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REGULAR ARTICLE

Study on Hydrophilicity/Hydrophobicity of Hydrogenated Diamond-Like Carbon Thin Film

Amit Kumar Kundu[1,2], Aniruddha Mondal[1,3], Hari Shankar Biswas[1,*], Dilip K. Maiti[4,†], Sandeep Poddar[5]

[1] *Department of Chemistry, Surendranath College, 700009 Kolkata, India*
[2] *Department of Chemistry, Sripat Singh College, Jiaganj, Murshidabad, 742123 Pin, India*
[3] *Harindanga High School, 743504 Falta, India*
[4] *Department of Chemistry, University of Calcutta, University College of Science, 700009 Kolkata, India*
[5] *Lincoln University College, Research & Innovation Division, 47301 Petaling Jaya, Malaysia*

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Hydrogenated Diamond-Like Carbon (HDLC) thin films find extensive applications in diverse fields, such as industrial settings, including biomedical coatings with bactericidal properties, as well as in mechanical, electronic, and biomolecule immobilization contexts. To enhance the surface properties of HDLC thin films, various methods are employed, including hydrogen plasma treatment, electrochemical hydrogenation, annealing, and biomolecule immobilization. The synthesis of HDLC films involves biased enhanced nucleation (BEN) under varying H_2 and CH_4 flow rates in the reactive gas-plasma process (RGPP). In this study, we investigated the wettability of both pristine HDLC thin films and modified HDLC thin films using the sessile drop technique, measuring contact angles with liquids of distinct physicochemical natures, such as water and glycerin. sp^3 and sp^2 content of the HDLC and modified samples were measured by Raman spectrum. The surface energy of the samples exhibited a slight increase in correlation with the sp^3 content of HDLC and modified HDLC samples. Notably, a strong correlation between hydrophilicity/hydrophobicity and the density of the sp^2/sp^3 ratio was observed across various HDLC surfaces, including as-prepared HDLC, electrochemically hydrogenated (ECHDLC), annealed HDLC surfaces, and surfaces modified through covalent immobilization of Bovine Serum Albumin (BSA) protein onto hydrogenated diamond-like carbon.

Keywords: Hydrophilicity, Hydrophobicity, HDLC, Contact angle, Raman spectra, Surface energy.

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1. INTRODUCTION

Diamond-like carbon (DLC) films have garnered significant attention over the past few decades owing to their exceptional mechanical properties, including a low coefficient of friction, high hardness, and strong adherence to various substrate materials [1-3]. These properties make DLC films highly desirable for a wide range of applications in both industrial settings and academic research. Understanding the surface properties of DLC films is crucial for comprehending their interactions with foreign materials. One key parameter influencing these interactions is surface energy, which is contingent upon the polarity of the surface. In the context of DLC films, investigating the hydrophobic/hydrophilic nature of the surfaces is of particular interest. This inquiry is typically addressed through the measurement of contact angles between water droplets and DLC surfaces.

Several strategies have been explored to modify the surface properties of DLC films, with notable studies focusing on hydrogenation [4], dehydrogenation [5], and the immobilization of biomolecules [1]. These modifications aim to enhance specific characteristics of the HDLC (hydrogenated DLC) surface, leading to improvements in stability, biocompatibility, cell adhesion, and lubricity [6-9]. Hydrogenation and dehydrogenation processes have been demonstrated as effective means to alter the surface of HDLC thin films. The resulting modifications impact the roughness of the film surfaces [10] [11-12]. Additionally, the hydrophobic or hydrophilic nature of the modified surfaces plays a pivotal role in influencing their properties [13].

The research community has extensively investigated the impact of these surface modifications on the performance of HDLC films. Notably, modifications have been shown to enhance the stability, biocompatibility, lubricity, and cell adhesion properties of HDLC films [6-9]. This is attributed to the inherent characteristics of the modified surfaces, which include changes in roughness and alterations in hydrophilicity or hydrophobicity [13].

The literature reflects a growing interest in the modification of HDLC film surfaces, exploring diverse methods such as hydrogenation, dehydrogenation, and biomolecule immobilization. These modifications have been shown to significantly impact the mechanical and biological properties of HDLC films, opening up new avenues for applications in various fields, from industry to academic research. Future research in this area holds the potential for further advancements in understand-

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[*] Correspondence e-mail: harishankarb7@gmail.com
[†] dkmchem@caluniv.ac.in

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ing and optimizing the properties of DLC films for specific applications.

2. EXPERIMENTAL

Pristine HDLC (PHDLC) thin films were synthesized by using the technique of biased enhanced nucleation (BEN) under the varying ratio of H_2 and CH_4 flow rates in the reactive gas-plasma process (RGPP) as described elsewhere [1]. In seven samples the flow rates of CH_4 are 25, 35, 45, 55, 65, 75, and 85 standard cubic centimeters per minute at STP (SCCM) and the flow rate of hydrogen is 500 SCCM, thus at room temperature (RT), the ratio of H_2 to CH_4 during deposition of the films will be represented as samples HDLC1.65, HDLC1.59, HDLC1.52, HDLC1.43, HDLC1.35, HDLC1.18, and HDLC1.22 respectively, in the rest of the paper. In the present experiment, the sample HDLC1.65 was hydrogenated electrochemically (ECHDLC) [4]. Dehydrogenated by annealing HDLC1.65 at 1050^{0}C (AHDLC) [5] and Bovine Serum Albumin modified HDLC1.65 (BDHDLC) [1]. Estimation of the surface energy of HDLC samples can be done by measuring the contact angle that a liquid makes at the surface of HDLC. Contact angle measurements were performed by using the contact angle (CA) goniometer of ramé hart instrument co. USA (model 250) with DROPimage Advanced v2.4 software. Measurements were made on three different spots for each surface of the HDLC samples and modified surfaces. Techniques of contact angle/surface energy measurements are explained below. The experimental parameters are summarized in Table 1.

The samples were rinsed with ethanol and with a mixture of cyclohexane and isopropyl alcohol using a ratio of 1:1. The samples were dried with agitated air.

The sessile drop technique was used to measure the equilibrium contact angle of different liquids listed in Table 2. A small drop of liquid was placed on the surface of the cleaned HDLC sample using a micropipette, and the contact angle was measured using the menu-based DROPimage Advanced v2.4 software in situ. The contact angle was measured at least ten times with different drops in order to increase the reproducibility of the measurement. The DROPimage contains a selection of tools to calculate the surface energies of solids by the contact angle measurement. There is an ‘Acid-Base Tool” to evaluate the surface energy parameters of a given solid by taking the contact angles of three different test liquids.

Van Oss et al. [14] [15] described the contribution of acid-base interaction which can be stated in terms of electron donor and electron acceptor of the acid-base component by using three liquids, two polar and one apolar. Methylene iodide for the apolar and either water and glycerol or water and formamide polar liquids are recommended test liquids.

According to Van Oss and coworkers [13, 15, 16], it can be included the weak forces come from polar (Keesom and Debye) forces in the dispersive contribution. The contribution of “combined” forces is denoted by LW–Lifschitz-van der Waals. Another part is a short-range interaction (SR) which is the result of acid-base interactions an example hydrogen bonding is a type of acid-base interaction.

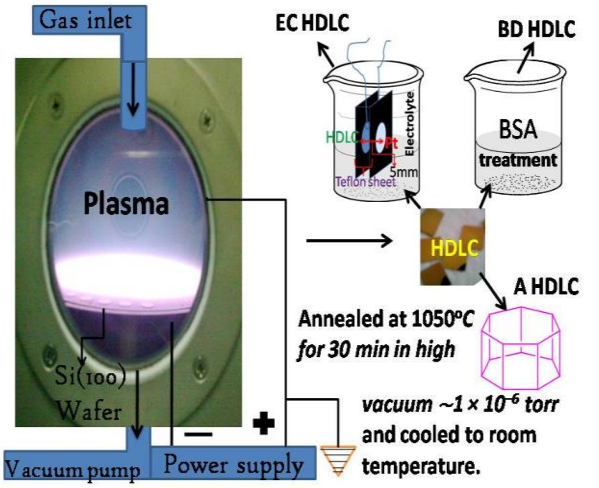

Fig. 1 – Schematic drawing with Plasma chamber photograph

The combined interaction can be written as $\gamma = \gamma^{LW} + \gamma^{AB}$

In which, W^{LW} is the geometric mean of (after Fowkes):

$$W_{12}^{LW} = 2(\gamma_1^{LW}\gamma_2^{LW})^{1/2} \quad (1)$$

But, in this way, we cannot express W^{AB} as only the surface interacts as a basic component with the liquid, and vice versa.

Therefore, Van Oss and coworkers write

$$W_{12}^{AB} = 2(\gamma_1^{+}\gamma_2^{-})^{1/2} + 2(\gamma_1^{-}\gamma_2^{+})^{1/2} \quad (2)$$

Whereas γ_i^{+} is the acidic part and is γ_i^{-}- the basic part.

After measuring the contact angle of particular three liquids viz. j = A, B, and C, with known LW, the acidic and the basic components, the surface energies of the corresponding solid can be calculated.

$$W_{12j} = \gamma_{1j}(1 + \cos\theta_j) = 2(\gamma_{1j}^{LW}\gamma_2^{LW})^{1/2} + \\ +2(\gamma_1^{+}\gamma_2^{-})^{1/2} + 2(\gamma_1^{-}\gamma_2^{+})^{1/2} \quad (3)$$

The solution of this equation is obtained by matrix inversion which is used in DROPimage’s Acid-Base tool.

Table 1 – Specification of liquid drop to measure the contact an-gle, samples surface, surface energy and polarity of different liquids

Parameter	Value
Test liquid	Ultrapure water (Milli-Q system of MilliporeCo.), methylene iodide, glycerol
Drop form	Dropimage advanced v2.4
Micro tip size and Drop Volume	250 µl and 4 µl
Drop type	Sessile
Micro tip diameter	0.50mm
Micro tip size	250 µl
Temperature	23 °C
Relative Humidity	56 %

We also use extended modified Fowke's equation

$$(1+\cos\theta)\frac{\gamma_1}{2(\gamma_1^d)^{1/2}} = (\gamma_2^p)^{1/2} + (\gamma_2^p)^{1/2}\left(\frac{\gamma_1^p}{\gamma_1^d}\right)^{1/2} \qquad (4)$$

to implement in the DROPimage surface energy tool for multi liquids.

3. RESULT AND DISCUSSION

The Figure 2 shows water contact angles on the samples. HDLC1.65, ECHDLC, AHDLC and BDHDLC. Hydrophilic surfaces have high surface energy w.r.t. that of water ~ 72 mJ·m^{-2} and hence water tends to spread over the solid surface, while hydrophobic surfaces have surface energy lower than that of water and hence beading up on the surface.

The surface energy of HDLC samples (Table 2), as estimated by the contact angle goniometer, which is ~ 40-44 ±2 mJ·m^{-2} with different three test liquids methods, shows the surface of HDLC samples is hydrophobic though polar part of the samples slightly increases from sample HDLC1.65 to HDLC1.22.

Table 2 – Samples, contact angle, surface energy and polarity by using different liquids

Sample	Contact Angle (°)	Surface Energy (mj/m^2)	Nonpolar	Polar
HDLC-1.65	71.1	40.83 ± 0.10	34.20	6.63
HDLC-1.59	74.0	41.90 ± 0.06	35.03	6.87
HDLC-1.52	75.1	41.67 ± 0.20	35.00	6.67
HDLC-1.43	75.5	42.73 ± 0.15	35.73	7.00
HDLC-1.35	79.0	42.87 ± 0.40	35.77	7.10
HDLC-1.18	78.3	43.35 ± 0.35	36.90	6.45
HDLC-1.22	82.0	44.20 ± 0.20	36.81	7.39
ECHDLC	81.2	44.77 ± 0.12	37.02	7.75
Annealed HDLC	93.4	51.11 ± 0.15	43.12	7.99
BD-HDLC	103.2	60.51 ± 0.25	52.60	7.91

Table 3 – Estimation of the ratio of sp^2/sp^3 for the samples

Sample	sp^3 (%)	sp^2 (%)	sp^2/sp^3
HDLC-1.65	37.70	62.30	1.65
HDLC-1.59	38.67	61.33	1.59
HDLC-1.52	39.65	60.35	1.52
HDLC-1.43	41.11	58.89	1.43
HDLC-1.35	42.58	57.42	1.35
HDLC-1.18	45.03	54.97	1.18
HDLC-1.22	46.00	54.00	1.22
ECHDLC	50.98	49.02	0.96
Annealed HDLC	15.54	84.46	5.44
BD-HDLC	–	–	–

It is seen that the roughness does not significantly influences the wetting properties of the solid surface of HDLC samples. The hydrophobic character increases due to the increment of surface energy as well as nonpolar part of the HDLC samples.

Estimation of the ratio of sp^2/sp^3 for the samples [17] sp^3 content = 0.24-48.9 (ωG – 0.1580) from the knowledge of G peak position (ωG) of Raman spectra (Figure 5) and the values are shown in Table 3.

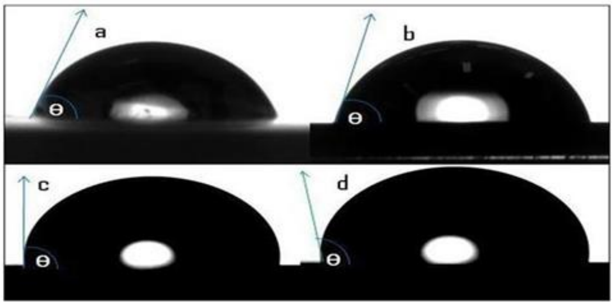

Fig. 2 – Typical contact angle of water with samples (a) HDLC1.65 (b) ECHDLC (c) AHDLC and (d) BDHDLC surfaces

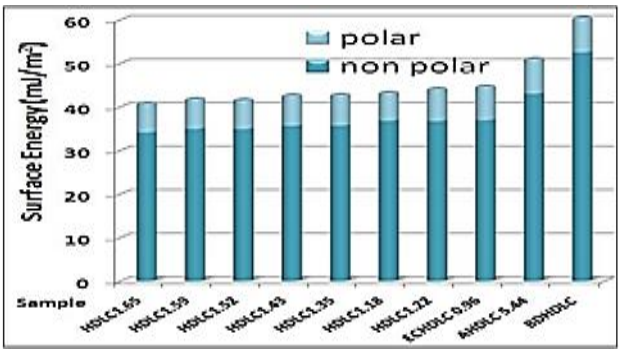

Fig. 3 – A bar graph: Surface energy vs HDLC samples and modified HDLC by different methods

The assessment of hydrophobicity in bulk High-Density Liquid Crystal (HDLC) using Raman spectroscopy reveals a noteworthy correlation with the sp^2/sp^3 ratio [17, 18]. However, the observed results in Table 3 fail to elucidate the alterations in hydrophobicity concerning changes in the sp^2/sp^3 ratio within the bulk HDLC.

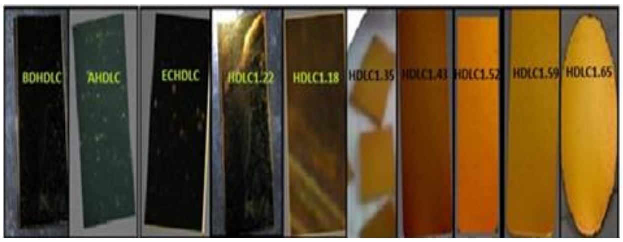

Fig. 4 – Photograph of HDLC and modified HDLC

Exploring techniques to reduce the sp^2/sp^3 ratio on the HDLC surface becomes imperative, given that an augmented hydrophobicity is anticipated due to the conversion of sp^2 C=C to sp^3 C-H during hydrogenation, leading to a decrease in the sp^2/sp^3 ratio on the HDLC surface. Although the surface roughness of HDLC does not significantly impact hydrophobicity, an innovative approach to enhance hydrophobicity, particularly for HDLC, involves reducing the sp^2/sp^3 ratio on the HDLC surface. This reduction can be achieved through electrochemical hydrogenation or the immobilization of biomolecules [19]. The potential of these techniques lies in their ability to modify the surface composition of HDLC, thereby influencing hydrophobicity. This avenue of exploration holds promise for advancing our understanding of hydrophobicity dynamics and opens up possibilities for tailored surface modifications in HDLC applications.

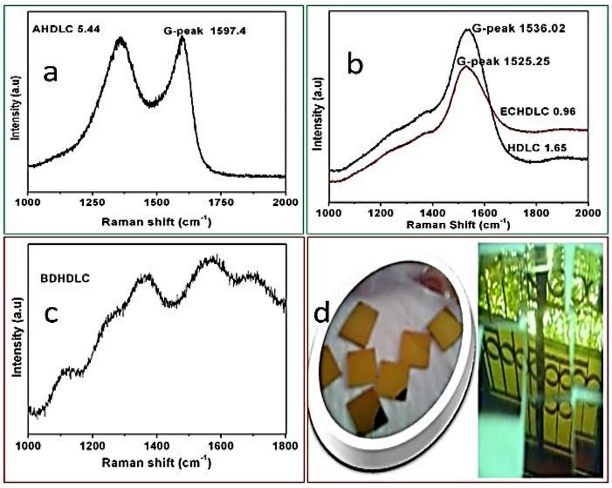

Fig. 5 – (a) Raman spectra of annealed HDLC (b) Raman spectrum of HDLC1.65 and ECHDLC (c) Raman spectra of BDHDLC (d) a photograph of HDLC and its reflection properties through the window

From Tables 2 and 3 it is clear that with the decrease of sp^2/sp^3 ratio surface energy as well as Contact angle gradually increases irrespective of methods used due to the increase of number density increases for hydrogen incorporation. Hence, by measuring the sp^2/sp^3 ratio we can predict the surface energy as well as the Contact angle of the HDLC surface.

4. CONCLUSION

This report elucidates the impact of surface energy, sp^2/sp^3 ratio, electrochemical hydrogenation, dehydrogenation by annealing, and surface modification through BSA protein on the hydrophobicity/hydrophilicity of HDLC surfaces. The investigation reveals crucial insights into predicting and discerning the polarity of HDLC thin film surfaces, offering a potential avenue for detecting biomolecules present on these surfaces. The interplay of surface energy and sp^2/sp^3 ratio emerges as a key determinant influencing the hydrophobic or hydrophilic nature of HDLC surfaces. Electrochemical hydrogenation and dehydrogenation through annealing further contribute to the modulation of surface properties, offering a versatile toolkit for tailoring surface characteristics. Moreover, the introduction of BSA protein as a surface modifier unveils a strategic approach to manipulate hydrophobicity/hydrophilicity, thereby presenting an innovative method for biomolecule detection on HDLC thin film surfaces. These distinctive properties position HDLC surfaces as promising candidates for advancements in surface chemistry, fostering future research and technological enhancements on a global scale.

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Дослідження гідрофільності/гідрофобності гідрогенізованої тонкої алмазоподібної вуглецевої плівки

Amit Kumar Kundu[1,2], Aniruddha Mondal[1,3], Hari Shankar Biswas[1], Dilip K. Maiti[4], Sandeep Poddar[5]

[1] *Department of Chemistry, Surendranath College, 700009 Kolkata, India*
[2] *Department of Chemistry, Sripat Singh College, Jiaganj, Murshidabad, 742123 Pin, India*
[3] *Harindanga High School, 743504 Falta, India*
[4] *Department of Chemistry, University of Calcutta, University College of Science, 700009 Kolkata, India*
[5] *Lincoln University College, Research & Innovation Division, 47301 Petaling Jaya, Malaysia*

Тонкі плівки з гідрогенізованого алмазоподібного вуглецю (HDLC) знаходять широке застосування в різноманітних сферах, включаючи біомедичні покриття з бактерицидними властивостями, а також у контексті механічної, електронної та іммобілізації біомолекул. Для покращення поверхневих властивостей тонких плівок HDLC використовуються різні методи: обробку водневою плазмою, електрохімічне гідрування, відпал та іммобілізацію біомолекул. Синтез плівок HDLC містить упереджене посилене зародження (BEN) при змінних швидкостях потоку H_2 і CH_4 в реактивному газоплазмовому процесі (RGPP). У цьому дослідженні ми досліджували змочуваність як первинних тонких плівок HDLC, так і модифікованих тонких плівок HDLC, використовуючи метод сидячої краплі, вимірюючи контактні кути з рідинами різної фізико-хімічної природи, такими як вода та гліцерин. Вміст sp^3 і sp^2 HDLC і модифікованих зразків вимірювали Раманівський спектр. Поверхнева енергія зразків продемонструвала незначне збільшення кореляції з вмістом sp^3 HDLC та модифікованих зразків HDLC. Примітно, що спостерігалася сильна кореляція між гідрофільністю/гідрофобністю та щільністю співвідношення sp^2/sp^3 на різних поверхнях HDLC, включаючи готові HDLC, електрохімічно гідрогенізовані (ECHDLC), відпалені поверхні HDLC та білок альбумін (BSA) на гідрогенізованому алмазоподібному вуглеці.

Ключові слова: Гідрофільність, Гідрофобність, HDLC, Контактний кут, Раманівські спектри, Поверхнева енергія.