Modification of Mechanical Strength of Octadecylphosphonic Acid on Mica by Hydrogen Bombardment

Ripon Kumar Dey[1*]

[1]*Department of Electrical and Computer Engineering (Nanotechnology), University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.*

Author's contribution

Research Article

ABSTRACT

Well-controlled, well-ordered and uniform Octadecylphosphonic acid (OPA) LB films on cleaved mica surfaces was formed, and their mechanical properties were characterized. A novel technology has been pioneered which utilizes a kinematic collision driven hydrogen abstraction using hyperthermal hydrogen molecules to induce cross-linking of hydrocarbon chains. The hyperthermal hydrogen-driven approach with proton energy as low as 5eV can induce cross-linking of the adsorbed OPA and can modify the hydrocarbon long chain chemical bonding formula and the actual ordered Langmuir-Blodgett lattice into an array of clusters of the virgin film. By increasing the kinematics-driven reaction time at fixed bombardment energy and at a modified fluence which initiates the degree of cross-linking can control the nanocluster growth of OPA thin film. Consequently, with a controllable bombardment condition with a function of fluence can modify the cluster shape and modify the mechanical strength as well.

Keywords: Langmuir-blodgett film; atomic force microscopy; self-assembled monolayers; octadecylphosphonic acid; contact angle; hydrogen bombardment.

[*]Corresponding author: Email: ripon4t@gmail.com;

ABBREVIATIONS

OPA: Octadecyl phosphonic acid; HHIC: Hyperthermal hydrogen induced cross-link; LB: Langmuir-blodgett.

1. INTRODUCTION

The production of polymeric molecular devices and biomedical devices both demand the synthesis of thin monolayer of cross-linked molecules with specific chemical and mechanical properties. Driven by these demands, various molecular layers with specific chemical functionalities have been developed by a number of innovative chemical synthetic approaches. Following these interests, this experimental work describes a simple approach for delivering Langmuir-Blodgett thin monolayer film of Octadecylphosphonic acid (OPA) on freshly cleaved hydrophilic muscovite surface. The result in the formation of approximately full-coverage of ultra-thin LB on Muscovite mica is especially useful because of the wide applications in the engineering of surfaces. Most Langmuir-Blodgett thin monolayer film possess homogeneous and well-ordered lattice structure and their mechanical, eletro-chemical properties can be fine tuned in incorporating different functional headgroups to their long hydrocarbon chain. As such, they regard as very important and promising system for nano-device applications towards the molecular level. In this work, the surface modification system was employed to enhance its mechanical strength which replaces the intermolecular van der Waals interaction force into cross-linking chemical bonding that induces the surface-molecular adsorption force as well.

OPA is an example of a phospholipid-like amphiphilic molecule that is used of as a material of many recent technologically important applications [1,2,3]. High stability of this OPA monolayer is found due to strong molecular interaction of phosphonic acid group with the insulating surface. As Phosphonic acid group shows their stronger adsorption and binding with the oxide surface rather than any other conventional carboxylic acid group, this alkylphosphonic acid group as of our organic molecules was chosen. Alkyl phosphonic acids have been examined to assemble onto several oxide surfaces, like, SiO_2, Al_2O_3, Ta_2O_5 and mica [4-13].

Molecular ordered thin organic films, ranging in thickness from about a few nanometres to several hundred nanometres, show a considerable technological promise. Specific layer thicknesses are required in the typical range between a monolayer and several mm depending on the intended purpose such as thin film waveguides, surface modifications, supramolecular architectures, and layer systems with planned functionalities. Highly ordered organic films can be prepared easily by means of the Langmuir-Blodgett technique, by which multilayer of a particular compound can be built up from monolayer, transferred from the air-water interface onto a solid substrate. OPA LB film on muscovite mica, Si oxide, Al oxide, and graphite surface was formed. The thickness of this multilayer can easily be controlled by the size of the compound and the number of deposited layers. The early investigations have been mainly related to the interfacial phenomena, but nowadays the interest is shifted to functional LB films with potential applications [14] in thin film optics, as sensors and transducers, as protective layers, as patternable materials, for surface preparation and modification, for chemically modified electrodes and as models for biological membranes. Traditionally, LB films have been prepared from low molecular-weight compounds, like fatty acids. These organic films have a poor mechanical, thermal and chemical stability, which reduces their application in practical devices. One way to overcome these obstacles is to

make use of polymeric LB films, which enhances the thermal, mechanical and chemical stability of these multilayer films [15,16] Considering these, OPA to form the LB films on different substrates was chosen. The monolayer characteristics of a compound can easily be obtained by measuring surface pressure-area/mol (π~A/mol.) isotherms at the air-water interface.

In this study, the hyperthermal hydrogen induced cross-linking technology (ion bombardment modification) [17] of our group was employed to OPA overlayer onto atomically flat muscovite which is a subject that has been studied by several research groups and continues to be an attractive topic under extensive investigation, though it is certainly challenging to control the degree and efficiency of collision-induced reactions with the monolayer. In this method, the lightest ion species, the proton, with hyperthermal (regime of 1-100 eV) energy of about 2-50 eV is used to bombard organic precursor molecules condensed on a substrate surface. After forming OPA LB film at controlled surface pressure and a particular temperature, then the film had been treated with the bombardment process where the cross link of each OPA carbon backbone chain happened. It experienced that on few substrates such as Poly(ethylene terephthalate) (PET), SiO_2, the thin monolayer LB films might be delicate because the balance of adsorption forces against very week van der Waals bond is inappropriate, and therefore they might be weak in the environment. Due to their nature, conventional wet-chemistry is not suitable for cross linking the OPA. Instead, surface-initiated atom transfer radical polymerization (ATRP) has been used for cross-linking LB. This process ensures the stability of the formation of cross-linked LB. Other undesirable issues with wet-chemistry for the synthesis of molecular layers such as the requirements of aggressive reactants, chemical additives and catalysts will also be eliminated. Dry reactions are more suitable because of the smallest amount of chemical reactants needed to reduce the risk of undesirable impurity and to improve the precision of process control. Here, hydrogen is introduced to the chamber to the magnetic induced plasma to ionize the hydrogen atom to hydrogen ion. The hydrogen ion containing kinetic energy then enters the second part of the chamber where more hydrogen molecules are present. These kinetic energy carrying ions cause the other hydrogen atoms to break to give hydrogen atoms. These neutralized atoms are then passed through the open the shutter and will reach the LB sample for bombardment. With the particular applied voltage, the energy is only sufficient to break the weaker C-H bonds and not the functional phosphonic group of OPA. As a result, carbon radicals will form without breaking the backbone chain of the OPA. The radicals will react to form a sheet of cross-linked network film. The modified surfaces of the OPA have then been analyzed in situ by X-ray photoemission spectroscopy.

2. METHODOLOGY

Solutions of concentrations 1mM, 2mM and 3mM of OPA [n-Octadecylphosphonic Acid, $CH_3(CH_2)_{17}P(O)(OH)_2$; Alfa Aesar, Ward Hill, MA] dissolved in chloroform (99.9%; Alfa Aesar, Ward Hill, MA) were prepared and heated to 60ºC for 25 min on a hot plate. Note that, if the solution is kept at room temperature for about 10 minutes, crystalline flakes would float on the surface of the solution. This can make aggregates on the surface which was easily observed using AFM. This can be eliminated by either using new solutions or reheat the solution to around 60ºC to completely re-dissolve the chemical. The Langmuir-Blodgett (LB) experiment was performed with a KSV Instrument (Company: Model: 5000) systems with a Teflon-coated trough operated with double barriers. The LB trough was filled with DI distilled water [A MilliQ (Boston, MA) purification system produced water with a resistivity of 17.5-18 MΩ-cm for all experiments] as subphase until it just brimmed over the top-about 2

mm over the rim of the trough. Then, 30 µL of solution was poured with a syringe over the subphase followed by waiting 10 min to allow solvent to vaporize at room temperature (23.4 $\pm$ 0.2ºC). The next step is to compress the subphase surface at a speed of 2.3-2.5cm min^{-1}. Freshly cleaved Muscovite mica was dipped through the subphase with controlling the barrier at different coverage. Y-type deposition method has been applied on hydrophilic substrate and X-type has been implemented on hydrophobic substrate to deposit the LB monolayer. Surface pressure was measured with a paper Wilhelmy plate suspended from a microbalance at 23.4 $\pm$ 0.2ºC. A dilute solution of OPA (dissolved in a volatile solvent) is spread at the air-water interface on a Langmuir trough. The solvent evaporates, leaving a monolayer of the compound at the air-water interface which, in turn, deposits on any substrates.

Dynamic Force mode atomic force microscopy (Park System; Model: XE-100) using silicon tips has been used to characterize the Langmuir-Blodgett film surface morphology and to measure the height of the LB film of OPA. Rectangular silicon cantilevers with a spring constant of ~40 N/m were used in dynamic force mode AFM. The cantilever was 125 µm long, 35 µm wide, and 4µm thick. The dynamic force mode AFM measures the surface morphology through a feedback mechanism of maintaining constant oscillation amplitude while the vibrating tip scans the contour of the surface. The images were obtained at a scan rate of 5µm/s.

The XPS analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al K (alpha) source (15mA, 14kV). XPS can detect all elements except hydrogen and helium (because the diameter of these orbitals is so small, reducing the catch probability to almost zero), probes the surface of the sample to a depth of 5-10 nanometres, and has detection limits ranging from 0.1 to 0.5 atomic percent depending on the element. The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f7/2 line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p3/2 line of metallic copper. The Kratos charge neutralizer system was used on all specimens. Survey scan analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 160 eV. High resolution analyses were carried out with an analysis area of 300 x 700 microns and pass energy of 20 eV. All analyses used an electron take-off angle of 90E. Spectra have been charge corrected to the main line of the carbon 1s spectrum (adventitious carbon) set to 285.0 eV. Spectra were analysed using CasaXPS software (version 2.3.14).

Hydrogen projectiles having kinetic energy around 5-8eV generated in a home-made reactor [18] was used bombard the surface of adsorbed hydrocarbon precursor. The hydrogen projectiles preferentially knock off C-H bonds without changing the other bonds. This creates carbon radicals, leading to formation of C-C bonds, i.e., cross-linking of hydrocarbon chains. To modify the surfaces of OPA overlayer, the bombardment has been carried out at H_2 pressure of around 8.0x10^{-4} Torr at ~5-8 eV for about 10 and 40s.

3. RESULTS AND DISCUSSION

3.1 Molecular Orientation and Proposed Bonding of OPA on Mica

Upon transferring the OPA molecules onto the substrates, nucleation, film growth, coalescence of 3D islands, isolated islands were observed on cleaved muscovite mica using the Langmuir-Blodgett deposition process. LB films seem to be different to those obtained

with spread-coated SAMs, the structure/morphology is found more ordered, homogeneous and uniform with controllable number of layer varying layer composition than using other ordinary self assembled monolayer method.

Fig. 1. shows AFM images dynamic of varying coverage samples transferred with 1 mM OPA solution in Chloroform spread on DI water (17.5-18 MΩ-cm) as the subphase at 23.4 ± 0.2ºC. The only changing parameter in Fig. 1a-d is LB trough area/molecule which formed with different area of tough controlled by sliding barrier. Though the OPA amphiphilic molecules spread uniformly immediately after injecting onto the DI water, 20μL (except 5% is with 10μL), within few minutes those make isolated island in sufficient area/molecules. After a while, the organized OPA molecules have sufficient time to rearrange themselves to make different shapes of island gathering the stable configuration for phosphonic acid group with mica surface. The uniform adsorption of OPA molecules enhances quick nucleation of 2D Island. Varying molecules area can control the coverage of molecules that transferred into the substrate. The rapid evaporation of chloroform (solvent) has lead to vary the structure of amphiphilic molecules on DI water. Fig. 1a shows at very surface area, low surface pressure enhanced the OPA molecules to make small monolayer domain with a thickness of ~1.5± 0.2nm with 5% coverage of molecules from analysis of numerous OPA/mica samples measured with AFM histogram method. Considering the thickness of OPA, 2.5nm [19] and geometry of molecules, it is logical to guess that OPA molecules definitely tilted on cleaved mica with 36.7 ± 3^0. And, it is very interesting to mention that the thickness, i.e., tilt, of OPA molecule is not in agreement with previous works [20,21,22,23] which is due to using different form of deposition method, LB technique. Those molecules make small isolated island due to short-range van der Waals interactions between the long-hydrocarbon chains of the amphiphilic organic molecules and the long-range dipole-dipole interactions acting between the polar phosphonic acid headgroups. However, The thickness of OPA monolayer on mica was previously found to be around 1.6± 0.2 nm [24,25] which indicates about tilted orientation and recently, HY Nie et al. [26] observed that the apparent thickness of OPA SAM layer on mica was 1.7 ± 0.2 nm which is approximately in agreement with our result.

In Fig. 1b and c, 90% coverage in different scales (10μm and μm) at 27cm^2, and Fig. 1 d) illustrated 97% surface coverage, the coalesced stage of LB film due to large surface pressure in small area at 10cm^2. It is verified that more surface pressure collapse the monolayer immediately and form the bi-layer and aggregates in some regions of film and eventually the complete surface was overlaid by lower coverage with different thickness. Fairly similar result was observed with different concentrations of OPA solution in corresponding surface area/molecule.

One other important concern is that, only a few crystal-like molecular ordering is observed during initial coverage, i.e., 5% and gradually higher molecular ordering can be found at higher surface pressure onwards. The morphology captured by non-contact mode AFM represents the situation where the lowest spring constant was applied to the monolayer in varying coverage, the increasing spring constant, more lattice spacing which results different molecular structure. Finally, the surface pressure, i.e. surface area/molecule control can make the well-organized OPA layers with different thickness on different surfaces. Apparently, OPA molecules interact with mica in short range van der Waals force as physio-adsorption whereas hydrocarbon methyl tail group directed exterior to the surface and phosphonic functional group interact with substrate.
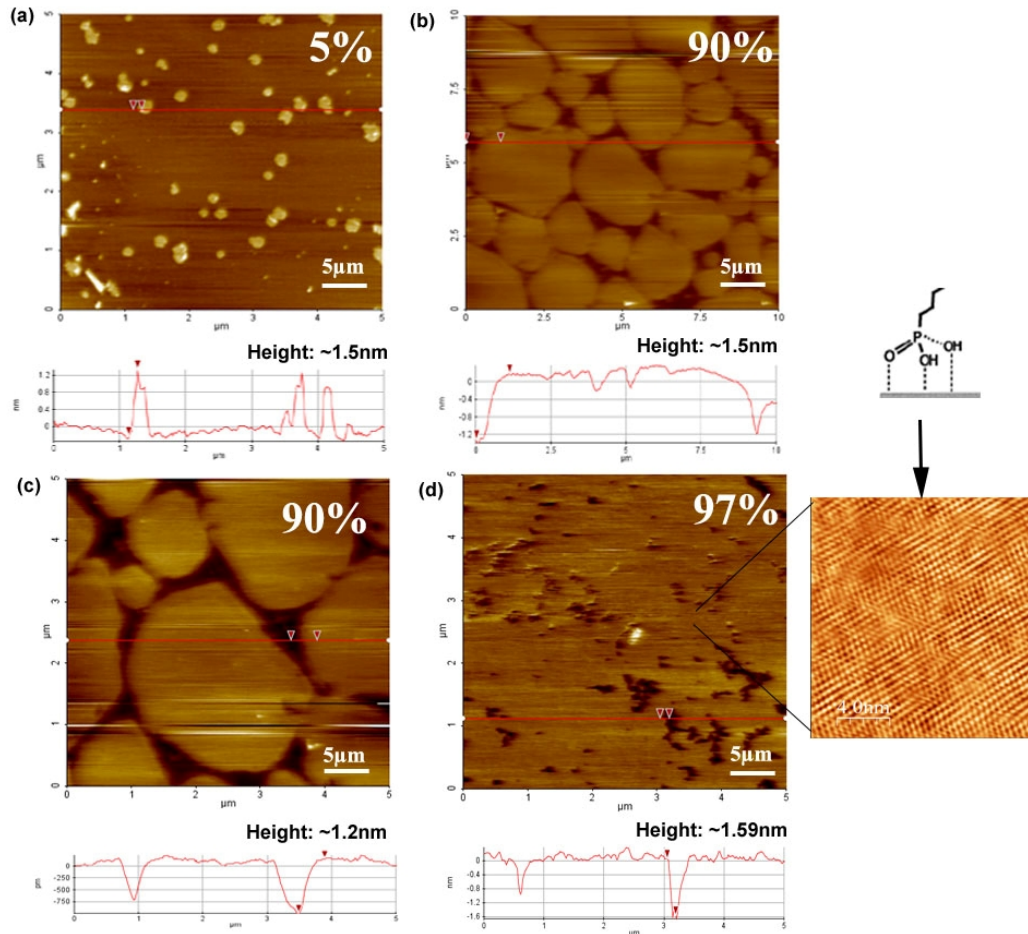
Fig. 1. AFM images (scan area: 5 µm × 5 µm) of varying coverage samples prepared with 1 mM OPA solution in Chloroform (1mM) at 23.4 ± 0.2^{0}C as a function of surface area/molecule, (a) 5% (b) 90%, (c) 90% and (d) 97% measured by AFM histogram respectively. In addition, molecular resolution of HR AFM image (20nm×20nm) of OPA on mica is shown in inset of d

The OPA molecules formed with Langmuir-Blodgett deposition method cannot be readily removed by washing with ethanol and Hexene that suggests the interaction in between OPA monolayers and muscovite is not weak, but strong enough, supposing it has not only van der Waals force, but also others. In fact, the elaborate analysis of bonding interaction is to be much more complicated to examine because of the nano-scale thickness of molecules. It also suggests after few seconds of transferring the OPA molecules on substrates, the two bindings of OH group and one binding of O phosphonic head group were executed with cleaved mica surface via van der Waals force apparently.

Fig. 2 shows tilted orientation of OPA molecule and proposed type of bonding of OPA on muscovite. This double and single bond of OH and O group configuration was also indicated by Reven et al. [27] which suggest strong bond between surface and functional phosphonic group. As consequence of these triple bindings, the fully extended zigzag long chain

encouraged to tilt, our result 36.7± 3º for muscovite with ~1.5± 0.2 nm thickness. The higher thickness of PET and HOPG shown in Table 1 indicated the weaker adsoption with OPA molecules. It is also noted that the contact angle experiment also suggests about the strong binding of OPA molecules with mica which discussed later in this article.
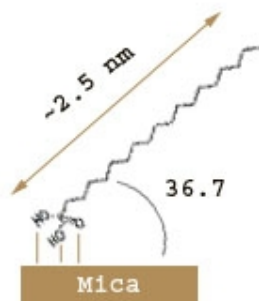

Fig. 2. Schematic representation of tilted orientation of OPA molecule and proposed type of bonding of OPA "Phosphonic functional acid" and "Methyl" group on mica surface.

3.1.1 XPS study of modified surface

Lau et al. implemented a novel technology which utilizes a kinematic collision driven hydrogen abstraction using hyperthermal hydrogen molecules to induce cross-linking. Hyperthermal Hydrogen Induced Cross-linking (HHIC) technology was used to cleave the C-H bonds of these adsorbed molecules and create new intermolecular C-C cross-links. The impact is expected to expand if the weak intermolecular van der Waals bonds can be practically replaced by covalent C-C cross-links. It has been shown that for the adsorbed molecules only weakly adsorbed on the substrate, the bond strains induced by the intermolecular C-C cross-links are strong enough to perturb the adsorbate-adsorbant bonding configuration. The original molecular monolayer adsorbate-adsorbant configuration changes to isolated islands of multilayers. However, for the monolayer adsorbate-adsorbant configuration with strong adsorption strength, the bond strains induced by the intermolecular C-C cross-links are not strong enough to destroy the two-dimensional monolayer configuration. A novel covalently cross-linked monolayer is thus formed. This is a ground-breaking approach of generating such a covalently cross-linked molecular monolayer. Proton energy was maintained 5-8eV while bombarding the samples.

Fig. 3 illustrated the OPA bonding with Muscovite mica elements with weak hydrogen-hydrogen bonding and hydrocarbon long chains structure before and after bombardment effect. In this experiment ~5 eV hydrogen proton with 8.0×10^{-4} torr was employed with a function of two bombardment fluence of about 7.24×10^{24} m^{-2} and 2.9×10^{25} m^{-2} respectively which implied C-C bonds replacing the CH_2 group. Taking advantage of the fact that phosphonic functional headgroup ($-P(O)(OH)_2$) bonds are stronger than C(1s)-H bonds, one can enhance the mechanical strength of the thin film without modifying the chemical functionalities of the molecules.

Cleaved muscovite mica surfaces were analyzed by XPS in complete coverage to isolated coverage formed with hyperthermal hydrogen bombardment. Some carbon on the surface of blank mica (0% coverage) which is attributable to adventitious carbon on the air exposed surface after cleaving was found.
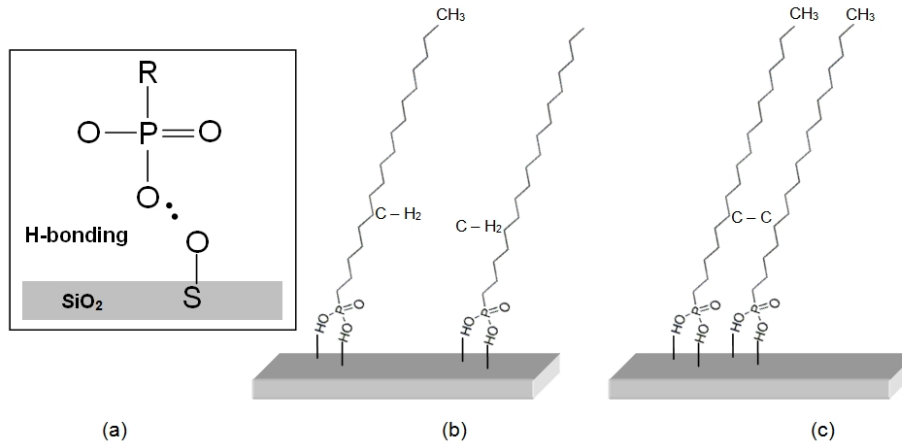
Fig. 3. (a) Proposed cross-linking chemical bonding (b) cross-linking of OPA molecules on Muscovite mica before bombardment; (c) cross--linking of OPA molecules on mica after bombardment.

Fig. 4 shows high-resolution C (1s) spectra of (a) freshly cleaved mica, OPA coated mica before (b) and after (c) HHIC for10 s. For the bare mica surface, i.e., the difference in binding energies between C (1s) core peak and K 2p3/2 peak was 7.93 ± 0.01 eV. However, for the complete coverage specimen, the distance between those two peaks before and after the bombardment was 8.19 ± 0.01 eV and 8.42 ± 0.01 eV, respectively, which demonstrates the sharp peaks of carbon existed in OPA molecules.

According to Table 1, high resolution binding energy area near carbon (1s) line position for freshly cleaved mica; OPA covered mica with ~95% coverage and cross-linked OPA with 10s bombarded respectively. The full width at half maximum of C-C, C-H bond of C (1s) for the cleaved blank sample, as shown in Fig 5(a), is nearly 1.44 eV and %area is 28.9; however, after depositing the OPA overlayer on that cleaved muscovite, the FWHM with 0s bombarded sample decreases to 1 eV (comparable with half widths of other polymers [28] with %area 46.1, then 0.95 eV for the 10s bombarded cross-linked OPA specimen with %area 58.5. It seems, the C-C, C-H bonding in the OPA thin film presents further homogeneous C(1s) than the adventitious C (1s) found on the 0% coverage of OPA on mica specimen.

K 2p1/2 follows same manner half width in XPS high resolution spectra. In uncoated muscovite, the C-O-C bonding was not observed which suggested that functional group was not existed there where O 1s and Si 2p also broadened as well. In addition, the half-width of C-O-C bonding in 0s bombarded OPA monolayer and 10s bombarded in coated monolayer is 1.88 eV and 1.67 eV respectively which also suggested narrowing the shape-peak of insulating surface gradually with a function of coverage and bombardment time respectively. The continuous line broadening of core shape-peak centroid from 10s bombarded towards uncoated mica surface results inhomogeneous surface bonding on the substrate. The area% of C-C, C-H was decreasing and K 2p3/2 and K 2p1/2 were increasing with function of coverage as well as bombardment time that is due to significant increasing of C(1s) concentration and C-C bonding forming respectively. Consequently, it can be said that cross-linking by bombardment had enhanced the homogeneity of OPA coated on atomically flat muscovite surface. Thus, it can be said that the weak intermolecular van der Waals

bonds has been practically replaced by covalent C-C cross-links of OPA on atomically flat muscovite surface. Also, later on, it proved that the mechanical strength would be significantly increased with a function of bombardment time through contact angle experiment.
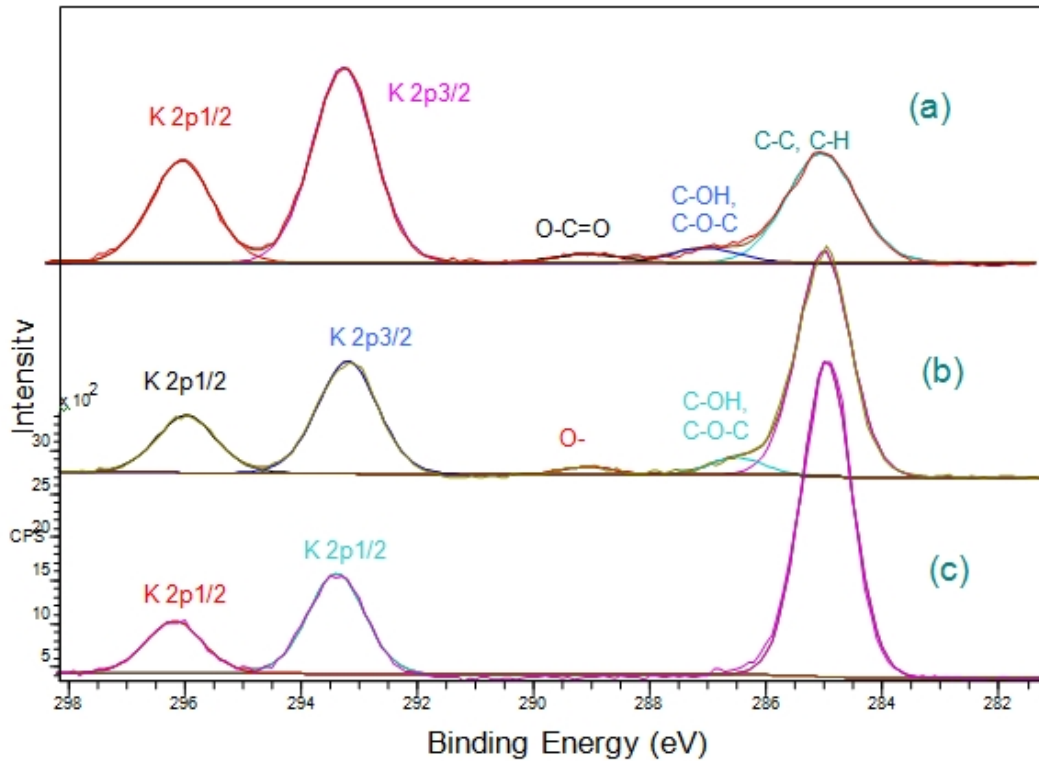

Fig. 4. XPS high resolution C (1s) core-level spectra of (a) freshly cleaved bare mica, (b) OPA prepared on mica surface (c) bombarded with ~19 eV hydrogen projectiles for 10 sec on OPA monolayer deposited on mica.

Table 1. Half-width and area of C-C, C-H, C-O-C, K 2p3/2, K 2p1/2 of 0s bombarded (0% coverage), 0s bombarded (~95% coverage) and 10s bombarded (97% coverage) samples

Bonding	C-C, C-H		C-O-C		O-C=O		K2p3/2		K 2p1/2	
	FWHM	%area	FWHM	%area	FWHM	%area	FWHM	%area	FWHM	%area
0s bombard (0% coverage)	1.40	62.8	1.40	5.6	1.54	4.3	1.35	27.4	1.37	0.0
0s bombard (~95% coverage)	1.07	78.8	1.07	6.0	1.07	2.6	1.21	12.6	1.20	0.0
10s bombard	1.02	90.5	---	---	---	---	1.17	9.5	1.15	0.0

From the Table 2 it is clearly observed that P 2p is increased in virgin OPA film with 72% which reduces after bombardment towards 45.7 for 10s and 43% for 40s indicates that some overlayer molecules are blown out due to hydrogen proton kinetic energy.

Table 2. The area (%) of P (2p) of mica, OPA/mica, 10s and 40s bombarded OPA are given below respectively

Surface	P 2p Area (%)
Muscovite	29.3
OPA on Muscovite	72.0
bombarded for 10s	45.7
bombarded for 40s	43.0

3.1.2 Morphology of modified surfaces

The LB film is composed of homogeneous and well-ordered molecular domains of the standing up phase. The uniform and ordered domain structures are turned into molecular cluster even with mildest (~5eV) kinematics-driven condition in this study. The changes are exemplified with the AFM images of the virgin OPA sample as shown in Fig. 5.
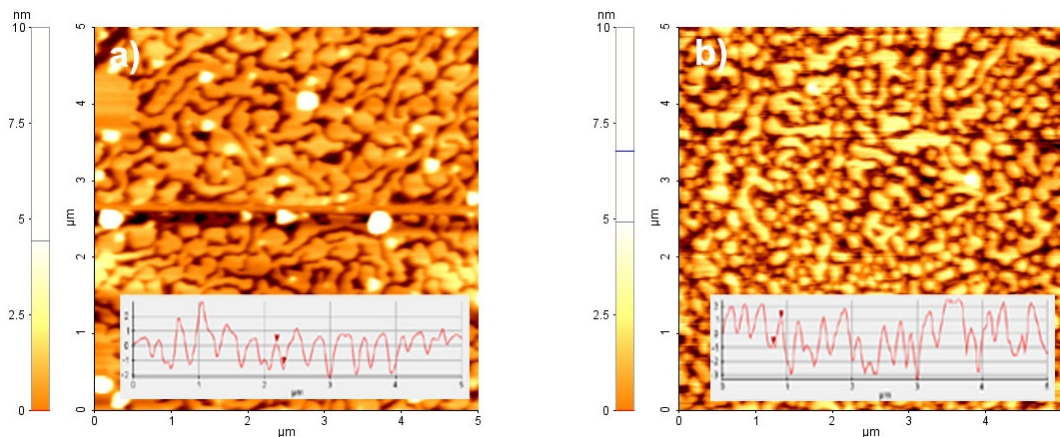

Fig. 5. Topography AFM images of (a) bombarded sample for 10 s and (b) 40 s respectively. Inset shows a profile of those corresponding film

Fig. 5 shows AFM images of 10s and 40s bombardment samples respectively. It is clearly observed the degree of residual defects was increased with increasing the degree of dry-reaction with a function of bombardment time. To modify OPA over-layer, the bombardment was carried out at H_2 pressure of around 8.0×10^{-4} torr at ~5eV with function of bombardment time of about 10 and 40 seconds, i.e., fluence of about 7.2×10^{24} m^{-2} and 2.9×10^{25} m^{-2} respectively. OPA on muscovite results significant changes after surface modification upon cross-linking with hydrogen bombardment. Root mean square roughness was varied after bombardment and cluster size became larger as bombardment time was increased. However, root mean square roughness for uncoated mica was observed about 0.2 nm and for coated virgin molecular film was 0.9nm. Clusters with an average thickness of around 2-4nm are observed following after 10s dry-reaction with a typical apparent area of about 0.2

µm^2, as shown Fig 5(c). According to Fig. 5(d), the apparent cluster area increased towards 0.5 µm^2 with a average height of 2-3 nm for 40s bombardment tuning on virgin sample. Lau et al.[17] suggested that HHIC leads to C-H cleavage preferentially with no cleavage of functional group of adsorbed hydrocarbon molecules. The inelastic kinetic energy of proton can transfer its energy to form C-C bond of long hydrocarbon chain which initiates cross-linking network upon mechanically adsorbed OPA molecules on muscovite. Briefly, when adjacent molecules go through C-H bond cleaving, they form x-linking C-C bond which brings the molecules much closer than virgin film separation occurred by weak van der Waals interaction force. The transferred kinetic energy of proton could replace the weak van der Waals force into cross-linking chemical bonding and probably lose the substrate-molecule adsorption force a bit. Increasing the degree of cross-linking with a function of time for 40s at fixed proton energy at around 5eV leads to turning uniform and well-ordered LB film to the larger isolated island clusters. Consequently, Fig. 5(d) shows larger clusters growth on OPA hydrocarbon chains in increased bombardment condition with additional 30s bombardment time. Later on, It is observed that cross-linking increases the mechanical strength/adsorption of over-layer with surface via ultrasonic bath experiment.

### 3.1.3 XPS spectrum under ultrasonic bath treatment

The hyperthermal hydrogen induced cross-linking technology of our group was used to cleave the C-H bonds of the monolayer and forming new intermolecular C-C cross-linking bonds. The mechanical strength of these thin films was thus improved. However, the bond strain induced by the intermolecular C-C cross-links was found to be strong enough to change the LB film morphology drastically for the LB layers on mica.

The cross-link-treated film survived the hexane dissolution test with an intact thickness with detectable phosphorus spectra of the washed sample. Conversely, virgin film was not mechanically strong to the extent that 3 min ultrasonic bathing with hexane could wash out overlayer whereas modified surface could survive these perturbations even after such dissolution experiment. This gave the significant qualitative results and evidence that stronger mechanical properties can be tuned by the degree of cross-linking. Through HHIC the impact is expected to expand as the weak intermolecular van der Waals bonds can be practically replaced by covalent C-C cross-links. The performance of the dry synthesis of cross-linked organic polymeric films with controllable time function can be also optimized with function of fluence of bombardment.

Fig. 6 shows the XPS survey spectrum of the virgin and kinematics-driven synthesis of cross-linked molecular films after ultrasonic bath with non-polar hexane and polar ethanol for 3 minutes. The P 2p signal was not detected from the virgin films while detected from the synthesized cross-linked film surface which concluded that the mechanical strength of modified films significantly increased due to dry chemistry reaction on cleaved muscovite surface. However, the area % of P 2p after washing with hexane and ethanol is 1.4 and 1.0 respectively which is less than the virgin film without wash. That probably for the transferred kinetic energy of proton could replace the weak van der Waals force into cross-linking chemical bonding and consequently loose the substrate-molecule adsorption force a bit. And nonpolar hexane may not wash out the non-polar organic molecules as like polar ethanol. Also according to Table 3, Fe 2p and N 1s are found in virgin films whereas in bombarded samples those are absent. Potassium (K) is the element of mica.
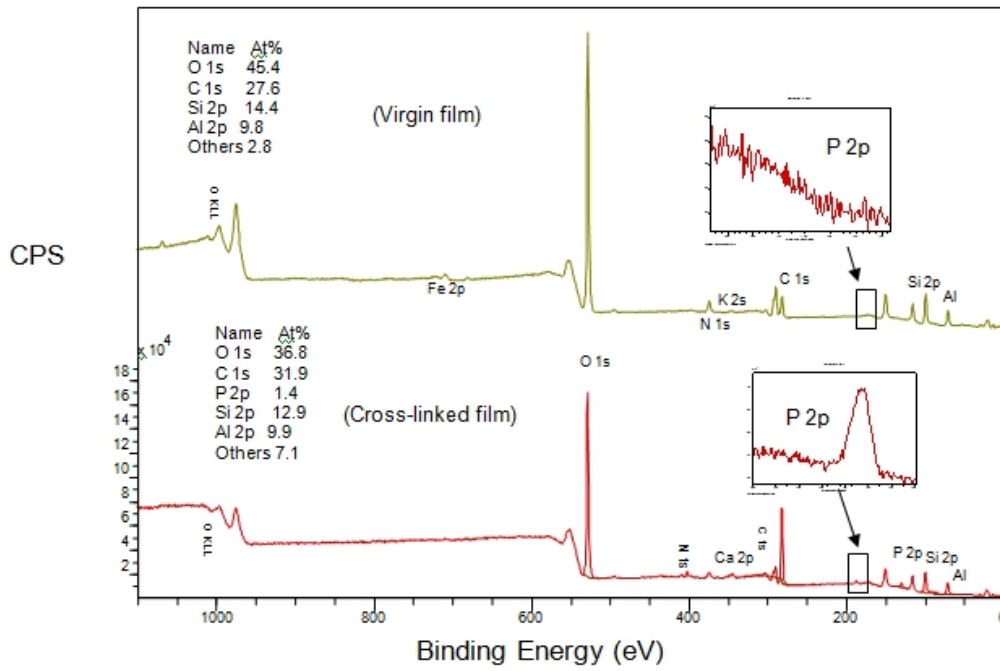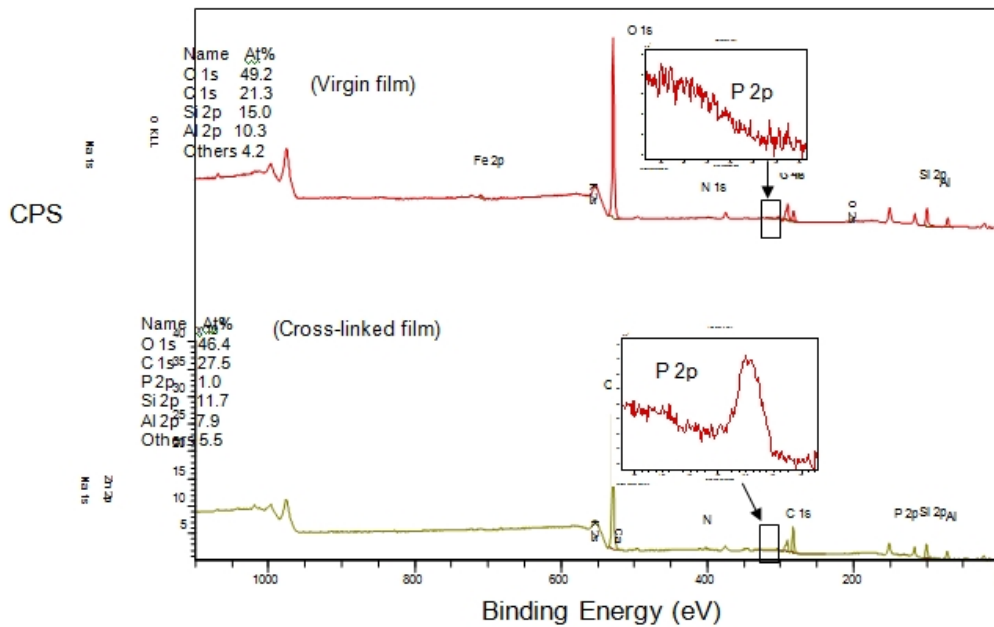
Fig. 6. (a) XPS wide scan spectra of virgin film (top) and Kinematics-driven synthesis of cross-linked OPA LB films on mica (bottom) after ultrasonic bath with hexane. (b) XPS wide scan spectra of virgin film (top) and kinematics-driven synthesis (40 s) of cross-linked molecular films on mica (bottom) after ultrasonic bath with ethanol

Table 3. Area of Fe, O, K, C, Si for virgin film and, kinematics-driven synthesis of cross-linked molecular films after ultrasonic bath with hexane; virgin film and, kinematics-driven synthesis (40s) of cross-linked molecular films after ultrasonic bath with ethanol

%Area	Fe 2p	O 1s	K 2s	C 1s	Si 2p
Virgin film (hexene)	0.4	45.4	2.2	27.6	14.4
40s bomb (hexene)	0	36.8	6.9	31.9	12.9
Virgin film (ethanol)	0.3	49.2	3.6	21.3	15.0
40 bomb (ethanol)	0	46.4	6.1	20.5	15.7

According to Fig. 7, the full width at half maximum of C-C, C-H bond of C (1s) for the virgin specimen washed with hexane is nearly 1.27 eV and % rea is 28.9; however, after cross-linking of the OPA overlayer, the washing experiment shows the FWHM of C-C, C-H bond sample is narrower valued 0.93 eV with % area 59.3 whereas after washing with polar ethanol, the half width of those bonds for virgin film is 1.31 eV, % area 25.1 and for cross-linked coated film the half width is 1.22 eV and % area 51.3 which suggests that virgin sample C 1s core line spectra is similar to the that of uncoated mica surface with adventitious C 1s.
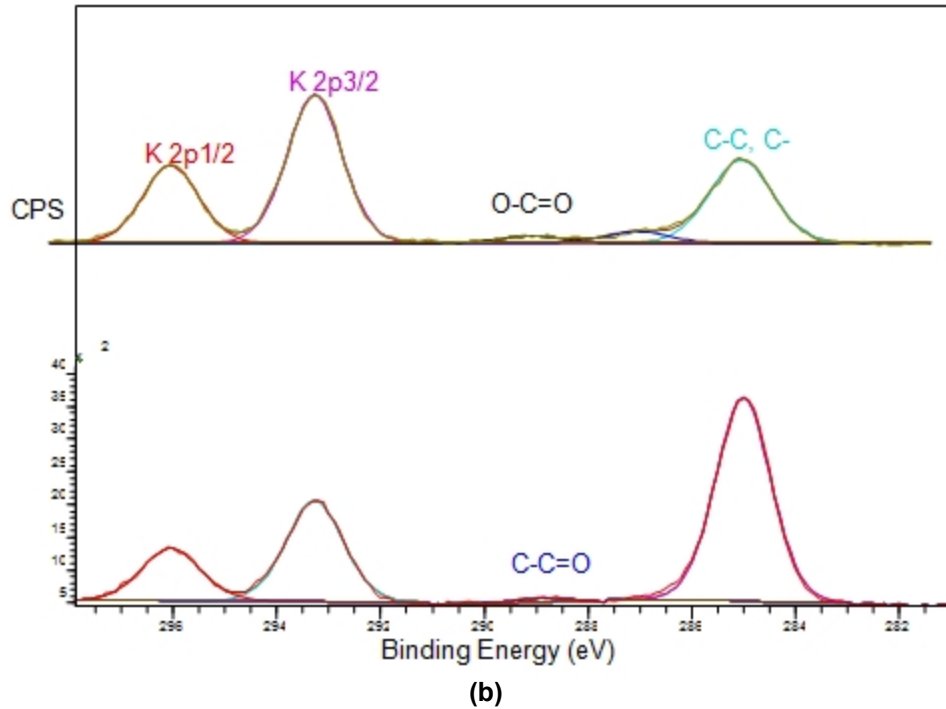

(a)

(b)
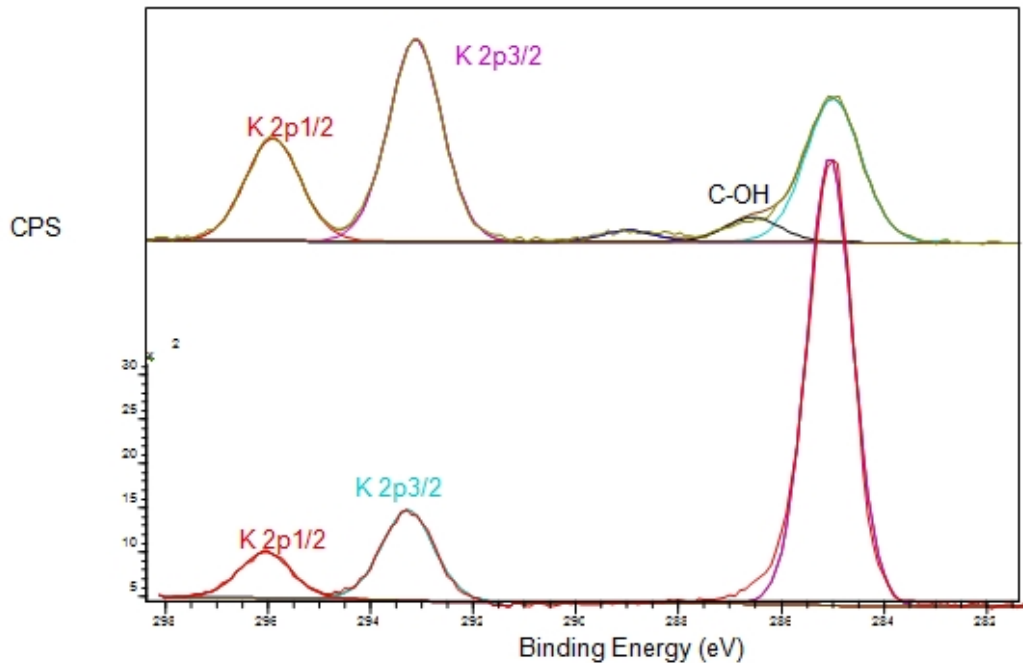
Fig. 7. XPS C 1s core-level spectra after ultrasonic bath of (a) virgin film and film bombarded for 40s by 5eV protons with hexane (non-polar solvent) [top to bottom]; (b) virgin film and 40s bombarded of OPA/mica with ethanol (polar solvent) [top to bottom]

And the cross-linked samples confirmed the existence of greater C 1s spectrum, i.e., greater OPA molecules with stronger mechanical strength. According to Table 4, for virgin film regards, i.e. 0s bombarded sample, the difference of binding energy between C (1s) shape-peak and K 2p3/2 shape-peak was 8.13 ± 0.01 eV; however, for modified OPA sample, the difference was 8.27 ± 0.01 eV after washing with hexane, and similarly 8.27 ± 0.01 eV for virgin and 8.28 ± 0.01 eV for cross-linked specimen after washing with ethanol respectively which indicated ethanol washed the molecules with more deliberately. O-C=O bonds also has been observed in virgin films after washing both polar and non-polar solvents for 3 min.

Table 4. Half-width and %area of C-C, C-H; C-O-C; O-C=O; K 2p3/2 and K 2p1/2 of samples after ultrasonic bath of virgin film, film bombarded for 40s by 5eV protons with hexane (non-polar solvent); virgin film, 40s bombarded of OPA/mica with ethanol (polar solvent)

Bonding	C-C, C-H		C-O-C		O-C=O		K2p3/2		K 2p1/2	
	FWHM	%area	FWHM	%area	FWHM	%area	FWHM	%area	FWHM	%area
Virgin film washed with hexene	1.27	61.2	---	---	1.27	4.9	1.21	23.3	1.25	0.0
Bombarded for 40s and washed with hexane	1.04	93.9	---	---	---	---	1.19	6.1	1.19	0.0
Virgin film washed with hexene	1.41	60.0	1.41	8.2	1.41	5.1	1.24	26.7	1.26	0.0
Bombarded for 40s and washed with ethanol	1.24	85.8	---	---	1.27	1.7	1.29	12.5	1.34	0.0

4. CONCLUSION

Uniform and well-ordered Octadecylphosphonic acid Langmuir-Blodgett film on freshly cleaved muscovite mica surface was formed and it demonstrated that modified hydrocarbon long chain chemical bonding with HHIC which induced cross-linking kept its functional group intact. These results suggest that kinematics-driven approach with proton energy as low as 5 eV can induce x-linking of the adsorbed OPA and can change the actual ordered LB lattice into an array of clusters of the modified film. The nanocluster growth is to be narrowed by increasing the dry-reaction time at fixed bombardment energy and at a modified fluence which indicates the degree of cross-linking can be controlled with a function of bombardment time. The effects of hyperthermal hydrogen bombardment on octa decylphosphonic acid Langmuir-Blodgett film on cleaved mica are studied with in situ X-ray photoemission spectroscopy and in situ atomic force microscopy. Thus with a controllable bombardment condition with function of time can modify the cluster shape and size and increase the mechanical strength.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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