Experimental Investigation and modeling of hydrogen storage in graphene nanplatelets incorporated silicon oxycarbide ceramics

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Abstract

The present work focuses on synthesizing graphene nanoplatelets (GNP) incorporated amorphous silicon oxycarbide ceramic (Si-O-C) for hydrogen adsorption. The changes in the structure of the ceramic upon addition of GNP has been studied using X-ray diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy and Fourier Transform Infrared (FT-IR) spectroscopy. A theoretical framework to quantify these changes is proposed in line with existing structural model. Hydrogen adsorption studies have been carried out at 100K and 2 bar using Sievert’s apparatus. Maximum gravimetric storage density (GD) of 0.16 wt.% was observed after adding 0.3 wt.% of GNP, in comparison to 0.35 wt.% for the non-GNP sample. Pores sized 2-5 nm were found to be critical for hydrogen adsorption. The study finds that GNP addition leads to an increase in the size of the silica nanodomains. This increase in nanodomain size results in increase in the pore sizes of the existing mesopores, thereby reducing the overall hydrogen uptake. Further, the addition of GNP beyond 3 wt.% is found to increase the coordination of mixed bonds (Si-O-C) in the interface which results in agglomeration and subsequent loss of porosity in the composite.
Keywords: Polymer derived ceramics; Hydrogen storage; Graphene nanoplatelets; Nanocomposites; Porous materials.

1. Introduction:

The growing energy needs and environmental concerns across the world require development and usage of green fuels in the near future. Hydrogen’s presence in abundance and high calorific value make it a promising fuel for the future, which can be used on a large scale. Various international organizations like Dept. of Energy (DoE), USA and the Task 32 team which reviews the “Hydrogen-based Energy Storage” for the International Energy Agency, have established their targets for hydrogen adsorption and hence continuously follow the developments in this area. Usage of hydrogen is risky given its inflammable nature but the biggest obstacle is its very low density, making its storage difficult. In the recent past, materials like metal-organic frameworks (MOF’s), carbonaceous materials (graphene, carbon nanotubes (CNT), activated carbons), and zeolites have been used as hydrogen adsorbents. Among these, MOF’s and carbonaceous materials having received maximum attention. A recent simulation work by A. Ahmed et. al. on MOF’s yielded results which exceeded even the targets of DoE, USA. They obtained maximum gravimetric storage density (GD) of 10.1 wt.% at 100 bar and 77K [1]. Simultaneously, several carbonaceous materials have also been tried for storing hydrogen. Studies by A. Ariharan et. al. on hydrogen storage through CNT involving the synthesis of nitrogen-doped CNT from polymeric precursors (polystyrene and polypyrrole) by poly-condensation resulted in GD of 2 wt.% at 100 bar and 298K [2]. Further, activated carbon (NAC-1.5-y) with specific surface area (SSA) and pore volume in the range of 526-2386 m²/g and 0.26-1.16 cm³/g, respectively, were prepared by treatment of a nitrogen-rich carbon with KOH. The adsorption studies resulted in a hydrogen uptake of 2.94 wt.% at 77K and 1 bar [3].
These were significant results at low pressures of just 1 bar. In another major study on chemically activated carbons, M. Jordá- Beneyto et. al. obtained hydrogen adsorption capacities of 1.2 wt.% and 2.7 wt.% at 20MPa and 50MPa, respectively at 298K. They observed that at 298K, the hydrogen adsorption capacity depends on both micro-pore volume and micro-pore size distribution [4]. Additionally, alongside these carbonaceous materials, graphene has also attracted attention as a hydrogen adsorbent because of the presence of carbon. In one of the early studies, first-principles plane-wave calculations were done. It was found that lithium covered graphene can serve as a high-capacity hydrogen storage medium amounting to a GD of 12.8 wt.% [5]. In a similar effort by Srinivas et. al., hydrogen adsorption on graphene-like nanosheets at 77 K and 1 bar were found to be 0.68 wt.% [6]. These results on pristine graphene were not promising and the major reason was the existence of weak interaction between molecular hydrogen and graphene. Therefore several routes like incorporating graphene in another structure, increasing the number of layers, and tuning the structure of graphene have been investigated to enhance both the binding energy and the gravimetric/volumetric storage capacity. In one such study, C. Zhou tried designing a Ni-graphene composite for hydrogen storage with Ni nanoparticles of 10 nm size, uniformly dispersed over the graphene substrate. At room temperature and 60 bar, the sorbent had a GD of 1.18 wt. % [7]. Further, a recent study by Sujith et. al. on the synthesis of graphene nanoplatelets (GNP) incorporated porous silicon oxycarbide ceramics established the effects of GNP addition in them. However, this study did not explore the hydrogen adsorption potential of these composites. Moreover, the study did not explore the effect of GNP addition on the pore morphology of the ceramic [8]. A similar study by A. Maheshwari et. al. reported an increase of electrical conductivity of amorphous silicon oxycarbide ceramics by incorporating GNP as a nano-filler. This is indicative of the increase in
the free carbon content in the ceramic that can be used for hydrogen adsorption [9]. Further, porous silicon oxycarbide ceramic derived carbon has been used by C. Vakifahmetoglu et. al. for storing hydrogen and they obtained GD of 5.5 wt.% at 25°C and 60 bar [10]. Before this study Nghiem et. al. also came up with a storage density of 1.1 wt.% for these ceramics at room temperature and 1 bar [11]. However, apart from these two studies, these ceramics which have thermo-mechanical and chemical stability have not been utilized for hydrogen storage [12]. Therefore, we try to combine its potential by mixing with GNP which has shown a promising GD of 2.47 wt.% in the pristine form [13].

Hence, we synthesize GNP incorporated porous silicon oxycarbide ceramics by polymer precursor route. In-depth studies of the effect of GNP on the pore morphology and structure of the ceramic have been carried out. These GNP incorporated ceramics have been further explored for their hydrogen adsorption capacity. Additionally, a theoretical model for describing the hydrogen adsorption in these GNP added amorphous ceramics has been obtained in line with the existing structural model. These studies of hydrogen adsorption on GNP incorporated porous silicon oxycarbide ceramics are probably one of the first attempts in these materials. Therefore, the study could further be significant for understanding and achieving an optimized material system for hydrogen storage.

2. Materials and Methods:

The synthesis of the GNP incorporated ceramic was carried out through the polymer precursor route which involves the curing of the polymeric mixture followed by pyrolysis till 1000°C. The polymeric precursors used were, linear polymethyl hydrosiloxane [PHMS,(CH₃)₃SiO{(CH₃)HSiO}ₙSi(CH₃)₃, viscosity: 15-40 mPa.s (20°C), CAS Number 63148-
and vinyl terminated polydimethylsiloxane [PDMS, \(\text{CH}_2\text{CH}[(\text{Si}(\text{CH}_3)_2\text{O})_n\text{Si}(\text{CH}_3)_2 \text{CHCH}_2\), viscosity: 850-1150 mPa.s (25°C), CAS Number 68083-19-2, Sigma Aldrich, USA]. Cyclic 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane [TMTVS, C\(_{12}\)H\(_{28}\)O\(_4\)Si\(_4\), CAS Number 2554-06-05, Sigma Aldrich, USA] with SiC=C moieties, hydrotalcite [LDH \{Mg\(_6\)Al\(_2\)(CO\(_3\))(OH)\(_{16}\)·4H\(_2\)O\}], CAS Number 11097-59-9, Sigma-Aldrich, St. Louis, MO, USA] and GNP (CAS NO.: 7782-42-5, United Nanotech Innovations Pvt. Ltd., Bangalore, India) were incorporated in the mixture before the curing stage. The hydrotalcite helps in synthesizing aligned pores in the ceramic [14]. The R18 sample discussed in reference [14] was chosen for the studies since it has the highest specific surface area and pore volume, which are key to hydrogen adsorption. GNP was added in different weight fractions of 0.3 wt.%, 3 wt.%, and 6 wt.% to the polymeric precursor mixture to establish its effect on the pore morphology and structure of the Si-O-C. The precursor mixture was then magnetically stirred for 20 min at 600 rpm. This was followed by the addition of platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt\(_2\)%%, \([\text{O}\{\text{Si}(\text{CH}_3)_2\text{CH=CH}_2\}_2 \text{Pt}, \text{Sigma Aldrich, USA}\], 100 ppm by weight of Pt relative to PHMS, as the catalyst for the curing reactions. After Pt addition, again the mixture was stirred for 15 min at 600 rpm. This was followed by pouring these stirred precursors blends in a ceramic crucible for overnight curing at 220°C [14]. The curing process was followed by pyrolysis till 1000°C. Pyrolysis was carried out in a tubular furnace at a heating rate of 4°C/min and in an atmosphere of argon, followed by a dwell time of 1 h.

The methodology followed for the synthesis is shown in Fig.1. The synthesis was followed by the hydrogen adsorption using Sievert’s apparatus, seen in ref. [13] and characterization studies on the composite. The mean value of GD obtained have been plotted, with the maximum
standard deviation being ±0.005 wt.%. Further, the Van-der Waals equation has been considered for describing the behavior of hydrogen at 100 K in the adsorption chamber [15]. It assumes a slow-motion of the hydrogen molecules from the reference chamber to the adsorption chamber due to low temperatures. The procedure and methodology for calculating and interpreting GD in this manner is detailed in [13].

Fig. 1: Process flow chart for synthesis of GNP incorporated Si-O-C.
2.1 Structural Characterization:

X-ray diffraction (XRD) was carried out using Rigaku - Ultima IV (Japan) with Cu: Kα (λ = 0.154 nm) to establish the effect of graphene on the pyrolysed samples. Raman spectroscopy (UniRAM, micro-Raman mapping system, laser λ=533nm) was carried on the pyrolysed samples to determine the type of carbon existing after GNP addition. Brunauer, Emmet, and Teller (BET, BESORP-mini II, Japan) analysis were carried out to find the SSA, average pore size, and total pore volume in the pyrolysed samples. The average pore diameter has been calculated as ratio of 4V/A, where V is the volume and A is the surface area of the nano-pores [16]. The mesopore size distribution in the samples was determined from the Barrett-Joyner-Halenda (BJH) curves. Further, Fourier Transform Infrared Spectroscopy (JASCO Japan, FT-IR 4200, Transmission type) studies were also carried out to study the effect of the GNP addition on to the structure of the Si-O-C.

2.2 Elemental Analysis

X-ray photoelectron spectroscopy (XPS) studies were taken up to find the effect of GNP addition on the structure of the Si-O-C through the change in the binding energies (B.E.) of atoms. Since the physisorption of hydrogen is a surface energy phenomenon hence it becomes relevant to associate it with the binding energy of the atoms at the surface and not in the bulk ceramic. Further, it was also used to find the average elemental composition on the surface of the material. The average elemental composition has been further used for calculating structural parameters for the material. The XPS used 180⁰ double-focusing hemispherical analyzer with an Al Kα radiation (1486.6 eV) [Thermo fisher scientific, USA] for the studies. Further, the full spectrum involved scanning for 60 seconds while the core spectrum involving individual
elements, scanned for 30 seconds. The XPS measurements were performed thrice to ensure the repeatability of the values.

3. Results and Discussions

FT-IR studies were conducted to confirm the formation of the ceramics at 1000°C. The FT-IR data was normalized and plotted (Fig. 2). It shows four distinguishable features for all the four samples. The first is a high-intensity absorption band at around 3500 cm\(^{-1}\), assigned to the hydroxyl group which represents adsorbed water on the surface. In addition, the bands near 1050 cm\(^{-1}\) and 800 cm\(^{-1}\) are attributed to Si-O-Si and Si-C, respectively [14]. The presence of the absorption band for Si–O stretching vibration mode and the absence of Si-H absorption band around 2150 cm\(^{-1}\) is an indication of the completion of the pyrolysis process and the formation of the ceramics.

![FT-IR spectra](image)

**Fig. 2:** FT-IR spectra (Transmission mode) for varying GNP compositions in Si-O-C.
Further, XRD studies were carried out to find the effect of GNP addition on the structure of the ceramic. The characteristic peak corresponding to carbon (2θ = 26°) can be observed in the samples containing GNP. The intensity of the carbon peak gets higher with an increase in the wt.% of GNP in the ceramic, as seen in Fig. 3. Further, the absence of any sharp peaks around 2θ = 36°, 72° and presence of a broad halo at 2θ = 23° (amorphous SiO2) for the GNP free SiOC ceramic sample (SiOC 1000C) confirms its amorphous nature. Moreover, it confirms that GNP is the sole contributor of crystallinity in the ceramics.

Fig. 3: XRD for pure and GNP incorporated Si-O-C; (a) SiOC 1000C (without GNP); (b) SiOC 1000C 0.3 wt.% GNP; (C) SiOC 1000C 3 wt.% and (d) SiOC 1000C 6 wt.% GNP.

Additionally, Raman spectroscopy (Supplementary Fig. 1) was carried out to find the nature of carbon existing in the composite after pyrolysis. The D and G peaks corresponding to the carbon from GNP were observed at 1336 cm⁻¹ and 1556 cm⁻¹, respectively. The I_D/I_G ratio was found to be 0.83 (Supplementary Fig. 1(b)), indicative of the orderness in the carbon of the incorporated GNP [17]. However, the peak intensities for D and G peaks were reduced when compared to
pure GNP (I_D/I_G= 0.43, Supplementary Fig. 1(a)). This is probably due to the strong background fluorescence of the amorphous ceramic samples [8, 18].

Having studied the characteristics of the GNP incorporated ceramic, further work focused on finding the elemental composition and the binding energies of the respective atoms on the surface of the specimens, using XPS. The resultant change in the ceramic surface structure upon addition of varying weight percentages of GNP is reflected through the changes in the binding energy values of the atoms, shown in Table 1 and Fig.4. We can observe from Table 1 that the binding energies for Si and C drop with addition of GNP upto 3 wt.%. For Si it reduces from 103.5 eV to 103.3 eV and for C it reduces from 285.5 eV to 285.2 eV. However, when the GNP addition is 6wt.%, the binding energies for the atoms, especially Si and O increase significantly. For Si, the binding energy increases from 103.3 eV to 103.9 eV and for O it increases from 533.2 eV to 533.5 eV. This increase in the binding energies at 6 wt.% GNP indicates strengthening of the Si-O bonds and a possible closing of the existing meso-micro pores (<5 nm).

Fig. 4: XPS graphs showing the Binding Energies for various atoms at surface of the pyrolysed samples; (a) SiOC 1000C; (b) SiOC 1000C 3wt.% GNP and (c) SiOC 1000C 6wt.% GNP.
Therefore, to find the effect of GNP addition on the porosity in the ceramics, BET and BJH studies were carried out. The effect on the porosity is reflected through adsorption-desorption and BJH curves, seen in Fig. 5. The adsorption-desorption curves obtained through BET studies resulted in Type IV N$_2$ sorption isotherms for all the samples, as per the IUPAC classification [19]. The hysteresis loops for the samples with GNP 0.3 wt.%, 3 wt.% and 6 wt.% begin at relative pressures ($p/p_0$) of 0.65, 0.75, and 0.83, respectively compared to 0.47 for without GNP sample. This indicates comparatively less volume of mesosized pores (<5 nm) in the samples containing GNP. However, the 0.3 wt.% , 3 wt.% GNP and without GNP samples have steep rise in hysteresis loops which is indicative of higher amount of N$_2$ adsorption through capillary condensation. This increased multilayer adsorption capability has resulted in higher SSA (Table 2) for these sample.

**Fig. 5** Shows the N$_2$ sorption isotherms for the samples obtained through BET studies; (a) adsorption-desorption isotherms; (b) Barrett-Joyner-Halenda (BJH) curves showing mesopore size distribution in the samples.
These characterization studies were followed by modeling the adsorption of hydrogen in these amorphous ceramics.

The property used to study the hydrogen storage capacity of the system is the gravimetric storage density (GD) which is defined as follows:

$$GD = \frac{\text{Mass of hydrogen adsorbed}}{\text{Mass of hydrogen adsorbed} + \text{Mass of adsorbent}}$$  \hspace{1cm} \text{Eq. 1}

For finding the adsorption storage capacity for the ceramic without GNP, where multilayer adsorption takes place through capillary condensation, the procedure and methodology required for calculating and interpreting GD is detailed in [13]. The role of the free carbon for hydrogen storage has been neglected because it is generally present in disordered form [17].

However, after addition of the GNP, the adsorbent is multicomponent and hence a new approach needs to be defined for establishing the GD of hydrogen in this material. The modeling of the GD requires finding microstructural features of the material and a framework to define the adsorption mechanism. Therefore, in this study, a model used by Saha et. al [20], hereafter referred to as the nanodomains model is used as a theoretical framework to define the microstructure of the composite. The Saha model is derived for bulk amorphous ceramic structure. Moreover, since our phenomenon only concerned with the surface of the ceramic, we hereby reference this model for calculation of our materials structural parameters by using the data obtained from the XPS technique. The two important parameters defined by the model are the domain size ($d^*$) of the silicon tetrahedra and the interface layer width ($\lambda$) consisting of the mixed bonds and the graphene layers.
Further, we have considered locally stable configurations of Si-O-C for finding the structural parameters [21]. Additionally, the modified expanded graphite model developed by the authors to evaluate the hydrogen storage capacity of GNP in their previous study [13] has been adapted in line with the proposed framework, for evaluating the GD of the composite.

The average surface composition obtained through XPS studies was used for the calculation of the empirical formula and subsequently, the stoichiometric and graphitic part tabulated in Table 3. The general factor “p”, which represents the coordination of the interfacial Si-O-C bonds for finding the model parameters is quite difficult to be determined from characterization experiments. Hence to find this factor, a comparison is done with the values used in [20] and B.E obtained from XPS. From Table 1, we can observe that there is a decrease in the B.E. of the atoms for the 0.3 wt.% and 3wt.% GNP sample. The decrease in the B.E. for Si2p (103.5 to 103.3 eV) and the C1s (285.3 to 285.2 eV) indicates lesser coordination between Si, O and C. Hence, we can qualitatively say that “p” value for 0.3 wt. % and 3 wt.% GNP sample must be lesser than the other 2 samples. Comparing with the values in [20], \( p_{(SiOC 1000C)} \), \( p_{(SiOC 1000C + 6wt\% GNP)} \) is 0.75 and \( p_{(SiOC 1000C + 0.3wt\% GNP)} \), \( p_{(SiOC 1000C + 3wt\% GNP)} \) is 0.5 respectively.

The model parameters \( d^*, \lambda \) and \( n_C \) are calculated by substituting the values and are shown in Table 4. The calculation of the structural parameters was followed by hydrogen adsorption studies.

The expanded graphite model is adapted for this system and the SiO\(_2\) nanodomains are assumed to be space fillers and not adsorbent of hydrogen. The assumption of SiO\(_2\) as merely space fillers comes from the observation of high reduction in mesopore (2-5 nm) volumes after addition of
GNP, as seen in Table 1. These mesopores are critical to hydrogen adsorption in these ceramics and are constituted by the Si-O bonds [22]. The G.D for these GNP incorporated ceramics is then calculated by incorporating the above considerations into the modified expanded graphite model as detailed below.

$$GD = \frac{\{\text{Volume of graphene interlayer spacing} - \text{Volume of SiO}_2 \text{ domain}\}}{\{V_m(P_{int}, T) + (\text{Volume of graphene interlayer spacing} - \text{Volume of SiO}_2 \text{ domain})\}} \times \text{(Correction factor)}$$  \hspace{1cm} \text{Eq. 2}

Where $V_m (P_{int}, T)$ is the molar volume of adsorbed hydrogen between the graphene layers. The adsorbed hydrogen is at a pressure of $P_{int}$ and temperature T where $P_{int}$ is defined as

$$P_{int} = \left(\frac{n_{ads}}{n_{des}}\right) \times P_{ext}.$$  \hspace{1cm} \text{Eq. 3}

Where $P_{ext}$ is the externally applied charging pressure of the hydrogen gas, $n_{ads}$ and $n_{des}$ are the moles of hydrogen adsorbed and desorbed recorded from the experiment respectively. The correction factor is established wrt. ref. [13] as $\text{CF} = (n - 1) \times e^{-\frac{E_{ads}/k_B T}{n}}$, where $n$ is the number of graphene layers and $E_{ads}$ is the adsorption energy of hydrogen with carbon in the graphitic domain.

The correction factor is calculated per interlayer spacing of the graphitic domain value. The adsorption energy ($E_{ads}$) depends on the composition of the interface layer ($p$) and is computed as follows,

$$E_{ads} = E_{bin}(H_2 + \text{Graphene}) - \frac{1}{2-p}E_{bin}(Si) - \frac{2(1-p)}{2-p}E_{bin}(O) - \frac{p}{2-p}E_{bin}(C) \hspace{1cm} \text{Eq (4)}$$

The value of $E_{bin}(H_2 + \text{Graphene})$ is obtained from molecular dynamics simulation as detailed in [13].
Therefore, the value of GD is calculated by the equation adapted from the modified expanded graphite model [13] as follows,

\[
GD = \frac{(0.2633(d')\lambda(n_C) - \frac{(d')^3}{6})}{\{V_m (P_{int,T}) + (0.2633(d')\lambda(n_C) - \frac{(d')^3}{6})\}} \times \left( e^{-\frac{E_{ads}/K_B T}{K_B T}} \right) \text{-------------------------Eq. (5)}
\]

From equation 5 we can refer that, the volume occupied by the SiO\textsubscript{2} nanodomains has been subtracted from the total volume available for hydrogen adsorption. Also seen from equation 5 is the dependence of GD on the structural parameters after addition of GNP. The above equation however does not consider the interdomain mixed Si-O-C bonds for hydrogen adsorption and only considers the ordered GNP which has been added in the ceramic. The presence of the ordered structure of GNP after pyrolysis at 1000°C has been reported in reference [17].

This establishment of the equation for gravimetric storage density was followed by the hydrogen adsorption studies on the composite.

**Hydrogen storage in GNP incorporated SiOC polymer derived ceramic**

Hydrogen storage studies were carried out on the synthesized composites at 100 K and pressure up to 2 bar using Sievert’s apparatus. The usage of pressure till 2 bar is an attempt to achieve promising uptake of hydrogen at low pressures, considering its practical usage in future. Gravimetric Density (GD) of hydrogen storage is then calculated and is then plotted with pressure ranging from 1 bar – 2 bar at 3 discrete pressures as shown in Fig. 6 (a) and Table 2.

Sample without GNP, SiOC 1000C showed the highest potential for hydrogen adsorption at 2 bar with GD being 0.35 wt.%. GNP added samples, SiOC 1000C 0.3 wt.%, 3 wt.% and 6 wt.% resulted in GD of 0.16 wt.%, 0.08 wt.% and 0.02 wt.% respectively.
Fig. 6: Shows the (a) Gravimetric storage densities(GD) of the samples at 100 K; (b) Mesopore volumes obtained through Barrett-Joyner-Halenda (BJH) studies.

As seen in Fig.6 (a), the hydrogen storage capacity decreases with addition of GNP. As discussed earlier, the adsorption in GNP free ceramic is largely due to capillary condensation in the mesopores (2-5 nm). However, after addition of GNP, this volume is exponentially reduced as seen in Fig. 6(b) and Table 2 leading to reduction in adsorption capacity. The highest GD of 0.16 wt.% was found to be for the 0.3 wt.% GNP sample. Further, this reduction in the mesopore (2 - 5 nm) volume can largely be attributed to changes in the electronegativity of the ceramic after addition of GNP, thereby affecting the interdomain bonding i.e., Si-O, Si-C, and the graphitic part(C) and size of the nanodomains in the ceramic [23, 24]. Further from Table 4 we can observe that for the ceramic without GNP addition, the silica nanodomain size is 1.4 nm, which is indicative of mesopores (<5 nm). These mesopores are key to multilayer adsorption in this material [22]. The effect of mesopores sized, 2-5 nm can also be seen through reference [22]. This results in a storage capacity of 0.35 wt.% for the ceramic. However, with the addition of GNP, the silica nanodomain size increases from 1.4 nm to 2.6 nm. The addition of GNP
increases the area of the graphitic domain bordering these SiO₂ nanodomains. This increase in the size of the nanodomain can be further correlated to the decrease in the B.E. for the Si, O and C atoms shown in Table 1. However, this increase in the openness in the structure reduces the pore volume of the mesopores sized, 2-5 nm (Fig. 6(b)), thus bringing down the storage capacity of the ceramic.

Contrary to the observations made above, for the 6 wt.% sample, the SSA and the GD both decrease, as seen in Table 2. This is probably due to partial refilling of pores by GNP which, due to addition in a sufficiently large quantity, loses capability of dispersion and tends to aggregate in the voids created by the pores [25]. This phenomenon of partial refilling of the pores reduces the hydrogen storage capacity by providing lesser 2D carbon phase at the surface as well as masking the Si-O-Si features at inner surface of the pore walls which is primarily responsible for hydrogen storage in pores. Similar observations were made by K. J. Kim et. al., reporting carbon precipitation in the Si-O-C matrix with the addition of free carbon [23].

4. Conclusions

The present work establishes the effects of GNP addition on the pore morphology, structure and hydrogen adsorption capability of the GNP incorporated ceramics. Type IV N₂ sorption isotherms were found for the ceramics. A maximum GD of 0.16 wt. % was observed for the sample with 0.3 wt.% GNP and it reduced further with an increase in the GNP content. This reduced GD for the GNP incorporated samples when compared to 0.35 wt.% for the without GNP sample, SiOC 1000C is largely due to increase in the relative size of the silica nanodomains compared to the non-stoichiometric graphitic domain after the addition of GNP. This enlargement leads to a reduction in the volume of mesopores sized in the range, 2-5 nm. Further,
the addition of GNP beyond 3wt.% led to a decrease in the total pore volume and SSA of the composite due to agglomeration of the GNP. Hence these studies find that the sizes of the nanodomains in the ceramic are critical for hydrogen uptake. Additionally, a suitable methodology in line with the nanodomains model for calculating the hydrogen storage capacity (GD) of the GNP added ceramic is formulated. Further, the finding of this study could be used for obtaining an optimized material for various applications.

5. Acknowledgements:
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6. References:


Table 1: Surface elemental composition and binding energies (B.E.) for the pyrolysed samples, obtained through XPS studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si2p</th>
<th>O1s</th>
<th>C1s</th>
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<tr>
<td></td>
<td>B.E.</td>
<td>Atomic %</td>
<td>B.E.</td>
</tr>
<tr>
<td>SiOC 1000C</td>
<td>103.5</td>
<td>25.4</td>
<td>533.2</td>
</tr>
<tr>
<td>SiOC 1000C 0.3 wt.% GNP</td>
<td>103.4</td>
<td>24.1</td>
<td>533.2</td>
</tr>
<tr>
<td>SiOC 1000C 3wt.% GNP</td>
<td>103.3</td>
<td>18.2</td>
<td>533.2</td>
</tr>
<tr>
<td>SiOC 1000C 6wt.% GNP</td>
<td>103.9</td>
<td>17.7</td>
<td>533.5</td>
</tr>
</tbody>
</table>

Table 2 Shows the pore morphology (pore volume, mean pore diameter) and gravimetric storage density (GD) of the pyrolyzed samples

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample Description</th>
<th>SSA (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Meso pore volume of pore size 2-5 nm (cm³/g)</th>
<th>Mean pore diameter (nm)</th>
<th>MeanGD (wt.%) at 2 bar and 100K</th>
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<tbody>
<tr>
<td>1.</td>
<td>SiOC 1000C</td>
<td>158.1</td>
<td>0.56</td>
<td>0.34</td>
<td>14.5</td>
<td>0.35</td>
</tr>
<tr>
<td>2.</td>
<td>SiOC 1000C 0.3wt.% GNP</td>
<td>212.6</td>
<td>0.876</td>
<td>0.07</td>
<td>16.4</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Table 3 shows the calculated values of the empirical formula, stoichiometric part and graphitic part.

<table>
<thead>
<tr>
<th>SI No</th>
<th>Sample</th>
<th>Atomic % Silicon</th>
<th>Atomic % Oxygen</th>
<th>Atomic % Carbon</th>
<th>Empirical formula ((SiO_xC_y))</th>
<th>Stoichiometric part ((SiO_xC_y(1-0.5x)))</th>
<th>Graphitic part ((y - (1 - 0.5x))C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiOC 1000C</td>
<td>25.4</td>
<td>41.5</td>
<td>33</td>
<td>(SiO_1C_{0.53})</td>
<td>(SiO_1C_{0.5})</td>
<td>0.03 C</td>
</tr>
<tr>
<td>2</td>
<td>SiOC 1000C</td>
<td>24.1</td>
<td>42.5</td>
<td>33.4</td>
<td>(SiO_{1.38}C_{0.81})</td>
<td>(SiO_{1.38}C_{0.31})</td>
<td>0.50 C</td>
</tr>
<tr>
<td></td>
<td>0.3wt% GNP</td>
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</tr>
<tr>
<td>3</td>
<td>SiOC 1000C</td>
<td>18.2</td>
<td>40.7</td>
<td>41.1</td>
<td>(SiO_{1.49}C_{1.25})</td>
<td>(SiO_{1.49}C_{0.255})</td>
<td>1.005 C</td>
</tr>
<tr>
<td></td>
<td>3wt% GNP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>SiOC 1000C</td>
<td>17.7</td>
<td>41.1</td>
<td>41.3</td>
<td>(SiO_{1.38}C_{1.02})</td>
<td>(SiO_{1.38}C_{0.31})</td>
<td>0.72 C</td>
</tr>
<tr>
<td></td>
<td>6wt% GNP</td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
Table 4 shows the calculated values of model parameters $d^*$, $\lambda$, and $n_C$.

<table>
<thead>
<tr>
<th>SI. No.</th>
<th>Sample</th>
<th>Empirical formula (SiO$_x$C$_y$)</th>
<th>p</th>
<th>$d^*$ (nm)</th>
<th>$\lambda$ (pm)</th>
<th>$n_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiOC 1000C</td>
<td>SiO$<em>1$C$</em>{0.53}$</td>
<td>0.75</td>
<td>1.4</td>
<td>27</td>
<td>5.292</td>
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<tr>
<td>2</td>
<td>SiOC 1000C 0.3wt.% GNP</td>
<td>SiO$<em>{1.38}$C$</em>{0.81}$</td>
<td>0.5</td>
<td>1.7</td>
<td>484</td>
<td>139.876</td>
</tr>
<tr>
<td>3</td>
<td>SiOC 1000C 3wt.% GNP</td>
<td>SiO$<em>{1.49}$C$</em>{1.25}$</td>
<td>0.5</td>
<td>2.6</td>
<td>1170</td>
<td>790.92</td>
</tr>
<tr>
<td>4</td>
<td>SiOC 1000C 6wt.% GNP</td>
<td>SiO$<em>{1.39}$C$</em>{1.02}$</td>
<td>0.75</td>
<td>3.9</td>
<td>1030</td>
<td>1566.63</td>
</tr>
</tbody>
</table>

**Supplementary Fig. 1:** Raman spectra for (a) Pure graphene nanoplatelets (GNP); (b) amorphous SiOC 3wt.% 1000C sample.