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ARTICLE TYPE

Fabrication of Morphology Controlled Graphene Oxide-Dye Composite Films at the Air-Water Interface

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This study presents a facile route for preparing two-dimensional (2D) graphene oxide-based composite films by Langmuir-Blodgett (LB) method. Graphene Oxide-Dye composites are formed with the incorporation of GO sheets and dye molecules (Pyronin Y) at the air-water interface, since GO sheets are perfectly capable of forming a floating-layer at the air-water interface. Graphene Oxide-Pyronin Y (PyY@GO) composites are successfully assembled as highly ordered thin films over a glass substrate by LB method. The surface pressure–area (π–A) isotherm studies reveal that pristine GO sheets and PyY@GO composites are capable of forming stable Langmuir films at the air–water interface. The limiting areas of pristine GO sheets and the composites are determined, and the area of pristine GO sheets are found to be larger than that found on PyY@GO composites. This observation clearly indicates the interaction of GO sheets with PyY molecules at the air-water interface, resulting in the formation of PyY@GO composites. Next, the floating layers of GO sheets and PyY@GO composites are successfully transferred to the glass substrate by LB method as mono- and multi-layer films. Their LB films are characterized by SEM and UV-Vis spectroscopy. SEM images reveal that the density of GO sheets and PyY@GO composites on the substrate are tuned by changing the film deposition pressure and the number of layers.

Introduction

The importance of graphite derivatives has been mentioned in many research articles after the discovery of graphene by Novoselov et al. in 2004.[1] These materials are main components of various technological applications including electronics, catalysis, supercapacitors, fuel cells sensors, etc.[2-4] Graphene oxide (GO) is one of the well-known graphite derivatives that has an excellent carrier platform for organic, inorganic and biomolecules.[5] The functional groups of GO, which possess hydroxyl and epoxy at the basal plane, carboxylic and carbonyl groups at the edges, allow its use in various applications due to easy modification of GO sheets.[6] GO sheets are in hydrophilic nature because of their functional groups containing oxygen and are perfectly dispersed in polar solvents such as water.[7] The stable dispersion of GO sheets in water are evaluated by the interaction types among GO sheets, which are edge-to-edge and face-to-face. The edge-to-edge interaction among GO sheets allows a stable dispersion of GO sheets in water.[8] Furthermore, the water-solubility of GO sheets sensitively depends on the variations in pH of the aqueous solution due to the fact that its hydrophobicity increases in acidic media (pH<2).[9] The functional groups of GO sheets enable the GO-based composites be successfully synthesized with nanoparticles, dye compounds, polymers, polyelectrolytes and biomaterials.[5,6,10] Thus, the surface properties of GO sheets can be adjusted by varying doped materials for the GO-based applications. These composites are widely-used in Li-ion battery, transistors, supercapacitors, photovoltaic devices, sensors and etc.[3, 10-13] In this respect, the preparation of the well-ordered thin films of GO and GO composites play crucial role for various applications mentioned.[14] To date, various methods have been developed to fabricate thin films namely: LBL (layer-by-layer assembly), LB (Langmuir–Blodgett) assembly, spin-coating, dip-coating, spraying, and solvent evaporation.[8,11,12] The fabrication of high-quality thin films of GO sheets and GO-based composites is rather difficult since ordinary thin films of GO includes folds and wrinkles as well as the aggregated and crumpled film. From this point of view, the use of LB film technique which gives an opportunity to form high quality thin films compared to the conventional film methods will be advantageous for the preparation of high-quality GO thin films with controllable thickness.[8] In the LB technique, the film architecture is easily controlled by adjusting the exchangeable parameters containing barrier speed, pulling speed, temperature and pH of the subphase, material composition, substrate, deposition pressure and evaporation time.[15] GO sheets are considered as a mimetic amphiphilic molecule with hydrophilic edges and hydrophobic basal plane at the interface[16] since the most suitable materials in LB technique are amphiphilic molecules having hydrophobic and hydrophilic parts. The desired quality of the LB film of GO sheets and GO based-composites can be achieved by adjusting the exchangeable parameters.[8,15] This work is of crucial role for preparing GO-based composite films by LB method, since controlling 2D structure of assembled GO sheets and GO-based composites are greatly desired for principal research and GO-based device applications. Considering the studies on the preparation and characterization of GO-based composite formations by LB method are limited,[17-18] we believe that the data presented by this manuscript will make important scientific contributions into the field.

In the present study, the preparation of PyY@GO composites at the air-water interface, and the 2D-thin films of pristine GO sheets and PyY@GO composites by using LB method have been reported. The floating-layers of pristine GO sheets and GO-based composites at the air-water interface are confirmed by π-A isotherm and spectroscopic studies. The characteristics of the LB films are examined by using SEM and UV-Vis spectroscopy.

Experimental

Materials

PyY (Scheme 1), $KMnO_4$ (potassium permanganate), H_2O_2 (hydrogen peroxide, 30%), $NaNO_3$ (sodium nitrate), H_2SO_4 (sulphuric acid, 98%) were purchased from Sigma–Aldrich. Natural graphite flakes (average particle size 325 mesh) were purchased from Alfa Aesar. All chemicals were used without further purification.

Apparatus

Absorption spectra of the samples were recorded with a Perkin-Elmer (Model Lambda 35) spectrophotometer at the room temperature. A commercially available LB trough (KSV, Minithrough system) was used to form LB films. Deionized (DI) water used for the subphase was obtained from a KrosClinic (KRS-R-75). The pH of the subphase was 6.3 and the temperature was ~20 ^oC. TEM (Transmission Electron Microscope) images were acquired using a JEM-2100 (JEOL) instrument operating at 200 kV. SEM (Scanning Electron Microscope) images were obtained with a Zeiss EVO40.

Assemblies of GO sheets and PyY@GO composites by using LB method

For LB films, a commercially available through (KSV minithrough) was cleaned with ethanol and DI water. After the through was filled with DI water, the as-prepared aqueous dispersion of GO sheets in water/methanol (1/5:v/v) as a spreading solvent was slowly spread on the surface of pure DI water subphase by Hamilton micro-glass syringe at 20±1 ^oC. 1.0 mL of GO aqueous dispersion (1.0 mg/mL) was totally spread with the speed of 100 μL/min. The change in the surface pressure was monitored with Wilhelmy plate balance. After allowing 20 min for the evaporation of the solvent (methanol) and to form a monolayer, GO sheets on the subphase was compressed by using moving barriers at a barrier speed of 5 cm^2/min. At the end of the process, GO monolayers with a weak brown colour was formed at the air-water interface. To prepare PyY@GO composite at the air-water interface, the same film procedure was performed as follows. The LB trough was filled with the aqueous solution of PyY ($1.0x10^{-6}$ M) and, then GO sheets dispersed in the spreading solvent were spread on the surface of the aqueous solution containing PyY by the micro-syringe. Consequently, PyY@GO composites were formed at the subphase surface due to the high affinity of the cationic dye molecules on the negatively charged surface of GO sheets. GO sheets and PyY@GO composites monolayers were transferred to the glass substrates at various surface pressures by vertically dip-coating method with a speed of 5 mm/min. The monolayer films of pristine GO sheets and PyY@GO composites on the glass substrate were transferred at 10, 20, 25, 30, 40 mN/m surfaces pressures. The transfer ratio of the monolayer of GO sheets and PyY@GO composites were determined to be approximately 1.0. The drying time for the multilayer LB films allowed between consecutive dips was ~10 min. The prepared LB films were stored in dust-free chamber for the characterization. The glass substrates were cleaned by a piranha solution (H_2SO_4/H_2O_2, (7:3)) for 30 min.

Results and Discussion

GO sheets used in this study was synthesized via modified Hummers method and characterized by various advanced analytical techniques which are reported elsewhere.[5,6] Herein, TEM and SEM images of as-prepared GO sheets were only shown in Fig. 1.

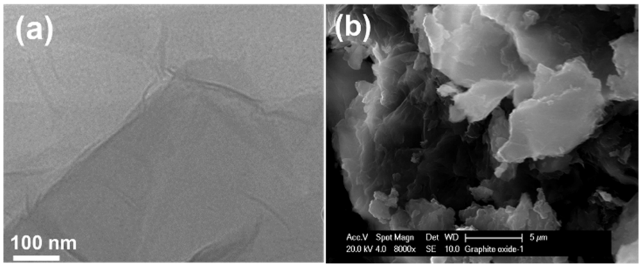


Fig. 1. TEM and SEM images of as-prepared GO sheets. (SEM belongs to the unexfoliated GO)

TEM image demonstrated a very thin layer of GO sheets with many wrinkles (Fig.1a). The porous morphology of pristine GO sheets was characterized with SEM study (Fig.1b) when it was compared to the common smooth surface and layered structure of graphite.[5] GO sheets are easily processed in various application due to the excellent physicochemical properties of GO sheets. For instance, the floating layers of pristine GO sheets on DI water subphase is well-known phenomenon because of the edge-to-edge interaction of GO sheets.[8] Spreading of the pristine GO sheets with an appropriate solvent (water/methanol, (1/5:v/v)) on DI water subphase to form a monolayer. The carboxylic and carbonyl groups of GO sheets at the edges sink into DI water subphase while its basal plane ensures to stay on the surface of subphase.[16] This property of GO sheets on the subphase was used to form GO-based composites via simple adsorption process. In general, the negatively charged surface of GO sheets interact easily with the oppositely charged molecules in aqueous dispersion. To synthesis PyY@GO composites at the air-water interface, the monolayer of pristine GO sheets on the subphase containing PyY ($1.0x10^{-6}$ M) were formed. During the procedure, PyY@GO composites at the air-water interface was formed due to the high affinity of the cationic dye molecules on the negatively charged surface of GO sheets. The monolayer formations of GO sheets on the subphase with and without PyY molecules were checked by π-A isotherms studies (Fig. 2).

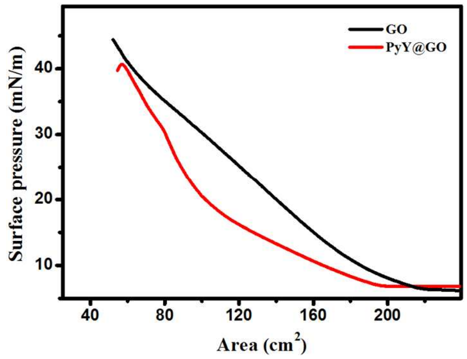
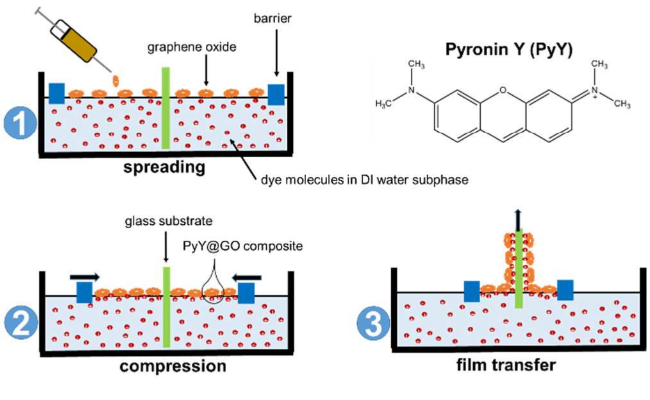


Fig. 2. π-A isotherms of GO sheets on DI water subphase with and without PyY ($1.0\text{x}10^{-6}$ M)

The π-A isotherms of GO sheets confirmed that the floating layer of GO sheets on the subphase with and without PyY molecules were formed as a Langmuir film.[8,18] The π-A isotherms revealed that the phases (gas, liquid, solid) can be clearly seen in the π-A isotherm of GO sheets on the subphase containing PyY molecules. The limiting molecular areas, determined by using "zero pressure" extrapolation of the π–A isotherms, were changed with the presence of PyY molecules in the subphase. This is due to interaction between the positively charged PyY molecules and the negatively charged oxygenated groups of GO sheets since the dye molecules were rapidly adsorbed on GO sheets in the aqueous solution.[5] The limiting areas of the pristine GO sheets on the subphase with and without PyY molecules were determined, and the area on pure DI water subphase was found to be larger than that found on the subphase containing PyY molecules, which clearly indicated the formation of PyY@GO composites. The adsorption of PyY molecules from DI water subphase onto GO sheets via the ionized carbocyclic acid groups at the edges decrease the repulsion among GO sheets. Thus, GO sheets adsorbing the dye molecules are closely packed than that of GO sheets.



Scheme 1. Schematic representation of preparing PyY@GO composites from the air-water interface to solid support, and the chemical structure of PyY.

This allows the fabrication of compact Langmuir-Blodgett (LB) films of GO-based composites at various thicknesses on the substrates. The floating layer of GO sheets is easily transferred to substrates at the desired deposition pressure that controls the density of GO sheets. To achieve this, the density of GO sheets at the air-water interface was adjusted by changing the surface pressure. First of all, GO sheets and PyY@GO composites were transferred to be LB films onto the glass substrate at a moderate surface pressure of 25 mN/m. A general procedure, which are the preparation of PyY@GO composites from the air-water interface to solid support, was shown in Scheme 1.

The density of GO sheets and PyY@GO composites on the glass surface were followed by a SEM study for their one-layer LB films (Fig. 3).

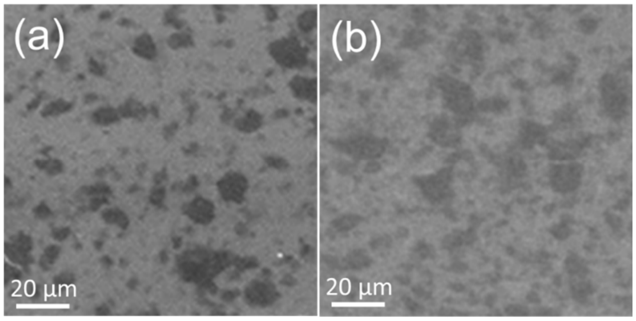


Fig. 3. SEM images of one-layer LB film of (a) GO sheets and (b) PyY@GO composites at 25 mN/m

The SEM images revealed that GO sheets and PyY@GO composites were successfully covered on the glass surface at 25 mN/m. As seen from the SEM image, PyY@GO composite sheets are closely packed than that of GO sheets at 25 mN/m. This observation supported the results obtained from the π-A isotherms, which PyY@GO composites were much closer to each other via decreasing the repulsion among GO sheets after the adsorption of dye molecules on the GO surface. The density of PyY@GO composites on the glass surface was also controlled with the increasing number of the PyY@GO composite layers transferred (Fig. 4).

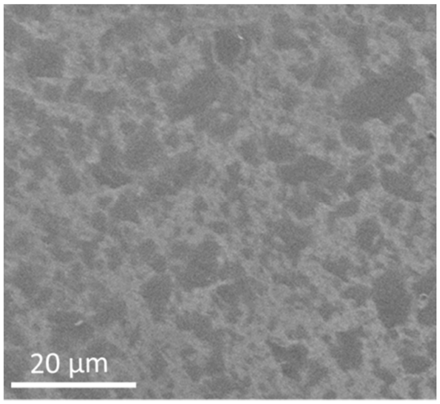


Fig. 4. SEM image of eleven-layer LB film of PyY@GO

composites at 25 mN/m

The density of PyY@GO composites on the LB film was successfully increased with the consecutive dips of floating-layer up to 11 layers, which is concluded by comparing the Fig.4 and Fig.3b. This result is crucial for the various applications including GO and GO-based composites since the desired porous and thickness of GO-based LB films are fabricated.

Furthermore, in the monolayer, the material density of PyY@GO composites was also controlled by changing the deposition surface pressure. For this aim, the specific regions of the π-A isotherm of PyY@GO composites were used to fabricate the LB films of the composites. The specific regions of the π-A isotherm of PyY@GO composites and SEM images of the composite LB films prepared at various surface pressure were shown in Fig. 5.

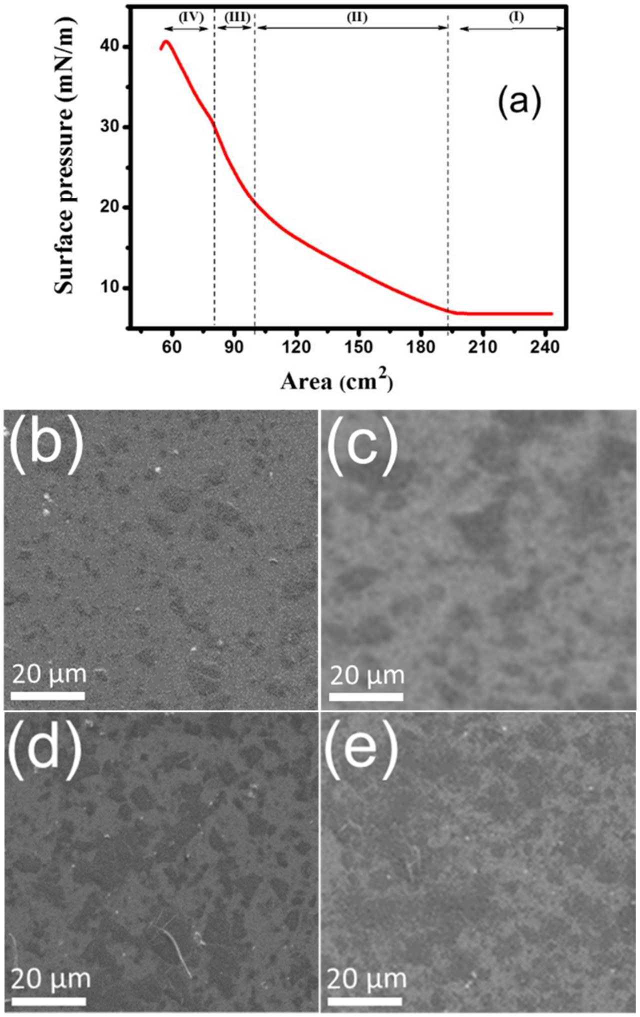


Fig. 5. The π-A isotherm of PyY@GO composites (a) and SEM images of one-layer LB film of PyY@GO composites at different regions of the π-A isotherm: (b) 10 mN/m for I. Region (c) 20 mN/m for II. Region (d) 30 mN/m for III. Region (e) 40 mN/m for IV. Region

The Langmuir films of PyY@GO composites compressed at 10, 20, 30 and 40 mN/m were transferred on the glass substrate as LB films. In these regions (I-IV), the density of PyY@GO composites on the surface is different as a function of film deposition pressure. SEM images of the LB films of PyY@GO composites revealed that the packing density of GO sheets attached PyY molecules on the as-fabricated LB films was successfully tuned by changing the film deposition pressure with the morphological properties transferred from loosely packed, closely packed to densely packed ones (Fig. 5b-e).[8] Thus, the PyY@GO composites on wide surfaces were homogeneously coated by LB technique at the desired material density. In GO-based thin films, some defects containing many wrinkles and folds of GO sheets can be observed, and the defects were also possible for GO-based composites. When the LB films of PyY@GO composites were coated at high surface pressure (>35 mN/m), the LB films contained many wrinkles and folds at some region (Fig. 6).

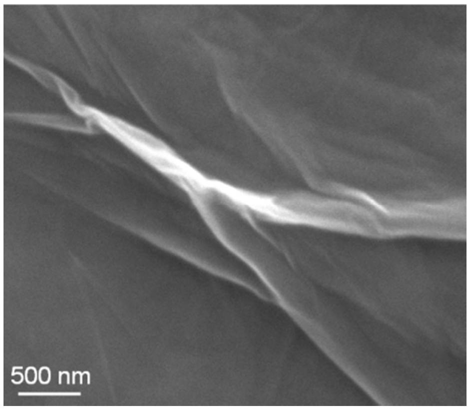


Fig. 6. SEM image of wrinkles on the LB film of PyY@GO composites deposited at high surface pressure

As seen in Fig. 6, the SEM image revealed that the LB film of PyY@GO composites transferred on glass substrate at 35-40 mN/m surface pressure included many wrinkles. The undesired states for LB coating of GO sheets were solved by decreasing the film deposition pressure. Consequently, the film coating processes have been executed at high surface pressure to fabricate the porous LB film of the composites. This type morphologic feature of GO-based materials are sometimes desired for their applications.

The transfer of the dye molecules from DI water subphase to the surface of GO sheets at the air-water interface were determined by UV-Vis spectroscopy since GO sheets weakly absorbed the visible light. The absorption spectra of LB films of GO sheets and PyY@GO composites were given in Fig. 7a. PyY molecules strongly absorb the visible light and their maximum absorption band in water is located at 546 nm at the diluted concentration.[19] In addition, the mixed LB film of PyY with stearic acid on glass substrate has an absorption band at 546 nm.[15] The LB films of GO sheets and PyY@GO composites were fabricated on the glass surface at 25 mN/m. The one-layer LB film of PyY@GO composite had an absorption band located at ~550 nm while the one-layer LB of GO sheets was not absorbed in the visible region (Fig. 7a). The absorption spectra confirmed that PyY@GO composites at the air-water interface are successfully formed, since the interaction between dye molecules and GO sheets leads to red-shifting of the absorption band maxima of dye molecules.[5,6]

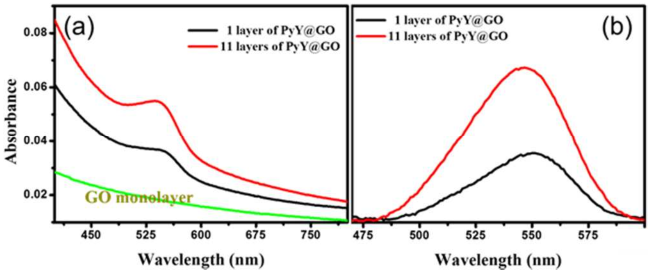


Fig. 7. The absorption spectra of LB films of GO sheets and PyY@GO composites: (a) raw (b) subtracted baseline

The maximum absorption band of PyY in the 11-layers LB film of the composite were formed at ~547 nm. The small shifting at the absorption band maximum of the composites was ascribed to the dye aggregation.[5] The adsorption of PyY molecules on GO sheets were clearly observed by the subtraction of baseline from the absorption spectra (Fig. 7b). The absorption properties of the LB films of PyY@GO composites were different since the material density on the LB film was controlled by chancing the film deposition pressure (Fig. 5). Fig. 8 showed that the absorbance of PyY in the composite LB film was increased by increasing the deposition pressure.

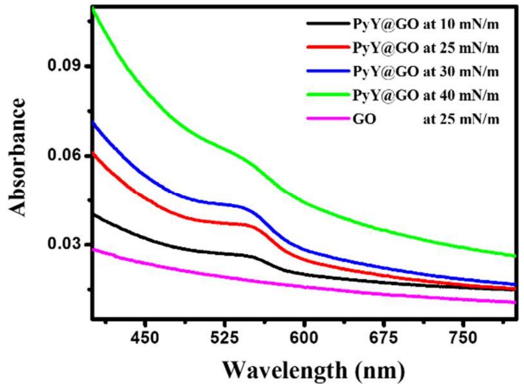


Fig. 8. The absorption spectra of one-layer LB film of GO and PyY@GO composite at various surface pressure

This was easily seen in the absorbance at 546 nm of LB films of PyY@GO composites versus deposition pressure (Fig. 9).

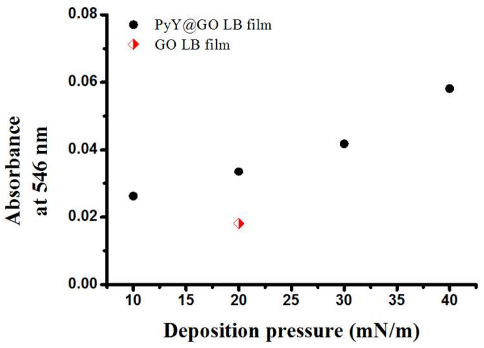


Fig. 9. The absorbance at 546 nm of LB films of PyY@GO composites versus deposition pressure (mN/m)

This figure revealed that a plot of the absorbance at 546 nm versus the surface pressure given a nearly straight line. The dye loading on the LB film of the composite were increased by increasing the film deposition pressure. Consequently, this study shows that the LB films of PyY@GO composite at various thicknesses and morphologies are homogeneously coated on a wide surface by LB film technique for various applications.[20]

Conclusions

In the present study, it was reported that the PyY@GO composites at the air-water interface were synthesized as Langmuir films. The π-A isotherms of GO sheets on DI water subphase with and without PyY molecules were confirmed to form the floating-layers of GO sheets and PyY@GO composites. The π-A isotherm of PyY@GO composites were different than that of GO sheets due to the interaction of GO sheets with the dye molecules. The Langmuir films of GO sheets and PyY@GO composites at the air-water interface were successfully transferred to the glass substrate as LB film. The absorption spectra of the LB films revealed that the loading of the dye on GO sheets was achieved. SEM images of GO sheets and PyY@GO composites showed that the morphologies of these films were readily controlled by manipulating the surface pressure during the film deposition as well as the number of layers. This is the first and a guide study showing that the LB films of the water soluble materials via GO sheets are simply formed at the air-water interface.

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Notes and references

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