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報告・学位記番号	甲第370号（甲バ第2号）
学位記授与の日付	平成26年9月25日
学位記授与の要件	本学学位規則第３条第１項該当
学位論文題目	Synthesis and Selective Patterning of Large Area Graphene-Oxide by Langmuir-Blodgett Technique for Bio-Nano Electronics Applications （和訳：バイオ・ナノ融合エレクトロニクスへの応用のためのLangmuir-Blodgett法による大型酸化グラフィーンの合成およびパターンニング）
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【論文審査】Review of the thesis

Graphene is a monolayer composed of SP^2-bonded carbon atoms. Graphene has recently been greatly focused on in both academia and industry thanks to its unique electrical, mechanical, optical and biocompatible characteristics. A significant progress has been made in the synthesis and applications of graphene in recent years. However, it is still extremely difficult to synthesise a large areal monolayer of graphene and graphene-oxide (GO) and form ultra fine patterns as designed using graphene and GO. Although the complex patterned structures can be formed using the current lithography and metal evaporation deposition techniques, contamination becomes a serious problem. What is worse, the above processes are time consuming and suffer from low throughput.

In this thesis, an eco-friendly approach is taken to the synthesis of GO and the reduction of GO for green electronics and bioscience applications. An efficient patterning of biocompatible GO on SiO_2/Si substrates is also demonstrated. The thesis consists of eight chapters, which deal with potential applications of a large areal monolayer of patterned GO to bio-nano electronics devices; “Chapter 1: Introduction”, "Chapter 2: Instrumentation and characterisation techniques", "Chapter 3: Synthesis of large area GO and organisation of monolayer GO at air-water interface using Langmuir Blodgett technique", "Chapter 4: Green reduction of GO for electronics and bioscience", "Chapter 5: Effect of N_2-plasma on hydrophilisation of SiO_2/Si", "Chapter 6: N_2-plasma assisted one-step alignment and patterning of GO on SiO_2/Si via LB technique", "Chapter 7: Specific area cellular growth enhancement on N_2-plasma patterned GO via LB technique" and "Chapter 8: Conclusions".

Chapter 1 Introduction

An overview of the fascinating features of graphene and GO and the synthetic strategies of two-dimensional ordered structures via self-assembly is given in this chapter. The theoretical understanding and processing routes available for patterning GO are also discussed and potential applications of patterned GO is highlighted. Finally, the motivation behind this thesis and the chapter-wise descriptions of the present protocol are summarised.

Chapter 2 Instrumentation and characterisation techniques

The physical principles of different instrumentation and characterisation techniques, which are extensively adapted for the present work, are summarised; that is, Langmuir Blodgett (LB) technique, UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, zeta potential measurement, optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), plasma system, optical omission spectroscopy (OES), contact angle measurements, electron beam lithography (EBL), photolithography (UVL), electron beam evaporator system, thermal resistive evaporator system and electrical conductivity measurement.

Chapter 3 Green reduction of GO for electronics and bioscience

A facile eco-friendly route to a green reduction of GO is discussed. Halophilic bacteria; *Halomonas* species, were an appropriate candidate for the removal of various toxic chemicals and organic compounds to reduce GO. Aerobic and anaerobic methodologies for GO reduction were demonstrated using bacterial culturing and the conductivity and biocompatibility of the reduced graphene was evaluated. Bacterially reduced GO (BRGO) was found to be highly conductive and supports mammalian cell growth under *in vitro* conditions. Electrical measurements carried out by the 3-probe method revealed that the conductivity of BRGO increased by 10^4-10^5 fold compared to that of GO. Biocompatibility assay using mouse fibroblast cell line showed that BRGO is non-cytotoxic and has a tendency to support and what is more, enhance the cell growth under laboratory conditions. The present large areal reduced GO, which is highly conductive, may well make a great contribution to the development of biomedical and electronic sensors and devices.

Chapter 4 Synthesis of large area GO and organisation of monolayer GO at air-water interface using Langmuir Blodgett technique

The synthesis of a large areal monolayer of GO in aqueous medium, its assembly at the air-water interface and the LB film formation are focused on in this chapter. A large areal monolayer of GO was formed using the Hummer's method with some minor modification. Several parameters such as the concentration of GO in the solution, volume and LB parameters were optimised to assemble a monolayer of GO at the air-water interface. A closely packed two-dimensional atomic layer was formed by the present method, which can significantly simplify the patterning process. The effectiveness of self-assembled monolayers of GO was characterised by various spectroscopic analysers.

Chapter 5 Effect of N_2-plasma on hydrophilisation of SiO_2/Si

The effect of different plasma systems on hydrophilisation of SiO_2/Si substrates are investigated under various chamber pressure conditions, noting that different types of gas and substrate determine the functional groups formed on the plasma-exposed substrates. A comparative study was performed between air and N_2 -plasma systems to check the effectiveness of the deposition of a monolayer of GO via LB technique. It was found that the hydrophilisation and surface modification were successfully performed when the SiO_2/Si surface was treated with both air and N_2-plasma. However, N_2-plasma was found to be more efficient for a specific placement of GO and for promoting its adhesion to the substrate. It is well known that the surface modification is in many cases very sensitive to the treatment time and environmental exposures and therefore aging study was also carried out to optimise the plasma-induced physical and chemical properties of the substrate prior to GO deposition.

Chapter 6 N_2 plasma assisted one-step alignment and patterning of GO on SiO_2/Si via LB technique

One-step facile technique using N_2-plasma, which stimulates the surface modification and enhances the surface wettability of the substrate, is proposed. The present technique was very successful to create a partially hydrophilic surface with the aid of various templates, thanks to which selective deposition, alignment and formation of a desired monolayer of GO could be performed via LB deposition technique. Various characterisation techniques were employed in order to understand the growth and patterning mechanism of GO. The present technique will definitely leads to the creation of patterns with controlled dimensions including the thickness of GO-sheets, which is one of the most important factors in designing and fabricating arrays and devices on wafer-scales.

Chapter 7 Specific area cellular growth enhancement on N_2-plasma patterned GO via LB technique

Specific area placement and patterning of GO on the surface of SiO_2/Si using the present N_2-plasma-assisted surface modification can contribute greatly to the development of electronics and biomedical devices. GO was successfully deposited on the pre-patterned surface of the electrodes. It was found that the as-synthesised large areal monolayer of GO was non-toxic to L929 and HCN cells and was highly biocompatible. The present facile and quick approach to precise assembly of GO sheets directly from dispersion to the desired area can reduce significantly a number of processing steps required for device fabrication and cell patterning.

Chapter 8 Conclusions

The results obtained in the present doctoral study are summarised.

(a) A high yield large areal monolayer of graphene-oxide was successfully synthesised using Langmuir Blodgett technique.

(b) Graphene-oxide was successfully reduced by extremophiles so that graphene of a high electric conductivity was produced. The graphene also showed a high biocompatibility.

(c) The optimal conditions for hydrophilisation of the surface of SiO_2/Si substrates using N_2-plasma was obtained so that the adhesion of graphene-oxide to the surface of the substrates was tremendously improved.

(d) One-step facile technique for the enhancement of the surface wettability of the substrates was developed. It became possible to fabricate hydrophilic patterns on the surface of substrates using both the hydrophilisation and LB deposition techniques so that exactly the same patterns were formed by GO.

(e) The as-synthesised large areal monolayer of GO was highly biocompatible. The present facile and quick approach made it possible to design some complicated cell patterning on the surface of substrates.

【審査結果】Summary and decision

The doctoral thesis entitled "Synthesis and selective patterning of large area graphene-oxide by Langmuir-Blodgett technique for bio-nano electronics applications" focuses on the synthesis of a large areal monolayer of graphene-oxide and precise patterning of graphene-oxide on the surface of SiO_2/Si substrates. The results shown in the thesis are outstanding from an international point of view and the significant points in the present study are summarised below;

(1) A very simple methodology for synthesising a large areal monolayer of graphene-oxide was developed based on Langmuir-Blodgett technique. A closely packed two-dimensional atomic layer of graphene-oxide was successfully formed, reducing a number of patterning processes.

(2) Graphene-oxide was reduced by Halophilic bacteria and it was found that the reduced graphene was highly conductive and biocompatible. The present eco-friendly bacterial reduction methodology may well make a great contribution to the development of biomedical and electronic sensors and devices.

(3) A facile methodology for hydrophilising the surface of substrates was successfully developed using N_2-plasma and a top-down ultra fine patterning technique. The optimal conditions were obtained for the deposition of graphene-oxide on the surface of substrates.

(4) Selective deposition, alignment and formation of a monolayer of graphene-oxide on the surface of substrates were successfully performed using the hydrophilic patterns fabricated on the surface of substrates. It may well become possible to form patterns of graphene-oxide as designed on electronic devices.

(5) The as-synthesised large areal monolayer of graphene-oxide was highly biocompatible. Therefore, it may also become possible to design some specific patterning of cells on the surface of substrates, which may make a great

contribution to the development of biomedical devices.

One first-authoring (equally contributed) paper has already been published in an international journal; *Part. Part Syst. Charact.*, whereas one co-authoring paper also published in *Part. Part Syst. Charact.* Judging by the quality of the research results shown in the thesis, the present results may well make a great contribution to the development of a new methodology for synthesising a large areal monolayer of graphene-oxide and patterning graphene-oxide as designed on the surface of substrates. As a result, the patterning of biological molecules and cells on the surface of substrates may also become possible, which may tremendously contribute to the design and development of electronic and biomedical devices. In conclusion, the quality of the present study and thesis is considered to be very high by international standards and therefore the thesis can be accepted as a doctoral one.