 6\text{H}_2\text{O}(l) + 2\text{NaOH}(aq) \rightarrow 2\text{Al(OH)}_3(aq) + 2\text{Na}^+(aq) + 3\text{H}_2(g) \] (5)

Such a system results in the dissolution of the passivating oxide shell and the continuous reaction of the aluminium to

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a Calculated based on methane. b Estimated using dodecane. c Estimated figure.

**Fig. 1** Reaction coordinate for the formation of H2 from Al17 and 2H2O molecules. (A) Al17. (B) An intact water molecule bound to the cluster. (C) The transition state for splitting the first water. (D) The cluster after water is split, with the LUMO + 2 charge density to show the induced Lewis acid site. (E) After the second water is bound. (F) The transition state for splitting the second water. (G) After the breaking of the second O–H bond. (H) A rearrangement of the cluster to facilitate the release of H2. (I) The transition state for releasing H2. (J) The final cluster after H2 is released. The total energies include zero point energies. Reprinted with permission from ref. 7; Copyright © 2010 American Chemical Society.
generate hydrogen as long as OH\textsuperscript{-} is available. While not nanoscale particles, Hu et al. performed a series of experiments that nicely demonstrated the effect of parameters such as [OH\textsuperscript{-}], temperature, and particle size.\textsuperscript{14} The work was performed using Ni-Al alloy particles prepared by a melt-spinning technique followed by milling. The highest rate (estimated from the data provided in ref. 14) was approximately 4 \times 10^{-4} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} Ni-Al. The authors showed a linear change in the rate with increased [OH\textsuperscript{-}], decreased particle size, and increased temperature when plotted as In (rate) vs. 1/T. A hydrogen generation rate of 10^{-5} to 10^{-4} g H\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1} Al is typical for the hydroxide ion assisted aluminium–water reaction given the nature of the particles most often used (i.e., micron scale).

A more technologically significant application of the aluminium–water reaction for hydrogen generation comes from efforts to modify the surface of the aluminium particles. The modification is most often achieved through mechanical milling with a suitable additive. Deng et al. have demonstrated a material they refer to as GMAP (\gamma-Al\textsubscript{2}O\textsubscript{3} modified Al powders),\textsuperscript{21–26} where aluminium particles are mixed with Al(OH)\textsubscript{3} powder, pressed at 120 MPa, sintered at 873 K, and then crushed into working powders. The authors have shown that the resulting powder consists of spherical Al nanoparticles (in the 100 to 200 nm range) with a rough, oxide modified surface.\textsuperscript{24} These particles are able to react in pure water; however, the authors found that the rate of hydrogen generation is highly dependent on both the oxide composition and the temperature of the water. The highest reported rate was for 37% Al\textsubscript{2}O\textsubscript{3} and a reaction temperature of 323 K, after a brief induction period, the material produced hydrogen at 5 \times 10^{-6} g H\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1} GMAP for ~two hours, then reduced to a rate of 1 \times 10^{-6} g H\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1} GMAP for ~six hours more. At room temperature, the hydrogen generation rate was much lower. The authors developed a physicochemical mechanism for the behavior of their particles following the model of Bunker,\textsuperscript{28} where the role of the oxide modifier is to lower the tensile strength of the passivation film.\textsuperscript{24} A number of other materials have been used as surface modifiers including TiO\textsubscript{2}, SiO\textsubscript{2}, CaO, Fe\textsubscript{2}O\textsubscript{3}, WO\textsubscript{3}, carbon, and salts (KCl and NaCl).\textsuperscript{25,27–31} For the oxides\textsuperscript{27} and carbon samples,\textsuperscript{28,29} hydrogen generation rates tended to be on the order of 10^{-5} to 10^{-4} with the application of temperature (e.g., ~1 \times 10^{-4} g H\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1} Al–C measured at 358 K\textsuperscript{30}). The salt-modified aluminium nanoparticles also produce hydrogen with rates on the order of 10^{-5} to 10^{-4}; however, this was accomplished at room temperature.\textsuperscript{30,31} Alinejad and Mahmoodi proposed a model in which the salt crystals acted to reduce the aluminium particle sizes during the milling process, damaged the passivating oxide shell, and formed salt gates (inclusions on the surface).\textsuperscript{30} When exposed to water, the small sizes, weakened shell, and dissolution of the salt gates which uncover aluminium metal all act to facilitate the aluminium–water reaction (Fig. 3).

In another approach used to modify the surface of aluminium metal, researchers have demonstrated the ability to liberate hydrogen at high rates (10^{-5} g H\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1} Al and higher with temperature) by mixing or dissolving the aluminium with other liquid metals (e.g., Ga, Ga–In, or Ga–In–Sn–Zn).\textsuperscript{32–36} The liquid metals prevent the formation of aluminium oxide and thus allow the aluminium–water reaction to proceed. It has been noted, however, that these materials will degrade under ambient conditions.

Many of the reports presented so far actually utilized micron-scale aluminium. This can be attributed in part to the extreme difficulty of synthesizing air-stable aluminium nanoparticles. Industrial methods can produce large quantities, but tend to suffer from broad and sometimes uncontrolled size distributions, agglomeration, and variable oxide content.\textsuperscript{37} Because of the potential value of nanoaluminium for a number of applications, researchers have been exploring new methods to prepare aluminium nanoparticles that can provide air stable particles, controllable properties (i.e., morphology, size, and size distribution), and high metal content. Significant progress has been made.\textsuperscript{38–50} Following the method of Haber and Buhro (i.e., the catalyzed thermal decomposition of alane),\textsuperscript{38} Jouet et al. demonstrated perfluorocarboxylic acid capped aluminium nanoparticles.\textsuperscript{39} The characterization of these materials showed large particles or broad size distributions, and indicated the possibility of agglomerations. Buckner and co-workers showed the synthesis of aluminium nanoparticles capped with alkyl-substituted epoxides that polymerized to yield a polyether cap.\textsuperscript{45} Epoxides with longer alkyl groups tended to show better air and moisture stability. Sun and co-workers produced aluminium nanoparticles within the ionomer membrane Nafion, where the nanoscale cavities within the Nafion membrane served as a template for the growth of the
particles. The Nafion itself acted to protect the particles from oxidation. In a slight modification of the synthesis method, Fernando et al. demonstrated the formation of aluminium nanoparticles capped with oleic acid via sonochemistry. The method yielded small nanoparticles with good metal content (~40% by mass), excellent size control (Fig. 4), and remarkable air, moisture, and solvent stability (no reaction observed in hexane, toluene, THF, chloroform, ethanol, and methanol); however, when the particles were exposed to room temperature water, they reacted to generate large quantities of hydrogen gas (reaction goes to near completion). The authors found that the rate of the reaction was easily tuned by controlling the Al to water ratio (Fig. 5), and reported the highest rate for controlled hydrogen generation yet shown (0.01 g H₂ s⁻¹ g⁻¹ Al). Analysis of the nanoparticles showed their composition to be 35% outer organic shell, 25% inner oxide shell, and 40% aluminium metal core. The authors have concluded that sonochemistry and the presence of both the organic and oxide shells are responsible for the air stability and water reactivity, but the high rate for hydrogen generation and excellent efficiency of the reaction are due to the nanoscale particles. The small particles possess very high surface areas, supporting enhanced mass and thermal transport and greater number densities of active sites (or defects). In addition, the small sizes ensure the ability to achieve complete reaction of the aluminium core before the process of aluminium oxide passivation can establish a viable oxide shell and stop the reaction.

**Nanoparticle catalysts for hydrogen storage materials**

There are a number of materials with high hydrogen content that are being explored for hydrogen generation. For the most part, these materials are stable and do not react with sufficient rate or with enough efficiency to warrant their application; however, when coupled with nanoscale catalysts, these materials can demonstrate excellent performance metrics. Sodium borohydride (NaBH₄) will react with water to yield hydrogen and sodium metaborate:

\[
\text{NaBH}_4(\text{aq}) + 2\text{H}_2\text{O}(l) \rightarrow \text{NaBO}_2(\text{s}) + 4\text{H}_2(\text{g})
\]

The reaction is relatively slow, producing \(~10^{-5} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} \text{NaBH}_4\) at room temperature. Liu et al. made significant improvement in the rate of this reaction by utilizing platinum nanoparticles on a LiCoO₂ support. The catalysts were prepared through an impregnation method, where a platinum salt and the oxide support were mixed at the desired ratio, heated at 523 K for 5 hours, mixed through grinding, and then sintered in air at 723 K for 5 hours. The authors report their particles to be on the order of 4 nm, and using a catalyst with a 5 wt% loading of platinum on LiCoO₂, they obtained a hydrogen generation rate of \(~1 \times 10^{-3} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} \text{Pt}\). The authors report for platinum nanoparticles alone (~5 nm) the rate of hydrogen generation was \(~5 \times 10^{-4} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} \text{Pt}\). They attributed the better response of the supported catalyst to the combined effect of both the platinum and the LiCoO₂ support (the support also showed good catalytic activity). In a different approach, where the catalyst is synthesized in situ, Zahmakiran and Özkär studied the performance of ruthenium nanoparticles grown within the supercage of zeolite-Y. To prepare the nanoparticles, the authors exposed the zeolite-Y to a solution of RuCl₃ with stirring for 72 h at room temperature, followed by washing. The Ru⁺⁺ ions within the zeolite structure were reduced by the NaBH₄, and then catalyzed the hydrolysis reaction. The authors showed the rate of hydrogen generation to be first order with ruthenium concentration (\(~1 \times 10^{-3} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} \text{Ru}\)) and strongly dependent on the reaction temperature (\(~5 \times 10^{-4}\) at 293 K to \(~2 \times 10^{-3} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} \text{Ru}\) at 318 K).

While useful in this form, the preferred method for hydrogen generation with NaBH₄ is as an alkaline solution (pH = 9). Under these conditions the solution is stable and requires a catalyst to react. Zahmakiran and Özkär examined the ruthenium/zeolite-Y catalyst with an alkaline solution and noted two significant differences in the behavior and performance. First, the reaction displays a prominent induction period, anywhere from 6 to 43 min depending on reaction conditions. The induction period was attributed to initial oxidation of the Ru nanoparticles followed by reduction to remake the catalyst. Second, the rate of the reaction is slower, \(~1.2 \times 10^{-4} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} \text{Ru}\) at room temperature, but again could be accelerated through the application of heat (\(~1 \times 10^{-3} \text{ g H}_2 \text{ s}^{-1} \text{ g}^{-1} \text{Ru}\) at 318 K).

Fig. 3 A schematic of hydration progress, for aluminium powders milled with different salt to aluminium mole ratios (\(a < b < c\)). Reprinted from ref. 30 with permission from Elsevier.
Similar work has been performed for other high hydrogen content materials such as ammonia borane (NH$_3$BH$_3$)$^{67-80}$ and hydrazine (N$_2$H$_4$)$^{81-83}$.

\[
\text{NH}_3\text{BH}_3(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{NH}_4^+(aq) + \text{BO}_2^-\text{(aq)} + 3\text{H}_2(g) \quad (7)
\]

\[
\text{H}_2\text{NNH}_2(aq) \rightarrow 2\text{H}_2(g) \quad (8)
\]

For hydrazine, however, there is a competing reaction that leads to no hydrogen generation:

\[
3\text{H}_2\text{NNH}_2(aq) \rightarrow 4\text{NH}_3(g) + \text{N}_2(g) \quad (9)
\]

For all of the high hydrogen content materials, there has been significant effort focused on developing catalysts made from less expensive, more abundant materials (e.g. Fe, Co, Ni, and Cu)$^{51-57,59,60,62,64,67-72,79,80}$ Shin et al. developed a procedure for attaching Co, Ni, and Pt nanoparticles to nitrogen doped carbon nitride nanotubes (CNNTs)$^{36}$ and Yan et al. demonstrated an in situ synthesis of amorphous Fe nanoparticles from the reaction of FeSO$_4$ with NaBH$_4$.$^{65}$ The immediate addition of NH$_3$BH$_3$ resulted in hydrogen generation with a rate of $\sim 2 \times 10^{-3}$ g H$_2$ s$^{-1}$ g$^{-1}$ Fe. In a separate report, the authors obtained a similar rate using Ni nanoparticles synthesized in the presence of starch.$^{66}$ When synthesized without the starch protection, the Ni nanoparticles reacted with NH$_3$BH$_3$ in air on the order of $10^{-2}$ g H$_2$ s$^{-1}$ g$^{-1}$ Ni, presumably due to the oxidation of the nanoparticles. Kalidindi et al. report a very high rate of hydrogen generation from NH$_3$BH$_3$ using freshly synthesized Cu$_2$O nanoparticles prepared via the solvated metal atom dispersion method.$^{69}$ The authors vaporized copper metal, condensed the metal vapor in the presence of 2-butane at 77 K, then purged the Cu-butane colloid with oxygen for 30 min to obtain the Cu$_2$O nanoparticles. Assuming the normalization procedures used by the authors in the presentation of their data is correct, then the data support a value of 0.05 g H$_2$ s$^{-1}$ g$^{-1}$ Cu$_2$O, one of the highest values for controlled hydrogen generation reported to date.

**Nanoparticle photocatalysts for water splitting**

The majority of work focused on developing nanoscale catalysts for hydrogen generation is found here, under the topic of photocatalysts. The number of reports is in the thousands and a careful review of the field is beyond the scope of this article. The work has been well documented in a number of recent reviews.$^{84-89}$ Including
a review in this journal by Kitano and Hara detailing heterogeneous photocatalytic water splitting. A recent report by Maeda et al. describes nicely the processes by which semiconductor photocatalytic nanomaterials can be used to generate hydrogen; they describe a single nanoparticle system, a dual nanoparticle system, and a more complex modular system that includes light-harvesting antenna functionality (Fig. 7). In addition, the authors provide experimental data for a series of GaN:ZnO nanomaterials modified with co-catalysts. The best activity for hydrogen generation using the visible spectrum reported by these authors was for a GaN:ZnO nanomaterial with Rh and Cr2O3 added through photodeposition. The rate was reported as 179 μmol H2 h⁻¹ for 0.15 g of catalyst using a 450 W high-pressure Hg lamp filtered to provide excitation >400 nm. The quantum efficiency of this catalyst was not reported. The hydrogen generation rate converts to 783 g H2 s⁻¹ g⁻¹ catalyst for the conditions employed by the authors, which is five orders of magnitude lower than the best values reported in the previous two sections. This should not be taken as a negative, but simply as the current state of a growing and highly important field. We should expect significant improvements in yield and rate of hydrogen generation as researchers work to develop these catalysts. Areas of research include the development of new catalyst materials, homogeneous catalysts systems, and systems that can utilize the full solar spectrum.

**Conclusions**

This Highlight article has summarized some of the more recent work involving nanoparticles for hydrogen generation. Significant progress has been made in the ability to generate hydrogen at high rates and with good efficiencies using the stored chemical potential of nanoaluminium and high hydrogen content materials such as sodium borohydride and ammonia borane catalyzed by nanoparticles. The performance metrics of these materials are likely sufficient for some specialized applications of power generation (i.e., emergency and/or portable power). The future of hydrogen generation technologies lies in the development of photocatalysts that can effectively harness the...
abundant and free energy provided by the sun. Coupled with the relative abundance of water, photocatalytic hydrogen generation offers the best solution for a portable or transportable renewable fuel. Should this be accomplished, the work presented in the first two sections could then become the storage, transport, and delivery technologies necessary to implement and support a true hydrogen economy.

References