Aggregation kinetics of nanosilver in different water conditions

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Received 24 February 2012
Accepted for publication 28 April 2012
Published 12 June 2012
Online at stacks.iop.org/ANSN/3/035006

Abstract

In this study the effect of different water conditions on the aggregation kinetics of nanosilver (nAg) is evaluated. The obtained results show that the aggregation rate of nAg increases with increasing electrolyte concentration. Divalent cation (Ca²⁺) can more effectively induce aggregation than monovalent cation (Na⁺). Critical coagulation concentration of nAg in NaCl solution is about 40 times higher than that in CaCl₂ solution. This study also indicates that aggregation rate of nAg in water condition containing high Ca²⁺ concentration in presence of humic acid is higher than that without humic acid due to the bridging effect of humic acid–Ca²⁺ complex. Finally, aggregation rate of nAg in seawater is higher than that in lake water.

Keywords: nanosilver, different water conditions, aggregation kinetics, critical coagulation concentration

Classification number: 4.02

1. Introduction

Nanotechnology is a rapidly growing field of global interest. With its fast development, a wide range of nanotechnology-based products are used in many industries such as clothing, cosmetics, water filtration and biomedicine [1–5]. Within all the nanomaterials, nanosilver-containing products are the most abundant due to its excellent antimicrobial activity [1–3]. Because of its wide applications, accidental or deliberate release of nanosilver (nAg) into the aquatic environment is inevitable and may cause environmental issues as its antimicrobial activity could threaten the natural microbial communities [5, 6].

The environmental effect of nAg is mainly dependent on its aggregation behavior in natural water bodies [5]. Recent investigations on the toxicity of nAg point out that large nAg aggregates could be less toxic than small nAg particles as large aggregates settle more easily [5, 7]. Therefore, the chances of contact between nAg aggregates and bacteria could be smaller in comparison with well-dispersed nAg [5, 7].

Recent studies on aggregation behaviors of nanomaterials in different water conditions indicate that divalent cations can increase aggregation rate of different nanoparticles including boron, silicon, iron oxides and silver nanoparticles [6, 8–10]. However, to the author’s knowledge, data on the aggregation kinetics of nAg with capping agent and its aggregation behavior in natural waters is still scarce.

In this study, nAg capped with polyvinyl pyrrolidone (PVP) was synthesized by Tollens method. PVP was chosen as a capping agent because PVP is environmentally friendly and is one of the most frequently used capping agents by other researchers. The morphology of nAg was characterized using transmission electron microscopy (TEM). Aggregation kinetics of nAg in different water conditions were measured using time-resolved dynamic light scattering technique. The result of this study may be referenced for risk assessment of the release of nAg into natural aquatic systems.

2. Experimental

2.1. Water sample preparation

NaCl and CaCl₂ solutions were prepared by adjusting the electrolyte concentrations from 10 to 4500 mM. Humic acid (HA) was added to the electrolyte solutions to mimic natural organic matter (NOM). Natural water samples were collected...
from lake water and seawater. The collected water samples were first filtered (0.45 µm) and then autoclaved to remove microorganisms in the water. HA and NOM contents in the synthetic and natural water were measured as total organic carbon (TOC) using a TOC analyzer (Apollo 9000, Tekmar Dohman). Major ions in natural water samples were analyzed using ion chromatography (IC) (DX-120, Dionex).

2.2. Preparation and characterization of silver nanoparticles

Nanogold stabilized with PVP (average molecular weight: 29 000, Sigma-Aldrich) was prepared via a Tollens method. The initial concentrations of the reactants were $1 \times 10^{-3}$ mol l$^{-1}$ and $1 \times 10^{-2}$ mol l$^{-1}$ for AgNO$_3$ and maltose, respectively [3]. The concentration of ammonia was $5 \times 10^{-3}$ mol l$^{-1}$ and PVP concentration was 0.35 w/w%. pH value of the reaction system was adjusted to 11.5 using NaOH. Nanogold solutions were cleaned with deionized (DI) water using a 10 kDa nominal molecular weight cut-off (NMWCO) ultrafiltration membrane (Millipore, Model 8200; NMWCO: 10 000). UV-Vis absorption spectrum was recorded using a spectrophotometer (Thermo Unicam). Concentration of nAg ($C_{\text{nAg}}$) was measured by ICP-MS (X series, Thermo Elemental). Cryo-transmission electron microscope (Cryo-TEM) was used to observe the morphology. $\xi$-potential of nAg was determined using a Zetasizer (Nano ZS, ZEN 3600, Malvern) at 25°C.

3. Results and discussion

3.1. Characterization of nanogold

Nanogold exhibits irregular round shape (figure 1). Figure 1(b) shows that the surface plasmon resonance band of nAg locates approximately at 400 nm. This observation agrees with previous studies [3, 4, 11].

3.2. Aggregation kinetics of nAg in different water conditions

Figure 2 shows that the aggregation rate of nAg in electrolyte solutions increases with increasing cationic concentrations. As the $\xi$-potential of nAg in DI water is negative ($-20.8$ mV), the increasing concentration of cations elevates the screening of surface charges of nAg. Therefore, the aggregation rates are increased due to the reduction of electric repulsion force and energy barrier between nanoparticles [12].

Figure 3 shows the attachment efficiency of nAg in different water conditions. As mentioned in the experimental section, at high electrolyte concentrations the surface charges of nAg are completely eliminated and the nanoparticles are thus in the fast aggregation (diffusion-limited) regime where $\alpha = 1$. In the diffusion-limited regime, the aggregation rates reached a maximum and are independent of the electrolyte concentration. When $\alpha < 1$ (figure 2), a reaction-limited regime occurs when the aggregation rates increase with increasing cationic concentrations due to the decreasing electrical repulsion force. Critical coagulation concentration (CCC) is used to define the minimum electrolyte concentration to reach the diffusion-limited
regimes. It is determined by calculating the intersection of the extrapolations through both diffusion-limited and reaction-limited regimes. Figure 3 and table 1 show that the CCC values of nAg in CaCl\(_2\) and NaCl solutions are in the following order: CCC(CaCl\(_2\)) < CCC(NaCl). The obtained result is consistent with the Schulze–Hardy rule, which indicates that the CCC of nanoparticle suspension is sensitive to the valence of the counter-ions. Consequently, divalent cation (Ca\(^{2+}\)) has a stronger effect to destabilize nano-suspension compared to monovalent cation (Na\(^{+}\)). Similarly, other studies indicate that CCC of Na\(^{+}\) is higher than that of Ca\(^{2+}\) for different nanomaterials [13–18]. Figure 3 and table 1 also show that humic acid (HA) could elevate CCC as HA macromolecules could be adsorbed onto nanoparticle surface and create steric repulsion forces preventing nAg from aggregating. This observation is also consistent with previous published data [13–18].

### 3.3. Effect of humic acid on the aggregation kinetics of nAg in the presence of Ca\(^{2+}\)

The aggregation behavior of nAg could be enhanced in water containing high Ca\(^{2+}\) with high concentration (figure 4). Figure 3 also shows that the attachment efficiency keeps increasing even to \(\alpha > 1\). Possible explanations have been raised by Chen and Elimelech [9], indicating that HA macromolecules and Ca\(^{2+}\) could form complex and the complex could cause bridging effect between nanoparticles.

### 3.4. Aggregation behavior of nAg in natural water conditions

A higher aggregation rate of nAg in seawater in comparison with that in lake water is observed (figure 5), which is likely because seawater contains divalent and monovalent cations at higher concentrations compared to lake water (table 2). In addition, concentration of natural organic matter (NOM) measured as TOC in lake water is much higher than in seawater (table 2), which could contribute a greater stabilizing effect according to the above-mentioned discussion. The result suggests that nAg in seawater could settle fast due to the

![Figure 2. Aggregation kinetics of nAg in CaCl\(_2\) and NaCl solutions (C\(_{nAg}\) = 10 mg l\(^{-1}\)).](image)

![Figure 3. Attachment efficiency of nAg in CaCl\(_2\) and NaCl solution in the presence and absence of humic acid (C\(_{nAg}\) = 10 mg l\(^{-1}\), C\(_{HA}\) = 1 mg l\(^{-1}\)).](image)

![Figure 4. Enhanced aggregation of nAg at high Ca\(^{2+}\) concentration of 200 mM (C\(_{nAg}\) = 10 mg l\(^{-1}\), C\(_{HA}\) = 1 mg l\(^{-1}\)).](image)

### Table 1. CCC of CaCl\(_2\) and NaCl in nAg suspension (C\(_{nAg}\) = 10 mg l\(^{-1}\), C\(_{HA}\) = 1 mg l\(^{-1}\)).

|           | CCC (without HA)/mM | CCC (with HA)/mM |
|-----------|---------------------|------------------|
| CaCl\(_2\) | 57.2                | 166.8            |
| NaCl      | 2322.5              | 4439.5           |

HA, humic acid.
Table 2. Water chemistries of the collected water samples.

| Water sample | TOC/(mg·l⁻¹) | Na⁺ | Mg²⁺ | Ca²⁺ | Cl⁻ |
|--------------|--------------|-----|------|------|-----|
| Lake water   | 7.60         | 0.90| 0.13 | 0.13 | 0.96|
| Seawater     | 1.00         | 573.90 | 45.83 | 7.50 | 538.03|

TOC, total organic carbon.

Figure 5. Aggregation kinetics of nAg in seawater and lake water ($C_{nAg} = 10$ mg l⁻¹).

formation of large aggregates. In contrast, nAg in lake water could settle slower because of its better dispersion.

4. Conclusions

In this study the aggregation kinetics of nAg was investigated. It can be concluded that: (i) aggregation rate of nAg increases with increasing concentration of cations; (ii) CCC of nAg in different water conditions follows the order: CCC(Na⁺) > CCC(Ca²⁺), CCC (with HA) > CCC (without HA); (iii) aggregation rate of nAg in water conditions containing high Ca²⁺ concentration in presence of HA is higher than that without HA due to the bridging effect of HA-Ca²⁺ complex and (iv) aggregation rate of nAg in seawater is higher than that in lake water.

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