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Colloidal properties and stability of aqueous suspensions of few-layer graphene: Importance of graphene concentration[☆]

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ABSTRACT

Understanding the colloidal stability of graphene is essential for predicting its transport and ecological risks in aquatic environments. We investigated the agglomeration of ¹⁴C-labeled few-layer graphene (FLG) at concentrations spanning nearly four orders of magnitude (2 µg/L to 10 mg/L) using dynamic light scattering and sedimentation measurements. FLG agglomerates formed rapidly in deionized water at concentrations >3 mg/L. From 1 mg/L to 3 mg/L, salt-induced agglomeration was decreased with dilution of FLG suspensions; the critical coagulation concentration of the more concentrated suspension (3 mg/L) was significantly lower than the dilute suspension (1 mg/L) in the presence of NaCl (1.6 mmol/L and 10 mmol/L, respectively). In contrast, FLG underwent slow agglomeration and settling at concentrations ≤0.1 mg/L in NaCl solutions and ambient waters with low ionic strength (<10 mmol/L). FLG nanoparticles with smaller lateral sizes (25 nm–75 nm) were shown to agglomerate more slowly than larger FLG, and these small FLG particles exhibited greater bioaccumulation in zebrafish embryo and stronger chorion penetration ability than larger FLG particles. These findings suggest that FLG at more environmentally relevant concentration is relatively stable and may have implications for exposure of small FLG to ecological receptors.

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1. Introduction

Graphene, a new carbon-based nanomaterial (CNM) that was first isolated by Novoselov et al., in 2004 (Novoselov et al., 2004), has attracted increasing attention because of its extraordinary properties and potential applications (Geim, 2009; Novoselov et al., 2012), such as in composites (Ramanathan et al., 2008; Stankovich et al., 2006), ultrasensitive sensors (Schedin et al., 2007), and transparent conductive films (Eda et al., 2008; Wang et al., 2008). Currently, graphene is rapidly being incorporated into a broad range of commercial products (Segal, 2009). The increasing production and use of graphene will inevitably lead to its release into the environment. Unfortunately, the environmental behaviors of graphene are still largely unknown. To date, the majority of studies have focused on the human health-related issues of graphene (Bussy et al., 2013; Duch et al., 2011; Schinwald et al., 2012; Seabra

et al., 2014; Yang et al., 2010, 2011; Zhang et al., 2010), with only a limited number of studies on potential ecological risks (Guo et al., 2013; Hu et al., 2014, 2015). The exposure of nanomaterials is directly determined by their transport and fate in the environment (Batley et al., 2012; Lowry et al., 2012; Maurer-Jones et al., 2013). Once released into aquatic systems, graphene is likely to interact with ubiquitous inorganic ions and natural organic matter (NOM). Changes in graphene size and shape resulting from agglomeration may subsequently alter its mobility as well as its reactivity and toxicity (e.g., to algal cells and wheat roots) (Hu et al., 2014, 2015). Therefore, knowledge of the agglomeration behavior of graphene in aquatic environments is essential for predicting its fate and potential for ecological exposure.

Agglomeration and stability of fullerene (nC₆₀) (Anderson and Barron, 2005; Bouchard et al., 2009; Chen and Elimelech, 2006, 2008, 2009), carbon nanotubes (CNT) (Sano et al., 2001; Smith et al., 2008, 2009), and graphene oxide (GO) (Chowdhury et al., 2013, 2015; Huang et al., 2016; Konkena and Vasudevan, 2012; Wu et al., 2013) have been extensively studied in the literature. These studies showed that the agglomeration of CNMs follows the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, and the CNM-

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specific properties have strong effects on the colloidal stability of CNMs. For example, the critical coagulation concentration (CCC) of cations was found to increase with the increasing surface oxygen contents of CNT and GO (Chowdhury et al., 2015; Smith et al., 2009; Yi and Chen, 2011). This suggests that pristine graphene with a hydrophobic lattice may undergo layer-to-layer agglomeration in water at low ionic strength (IS). As mass concentration affects particle number and the rate of collisions between colloids that have small Hamaker constants and low surface potentials (Hsu and Liu, 1998), salt-induced agglomeration is expected to be reduced at a low graphene concentration. However, no study has yet been conducted to quantitatively establish the agglomeration kinetics of graphene as a function of electrolyte concentration or to test the impact of mass concentration on its colloidal stability. In addition, agglomeration and settling of nanomaterials such as graphene during ecotoxicology experiments with pelagic organisms in the water column can cause increased heterogeneity in the exposure concentrations (Petersen et al., 2015). It is likely that graphene particles remain suspended for longer time periods in dilute suspensions than in more concentrated ones. The impact of the particle size of suspended CNMs on their stability has not been studied during most previous investigations. Moreover, nanomaterial size is one factor that may influence their potential ecotoxicological effects and thus additional research on this topic is important (Mu et al., 2012; Silva et al., 2014; Zhao and Wang, 2012).

The primary objective of this paper is to ascertain the impact of mass concentration on agglomeration and stability of ^{14}C -labeled graphene. The graphene utilized in this study was mainly comprised four graphene layers (Guo et al., 2013) and were defined as few-layer graphene (FLG) in our previous work (Feng et al., 2015; Lu et al., 2015; Mao et al., 2016a, 2016b). The agglomeration kinetics of FLG (0.1 mg/L to 10 mg/L) at varying IS were investigated by using a dynamic light scattering (DLS) method. To investigate the state of agglomeration of FLG at concentrations (2 $\mu\text{g/L}$ to 107 $\mu\text{g/L}$) that are below the detection limit of DLS and most other analytical techniques, sedimentation kinetics in simple electrolyte solutions and ambient water samples were determined via radioactivity measurements. While performing experiments using waters with defined yet varying compositions is necessary to yield a mechanistic understanding, it is critical to verify that those trends are still observed in water samples from natural and engineered environments because some factors such as the type of NOM vary widely among water sources and the NOM composition can impact the fate of environmental pollutants such as nanomaterials (Akkanen et al., 2001; Pakarinen et al., 2013). We also evaluated if FLG lateral size impacts their agglomeration rate, sedimentation rate, or biological uptake by zebrafish (*Denio rerio*) embryos.

2. Materials and methods

2.1. Graphene synthesis and characterization

Synthesis of ^{14}C -labeled FLG by graphitization and exfoliation of sandwich-like $\text{FePO}_4/\text{dodecylamine}$ hybrid nanosheets has been described in our previous study (Guo et al., 2013). Using X-ray photoelectron spectroscopy (XPS), the atomic ratio of C:O in the FLG was determined to be 89:6 (the remaining 5% is 1.4% of H and 3.6% of N) (Guo et al., 2013), and carbonyl (C=O), hydroxyl (C–OH), and carboxyl (COOH) functional groups were found on the FLG surface (Feng et al., 2015). Notably, the oxygen was introduced by the addition of ^{14}C -phenol during the FLG synthesis, not by oxidation. The specific radioactivity of FLG was determined to be (16.0 \pm 0.6) mCi/g ($n = 3$; uncertainties always indicate standard deviation values if not specified). A stock suspension of FLG (20 mg/L) was prepared following the procedures that are provided in the

Supporting Information (SI). Prolonged probe tip sonication (up to 60 h) was conducted to prepare a small FLG (S-FLG) stock suspension; the sonication procedure was the same as that used for the stock FLG except for the sonication duration. The stock suspensions of FLG and S-FLG (1 mL) were mixed with 3 mL of scintillation cocktail (Gold Star, Meridian), and radioactivities of the stocks were determined via liquid scintillation counting (LSC) (LS 6500, Beckman Coulter). A PHI 5000 Versa Probe XPS instrument with a monochromatic Al K α X-ray source was used to measure the elemental composition of FLG and S-FLG. To measure the size distribution of FLG and S-FLG, 3 μL of a 20 mg/L stock suspension was deposited on a mica plate, air dried, and then analyzed by an atomic force microscopy (AFM) (Bruker, U.S.A). Subsamples of the FLG and the S-FLG stock suspensions were centrifuged (49,000 g, 30 min); supernatants were then analyzed by LSC and a gas chromatography-mass spectrometry (GC-MS) to evaluate if carbon-14 byproducts formed during the sonication processes using methods previously described (Mao et al., 2016a). Analysis of the supernatants using LSC and GC-MS did not show a significant increase in the radioactivity or obvious chemical peaks in the GC-MS chromatogram, indicating that degradation products did not form during the sonication process.

2.2. Electrophoretic mobility measurements

The electrophoretic mobility (EPM) of FLG (1 mg/L to 10 mg/L) was measured at varying NaCl and NOM concentration at pH 7.0 and 25 $^\circ\text{C}$ using a disposable folded capillary cell (Nano ZS, Malvern). Because the calculation of zeta potential values from EPM measurements uses the Henry equation and the Smoluchowski approximation which assumes spherical particles, it is problematic to use this approach for non-spherical CNMs (Petersen and Henry, 2012); EPM values are reported instead. As described in the SI, Suwannee River NOM (SRNOM) (RO isolation, International Humic Substances Society) was used as a model NOM and a stock solution of SRNOM was prepared, which had a total organic carbon (TOC) content of 8.6 mg/L \pm 0.1 mg/L ($n = 3$). The background TOC content in the DI water was around 0.3 mg/L. For each solution condition, six EPM measurements were conducted for each of three samples.

2.3. Graphene agglomeration and sedimentation kinetics

DLS (Nano ZS, Malvern) was used to measure the intensity-averaged hydrodynamic diameter (D_h) of FLG as functions of time and NaCl concentration in the absence and presence of SRNOM. For each agglomeration experiment, equal volumes (0.5 mL) of the diluted FLG stock suspension and NaCl solution in the absence and presence of SRNOM were separately pipetted into a disposable polystyrene cuvette to yield a specific FLG, electrolyte and/or SRNOM concentration. The capped cuvette was then briefly vortexed, placed in the DLS instrument, and the measurements were started immediately. The scattered light intensity was detected by a photodetector at a scattering angle of 90 $^\circ$, and the D_h was recorded every 10 s by autocorrelation function until D_h reached 1.5-fold of the initial D_h or until 360 data points had been acquired (Chowdhury et al., 2013; Smith et al., 2008). All agglomeration experiments were conducted in triplicate at pH 7.0. Detailed equations and parameters for calculation attachment efficiency (α_a) and CCC values are provided in the SI. The FLG concentration in the DLS measurements was quantified by radioactivity measurements and ranged from 0.1 mg/L to 10 mg/L. However, FLG concentrations below 1 mg/L did not provide a sufficient signal for accurate DLS measurements and were not included in further analysis.

The long-term stability of FLG at low concentrations (2 $\mu\text{g/L}$ to 107 $\mu\text{g/L}$) were evaluated both in well-controlled simple electrolyte

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