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## 学位論文題名

Development of high-performance water-decontamination systems by using graphene oxide as the functioning element (酸化グラフェンを機能場として用いた高性能水浄化システムの開発)

## 学位論文内容の要旨

High-performance water-decontamination systems were developed by using graphene oxide (GO) as the functioning elements. GO is heavily oxygenated graphene bearing hydroxyl and epoxide functional groups on the basal planes and carbonyl and carboxyl groups at the edges. GO have attracted a great deal of attention in recent years for a number of reasons. First, GO belongs to a class of truly sheet-shaped molecules. A single GO sheet has a length or breadth that is typically larger than micrometers while its thickness is only one or a few atoms thick; therefore, it is possible to cover or overlap chemical pollutants with an atom-thick sheet. Second, in comparison with carbon nanotubes, GO is highly soluble in both aqueous and organic media; therefore, it is easier to introduce GO into water and other matrixes with GO being ideally dispersed. Third, GO can be ' converted to graphene through chemical reductions or with heating. Graphene has many unusual properties, for example, graphene has high in-plane thermal (~3000 W/mK) and electrical conductivity (~10<sup>4</sup>  $\Omega^{-1}$  cm<sup>-1</sup>) and the extremely high surface areas (~2600 m<sup>2</sup>/g), which enable us to create a broad new class of high-performance systems and/or materials for environmental remediation applications. Moreover, GO is commonly produced by exfoliating graphite, an abundant material, through chemical and/or physical reactions; thus, GO has the advantages of low cost and plentiful supply of the starting material.

This dissertation consists of five chapters. In Chapter 1, a brief introduction to the hottest topic on investigation of the carbon based nano-sized adsorbents was described. In Chapter 2, a method for massive production of GO was introduced with commercially available expanded graphite as starting materials. The typical intercalating agent ( $H_2SO_4$ ) was capable of penetrating into the expanded graphite; this has further expanded internal distance between the basal planes and as a result, a foam-like intermediate was obtained. The foam-like intermediate was more easily oxidized in reaction with the oxidant (KMnO<sub>4</sub>) to form GO. Fully exfoliated GO was obtained

with the expanded graphite having the median diameter  $\sim 15$  µm as the precursors. This procedure was much safer and productive in scalable applications than the conventional Hummers methods. In Chapter 3, an in situ reduction approach was introduced for enhancing the GO adsorptive capability in the removal of organic dyes from contaminated water samples. GO was directly used as the adsorbent and its absorptive capability toward the organic dye was largely enhanced through its in situ reduction with sodium hydrosulfite as the reductant. Acridine orange was the selected target to eliminate with GO as the adsorbent. Under identical conditions, GO without the in situ reduction showed a maximum adsorption capacity of 1.4 g g<sup>-1</sup> while GO with the *in situ* reduction provided a maximum adsorption capacity of 3.3 g  $g^{-1}$ . Sodium hydrosulfite converted carbonyl groups on GO into hydroxyl groups which functioned as the key sites for the adsorption enhancement. In Chapter 4, an encapsulation approach was introduced, which enabled GO to be used as adsorbent insides of macro-sized beads. The beads were prepared by using alginate as the backbone polymers and calcium ion  $(Ca^{2+})$  or hydronium ion  $(H^{+})$  as the cross-linker. The adsorption capabilities of the GO contained alginate beads had been studied in terms of their kinetics and the isotherms based on their time and concentration dependencies with acridine orange as the typical pollutant species. The pseudo-first-order rate model nicely reproduced the time-dependent adsorption for the calcium crosslinked beads, and the pseudo-second-order rate model for the hydronium beads, while the Langmuir isotherm described well the influence in term of the pollutant loading. As inferred from the adsorption model assumptions, (1) their capacities were proportionally related to the available active sites exposed to the pollutant, and (2) the physiochemical sorption was likely to be the main mechanism. Interactions with the oxygencontained functional groups together with the sorption onto the basal planes were considered to be the key reasons for the GO contained beads to undergo the absorption. In Chapter 5, the overall achievements obtained in this study were summarized and the possibilities for practical environmental remediation applications were discussed.

In conclusion, as the adsorbent, graphene oxide, the two-dimensional, carbon based nanomaterial, showed multi-functionalities in the elimination of chemical pollutants. Highperformance water-decontamination systems were obtainable through either the direct utilization or the direct utilization of graphene oxide as the functioning elements. These new findings reported in this dissertation are beneficial to the field of environmental remediation.

## 学位論文審査の要旨

È	査	教	授	古	月	文	志	
副	査	教	授	田	中	俊	逸	
副	査	教	授	齌	藤		健	(大学院保健科学研究院)
副	査	助	教	藏	崎	正	明	

学位論文題名

Development of high-performance water-decontamination systems by using graphene oxide as the functioning element

(酸化グラフェンを機能場として用いた高性能水浄化システムの開発)

In this study, the candidate has established a high-performance water-decontamination system with graphene oxide (GO) being used as the functioning elements. GO is heavily oxygenated graphene bearing hydroxyl and epoxide functional groups on the basal planes and carbonyl and carboxyl groups at the edges. GO have attracted great attentions in recent years for a number of reasons: i) GO belongs to a class of truly sheet-shaped molecules; a single GO sheet has a length or breadth that is typically larger than micrometers while its thickness is only one or a few atoms thick; therefore, it is possible to cover or overlap chemical pollutants with an atom-thick sheet; ii) in comparison with carbon nanotubes, GO is highly soluble in both aqueous and organic media; therefore, it is easier to introduce GO into water and other matrixes with GO being ideally dispersed; iii) GO can be converted to graphene through chemical reductions or with heating; furthermore, GO is commonly produced by exfoliating graphite, an abundant material, through chemical and/or physical reactions; thus, GO has the advantages of low cost and plentiful supply of the starting material.

The candidate has firstly introduced a method for the massive production of GO with commercially available expanded graphite as starting materials. The typical intercalating agent (H<sub>2</sub>SO<sub>4</sub>) was found to be capable of penetrating into the expanded graphite; this has further expanded the internal distance between the basal planes and as a result, a foam-like intermediate was obtained. The foam-like intermediate was more easily oxidized in the reaction with KMnO<sub>4</sub> (the oxidant) to form GO. Fully exfoliated GO was obtained with the expanded graphite having the median diameter ~ 15  $\mu$ m as the precursors. This procedure was much safer and productive in scalable applications than the conventional Hummers methods.

The candidate has consequently established an *in situ* reduction approach for enhancing the GO adsorptive capability in the removal of organic dyes from contaminated water samples. GO was directly used as the adsorbent and its absorptive capability toward the organic dye was largely enhanced through its *in situ* reduction with sodium hydrosulfite as the reductant. Acridine orange was the selected target to eliminate with GO as the adsorbent. Under identical conditions, GO without the *in situ* reduction provided a maximum adsorption capacity of 1.4 g g<sup>-1</sup> while GO with the *in situ* reduction provided a maximum adsorption capacity of 3.3 g g<sup>-1</sup>. Sodium hydrosulfite converted carbonyl groups on GO into hydroxyl groups which functioned as the key sites in the adsorption enhancement.

The candidate has also created an encapsulation approach with which GO was able to use as adsorbent insides of macro-sized beads. Alginate was chosen as the backbone polymers and calcium ion  $(Ca^{2+})$  or hydronium ion  $(H^+)$  as the cross-linker; GO was encapsulated insides of the alginate-based beads through an one-step encapsulation process. Adsorptive capabilities of the GO contained alginate beads were studied with acridine orange as the typical pollutant chemicals. The pseudo-second-rate model fitted nicely the data on the time-dependent adsorption; while the Langmuir model was found to be applicable to specify the sorption isotherms. Interactions with the oxygen-contained functional groups on GO and that of the interactions with the GO basal planes were the key driving-forces considerably of the GO contained beads to undertake the absorption of the pollutant chemicals.

In conclusion, the candidate showed familiarity with, and critical understanding of the relevant literatures; the methods adopted were appropriate to the subject matter and properly applied; the research findings were suitable set out, accompanied by adequate exposition and discussion, and the quality of English and the general presentation were satisfactory. The recommendation made by the examination committee was that "the degree be awarded".