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Adsorption of Ca^{2+} on single layer graphene oxide

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ABSTRACT

Graphene oxide (GO) holds great promise for a broad array of applications in many fields, but also poses serious potential risks to human health and the environment. In this study, the adsorptive properties of GO toward Ca^{2+} and Na^+ were investigated using batch adsorption experiments, zeta potential measurements, and spectroscopic analysis. When pH increased from 4 to 9, Ca^{2+} adsorption by GO and the zeta potential of GO increased significantly. Raman spectra suggest that Ca^{2+} was strongly adsorbed on the GO *via* $–COOCa^+$ formation. On the other hand, Na^+ was adsorbed into the electrical diffuse layer as an inert counterion to increase the diffuse layer zeta potential. While the GO suspension became unstable with increasing pH from 4 to 10 in the presence of Ca^{2+}, it was more stable at higher pH in the NaCl solution. The findings of this research provide insights in the adsorption of Ca^{2+} on GO and fundamental basis for prediction of its effect on the colloidal stability of GO in the environment.

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Introduction

Nanomaterials have attracted great attention and research interest due to their large specific surface area and abundant active groups. Among these, graphene and its derivatives have been in the spotlight in recent years. Graphene is a two-dimensional nanomaterial with one to ten layers of sp^2-hybridized carbon atoms arranged in six-membered rings, that has attracted tremendous attention due to its high mechanical strength (125 GPa fracture strength and 1100 GPa Young's modulus) (Lee et al., 2008), large specific surface area (theoretical value of 2600 m^2/g) (Rao et al., 2009) and exceptionally high electronic and thermal conductivity (200,000 $cm^2/(V·sec)$) and approximately (5000 W/(m·K), respectively) (Balandin et al., 2008; Park and Ruoff, 2009) as well as many other remarkable properties. Graphene oxide (GO), as part of the graphene-based nanomaterials family (GNFs), has hexagonal carbon rings similar to those in graphene, but with many oxygen-containing functional groups, such as carboxyl (–COOH), hydroxyl (–OH), and epoxy (–O–) groups, at the edges and on the face of the GO nanosheets (Lerf et al., 1998; Lee et al., 2010), which can be differentially functionalized (Stankovich et al., 2006; Niyogi et al., 2006). The potential applications of GO and its functionalized derivatives include optoelectronics, biodevices, drug delivery systems and reinforced composites (Xu et al., 2009; Dreyer et al., 2010).

Although the applications of GO are exciting (Singh et al., 2011a), it may cause significant pathological effects for the

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environment and human health. In particular, GO nanoparticles can cause thrombus (Singh et al., 2011b), severe and persistent lung injury (Schinwald et al., 2012; Li et al., 2013) and damage to fetal growth, since their size allows them to cross the placenta (Arvidsson et al., 2013). Ecosystem equilibria could be seriously affected by the high antibacterial capacity and cytotoxicity of GO (Chen et al., 2012). The toxicity of GO to a series of common terrestrial plants (cabbage, tomato and red spinach) has also been reported (Zhao et al., 2014).

The effectiveness of GO has been demonstrated for removal of a wide range of environmental pollutants from wastewater. Several studies reported high adsorption capacity for GO toward different heavy metals such as Cu^{2+}, Cd^{2+}, Co^{2+}, $Ni^{2+}$and Pb^{2+} (Chandra et al., 2010; Li et al., 2011; Zhao et al., 2011a; Guo et al., 2012; Luo et al., 2012; Wang et al., 2013; Pei et al., 2013; Gu and Fein, 2015; Tan et al., 2015). The adsorption capacity was higher than for any other known material, which suggests promising prospects for applications in wastewater treatment and contaminant remediation (Yang et al., 2010; Zhao et al., 2011b; Chowdhury et al., 2013; Sitko et al., 2013). Since GO is highly hydrophilic and readily dispersed in water, studies have been conducted on the colloidal stability and mobility of GO nanoparticles in the aquatic environment, especially in the presence of electrolytes (Feriancikova and Xu, 2012; Chowdhury et al., 2014; Lanphere et al., 2014). Divalent and monovalent cations such as Ca^{2+} and Na^{+} are the most abundant cations, with a concentration range of about 1–135 mg/L (0.025–3.4 mmol/L) and 1–402 mg/L (0.043–17.5 mmol/L), in most freshwater (National Academy of Sciences, 1977; Hem, 1992; Lanphere et al., 2013). The results indicated that GO could be highly mobile in aquatic environments; however its mobility was significantly affected by the ionic strength (Stumm, 1992). The results obtained for divalent cation solutions indicated that Ca^{2+} can significantly influence the stability and mobility of GO in natural water. Although the effect of Ca^{2+} on the colloidal stability of GO has been generally attributed to electrostatic interaction, the nature of Ca^{2+} interactions with GO has not been studied.

In the present study, the mechanism of Ca^{2+} adsorption on GO was evaluated using adsorption tests and Raman spectroscopic analysis; results from zeta potential measurements also showed differences in the effect of Ca^{2+} adsorption on the zeta potential of the GO nanoparticles compared to Na^{+}.

1. Materials and methods

1.1. *Materials*

Single layer GO (SLGO) with purity >90%wt, XY dimensions (lateral) of 300–800 nm, thickness (Z dimension) of 0.7–1.2 nm and specific surface area (SSA) of 350–400 m^2/g was purchased from Cheap Tubes Inc. (Brattleboro, VT). The stock solution of GO was prepared by transferring 10 mg GO nanoparticles into 100 mL deionized (DI) water (nanopure water at >18.2 MΩ·cm at 25°C) and then dispersing the nanoparticles using a Sonic Dismembrator (Fisher Scientific, Model F550) at 25% power for 30 min. $MgCl_2$, NaCl, and $CaCl_2$ solutions, and 0.1 mol/L NaOH and HCl solutions used for pH adjustment, were prepared using ACS grade chemicals and DI water.

1.2. *Batch adsorption experiments*

A GO working solution was prepared by addition of the stock solution into DI water to reach a GO concentration of 20 mg/L. The working solution was dispersed with ultrasonication for 10 min before it was used in the experiments. Adsorption of Ca^{2+} and Na^{+} by GO nanoparticles was tested by mixing solutions containing 10 mg/L of GO and 1–4 mmol/L of Ca^{2+} or Na^{+} in 50 mL centrifuge tubes on a rotary mixer. After overnight mixing, the samples were centrifuged at 10,000 r/min for 30 min. The supernatant samples were collected and passed through a 0.22 μm syringe filter for analysis of soluble Ca^{2+} and Na^{+} concentrations using an inductively coupled plasma optical emission spectrometer (ICP–OES) (Varian Vista MPX). The amount of metal ions adsorbed on GO, q_e (mmol/g), was calculated from the difference between the initial concentration C_0 (mmol/L) in aqueous solution and the equilibrium concentration C_e (mmol/L) determined in solution after filtration: $q_e = (C_0 - C_e)V / m_{adsorbent}$, where V (L) is the volume of the suspension and $m_{adsorbent}$ (g) is the mass of GO.

1.3. *Raman spectroscopy analysis*

The Raman spectra were collected in high resolution mode with a dispersive Raman spectrometer (Thermo Nicolet Almega XR) equipped with a CCD detector, optical microscope, digital camera, and 780 nm laser line with a laser source power of 30 mW (50% power was applied in the analysis). The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. All the measurements were conducted in the backscattering geometry. A 10× microscope objective was used, providing a laser spot size of 3.1 μm. The data acquisition time was 3 sec per scan, and 100 scans were used for each spectrum collection.

1.4. *Effect of pH and cations on GO aggregation*

The NaCl and $CaCl_2$ solutions were added into the GO working solution to reach the desired salt concentrations. An initial concentration of 10 mg/L of GO was used for all tests. The solution pH was adjusted to desired values using NaOH and HCl solutions at 0.1 mol/L. After 15 min of mixing, 2.5 mL samples were taken for measurement of the zeta potential and the hydrodynamic diameter (Dh) using a Nano ZetaSizer ZEN3600 (Malvern Instrument, UK).

2. Results and discussion

2.1. *Adsorption of Ca^{2+} on GO*

Batch adsorption experiments were carried out in order to assess the adsorption behavior of GO for Ca^{2+}. Adsorption kinetic results in Appendix A Fig. S1 showed that Ca^{2+} was

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