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授与した学位	博　士
専攻分野の名称	学　術
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学位授与の要件	自然科学研究科　　応用化学専攻 （学位規則第４条第１項該当）
学位論文の題目	Robust functionalization of graphene for organic electrode materials （グラフェンの化学修飾による有機系電極材料の創出）
論文審査委員	准教授　仁科　勇太　　教授　　菅　誠治　　教授　　藤井　達生

学位論文内容の要旨

Two-dimensional nanocarbons, as represented by graphene, have been the active research subject owing to their outstanding physical properties, such as toughness, high specific surface area, and high electrical and thermal conductivities. As the basic physical properties of graphene and its analogs have mostly been elucidated by intense research over more than 15 years, the development of functionalization methods to further enhance their physical/chemical properties is in great demand.

The present study aims to robust functionalization of graphene for organic electrode materials. The thesis is composed of three achievements.

In the first achievement, a new concept for graphene functionalization using brominated graphene has been developed, in which brominated graphene is successfully functionalized by heteroatom-containing molecules to form onium bonds, such as pyridinium or ammonium. The counterion bromide is replaced with other anions, such as sulfate, by treating with sulfuric acid while retaining the cationic molecules on the graphene surface, demonstrating the durable properties of onium bonding. To emphasize the advantages of this strategy for graphene functionalization, the performance for energy-related applications, such as biofuel cells, supercapacitors (SCs), and lithium-ion batteries are evaluated.

In the second achievement, a three-step reaction furnished a composite of graphene and a conductive polymer. In the first step, graphene oxide (GO) was modified with a diamine, which acted as a linker for polymer attachment. In the second step, an initiating site was attached to the free amine of the linker. Finally, a polymer was grown from the initiation site, and GO was reduced during polymer growth. The electrical properties of the composite were evaluated to determine its suitability as an electrode material for SCs.

In the third achievement, a series of organic molecules was functionalized on GO by using stepwise covalent double functionalization method. The functionalization was performed by the stepwise reaction of epoxide and hydroxyl groups on GO. The first step consists of ring-opening reaction of epoxide group by amine compounds. The mono functionalized GO, containing more OH groups compared to pristine GO, was modified with α,β-unsaturated carbonyl compounds via Michael reaction. The double functionalization enabled the production of multifunctional graphene with proton conductivity and improved capacitance.

論文審査結果の要旨

グラフェンは，電極材料，触媒，吸着材など広範な用途に用いられるナノカーボンである。グラフェンの高い電気伝導性や強度などの優れた物性を活かしつつ，新機能化や高機能化のための化学修飾法が広く検討されている。本学位論文の研究では，入手容易な黒鉛から安全かつ大量に製造可能な酸化グラフェンを用い，オニウム結合，ポリマーグラフト，多重官能基化により化学修飾した新たなグラフェン系材料を創出した。各反応で得られたグラフェン系材料について，XPS，FT-IR，AFM等の分析により，目的の構造が構築できていることを確認している。グラフェン上に酸化還元特性を有する官能基を付与することにより，スーパーキャパシタの電極材料としての性能を評価した。また，多重官能基化では，プロトン導電性と酸化還元性の両方を付与することにより，ナフィオンの添加が不要な電極材料を創出することができた。本研究では，強固な化学結合によりグラフェンを化学修飾しているため，単にグラフェンと分子を混合しただけの場合に比べて安定性が向上するという利点もある。

以上，本研究は新規グラフェン材料を作製するための新手法の開発やその用途開拓を実証したものであり，博士（学術）の学位に値する。