was produced to enhance the regenerative cooling capacity of the ATF. The study, which was comparative in nature, revealed a meagre increase in the ignition delay of the nano-fuel with respect to ATF (base-fuel), at temperatures (T) > 950 K. The study indicates a negligible compromise on the ignition delay, as against a substantial improvement in the regenerative cooling capacity of the fuel.

1. Nagaboopathy, M., Vijayanand, C., Hegde, G., Reddy, K. P. J. and Arunan, E., Single-pulse chemical shock tube for ignition delay measurements. *Curr. Sci.*, 2008, **95**(1), 78–82.
2. Sonawane, S., Bhandarkar, U., Puranik, B. and Kumar, S. S., Convective heat transfer characterization of aviation turbine fuel–metal oxide nano-fluids. *J. Thermophys. Heat Transfer*, 2012, **26**(4), 619–628.
3. Milton, B. E., Atomization of liquid droplets on surfaces exposed to moving shock waves. *Shock Waves*, 2006, **16**(2), 95–107.
4. Anderson Jr, J. D., In *Modern Compressible Flow: With Historical Perspective* (eds Beamesderfer, L. and Morriss, J. M.), McGraw-Hill, Singapore, 1990, 2nd edn, pp. 209–212.
5. Gauthier, B. M., Davidson, D. F. and Hanson, R. K., Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures. *Combus. Flame*, 2004, **139**(4), 300–311.
6. Vandersickel, A. *et al.*, The autoignition of practical fuels at HCCI conditions: high-pressure shock tube experiments and phenomenological modeling. *Fuel*, 2012, **93**, 492–501.
7. Litke, P. J., Schauer, F. R., Paxson, D. E., Bradley, R. P. and Hoke, J. L., Assessment of the performance of a pulsejet and comparison with a pulsed-detonation engine. AIAA paper No. 2005-0228.
8. Ma, F., Choi, J. Y. and Yang, V., Thrust chamber dynamics and propulsive performance of single-tube pulse detonation engines. *J. Propulsion Power*, 2005, **21**(3), 512–526.
9. Bussing, T. R. A., Bratkovich, T. E. and Hinkey, J. B., Practical implementation of pulse detonations engines. AIAA paper No. 1997-2748.

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Atomic hydrogen storage in a two-dimensional hydrogenated diamond-like carbon film

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The present communication describes the two-dimensional hydrogenated diamond-like carbon (2D-HDLC) film as a system for storing atomic hydrogen, having hydrogen content in atomic per cent ~37.5 corresponding to gravimetric density of hydrogen ~5.8 wt%.

Keywords: Graphane, gravimetric density, green fuel, hydrogen storage.

HYDROGEN is the most promising environmental-friendly 'green' fuel. This is due to the fact that its energy content of 142 MJ per kg exceeds that of petroleum by several factors of magnitude and its combustion produces water vapour only[1]. Electrical energy is produced in a fuel cell due to chemical reaction between oxygen (in air) and hydrogen[2]. Fuel cells are expected to be a practical means for supplying power to road/space vehicles. Therefore, it is necessary for a viable method of on-board hydrogen storage. Currently the methodologies for storing hydrogen in a suitable container are of primary concern. Several means of hydrogen storage were considered using two parameters, viz. gravimetric density (GD), i.e. ratio of weight percentage of hydrogen stored to the total weight of the system (hydrogen + container), and volumetric density (VD), i.e. stored hydrogen mass per unit volume of the system. Till date, hydrogen storage as gas at high pressure or as a liquid at cryogenic temperatures is not found to be suitable for safety and economic reasons. Also, the methods of storing hydrogen in or on solid phase do not fulfil the Department of Energy (DOE), USA targets for GD and VD[3,4]. The well-known diamond-like carbon (DLC) film is referred to as amorphous hydrogenated carbon (a-C: H) film having sp^2 C=C and sp^3 C–H carbons and some films containing up to 50 at% hydrogen[5,6]. The unique properties of a-C: H films make them suitable for various industrial applications[5–7], viz. antireflective, scratch-resistant wear-protective coating, cold cathode material in electron devices, biomedical devices, etc. The amorphous DLC (a-C: H) film was not reported[5–7] for application as hydrogen-storage material[8] in hydrogen-fuel technologies[1]. Since the discoveries of (i) experimental synthesis of graphene[9] (two-dimensional one-atom-thick layer of carbon in hexagonal crystalline structure), and (ii) theoretical prediction of graphane[10]

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(hydrogenation of both sides of graphene alternately), followed by experimental hydrogenation of one side of graphene by hydrogen plasmas[11] created a focused interest among researchers for the laboratory synthesis of graphane[10,12], which is considered as one of the thinnest DLC films due to pure sp^3 hybridization of all carbon–carbon σ-bonds/carbon–hydrogen σ-bonds and absence of conductive π-bonds (Figure 1). It was estimated[12,13] that single-layer graphane, a graphene-based material, having very high hydrogen density[10] can be used for hydrogen storage in hydrogen-fuel technologies. A detailed demonstration was provided earlier[14,15] that hydrogenated diamond-like carbon (HDLC) films, having an estimated value[15] of specific surface area $\sim 10^{12}$ nm^2/g, deposited onto a large area Si (100) substrate at room temperature by reactive gas–plasma process, are composed of an ordered hexagonal structure of carbon atoms with lattice parameters $a = 2.62$ Å and $c = 6.752$ Å, different from those present in a hexagonal graphite structure. Figure 2 provides a typical view of HDLC films onto Si substrate. Detailed characterization confirmed the existence of misoriented bilayer graphene-like (sp^2 C=C) and graphane-like (sp^3 C–H) structures in the HDLC films, having interlayer disorder[16,17]. Due to existence of interlayer disorder, the layers of HDLC film stay perfectly parallel but their mutual orientation in the direction of planes is random and hence the 3D crystallinity of the HDLC films should be lost, while only the 2D crystallinity should be preserved[18]. These results imply two-dimensional behaviour of each layer of a typical HDLC film, also known as 2D-HDLC films[16,17]. Three representative electron energy loss (EEL) spectra at the carbon *K*-edge of 2D-HDLC film in cross-section geometry were examined at different depths of the film by a high resolution transmission electron microscope (HRTEM; JEOL-EM-2010; with LaB_6 emitter) operating at 200 kV. Figure 3 shows the recorded spectra with the electron probe positioned approximately 26, 88 and 163 nm above the interface of the 2D-HDLC film onto the Si substrate. There is no significant difference among the spectra. All spectra have a peak at the onset of the *K*-edge followed by a broad maximum that spreads between 290 and 310 eV. The peak at 285.5 eV is due to transition from the core 1s state to the π^* state above the Fermi level and its sharpness clearly indicates crystalline nature of sp^2-bonded carbon as in the hexagonal graphitized C in comparison to amorphous carbon (a-C); the broad peak is due to transition from 1s to σ^* states[19,20]. Thus, the EEL spectra also confirm hexagonal crystallinity at different depths of the typical 2D-HDLC film (Figure 2). The aim of the present communication is a critical evaluation of the 2D-HDLC film as a system for storage of atomic hydrogen[14–17].

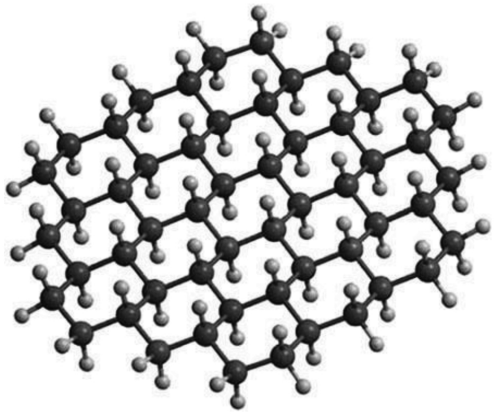

Figure 1. Schematic structure of graphane (1.54 Å C–C) layer produced via functionalization of graphene (1.42 Å C–C) with atomic hydrogen (small white balls) in a chair configuration[10].

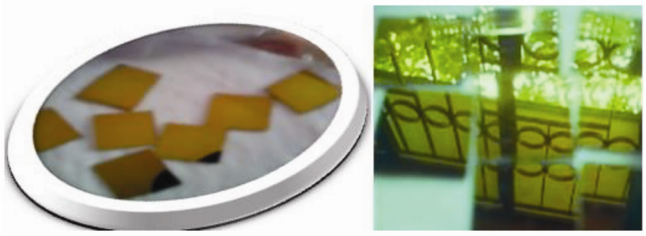

Figure 2. Photographs of 2D-hydrogenerated diamond-like carbon (HDLC) films and typical mirror image of surrounding objects due to reflection of light from the films.

The basic condition for the realization of hydrogen storage material for practical uses is that it should be reversible, i.e. able to load and unload hydrogen under ambient temperature and pressure. The theoretically predicted crystalline lattice of graphane consists of a hexagonal carbon–hydrogen network in which each carbon atom of graphene is bounded with atomic hydrogen in a chair configuration (Figure 1). The estimated value of GD of hydrogen in a single-layer graphane[10] is 7.7 wt%, which corresponds to ~50 at%. Since graphane is a 2D material, its VD is not relevant herein. According to current DOE targets for commercial automotive applications[3,4], the GD of hydrogen storage material should reach the level of 6.5 wt%. It has been found that desorption energy[21] of hydrogen atoms is largest in graphane (C : H=1), being a saturated hydrocarbon[21] and that depends upon the degree of hydrogenation in the partially hydrogenated graphene (C : H > 1), being an unsaturated hydrocarbon. Thus the hydrocarbon thin film made in the present author's laboratory[17], having interlayer disorder and consisting of graphane-like and graphene-like structures in each layer of the film, may be considered as partially hydrogenated graphene and this material should be suitable for atomic hydrogen (H) storage[1]. Due to the stable structure and small size of graphane, it has been estimated that molecular hydrogen (H_2) can be stored if graphane is doped with alkaline earth metals (AEMs)[22,23]. In this respect, 2D-HDLC film, containing graphane-like structure should be suitable for doping with AEMs followed by hydrogen storage in molecular form[17]. In the

earlier study[24], the concentration of bonded hydrogen atoms in HDLC films under different deposition conditions was measured (by visible Raman spectroscopy) to be in the range 26–36 at%. The main effect of hydrogen in an HDLC film is to modify the C–C network at different depths of the film. How these modifications occur at various depth of the HDLC film during its synthesis onto Si(100) substrate cannot be studied by Raman spectroscopy or X-ray photoelectron (XP) spectroscopy method because: (i) the skin depth of the 488 nm excitation source used in Raman measurements, is ~6 μm and using this technique one can get information for the whole material rather than at different depths of the thin film having thickness ~168 nm, and (ii) XP spectroscopy is a surface-sensitive probe for the 2D-HDLC film, because here the skin depth for X-rays is 5 nm (ref. 25). Thus in order to explore the distribution of hydrogen in the 2D-HDLC film along its depth, the well-known ion beam analysis (IBA) techniques, viz. nuclear reaction analysis (NRA)[26] and Rutherford backscattering (RBS)[27] were used. Datta *et al.*[28] provided a detailed description of measuring depth profile of hydrogen in the 2D-HDLC film using the IBA technique, with resonance at 6.44 MeV in $^{1}H(^{19}F, \alpha\gamma)^{16}O$ nuclear reaction. Figure 4 shows typical concentration of hydrogen atoms as a function of depth in the 2D-HDLC film synthesized under different deposition conditions of $H_2 : CH_4$ ratio, viz. ~25 (film A), ~17 (film B), ~13 (film C) and ~7 (film D) respectively. The typical concentration profile of hydrogen in film D ~ 37.5 at% was found to be quasi-uniform; similar result for HDLC film under typical deposition condition of H_2:CH_4 ratio ~10 was found using Raman spectroscopy[24]. In the IBA techniques the depth resolution is ~10 nm; thickness of single layer of 2D-HDLC film is ~0.5 nm, i.e. the number of layers within 10 nm will be ~20. Thus the measured concentration profile of hydrogen atoms (Figure 4) corresponds to several number of layers in the 2D-HDLC film. For the fully hydrogenated graphene, i.e. pure single-layer graphane (C : H=1)[10], the GD of hydrogen is 7.7 wt% which corresponds to hydrogen atom content in atomic percent at ~50. Thus GD of H can be estimated, using the measured value of hydrogen atom content in ~37.5 at% in film D, to be ~5.8 wt%. Since 2D-HDLC film is not a pure single-layer graphane, but multi-layers of graphene-like and graphane-like structures with interlayer disorder, the measured value of death profile of hydrogen content (Figure 4) corresponds to that in different layers of the 2D-HDLC films. Considering 2D-HDLC as a binary film C_xH_y, it can be said that the H : C ratio is close to 30 at% for the typical as-prepared film B, and to 5 at% for the typical annealed film B (Figure 5), which implies unloading of atomic hydrogen from 2D-HDLC film. Unloading of H is also evident from the constant current STM image of the annealed 2D-HDLC film, as shown in Figure 6, which is more conductive than the fully hydrogenated graphene, i.e. pure graphane (which is an insulator). The observed bright spots in Figure 6 seem to correspond to the simulated constant-current STM image of the conducting sp^2 C=C carbons, and the dark spots correspond to non-conducting sp^3 C–H carbons. Bright spots are interconnected by dark spots, indicating that the 2D-HDLC film comprises coherent

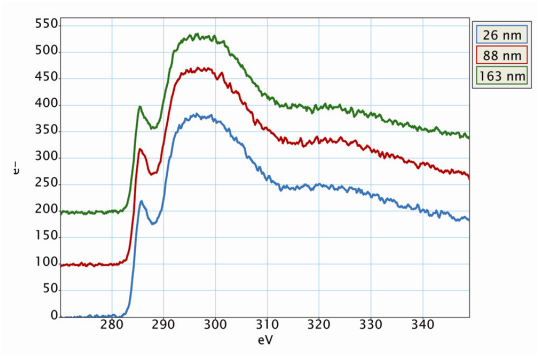

Figure 3. Typical electron energy loss spectra of 2D-HDLC film in cross-section geometry at three different depths from the interface of the film-D (vide Figure 4) onto Si substrate.

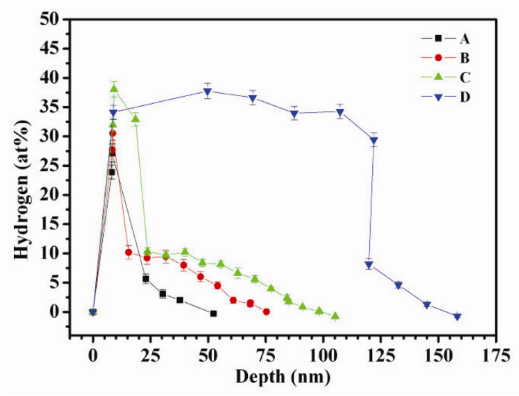

Figure 4. Typical depth profiles of hydrogen as measured by ion beam analysis techniques in the 2D-HDLC films (A–D), synthesized under different deposition conditions of $H_2 : CH_4$ ratio.

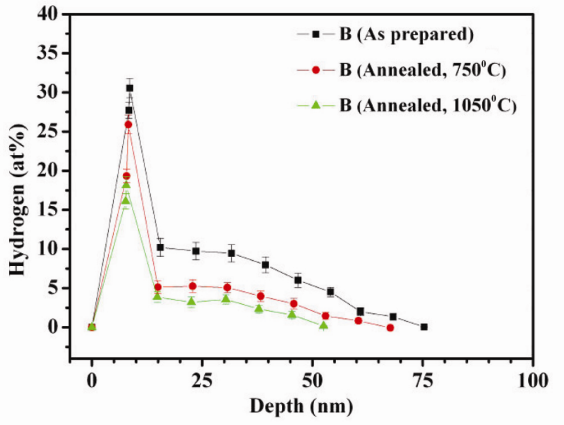

Figure 5. Typical depth profiles of hydrogen as measured by IBA techniques in the as-prepared and annealed 2D-HDLC film (film B).

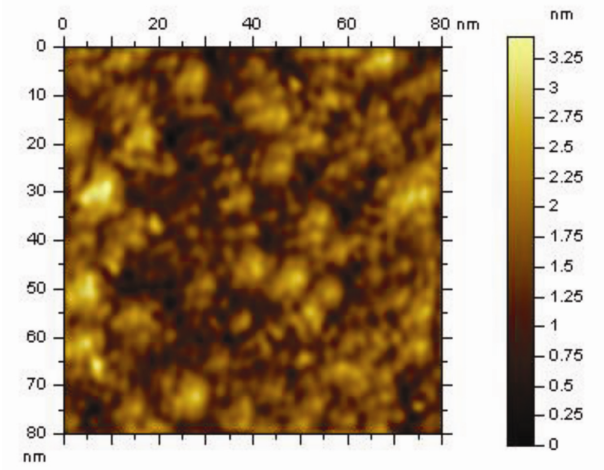

Figure 6. Typical STM image of annealed 2D-HDLC film.

domains of sp^2 and sp^3 carbons, as reported in an earlier study[16]. Since the annealed 2D-HDLC film is partially hydrogenated graphene (C : H>1) for which the desorption energy of hydrogen is found to be much smaller than that for graphane (C : H=1), AEM can be doped with the sp^3 C–H carbons in the annealed sample using the electrochemical process[3] for storing molecular hydrogen[22,23]. Many methods have been proposed for efficient storage of molecular hydrogen in graphene-based materials for fuel-cell applications[4,29]. Despite intense research efforts, DOE, USA, goal of 6.5 wt% GD of hydrogen[4] has not been achieved till date either experimentally or using theoretical simulations on reversible (hydrogenation/dehydrogenation) model system[8,29].

In conclusion, the 2D-HDLC films, having hydrogen content ~37.5 at% which corresponds to GD of H ~5.8 wt%, can be used for storage of atomic hydrogen. This result is close to the target value set by DOE, USA[4] for automotive applications[1]. Thus the 2D-HDLC film is proposed in making prototype practical devices for implementation of commercial uses in future.

1. Schlapbach, L. and Züttel, A., Hydrogen-storage materials for mobile applications. *Nature*, 2001, **414**, 353–358.
2. Das, A. K., *Fundamental Concepts of Inorganic Chemistry-Part II*, CBS Publishers & Distributors, New Delhi, 2004, pp. 838–846.
3. Ströbel, R. *et al.*, Hydrogen storage by carbon materials. *J. Power Sources*, 2006, **159**, 781–801.
4. D.O.E. Office of Energy Efficiency and Renewable Energy Hydrogen, Fuel cells and infrastructure technologies program multi-year research, development and demonstration plan. Available at https://energy.gov/sites/prod/files/2015/05/f22/fcto_myrdd_storage.pdf (accessed on 12 July 2016).
5. Robertson, J., Diamond-like carbon. *Pure Appl. Chem.*, 1994, **66**, 1789–1796.
6. Grill, A., Diamond-like carbon: state of the art. *Diamond Relat. Mater.*, 1999, **8**, 428–434.
7. Zeng, A., Diamond-like carbon (DLC) films as electrochemical electrodes. *Diamond Relat. Mater.*, 2014, **43**, 12–22.
8. Steele, B. C. H. *et al.*, Materials for fuel-cell technologies. *Nature*, 2001, **414**, 345–352.
9. Novoselov, K. S. *et al.*, Electric field effect in atomically thin carbon films. *Science*, 2004, **306**, 666–669.
10. Sofo, J. O. *et al.*, Graphane: a two-dimensional hydrocarbon. *Phys. Rev. B*, 2005, **75**, 153401-1–153404-4.
11. Elias, D. C. *et al.*, Control of graphene's properties by reversible hydrogenation: evidence for graphane. *Science*, 2009, **323**, 610–613.
12. Savchenko, A., Transforming graphene. *Science*, 2009, **323**, 589–590.
13. Srinivas, G. *et al.*, Graphene-based materials: synthesis and gas sorption, storage and separation. *Prog. Mater. Sci.*, 2015, **69**, 1–60.
14. Ray, N. R. *et al.*, In search of graphane – a two-dimensional hydrocarbon. *Cond. Mat. Mtrl. Sci.*, 2008, preprint; arXiv: 0802-3998v1.
15. Biswas, H. S. *et al.*, Covalent immobilization of protein onto a functionalized hydrogenated diamond-like carbon substrate, *Langmuir*, 2010, **26**, 17413–17418.
16. Datta, J. *et al.*, Structure of hydrogenated diamond like carbon by micro-Raman spectroscopy. *Mater. Lett.*, 2012, **71**, 131–133.
17. Ray, N. R. *et al.*, Signature of misoriented bilayer graphene-like and graphane-like structure in the hydrogenated diamond like carbon film. *IEEE Trans. Plasma Sci.*, 2012, **40**, 1789–1793.
18. Tuinstra, F., Raman spectrum of graphite. *J. Chem. Phys.*, 1970, **53**, 1126–1130.
19. Lifshitz, Y. *et al.*, Visualization of diamond nucleation and growth from energetic species. *Phys. Rev. Lett.*, 2004, **93**, 056101-1–056101-4.
20. Murooka, Y. *et al.*, Electron energy loss spectroscopy of carbon films prepared by electron cyclotron resonance plasma sputtering. *Mater. Trans.*, 2002, **43**, 2092–2096.
21. Openov, L. A. and Podlivaev, A. I., Thermal desorption of hydrogen from graphane. *Cond. Mat.* Mes-Hall, 2010, preprint; arXiv: 1001-1124v1.
22. Antipina, L. Y. *et al.*, High hydrogen-adsorption-rate material based on graphane decorated with alkali metals. *Phys. Rev. B*, 2012, **86**, 085435-1–085435-7.
23. Hussain, T. *et al.*, Calcium doped graphane as a hydrogen storage material. *Appl. Phys. Lett.*, 2012, **100**, 183902-1–183902-5.
24. Singha, A. *et al.*, Quantative analysis of hydrogenated diamond-like carbon films by visible Raman spectroscopy. *J. Appl. Phys.*, 2006, **100**, 044910-1–044910-8.
25. Nebesny, K. W. *et al.*, Quantitation of auger and X-ray photoelectron spectroscopies. *Anal. Chem.*, 1989, **61**, 469A–477A.
26. Liech, D. A. *et al.*, A technique for measuring hydrogen concentration versus depth in solid samples. *Nucl. Instrum. Methods*, 1973, **108**, 67–71.
27. Ziegler, J. F., Profiling hydrogen in materials using ion beams. *Nucl. Instrum. Methods*, 1978, **149**, 19–39.
28. Datta, J. *et al.*, Study of depth profile of hydrogen in hydrogenated diamond like carbon thin film using ion beam analysis techniques. *Nucl. Inst. Methods Phys. Res. B*, 2014, **328**, 27–32.
29. Spyrou, K. *et al.*, Hydrogen storage in graphene-based materials: efforts towards enhanced hydrogen absorption. *ECS J. Solid State Sci. Technol.*, 2013, **2**, M3160–M3169.

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