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# Effect of water chemistry on the aggregation and photoluminescence behavior of carbon dots

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## ABSTRACT

Carbon dots are rapidly emerging carbon-based nanomaterials that, due to their growing applications, will inevitably find their way to natural waters; however, their environmental fate is mostly unknown. Carbon dots with different surface functionality were fabricated and characterized by TEM and FT-IR. Their surface charge, given by the zeta potential, and their hydrodynamic diameter in suspension were investigated under a variety of environmentally relevant conditions. The effect of ionic strength was studied in the presence of monovalent (NaCl) and divalent (CaCl<sub>2</sub>) cations, for pH levels from 3 to 11; humic acid was used as a model for dissolved natural organic matter. Total potential energies of interactions were modeled by classical DLVO theory. The experimental results showed that water chemistry altered the surface charge of the nanomaterials, but their hydrodynamic size could not be correlated to those changes. Evidence of specific interactions was found for the amino functionalized particles in most cases, as well as the plain carbon dots in the presence of Ca<sup>2+</sup> and humic acid. Nanoparticles remained largely stable in suspension, with some exception at the highest ionic strength considered. DLVO theory did not adequately capture the aggregation behavior of the system. Moreover, cation and/or humic acid adsorption negatively affected the emission intensity of the particles, suggesting limitations to their use in natural water sensing applications. The particular stability shown by the carbon dots results in exposure to organisms in the water column and the possibility of contamination transported to significant distances from their source.

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## Introduction

Carbon dots (CDs) constitute a class of quasi-spherical, photoluminescence (PL) carbon nanoparticles with sizes below 10 nm (Baker, and Baker, 2010). Their easy fabrication and presumably negligible environmental impact make them an attractive alternative to inorganic quantum dots (Li and Kaner, 2008; Rao et al., 2009). Early studies have shown that CDs are biocompatible and less cytotoxic than Cd-based quantum dots and may even inhibit cancer cells (Qu et al.,

2012; Song et al., 2013; Hsu et al., 2013). These fluorescent nanoparticles have been successfully utilized in biomedicine, optoelectronics, catalysis, and chemical sensors (Wang and Hu, 2014). Their application in the environmental field is particularly promising. Semiconductor quantum dots (SQDs) and graphene quantum dots (GQDs) can be distinguished within the large group of carbon-based nanoparticles since SQDs and GQDs are perfect spherical nanocrystals of metallic atoms and nanosheets of sp<sup>2</sup> carbons, respectively, while the other types of CDs have an undefined carbogenic structure,

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being in some situations a combination of crystalline structures resembling graphene layers combined with amorphous carbon. Carbon particles exhibiting a crystalline core based on a mixture of  $sp^2$  and  $sp^3$  carbons are termed carbon quantum dots (CQDs) while those composed of a mixture of primarily  $sp^3$  carbons in a disordered structure carbon nanodots (CNDs) (Cayuela et al., 2016).

The PL properties of CDs vary sensitively with size, and emissions are red-shifted with increasing size (Wang and Hu, 2014). At present, the PL mechanism of CDs is still under debate (Zhu et al., 2015), although different researchers have attributed their emission properties to quantum confinement effect (Li et al., 2010), surface states determined by hybridization of the carbon backbone and the connected chemical groups (Fang et al., 2011; Hsu et al., 2009), fluorophores with different degrees of p-conjugation (Mao et al., 2010; Bourlinos et al., 2012), and the recombination of electron-hole pairs localized within small  $sp^2$  carbon clusters embedded within a  $sp^3$  matrix (Srivastava and Gajbhiye, 2011). Furthermore, the PL can be tuned via surface modification or via electron/energy transfer, and numerous capping strategies have been reported (Wang and Hu, 2014).

CDs characteristics can be tuned by the choice of precursors during synthesis, surface passivation and functionalization. Two types of synthesis methods, top-down and bottom-up, have been reported (Esteves da Silva and Gonçalves, 2012). The top-down methods involve cutting carbon resources, most commonly using concentrated oxidizing acid ( $HNO_3$  or  $H_2SO_4/HNO_3$  mixture) (Tao et al., 2012). The bottom-up synthesis methods consist of thermal carbonization and acid dehydration of suitable molecular precursors (Liu et al., 2012); passivation and/or the functionalization may be required to create highly PL CDs with tunable fluorescent features (Cayuela et al., 2015). CDs possess numerous surface reactive groups, that offer the chance for surface modifications. Passivation can enhance the quantum yields (QYs) of the CDs, changing the PL emission and meeting the requirements of selected applications (Zhu et al., 2015). Different strategies have been used to functionalize CDs with different types of molecules; for instance, macromolecules, chelating ligands, specific oligonucleotides, and metal ion or metal-mediated DNA binding for heavy metal detection (Vázquez-González and Carrillo-Carrión, 2014; Cayuela et al., 2016). Acid oxidative treatment, typically using  $HNO_3$ , can introduce carbonyl functionalities at several carbon surfaces. These groups enhance the CDs water solubility, which is very important for biologically applications. Furthermore, the PL can be increased significantly by surface passivation agents, as for example, amino-terminated reagents (Baker, and Baker, 2010).

As interest for both fundamental research and applications has surged dramatically in the last few years, it is inevitable that CDs will find their way to natural water sources where, unlike the more well studied fullerenes and carbon nanotubes, their environmental impact and fate is mostly unknown. The presumed negligible environmental impact of CDs can only be confirmed if their behavior in natural systems is fully understood. However, the colloidal stability of CDs in environmentally relevant aqueous suspensions has not been investigated, and neither the effect of those conditions on their PL properties.

Due to their small size and large surface area, adsorption processes are expected to play a key role in determining the physicochemical properties of CDs (Chowdhury et al. 2013).

Adsorption may alter the surface characteristics of the nanoparticles so that they become dispersed and thus, mobile in aqueous media (Lanphere et al., 2013). Natural organic matter, e.g., humic acid (HA), and exopolymeric substances, e.g., proteins and polysaccharides, have been shown to adsorb onto carbon nanotubes and act as stabilization agents (Saleh et al., 2010); these macromolecules can potentially interact with CDs surfaces by  $\pi$ - $\pi$  bonding and hydrophobic effects, due to the presence of C=C double bonds as well as aromatic rings (Dimiev et al., 2013).

CDs are well known for their colloidal stability in water suspensions at low ionic strength (IS); their PL is stable under those conditions but generally expected to decline if aggregation occurs. Other matrix chemistry effects have been reported. For example, their fluorescence intensities were shown to be pH-dependent, decreasing with increasing pH (Jelinek, 2017). Furthermore, a study showed no significant change in fluorescence quenching of CDs by HA up to a concentration of 10 ppm (Cayuela et al., 2015), while another study reported that the quenched fluorescence intensity of surface functionalized QDs was linearly proportional to the concentration of  $Hg^{2+}$  under optimum conditions (Vázquez-González and Carrillo-Carrión, 2014).

In summary, there is extensive literature on inorganic nanoparticle stability in natural waters, as well as for some common carbon-based particles such as carbon nanotubes, fullerenes and a few studies on graphene oxides, but the aggregation and surface properties of CDs under environmental conditions have not been investigated. In view of the increasing amount of research devoted to CDs applications for sensing and imaging, an understanding of the colloidal stability is needed as a first step towards the prediction of environmental fate, transport and potential toxicity of these nanomaterials. It has been recognized that our knowledge on nanoparticle environmental behavior needs to be continuously revised and extended to account for new materials or novel commercial applications as they emerge, in order to accurately assess the associated risks (Troester et al., 2016).

The objective of this work is to investigate for the first time the colloidal stability of CDs, an emerging carbon nanomaterial, in natural water conditions (i.e., variable salinity, pH, dissolved organic matter) and the effect of the transformations they undergo under such circumstances on their fluorescence properties. Two types of CDs were considered: as obtained from thermal treatment of organic molecules, and surface functionalized, to represent differences in their surface chemistry. The particles were synthesized and characterized with respect to size and surface chemistry. Aggregation was investigated under environmental relevant conditions and DLVO theory was applied to the modeling of particle stability.

## 1. Materials and methods

### 1.1. Synthesis

Unfunctionalized or plain CDs were synthesized following a modification of a previously published method (Wang et al., 2011). A 70% (W/W) glycerol solution (Sigma, >99.5%) was mixed with a 20% (W/W) solution of  $NaH_2PO_4$  (Fisher Scientific) in a 10:1 volume ratio. The solution was heated for 20 min at 900 W

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