Humic acid disaggregation with/of gold nanoparticles: Effects of nanoparticle size and pH

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ABSTRACT

Humic acid (HA) polyelectrolytes are natural colloids whose chemistry features carboxylic, phenolic and even amine functionalities. Gold nanoparticles may interact with the acidic functionalities, leading to HA disaggregation. In the current study, the aggregation behavior and surface charge characteristics of HA and citrate-coated gold nanoparticles (CT-GNPs) having core sizes 10 and 50 nm were investigated at varying pH to determine the effect of nanoparticle size on disaggregation. Dynamic light scattering and zeta potential analyses are described. The significance of this research is that detector response in the field of new plasmon-enhanced spectroscopy (for monitoring of Hg^{2+} among other pollutants) may undergo fouling by the interactions of GNPs with natural organic matter, and fate and transformation of GNPs released into the environment will certainly be driven by those same interactions. Simultaneous studies of both GNP and HA states of aggregation are therefore vital.

HA formed supramicrometer aggregates (>1 μm) at 2 ppm DOC (dissolved organic carbon concentrations) when titrated from pH 12–1. In the presence of citrate-coated GNPs (11 ppm gold mass concentration) having 50 nm core size the HA disaggregated, potentially forming primary particles. The control GNPs-50 aggregated at low pH, but the mixture with HA facilitated disaggregation of GNPs-50 at lower pHs. The pI of this mixture shifted synergistically. This interesting shift may arise from localized charge at NP surface affecting apparent pKa, and was not evident for HA + GNPs-10 (10 nm core size). GNP size effects were observed. GNPs-10 appeared to disaggregate the HA only in the pH range 3–6, and CT-GNPs-10 aggregates were themselves unaffected by HA.

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1. Introduction

Gold nanoparticles (GNPs) are researched and used extensively for a variety of commercial applications including biomedical imaging, therapeutics, chemical sensing, catalysis, photonics and in semi-conductor manufacturing (Aitken et al., 2006; Eustis and El-Sayed, 2006; Murphy et al., 2008; Sardar et al., 2009). Of relevance to environmental monitoring, gold nanoparticles represent an emerging platform for development of new highly sensitive analytical methods for detection of chemical pollutants in the environment ranging from Hg^{2+} to Pb^{2+} to nitrates to pesticides. These colorimetric analyses rely on the state of gold nanoparticle aggregation. (The basis for detection may be plasmon resonance, surface enhanced Raman spectroscopy (SERS) and/or fluorescence reso-

nance energy transfer (FRET), as reviewed quite recently (Wei et al., 2015; Wang and Yu, 2013; Darbha et al., 2008; Saha et al., 2012; Thatai et al., 2016; Pradeep and Anshup, 2009). In a recent review, Liu et al. have very clearly pointed out that dozens of articles detail the performance of these field-type assays (based on GNPs) using pristine samples, yet real water samples will present interferences from the complex mixture and these should be studied (Liu et al., 2011). As the production of nanomaterials rises to several thousand tons per year (Pitkethly, 2004; Stretz et al., 2013), higher quantities of nanomaterial waste will also be released into the environment. The toxicity of GNPs in the environment is not yet well understood, but recent reports do indicate environmental toxicity associated with certain capping agents and with GNPs in which edges play a role in toxicity (Pradeep and Anshup, 2009; Li et al., 2014; Bozich et al., 2014; Tedesco et al., 2010). Fate and transformation will ultimately depend on the interactions between nanoparticles and surface-water borne NOM (Klaine et al., 2008; Fabrega et al., 2009; Nowack and Bucheli, 2007; Navarro et al., 2009). Therefore, the

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significance of the present research is to illuminate GNP colloidal behavior as a function of pH and nanoparticle size in an aqueous environment containing NOM. Several reports describe the aggregation behavior of metallic nanoparticles in the presence of varying pH, ionic strength and NOM (Domingos et al., 2009; Baalousha, 2009; Ghosh et al., 2008; El Badawy et al., 2010; Illes and Tombacz, 2006), but none have simultaneously described both humic acid (HA) and GNP aggregation (HA being one example of NOM). Loosli et al. have described the disaggregation of Suwanee River HA by TiO₂ nanoparticles (15 nm) (Loosli et al., 2014). However, literature on the effects of GNPs on HA aggregation is limited (Pallem et al., 2009; Esfahani et al., 2016b; Diegoli et al., 2008). The purpose of this study was to explore the fundamental relationship between pH and aggregation state for GNP/HA mixtures as a function of GNP diameter. To examine this relationship thoroughly, two aspects of the mixture behavior must be explored: under what conditions would GNPs aggregate in the mixture, and under what conditions would HAs aggregate in the mixture. The first perspective has implication for fate and transformation of GNPs in surface water, and the second perspective has implication for HA fouling of surface-attached GNPs used for water monitoring.

In a previous publication we described the interactions between GNP and HA as a function of the compatibilizer composition at pH 6.0–6.5 (Pallem et al., 2009). The current research broadens the fundamental understanding of colloidal behavior of this mixture under varying pH conditions. While the pH range explored was much wider than that found in surface waters, this type of study nevertheless will serve to illuminate more fully the mechanism by which the observed disaggregation of HA occurred. The state of aggregation was characterized using dynamic light scattering (DLS), and the surface charge properties were characterized using zeta potential measurements.

2. Materials and methods

2.1. Materials

HA (humic acid sodium salt, technical grade) was purchased from Sigma Aldrich (MO, USA). HPLC grade water was obtained from Fisher Scientific (NJ, USA). CT-GNPs having core sizes 10 and 50 nm were purchased from Ted Pella (CA, USA) in aqueous dispersions.

2.2. Methods

2.2.1. Preparation of humic acid solution

The HA stock solution was prepared by dissolving 7.6 mg of HA in 130 mL of HPLC grade water and stirring for 24 h in the dark. The dissolved organic carbon (DOC) concentration of the HA sample was measured on a Shimadzu TOC-VCPH (combustion catalytic oxidation PC-controlled high sensitivity model, Shimadzu Scientific Instruments, Columbia, MD, USA) analyzer after filtering through a 0.45 μm nylon fiber filter (GE Water & Process Technologies, MA, USA). The stock solution was diluted to 2 ppm with HPLC grade water.

2.2.2. Dynamic light scattering

Dynamic light scattering (DLS) size measurements of all samples were performed using a ZetaSizer Nano ZS (Malvern Instruments, Worcestershire, UK). A He-Ne laser beam having wavelength 633 nm with a scattering angle of 173° was employed. The intensity average (Z-average) hydrodynamic diameter (D_H) of the particles was calculated using the Stokes-Einstein equation and the measured diffusivities of the particles (Malvern Instruments Ltd, 2005). The controls for 2 ppm HA, CT-GNPs having core sizes 10 and 50 nm

(CT-GNPs-10, −50), and the samples consisting of 2 ppm HA + CT-GNPs were titrated in the pH range 12–1. The pH titrations were performed with CT-GNPs gold mass concentration equal to 11 mg/L. All titrations were performed in triplicate and the procedure followed by Ma and Bouchard (2009) and Bouchard et al. (2009) was used. One set of titrants including a concentrated acid, a concentrated base, and a dilute acid were chosen for adjusting the pH from the pairs of titrants involving 0.5, 0.75 M HCl; 0.1, 0.5 M NaOH; and 0.05, 0.1 M HCl. The titrants were degassed prior to autotitration and primed to exclude any bubbles in the transfer tubes. The pH probe was calibrated in the autotitrator at the beginning of each titration session and the sample loop was cleaned well with methanol and double deionized water (DDI) before and after each titration session. The particle sizes for controls and samples were determined using the ZetaSizer Nano ZS. The intensity average (Z-average) hydrodynamic diameter (D_H) for the controls comprised of 2 ppm HA, CT-GNPs and the mixture of HA + CT-GNPs were plotted for the measured pH range. The D_H of 2 ppm HA in the presence of CT-GNPs-50 having different gold mass concentrations was also measured to verify the effect of CT-GNPs concentration on the aggregation behavior of the mixture.

Z-average size was calculated using the formalism in equation

$$D_H = \frac{\sum\limits_x N_x D_x^3}{\sum\limits_x N_x D_x^2} \tag{1.1}$$

here, D_H is the Z-average hydrodynamic diameter of the particles, D_x is the diameter of an individual particle, N_x is the number of particles measured at a given diameter. Z-average hydrodynamic size is the harmonic mean of the particle size distribution. Moreover, the intensity based particle size distributions were converted to the volume based particle size distributions using the Mie theory for more accurate representation of relative proportion of multiple components in the sample based on their volume rather than based on their intensity (Anon, 2005).

2.2.3. Zeta potential

The zeta potential values for all samples were also measured in the pH range 12–1 on the same instrument, which used phase analysis light scattering (PALS) to measure the electrophoretic mobility of charged particles. The electrophoretic mobility was subsequently converted into zeta potential using the Smoluchowski equation (Malvern Instruments Ltd, 2005). To determine the influence of HA on the zeta potential of CT-GNPs with the two different core sizes, the zeta potential of mixtures of HA + CT-GNPs, and control CT-GNPs and 2 ppm HA were measured across the entire pH range, starting at pH = 6.1. The gold mass concentration of the CT-GNPs with the two different core sizes was approximately 11 ppm as estimated from the particle concentrations reported by the manufacturer. Instrument performance was verified using National Institute of Standards and Technology (NIST)-traceable latex microsphere and polystyrene microsphere standards.

3. Results and discussion

3.1. Dynamic light scattering size results

In the literature, intensity-based DLS data are more commonly reported than volume-based results. In our research, we have found that intensity-based and volume-based DLS spectra are each useful, but must be carefully interpreted. Because the intensity-based data are biased toward larger particles due to their ability to scatter light thousands of times more than smaller particles, the volume-based particle size distribution spectra provide a more realistic