

Metal Hydrides and Graphene Supports

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Energy production, distribution, and storage remain paramount to a variety of applications that reflect on our daily lives, from renewable energy systems, to electric vehicles and consumer electronics. Hydrogen is the sole element promising high energy, emission-free, and sustainable energy, and metal hydrides in particular have been investigated as promising materials for this purpose. While offering the highest gravimetric and volumetric hydrogen storage capacity of all known materials, metal hydrides are plagued by some serious deficiencies, such as poor kinetics, high activation energies that lead to high operating temperatures, poor recyclability, and/or stability, while environmental considerations related to the treatment of end-of-life fuel disposal are also of concern. Graphene is a 2D material with very appealing properties, highlighting its potential use as support for various reactive species, including metals and metal hydrides. By embedding hydride species into graphene supports, valuable nanocomposites can be obtained with direct use for energy storage applications.

Keywords: graphene ; energy storage ; hydrogen ; metal hydrides ; composites

1. Metal-Decorated Graphene

An important strategy for tuning graphene for energy storage applications has been to decorate the support with metals or clusters of metals. Among the investigated materials are metallized siligraphene nanosheets (SiG) with varying light metal decorations (Li, Na, K, Mg, Ca, Sc, Ti) [1], metal-decorated graphene (Li, Na, Mg)/G, DFT study [2], or K in K @ B-substituted G [3]. Given the potential of AlH₃ for hydrogen storage, Al-doping has also been explored in Al/G composites [4] [5], Al_n clusters supported by coronene and graphene G (DFT study) [5], and Al/Si –SLG (SLG, single layer graphene + Si +Al) [6].

Palladium is well known for its high affinity for H₂, and many studies have been devoted to the theoretical modelling of this interaction; Pd-decorated N-doped G, DFT study [7]; Pd_n @ G (n = 1–4) in BC3 variant [8], and Cu- and Pd-decorated G, DFT study [9]. Titanium and its clusters have also been investigated: Ti₃ clusters [10]; Ti₄—decorated B/N-doped G [11]; Ti₄ & Ni₄—doped G nanoplatelets [12]; and Ti–Al subnanoclusters on G [13].

Most reports, however, focus on Mg-doped porous carbonaceous materials, such as Mg@ G flake nanocomposites (H₂ generation from H₂O) [14], Mg@graphite for comparison purposes [15], Mg@rGO layers [16][17], Mg@Heteroatom–doped G [18], Mg@B–doped G [19], and Mg/defected GO [20]. Additionally, various alloys have also been studied for graphene supports: Mg alloy @rGO–V₂O₃ [21], rGO–EC@AB5 hybrid material (EC = ethyl cellulose, AB5 = La(Ni_{0.95}Fe_{0.05})₅) (LNF) [22], or MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}/G nanoplatelets (Mm denotes mischmetals) [23].

2. Mechanistic Insight and Kinetics of H₂...Support Interaction

Pristine graphene can chemically absorb H₂ and its theoretical storage capacity is 7.7 wt.%; the hydrogenated graphene (graphane, (CH)_n, a sp³ hybridized analog of graphene) releases H₂(g) at ~400 °C, with an E_a = 158 kJ/mol (1.64 eV) [24]. While an intriguing material in its pristine form, its thermodynamic parameters make it less feasible for scaling up processes aimed at vehicular applications; however, it is worth noting the similarity of the activation energy deduced for graphane and that of metal hydrides.

The fundamental understanding of the adsorption/desorption mechanism of H₂ in graphene is paramount to developing new materials aimed at this task; a pertinent comparison between physisorption and chemisorption on graphene was reported in 2011, where the physical limitations of G (5 wt.% H₂ storage) were correlated to the entropy contribution TΔS and the large van der Waals distance between two H₂ molecules (0.3 nm), further preventing the increase in gravimetric storage capacity of pristine graphene [25]. The interaction H₂...G was studied by DFT in single- and double-vacancy graphene by Wu et al., with direct implications for the behavior of defected graphene during hydrogenation studies [26]. The mechanism of H₂ interaction with Al-doped porous graphene has been reported by Ao et al., showing by DFT that

Al/G can store up to 10.5 wt.% H₂, with a relatively low H₂ adsorption energy of -1.11 to -0.41 eV/H₂, which would potentially allow hydrogen absorption/desorption near room temperature conditions, in agreement with the findings from the analysis of atomic charges, electronic distribution, and density of states (DOS) of the system [4]. The enhanced interaction was potentially due to the polarization of the adsorbed H₂ molecules.

Akilan et al. have studied by DFT the adsorption of H₂ molecules on B/N-doped defected (5-8-5, 55-77, 555-777 and 5555-6-7777 defects) graphene sheets [27]. The N-atom addition (donor behavior, n-type semiconductor) increases the delocalized electrons, while the B atoms (acceptor, p-type semiconductor) increase the localized electrons in the considered system. The most efficient adsorption was modelled when the H₂ molecule approached the sheet in a perpendicular direction (-80 meV), while the least efficient interaction was observed in a parallel orientation (-9 meV), while the delocalized electron density was higher on the fusion points of the pentagonal and hexagonal rings and would therefore enhance H₂ adsorption [27]. Another supporting DFT study of H₂ storage on TM-doped defected graphene (TM = transition metal) revealed that in the case of TM = Sc, the 555-777/Sc structure doped with Sc showed the maximum H₂ capacity, with H₂ binding energies in the range 0.2–0.4 eV/H₂ [28].

The advances regarding TM-loaded Mg-based alloys/G have been reviewed recently [29]. A few important points are attributed to graphene: It can inhibit grain growth, thus aiding the overall cyclability of the composite, and it can (co-)catalyze the hydrogenation process, in which the electron transfer between Mg and C plays a key role [29].

The cyclic behavior of metal hydrides can be affected by issues related to grain growth. This can be partly overcome with the formation of G layers encapsulating MgH₂ to prevent grain growth [30]. In this report, Lototsky et al. used various carbon sources (graphite, AC, MWCNTs, etc.) and showed that the formation of graphene sheets during high-energy reactive ball milling in hydrogen (HRBM) is responsible for the encapsulation of MgH₂, noting an increase in a/d cycling behavior along with a more reduced size of the MgH₂ crystallites (40–125 nm vs. 180 nm in pristine form) [30]. The catalytic role of graphene nanoplatelets (GNP) over H₂ storage kinetics in Mg has been studied by Ruse et al. [31]. The enhancement of more than an order of magnitude was attributed to GNP properties (size, thickness, defect density, and specific surface area), and these can be further tuned to alter H₂ storage kinetics in Mg–GNP nanocomposites [31]. A carbon-neutral, reversible, and sustainable process that produces H₂ is the formate-bicarbonate system, where graphene has also served as a support of Pd and Ru metals [32].

3. Manufacturing Techniques

Several techniques have been utilized to introduce metal catalysts into graphene, synthesizing (nano)composites containing graphene and carbonaceous materials [33]. While ball milling and its variants remain a key technique, other options have been explored: Electrostatic layer-by-layer self-assembled G/MWCNTs [34], Uranium U-decorated G (H₂ and D₂ adsorption) [35], and plasma-assisted milling in Mg@FLG composites (few-layer graphene nanosheets) [36]. Given the remarkable properties of 2D graphene on hydride storing materials, the synthesis of 2D MgH₂ has also been proposed in DFT studies [37].

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