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Silver nanoparticle synthesis using lignin as reducing and capping agents: A kinetic and mechanistic study

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ABSTRACT

Silver nanoparticles (AgNPs) were robustly synthesized from aqueous AgNO_3 with alkali lignin (low sulfonate) (AL_{LS}) severing as dual reducing and capping agent. The AgNP synthesis mechanisms were highly pH dependent. Under neutral and acidic conditions, polydispersed AgNPs were synthesized via the self-catalyzed reduction of Ag^+ on instantaneously formed Ag_2O surfaces followed by the slower pseudo-first order reduction. The Ag_2O nanoparticles functioned as the nucleating sites for the reduction of remaining silver cations to form AgNPs whose size and size distribution strongly dependent of lignin concentrations. AgNPs were optimally synthesized by reducing 2 mmol/L AgNO_3 with 0.16 wt% AL_{LS} at pH 10 and 85 °C in 30 min to near 100% yield in bimodal distributed sizes with 23% and 77% in feret diameters of 7.3 (± 2.2) nm and 14.3 (± 1.8) nm, respectively.

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1. Introduction

Silver nanoparticles have drawn much attention in research due to their many desirable properties including high electrical conductivity [23], excellent catalytic activity in organic redox reactions [16,24], surface plasmon resonance [3,10] and anti-microbial properties [7,14]. Synthesis of silver nanoparticles typically involves “bottom-up” reduction of silver salts, most commonly silver nitrate, often in the presence of capping agents to fine-tune particle sizes and shapes [11,12,19–21,25,26]. Using poly(vinyl pyrrolidone) (PVP) as a capping agent, larger and more uniformly sized nanospheres have been synthesized with increasing temperatures (200–260 °C) and silver/PVP molar ratios (1/16 to 1/8) with ethylene glycol as a reducing agent [11], larger nanocubes with longer reaction times (14–45 min) at over 0.1 M silver nitrate concentrations [21] and nanowires with the highest 1000 aspect ratio at 160 °C (100–185 °C) [19]. It is generally accepted that PVP regulates particle growth and promotes nanowire formation by capping the {100} facets of multi-twined silver seeds to inhibit growth in the direction perpendicular to those facets [12,20,26]. Di-carboxylates and tri-carboxylates with two nearest carboxylate groups separated by two or three carbon atoms, such as sodium citrate, oxalate, succinate and malnate, have shown to cap the {111} facets, causing their stacking into nanoplates [25]. Nanocubes

have also been synthesized using structural regular polymers with defined intra/inter-molecular spacings, such as 2-butyne-1,4-diol dendrimers with 3,5-dihydroxybenzyl alcohol branches [22].

Natural compounds and plant extracts have also been used as reducing and/or capping agents in the synthesis of silver nanoparticles, i.e., β -D-glucose and starch as reducing and capping agents, respectively [17], and aloe vera extracts in the presence of ammonia as reducing agents [2]. Tannic acid [18], grape pomace extracts [1], *Azadirachta indica* leaf extract [13] and wheat bran xylan [4] have served as both reducing and capping agents to prepare silver nanoparticles. The silver nanoparticles so prepared tend to vary widely in shapes and sizes with coefficients of variation greater than 0.3, attributed to the structural and chemical complexity of these natural compounds [2,15,17,18]. While the ease and effectiveness of these natural compounds and plant extracts in reducing and/or capping are attractive, many aspects of such reactions including the exact responsible compound of the plant extracts, the control over particle shape and sizes, and the kinetics and mechanisms have not been analyzed.

Lignin, one of the most abundant biopolymers in nature, is a significantly under-utilized agricultural and industrial waste from pulping. Although lignin is chemical heterogeneous and structurally complex, it possesses multiple functional groups, i.e., reductive aliphatic hydroxyls, phenolic hydroxyls and thiols, each of these can potentially reduce and/or cap in silver nanoparticle synthesis. Hydroxyl containing compounds, such as ethanol, glucose and tannin have successfully reduced silver cations into silver nanospheres [11,18]. Thiols, such as n-alkanethiols, have shown

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strong affinity to silver nanoparticles, hence facilitating its adsorption and capping onto particle surface [9]. Lignin's polar sulfonate groups can also help to disperse the formed nanoparticles in aqueous solutions. We have demonstrated that alkali lignin could serve as multi-functional binding, complexing and reducing agents for silver cations as well as capping agents for the synthesis of silver nanoparticles on ultra-fine cellulose fibrous membranes [5]. This study was to investigate the underlying reaction mechanism and kinetics of silver nanoparticle synthesis using AL_{IS} as reducing and capping agent as well as to optimize a simple and highly efficient one-pot reaction to synthesize uniform spherical silver nanoparticles in high yields. The reaction kinetics and mechanism were investigated by analyzing how silver nanoparticle size, size distribution and yield were influenced by reaction conditions of pH, temperature and time, lignin quantities at both fixed silver nitrate concentration and lignin/silver ratio.

2. Experimental

2.1. Chemicals

Alkali lignin (low sulfonate) (AL_{IS}) ($M_w = 60$ kDa, spruce origin, Sigma-Aldrich), sodium hydroxide (NaOH, 1 N, Fisher Scientific), sodium borohydride ($NaBH_4$, MP Biomedics) and silver nitrate ($AgNO_3$, practical grade, Acros Organic) were used as received. Water used was purified by Milli-Q plus water purification system (Millipore Corporate, Billerica, MA).

2.2. Synthesis of silver nanoparticles (Ag NPs)

Silver nanoparticles were synthesized from aqueous $AgNO_3$ in the presence of AL_{IS} at varied $AgNO_3$ and AL_{IS} concentrations, $AL_{IS}/AgNO_3$ ratios and under different reaction conditions of pHs, time and temperatures. Their effects on obtained silver nanoparticles sizes and distributions were closely examined. All pH values indicated were measured at the ambient temperature and recorded to 0.01 for $[OH^-]$ calculation.

2.2.1. Reaction mechanism

Aqueous $AgNO_3$ solution was prepared by adding 0.5 mL 20 mmol/L $AgNO_3$ into 4.5 mL pH 10.01 deionized water to make 5 mL 2 mmol/L solution. This as-prepared $AgNO_3$ solution was monitored at 85 °C for up to 30 min without AL_{IS} to validate the role of lignin as the reductant. 0.01 wt% AL_{IS} aqueous solutions were prepared at 85 °C with pH adjusted to 5.98, 7.54, 8.71, 9.68 and 10.01 by adding 0, 0.5, 1.5, 2 and 3 μ L 1 N NaOH. To each of the as-prepared 4.5 mL AL_{IS} solution, 0.5 mL 20 mmol/L $AgNO_3$ was added for 10 min. AL_{IS} and $AgNO_3$ mixtures were also prepared at 0.04 wt% AL_{IS} with pH adjusted by 1 N NaOH: (1) 0.4 mL of 0.5 wt% AL_{IS} was added into 4.1 mL deionized water with pH adjusted to 10.01 by adding 3 μ L 1 N NaOH. Then 0.5 mL 20 mmol/L $AgNO_3$ was added into the as-prepared 4.5 mL AL_{IS} solutions for 60 min. (2) 0.4 mL of 0.5 wt% AL_{IS} was added into 4.1 mL deionized water and immediately mixed with 0.5 mL 20 mmol/L $AgNO_3$ under constant stirring for 2 min, and then 3 μ L 1 N NaOH was added into the mixture solutions for 60 min.

2.2.2. Reaction kinetics

The reaction kinetics were studied at three pHs of 9.03, 10.01 and 11.28 and reaction temperatures of 20, 60 and 85 °C as reaction proceeded up to 180 min as follows: 5 mL of 0.16 wt% AL_{IS} – 2 mmol/L $AgNO_3$ solutions were prepared by adding 0.8 mL of 0.5 wt% AL_{IS} into 3.7 mL deionized water with pH adjusted by adding 0, 1 and 2 μ L 1 N NaOH. Then 0.5 mL 20 mmol/L $AgNO_3$ was added into the as-prepared 4.5 mL AL_{IS} solutions for up to 30 min. 5 mL of 0.16 wt% AL_{IS} – 2 mmol/L $AgNO_3$ solutions were prepared at 20, 60 and 85 °C,

with pH adjusted to 10.01. Then 0.5 mL 20 mmol/L $AgNO_3$ was added into the as-prepared 4.5 mL AL_{IS} solutions for up to 180 min.

2.2.3. Lignin concentration effects

The effects of AL_{IS} concentration was studied from 0.01 to 0.2 wt% AL_{IS} at fixed 2 mmol/L $AgNO_3$ concentration at 85 °C. 4.5 mL of 0.01, 0.02, 0.04, 0.08, 0.12, 0.16 and 0.2 wt% AL_{IS} solutions were prepared at pH 10.01, then 0.5 mL 20 mmol/L $AgNO_3$ was added for 10, 30 and 60 min. The silver nanoparticle synthesis reference for the 100% yields was prepared by adding 0.1 g $NaBH_4$ to 0.16 wt% AL_{IS} – 2 mmol/L $AgNO_3$ mixture at 85 °C for 60 min to ensure full reduction of silver cations. The reaction was also studied at varied lignin concentrations from 0.04 to 0.32 wt% at a fixed 0.8 $AL_{IS}/AgNO_3$ wt%/mmol/L ratio 10, 30 and 60 min.

2.3. Analytical methods

Silver nanoparticle synthesis was monitored by measuring its characteristic absorbance peak around 420 nm using ultraviolet–visible spectroscopy (UV–vis) (Evolution 600, Thermo Scientific). All aqueous solutions were diluted to 0.2 mmol/L Ag molar concentration and measured in quartz cuvettes with 1-cm path length. The size and size distribution of silver nanoparticles synthesized were measured on a transmission electron microscopy (TEM) (JEOL 3000, JEOL). TEM samples were prepared by placing 5 μ L onto a carbon grid, then letting dry in air. Particles size and distribution were derived from imaging at least 400 particles using software ImageJ (Version 1.46r).

3. Results and discussion

3.1. Reaction mechanism

The role of lignin as a reducing agent for silver nanoparticle (AgNP) synthesis under varying pH conditions (85 °C, 10 min) was first verified by UV–vis observation (Fig. 1). Without lignin, the control showed no AgNP characteristic surface plasmon resonance peak between 250 and 800 nm, confirming none was synthesized without lignin or any other reducing agent. With 0.01 wt% AL_{IS} at pHs from 5.98 to 10.01, broad absorbance bands centering between ca. 411 and 421 nm appeared (Fig. 1), clearly evident of AgNP formation. At pH 5.98 and 7.54, UV–vis absorbance peaks at 421 nm with similar 0.267 and 0.304 intensities appeared, respectively, indicating synthesis of some AgNPs under these slightly acidic to just above neutral conditions. The AgNP synthesized at pH 8.71 showed surface plasmon resonance peak to be more than doubled to 0.66 and blue-shifted to 416 nm, indicating reduced particle sizes that are known to exhibit higher frequency [8]. The characteristic AgNP surface plasmon resonance peaks further intensified to 0.882 and 1.089 while also blue shifted to 412 nm and 421 nm as pH increased to 9.68 and 10.01, respectively, showing increasingly numbers of smaller AgNPs. This confirmed not only the role of lignin as the reducing agent in AgNP synthesis but also its greater effect under increasing pH.

While AgNP synthesis was observed at all pHs studied, the greater numbers of smaller AgNPs synthesized at pHs > 8.71 suggested a different mechanism than that at the lower pHs of 5.98 and 7.54. Another distinction at this pH transition was the same yellowish color reaction mixtures turned from clear at and below pH 7.54 to slightly colloidal at and above pH 8.71. Such colloidal appearance at and above pH 8.71 indicated the presence of silver oxide (Ag_2O), the more energetically favorable product of silver hydroxide (AgOH). The $[Ag^+] \times [OH^-]$ values were estimated from silver cation $[Ag^+]$ (2×10^{-3} M) and hydroxide anion $[OH^-]$ (10^{-pOH}) to be 1.9×10^{-11} , 6.93×10^{-10} , 1.02×10^{-8} , 9.57×10^{-8} , 2.09×10^{-7} at pH 5.98, 7.54, 8.71, 9.68 and 10.01, respectively. Comparing to

Fig. 1. TEM and UV-vis spectrum of AgNPs synthesized by reducing AgNO_3 (2 mmol/L) with 0.01 wt% ALIS at varied pHs (85 °C, 10 min).

the 1.52×10^{-8} solubility constant for AgOH (K_{sp} at 20 °C), the $[\text{Ag}^+] \times [\text{OH}^-]$ values of AgNO_3 - ALIS mixtures at $\text{pH} \leq 7.54$ were much smaller, that at $\text{pH} 8.71$ was similar and those at and above $\text{pH} 9.68$ far exceeded the K_{sp} . These observations seem to fit the self-catalyzed reduction mechanism in which AgNPs adsorbed on silver oxide would induce autocatalytic reduction of silver cations on its surfaces [6]. In the simultaneous Ag^+ reduction to zero-valence silver and AgOH formation with NaOH , AgNPs adsorbed onto the large Ag_2O particle surfaces would continuously transfer electrons to catalyze further Ag^+ reduction. At pH above 8.71, Ag^+ can be instantly reduced into AgNPs by ALIS on Ag_2O particle surfaces via this much faster autocatalytic mechanism, as shown by the much higher yields. Under basic conditions, the mechanism by which lignin catalyzed AgNP synthesis was on the intermediate Ag_2O surfaces. Under neutral and acid condition, Ag^+ were thought to be directly reduced by ALIS into AgNPs, but not by the autocatalytic mechanism due to the absence of Ag_2O .

AgNPs prepared at $\text{pH} 5.98$ were few and varied greatly in shapes and sizes from 20 to 300 nm, while more spherical nanoparticles in less than 20 nm diameter were synthesized at $\text{pH} 10.01$. Particles larger than 100 nm were observed in both and could be aggregated AgNPs and/or unreduced silver-lignin complexes from drying in TEM sample preparation. The presence of these large particles suggested there might not be sufficient lignin to stabilize the AgNPs or fully reduce Ag^+ in such short reaction times. The mechanism and kinetics were therefore studied by raising lignin concentration to 0.04 wt% and above and at higher $\text{pH} 10.01$.

To further confirm the AgNP synthesis mechanism via the Ag_2O route, AgNPs were synthesized with 2 mmol/L AgNO_3 and 0.4 wt% ALIS at 85 °C via two procedures: (1) direct mixing of AgNO_3 and ALIS at $\text{pH} 10.01$ for 60 min; (2) mixing AgNO_3 with neutral ALIS solution for 30 min then adding NaOH for another 60 min. The TEMs showed AgNPs obtained via direct mixing at $\text{pH} 10.01$ ranged from 3 to 40 nm in sizes with an average feret diameter of 9.9 (± 3.8) nm (Fig. 2a and b), whereas those with NaOH added after mixing were larger in 17.8 (± 24.4) nm average feret diameter and much broadly distributed from 4 to 300 nm (Fig. 2c and d). Under

neutral condition, some Ag^+ could ionically bond with the lignin phenolic hydroxyl and sulfonate groups to form tightly associated complexes which could not form Ag_2O following addition of NaOH . These silver-lignin complexes would be irregularly shaped and sized similar to the heterogeneous lignin structures and, when reduced by lignin's reductive groups into zero-covalent nanoparticles, remained irregularly shaped and polydispersely sized. With addition of NaOH , those unassociated Ag^+ could be instantly converted to Ag_2O then autocatalyzed reduced into AgNPs. Therefore, due to the various sized and shaped nucleating sites formed via these two mechanisms, nanoparticles grown tend to be polydispersed as observed.

The mechanistic studies have shown that faster overall reaction and more uniformly sized AgNPs were facilitated under increasingly basic conditions where Ag_2O formation and the adsorbed AgNPs on the Ag_2O surfaces catalyzed faster Ag^+ reduction. AgNPs formed via such mechanism were not affected by the lignin structure as Ag^+ did not complex with lignin, thus were more monodispersed in their sizes.

3.2. Reaction kinetics

The kinetics of lignin catalyzed AgNP synthesis was studied at 0.04–0.16 wt% lignin concentrations at a fixed 2 mmol/L AgNO_3 concentration, under several basic conditions including an even higher pH of 11.28 and temperatures. The control was prepared by adding 0.1 g NaBH_4 to 0.16 wt% ALIS – 2 mmol/L AgNO_3 mixture at 85 °C for 60 min and exhibited a peak intensity of 2.71 at 419 nm. The 419 nm peak intensity was normalized by that of the control to calculate the yield as in Eq. (1). The remaining silver not in the form of AgNPs included all silver species, i.e., Ag_2O , atomic Ag and Ag^+ , were expressed as Eq. (2). As the conversion from Ag_2O to atomic Ag then AgNPs was instantaneous, remaining silver was assumed to silver cations at +1 oxidative state or Ag^+ .

$$\text{Yields (\%)} = \left(\frac{419 \text{ nm peak intensity of sample}}{2.71} \right) \times 100 \quad (1)$$

Fig. 2. TEM (a, c) and size distribution (b, d) of AgNPs synthesized with AgNO_3 (2 mmol/L) and AL_{15} (0.04 wt%) at 85°C for 60 min: (a, b) mixing at pH 10.01; (c, d) pH adjusted to 10.01 after mixing.

$$\text{Remaining silver (\%)} = 100 - \text{Yield} \quad (2)$$

Under varied basicity, the AgNP yields increased exponentially with reaction times up to 3 h at pH 9.03 and 10.01 and reached almost 100% within 3 min at pH 11.28 (Fig. 3a). The natural logarithm of the remaining Ag^+ decreased linearly with reaction time, suggesting a pseudo-first order kinetic for the reduction reaction (Fig. 3b). However, the amount of Ag^+ at the beginning of the reaction determined by the intercept of the fitted line at $x=0$ was not 100%, indicating some Ag^+ were reduced into AgNPs instantaneously (Fig. 2). These instantaneously formed AgNPs are consistent with autocatalytic reduction of Ag^+ by lignin on the Ag_2O surface discussed earlier. From the intercepts, increasing Ag_2O as the approximate $[\text{OH}^-]$ of AgNO_3 - AL_{15} mixtures increased from 1.07×10^{-5} to 1.02×10^{-4} and 1.9×10^{-3} mol/L at pH 9.03–10.01 and 11.28 corresponded to 35.0, 59.0 and 99.3% of the instantly converted nanoparticles, respectively (Fig. 3b). However, the reaction rate constants determined by the slope of the fitted lines varied little at these pHs, indicating the pH played little roles in the reduction of remaining Ag^+ to zero-covalent AgNPs over time. The observations under basic conditions supported the notion that Ag^+ were reduced by AL_{15} into AgNPs via two simultaneous processes: fast pH-dependent autocatalytic reduction of Ag^+ on the instantaneously formed Ag_2O surfaces; considerably slower direct reduction of remaining Ag^+ that is independent of pH.

Under varied temperatures, AgNP yields also increased exponentially with reaction times at pH 10.01 (Fig. 3c). The amount of instantaneously formed AgNPs via Ag_2O determined from the intercepts increased from 23.1%, 33.5% to 59.0% with increasing temperatures from 25°C , 60°C to 85°C , showing significant temperature effects on this instant reduction process. This increasing Ag_2O formation could be due to increasing self-ionization constant (k_w) of water as temperature increases, leading to higher $[\text{OH}^-]$ concentration. Residual Ag^+ also reduced linearly with reaction time at these temperatures (Fig. 3b), consistent with the pseudo-first order kinetics in the reduction of remaining Ag^+ by lignin. The reaction rates increased greatly from $2.19 \times 10^{-5} \text{ s}^{-1}$, $1.72 \times 10^{-4} \text{ s}^{-1}$ to $8.68 \times 10^{-4} \text{ s}^{-1}$ with increasing temperatures from 25°C , 60°C to

85°C . At a higher temperature, AgNPs synthesized via both reaction reached 100% in shorter time.

The kinetic data under varied temperatures clearly showed the rate of AgNP synthesis by autocatalytic reduction of Ag^+ on the instantaneously formed Ag_2O surfaces to be significantly affected by temperature in addition to pH, evident of their direct effects on $[\text{OH}^-]$ hence Ag_2O that catalyzes the instant reduction of Ag^+ . The reduction of the remaining silver cations was shown to be pseudo-first order reaction as the rate of which was mainly determined by temperature rather than pH.

3.3. Optimization of yield and size

A systematic survey of AL_{15} concentrations (0.01–0.2 wt%) and reaction time (10–60 min) (Fig. 1S) further supported the catalytic role of AL_{15} in synthesizing AgNP from AgNO_3 presented earlier at the lowest 0.01 wt% AL_{15} concentration and shortest 10 min reaction (Fig. 1). Given a fixed 60 min reaction time, the peak position red shifted from 413 to 419 nm as lignin concentrations increased from 0.01 to 0.2 wt%, indicating larger AgNPs (Fig. 1S). The AgNP yields also increased from 43 to 99% with increasing lignin concentrations and peaked 0.12 wt%, showing lignin quantity to be the limiting factor at below 0.12 wt% (Fig. 4). Also, the time taken to reach 99% yields remained 60 min at 0.12 and 0.16 wt% AL_{15} and decreased to 30 min at 0.2 wt%, respectively. As lignin is a weak base, the reaction between OH^- and Ag^+ would drive the ionization of lignin phenolic groups to form more hydroxide anions, leading to more Ag_2O at higher AL_{15} concentrations and catalyzing more reduction of surface Ag^+ to AgNPs. Higher lignin concentration would also lead to a higher rate of reducing the remaining silver cations, resulting in faster particle growth. At a fixed lignin concentration, the yields increased with reaction time, again consistent with the kinetic data presented previously.

As yields increased from 75.6 to 91.9 then 99% with longer reaction times (2 mmol/L AgNO_3 , 0.16 wt% AL_{15} , pH 10.01, 85°C), the AgNPs also increased in sizes and size distribution (Fig. 5). While similar in their coefficients of variance, the increasing sizes and broadening size distribution were consistent with the dominance

Fig. 3. AgNP synthesis (2 mmol/L AgNO₃, 0.16 wt% AL₅, pH 10.1, 85 °C) under varied pH (9.03 ●, 10.01 ▼, 11.28 ▲ and temperatures (20 °C ■, 55 °C ◆, 85 °C ▼): (a, c) yield; (b, d) residual silver and cations. Inset in a: UV–vis spectrum over time in min.

of instant autocatalytic AgNP formation coupled with continuing particle growth from the slower reduction of the remaining Ag⁺ in which Ag NPs served as nucleating sites and could also be from the coalescence of smaller particles into bigger ones.

While AgNP yields increased with AL₅ concentrations at a given reaction time (Fig. 4), AgNP sizes remained mostly in the similar ca. 4–20 nm range but their sizes transformed from mono-distribution in 9.9 (±3.8) nm average feret diameter at 0.04 wt%

AL₅ to bimodally distributed at higher AL₅ concentrations (Fig. 6). AgNPs synthesized at 0.8 wt% AL₅ consisted ca. 25% in 6.9 (±2) nm average feret diameter and 75% majority in 14.6 (±1.7) nm average feret diameter. Similarly, 23% and 77% of the AgNPs synthesized with 0.16 wt% AL₅ had average feret diameter of 7.3 (±2.2) nm and 14.3 (±1.8) nm, respectively. In essence, both UV–vis and TEM data were consistent and clear in showing increasing AgNP sizes with increasing AL₅ concentrations while the size distribution became narrower and bimodally distributed. Therefore, AL₅ exhibited capabilities in not only catalyzing synthesis of larger AgNPs in faster reaction rates, but also capped and stabilized the synthesized AgNPs from aggregation, resulting in more narrowly distributed sizes.

Additional observations at a fixed 0.8 wt%/mmol/L AL₅/AgNO₃ also showed increasing AgNP yields from 68.3 to 75.6% and 95.3% at 0.04, 0.16 and 0.32 AL₅ concentrations at 10 min reaction time, respectively (Fig. 2S). As both initial pH and AL₅/AgNO₃ ratio were fixed, the overall reaction rate increases could only be attributed to AL₅ quantity as previously discussed, e.g. more Ag NPs would be instantly formed via Ag₂O intermediate, more AL₅ phenolic groups would be ionized to give more hydroxide anions, while reduction rate of the remaining Ag⁺ would also increase.

Overall, both reaction time and AL₅ concentration have shown strong effects on AgNP yields, particle sizes and size distribution. As a reducing agent, lignin content determines the amount of AgNPs formed via silver oxides as well as the reduction rate of the remaining silver cations. The AgNP size distribution was determined upon the instantaneously formed AgNP nanoparticles via the autocatalytic reduction on Ag₂O nanoparticle surfaces whereas the reduction of remaining Ag⁺ mainly increased particle size and

Fig. 4. AgNP yields with varying AL₅ in 10 (●), 30 (▲) and 60 (◆) min (2 mmol/L AgNO₃, 85 °C, pH 10.01).

Fig. 5. TEM and size distribution of AgNPs synthesized over time in 0, 5, 30 and 60 min (2 mmol/L AgNO_3 , 0.16 wt% ALi_5 , 85 °C, pH 10.01).

Fig. 6. TEM and size distribution of AgNPs synthesized from 0.04, 0.08 and 0.16 wt% ALi_5 (2 mmol/L AgNO_3 , 85 °C, pH 10.01, 60 min).

slightly changed distribution from unimodal to bimodal possibly from coalescing small AgNPs over time.

4. Conclusion

Silver nanoparticles (AgNPs) were robustly synthesized in high yields from aqueous AgNO₃ precursor using AL₁₅ as dual reducing and capping agent. The AgNP synthesis mechanisms were highly pH dependent. At pH < 7.54, silver cations associated with lignin into irregularly shaped nucleating sites to be reduced into polydispersed AgNPs. At pH > 8.7, monodispersed AgNPs were formed through instantaneous self-catalytic reduction of Ag⁺ via Ag₂O intermediates whose quantities were dependent of pH, reaction temperature, silver and AL₁₅ concentrations. The remaining Ag⁺ was reduced to AgNPs via the pseudo-first order reaction, which depended mainly on the rate-determining reaction temperature and AL₁₅ concentrations. Bimodally distributed AgNPs could be synthesized at near 100% yield within 60 min at 85 °C by reducing 2 mmol/L AgNO₃ with a minimum 0.12 wt% AL₁₅ at pH 10. The average AgNP sizes increased with reaction times, while their size distributions narrowed with increasing AL₁₅ concentrations due to their highly desirable capping and stabilizing effect. This eco-friendly approach shows that other natural occurring polyphenolics may also serve as reducing and capping agents for the synthesis of silver and other nanoparticles to eliminate the use of hazardous and petroleum based chemicals, as green chemistry strives for.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ijbiomac.2015.09.066>.

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