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ISOTHERMS AND MORPHOLOGY OF NANOCOMPOSITE THIN FILMS DEPOSITED USING MODIFIED LANGMUIR-SCHAEFER TECHNIQUE

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*S.Malik**, Fatin Hana Naning, Azyuni Aziz*

[a]Physics Department, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

*Corresponding author
syed.malik@fsmt.upsi.edu.my

Abstract

Various techniques have been used to prepare polymer nanocomposite thin films that involve tedious work and consume considerable amount of materials and time. In this study, nanocomposite thin films of poly (3-hexylthiophene -2, 5-diyl) (P3HT), stearic acid and CdSe nanoparticles were fabricated by a stamping method which is a modification of Langmuir Schaefer technique. The CdSe nanoparticles were then grown in-situ between subsequent layers of thin film by gas exposure technique. Their surface-pressure (π-A) isotherms and morphology were investigated. The surface-pressure isotherms revealed that, impurities in water subphase affect the profile of Langmuir monolayer. Stearic acid was found to be more dominant as compared to P3HT. The modified Langmuir Schaefer technique produced fairly smooth, large area nanocomposite thin films as shown by the AFM images. A prominent advantage of this procedure is that it requires only small amount of materials.

Keywords: Nanocomposite thin-film; P3HT;CdSe nanoparticles; surface-pressure isotherm

Abstrak

Pelbagai teknik telah digunakan untuk menyediakan filem nipis komposit-nano polimer yang melibatkan kerja yang rumit dan mengunakan banyak bahan dan masa. Dalam kajian ini, filem nipis komposit-nano poly (3-hexylthiophene -2, 5-diyl) atau P3HT, asid stearik dan partikel-nano CdSe difabrikasikan dengan mengunakan kaedah petekapan yang merupakan modifikasi kepada teknik Langmuir Schafer. Partikel nano CdSe di tanam secara terus diantara lapisan-lapisan filem nipis dengan teknik pendehahan gas. Isotem tekanan-permukaan (π-A) dan morfologi mereka disiasat. Isotem tekanan-permukaan menunjukkan bendasing dalam subfasa air memberi kesan kepada profil lapisan nano Langmuir. Asid stearik didapati lebih dominan berbanding P3HT. Teknik Langmuir-Schaefer yang telah dimodifikasi ini menghasilkan filem nipis yang agak serata seperti yang dipaparkan oleh imej-imej AFM. Satu kelebihan yang unggul prosedur ini adalah hanya sedikit bahan digunakan.

Kata kunci: Filem nipis komposit-nano; P3HT;CdSe partikel-nano; permukaan-tekanan isotem

1.0 INTRODUCTION

Advancements in nanomaterials have resulted in development of polymer nanocomposites (PNC), which are used in various applications such as solar cells [1, 2], drug delivery system [3], water membrane [4], and automotive components [5]. PNC are basically mixtures of nanomaterials in polymer matrices. The addition of specific types of nanomaterials into the polymer matrices gives rise to composite materials physical, electrical and chemical properties.

Among the popular PNC materials mixture are cadmium selenide (CdSe) and conjugated polymer, poly (3-hexylthiophene-2,5-diyl) or P3HT due to its potential in optoelectronic devices [6]. The PNC are usually fabricated as thin film through three common methods. The first method is by physical mixing of the nanoparticles (such as CdSe) with a polymer matrix [7]. Hence, CdSe Nanoparticles have to be prepared in advanced by reacting dimethylcadmium

($(CH_3)_2Cd$) with a selenium reagent in the presence of trioctylphosphine oxide (TOPO) [8], or by injecting selenium solution into a heated cadmium solution [9].

The second way is by grafting, where the ligands on the Nanoparticles were replaced and grafted according to the reactive group type in the ligand and the grafting molecule [10, 11]. The third method is by growing the nanoparticles in the polymer matrix in order to have intimate contact between the polymers and the Nanoparticles [12, 13]. However, these methods are tedious and time consuming and use substantial amounts of materials. In our study, the CdSe nanoparticles were directly grown in P3HT mixed with stearic acid (SA) and a modified Langmuir-Schaeffer (LS) method was used to fabricate the thin film. We investigated the surface pressure (Π)-area (A) isotherm of Langmuir monolayer of different materials on different subphases, as well as the changes in morphology of nanocomposite thin film.

2.0 MODEL DESCRIPTION

A similar technique to fabricate the thin film as published earlier [14] is used. In the previous report, however, the nanoparticles impregnated in the polymer matrix were cadmium sulfide nanoparticles. The procedure is described as follows.

The conjugated polymer, poly (3-hexylthiophene - 2, 5-diyl) or P3HT and stearic acid (SA) were used as the matrix for the thin film, whilst cadmium (II) chloride ($CdCl_2$) was the seed for the nanoparticles. Chloroform was used as the solvent for P3HT and stearic acid. All materials were purchased from Sigma Aldrich and used as-received unless stated otherwise.

The technique employed in fabricating the thin film adopting Langmuir layer principle to transfer the floating polymer monolayer onto a solid substrate. Two common approaches are Langmuir-Blodgett (LB) and Langmuir-Schaeffer (LS) method. Whilst LB method deposits films vertically and LS horizontally, modified Langmuir-Schaefer (m-LS) method utilized angle in depositing thin films onto substrate. The films were deposited by carefully touching one edge of substrate onto floating film surface at an angle of 45°, and slowly dropping it on the solid monolayer before lifting the substrate again by raising it the same manner it was dropped. The m-LS technique allows us to construct large-area nanocomposite thin films, and at the same time control the polymer ordering.

In our study, KSV 2002 System 2 hydrophobic trough was used and filled with de-ionized water containing 0.5 mM $CdCl_2$. The Langmuir monolayer was formed by dispensing 100 µl stearic acid (0.14 mg/ml) and 400 µl P3HT (0.2 mg/ml) onto the water subphase, and set at rest for 10 minutes to allow chloroform to evaporate. The floating layer was compressed with one barrier at a constant rate of 1 cm/min until it attained solid phase called Langmuir film. The deposition was performed at a constant surface pressure that was monitored by an electronic balance attached to Wilhemy plate. Thirteen layers of film were deposited in which after every deposition, hot air was blown to the film for 15 seconds to ensure the film is fully dry and to initiate polymerization. After the last deposition, the film was exposed to H_2Se gas to implant CdSe in the matrix. Morphological study was done using Atomic Force Spectroscopy (AFM) Seiko instrument model SPA 200.

3.0 RESULTS AND DISCUSSION

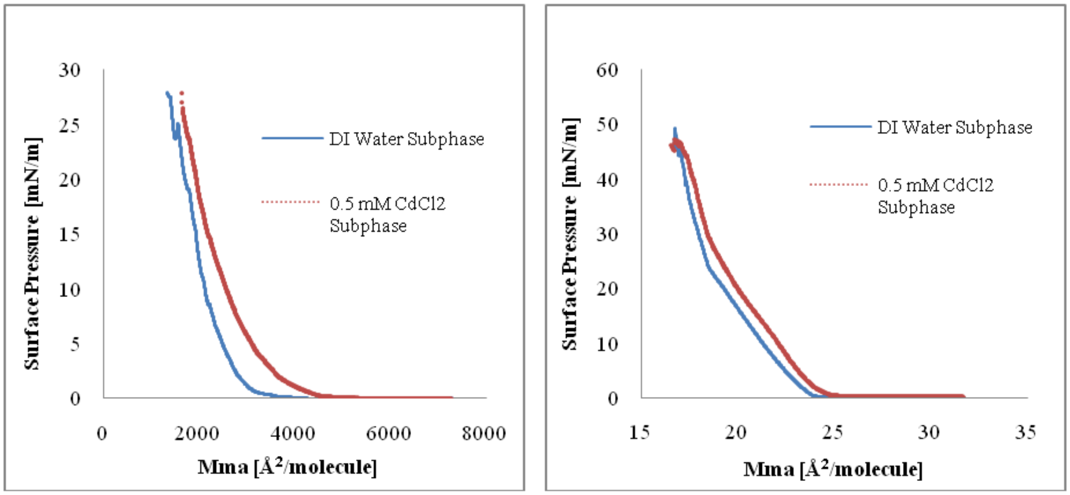
Modified Langmuir-Schaeffer technique (m-LS) utilizes Langmuir monolayer in characterization of gas-liquid-solid phase transformation, and measuring the dependency of surface pressure (Π) on the mean molecular area per molecule (A). The surface pressure-area (Π-A) isotherm graph is achieved by moving the barrier very slowly at a constant speed to decrease of the through area, at constant temperature, 25°C.

Figure 1 (a) show the Π-A isotherm of Langmuir monolayer of pristine Poly(3-hexylthiophene-2,5-diyl) or P3HT with concentration 0.2 mg/ml in chloroform on different subphases – deionized water (DI-water), and deionized-water containing $CdCl_2$.No distinct gas-liquid-solid phase developmentcan be observed from the isotherm of the pristine P3HT. This phenomenon is due to the long polymer chains that cause a two-dimensional lattice to form [15]. The addition of cadmium (II) chloride into water subphase resulted in smoother Π-A graph and larger mean molecular area, A_o. The "impurities" in the subphase cause the surface pressure to increase earlier than that of DI water. Similar trend can be observed in two other materials – SA and P3HT:SA. The proclivity is apparent for pristine P3HT, even the amount $CdCl_2$ added were very small.

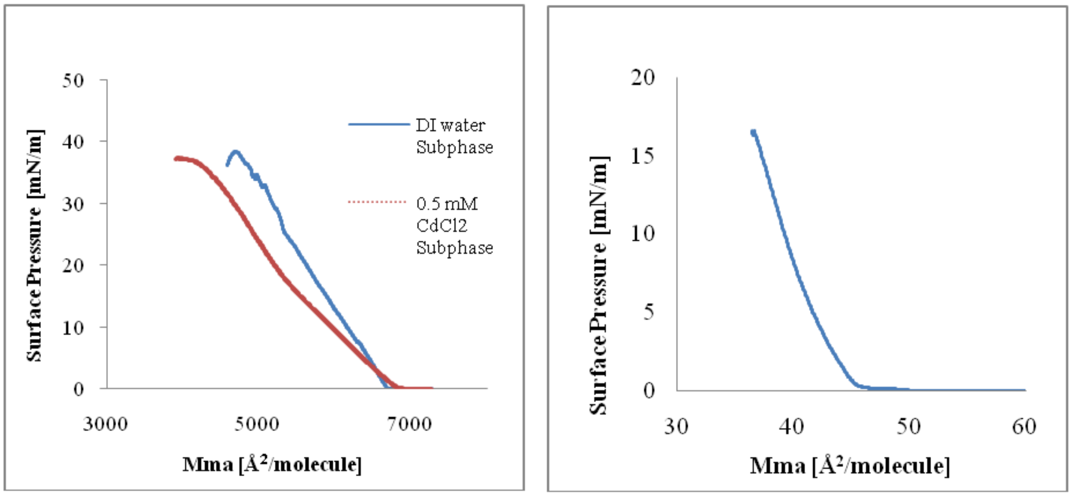
The Π-A isotherm graph of pristine SA of concentration 0.14 mg/ml with different spreading volume are shown in Figure 1 (b) and Figure 1 (d). In Figure 1 (b), the spreading volume was 600 µl even the volume of SA spread throughout this study were 100 µl (Figure 1 (d)). The 600 µl SA Π-A isotherm graph was shown as to display the complete phase transformation of the SA. When only 100 µl of SA were spread, the phase transformations could not be discerned due to the limitation of number of SA molecules. The monolayer behavior of the pristine SA (600 µl) shows a distinct gas-liquid-solid phase development. Liquid-solid phase transition occurs at a surface pressure 24 mN/m. By extrapolating the solid phase linear section of the graph, it was found that a stearic acid molecule occupied at a molecular area (A_o) of approximately 20.5 Å^2/molecule. Apart by extrapolating the solid phase linear section of the graph to get the area per molecule for pristine P3HT and Stearic Acid, the area per molecule a_{tm}, can also be calculated using:

$$a_{tm} = \frac{AM_w}{cN_AV} \qquad (1)$$

Where A is the area of water surface confined by the barriers, M_W is the molecular weight, c is the solution concentration, N_A is the Avogadro's number, and V is the spreading volume. The experimental and theoretical values of the mean molecular area are tabulated in Table 1. When 400 µl of P3HT is mixed with 100 µl SA, the Π-A isotherm of P3HT:SA on water subphase follows the stearic acid monolayer trend – higher surface pressure and distinguishable phase changes, even though the volume of stearic acid added and stearic acid molecule size's is very small as compared to P3HT. The effect of $CdCl_2$ addition in water subphase towards the gas-liquid-solid phase transformation is summarized in Table 2



(a) P3HT (400 µl) **(b) Stearic Acid (600 µl)**



(c) P3HT:SA **(d) Stearic Acid (100 µl)**

Figure 1 Isotherm of (a) 400 µl P3HT, (b) 600µl stearic acid, (c) 400 µl P3HT: 100 µl SA, and (d) 100 µl SA

Table 1 Mean molecular area (Mma) of P3HT and stearic acid on DI water subphase.

Material	MmA at 27 mN (experimental) (Å²/molecule)	MmA at 27 mN (theoretical) (Å²/molecule)	Deviation (Å²/molecule)
P3HT	~ 2600	2892.00	~ 292
Stearic Acid (600 µl)	~ 20.5	22.60	~ 2.1

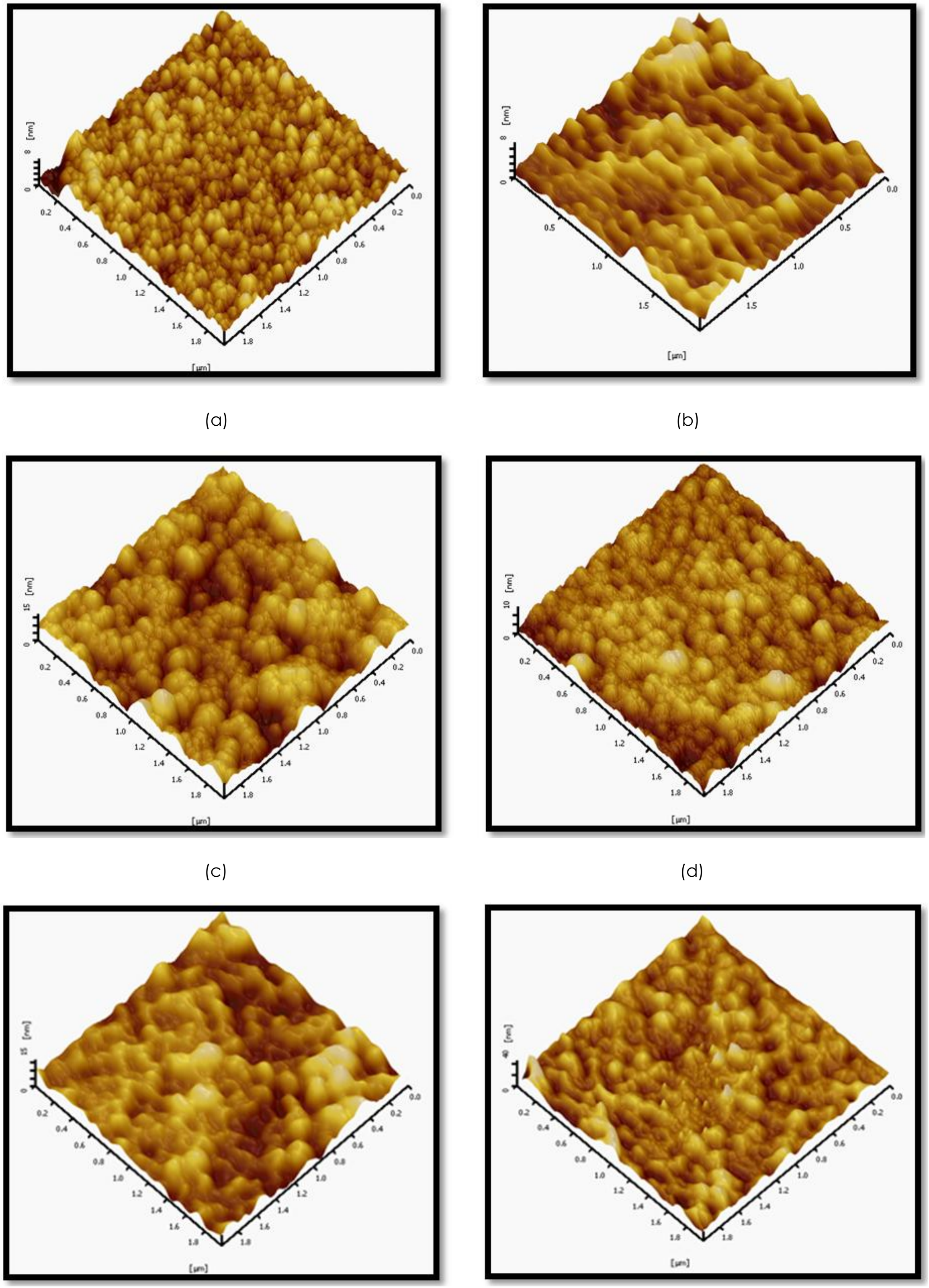
Table 2 Summary of gas–liquid–solid phase transformation.

Material	Subphase	Gas Phase (mN/m)	Liquid Phase (mN/m)	Solid Phase (mN/m)	Collapse (mN/m)	MmA (Å²/molecule)
P3HT (400 µl)	DI Water	~ 0 – 2	~ 2 – 9	~ 9 – 27	~ 27	2600
	0.5 mM $CdCl_2$	~ 0 – 2	~ 2 – 13	~ 13 – 27	~ 27	3000
Stearic Acid (100 µl)	DI Water	~ 0 – 1	~ 2 – 24	NA	NA	NA
Stearic Acid (600 µl)	DI Water	~ 0 – 1	~ 2 - 24	~ 24 - 48	~ 48	20.5
	0.5 mM $CdCl_2$	~ 0 – 1	~ 2 - 30	~ 30 - 47	~ 47	20.7
P3HT:SA (400 µl:100 µl)	DI Water	~ 0 – 2	~ 2 - 26	~ 26 - 37	~ 37	6000
	0.5 mM $CdCl_2$	~ 0 – 2	~ 2 - 18	~ 18 - 36	~ 36	6250

The morphology of the nanocomposite thin films was determined using Atomic Force Spectroscopy (AFM) as portrayed in Figure 2. Six samples of thin film have been prepared to study the morphological changes of the pristine P3HT thin film until it becoming nanocomposite thin film. Figure 2 (a) shows the image of pristine P3HT thin film deposited on DI-water subphase. The polymer is clearly ordered and the rms surface roughness is ~ 1.100 nm. When SA was mixed with P3HT and the depositions were done on DI-water subphase, the thin film rms surface roughness increased to 1.117 nm. The slight increment in roughness is due to the small SA's molecular size and limited amount of SA. However, the presence of SA caused disarray in the polymer ordering as evidence in Figure 2 (b).

The third step was the introduction of $CdCl_2$ in DI water subphase to fabricate P3HT:SA:Cd thin film as in Figure 2 (c). Stearic acid molecules trapped Cd^{2+} ions, and transferred together onto the substrate as thin film. Cl^{2-} ions remain in water causing it to be more acidic. On the other hand, P3HT has no obvious effect with Cd^{2+} ions since the S atom in the P3HT molecular chain have relatively weak coordination abilities with metal ions. However, the capping of Cd^{2+} ion by SA in between the polymer matrix caused discontinuity in the P3HT long chain and consequently, the surface roughness hiked to 1.813 nm.

To create CdSe nanoparticles in the thin film, the thin film were exposed to H_2Se gas. The exposure time was varied in order to monitor the affects towards film roughness. When the thin film was exposed to H_2Se gas, the Cd^{2+} ions reacted with selenide to produce CdSe nanoparticles. Two hours H_2Se gas exposure created nanoparticles in the thin film (Figure 2 (d)). Small size and small amount of nanoparticles produced leverage the rms surface roughness caused it to decrease slightly to 1.639 nm. However, as the exposure time increased, more nanoparticles created and some of the nanoparticles further aggregated to form larger CdSe clusters. The rms surface roughness increased to 2.359 nm and 3.964 nm when exposed to H_2Se gas for 4 and 6 hours, respectively. It is clearly visible from the AFM image in Figure 2 (e) and Figure (f) that more nanoparticles are created and the investigated area are more compact. The change in surface roughness is wrapped up in Figure 3.



(a) (b)

(c) (d)

(e) (f)

Figure 2 3D- AFM image for thin film of (a) Pristine P3HT, (b) P3HT:SA (c) P3HT:SA:Cd (d) After 2 hours exposure, (e)After 4 hours exposure, (f) After 6 hours exposure, at frame size 2000nm

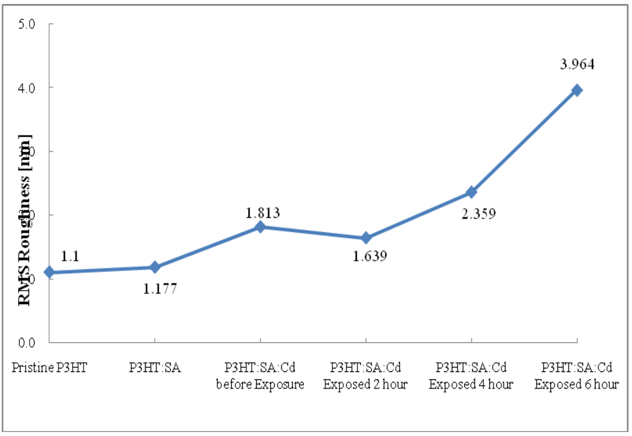


Figure 3 Changes in thin films' surface roughness

4.0 CONCLUSION

Modified Langmuir-Schaefer (m-LS) method was used to create nanocomposite thin film. The procedure started by examining the isotherm profile of every materials used as the matrix to embed the CdSe nanoparticles. The small molecule stearic acid influenced the isotherm of much higher molecular weight polymer. This may be due to its amhiphilic nature as compared to hydrophobic nature of P3HT.

The chronological order of thin film morphology was revealed through AFM image. The rms roughness of the thin film keep increasing as more materials were added into the thin film, except when the thin film were exposed for 2 hours. Nevertheless, we managed to achieve reasonably smooth thin film (< 4 nm) by using m-LS method. Surface roughness plays important role in many electronic devices like solar cell where it significantly affects the short circuit current density [16].

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