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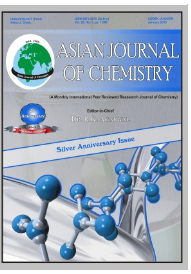

# Aggregation and Dissolution Kinetics of Nanosilver in Seawater

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This study shows the synthesis of citrate capped nanosilver using Tollens method and the effect of seawater on its physcochemical properties. The results show that the average particle size of nanosilver is 66 nm in deionized water condition and 1800 nm in seawater condition. ξ-Potentials of nanosilver in deionized water is more negative than that in seawater. This study also indicates that aggregation rate of nanosilver in seawater is higher than that in deionized water. At last, more dissolution of nanosilver was measured in deionized water than that in seawater.

**Key Words: Nanosilver, ξ-Potential, Aggregation rate, Dissolution.**

## INTRODUCTION

Nanosilver (nAg) has been widely investigated due to its potential applications in catalytic and antimicrobial properties[1-8]. In 2010, commercial products containing nanosilver are among the mostly used nanomaterials around the world.

Previous studies have demonstrated the excellent antimicrobial activity of nanosilver. The proposed mechanisms of the antimicrobial activity include the lysis of cells caused by the released silver ions and the damage of cell walls by pitting of nanosilver[3-5]. Recent investigations have reported that nanosilver could be toxic to microorganisms in different water conditions and attributed the toxicity to different physicochemical parameters including particle size, surface charge and release of silver ions[3,4].

As the release of nanosilver into seawater may pose potential threat to the local microorganisms due to its antimicrobial activity, it is important to study the fate of nanosilver in seawater. Previous studies have investigated the above mentioned physicochemical parameters in deionized water or other synthetic water conditions[3,6,7]. However, studies on the fate of nanosilver in seawater are still scarce.

In this study, nanosilver was synthesized by Tollens method. The morphology of nanosilver was characterized using transmission electron microscopy. Average hydrodynamic size was measured using dynamic light scattering technique. Dissolution of nanosilver was measured as total silver by Inductively coupled plasma mass spectrometry (ICP-MS). Aggregation kinetics in original and diluted seawater was measured using a time-resolved dynamic light scattering to investigate the effect of different ionic strength on nanosilver aggregation. This study may be served as important reference on the risk assessment of release of nanosilver into oceans.

## EXPERIMENTAL

**Synthesis of nanosilver:** Nanosilver was synthesized using Tollens method. The concentrations of the reactants were $1 \times 10^{-3}$ mol/L, $1 \times 10^{-2}$ mol/L and $5 \times 10^{-3}$ for $AgNO_3$, maltose and ammonia, respectively[9]. pH Value of the reaction system was adjusted to 11.5 using NaOH. Then, sodium citrate was added as capping agent. Sodium citrate was used in this study because it is environmentally friendly and is frequently used by other researchers. The obtained nanosilver solutions were cleaned with deionized 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). Transmission electron microscope was used to characterize the shape of nanosilver. ξ-potential of nanosilver was determined using a Zetasizer (Nano ZS, ZEN 3600, Malvern) at 25 ºC. Concentration of nanosilver was measured by ICP-MS (X series, Thermo Elemental).

**Natural water preparation:** Natural seawater was collected in Atlantic Ocean. The seawater samples was filtered via a 0.45 µm filter paper and then sterilized by boiling to remove any microbial contaminations. Natural organic matter content in the seawater was measured as total organic carbon using a total organic carbon analyzer (Apollo 9000, Tekmar Dohman).

Major ions in seawater sample were analyzed using ion chromatography (IC) (DX-120, Dionex) (Table-1). The ionic strength of the original seawater is 662 mM. Seawater with 2 and 10 times dilutions were used to study the effect of different ionic strength on the aggregation kinetics of nanosilver.

**Dissolution and aggregation rate of nanosilver:** Dissolution of nanosilver in deionized water and seawater was measured as total silver using ICP-MS (X series, thermo elemental) during 5 days. Aggregation rate were acquired as rate of change of hydrodynamic diameter *versus* time. In brief, nanosilver was injected into glass tubes containing original and diluted seawater solutions. The mixture was introduced into a cuvette, hand-shaken and transferred into the zetasizer (Nano ZS, ZEN 3600, Malvern). Measurements were started immediately and the changes in diameter of nanosilver were recorded over 500 s at 25 ºC.

TABLE-1
WATER CHEMISTRIES OF THE COLLECTED WATER SAMPLES

| Water sample | TOC (mg L$^{-1}$) | Major ions (mg L$^{-1}$) | | | |
|---|---|---|---|---|---|
| | | Na$^+$ | Mg$^{2+}$ | Ca$^{2+}$ | Cl$^-$ |
| Seawater | 0.2 | 14420 | 1200 | 462 | 20400 |

Total organic carbon (TOC)

## RESULTS AND DISCUSSION

**Characterization of fabricated nanosilver:** The surface plasmon resonance band of nanosilver locates approximately at 400 nm (Fig. 1a). This observation agrees with previous studies[8,9]. Fig. 1(b) shows that the shape of nanosilver is irregularly spherical. The particle size distribution of nanosilver is recorded by dynamic light scattering (Fig. 1c). The average particle size obtained is 66.04 nm.

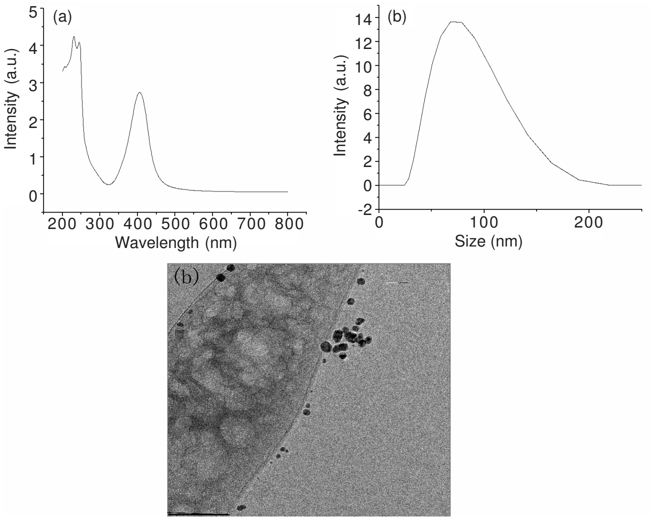

Fig. 1. (a) UV-VIS spectra (b) TEM image (black line = 200 nm) and (c) particle size distribution of nanosilver

**Aggregation kinetics of nanosilver:** To simulate the potential fate of nanosilver in seawater, aggregation kinetics of nanosilver was recorded. Deionized water and diluted seawater was used to measure the effect of ionic strength on the aggregation kinetics. As shown in Fig. 2, increasing ionic strength elevates the aggregation rate. Li *et al.*[17] indicated that aggregation rate of nanosilver without capping agent in both monovalent and divalent electrolyte solutions increased with increasing ionic strength[6]. Similarly, Huynh and Chen. reported a similar behaviour of nanosilver coated with sodium citrate and polyvinyl pyrrolidone[7]. In addition to nanosilver, researchers also found that aggregation kinetics of boron, fullerene, iron oxides and silicon nanoparticles follow similar pattern in electrolyte solutions[10-18]. These consistent observations agree with Shulze-Hardy rule, which indicates that the stability of a nanosuspension highly depends on the valence of its counter-ion[3]. In present case, the counter-ions are the cations present in seawater since ξ-potential of nanosilver is negative (Table-2). The cations present in seawater can eliminate the negative surface charges of nanosilver and reduces the electric repulsion force and energy barrier between nanoparticles, which enhances the aggregation of nanosilver[6,7]. As ξ-potential is related to the stability of a nano-suspension (higher absolute ξ-potential values indicate better stability), Table-2 shows that stability of nanosilver decreases with increasing ionic strength. ξ-Potential of nanosilver in deionized water is about 43 times higher than that in pure seawater. Fig. 3 shows the particle size of nanosilver after 2 h storage time. The recorded particle size is consistent with the aggregation kinetics. Similarly, Gao *et al.* reported a much larger size of nanosilver in seawater (>1000 nm) than that in deionized water (<100 nm)[4].

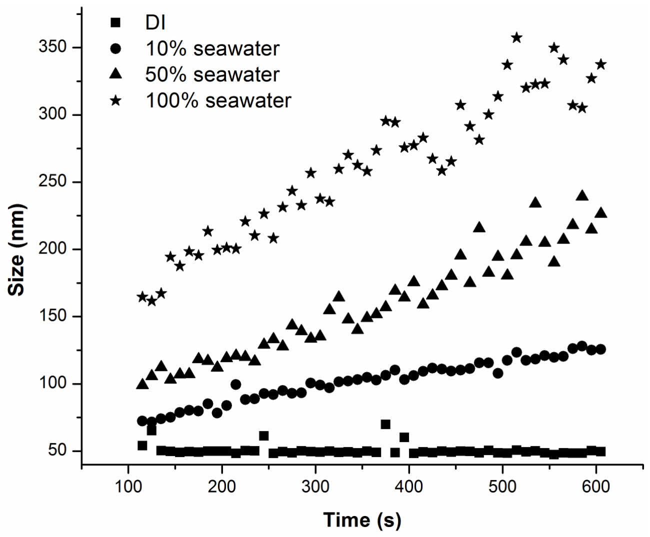

Fig. 2. Aggregation kinetics of nanosilver in original and diluted seawater samples (water compositions include pure deionized water (DI); 10 % seawater and 90 % deionized water (10 % seawater); 50 % seawater and 50 % deionized water (50 % seawater); original seawater sample (100 % seawater). Original nanosilver concentration: 5 mg × L$^{-1}$)

TABLE-2
ξ-POTENTIAL OF NANOSILVER IN DEIONIZED WATER AND SEAWATER SAMPLE

| | ξ-Potential (mV) |
|---|---|
| Deionized water | -25.6 |
| 10 % seawater | -20.6 |
| 50 % seawater | -7.2 |
| 100 % seawater | -0.6 |

**Ion release of nanosilver in seawater:** Fig. 4 shows the ion release kinetics of nanosilver in deionized water and seawater at 25 ºC during 5 days. The mechanism of ion release from nanosilver is associated with the redox reaction happens on its surface:

$$2Ag+\frac{1}{2}O_2 \rightarrow Ag_2O(s) \tag{1}$$

$$Ag_2O(s) + H_2O \rightarrow 2Ag^+ + 2OH^- \tag{2}$$

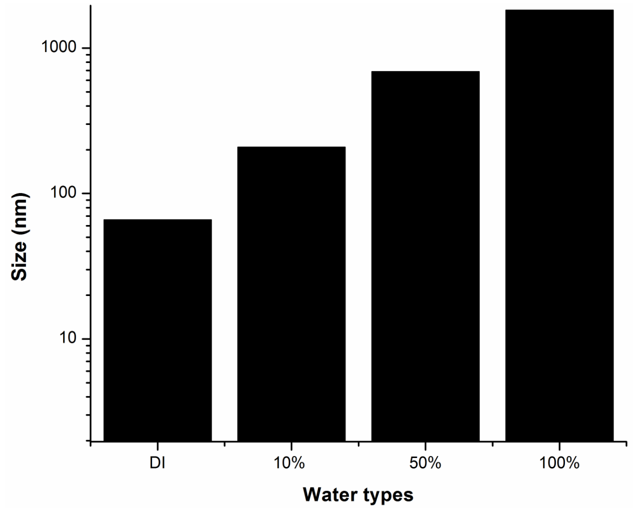

Fig. 3. Size of nanosilver in original and diluted seawater samples (water compositions include pure deionized water (DI); 10 % seawater and 90 % deionized water (10 % seawater); 50 % seawater and 50 % deionized water (50 % seawater); original seawater sample (100 % seawater). Original nanosilver concentration: 5 mg × $L^{-1}$)

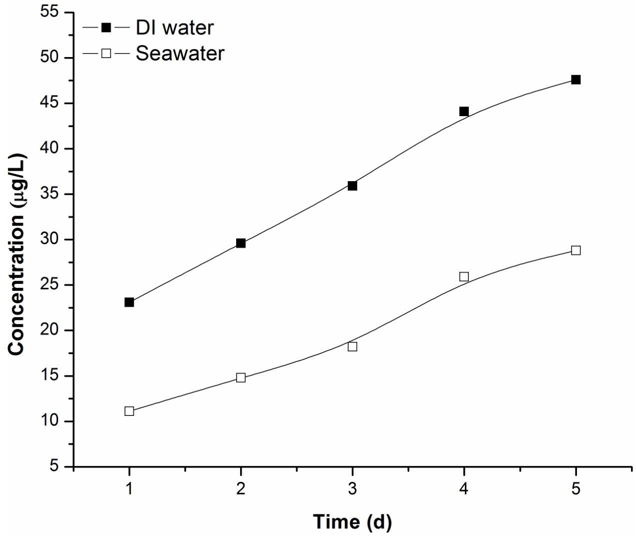

Fig. 4. Dissolution of nanosilver in deionized water and seawater (original nanosilver concentration: 5 mg/L)

During the first 3 days, an initial rapid increase in $Ag^+$ concentration is observed in both deionized water and seawater conditions. However, the final concentration of $Ag^+$ in deionized water is more than twice that in seawater. The difference is likely due to the high ionic strength leading to nanosilver aggregation[8]. In addition, the natural organic matter in seawater may coat on the surface of nanoparticles and prevent their dissolution[4,8]. Similarly, previous studies also reported higher silver ion concentration in deionized water than that in seawater[4,8].

## Conclusion

In this study, nanosilver was synthesized using Tollens method. The obtained nanosilver was characterized by UV-VIS spectrometry, TEM and dynamic light scattering. Aggregation kinetics of nanosilver was measured using a time-resolved dynamic light scattering. The result indicates that aggregation rate increases with increasing ionic strength. Stability of nanosilver in seawater sample was measured using zetasizer. The obtained result shows that the absolute values of ξ-potential decreases with increasing ionic strength. Dissolution of nanosilver in seawater is about half of that in deionized water, which is attributed to the high ionic strength and natural organic matter content in seawater.

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