Carbon Based Hydrogen Storage Materials

Ph. D Synopsis Report

Submitted by

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Rapid consumption along with the limited availability of fossil fuels has driven the need to explore alternative and renewable sources of energy. Hydrogen has been explored as an alternative source of energy due to its various advantages, such as higher energy density, non–polluting characteristics and renewable nature. The main concern regarding using hydrogen as fuel is its storage. The solid material based hydrogen storage system has been reported as one of the safest options. Usually, the hydrogen is stored either as hydrides or in adsorbed condition. Porous carbon materials have been used for gas storage applications. The principal properties that determine their performance include surface area, pore size and pore volume. Comparatively low cost, easy availability and good chemical stability are added advantages. Researchers have reported various porous carbon materials for hydrogen storage application, such as carbon nanotube, activated carbon, metal-organic framework, and templated carbons. Majority of the reported hydrogen storage materials are microporous having high surface area. However, the high surface area mesoporous carbons (2–20 nm) are also reported recently. A major advantage of mesoporous carbons compared to that of microporous carbons is that the former can facilitate incorporation of larger dopants in carbon matrix, resulting in their higher dispersion and better performance in applications. The diffusion limitation is reported to be higher in microporous carbon. Recently, graphene has also generated interest as a potential hydrogen storage material. The graphene–based materials are reported to be prepared by chemical, thermal and electrochemical treatment of graphene oxide (GO). The difference in preparation is expected to affect physicochemical properties. Incorporation of nonmetals and metals in the carbon matrix has been reported to affect the hydrogen uptake property of templated carbon. However, very few studies have been reported on graphene modified with different metals for hydrogen storage. Metals are reported to act as additional adsorption sites as well as promote spillover phenomenon for hydrogen adsorption.

The objective of this study was to develop carbon based hydrogen storage materials. Mesoporous templated carbon and graphene based structures were investigated. The mesoporous low cost alumina and surfactant modified alumina templates were developed. The corresponding undoped and doped mesoporous templated carbons were compared with templated carbons prepared using commercially available microporous zeolite and mesoporous silica gel as templates. The effects of non-metal (nitrogen) and metal (platinum, palladium or nickel) doping on templated carbons were investigated. Graphene like structures were prepared by chemical and thermal treatments and its physicochemical properties and hydrogen uptakes were compared. The effects of preparation conditions and incorporation of metals (platinum, palladium or nickel) were also investigated. Hydrogen uptake capacities of prepared samples were determined at different temperatures and pressures using volumetric adsorption analysis. The heat of adsorption, reversibility and cycle stability of samples were also determined. Figure 1 represents the overall work done in this study.
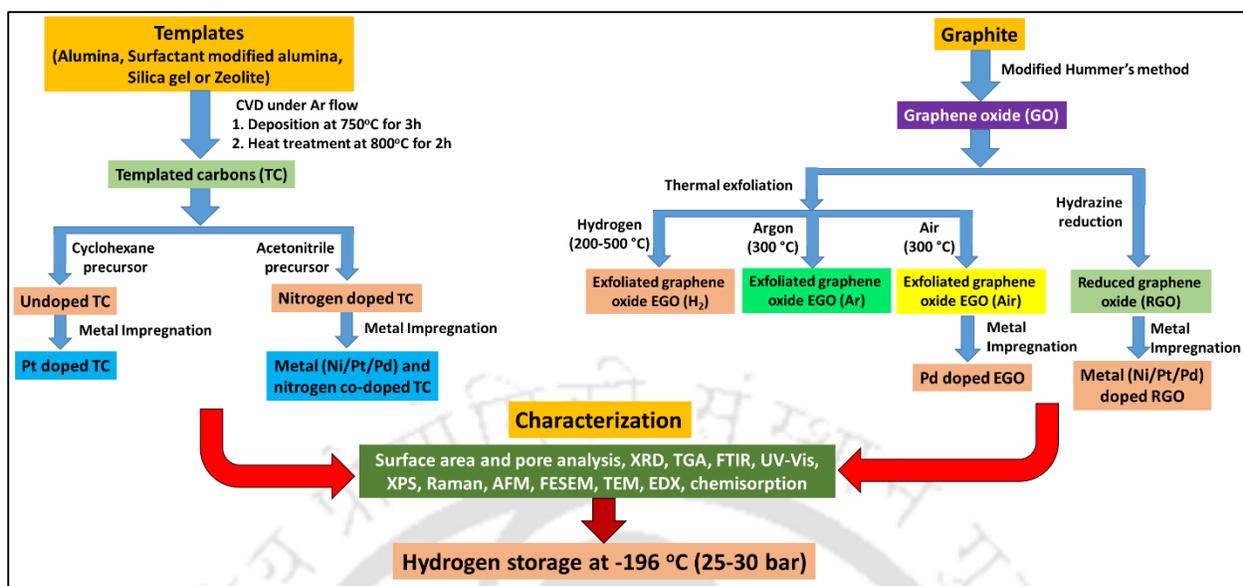
Figure 1: Representation of overall work done in this study.

Alumina and surfactant modified alumina were prepared in the laboratory and used as templates in the chemical vapor deposition process. Commercially available zeolite and silica gel were used for comparative study. For the preparation of undoped templated carbons, cyclohexane was used as the carbon precursor while nitrogen doped templated carbons were prepared using acetonitrile as a source of both carbon and nitrogen. The metals platinum, palladium and nickel were incorporated by impregnation in templates before carbon and nitrogen deposition. The graphene based materials were prepared from graphite oxide by two methods; chemical reduction and thermal exfoliation. The effect of exfoliation temperature on properties of exfoliated graphene oxide (EGO) was studied by varying the temperature between 200 – 500 ºC in a hydrogen atmosphere. The effect of exfoliation atmosphere was studied by varying the carrier gas. Reductive, inert and oxidative atmospheres were created by using hydrogen, argon and air respectively. The metals were incorporated in graphite oxide before reduction or exfoliation to prepare doped graphene based materials. The physicochemical properties of the samples were determined by various characterization techniques including XRD, Raman Spectroscopy, TGA, Carbon monoxide chemisorption, EDX, FESEM, TEM and surface area and pore analyzer. The hydrogen storage properties of the prepared samples were determined at –196 °C at 25 or 30 bar by volumetric adsorption analysis.

The alumina based templated carbons were mainly mesoporous with pores in the range of 2–7 nm, having mainly agglomerated tubular/noodle like structures (Figure 2). The surface area was 1050 m^2/g. When the surfactant modified alumina was used as the template, the surface area increased to 1221 m^2/g and pore range increased to 2-10 nm. This agreed with more voidage observed within its agglomerated tubular structure. In comparison, the mesoporous silica gel (736 m^2/g) and microporous zeolite templated carbon

(1462 m^2/g) showed spherical agglomerates and particle structure respectively. The surfactant modified alumina templated carbon gave the highest hydrogen uptake capacity of 4.3 wt.%, in spite of lower surface area than zeolite templated carbon. Higher hydrogen uptake capacity of surfactant modified alumina templated carbon may be attributed to its higher pore volume, highest average pore size and presence of tubular structures. The isosteric heat of adsorption was highest for this templated carbon; 13 kJ/mol at lower hydrogen uptake.
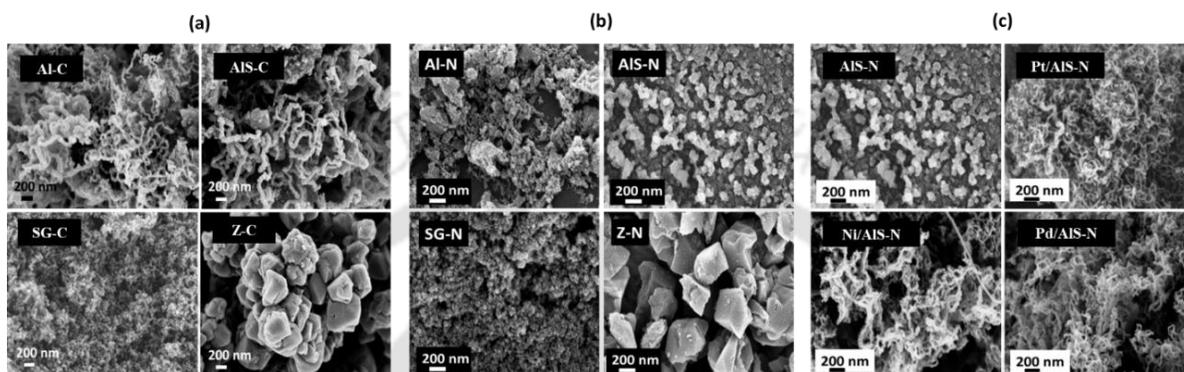

Figure 2: FESEM images of (a) undoped (b) nitrogen doped and (c) metal (Ni/Pt/Pd) and nitrogen co-doped templated carbons.

The nitrogen doped templated carbons were mesoporous with narrow pore size range (2-8 nm). The surface area and pore volume increased for all the nitrogen doped templated carbons. The surface areas were in the range of 908–1664 m^2/g. The hydrogen uptake capacity of microporous zeolite templated increased to 4.0 wt.% however for the alumina-SDS templated carbon it slightly decreased to 3.9 wt.%. On co-doping nitrogen with 3 wt.% platinum, the surface area decreased to 496-1173 m^2/g with pore volume to 0.47-1.24 cm^3/g for all the templated carbons. However, the drop for mesoporous surfactant modified alumina templated carbon was least. This may be associated with the highest dispersion of the Pt metal within the mesoporous matrix of surfactant modified alumina templated carbon. Co-doping nitrogen and platinum resulted in noddle like morphology. The hydrogen uptake increased to 4.1 wt.% for surfactant modified alumina templated nitrogen and platinum co-doped carbon. This highest uptake capacity may be attributed to the synergistic effect of significant surface area, highest pore volume and highly dispersed platinum. Co-doping of nitrogen and platinum resulted in increase of heat of adsorption up to 15.9 kJ/mol at lower hydrogen uptake for surfactant modified alumina templated carbon.

The mesoporous surfactant modified alumina templated carbon were also co-doped with other metals, such as nickel or palladium with nitrogen. All the metals were selected based on their reported strong interaction with hydrogen. The co–doping with metals reduced both the area as well as pore volume as before. The highest dispersion of metal was observed for palladium and nitrogen co–doped carbon. The co–doping of

palladium and nitrogen also resulted in the appearance of noddle or tubular like structure in contrast to the aggregated structure of nitrogen–doped carbon. The palladium and nitrogen co–doped carbon with 2 wt.% palladium showed the highest hydrogen uptake of 5.0 wt.%. This may be attributed to its highest number of active sites corresponding to the highest metal dispersion and amount of nitrogen present. Also, the highest heat of adsorption of 22.9 kJ/mol was obtained for the same sample. The palladium loading lower or higher than 2 wt.% was found to be less efficient for hydrogen storage.
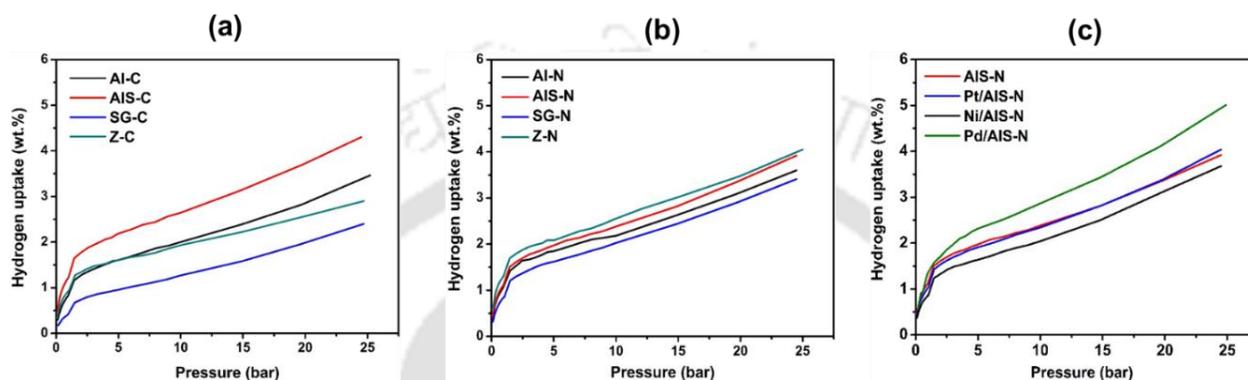

Figure 3: Hydrogen uptake isotherms of (a) undoped (b) nitrogen doped (c) metal and nitrogen co-doped templated carbons (at -196 °C & 25 bar)

Surfactant modified alumina was observed to be an effective and economic template for synthesis of mesoporous templated carbons. Significant surface area, pore volume, relatively narrow pore size distribution, the tubular structure gave unique physicochemical characteristic to surfactant modified alumina based templated carbon. Its mesoporous structure facilitated higher metal dispersion. In this study, the surfactant modified alumina templated carbon showed the maximum surface area of 1508 m^2/g and pore volume of 1.64 cm^3/g. The incorporation of non-metal and metals changed the surface area, pore structure, morphology and consequently hydrogen uptake capacity of the templated carbons. Though surface area and pore volume increased on the incorporation of nitrogen, however, the values dropped by co-doping of metals. Co-doping of nitrogen and metal also resulted in tubular or noodles like structure for mesoporous templated carbons. The effect of co-doping of nitrogen and metals on hydrogen uptake capacity, depended on the metal as well as template type. The most effective improvement was observed for nitrogen and palladium co-doped on surfactant modified alumina templated carbon that showed the highest hydrogen uptake capacity of 5 wt.% at -196 °C and 25 bar (Figure 3).

The graphene based hydrogen storage materials, prepared from graphene oxide by thermal exfoliation and chemical hydrazine treatment, and were compared for physical properties and hydrogen uptake. Exfoliation temperature was observed to have a significant effect on the surface and structural properties of the samples. Decrease in oxygen content was observed on increasing the exfoliation temperature. All the exfoliated

graphene oxide samples had a fluffy layered structure as observed from Figure 4. The graphene oxide exfoliated at 300 °C, having surface area of 248 m^2/g and total pore volume of 1.64 cm^3/g, showed the hydrogen uptake of 3.12 wt.% as shown in Figure 5(a). The considerable hydrogen uptake of this sample in spite of lower surface area may be the combined effect of high pore volume, mesoporous fluffy layered structure, and significant content of surface oxygen heteroatom.

The method of preparation by chemical and thermal treatments was also observed to have an effect on the physicochemical properties of resultant graphene materials. A part of the synthesized graphene oxide (GO) was subjected to hydrazine treatment and the remaining part was thermally treated in different gaseous (H_2, Ar or air) environments. Structurally hydrazine reduced graphene oxide (RGO) was similar to parent graphene oxide but Oxygen to Carbon (O/C) ratio value was significantly lower than that of exfoliated graphene oxide samples suggesting more retainment of oxygen–containing functional groups in the latter.
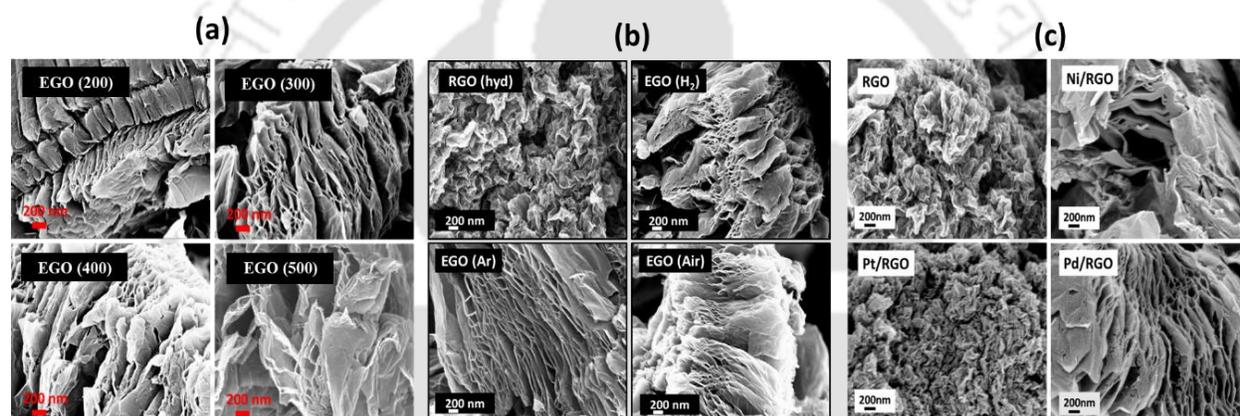

Figure 4: FESEM images of (a) exfoliated graphene oxide (EGO) prepared at different temperatures (b) hydrazine reduced graphene oxide (RGO) and graphene oxide (EGO) samples exfoliated in H_2, Ar or air environment (c) metal doped RGO samples

The pore size distribution revealed the microporous nature for RGO and mesoporous for EGO samples. The RGO had an average pore size of 2.0 nm, whereas EGO samples had an average pore size between 2.8–4.1 nm. The fluffier and distinct multi–layered structure for thermally exfoliated graphene was in contract to the wrinkled layered structure of hydrazine reduced graphene oxide. The BET surface area was highest for RGO (461 m^2/g) but the EGO (H_2) showed the highest pore volume (1.63 cm^3/g), while O/C value was highest for EGO (Air).

The maximum hydrogen uptake of 3.3 wt.% was obtained for EGO (Air) at -196 °C and 30 bar followed by that of RGO (Figure 5). The hydrogen uptake capacity was observed to increase with O/C ratio because the presence of highly electronegative oxygen may have facilitated interaction with incoming highly electropositive hydrogen. The results suggested that the combined effect of surface area, pore volume,

nature of layered structure and oxygen content contributed to hydrogen uptake characteristics of graphene based materials.
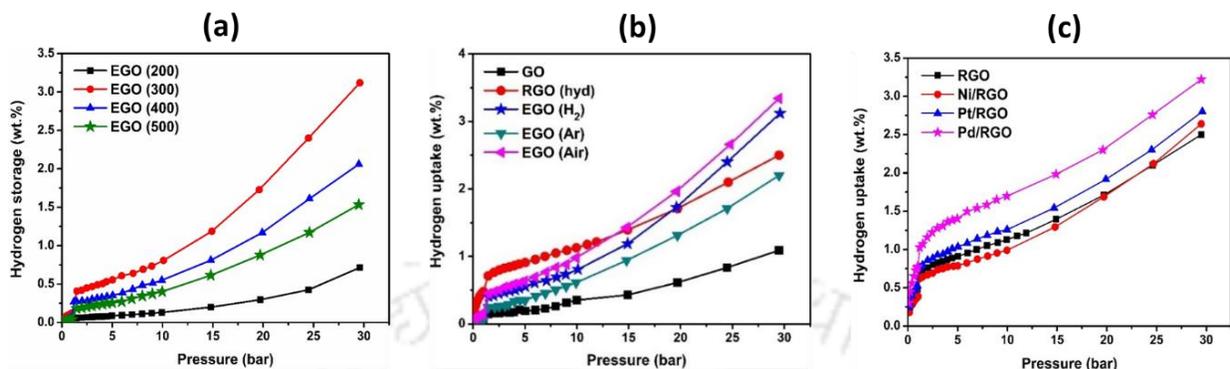

Figure 5: Hydrogen uptake isotherm (at -196 °C upto 30 bar) of (a) exfoliated graphene oxide (EGO) prepared at different temperatures (b) hydrazine reduced graphene oxide (RGO) and graphene oxide (EGO) samples exfoliated in H₂, Ar or air environment (c) metal doped RGO samples

Among graphene based materials the highest surface area of 461 m^2/g was observed for hydrazine reduced graphene oxide sample but the highest pore volume of 1.63 cm^3/g was observed for exfoliated graphene oxide in air. This characteristic can be correlated with the fluffy layer structure of the exfoliated graphene oxide compared to dense wrinkled layered structure for hydrazine reduced graphene oxide. The air exfoliated graphene oxide displayed maximum hydrogen uptake capacity of 3.3 wt.% among graphene based materials. On addition of palladium metal to RGO and EGO, the hydrogen uptake capacity was enhanced from 2.50 to 3.22 wt.% and 3.2 to 3.5 wt.% respectively.

For templated carbon, the hydrogen uptake capacity was observed to be depended not only on the surface area but also on pore volume. For doped templated carbon amount of nitrogen and dispersion of metal was observed to be important criteria for hydrogen uptake; higher nitrogen content and higher dispersion resulted in higher hydrogen uptake. For graphene based materials, in addition to the above parameters, presence of oxygen–containing surface functional groups was observed to play a positive role in hydrogen uptake of these samples. Higher oxygen content usually favored hydrogen uptake. All the templated carbon and graphene based adsorbents showed good reversibility and cyclic stability for hydrogen storage at -196 ºC and moderate pressure up to 30 bar.