

Review Article

Nanomaterials for Hydrogen Storage Applications: A Review

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Nanomaterials have attracted great interest in recent years because of the unusual mechanical, electrical, electronic, optical, magnetic and surface properties. The high surface/volume ratio of these materials has significant implications with respect to energy storage. Both the high surface area and the opportunity for nanomaterial consolidation are key attributes of this new class of materials for hydrogen storage devices. Nanostructured systems including carbon nanotubes, nano-magnesium based hydrides, complex hydride/carbon nanocomposites, boron nitride nanotubes, TiS₂/MoS₂ nanotubes, aluminates, polymer nanocomposites, and metal organic frameworks are considered to be potential candidates for storing large quantities of hydrogen. Recent investigations have shown that nanoscale materials may offer advantages if certain physical and chemical effects related to the nanoscale can be used efficiently. The present review focuses the application of nanostructured materials for storing atomic or molecular hydrogen. The synergistic effects of nanocrystallinity and nanocatalyst doping on the metal or complex hydrides for improving the thermodynamics and hydrogen reaction kinetics are discussed. In addition, various carbonaceous nanomaterials and novel sorbent systems (e.g. carbon nanotubes, fullerenes, nanofibers, polyaniline nanospheres and metal organic frameworks etc.) and their hydrogen storage characteristics are outlined.

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1. INTRODUCTION

The increase in threats from global warming due to the consumption of fossil fuels requires our planet to adopt new strategies to harness the inexhaustible sources of energy [1, 2]. Hydrogen is an energy carrier which holds tremendous promise as a new renewable and clean energy option [3]. Hydrogen is a convenient, safe, versatile fuel source that can be easily converted to a desired form of energy without releasing harmful emissions. Hydrogen is the ideal fuel for the future since it significantly reduces the greenhouse gas emissions, reduces the global dependence on fossil fuels, and increases the efficiency of the energy conversion process for both internal combustion engines and proton exchange membrane fuel cells [4, 5]. Hydrogen used in the fuel cell directly converts the chemical energy of hydrogen into water, electricity, and heat [6] as represented by



Hydrogen storage cuts across both hydrogen production and hydrogen applications and thus assumes a critical role in initiating a hydrogen economy [7–10]. For catering today's fuel cell cars, the onboard hydrogen storage is inevitable and an integral part of the system to be reengineered [11, 12]. The critical properties of the hydrogen storage materials to be evaluated for automotive applications are (i) light weight, (ii) cost and availability, (iii) high volumetric and gravimetric density of hydrogen, (iv) fast kinetics, (v) ease of activation, (vi) low temperature of dissociation or decomposition, (vii) appropriate thermodynamic properties, (viii) long-term cycling stability, and (ix) high degree of reversibility. All the said properties greatly demand from us to understand the fundamental mechanistic behavior of materials involving catalysts and their physicochemical reaction toward hydrogen at an atomic or molecular scale.

Various hydrogen storage systems (see Figure 1), such as metal hydrides, complex hydrides, chemical hydrides, adsorbents and nanomaterials (nanotubes, nanofibers,

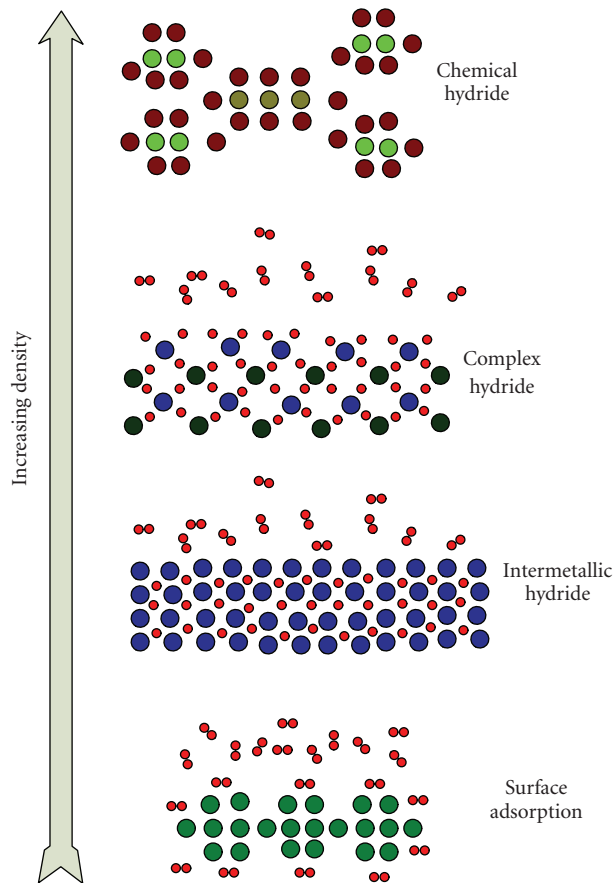


FIGURE 1: Hydrogen storage density in physisorbed materials, metal/complex, and chemical hydrides.

nanohorns, nanospheres, and nanoparticles), clathrate hydrates, polymer nanocomposites, metal organic frameworks, and so on [13–19], have been explored for onboard hydrogen storage applications. However, none of these materials qualifies and fulfill all hydrogen storage criteria such as (1) high hydrogen content (>6.0 wt.%), (2) favorable or tuning thermodynamics ($30\text{--}55$ kJ/mol H_2) (3) operate below 100°C for H_2 delivery, (4) onboard refueling option for a hydrogen-based infrastructure, (5) cyclic reversibility (~ 1000 cycles) at moderate temperatures, and so on. Among the various hydrogen storage systems, the concept of nanomaterials and their wide applications for energy storage [20] are discussed in the present paper.

2. NANOSTRUCTURED MATERIALS

Nanostructured materials have potential promise in hydrogen storage because of their unique features such as adsorption on the surface, inter- and intragrain boundaries, and bulk absorption [21, 22]. Nanostructured and nanoscale materials strongly influence the thermodynamics and kinetics of hydrogen absorption and dissociation by increasing the diffusion rate as well as by decreasing the required diffusion length. Additionally, the materials at the nanoscale offer the possibility of controlling material tailoring parameters

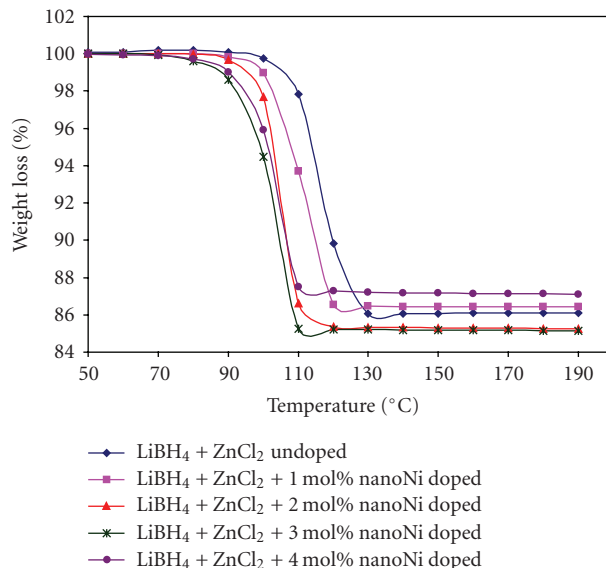


FIGURE 2: TGA curves for the $\text{LiBH}_4 + 1/2 \text{ZnCl}_2$ undoped and X mol% nano-Ni doped system ($X = 1, 2, 3, 4$).

independently of their bulk counterparts. They also lead to the design of light weight hydrogen storage systems with better hydrogen storage characteristics.

2.1. Nanocatalyst doping in complex borohydrides

Advanced complex hydrides that are light weight, low cost, and have high-hydrogen density are essential for onboard vehicular storage [8, 23, 24]. Some of the complex hydrides with reversible capacities achieved are Alanates [25, 26], Amides [27, 28], Borohydrides [29–31], and combinations thereof [32, 33]. The challenging tasks to design and develop the complex hydrides mandate an optimization and overcoming of kinetic and thermodynamic limitations [18, 34]. The enhancement of reaction kinetics at low temperatures and the requirement for high hydrogen storage capacity (>6.0 wt%) of hydrogen storage materials could be made possible by catalytic doping. If nanostructured materials with high surface area are used as the catalytic dopants, they may offer several advantages for the physicochemical reactions, such as surface interactions, adsorption in addition to bulk absorption, rapid kinetics, low-temperature sorption, hydrogen atom dissociation, and molecular diffusion via the surface catalyst. The intrinsically large surface areas and unique adsorbing properties of nanophase catalysts can assist the dissociation of gaseous hydrogen and the small volume of individual nanoparticles can produce short diffusion paths to the materials' interiors. The use of nanosized dopants enables a higher dispersion of the catalytically active species [35] and thus facilitates higher mass transfer reactions.

Figure 2 depicts the thermogravimetric weight loss profiles of the new complex borohydride ($\text{LiBH}_4 + 1/2 \text{ZnCl}_2$) system undoped and doped with different nanocatalyst (e.g., nano-Ni) concentrations.

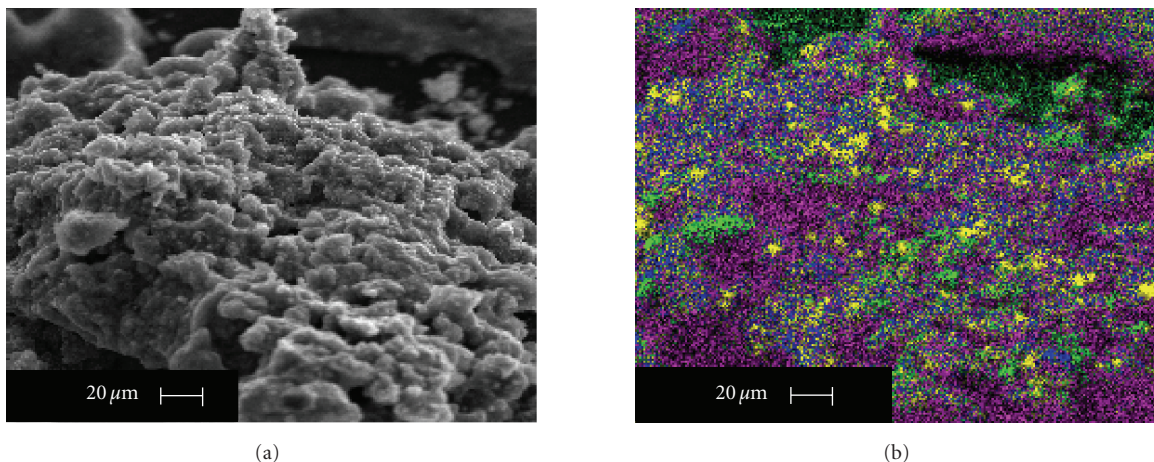


FIGURE 3: (a) SEM imaging and (b) EDS mapping of the sample $\text{LiBH}_4 + 1/2 \text{ZnCl}_2 + 10 \text{ mol\% nano-Ni}$ (mapping elements—green: oxygen, yellow: nano-Ni, blue: chlorine, purple: zinc).

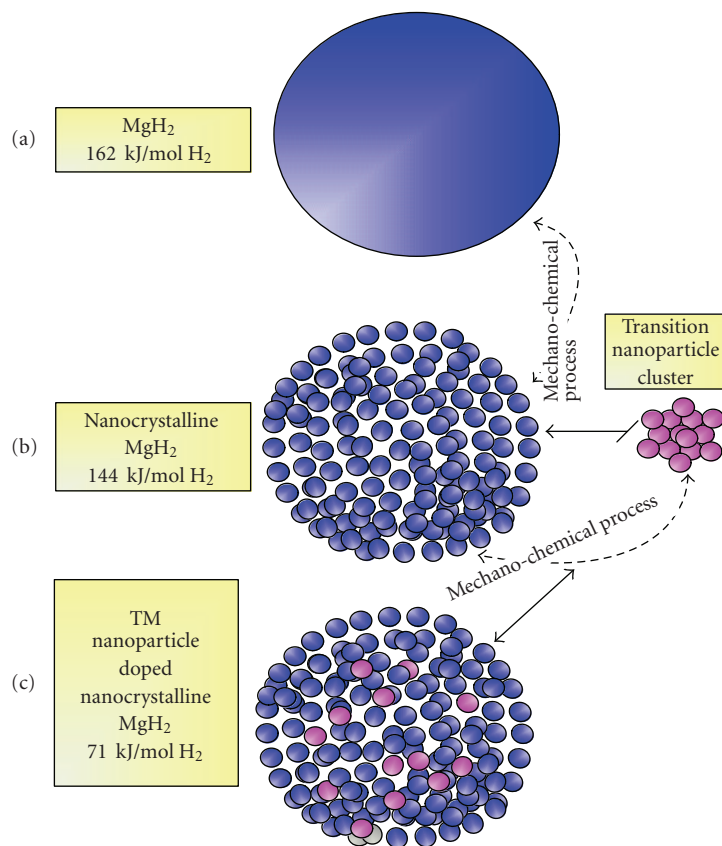


FIGURE 4: Conceptual model of MgH_2 cluster (a) plain, (b) nanocrystalline, and (c) nanocatalyst-doped materials.

The $\text{Zn}(\text{BH}_4)_2$, as obtained from the mechanochemical reaction of $(\text{LiBH}_4 + 1/2 \text{ZnCl}_2)$, exhibits an endothermic melting transition at around $80\text{--}90^\circ\text{C}$ (DSC signals are not shown in the figure) and a clear-cut weight loss occurs due to the thermal hydrogen decomposition at around 120°C . Trial experiments were conducted by introducing different

nanocatalyst (nano-Ni (particle size of $3\text{--}10 \text{ nm}$) obtained from QuantumSphere Inc., Calif, USA) concentrations ($X = 1, 2, 3, 4 \text{ mol\%}$) in this complex system. It is clearly discernible from this figure that nanocatalyst doping helps to lower the temperature of decomposition from 120°C down to 100°C . A concentration of 3 mol\% nano-Ni was found to

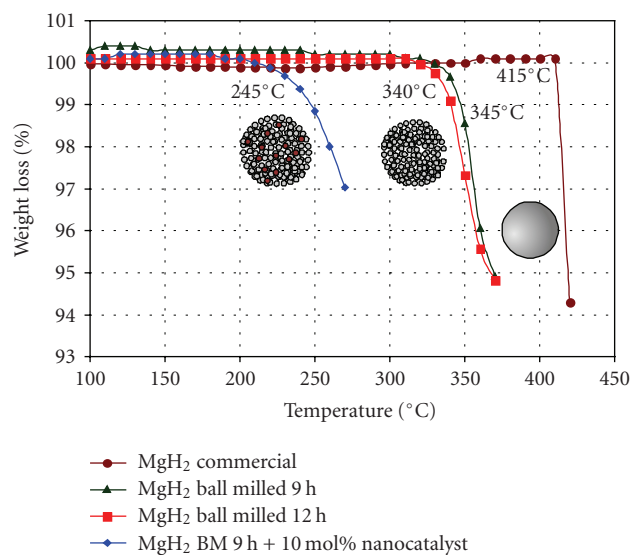


FIGURE 5: TGA curves for the (a) commercial; (b) micro-/nanocrystalline, and (c) 10 mol% nanocatalyst-doped nanocrystalline MgH_2 .

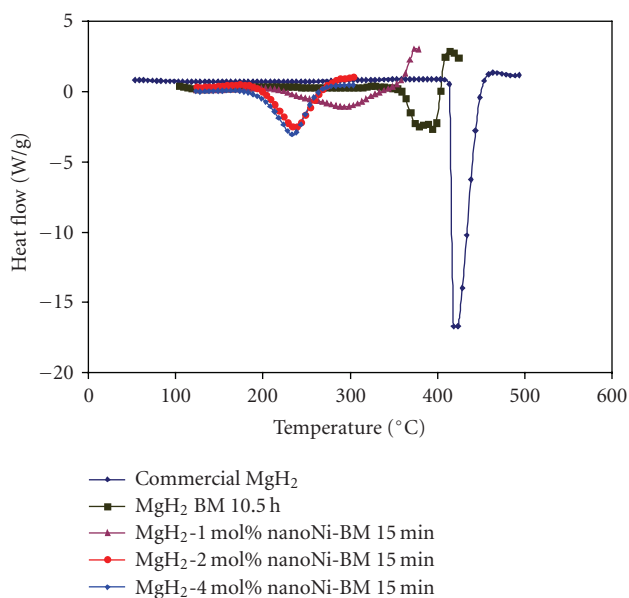


FIGURE 6: DSC profiles of (a) commercial, (b) ball milled for 10.5 hours, and (c) 10 mol% nano-Ni-doped nanocrystalline MgH_2 .

be optimum for the gravimetric weight loss due to thermal decomposition at low temperature. It is also confirmed from the gravimetric analysis that nanocatalyst doping enhances the hydrogen storage characteristics such as reaction kinetics at low-decomposition temperatures (T_{dec}). The microstructures of the nanocatalyst doped complex hydride both in imaging mode and EDS mapping (distribution of different elements) mode as obtained from SEM are shown in Figures 3(a) and 3(b).

2.2. Synergistic behavior of nanocatalyst doping and nanocrystalline form of MgH_2

It is generally known that pristine MgH_2 theoretically can store ~ 7.6 wt.% hydrogen [36]. However, so far, magnesium hydride-based materials have limited practical applications because both hydrogenation and dehydrogenation reactions are very slow and, hence, relatively high temperatures are required [23]. Magnesium hydride forms ternary and quaternary hydride structures by reacting with various transition metals (Fe, Co, Ni, etc.) and thus improved kinetics. Moreover, the nanoscale version of these transition metal particles offers an additional hydrogen sorption mechanism via its active surface sites [36, 37]. In a similar way, the synergistic approach of doping nanoparticles of Fe and Ti with a few mol% of carbon nanotubes (CNTs) on the sorption behavior of MgH_2 has recently been investigated [38]. The addition of CNT significantly promotes hydrogen diffusion in the host metal lattice of MgH_2 due to the short pathway length and creation of fast diffusion channels [39]. The dramatic enhancement of kinetics of MgH_2 has also been explored through reaction with small amounts of LiBH_4 [40]. Though the MgH_2 admixing increases the equilibrium plateau pressure of LiNH_2 [41] or LiBH_4 [29], catalytic doping of these complex hydrides has not yet been investigated. It is generally believed that the role of the CNT/nanocatalyst on either NaAlH_4 or MgH_2 is to stabilize the structure and facilitate a reversible hydrogen storage behavior.

The phenomenon of mechanical milling helps to pulverize the particles of MgH_2 into micro- or nanocrystalline phases and thus leads to lowering the activation energy of desorption [42]. The height of the activation energy barrier depends on the surface elements. Without using the catalysts, the activation energy of absorption corresponds to the activation barrier for the dissociation of the H_2 molecule and the formation of hydrogen atoms. The activation energies of the H_2 sorption for the bulk MgH_2 , mechanically milled MgH_2 and nanocatalyst-doped MgH_2 , are shown in Figures 4(a) and 4(c).

It is undoubtedly seen that the activation barrier has been drastically lowered by nanocatalyst doping which suggests that the collision frequency between the H_2 molecules and transition metal nanoparticles increases with decreasing size of the catalyst. In addition, Figure 4 shows the conceptual model of an MgH_2 nanocluster and the distribution of nanocatalyst over the active surface sites for efficient hydrogen storage.

Recently, we have attempted to establish the above “proof of concept.” Commercial MgH_2 exhibits weight loss due to hydrogen decomposition at higher temperature (e.g., 415°C) (see Figure 5).

However, the mechanochemical milling of MgH_2 introduces defects and particle size reduction. Thus, obtained micro-/nanocrystalline MgH_2 grains show endothermic hydrogen decomposition (see Figure 6) at an earlier temperature of 340°C. In addition, to nanoscale formation, the doping by a nanocatalyst certainly decreases the onset transition temperature by as much as 100°C (Figures 5 and 6).

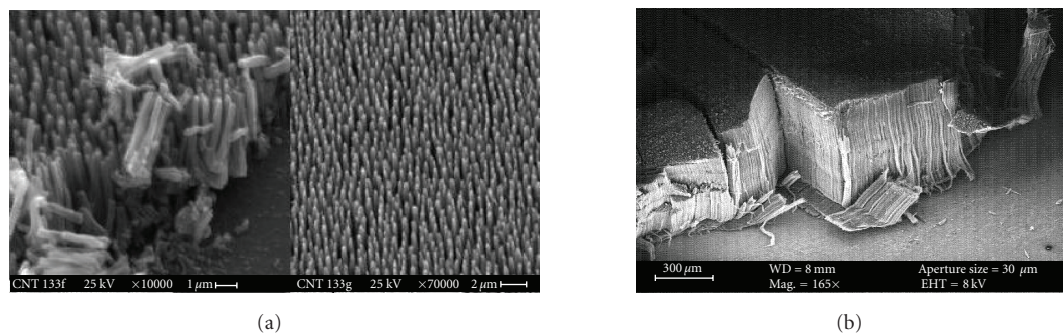


FIGURE 7: SEM micrographs of (a) carbon nanotubes grown by MPECVD and (b) high density of aligned carbon nanotubes.

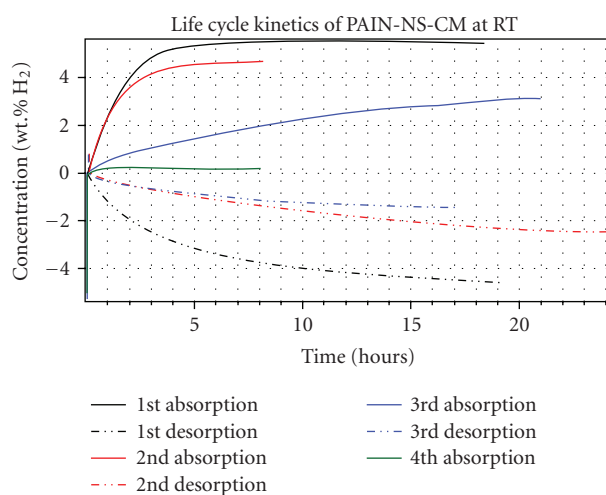


FIGURE 8: Hydrogen sorption kinetics of polyaniline nanospheres at room temperature showing good reversibility in the initial runs.

2.3. Carbonaceous nanomaterials (carbon nanotubes, fullerenes, and nanofibers)

Carbonaceous materials are attractive candidates for hydrogen storage because of a combination of adsorption ability, high specific surface area, pore microstructure, and low-mass density. In spite of extensive results available on hydrogen uptake by carbonaceous materials, the actual mechanism of storage still remains a mystery. The interaction may either be based on van der Waals attractive forces (physisorption) or on the overlap of the highest occupied molecular orbital of carbon with occupied electronic wave function of the hydrogen electron, overcoming the activation energy barrier for hydrogen dissociation (chemisorption). The physisorption of hydrogen limits the hydrogen-to-carbon ratio to less than one hydrogen atom per two carbon atoms (i.e., 4.2 mass %). While in chemisorption, the ratio of two hydrogen atoms per one carbon atom is realized as in the case of polyethylene [43–45]. Physisorbed hydrogen has a binding energy normally of the order of 0.1 eV, while chemisorbed hydrogen has C–H covalent bonding, with a binding energy of more than 2–3 eV.

Dillon et al. presented the first report on hydrogen storage in carbon nanotubes [46] and triggered a worldwide tide of research on carbonaceous materials. Hydrogen can be physically adsorbed on activated carbon and be “packed” on the surface and inside the carbon structure more densely than if it has just been compressed. The best results achieved with carbon nanotubes to date confirmed by the National Renewable Energy Laboratory are hydrogen storage density corresponding to about 10% of the nanotube weight [47].

In the present study, carbon nanotubes have been successfully grown by microwave plasma-enhanced chemical vapor deposition (MPECVD), a well-established method [46, 47]. Figure 7(a) represents the as-grown carbon nanotubes on a substrate using optimized processing conditions such as temperature, gas flow, gas concentrations, and pressure. Aligned nanotubes, as seen in Figure 7(b), have been grown to ensure uniformity in the nanotubes’ dimensions. Various seed materials have been investigated to grow carbon nanotubes and attempted to determine any effect on the hydrogen sorption capacities.

Fullerenes, on the other hand, a new form of carbon with close-caged molecular structure were first reported by Kroto et al. in 1985 [48]. It is a potential hydrogen storage material based on the ability to react with hydrogen via hydrogenation of carbon-carbon double bonds. The theory predicts that a maximum of 60 hydrogen atoms can be attached to both the inside (endohedrally) and outside (exohedrally) of the fullerene spherical surface. Thus, a stable $C_{60}H_{60}$ isomer can be formed with the 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. However, this reaction is not possible because it requires high temperature, about 823–873 K [49]. Solid C_{60} has face-centered cubic lattice at room temperature and its density is ~ 1.69 g/sm³. Molecules are freely rotating due to weak intermolecular interaction. Fullerene is an allotropic modification of carbon. Fullerene molecules are composed of pentagons and hexagons whose vertexes contain carbon atoms. Fullerene, C_{60} , is the smallest and the most stable structure (owing to high degree of its symmetry).

Hydrogen can be stored in glass microspheres of approximately 50 μ m diameter. The microspheres can be filled with

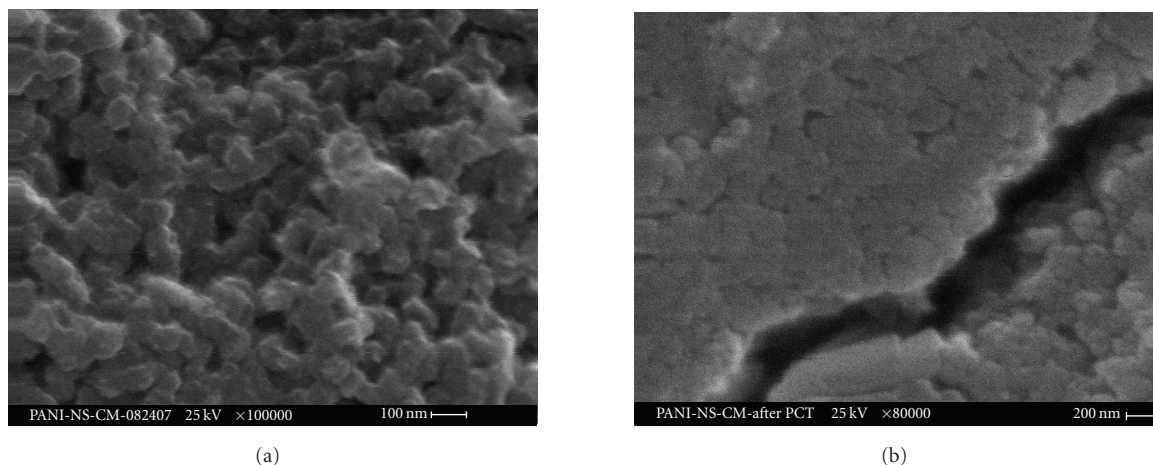


FIGURE 9: SEM images of polyaniline nanospheres (a) as-prepared and (b) after hydrogen sorption cycles.

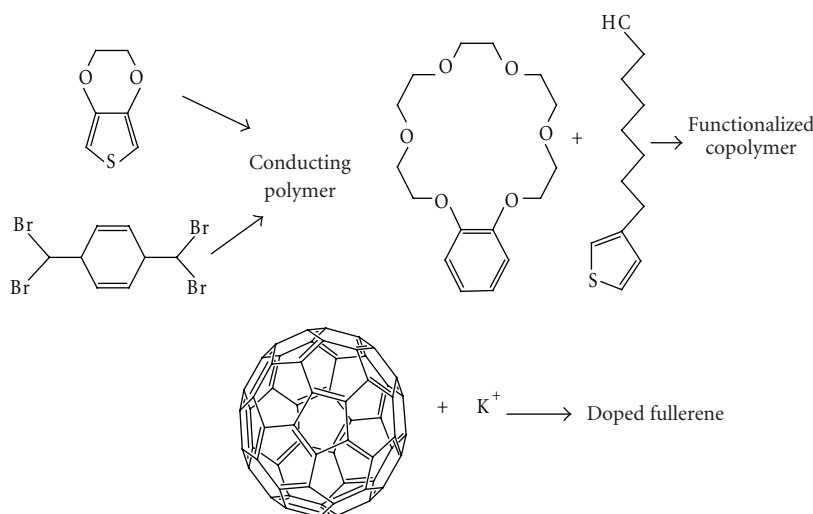


FIGURE 10: Schematics for the development of functionalized conducting polymer.

hydrogen by heating them to increase the glass permeability to hydrogen. At room temperature, a pressure of approximately 25 MPa is achieved resulting in storage density of 14% mass fraction and $10 \text{ kg H}_2/\text{m}^3$ [49]. At 62 MPa, a bed of glass microspheres can store $20 \text{ kg H}_2/\text{m}^3$. The release of hydrogen occurs by reheating the spheres to again increase the permeability.

2.4. Nanocomposite conducting polymers

Nanocomposite material consisting of a polyaniline matrix, which can be functionalized by either catalytic doping or incorporation of nanovariants, is considered to be a potential promise for hydrogen storage. It was reported that polyaniline could store as much as 6–8 wt% of hydrogen [50], which, however, another team of scientists could not reproduce [51]. Yet another recent study reveals that a hydrogen uptake of 1.4–1.7 wt% H_2 has been reported for

the polymers of intrinsic microscopy [52]. Polyaniline is a conductive polymer, with conductivity on the order of 10^0 S/cm . This is higher than that of typical nonconducting polymers, but much lower than that of metals [53]. In addition to its conductivity, polyaniline emeraldine base (EB) is very simple and inexpensive to polymerize. It is because of this simplicity that it was chosen as a matrix material for the nanocomposite structure.

Figure 8 represents the hydrogen sorption kinetics of polyaniline nanospheres at room temperature. From this figure, it is discernible that the hydrogen uptake and release of $\sim 4.0 \text{ wt.}\%$ occurs in the initial run. However, during the consecutive cycles, the hydrogen storage capacity and kinetics were decreased. The SEM microstructure of polyaniline nanospheres are shown in Figure 9(a). Uniform cluster sizes of 50–100 nm are widely distributed over the surface. The microstructures after hydrogen sorption cycles exhibit microchannels or microcrack formation (see Figure 9(b)).

This correlates very well with effective hydrogenation as observed from sorption kinetic profiles (see Figure 8). Further cyclic reversibility and associated mechanistic behavior for hydrogen uptake and release kinetics are still underway.

Functionalization (see schematic Figure 10) has been carried out by the introduction of chemical groups into a polymer molecule or conversion of one chemical group to another group, which leads to a polymer with chemical, physical, or other functions. Functional polymers act as a catalyst to bind selectively to particular species, to capture and transport electric charge or energy, and to convert light into charge carriers and vice versa.

2.5. High-surface area sorbents and new materials concepts

There is a pressing need for the discovery and development of new reversible materials. One new area that may be promising is that of high-surface area hydrogen sorbents based on microporous metal-organic frameworks (MOFs). Such materials are synthetic, crystalline, and microporous and are composed of metal/oxide groups linked together by organic struts. Hydrogen storage capacity at 78 K (-195°C) has been reported as high as 4 wt% via an adsorptive mechanism, with a room temperature capacity of approximately 1 wt% [54]. However, due to the highly porous nature of these materials, volumetric capacity may still be a significant issue.

Another class of materials for hydrogen storage may be clathrates [15], which are primarily hydrogen-bonded H_2O frameworks. Initial studies have indicated that significant amounts of hydrogen molecules can be incorporated into the sII clathrate. Such materials may be particularly viable for off-board storage of hydrogen without the need for high pressure or liquid hydrogen tanks.

3. SUMMARY

Nanostructured materials such as nanotubes, nanofibers, and nanospheres show potential promise for hydrogen storage due to high-surface area, and they may offer several advantages for the physicochemical reactions, such as surface interactions, adsorption in addition to bulk absorption, rapid kinetics, low-temperature sorption, hydrogen atom dissociation, and molecular diffusion via the surface catalyst. The intrinsically large surface areas and unique adsorbing properties of nanophase materials can assist the dissociation of gaseous hydrogen, and the small volume of individual nanoparticles can produce short diffusion paths to the materials' interiors. The use of nanosized dopants enables a higher dispersion of the catalytically active species, and thus facilitates higher mass transfer reactions. Nanocomposites based on polymer matrix and functionalized carbon nanotubes possess unique microstructure for physisorption of hydrogen atom/molecule on the surface and inside the bulk. This review paper discussed briefly various nanomaterials for hydrogen storage and also presented hydrogen uptake and release characteristics for polyaniline nanospheres at room temperature.

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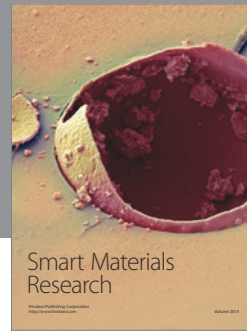
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