科学研究費助成事業　　研究成果報告書

平成 ２６ 年　 ６ 月 １７ 日現在

機関番号：１４３０１
研究種目：若手研究(A)
研究期間：2012～2013
課題番号：２４６８１０１９

研究課題名（和文）ラングミュア‐ブロジェット法を用いたＤＮＡ折り紙二次元集積体の構築

研究課題名（英文）Preparation of well-controlled 2D assemblies of DNA origami using Langmuir-Blodgett technique

研究代表者
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研究者番号：１０６０８５６６

交付決定額（研究期間全体）：（直接経費）　　20,700,000円、（間接経費）　　6,210,000円

研究成果の概要（和文）：We proposed a new assembly technique, namely "diffusion driven layer-by-layer assembly", and showed how it can be used for creating diverse nanosheet architectures with good control in shape and properties.

研究成果の概要（英文）：The original aim of this project was to utilize liquid-air interfaces as a platform to construct DNA origami into diverse 2D assemblies. However, during this study we discovered an unexpected but interesting assembly behavior of nanosheets, which became our new focus. In 2012, we developed a novel strategy for directing the assembly of nanosheets through interfacial complexation with oppositely charged polyelectrolytes. Using this method, we demonstrated the assembly of nanosheets into various macrostructures such as films, fibers, and capsules.
In 2013, we further found that the diffusion of polyelectrolyte could drive continuous growth of the nanosheet complex into 3D porous foam-like frameworks which porosity could be easily adjusted. From such discovery, we proposed a new assembly technique, namely "diffusion driven layer-by-layer assembly", and showed how it can be used for creating diverse nanosheet architectures with good control in shape and properties.

研究分野：ナノ・メゾ合成化学、自己組織化

科研費の分科・細目：ナノ・マイクロ科学、ナノ材料・ナノバイオサイエンス

キーワード：Self-Assembly　Nanomaterial　Langmuir-Blodgett　DNA Origami　Interfacial Assembly　Graphene

１．研究開始当初の背景

For practical applications of nanomaterials, it is often necessary to construct the small building blocks into 2D or 3D macrostructures which can be integrated into conventional real-life devices. During this process, the properties of the material are often significantly altered, which can be either beneficial or detrimental. As a result, it is critical to gain the ability to assemble the nanomaterials into functional architectures with good control and efficiency. For this purpose, we have long investigated the use of air-liquid and liquid-liquid interfaces as an assembly platform.

One building block of interest is DNA origami. DNA has been actively investigated not only as a genetic material, but also recently as a starting material for creating novel structures. It is now possible to mold DNA strands into precisely controlled forms such as nanotubes and polyhedrons, typically in the size range of tens to hundreds of nanometers. With unique molecular recognition capacity and biocompatibility, these DNA nanostructures are actively explored for applications such as biomedical diagnostics. However, to realize this potential, it becomes necessary to construct the DNA into even higher order functional architectures. In this project, we proposed to utilize Langmuir-Blodgett technique to demonstrate the assembly of DNA origami on water surfaces into 2D macrostructures.

２．研究の目的

Initial research goals:
Our original goals were to 1) demonstrate the application of Langmuir-Blodgett (LB) technique for preparing well-ordered DNA superstructures with good control and reliability, and 2) gain fundamental understandings on how the structure and surface properties of nanomaterials influence their self-assembly behavior.

Modified research goals:
However, during the studies we experienced much difficulty with the instability of DNA origami on water surfaces. Extreme scrolling and aggregation of the origami structure was observed, which made it somewhat unsuitable for LB assembly. Therefore, *we decided to change the material of focus from DNA origami to nanosheets such as graphene, WS_2, and MoS_2,* which have been gaining strong interest for energy related applications. At the same time, instead of relying on LB technique, *we started to investigate the application of interfacial polyionic complexation for the nanosheet assembly based on new discoveries made in the group.*

３．研究の方法

Three types of nanosheets were prepared using chemical and physical exfoliation methods, namely, graphene oxide (GO), tungsten sulfide (WS_2), and molybdenum disulfide (MoS_2). While these nanosheets are not as uniform in size and shape compared to DNA origami, it can be produced in large quantities and are stable on liquid surfaces.

The nanosheets were deposited to various air-liquid and liquid-liquid interfaces. During that process, by inducing complexation with an oppositely charged polyelectrolyte, we were able to observe interesting assembly behaviors as discussed below.

４．研究成果

In FY2012, we reported in *ACS Nano* a new strategy for directing the assembly of nanosheets into various macrostructures through interfacial polyionic complexation (Figure 1). A key point of the study was that nanosheets often behave as charged macromolecules and therefore can form a stable complex with oppositely charged polyelectrolytes. Such characteristic was explored using chitosan, a positively charged biopolymer, which readily interacted with nanosheets that have negative surface charges such as GO, WS_2, and MoS_2.

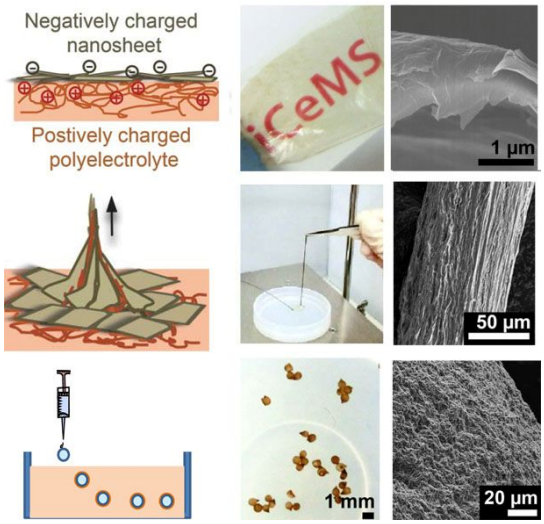
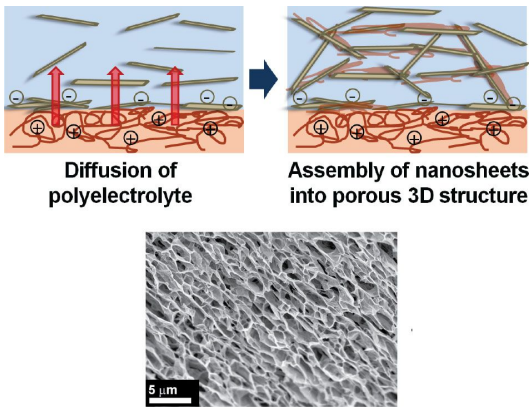


Figure 1. Assembly of graphene oxide nanosheets into thin film, fiber, and capsule forms using interfacial polyionic complexation.

We found that the complexation could be confined at liquid-liquid or air-liquid interfaces, which allowed control over the nanosheet assembly into forms such as films, fibers, and capsules. Furthermore, additional components such as nanoparticles and small molecules could also be easily integrated to the structure for further tailoring of material properties. Such results suggest that the complexation with polyelectrolytes can serve as a simple yet useful tool for guiding the assembly of nanosheets into various architectures.

During FY 2013, we were able to further expand our previous report. The key new discovery was that diffusion of polyelectrolyte could induce continuous growth of the nanosheet complex formed at the interface into 3D macroscopic structures (Figure 2). Interestingly, the assembled nanosheets form a foam-like porous network, which porosity can be tuned from ultra-light (5.6 mg/cm^3) to tightly packed (~ 1800 mg/cm^3) through simple adjustments in experimental condition. Furthermore, the assembly process can be utilized in various configurations such as to create free-standing architectures with tailored shapes or patterned GO films on a substrate. Based on such discovery, we have proposed a



novel assembly technique which we termed as "diffusion driven layer-by-layer assembly". This result is currently submitted and under revision.

Figure 2. Construction of GO nanosheets into porous macrostructures through diffusion driven layer-by-layer assembly

The simplicity and versatility of this process should be useful in constructing a wide range of 3D graphene-based architectures. At the same time, we believe that this concept of utilizing the diffusion of polyelectrolyte for the assembly of nanomaterials into macrostructures should also be applicable to a much wider range of materials.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　　1 件）

Author: Jianli Zou, Franklin Kim
Title: Self-Assembly of Two-Dimensional Nanosheets Induced by Interfacial Polyionic Complexation
Journal Name: ACS Nano (Peer reviewed), issue 6, 2012, 10606 – 10613
DOI: 10.1021/nn303608g

〔学会発表〕（計　　3 件）

Presenter name: Franklin Kim
Presentation title: Self-assembly of two-dimensional nanosheets induced by interfacial polyionic complexation
Conference name: International conference on Metallurgical coatings and thin films (ICMCTF)
Date: 2013/04/28 to 2013/05/02
Location: San Diego, USA

Presenter name: Franklin Kim
Presentation title: Self-Assembly of Two-Dimensional Nanosheets Induced by Interfacial Polyionic Complexation
Conference name: 7th Annual Symposium on Nanobiotechnology
Date: 2013/11/05 to 2013/11/07
Location: Bristol, UK

Presenter name: Franklin Kim
Presentation title: Self-Assembly of Two-Dimensional Nanosheets Induced by Interfacial Polyionic Complexation
Conference name: 2013 UST-Kyoto University iCeMS International Symposium
Date: 2013/11/17 to 2013/11/19
Location: Hsinchu, Taiwan

〔図書〕（計　　0 件）

〔産業財産権〕

○出願状況（計　　件）

名称：
発明者：
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種類：
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国内外の別：

○取得状況（計　　件）

名称：
発明者：
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取得年月日：
国内外の別：

〔その他〕

ホームページ等

６．研究組織

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