氏　　名	TON, Nu Thanh Nhan
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論文審査委員	主査　谷池俊明　北陸先端科学技術大学院大学　准教授
	前之園信也　同　教授
	松見紀佳　同　教授
	都英次郎　同　准教授
	中谷久之　長崎大学大学院　教授

論文の内容の要旨

Research Content

Heterogeneous photocatalysis using titanium dioxide is a well-known advanced oxidation process for water treatment. However, the large band gap, a short lifetime of photo-excited electron-hole pairs, and the ability as an absorbent limit its applications. Hybridization of TiO2 with graphene emerges as a promising approach to diminish these drawbacks. Many efforts have been reported on the preparation of TiO2/graphene composites, but most of them utilized graphene oxide (GO) as a starting material. Subsequent reduction of GO into so-called reduced graphene oxide (rGO) leads to the formation of defect-rich graphene with disadvantageous electronic properties. Furthermore, the aggregation of TiO2 is usually observed because the sensitivity of titanium alkoxide to water (GO usually contains) significantly impedes the uniform and controlled growth of TiO2 on graphene. Hence, the aim of this thesis is to explore a novel and effective approach for the preparation of the TiO2/graphene nanocomposites to obtain excellent visible-light photocatalysts for water treatment application.

In Chapter 2, a novel GO-free route for the fabrication of TiO2/graphene nanocomposites was explored. This route involved the ultrasonication-assisted exfoliation of graphite in a titanium tetra-n-butoxide and subsequent sol-gel reaction to form TiO2 using the graphene dispersion. Featured with various advantageous characteristics including i) a morphology in which TiO2 nanolayers uniformly and thinly covered graphene sheets, ii) a trace amount of defects on the graphene frameworks, iii) a dramatic inhibition of charge carriers recombination, and iv) a significant extension of absorption edge into visible-light area, the obtained the TiO2/graphene nanocomposites exhibited an excellent performance for the visible-light photocatalytic decomposition of methylene blue in an aqueous medium.

Chapter 3 concentrated on the exploration of new solvents for liquid-phase exfoliation of graphite via ultrasonication. Various new exfoliating solvents were found through screening of different solvents and

their mixtures. Particularly, chlorobenzylamine, which is a combination of the molecular structure of chlorobenzene and benzylamine, known as famous exfoliating solvents, presented the highest graphene yield. More importantly, a synergistic effect among different functional groups e.g. aromatic, amine, and halogen groups was identified, and this was more effectively exploited in a form of solvent mixtures. In addition, the preparation of a graphene dispersion in the presence of different metal alkoxides was demonstrated, which could be useful as a direct precursor of various oxide@graphene nanocomposites without mediating GO.

In Chapter 4, further improvement in the visible-light photocatalytic performance of the TiO2/graphene nanocomposites was achieved by chlorine doping. The chlorine-doped TiO2/graphene nanocomposites were synthesized based on the synthetic method established in Chapter 2. With the aid of chlorine radicals in accelerating the photodecomposition of target organic compounds and a significant reduction of the amount of graphene defects, the chlorine-doped TiO2/graphene nanocomposites exhibited a significant improvement in the photocatalytic performance compared to that of the undoped TiO2/graphene nanocomposite (Figure 1).

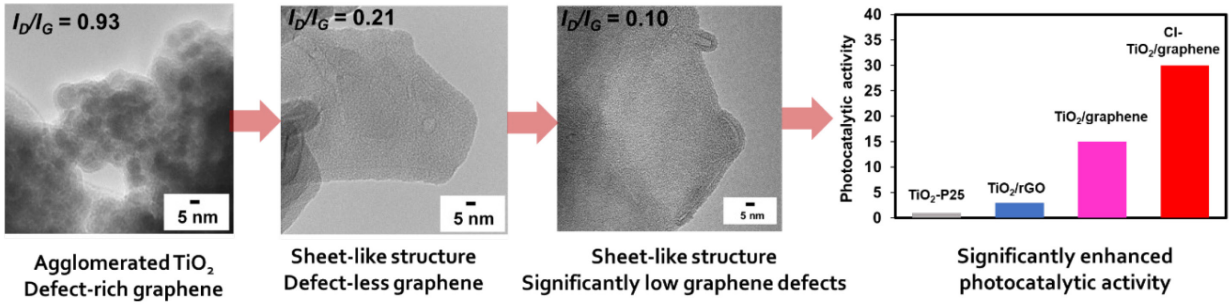

Figure 1. Development of TiO_2/graphene nanocomposites for the enhancement of visible-light photocatalytic activity.

Research Purpose

Because of the limitations of the conventional TiO2/rGO nanocomposites which restrained their photocatalytic activity, in this research, I have found a novel GO-free route to synthesize TiO2/graphene nanocomposites. Eliminating most of the problems of TiO2/rGO, I have synthesized the TiO2/graphene nanocomposites with an excellent visible-light photocatalytic activity.

Owing to my finding about the importance of solvents in the preparation of the nanocomposites, in which their ability to stabilize graphene played a key role, I have investigated deeper about the solvents for the liquid-phase exfoliation of graphite under ultrasonication. In this research, I have explored a series of new exfoliating solvents. More importantly, the relation between functional groups of solvents and their exfoliation ability has been found. A synergy between effective functional groups introduced not only in the molecular structure of single solvents but also more exploited through solvent mixtures. This finding

is meaningful for chemists in investigating a proper exfoliation medium for specific purposes in term of the availability, diversity, and tunability.

According to the finding of the synthetic method for TiO2/graphene nanocomposites as well as the available solvents for the preparation of the nanocomposite. With the ambitious to further improve the photocatalytic activity of the TiO2/graphene nanocomposites by chlorine doping, I have investigated a novel synthetic method for Cl-doped TiO2/graphene nanocomposite. The Cl-doped TiO2/graphene nanocomposites successfully prepared by this new method exhibited an excellent enhancement in the visible-light photocatalytic activity compared to the undoped ones.

In general, this thesis has established a novel and effective route for the synthesis of the TiO2/graphene nanocomposites and demonstrated its usefulness in the field of water treatment based on excellent visible-light photocatalysis. It was also suggested that a similar method is applicable for the synthesis of different oxide@graphene nanocomposites with advantageous features.

Keywords

TiO2/graphene, Chemical exfoliation, Sol-gel, Photocatalysis, Water treatment

論文審査の結果の要旨

今日に至る多様な水質汚染は人口増加や経済活動に起因するが、中でも持続性が高く広範囲に拡散し生体に取り込まれやすい有機汚染物質は深刻な問題である。有機汚染物質を持続的に除去する手段として、副生成物を産することなく様々な有機分子の無機化を可能とする促進酸化処理（AOP）が注目を集めている。特に、二酸化チタン（TiO2）などの固体光触媒を用いたAOPは、コストやプロセスの点で有望視されている。しかし、豊富に存在し無害なTiO2は、①バンドギャップが広く太陽光の利用効率が低い、②励起電子・ホールの寿命が短い、③親水性が高く有機分子を十分に吸着しない問題があり、TiO2単独でのAOP応用は困難である。これらの問題を一手に解決する手段として、TiO2とグラフェンの複合材料が近年精力的に研究されている。同複合材料は、一般に高い表面積と長波長側に延長された吸収端を有し、グラフェンが励起電子を補足することで、有機分子分解に関しTiO2と比べて最大で数倍の活性を示す。欠陥の少ないグラフェンをTiO2ナノ薄膜が均一に覆った構造が理想的であるが、これまでに報告された合成法は全て酸化グラフェンを始物質として用いていたため、このような構造は達成されていなかった。

本論文では、特定の溶媒の存在下、超音波の照射などによりグラファイトを剥離させる化学剥離法を活用することで、有機分子分解に対して極めて高い活性を示すTiO2/グラフェン複合材料の開発に成功した。成功のきっかけは、化学剥離法において質の高いグラフェンを高効率製造可能な溶媒を探索する中で、TiO2の前駆体であるTi(OnBu)4が溶媒として有効なこと、及び、複数の溶媒を混合する規則を見出したことにあった（3章）。斯くして得たTi(OnBu)4/グラフェン分散液に、同じく剥離能を有するベンジルアミンをゾルーゲル反応の触媒として添加し反応させることで、欠陥の少ないグラフェンがTiO2ナノ粒子に均一に覆われた複合材料を合成することに成功した。ベンジルアミンは表面上に固定化され増

感剤として働き、吸収端を TiO2 の 390 nm から 580 nm まで延長した。高表面積により有機分子の吸着量が 9 倍増加しただけでなく、グラフェンが励起電子を捕捉することで励起ホールの利用効率が著しく改善した。本研究で開発した複合材料は水中での有機分子分解に関し TiO2 と比べて 15 倍程度の活性を示した（2章）。4章では、ベンジルアミンの分子構造を検討し、触媒活性を32倍まで向上することに成功した。

以上、本論文では、グラフェン製造に着目することで理想的な構造を有する可視光応答型 TiO2/グラフェン複合材料を酸化グラフェンを経ずに初めて合成し、触媒活性を劇的に向上することに成功し、また、そのメカニズムも解明した。よって、博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。