# Aggregation kinetics of citrate coated nanosilver in seawater

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## Abstract

This study shows the synthesis of citrate capped nanosilver using Tollens method and the effect of seawater on its physicochemical properties. The obtained results show that the average particle size of nAg is 66 nm in DI water condition and 1800 nm in seawater condition. $\xi$-potentials of nAg in DI water is more negative than that in seawater. This study also indicates that aggregation rate of nAg in seawater is higher than that in DI water.

*Keywords:* nanosilver, Tollens' method, seawater, physicochemical properties.

## Introduction

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

Previous studies have demonstrated the excellent antimicrobial activity of nAg. 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 nAg particles [3-5]. Recent investigations have reported that nAg 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 ion [3,4].

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

In this study, nAg was synthesized by Tollens method. The morphology of nAg was characterized using transmission electron microscopy (TEM). Average hydrodynamic size was measured using dynamic light scattering (DLS) technique. 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 nAg aggregation. Aggregation of nAg directly links to the toxicity of nAg. This study may be served as important reference on the risk assessment of release of nAg into oceans.

## 2. Materials and methods

### 2.1. nAg synthesis

nAg was synthesized using Tollens method. Tollens' method reduces silver ions to elemental silver using tollens' reagents such as saccharides. The concentrations of the reactants were $1 \times 10^{-3}$ M, $1 \times 10^{-2}$ M and $5 \times 10^{-3}$ M 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 nAg 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). Transmission electron microscope (TEM) was used to characterize the shape of nAg. $\xi$-potential of nAg was determined using a Zetasizer (Nano ZS, ZEN 3600, Malvern) at 25 $^0$C. Concentration of nAg was measured by ICP-MS (X series, Thermo Elemental).

*2.2 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 (NOM) content in the seawater was measured as total organic carbon (TOC) using a TOC 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 nAg.

**Table 1** Water chemistries of the collected water samples

| Water sample | TOC/(mg/L) | Major ions/(mg/L) | | | |
|---|---|---|---|---|---|
| | | $Na^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Cl^-$ |
| Seawater | 0.2 | 12420 | 1200 | 400 | 19400 |

TOC: Total organic carbon

*2.3 Aggregation rate of nanosilver*

Aggregation rate were acquired as rate of change of hydrodynamic diameter versus time. In brief, nAg 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 nAg were recorded over 500 s at 25 $^0$C.

## 3. Results and discussion
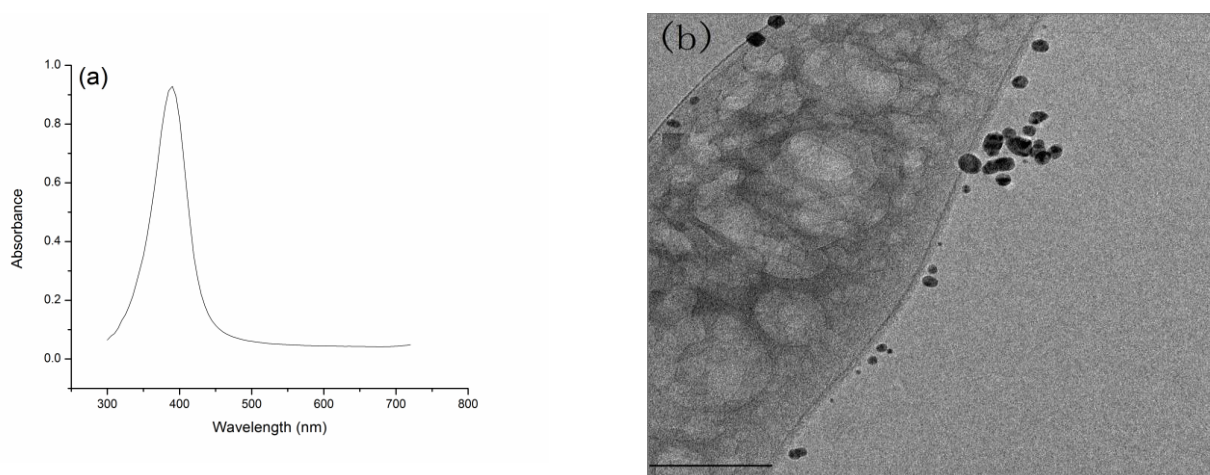


**Figure 1.** UV-vis spectrum (a) and TEM image (b) of nAg

Fig. 1 shows the UV-Vis spectrum and TEM image of the obtained nAg. The characteristic peak in the UV-Vis spectrum in Fig. 1(a) agrees well with previous published data [1]. TEM image presented in Fig. 1(b) shows that the nanoparticles exhibited near spherical shape.

Aggregation kinetics of nAg can elucidate the physicochemical properties of nAg, which is closely related to the ecotoxicity of nAg. To simulate the potential fate of nAg in seawater, aggregation kinetics of nAg was recorded. DI water and diluted seawater was used to measure the effect of ionic strength on the aggregation kinetics. As shown in Fig. 2 and Fig. 3, increasing ionic strength elevates the aggregation rate and particle size. Li et al. (2010) 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 (2011) reported a similar behavior of nanosilver coated with sodium citrate and polyvinyl pyrrolidone (PVP) [7]. In addition to nAg, researchers also found that aggregation kinetics of boron, fullerene, iron oxides and silicon nanoparticles follow similar pattern in electrolyte solutions [10-20]. These consistent observations agree with Shulze-Hardy rule, which indicates that the stability of a nano-suspension highly depends on the valence of its counter-ion [3].
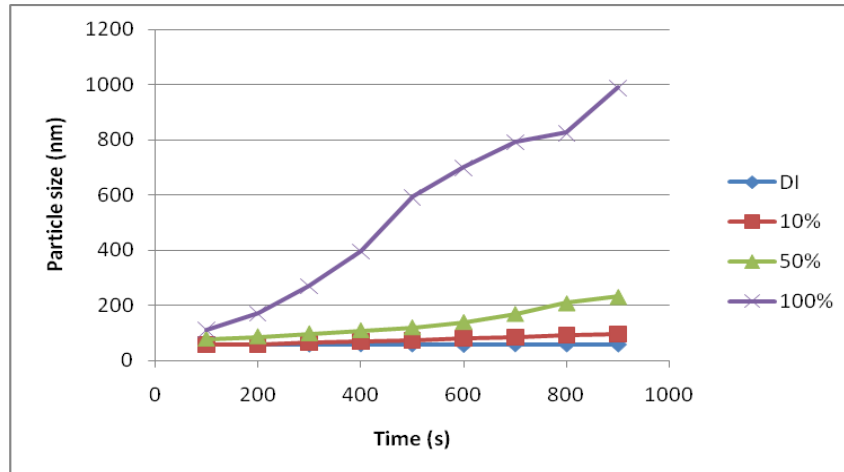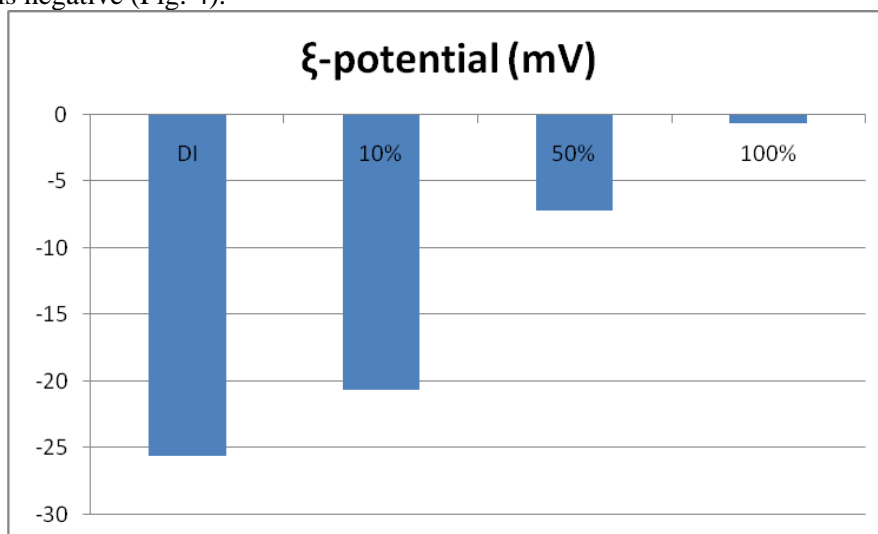
**Figure 2.** Aggregation kinetics of nAg in original and diluted seawater samples (10%: 10% seawater 90% DI water; 50% 50% seawater 50% DI water; 100%: original seawater sample)
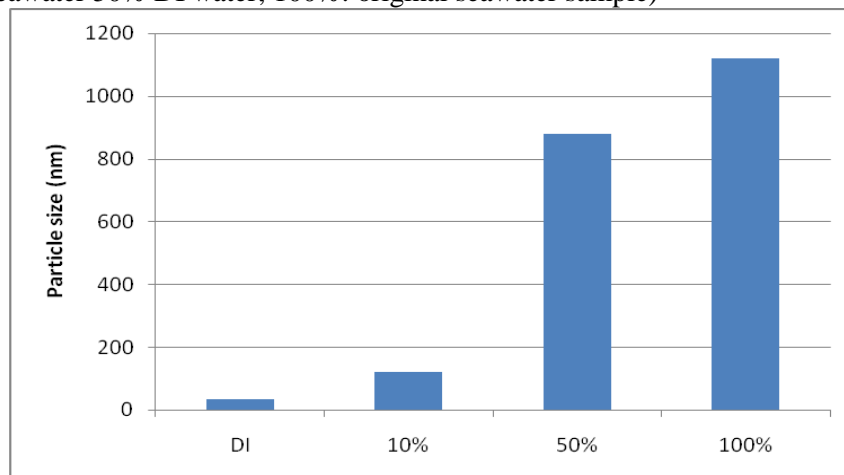


**Figure 3.** Size of nAg in original and diluted seawater samples (10%: 10% seawater 90% DI water; 50% 50% seawater 50% DI water; 100%: original seawater sample)

Fig.3 shows the particle size of nAg after 2 h storage time. The recorded particle size is consistent with the aggregation kinetics. Similarly, Gao et al. (2009) reported a much larger size of nAg in seawater (>1000 nm) than that in DI water (<100 nm) [4]. In our case, the counter-ions are the cations present in seawater since $\xi$-potential of nAg is negative (Fig. 4).



**Figure 4.** $\xi$-potential of nAg in original and diluted seawater samples (10%: 10% seawater 90% DI water; 50% 50% seawater 50% DI water; 100%: original seawater sample)

The cations present in seawater can eliminate the negative surface charges of nAg and reduces the electric repulsion force and energy barrier between nanoparticles, which enhances the aggregation of nAg [6,7]. As $\xi$-potential is related to the stability of a nano-suspension (higher absolute $\xi$-potential values indicate better stability), Fig. 4 shows that stability of nAg decreases with increasing ionic strength. $\xi$-potential of nAg in DI water is about 43 times higher than that in pure seawater.

**Conclusion**

In this study, nAg was synthesized using Tollens method. The obtained nAg was characterized by UV-vis spectrometry, TEM and DLS. Aggregation kinetics of nAg was measured using a time-resolved DLS. The result indicates that aggregation rate increases with increasing ionic strength. Stability of nAg in seawater sample was measured using zetasizer. The obtained result shows that the absolute values of $\xi$-potential decreases with increasing ionic strength.

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