Structural and surface modification of carbon nanotubes for enhanced hydrogen storage density

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HIGHLIGHTS

- Functionalization of carbon nanotubes was done using chemical oxidative method.
- Structure and morphology of P-CNTs has been modified after being open acid treatment.
- Sievert's type storage setup is designed, fabricated and installed indigenously.
- CNTs were characterized by SEM, TEM, XRD, Raman and FTIR spectroscopy.
- Storage capacity enhanced due to presence of structural defects in F-CNTs.

GRAPHICAL ABSTRACT
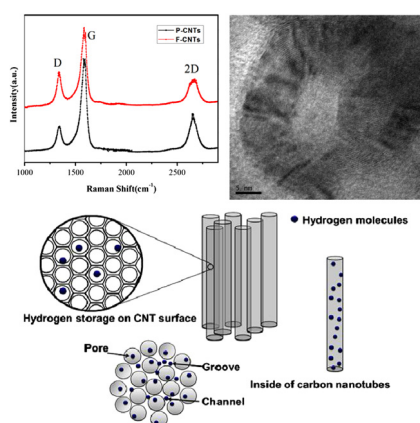
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ABSTRACT

In this paper, we report the synthesis of functionalized carbon nanotubes (F-CNTs) by acid treatment and their hydrogen storage properties. These F-CNTs have been characterized by XRD, FTIR, Raman spectroscopy and electron microscopy techniques. The results show that the structure and morphology of P-CNTs have been modified after the acid treatment. The hydrogen storage capacity was determined by volumetric measurements at room temperature and experimental results showed that the storage capacities of P-CNTs and F-CNTs were 0.65 wt% and 0.89 wt%, respectively. A notable enhancement in hydrogen storage capacity of F-CNTs was observed which could be attributed to the enhanced oxygen functionalities, opening of end caps and presence of surface defects that offered enhanced surface area for hydrogen adsorption. The key results of present research show that structural, morphological and chemical changes are responsible factors to enhance the hydrogen storage density.

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1. Introduction

The ever-increasing worldwide demand of energy consumption, as well as concern about shortage of non-renewable fossil fuels (petroleum, coal, oil and gas) and global warming has inspired scientific community to do intensive research to develop

new alternative sustainable energy sources that can replace carbon based fossil fuels [1]. There are number of alternative energy sources such as solar, wind, ocean, geothermal and hydrogen [2]. Hydrogen is one of the potential green fuels because it is lightweight, eco-friendly, renewable, and four times more efficient than petroleum [3,4]. For the utilization of molecular hydrogen as energy carrier, its production, storage and transportation crucial. Hydrogen storage is one of the major challenges because hydrogen is present in the gaseous form in ambient condition. Hydrogen is the lightest gas in the atmosphere. Hydrogen gas can be stored as (i) pressurized gas, (ii) cryogenic liquid, (iii) solid fuel as chemical (metal hydrate) or physical combination (carbon material) [5]. All the storage methods are discussed in the following reviews [6,7]. The cryogenic hydrogen storage requires cryogenic unit to maintain the temperature that makes it an energy consuming process. The high pressure hydrogen storage requires high pressure and high mechanical strength piston pump. Although each of above storage methods have some advantages but none of them satisfy the size, efficiency, weight, and safety necessities for own transportation vehicle [8]. Solid fuel by means of physical combination in which hydrogen is physically bonded to the surface of potential materials is another alternative for hydrogen storage.

Carbon is one of the adsorbent for gases because these materials demonstrate unusual properties with highly spongy structure and the existence of specific interfaces among the carbon atoms and hydrogen gas [9–11]. The properties of carbon such as high mechanical strength, long life, efficient heat transfer coefficient, fast thermodynamics kinetics (quick uptake and release) make it a desirable material for hydrogen storage. In addition, carbon materials have the advantage of being lighter than the inorganic compounds that are available in the market [12–14]. In 1991, Iijima et al. added a new member of carbon family, namely carbon nanotubes that have the ability of high hydrogen storage density [15]. The variety of carbon nanostructured materials, such as multiwalled carbon nanotubes [10], single walled carbon nanotubes [11], graphene based derivative [14] and other varies carbon [13] materials have been investigated experimentally as well as theoretically for various energy applications including hydrogen storage. For instance, ammonia boranes have received significant attention in recent years as a source of hydrogen [16]. Sen et al. have extensively investigated various carbon nanocomposite materials for hydrogen generation from ammonia boranes [17–20]. The novel carbon nanomaterials namely CNT, graphene and graphene oxide were mixed with metallic and metallicalloy nanomaterials to prepare the nanocomposites [21,22]. Ruthenium-cobalt alloy nanoparticles-functionalized MWCNTs (RuCo-FMWCNT) composites have been demonstrated to be the best catalyst for the dehydrogenation of dimethylamine borane (100% conversion, turn over frequency 775.28 h^{-1}) [23]. Carbon-metal composites have also been explored for other application including solar cell and organic synthesis [24,25]. Darkrim and Wang groups using computational methods proposed that the hydrogen molecules are absorbed by the carbon structure due to the Van der Waal's force on the surface of the material [26,27]. Cheng et al. reported that storage capacity of carbon nanotube increases by the optimization of CNT diameter, inter-tube spacing and array configuration. They demonstrated that single walled carbon nanotubes can store more than 10.0 wt% hydrogen at 298 K and 10 MPa [28]. Carbon nanotube is one of the most interesting material due to their structural characteristics, such as high theoretical surface area, porosity, high mechanical strength and durability, effective heat transfer, narrow pore size distribution and low mass density [29]. Durgun et al. studied the hydrogen storage capacity theoretically using first principle method and showed transition metals decorated carbon nanotube may bind multiple H_2 molecules which could be correlated with enhanced hydrogen

storage capacity [30]. Zuttle et al. Experimentally investigated the hydrogen absorption through the surface of carbon nanotubes [31]. Hydrogen storage study has been carried out for CNT at 10.5 MP pressure is 0.7 wt% [32] and in CNT film is 8 wt% [33] at room temperature and ambient pressure. Recently, Reddy et al. [34] reported the platinum dispersion on single walled carbon nanotubes enhances the storage capacity. Gayathri et al. have been studied the H_2 adsorption in defected CNTs and reported that hydrogen can be adsorbed on carbon nanotube in two manners physical adsorption and chemisorption [35]. Interconnected carbon nanotubes (CNT) composed a newly diamond-like architecture namely super diamond. It has been designed by tunable pores and controlling the location of defects. The hydrogen storage properties were studied thoroughly via ab-initio and Grand Canonical Monte Carlo simulations and results showed the gravimetric capacity of 20% at 77 K and can reach the high value of 8% at room temperature [36]. Sharma et al. Showed a comparative study of hydrogen storage capacity of GO and Go-PANI nanocomposite and reported the GO-PANI nanocomposite has low storage capacity in comparison to GO [37]. Interlayer spacing, functional group and defect density also play a major for enhance the hydrogen storage density [38,28].

Yildrim etal. studied the hydrogen storage capacity theoretically and predict the functionalized the carbon nanotube with Sc, V and Ti holds high theoretical gravimetric densities of 9.8, 9.2 and 7.8 wt% respectively [39]. However, Liu et al. reported the 2.9 wt% hydrogen storage capacity of hybrid GO-MWCNTs nanocomposites [40]. Ruoff etal.synthesized the graphene like nanosheets reduction of exfoliated graphite and studied the hydrogen storage behavior [41]. Similarly, Kim et al. thermally reduced the graphene oxide, note the hydrogen storage capacity, and explore the functional group play a major role to enhance the hydrogen storage [42]. Rao et al. study the effect of acid treatment of CNTs and their hydrogen storage behavior [43]. Cheng et al. activated CNT via various chemical and physical techniques and report the opening the defective site and surface modification after activation a major way to enhance the modified carbon nanotubes [44]. Nanostructure graphite was prepared by mechanical milling under hydrogen atmosphere and the hydrogen storage performance was recorded [45]. A high hydrogen storage capacity of graphene, nitrogen-doped graphene and Pd decorated nitrogen-doped hydrogen exfoliated graphene nanocomposite is demonstrated under moderate temperature and pressure conditions [46]. High-pressure hydrogen sorption isotherms were investigated on by thermally reduced GP (TR-GO), chemically reduced GO (CR-GO) and graphene sheets decorated with Fe nanoclusters (Fe-GS) [47]. Li and K doped CNTs can hold 20 wt% and 14 wt% hydrogen at moderate or room temperatures, respectively, under ambient pressure [48]. The high hydrogen-uptake capacity of these systems may be derived from the special open-edged, layered structure of the carbon nanotubes and used carbon precursor source and catalysis. G.E. Froudakis et al. investigate the hydrogen storage capacity in silicon–carbon nanotube using Ab initio simulation and report the hydrogen storage capacity 3.6 wt% at high pressure [49]. M. Rodriguez et al. synthesis the graphite nanofiber by dissociation of carbon containing gas on metal surface and synthesis the graphite nanofiber and report the hydrogen storage behavior [50]. The earlier reported hydrogen uptake capacity and some related parameters of carbon nanostructures have been summarized in Table 1.

Many reports stated above used more than one-step for the activation of CNTs for hydrogen storage. Aiming towards simple activation procedure for CNTs, current research focus on enhancing the hydrogen storage density economically in graphene based derivatives. The activation can be achieved from different chemical and physical techniques, which results in increasing porosity, active sites, interlayer spacing and defects in the structure [51,52].