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Core-size regulated aggregation/disaggregation of citrate-coated gold nanoparticles (5–50 nm) and dissolved organic matter: Extinction, emission, and scattering evidence

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ABSTRACT

Knowledge of the interactions between gold nanoparticles (GNPs) and dissolved organic matter (DOM) is significant in the development of detection devices for environmental sensing, studies of environmental fate and transport, and advances in antifouling water treatment membranes. The specific objective of this research was to spectroscopically investigate the fundamental interactions between citrate-stabilized gold nanoparticles (CT-GNPs) and DOM. Studies indicated that 30 and 50 nm diameter GNPs promoted disaggregation of the DOM. This result—disaggregation of an environmentally important polyelectrolyte—will be quite useful regarding antifouling properties in water treatment and water-based sensing applications. Furthermore, resonance Rayleigh scattering results showed significant enhancement in the UV range which can be useful to characterize DOM and can be exploited as an analytical tool to better sense and improve our comprehension of nanomaterial interactions with environmental systems. CT-GNPs having core size diameters of 5, 10, 30, and 50 nm were studied in the absence and presence of added DOM at 2 and 8 ppm at low ionic strength and near neutral pH (6.0–6.5) approximating surface water conditions. Interactions were monitored by cross-interpretation among ultraviolet (UV)-visible extinction spectroscopy, excitation-emission matrix (EEM) spectroscopy (emission and Rayleigh scattering), and dynamic light scattering (DLS). This comprehensive combination of spectroscopic analyses lends new insights into the antifouling behavior of GNPs. The CT-GNP-5 and -10 controls emitted light and aggregated. In contrast, the CT-GNP-30 and CT-GNP-50 controls scattered light intensely, but did not aggregate and did not emit light. The presence of any CT-GNP did not affect the extinction spectra of DOM, and the presence of DOM did not affect the extinction spectra of the CT-GNPs. The emission spectra (visible range) differed only slightly between calculated and actual mixtures of CT-GNP-5 or -10 with DOM, whereas emissions for mixtures of CT-GNP-30 or -50 with DOM were enhanced at the surface plasmon resonance (SPR) wavelength. The emission spectra (ultraviolet range) for protein-like constituents of DOM were quenched. Resonance Rayleigh scattering (RRS) was more intense for the CT-GNP-30 and -50 than for the CT-GNP-5 and -10 controls. Intensity-based DLS particle size distributions (PSDs) of DOM controls, CT-GNP-5 and -10 nm controls, and 5- and 10 nm GNP-DOM mixtures exhibited multimodal aggregation. Analyses of CT-GNP-5 and CT-GNP-10 nm mixtures with DOM indicated overcoating of DOM molecules occurred in close proximity (<10 nm) to GNPs, whereas similar overcoating was not supported for the CT-GNP-30 or -50 mixtures with DOM. These fundamental observations can be exploited to improve our comprehension of nanomaterial interactions with environmental systems.

1. Introduction

Enviro- and bio-sensing applications using plasmonic nanoparticles such as gold nanoparticles are rapidly expanding [1]. In the present research, gold nanoparticles having a citrate compatibilizer coating (CT-GNPs) and their interactions with dissolved organic matter (DOM) were investigated due to the possibility of DOM presenting an interference in a sensing application. In the environment, the surface-mediated interactions of engineered nanoparticles (ENPs) with DOM will depend on critical physicochemical properties of each—individually and in combination—and of the matrix [2,3]. Because nanoparticle size, in general, is known to affect cellular uptake, activity, and toxicity, the need also exists to understand the effects of core diameter size on the interaction of GNPs with DOM when found in surface waters.

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Most inquiries to date into ENP-DOM interactions, in general, and for CT-GNP-DOM interactions in particular [4–10] has focused on the effects of DOM on ENP stability, probably because most studies have been conducted on smaller core sized NPs (<20 nm). In this report, emphasis on the inverse perspective was also determined to be important, that is, the effects of GNPs on DOM stability were also of interest, particularly if the DOM might interfere with a sensing technique.

In related research, we investigated the core size differences in self-aggregation among 5–50 nm citrate-coated GNPs separately without added DOM [11] and the abiotic, reversible, self-assembly of DOM-DOM aggregates without added GNPs [12]. We also reported the influence of core size and solution pH [13] in determining GNP-DOM aggregation behavior. The present study provides new information concerning the transformations of GNP-DOM solutions as affected by GNP core diameter. Using extinction spectroscopy, excitation-emission matrix (EEM) spectroscopy (emission and Rayleigh scattering), and dynamic light scattering (DLS), the effects of CT-GNP core size on GNP-GNP, DOM-DOM, and GNP-DOM interactions at low ionic strength and near neutral pH (6.0–6.5) were examined to emulate surface water conditions.

This research identifies for the first time, the GNP core-size-dependent enhancement of surface plasmon resonance (SPR) and resonance Rayleigh scattering (RRS) phenomena in the presence of DOM that can be exploited to improve our comprehension of nanomaterial interactions with environmental systems.

2. Materials and Methods

CT-GNPs having core sizes 5, 10, 30, and 50 nm were purchased from Ted Pella, Inc. (Redding, CA, USA) in aqueous dispersions having trace amounts of sodium citrate (0.00001%), tannic acid (0.0000001%), and potassium carbonate. HPLC grade water was obtained from Fisher Scientific (Fisher Scientific, Fair Lawn, NJ, USA). The background dissolved organic carbon (DOC) of the HPLC grade water was 0.6 ppm. The dissolved organic matter (DOM) used in this research consisted of Aldrich humic acid (HA sodium salt, technical grade) purchased from Sigma Aldrich (Sigma-Aldrich, Saint Louis, MO, USA). The commercial product Aldrich humic acid is unfortunately misnamed—it does not consist of 100% HA. Any humic substance derived from sedimentation of ancient aquatic deposits can be expected to consist of both fulvic and humic acids, which is evident for Aldrich HA in the EEM spectra in Fig. S1 and as further discussed in Section 4.3.

2.1. Preparation of CT-GNP Solutions

Four different dispersions containing CT-GNPs with core sizes 5, 10, 30, and 50 nm were prepared. The mass concentration of gold in all dispersions containing different core sizes of nanoparticles in the range of 11.9–12.6 μg mL^{-1} were prepared by dilution with HPLC grade water from stock solutions of 54–63 μg mL^{-1} CT-GNPs obtained from the manufacturer [11].

2.2. Preparation of HA Solutions

The organic matter 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 after filtering through a 0.45 μm nylon fiber filter (GE Water & Process Technologies, Watertown, MA, USA). Total organic carbon (TOC) and DOC of the HA solution were measured by a Shimadzu TOC-VCPH (Shimadzu Scientific Instruments, Columbia, MD, USA) total organic carbon analyzer. Solutions of 2 and 8 ppm DOC of aqueous HA were prepared from the filtered stock solution as representative of typical humic substance concentrations in surface water.

2.3. Preparation of Mixtures of HA + CT-GNPs

For each of the HA concentrations (2 and 8 ppm), four different dispersions containing CT-GNPs with core sizes 5, 10, 30, and 50 nm (11.9–12.6 μg mL^{-1}) were prepared. The samples containing HA and CT-GNPs were allowed to equilibrate at room temperature for 4 h in glass vials. The pH of all samples was measured to be in the range of 6–6.5. No control of ionic strength was implemented other than the contributions of the HA and CT-GNPs themselves.

2.4. UV–Visible Extinction and Emission Measurements

All samples were subsequently analyzed for UV–visible extinction and emission. UV–visible extinction spectra were recorded from 200 to 800 nm using a UV–visible spectrophotometer (Varian Cary 3E, Agilent, Santa Clara, CA, USA) and a quartz cuvette having a 1 cm path length. Three-dimensional EEM spectra were generated by collecting emission (EM) spectra over a range of excitation (EX) wavelengths (200 to 800 nm in increments of 3 nm) and EM wavelengths (200 to 850 nm in increments of 2 nm). A Varian Cary Eclipse fluorescence spectrophotometer (VarianCary Eclipse, Agilent, Santa Clara, CA, USA) with a full spectrum xenon pulse single source lamp was employed. The EX and EM slit widths were set to 10 nm. Controls of HPLC grade water were checked regularly. The second order Rayleigh scattering of all samples was removed instrumentally. The spectra of all samples and controls were corrected (using a MATLAB program developed in house) for primary and secondary inner filtering effects according to Tucker et al. [14]. Further, the spectrum of HPLC grade water was subtracted from the EEM spectra of samples and controls to correct for the Raman spectrum of water and the first order Rayleigh scattering spectrum of water. The corrected 2D emission spectra at constant EX wavelength $\lambda_{ex} = 221$ nm and the corrected Rayleigh scattering spectra (EX = EM) were extracted from the EEM data and plotted for all samples.

2.5. Dynamic Light Scattering (DLS) and Zeta Potential

All samples were analyzed for size changes using DLS data collected on a Malvern ZetaSizer Nano ZS (Malvern Instruments Ltd., Malvern, United Kingdom). For the light scattering measurements, a He—Ne laser beam having wavelength 633 nm with a scattering angle of 173 degrees was used to take advantage of the backscattering mode. Intensity- and volume-based size distributions were measured. The same instrument was used to determine the zeta potential as previously reported [13].

3. Theory

Particles that scatter but do not absorb light are referred to as pure light scatterers, and those that both absorb and scatter light are called light-absorbing particles. The combined processes of absorbing and scattering light are referred to as light extinction [15–17] defined as:

$$C_{ext} = C_{sca} + C_{abs} \tag{1}$$

where C_{sca} and C_{abs} represent the hypothetical cross-sectional area surrounding a particle such that every photon of light entering that area is scattered or absorbed, respectively. Without the absorbance of light, there can be no emission. Thus the extinction, scattering, and emission spectra are interdependent. Therefore, extinction and emission behaviors must be considered holistically. The extinction, scattering, and emission of plasmonic particles were discussed previously [11].

4. Results

UV–visible extinction spectroscopy, EEM spectroscopy (emission and Rayleigh scattering), and DLS were explored to investigate the