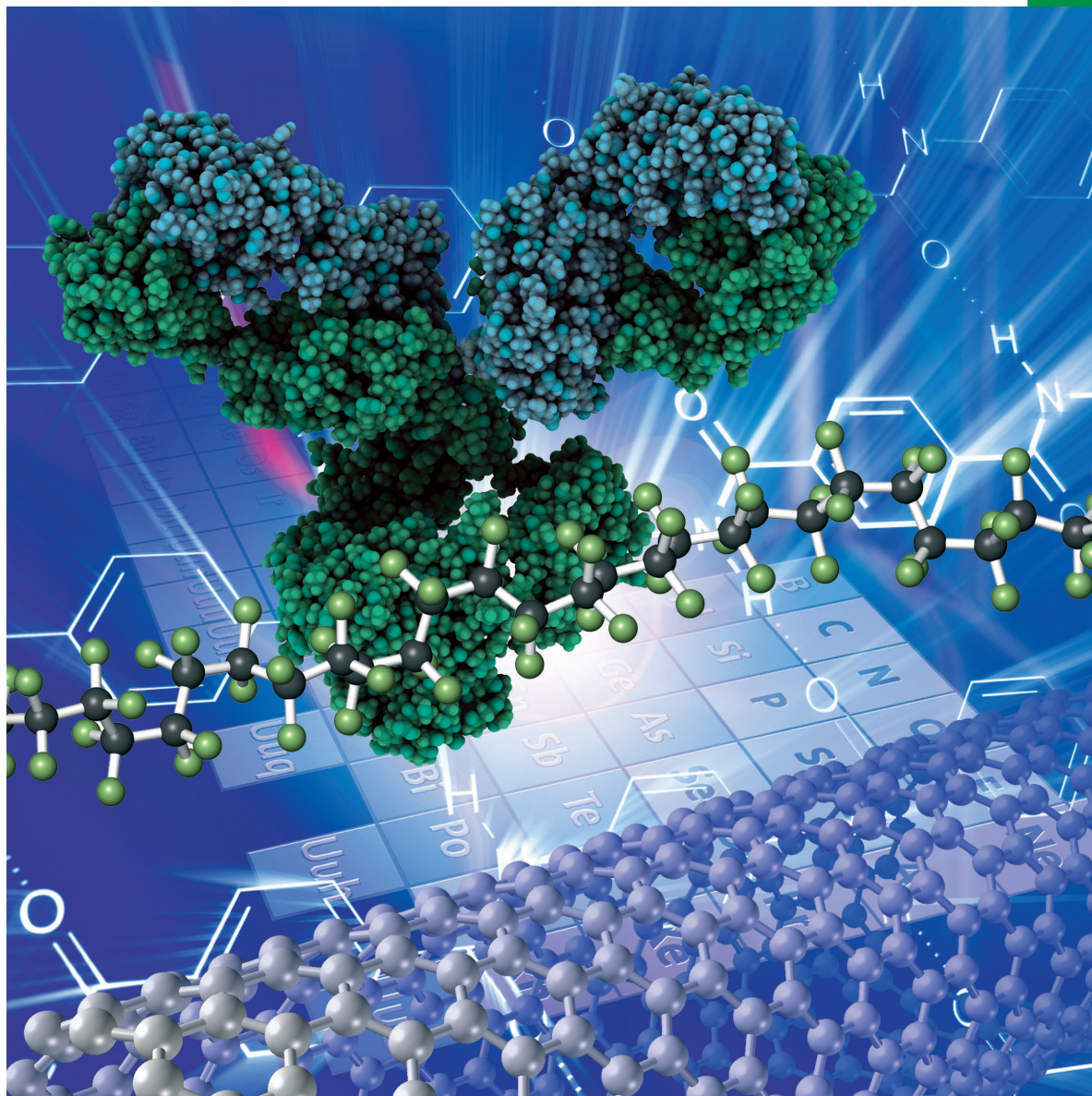


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Enhanced Room-Temperature Synthesis of Li@f-MWCNTs for Hydrogen Storage Application

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The adsorption capacities of hydrogen in Li decorated MWCNTs (Multi Walled Carbon Nano Tubes) i.e. Li@f-MWCNTs was examined at 70 bar pressure at 253 K and 298 K temperatures. The Experimental conditions were altered by changing the concentrations of metals and solvents such as Dimethyl formamide (DMF), Triethyl amine (TEA) and Water to facilitate the adsorption/desorption of Hydrogen. TEM and SEM were used to study morphology and their structures. At different

experimental conditions i.e. 70 bar pressure and 253 K, the adsorption isotherms revealed that 1.13 wt% (DMF), 0.85 wt% (TEA) and 0.63 wt% (water), of hydrogen uptake capacities, was achieved by Li@f-MWCNTs. In comparison with 298 K, at 253 K two to three-fold increase of hydrogen storage capacity was found in all samples. Additionally, fourfold increase in hydrogen storage capacities was found in comparison with pristine materials.

1. Introduction

Energy is considered as one of the significant factors for any country's economic growth. In a scenario of continuously diminishing fossil fuels and growing demand for sustainable energy, hydrogen fulfils the energy needs as a fuel. Hydrogen is deemed as an ideal substitute to the current fossil fuels as it is light in weight, regenerative in nature, largely available and eco-friendly.^[1] Hydrogen possesses high energy per mass and upon its combustion, the obtained by-product is water. Hence it operates as a clean carrier of energy thereby reducing the emissions of greenhouse gases.^[2] But the hydrogen technology faces a major setback in terms of Hydrogen storage, especially for on-board transportation. The storage of hydrogen needs to be efficient, safe and compact.^[3] This is possible only by solid-state storage of hydrogen through adsorption on materials. The hydrogen in solid form merges with materials by chemisorption/physisorption.^[1] This is believed as the safest technique of hydrogen storage.^[4] Moreover, for storing hydrogen in diverse materials for on-board applications, the technical objectives established by the US Department of Energy (DOE) should be satisfied. The goal for gravimetric hydrogen storage capacity is 5.5 wt% as established by the DOE for 2020.^[5,6] But the materials abiding by the DOE requisites are limited. Therefore, extensive research has been carried out to identify the materials for storing hydrogen.

The nanomaterials of carbon such as templated carbons, graphene and its allotropes, carbon aerogel, carbon nanotubes (CNTs) etc. have been extensively analysed for hydrogen storage.^[7] The physisorption of hydrogen in porous nanomaterials like zeolites, fullerenes, clathrate hydrates and CNTs is considered extremely efficient and widely approved technique for hydrogen storage.^[2] The material properties like simplicity, porosity, low density, high chemical and thermal stability with economical manufacturing have been attributed for the endorsement of these carbonaceous nanomaterials. It is the CNTs that possess capillary qualities, superior mechanical strength and novel electrical properties apart from the aforementioned characteristics.^[8,9,10] Therefore, they gained popularity among various researchers across the world.

Multi-walled carbon nanotubes (MWCNTs) can effectively store hydrogen at non-cryogenic temperatures and ambient pressures because of chemical stability, tuneable characteristics, low resistivity, high surface area and pore volume and cage-like structure.^[11,12] Hydrogen storage is possible among the graphitic layers, within the tube cavity and interspersing bundles of MWCNTs. Moreover, the parameters like pre-treatments, geometry, purifications, and structure defects influence the effective storage of hydrogen in MWCNTs. But the lack of strong bonding between the molecules of hydrogen and CNTs, allows a maximum of 1 wt% adsorption despite the high surface area of CNTs.^[13] Decorating the CNTs with metal nanoparticles has been considered as an efficient approach for enhancing hydrogen storage efficacy. This improves the interaction of hydrogen substrate with the tubes facilitating spill over of hydrogen to CNTs thereby enhancing the storage capacity. Metal decorated MWCNTs adsorb molecular hydrogen via Kubas interaction (low binding energy) or spill over mechanism via dissociation of H₂ molecules to atomic hydrogen on metal particles (high binding energy).^[14] So the hydrogen uptake capacity, as well as binding energy of M@MWCNTs, can be enhanced after incorporating more dopant.^[15]

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It is reported that there is 5-fold increase (3.5 wt%) in capacity of storing hydrogen in comparison to pristine CNTs. Previous research suggests substantial enhancement of the hydrogen storage capacity of MWCNTs by doping them with various metals like Fe, Ni, Cu, Li, Co and Pd under ambient conditions.^[16,17,18]

Konni et al., 2019 experimented on MWCNTs doped with Fe and Cu at non-cryogenic temperatures and obtained an enhancement in the hydrogen uptake by 2 to 5 times in comparison to pristine MWCNTs. The readings were observed at 253 K and 298 K temperatures respectively for a 70-bar pressure.^[19] But among all of these elements, lithium has higher prospects as it possesses a high nucleation barrier. Previous findings of Cabria et al., 2005 on physisorption energy of hydrogen on CNTs doped with Li suggest a twofold increment in comparison to pristine single-walled carbon nanotubes (SWCNTs).^[20] This has been attributed to transfer of charge between Li and the surrounding graphitic surface. The CNTs doped with Li acts as acidic for attracting the molecules of hydrogen. The strong affinity of sp^2 carbon framework towards electrons, results in easy separation of charge from Li leading to enhanced stabilization of H_2 molecules. Literature supports this effect for Li doped SWCNTs with the capacity of hydrogen storage increasing to 6 wt% at a pressure of 50 bar.^[21] Similar

results were obtained with Li doped MWCNTs which exhibited high chemical stability. They have the ability to adsorb or desorb hydrogen at extreme temperatures (473–673 K). A maximum of 20 wt% capacity of hydrogen storage was exhibited by the Li doped MWCNTs.^[22,23] Many theories on hydrogen storage capacity have been proposed at extreme pressures and cryogenic temperatures but very few have been reported at room temperatures. Except for this outstanding result mentioned above, research across the world does not approve of this. Hence, there is a certain ambiguity in the storage of hydrogen i.e. doped MWCNTs. Therefore, the present study focuses on the evaluation of uptake capacities of hydrogen on Lithium doped MWCNTs at diverse experimental conditions, particularly at non-cryogenic temperatures.

2. Results and Discussion

2.1. Structural and Morphological Studies

Figure 1[a] depicts p-MWCNTs TEM image and the magnified view can be seen in Figure 1[b] the carbon nanotube average diameter is 30 nm. Generally, f-CNTs produced through the techniques of chemical oxidation, exhibit textural changes with substantially reduced tube length, having the structure of open

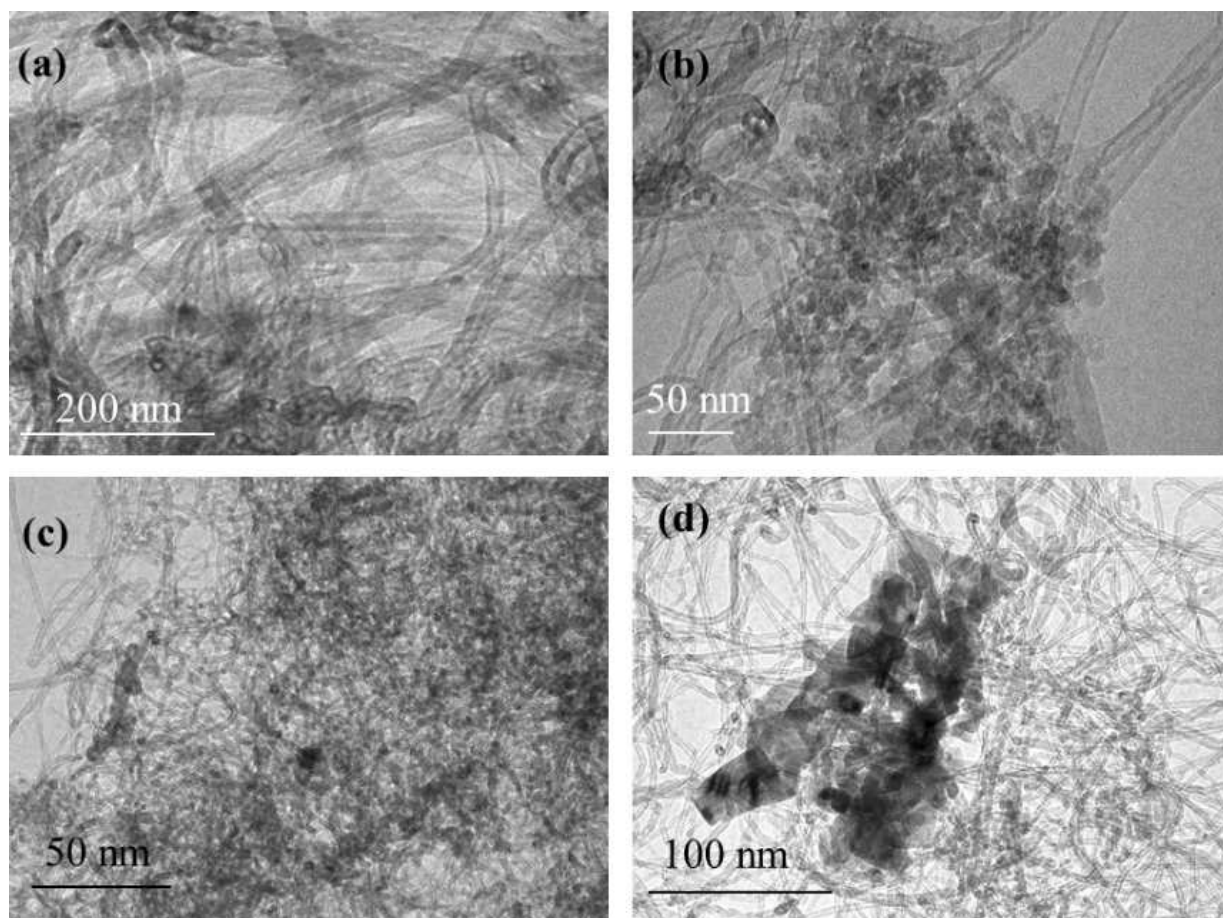


Figure 1. [a] TEM image of p-MWCNTs, [b] Magnified TEM image of p-MWCNTs, [c], [d] TEM images of Li@f-MWCNTs.

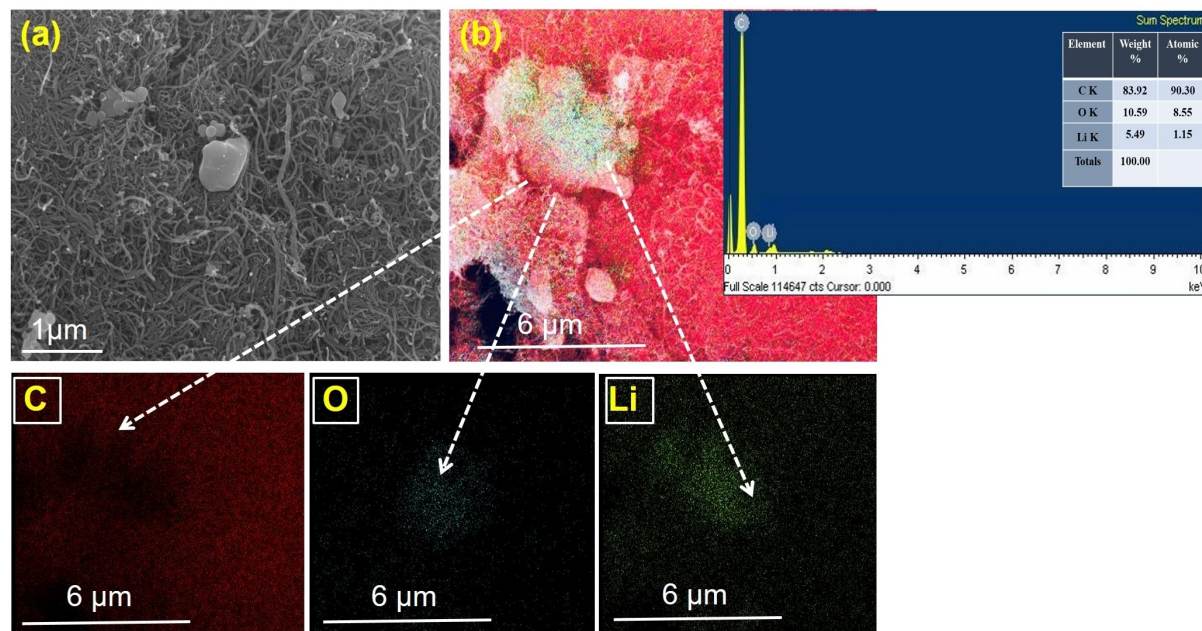


Figure 2. [a] SEM image of Li@f-MWCNTs and [b] Elemental mapping of Li@f-MWCNTs.

end-cap. In our experiment, these parameters are restored within carboxylate f-MWCNTs. Detailed analysis of TEM (Transmission Electron Microscope) images shows that the Morphology and texture of CNTs with end-cap diameters (30 nm) are well reserved in f-MWCNTs. To enhance the sorption capacities and to identify the optimum conditions to produce Li@f-MWCNTs reactions between several chemicals were done by modifying the metal concentrations with media. Figure 1[c] and 1[d] depict TEM images of Li@f-MWCNTs. The presence of lithium is clearly visible on the MWCNTs surface.

As shown in EDS Spectrum Figure 2 [b], weight percentage of Li nanoparticles loaded on MWCNTs is about 5%. Elemental mapping of Li@f-MWCNTs measured through SEM (Scanning Electron Microscope) (Figure 2 [a]) reveals the distribution of C, O, and Li, preliminarily confirmed the presence of the dopant of lithium oxide nanoparticles.

The FT-IR (Fourier-transform infrared spectroscopy) spectra of p-MWCNTs, f-MWCNTs, Li@f-MWCNTs are represented within Figure 3. The two peaks at 2920 cm^{-1} and 2854 cm^{-1} correspond to C–H stretching vibrations. The adsorption peak at 1682 cm^{-1} correspond to stretching vibration of C=O from –COOH. The adsorption peak at 1423 cm^{-1} corresponds to stretching vibration of –CH₂. The adsorption peak at 1288 cm^{-1} corresponds to stretching vibration of C–H. This indicates formation of functionalized MWCNTs (COOH-MWCNTs/f-MWCNTs) (Figure 3 [a] and 3 [b]). Peak obtained at 655 cm^{-1} represents Li–O bond.

2.2. Surface area

At 77 K, N₂ sorption measurements are used to determine surface areas (BET: Brunauer–Emmett–Teller surface area) of

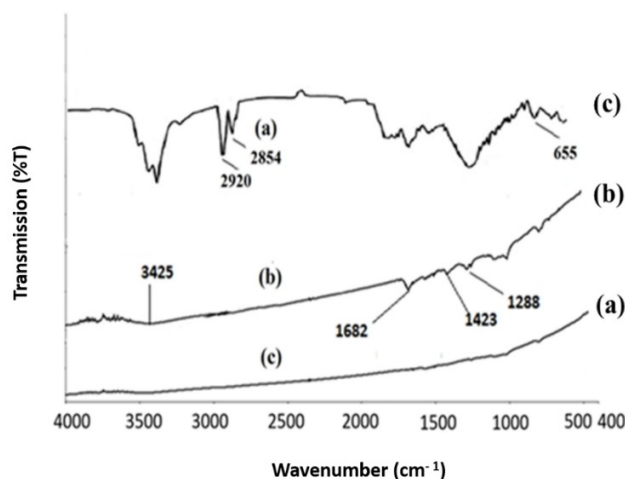


Figure 3. FT-IR spectra of [a] p-MWCNTs [b] f-MWCNTs, [c] Li@f-MWCNTs.

Li@f-MWCNTs, p-MWCNTs and f-MWCNTs (Table 1). The p-MWCNTs and f-MWCNTs have $360\text{ m}^2/\text{g}$ and $236\text{ m}^2/\text{g}$ surface area respectively. Functional groups (COOH) blocked the pores thereby reducing the surface area from $236\text{ m}^2/\text{g}$ to $221, 164$ and $13\text{ m}^2/\text{g}$ for Li@f-MWCNTs prepared in all three solvents. The shortfall of these surface areas is due to pore blockage by lithium nanoparticles.

2.3. Hydrogen sorption properties

(BELSORP-HP) is used in this experimental setting to measure the hydrogen sorption (volumetric) behaviour of Li@f-MWCNTs at non-cryogenic temperatures (253 K, 298 K) for a pressure of 70 bar. Table 1 represents the storage capacity of hydrogen in

Sample	Solvents	^s BET (m ² /g)	H ₂ storage in wt % (253 K, 70 bar)	H ₂ storage in wt % (298 K, 70 bar)
p-MWCNTs	–	360	0.30	0.12
f-MWCNTs	–	236	0.09	0.06
Li@f-MWCNTs	Water	221	0.20 ^[a]	0.17 ^[a]
Li@f-MWCNTs	Water		0.63 ^[b]	0.50 ^[b]
Li@f-MWCNTs	TEA	164	0.42 ^[a]	0.22 ^[a]
Li@f-MWCNTs	TEA		0.85 ^[b]	0.68 ^[b]
Li@f-MWCNTs	DMF	13	0.46 ^[a]	0.31 ^[a]
Li@f-MWCNTs	DMF		1.13 ^[b]	0.87 ^[b]

[a] MLC-Metal of low concentration [b] MHC- Metal of high concentration

Li@f-MWCNTs synthesized in various solvents by combining p-MWCNTs and f-MWCNTs. At 253 and 298 K temperatures, all the samples in the experiment exhibited reversible adsorption/desorption behaviour. Due to the monolayer adsorption of these materials, linear curves in adsorption isotherms are obtained. Metal nanoparticles and functional groups used for functionalization of CNTs play a vital role in hydrogen adsorption. So, decorating MWCNTs with lithium significantly enhances the hydrogen sorption.

P-MWCNTs at 253 K 0.3 wt% of hydrogen were adsorbing and at 298 K it is 0.12 wt%. The hydrogen of 0.09 and 0.06 wt% was adsorbed by CNTs post the functionalization with acid. The hydrogen reduction is because of the decrease in the CNT surface area. Hydrogen storage behaviour of Li@f-MWCNTs produced in different experimentation settings is studied. For 253 K temperature, the hydrogen storage capacity for a metal of low concentration (MLC) was observed to be 0.20, 0.42 and 0.46 wt% (Figure 4) in each of the three solvents (water, TEA & DMF). In metal of high concentration (MHC), for the same solvents and temperature, 0.63, 0.85 and 1.13 wt%, respectively

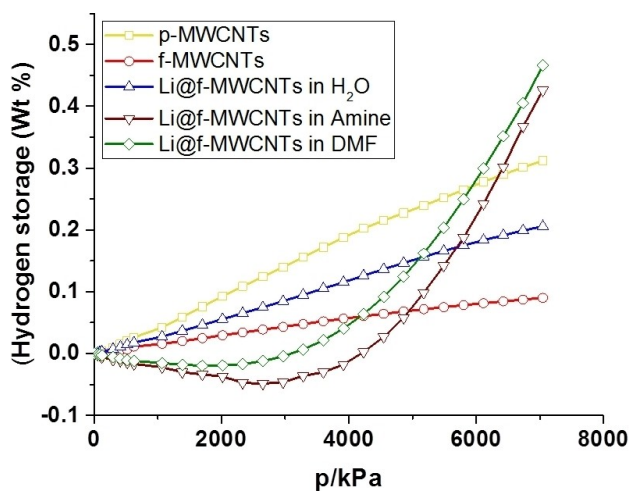


Figure 4. Hydrogen storage by p-MWCNTs, f-MWCNTs and Li@f-MWCNTs at 253 K at MLC.

were obtained hydrogen storage capacities (Figure 5). For 298 K temperature, the hydrogen storage capacity for the metal of low concentration (MLC) was observed to be 0.17, 0.22 and 0.31 wt% (Figure 6) in each of the three solvents (water, TEA & DMF). In metal of high concentration (MHC), for the same solvents and temperature 0.5, 0.68 and 0.87 wt %, respectively are the obtained hydrogen storage capacities (Figure 7). The hydrogen storage capacity in DMF synthesized Li@f-MWCNTs is 2–3 times superior to p-MWCNTs. DMF is a polar aprotic solvent plays an important role in uniform loading and decoration of lithium nanoparticles on the surface of MWCNTs.^[24] Due to this reason, high uptake of hydrogen was observed in the case of Li@f-MWCNTs prepared in DMF solvent. The lowest surface area observed in the case of Li@f-MWCNTs prepared in DMF medium due to the blocking of pores by the solvent molecules.^[22]

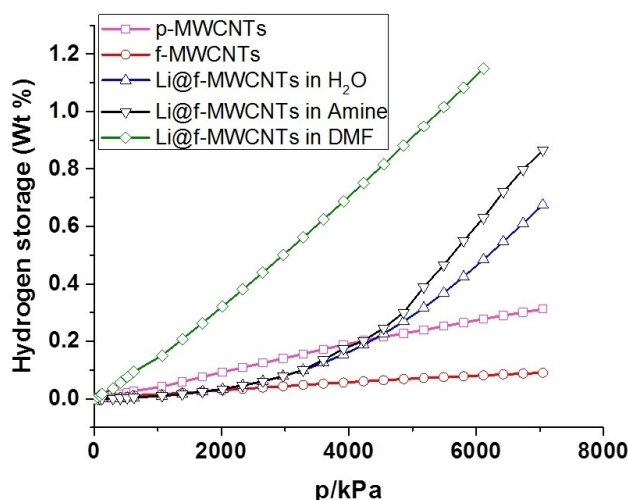


Figure 5. Hydrogen storage by p-MWCNTs, f-MWCNTs and Li@f-MWCNTs at 253 K at MHC.

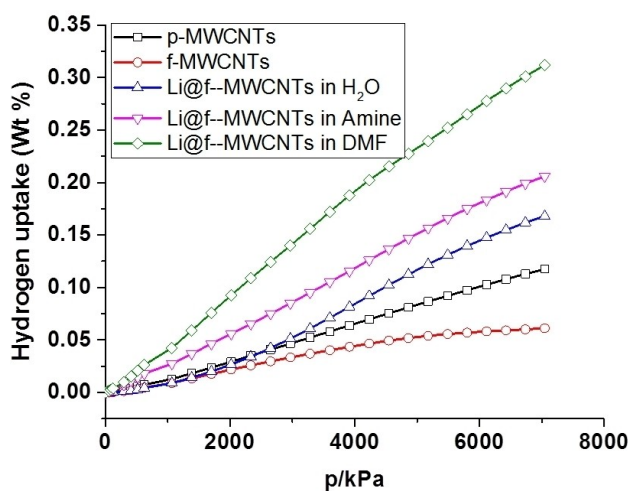


Figure 6. Hydrogen storage by p-MWCNTs, f-MWCNTs and Li@f-MWCNTs at 298 K at MLC.

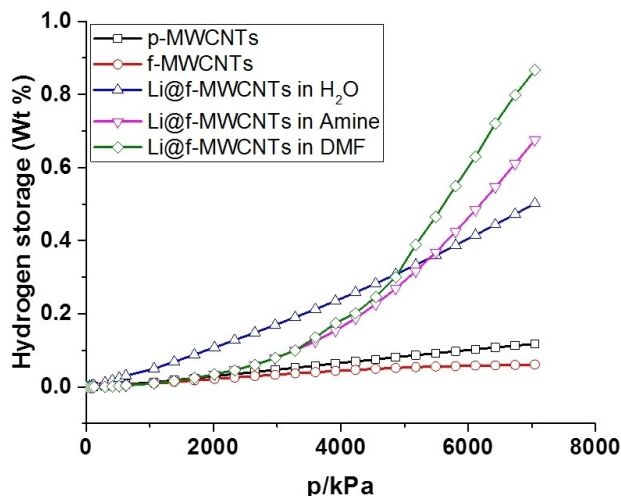


Figure 7. Hydrogen storage by p-MWCNTs, f-MWCNTs and Li@f-MWCNTs at 298 K at MHC.

Paucity in the literature exists while comparing the present study with similar previous studies. Though some studies presented synthesis and measurements of nanotubes at different conditions, those are indifferent to the present study. For instance Deng et al., 2004^[22] used Lithium doped SWCNTs and obtained 6 wt% at 50 bar pressure, due to its unstable nature along with inconsistent repeatability this procedure has not been adopted by researchers. Yang et al., 2000^[24] doped Li with SWCNTs and achieved 20 wt% at 200–400 °C (1 atm pressure) these conditions are generally fit for bench scale studies but not for real time applications, further these conditions are not adoptable for large scale studies. The present study is unique as Lithium is doped with f-MWCNTs and obtained good hydrogen storage capacity at non-cryogenic temperatures with low metal concentration in comparison with the literature available.

3. Conclusions

The capacities of hydrogen storage in Li@f-MWCNTs under various experimental conditions have been studied. The obtained results support the enhancement of hydrogen storage capacity in Li@f-MWCNTs by a factor of 2–3 in comparison to its associates p-MWCNTs and f-MWCNTs. The concentrations of metal and solvent type considerably influence the hydrogen storage capacity. The uniformity in the dispersion of lithium nanoparticles is influenced by DMF for hydrogen uptake enhancement. The enhanced storage capacity is attributed to the hydrogen spillover mechanism from lithium to MWCNTs.

Supporting Information Summary

Supporting information illustrates the methodology that has been used in the present study which includes Materials and synthesis, purification of MWCNTs (p-MWCNTs), Functionaliza-

tion of MWCNTs (f-MWCNTs), and Decoration of Li nanoparticles on f-MWCNTs, Characterization techniques and Hydrogen sorption studies. All the above information has been provide in detail for effective reproducing.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbon Nanotubes · Doping · Functionalization · Hydrogen Storage · Lithium Nanoparticles

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