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Investigation of graphene-based systems for hydrogen storage

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ABSTRACT

Todays, environmental impacts as well as depletion of fossil fuels have simulated scientist's efforts to find alternative, renewable, and neat energy resources. Recently, hydrogen has been introduced as a clean and high-density energy resource which has satisfied all foregoing demands. There are many challenges which has been defined in storage sector. Recently, nanomaterials, especially graphene, have been employed in this regard. In this study, the potential of graphene-based materials have been embossed. It has been proved that heteroatoms, especially nitrogen as dopant in graphene nanosheet, assist the Gravimetric hydrogen density (GHD). Also, decorated graphene by both alkali and transition metals (TMs) have shown promise results. Furthermore, dopant-decorated systems have been defined desirable toward higher HSC; e.g. nitrogen-doped Pd decorated graphene has been studied as one of the best hybrid system in this manner. In addition, density functional theory (DFT) has been considered and confirmed the assessment.

1. Introduction

Recently, depletion of fossil fuels has actuated scientists in search of renewable energy resource. Apart from that, several evidences can be progressed for demonstrating the importance of alternative sustainable energy resource in the global energy supply system. One of the major points that should be assigned is the inequity of energy (especially electricity) supply, e.g. several villages in India will likely never be grid-connected due to their remoteness. The other reason that should not be left unmentioned is the high cost of extending the electricity grid to off-grid areas; this requires the use of alternative energy resource such as hydrogen. Moreover, the harmful environmental impacts of conventional energy resources, such as global warming should not be ignored. In order to overcome the aforementioned challenges, according to the report of the European Commission and the US Department of Energy, several countries consider hydrogen as an important alternative energy resource. Therefore, investigation on hydrogen storage, as a key element of hydrogen economy, comes significant. Hydrogen, as environmental friendly resource, possesses high content of energy and can meet the objectives of distributed energy production. Although, several systems have developed for hydrogen production and combustion, most of storage systems have encountered challenges [1–3]. Therefore, investigation on hydrogen storage, as a key element of hydrogen economy, comes significant along with global current and future energy policies. According to the report of International Energy Agency, nanotechnology as a new tool comes as a remedy to hydrogen storage [4,5]. It has assisted GHD through porous substrate as well as extended surfaces [6]. Carbonaceous nanomaterials such as graphyne and graphene can purpose as efficient storage system through development of C-H bonds, physisorption [7]. Graphene nanosheets as a 2-dimension nanostructure offer broad surface area for gas adsorption. Although the structures such as graphyne have developed, some experimental limitations lie ahead. On the other hand, the optimization of theoretical- and experimental-developed efficient systems such as graphene has attracted many attentions.

In this regard, activation of graphene nanosheet is considered as a necessity. Metal particles especially transition metals (TMs) have shown more interest to hydrogen storage [8]. The improvement could be defined as (i) dissociation of molecules to atoms, as catalysis; (2) spillover mechanism [9]. Nair et al. [10] studied the Pd/graphitic carbon nitride as an efficient hydrogen storage system. They found that uniform dispersion and strengthened interaction between Pd and substrate makes efficient hydrogen storage system through catalysis and/or spillover. Also, the doping of heteroatoms has been defined as a decisive factor for estimation of hydrogen storage capacity. Zhang et al. [11] have developed an efficient hydrogen storage system of titanium decorated graphitic carbon nitride. They concluded that the GDH obtained 9.7 wt%; also, the reversibility could be progressed at the temperature range close to practical applications. Therefore, there is high potential for hydrogen to be stored in graphene-based systems. Also, these systems can eliminate the problems associated with the full chemisorption (extreme operational condition and irreversibility) or full physisorption (instability and low efficiency).

Literature review shows that several scientists all over the world are

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examining many structures to find a hydrogen storage system that complies the DOE policies, light and efficient hydrogen reservoir. On the other hand, there is no rich as well as comprehensive reference for scholars. In this investigation, we review the aforementioned concepts and structures in the case of graphene-based hydrogen storage system. The recent researches over hydrogen storage capacity of graphene and its derivatives were considered (Section 2). Also, with the focus on hydrogen storage, optimization treatments such as metal (TM and alkali) decoration (Sections 2.1.1 and 2.1.2), heteroatom doping (Sections 2.2. and 2.2.2) and doping-decoration (Sections 2.2.1, 2.2.2.1, and 2.2.2.2) have been reviewed, theoretically and experimentally. Moreover, the multi-component graphene-based systems (Section 2.3.) were considered.

2. Graphene and usual derivatives

Density functional theory (DFT) as a theoretical method has become a valuable tool. In fact, it can predict the hydrogen bond capacity in various conditions. It has greatly expanded our understanding of the properties of known hydrides, including electronic structure, hydrogen bonding character, enthalpy of formation, etc [12–14].. In the case of graphene, calculations of the binding capacity of hydrogen in terms of materials microstructure at ambient condition including quantum effects may propose an interesting behavior. Fig. 1 demonstrates the change of energy bonding in the wide range of interlayer gap. There is an optimum in adsorption; round 6 Å of interlayer distance, there is a minimum for bonding energy and maximum for equilibrium constant at ambient condition, simultaneously. Also, Fig. 1 presents desirable proceedings to Gibbs free energy; as the interlayer gap increases binding energy increases too, consequently physisorption overcomes [8].

In the interlayer gap of 6 Å, chemisorption percentage increased, significantly. Thus, hydrogen adsorption can be promoted at ambient conditions [8]. Recently, scientists have simulated hydrogen storage of corrugated graphene to study the chemisorption interactions [15]. They found that GHD of 8% could obtain; fortunately, reversibility was satisfactory. As a further step, they found that control in local curvature of graphene could offer a proper system for hydrogen storage [16]. Also, the environment conditions could be a decisive factor for the hydrogen storage system. It was demonstrated that humid [17], in the form of either humid oxygen or humid air, could propose detrimental effects on the graphene-based hydrogen storage system. Moreover, thermal desorption experiments proved that release of hydrogen could be carried out at relatively low temperature [17]; this can gradually deplete the graphene-based hydrogen reservoir. Graphene derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) can propose as the promise systems to hydrogen adsorption. Obviously, Modification techniques such as doping of heteroatoms and metal

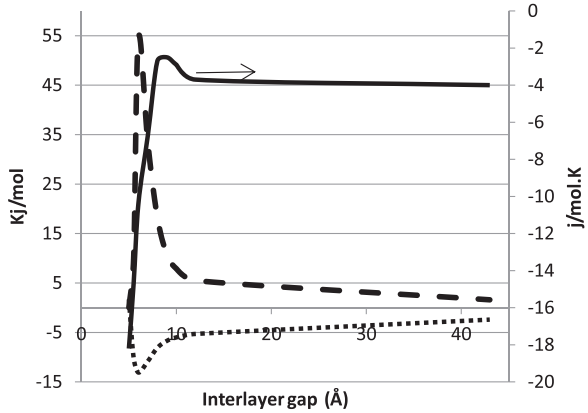

Fig. 1. ab initio calculations result; bonding energy (dot), equilibrium constant (dash) and Gibbs free energy (line) in term of interlayer gap.

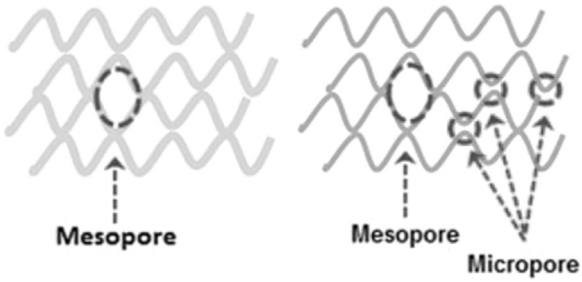

Fig. 2. Graphite oxide exfoliation: [left] sample (I); [right] sample (II) (adoption from ref [20].).

decorating can optimize adsorption parameters such as enthalpies and surface area [18].

Functional groups especially oxygen-containing groups can contribute on hydrogen adsorption through Hydrogen bonds which is stronger than simple Van der Waals [18].

The existence of the groups on the surface, active sites, and the edges of the nanosheets can moderate conditions to accommodate chemical species such as metal particles and eventually boost the GHD. For example, immobilization of titanium particles in graphene oxide could interact with surface hydroxyl groups and improve the GHD, compared to initial [19]. In fact, synergy effect of oxygen-containing groups and metal particles enhanced the GHD. Also, thermal treatments have been defined impressive on the GHD. Guo et al. [20] examined a hierarchically thermal exfoliation of graphite oxide. The procedure was performed by heating in vacuum at 150 °C (I) and followed at 600 °C (II) in Ar atmosphere. Characterizations demonstrated the existence of just mesopores in the case of the sample (I) while both micro- and mesopores were recognized for the sample (II) (Fig. 2).

The measurement revealed that sample (I) could achieve just 37% of GHD of (II) (4 wt%). The improvement is ascribed to the porous nature which offers a high void volume that could be charged for hydrogen uptake. As we see in the previous study, moderate annealing could not be efficient for untwining of nanosheets. On the other hand, graphene GDH could vary by treatment method. Recently, scientists investigate the hydrogen storage capacity of graphene samples obtained using graphite oxide thermal-exfoliation (G1). The measurements demonstrated that KOH activation of G1 could improve the available surface area by a factor of 4. This led to maximum GHD of ~5 wt% [21], further value compared to G1, for the broad surface area of 2300 m^2/g. The surface characterizations showed that separation of few-layered graphene in single sheets (and extending surface area) could not be carried out using thermal exfoliation. The broad surface area can ascribe to the significant number of defects, mainly holes, which are capable to prepare interconnected network of pores. Therefore, chemically activation or relatively extreme annealing can improve the GDH. Also, reduced graphene oxide has emerged as one of promise systems. Rajaura et al. [22] studied the effect of interlayer space in graphene-based systems. They employed Modified Hummer method for fabrication of GO and rGO. The hydrogen storage measurements were carried out using high pressure Sievert method at room temperature. Results showed that the GO is capable to uptake higher amount of hydrogen (1.9 wt%), compared to rGO (1.34 wt%). The main reason for higher GDH is that the oxygen functional groups act as spacer between the graphene sheets; these groups increase the amount of hydrogen storage through higher inter-layer gap.

Hydrogenated few-layer graphene as reduced form of graphene oxide, which had been prepared using Birch reaction with lithium in liquid ammonia, was introduced to hydrogen storage. BET characterization demonstrated high surface area. The measurements explained GHD of 5 wt% under excess Li values [23]. It seems rGO storage capacity is lower than GO. In fact, the introduction of oxygen-contain-