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Observation of the interactions of Silver nanoparticles (AgNPs) mediated by acid in the aquatic matrices using in-situ liquid cell transmission electron microscopy

Ishara Fernando[1,2], Yee Yan Tay[3,4], Hasith Karunasekera[5], Yan Zhou[2,6]*

[1]Interdisciplinary Graduate School, Nanyang Technological University, Singapore 639798.

[2]Nanyang Environment & Water Research Institute, Advanced Environmental Biotechnology Centre, Nanyang Technological University, 1 Cleantech Loop, CleanTech One, Singapore 637141.

[3]Facility for Analysis, Characterization, Testing and Simulation, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798.

[4]School of Materials Science and Engineering, College of Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

[5]School of Electrical & Electronic Engineering, College of Engineering, Nanyang Technological University, Singapore 639798.

[6]School of Civil & Environmental Engineering, College of Engineering, Nanyang Technological University, Singapore 639798.

*Corresponding author at: Tel.: +65 6790 6103; E-mail address: zhouyan@ntu.edu.sg

Abstract

The properties of the solution matrix play a prominent role in determining the interactions between the silver nanoparticles (AgNPs) when they are present in the aquatic environment. Here, using in situ liquid cell transmission electron microscopy (LCTEM), we show that the interaction of AgNPs is predominantly affected by the solution pH. Reducing the pH in the solution will accelerate the aggregation of AgNPs due to the alteration of the charge cloud around the NPs. Aggregates formed in this scenario were non spherical and irregular shaped and were stable under the electron beam irradiation. Individual AgNPs and smaller aggregates moved randomly and approached the larger aggregates before the aggregation process came to an end. We found that during the aggregation process, the mode of jump to contact and the pairwise approach of aggregation differed according to the composition of the solution. Observations made using the LCTEM were further explained using empirical formulae. Our observation on the pH induced interactions provides important insights on predicting the behavior of AgNPs released through many anthropogenic activities in the environment.

Keywords: Liquid cell transmission electron microscopy, aggregation, interactions, Silver nanoparticles

Introduction

Interactions between nanoparticles (NPs) in solution play an important role in understanding their transformation and subsequent fate in engineered systems. For example, they are responsible for colloidal stability [1], aggregation [2], dissolution [3] and reactions with biological macromolecules [4]. These interactions are regulated by the attractive and repulsive electrostatic forces between two interactive surfaces in water [5]. It is known that these short-range forces may prevent the surfaces from approaching closer than several water molecules [6]. However, the exact origin and mechanism of these forces is still not fully-understood. For example, the classical continuum models account only for a repulsive diffuse double layer and the attractive van der Waals (vdW) forces in the matrix [7]. Even though the two macroscopic hydrophilic surfaces are just a short-distance apart, these forces may dominate other intermolecular forces [8, 9]. It is unclear how the repulsive diffuse double layer exactly affects the interaction dynamics of NPs.

The properties of the solution matrix, where silver NPs (AgNPs) are present, have a significant impact on various interactions, such as absorption, oxidation reactions and dissolution. Hence, determining the transformations of AgNPs, widely used in the consumer products which are subsequently released into the aquatic environment [10] is critical.

Recently, the correlation between the pH with the colloidal stability, dissolution and aggregation kinetic of these AgNPs has been evaluated [11]. This was done in the environmentally relevant conditions from acidic to basic using different analytical techniques such as UV vis, DLS and TEM. Empirical formulae have also been used to relate the chemistry behind the phenomenon of aggregation of AgNPs with the experimental results. It

was found that AgNPs aggregated rapidly in the acidic conditions whereas they only dissolved in the alkaline conditions.

The synthesized NPs will have their own surface charge when present in the environment. The surface charges act like a cloud of electrons surrounding the NPs when the latter is present in the liquid. It creates a metastable state, preventing the NPs from aggregating to each other due to vdW forces. Therefore, when differentiating the interactions of AgNPs in the absence and presence of acid, we found that the presence of acid in the solution alter the surface charge of the AgNPs changing the electrostatic potential of the AgNPs. Thus, this charge cloud is altered or disturbed affecting the stability of the NPs. As a result, aggregation will take place. While the aggregation kinetics is recorded systematically with time [11], there is little information on the path observation of the aggregation interaction of the AgNPs in solution when the pH is varied. Path observation has been made possible in the recent years using the in-situ liquid cell transmission electron microscopy (LCTEM) [12], which can potentially be applied in geochemical and environmental studies. LCTEM directly helps in quantifying and structuring the NPs dispersed in a solution, while also simplifying the tracking of real-time interactions between individual NPs. Advantages of using LCTEM include, firstly, the ability to visualize dynamic processes depending on the total number of NPs. Secondly, it allows exploring how liquid flows through the cell and the solution-properties that affect the interactions of NPs. Finally, with the capability to observe such in-situ processes in the electron microscope, the presence of the electrostatic forces between NPs, vital in the attachment [13], growth [14] and assembly [15] of NPs, is also observable. In these studies, tracking the movement of interacting NPs within few nanometers, showed that electrostatic interactions facilitate the pairwise approach and the subsequent alignment of NPs. LCTEM enables investigating the impact of an external stimuli directly on the interactions and the dynamics of NPs in a solution [16, 17].

The objectives of this study include (1) evaluating the mechanism of aggregation of AgNPs in water and acid with respect to the change in the interactive forces; (2) assessing the impact of intermolecular forces on interactions of NPs, and (3) appraising the suitability of LCTEM as a technique for in-situ studies in environment-related subjects. Here, using the in-situ LCTEM imaging [18-21], we visualized the time-resolved pH-induced dynamic interactions of AgNPs in water, showing that their mutual approach was hindered by the primary hydration shell of individual AgNPs.

Materials and Methods

The AgNPs used during the experiments were synthesized via oxidation-reduction of $AgNO_3$ using $NaBH_4$ [11] as mentioned in SI, characterized according to Fernando et al [22] and the typical size of the NPs used were about 40-75 nm.

Our experimental setup included a thin layer of liquid specimen [23] with AgNPs sandwiched between the two-electron transparent Silicon Nitride (Si_3N_4) membranes (~50nm thick on each side) of a liquid cell with the help of the Au spacer of (~50 nm) in thickness. The diffusion of NPs due to translation and rotation within these thin liquid films near liquid-solid interfaces is strongly suppressed [24, 25]. As such, the real time imaging and quantification of the interaction force fields of an otherwise rapid phenomenon can be facilitated.

We carried out the flow experiment using the Protochip Poseidon Liquid Cell Holder with two kinds of solutions: freshly-synthesized, uncoated 10 mg/L AgNP solution (final pH ~8) and 10% (w/v %) Nitric (V) acid solution. Before loading the AgNPs onto the grids, they were adequately rinsed using acetone and methanol at least for 5 min respectively. The e-

chips were, then, plasma-cleaned (3:1Argon/Oxygen mixture) for about 5 min using the Fishione Plasma Cleaner Nanoclean Model 1070 for surface treatment to change the Si_3N_4 membranes from hydrophobic to hydrophilic and to remove possible organic contaminants on the surfaces [26]. Right after the hydrophilic treatment, the sample of 0.3 µL was drop-cast onto the chips before sealing up for the experiment.

First, the AgNPs in the fluid cell e-chips were observed through the JEOL 2010 TEM with a high-resolution pole piece operated at 200 kV and the JEOL GrandARM TEM operated at 300 kV with a wide gap pole piece, mounted with an image corrector. The camera used are the AMT XR40B CCD (JEOL 2010HR) and Gatan Oneview CMOS camera (JEOL GrandARM) at a rate of 4-10 frames per second. The electron doses range from 0.75 to 58.5 e/(Å^2.s). In order to observe the aggregation dynamically, fresh AgNPs was first pumped through the liquid cell holder to the fluid cell using a syringe pump (Harvard Apparatus, Pump 11 Elite) at an infuse rate of 300 µl/h. After allowing ample time for the AgNPs to reach the fluid cell, the movement of AgNPs in the matrix was observed. Subsequently, Nitric (V) acid was pumped into the fluid cell using a syringe pump at an infuse rate of 150 µl/h. As such the observation of the aggregation occurs in a situation where the pH is continuously changing. The impact of the beam on the movement of NPs in liquid cells due to heating or momentum transfer from energetic electrons is negligible under these imaging conditions. However, charging during the imaging may enhance the movement of the NPs [27]. The images obtained during different scenario were processed as mentioned in SI.

Results and Discussion

Temporal observation on the mobility of the AgNPs in different environment

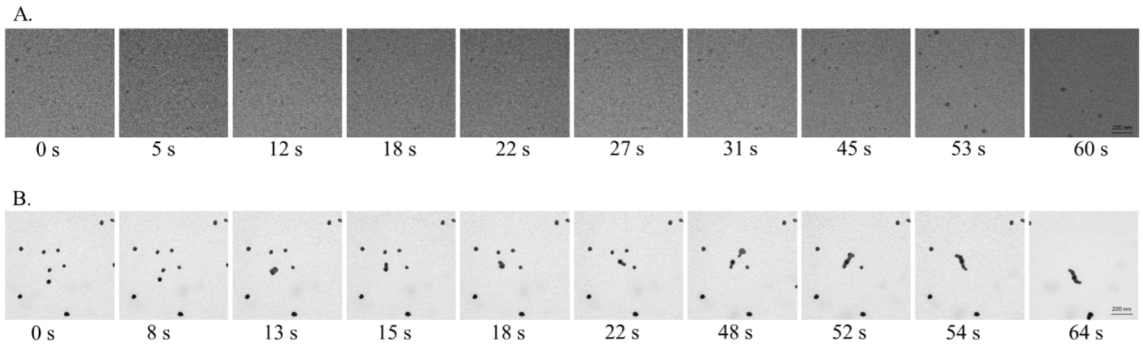

Figure 1. Time series images showing the interactions of individual AgNPs in the (A) de-ionized (DI) water and (B) in the presence of acid (processed images). AgNP concentration : 10 mg/L.

Time resolved TEM images of the AgNPs interacting in water (Figure 1A) are compared with those in the presence of acid (Figure 1B). According to Figure 1A, the distance between the single NPs and the clusters changed irregularly with time. It is also apparent from Movie S1 which demonstrates that the movement of AgNPs was non-directional, suggesting the random movement of AgNPs in the liquid over time. A striking difference between Figure 1A and 1B is the time-taken for the aggregation of AgNPs in water and in the presence of acid. It took longer for particle-aggregation in water (aggregation starts at 53s in water vs aggregation start at 13s in acid) compared to acid. The liquid cell holder was not electronically designed to measure the varying pH physically over the time while the acid/water was introduced during the experiment. pH was estimated based on an approximation using the flowrates, length of the tubes and the area of the chip. According to the approximation, the pH of the solution at the time where the images in the acidic condition of the Fig. 1B was taken lies around 5.5. This is also consistent with the result that was previously published using UV-vis

[11] where the spectra starts to indicate a change in the surface plasmon peak profile in the UV-vis spectrum with the reducing pH.

The distance between the single AgNPs decreased with time in the presence of the acid (Figure 1B). In addition, rotational and translational as well as translational-rotational coupled movements of these small AgNP aggregates were also observed (Movie 1 & 2). The change in the UV vis spectrum of the AgNPs with the solution pH is illustrated in Figure S4, which is also consistent with the LCTEM results. Variation in the solution pH also changed the behavior of the AgNPs resulting in rapid attachment of the smaller aggregates with each other forming larger aggregates consequently. Figure S3 shows the growth of these large aggregates of AgNPs changing with time in the presence of acid.

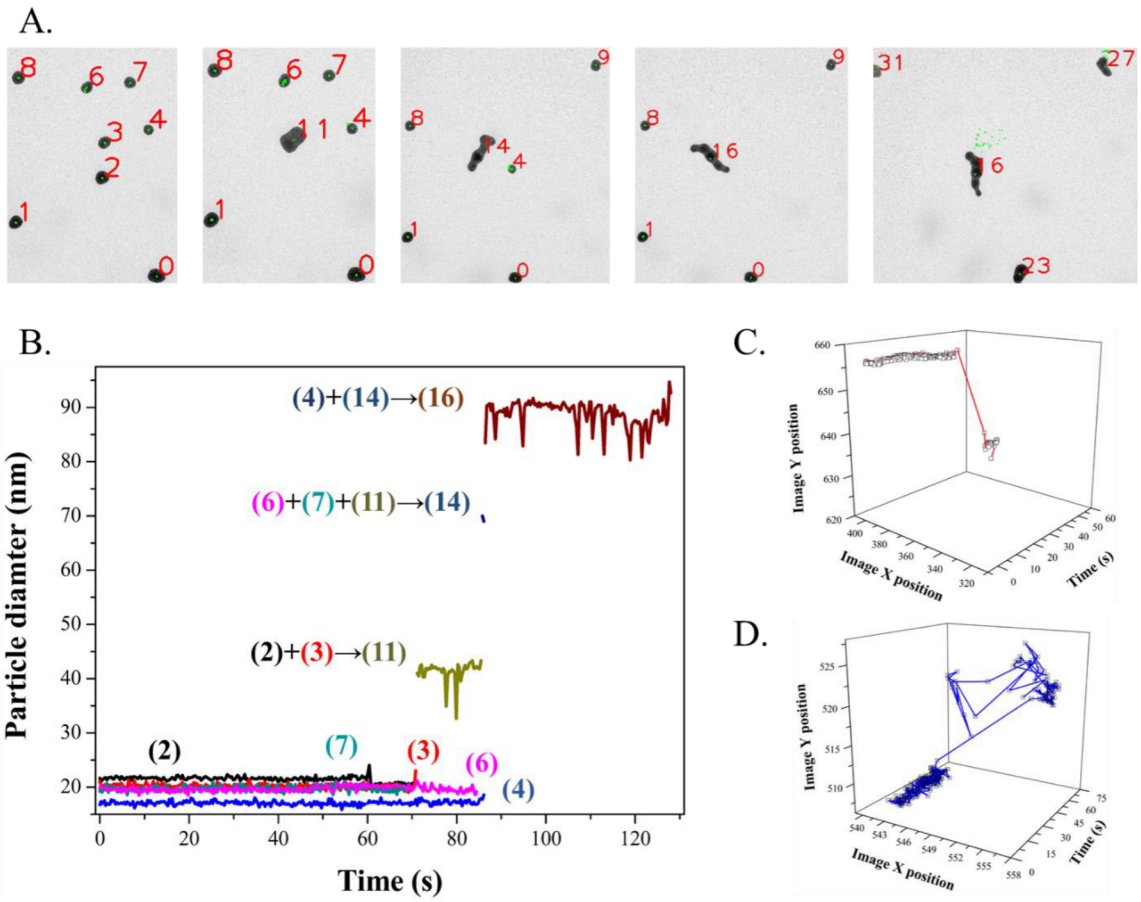

Figure 2. (A) Images with the tracking IDs showing movement of AgNPs in forming aggregates, (B) the change in the particle diameter of the AgNPs in (A) in the acidic solution, (C) Mobility of the particle with the Track ID (2) in (A) and (D) Mobility of the particle with the Track ID (4) in (A). AgNP concentration: 10 mg/L.

We further evaluated the aggregation process for the AgNPs in the presence of acid (Figure 1B) by carefully tracking the individual particles. The TEM images of the AgNPs with tracking IDs before and after the addition of Nitric (V) acid are shown in Figure 2A. At the beginning, the NPs were distributed evenly within the field of view. Aggregation subsequently happened with particles of different mobility albeit these AgNPs moved in random directions before the attachment (Figure 2C & D). According to the Figure 2C & D, the mobility exhibited by the particle with the track ID (4) was higher than that of the particle with the track ID (2). Particle with the track ID (2), moved for a limited time as an individual particle before aggregation. The particle with the tracking ID (4), however, moved randomly for a considerable time before the aggregation as observed in Figure 2D.

Interaction of AgNPs with Water vs Acid

The random movements of the AgNPs and their attractive and repulsive interactions in water are observed in Movie S1 such as some particles disappearing and reappearing again. Furthermore, it is observed that the movement of the individual NPs in DI water is more vigorous as compared to the one the acidic condition under similar dose of irradiation (SI Movie 1 vs Movie 2). It is not clear why this happened but may be related to the explanation

as follows. Since the point of zero charge of bare Si_3N_4 is about pH 4.1, AgNPs initially adhered to the positively-charged Si_3N_4 membrane [28] when they were in the DI water ($pH \approx 6.5$), via electrostatic attraction and vdW forces. After several seconds of exposure to the electron beam, some of the particles or aggregates detached from the Si_3N_4 membrane and moved in a quasi 2D plane closer to the membrane in the focal plane making it visible under the TEM. This could be due to the increasingly negative electrical charges built up on the Si_3N_4 membrane and the secondary emission of the electron beam irradiation, the negatively charged AgNPs repulsed and detached from the membrane permanently, initiating the aggregation. Many of these observations can be described by the attractive forces between a membrane and the particles as expressed in Eqn. (1).

$$F = -\frac{k_A R}{6z^2} \quad (1)$$

Where k_A is the Hamaker constant of water which is 1.5 x 10^{-19}, R is the radius of the AgNPs or the aggregates and z is the distance between the membrane and the aggregate.

The charging of the Si_3N_4 membrane and NPs, which caused electrostatic repulsions between the membrane and the charged AgNP aggregates can be the driving force to the fast movement of the NPs and aggregates in the water (Figure 1A, Movie S1). On the other hand, due to the introduction of the acid, the presence of H^+ can increase the conductivity of the solution and reduce the negative electrical charge built-up by the membrane. As the H^+ ions have positive charges, the negative charges or the electrons attract towards them in the solution. Subsequently the charge cloud around the AgNPs will be destabilized resulting in a reduced and inhomogeneous amount of negative charges among the AgNPs, thus altering the resultant surface charge of the AgNPs. For further clarification, we have explained the phenomena in a pictorial way below in Figure 3.

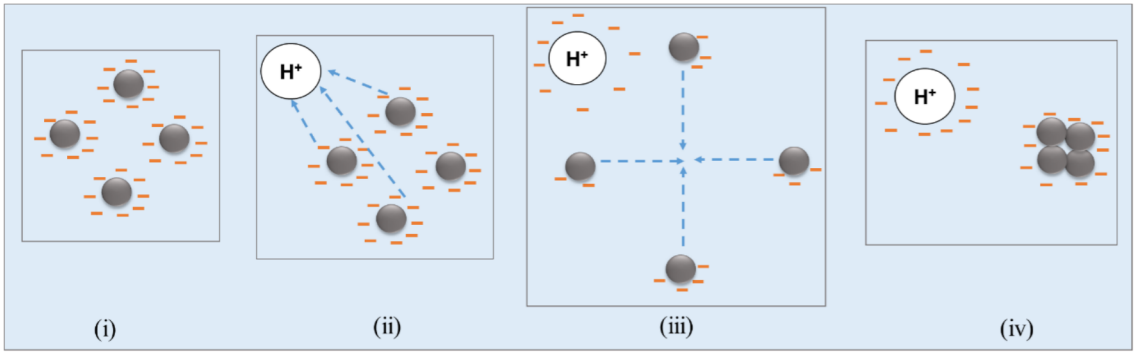

Figure 3. Mechanism involved in the change of the particle behavior with pH in acidic region (i) AgNPs in the aquatic solution (ii) Introduction of a proton to the system (iii) Deterioration of the electron cloud around the particles and attraction of the electrons towards the proton (iv) Formation of the aggregates by the destabilized AgNPs which is enhanced by the increasing amount of protons

Moreover, aggregates with an increased size were observed in the presence of high concentration of H^+ ions, as the vdW attractive force between the AgNPs and Si_3N_4 membrane increased (Eqn.(1)). The addition of H^+ ions weakened this electrostatic repulsive force and decreased the distance (z) between the AgNPs. The interactive force between the membrane and the particles/aggregates is inversely proportional to z^2 (Eqn.(1)). Therefore, the increased traction from the membrane probably limited the random motion of the aggregates in the acidic solution. This phenomenon could suppress the detachment and mobility of the AgNPs.

As the aggregates grew considerably in size, such as the one observed in Figure S3, the larger aggregates were attracted strongly towards the membrane. Therefore, larger aggregates (Figure S3) were stationary during observation with the electrostatic repulsive force between the Si_3N_4 membrane and AgNPs being lower than the vdW attractive forces between the

membrane and the particles. There were, however, some remaining AgNPs and smaller aggregates moving continuously in a random manner (Figure S3).

Behavior of aggregation of AgNPs

As we temporally resolved the difference in the way AgNPs behave in different environments and their mobility difference, it is also possible to observe the difference in the movement of the NP aggregates in the solution using LCTEM and considering these other interactions are worthwhile. For example, we observed the randomly-moving AgNPs jumped back and forth several times before aggregation between AgNPs occurred in water (Figure 1A). Such behavior of AgNPs in water can be explained in the following way. Each of the AgNP aggregate was enclosed in a repulsive and anisotropic charge cloud in water. When the repulsive clouds of two AgNPs or aggregates overlapped, they approached each other closely. According to Movie S1 & Figure 1A, individual NPs moved nearer to the aggregates and approached them from different directions before the aggregation. As the AgNPs were nearer to each other, the individual AgNPs were repulsed by the repulsive cloud of the aggregates. AgNPs would then try different ways to overcome the energy barrier for interaction such as the rotation and translational behavior of these individual AgNPs. It is not clear why in the end the AgNPs aggregated despite that the solution pH was around 8. It might be due to the radiolysis of the solution by the electron beam which produced different radicals reducing the pH locally[29]. When the repulsive forces between the charged NPs were finally screened, the stronger short-range attractive vdW forces enable the particles to aggregate.

In the presence of acid, the aggregation behavior and mechanism are different from the one in DI water. As shown in Figure 1B (Figure 1B, Movie S2), in the acidic environment,

266 individual AgNPs exhibited directional interaction with each other and had interesting
267 aggregation behavior. We observed that in the presence of the H^+ ions, as the distance
268 between the isolated AgNPs changed, the pairwise interactions can be observed initially.
269 Then, it promoted the AgNPs to form multiple pairwise aggregates. The pairwise distance
270 (coupling proximity) changed differently depicting the change in the solution matrix affecting
271 the interactions. Thereafter, these multiple pairwise aggregates rotated first before
272 aggregating with each other or other AgNPs indicating the presence of a directional
273 interaction behavior. Followed by the formation of multiple paired AgNPs, a sudden jump
274 occurred, allowing these paired AgNPs to contact each other, which resulted in the mutual
275 attachment of these AgNP-pairs increasing their overall diameter (Figure 2B). The
276 observation shows that aggregation of individual AgNPs increased in the presence of H^+ ions
277 at the same concentration of AgNPs (Figure 1A vs 1B), although the mobility reduces with
278 increasing aggregate-sizes (Figure 1B vs S3). This establishes that the presence of H^+ ions
279 affected the aggregation state of the individual AgNPs and aggregates, determining their
280 interactions in the solution.
281
282 It is likely that the origin of the aggregation mechanism is due to the electrostatic repulsion
283 being screened in the presence of H^+ ions (Figure 1B). The short-range interactions between
284 the aggregates were dominated by the vdW attractions, which facilitated the final attachment
285 process. On the other hand, the long-range attractions would take place when the distance
286 between two AgNPs become larger than the range of the vdW forces. These long-range
287 attractions are usually observed between identically charged NPs in confined geometries [30]
288 similar to the liquid cell used in the LCTEM study. The long-range attractions are mediated
289 by the redistribution of the ions and counter ions by the confining walls in the solution around
290 the AgNPs, becoming the driving force for two AgNPs or aggregates to move together.

Therefore, the long-range, like-charge attractions and the short-range vdW attractions worked together in governing the direct attachment of AgNPs and smaller aggregates to the larger aggregates in the presence of H^+ ions. This finding could give insights in understanding how the change in the size of the aggregates affect their colloidal stability and toxicity [31] in the environmental matrices.

Conclusions

This study reveals that randomly moving AgNPs in an aquatic matrix tend to aggregate due to the repulsive electrostatic and attractive vdW forces. The aggregation of AgNPs induced by the chemical composition of the solution matrix will have important implications on the kinetics of the transformations of the AgNPs in the aquatic environment. The difference in the time taken for the inter-particle attachment in these two scenarios indicates that the jump-to-contact phenomenon observed during particle-attachment occurs almost instantaneously when the electron layer around the AgNPs is affected, which is governed by the properties of the solution such as acidity. The formation of transient pairs before the direct contact may provide enough time for AgNPs to change their orientation and explore optimal configuration to attach completely. This phenomenon may be critical in different processes such as the oriented-attachment of crystals or site-specific binding between biological macromolecules. We believe that future studies exploiting LCTEM will provide important insights into details of interaction mechanisms among other properties of the solution matrix and the AgNPs, which will be important in the areas of environmental science and engineering.

Conflicts of interest

There are no conflicts to declare.

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