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Silver Nanoparticles: Green Route, Stability and Effect of Additives

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ABSTRACT

Colloidal silver nanoparticles were prepared by reducing silver nitrate with oxalic acid in presence of cetyltrimethylammonium bromide (CTAB). The synthesized silver particles show an intense surface plasmon band in the visible region. The work reported in this paper describes the effect of concentration of various additives (NaCl, NaBr, NaNO$_3$, Na$_2$SO$_4$ and NaH$_2$PO$_4$) and ammonia on the growth and stability of Ag-nanoparticles. In all the cases the rate decreases as the [electrolytes] or [ammonia] increases. The nature, polarizability and coordinating ability of the anions play vital roles for nucleus formation and the growth process, which subsequently form different size particles. Transmission electron microscopy, selected areas electron diffraction, and UV-visible spectroscopy have been employed to characterize Ag-nanoparticles. The effect of the following variables on the particle size and size distribution was investigated: the [oxalic acid], [CTAB] and [Ag$^+$]. The nanoparticles are stable in NaNO$_3$ and NaH$_2$PO$_4$ solutions; but NaCl, NaBr and Na$_2$SO$_4$ causes their aggregation.

Keywords: *Silver Nanoparticles, Stability, Oxalic Acid, Additives, Ammonia*

1. Introduction

The literature is replete with the investigations of the use of noble metal nanoparticles(NP) (silver, gold and platinum) deposited on nanosized TiO$_2$ and/or WO$_3$ for carrying out the photocatalytic destruction of oxalic acid in aqueous solution [1-4]; but the preparation and characterization of Ag-NP involving oxalic acid (sacrificial electron donors) has been neglected. Oxalic acid, an important reductant in many organic and bioorganic redox reactions and its reduction process is eco-friendly and has gained importance in green chemistry. It is found naturally in varying concentrations, occurring in many plants such as tea, rhubarb, spinach, cocoa, nuts, berries and beans. Organic oxalic acid is essential for human body and is completely harmless if consumed in organic form. Inorganic oxalic acid causes trouble to human body. When ingested, oxalic acid removes calcium from the blood. Kidney damage can be expected as the calcium is removed from the blood in the form of calcium oxalate. Within the sub-group of 'weak acids', it is relatively strong (pK$_1$ = 1.22; pK$_2$ = 4.28; E$_0$ = +0.49 V for C$_2$O$_4$H$_2$/CO$_2$ system in acid solution).

Advanced Ag-NP have been synthesized by thermal decomposition and microwave irradiation methods by the decomposition of silver oxalate in a glycol medium using polyvinyl alcohol and polyvinyl pyrolidone as the capping agents, respectively [5,6]. Itoh, *et al* prepared silver nanoparticles via thermal decomposition of oxalate-bridging silver oleylamine complexes at 150˚C [7]. Even though many methods have been reported in the literature, the interest in the field of genesis of Ag-NP has not diminished. Among the various methods available, chemical reduction of metal salts is one of the possible ways of producing Ag-nanostructures as stable, colloidal dispersions in water or organic solvents [8]. The chemical reduction methods are probably the most versatile, economical and easy to control the shape and size of metal-NP. For stabilization of small particles, the use of polymers, phospholipids, triblock polymers, ligands, solid matrix and surfactants has also been suggested [9-14]. Although a number of stabilizers are available for the stabilization of nanosize particles in solution, these are associated with some demerits [15]. The preparation of these materials in green solvents, such as water [16] and other non-toxic solvents is becoming popular. In this content, surfactant aggregates, especially micelles, reverse micelles and macro emulsions, will get

an edge over other stabilizers [17-20].

Henglein prepared the colloidal silver particles by radiation method using 2-propanol, $AgClO_4$ and polyphosphate as reductant, oxidant and stabilizer, respectively, discussed the effects of adsorbed additives, organic solvent, and some metal cations (KI, NaSH, C_6H_5SH, H_2S, O_2, CCl_4, Na^+, Ag^+, Ba^{2+}, Cd^{2+}, Ni^{2+}, Hg^{2+}) on the stability of resulting silver particles, and suggested that Ag_4^{2+} species can be stabilized for along time in presence of a polyanion even under air and growth stops at the stage of this species [21-25]. Chemisorbed metal cations effect was interpreted in terms of the donation of electron density from the silver particles to the adsorbed cations. Henglein also monitored the stepwise growth of first silver clusters Ag^+ ion reduction in aqueous solution by spectroscopic methods [26]. Considerable spectroscopic data have accumulated on the synthesis of various Ag-NP by silver-mirror reaction. It has been established that ammonia concentrations and nature of reducing agents play an important role in controlling the morphologies of NP [27,28]. However, details of silver(I) reduction (Ag-NP formation) involving oxalic acid as reductant are not yet well-known in the absence and presence of additives or ammonia. We have chosen oxalic acid to see the effects of different additives, because its oxidation product, *i.e.*, CO_2, has no complex-forming tendency. A study of such a redox reaction should provide information relevant to the hypothesis previously advanced to the silver-mirror reaction [29,30]. We have carried out the present study with the following aims: (1) to determine the effects of different variables on the rates of Ag-NP; (2) to establish the role of different additives and ammonia on the growth of Ag-NP; and (3) to determine the effects of inorganic salts on the stability of silver sol. The observed results and the probable explanations detailed in this paper.

2. Experimental Section

2.1. Chemicals

Oxalic acid ($C_2H_2O_4.2H_2O$, reductant, 99%), silver nitrate ($AgNO_3$, oxidant, 99%), ammonia, cetyltrimethylammonium bromide (CTAB), ammonia, and inorganic electrolytes (NaCl, NaBr, $NaNO_3$, Na_2SO_4 and NaH_2PO_4) were obtained from Merck India and used with out further purification. Deionized water was used to prepare all of the aqueous solutions. $AgNO_3$ solutions were stored in a dark glass bottle.

2.2. Preparation and Characterization of Ag-NP

CTAB solution (0.01 $mol \cdot dm^{-3}$, 4.0 ml) was mixed with 0.01 $mol \cdot dm^{-3}$ $AgNO_3$ (10.0 ml). A 0.01 $mol \cdot dm^{-3}$ oxalic acid (2.0 ml) was added to this solution. The color of the reaction mixture gradually changed from colorless to prefect transparent yellow, indicating the formation of Ag-NP [5]. UV-260 Shimadzu, with 1cm quartz cuvettes spectrophotometer was used to monitor the optical transmission spectra of the silver sol under different experimental conditions. The prepared NP was analyzed by transmission electron microscopy (TEM) on a transmission electron microscope (JEOL, JEM-1011; Japan). Samples were prepared by placing a drop of working solution on a carbon-coated standard copper grid (300 mesh) operating at 80 kV. An Accumet, fisher scientific digital pH meter 910 fitted with a combination electrode was used for pH measurements.

2.3. Determination of Critical Micelle Concentration (CMC)

The cmc values were determined from plots of the specific conductivity versus [CTAB] in the absence and presence of $AgNO_3$ and oxalic acid. The break point of nearly two straight-line portions in the plot are taken as an indication of micelle formation and this corresponds to the cmc of CTAB [31] and found to be 10.1×10^{-4}, 8.7×10^{-4}, 8.8×10^{-4}, 8.8×10^{-4} and 8.9×10^{-4} $mol \cdot dm^{-3}$ for water + CTAB, CTAB + oxalic acid (2.0×10^{-4} $mol \cdot dm^{-3}$), CTAB + $AgNO_3$ (2.0×10^{-4} $mol \cdot dm^{-3}$), CTAB + oxalic acid + $AgNO_3$, respectively, at 30°C.

3. Results and Discussion

3.1. Optimization of Reaction Conditions for Transparent Ag-Sol

Generally, aqueous solutions of oxalic acid and $AgNO_3$ were used to the preparation of silver oxalate (white precipitate) [5-7]. Therefore, choice of the best conditions for the preparation of Ag-NP is a crucial problem that we address first. Under our experimental conditions used ([oxalic acid (from 4.0×10^{-4} $mol \cdot dm^{-3}$ to 14.0×10^{-4} $mol \cdot dm^{-3}$), [Ag^+] (from 4.0×10^{-4} $mol \cdot dm^{-3}$ to 20.0×10^{-4} $mol \cdot dm^{-3}$, [CTAB] (from 2.0×10^{-4} $mol \cdot dm^{-3}$ to 14.0×10^{-4} $mol \cdot dm^{-3}$ at 30°C), we did not observe the appearance of white precipitate, ruled out the possibility of silver oxalate as the reaction product. It is well known that colloidal aqueous solution of metal particles undergoes acid hydrolysis or is unstable in acidic medium, stability of metal nanoparticles depends strongly on the pH of the working reaction mixture and its growth can be stopped by adding the small amounts of minerals acids [23,32,33]. Control of pH is not as straightforward in micellar solutions as in ordinary solvents [34,35]. However, a series of experiments were performed in order to see any change in the pH of the working solution. The pH values were found to be nearly constant with increasing [oxalic acid] (**Table 1**). It is not surprising from

Table 1. Values of k_{obs} as a function of [oxalic acid], [CTAB] and [Ag+] for the Ag-NP formation at 30°C.

10^4 [oxalic acid] (mol·dm^{-3})	10^4[CTAB] (mol·dm^{-3})	10^4[Ag$^+$] (mol·dm^{-3})	pH	$10^4\ k_{obs}$ (s^{-1})
0.0	8.0	2.0	3.2	0.0
4.0			3.2	7.2
6.0			3.4	7.2
8.0			3.3	7.1
10.0			3.3	7.0
12.0			3.2	7.4
14.0			3.3	7.3
20.0			3.2	7.3
4.0	2.0	20	3.3	3.1
	4.0		3.2	4.6
	6.0		3.1	5.8
	8.0		3.2	7.2
	10.0		3.1	6.2
	12.0		3.0	4.8
	14.0		3.3	3.6
	16.0		3.2	yellowish turbidity
	20.0		3.1	yellowish turbidity
4.0	8.0	4.0	3.1	no yellow color
		8.0	3.3	4.1
		10.0	3.3	5.4
		12.0	3.1	6.6
		14.0	3.2	6.6
		16.0	3.1	6.8
		20.0	3.2	7.2

the fact that oxalic acid is a weak acid. Spectra of silver sol solution possess a surface resonance plasmon (SPR) band in the vicinity of 375 to 450 nm [36]. When AgNO$_3$ (20.0×10^{-4} mol·dm^{-3}) and CTAB (10.0×10^{-4} mol·dm^{-3}) reaction solution was allowed to react with oxalic acid (4.0×10^{-4} mol·dm^{-3}) in the absence and/or presence of ammonia (from 0.0 to 60.0×10^{-4} mol·dm^{-3}), the colorless reaction solution became transparent yellow. UV-visible spectral studies (**Figure 1**) showed that the AgNO$_3$-oxalic acid redox reaction resulted in SRP band at 425 nm which was assigned to the Ag-NP [36]. It should be emphasized here that before examining the effect of electrolytes and ammonia on the stability and growth of Ag-NP, the reaction was studied without adding any agents too.

3.2. Effect of Reactant Concentrations and Mechanism

Reduction of Ag$^+$ ions by oxalic acid has been studied kinetically as a function of [oxalic acid], [AgNO$_3$] and
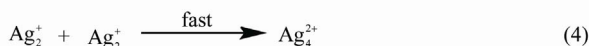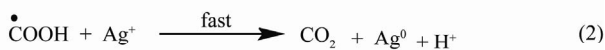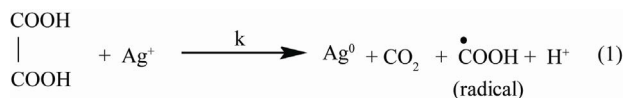
[CTAB]. The apparent first-order rate constant (k_{obs}, s^{-1}) were determined from the slopes of ln[a/(1-a) versus time plots [37,38]. The rate constant remained unchanged with increase in [oxalic acid] (**Table 1**), showing first-order dependence with respect to [oxalic acid]. Interestingly, as the [CTAB] increased from 2.0×10^{-4} mol·dm^{-3} to 14.0×10^{-4} mol·dm^{-3}, k_{obs} increases, until it reaches a maximum, and then decreases monotonically due to the dilution effect. Kinetic determinations at higher [CTAB] ($\geq 16.0 \times 10^{-4}$ mol·dm^{-3}) were hampered due to the formation of yellowish turbidity (**Table 1**). We did not observed the formation of yellow color at [AgNO$_3$] = 2.0×10^{-4} mol·dm^{-3}. From these data, the over all mechanism for the reaction can be represented in **Scheme 1**.

3.3. Salt Effect Results

Inert salts, especially the inorganic ones, act as catalysts or inhibitors in the micelle mediated reactions [39,40]. Therefore, to see the effects of NaCl, NaBr, NaNO$_3$, Na$_2$SO$_4$ and NaH$_2$PO$_4$ on the rate of Ag-NP, different
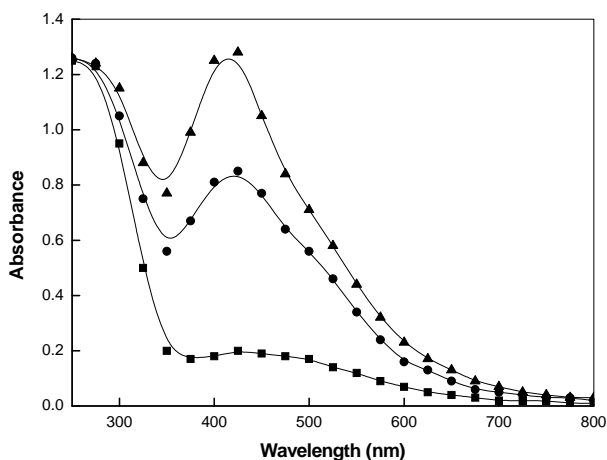
Figure 1. UV-visible spectra of Ag-NP for [oxalic acid] = 4.0 × 10⁻⁴ mol·dm⁻³, [Ag⁺] = 20.0 × 10⁻⁴ mol·dm⁻³ and CTAB = 10.0 × 10⁻⁴ mol·dm⁻³ as a function of time 20 (■), 40 (●) and 60 min (▲) at 30°C.

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + Ag^+ \xrightarrow{k} Ag^0 + CO_2 + \overset{\bullet}{C}OOH + H^+ \quad (1)$$
$$\text{(radical)}$$

$$\overset{\bullet}{C}OOH + Ag^+ \xrightarrow{fast} CO_2 + Ag^0 + H^+ \quad (2)$$

$$Ag^0 + Ag^+ \xrightarrow{fast} Ag_2^+ \quad (3)$$

$$Ag_2^+ + Ag_2^+ \xrightarrow{fast} Ag_4^{2+} \quad (4)$$

Scheme 1. Reduction of Ag⁺ by oxalic acid.

amounts of these salts were added to the reaction mixture at 8.0×10^{-4} mol·dm⁻³ CTAB. Reaction solution became turbid in presence of NaCl or NaBr ($\geq 2.0 \times 10^{-2}$ mol·dm⁻³), which increases with these salts due to the strong Cl⁻ or Br⁻ ions affinity for Ag⁺ ions. The curves are explained by taking into account two effects of anions, First, exclusion of reactants from the reaction site (*i.e.*, Stern layer, as most of the ionic micelle mediated reactions are believed to occur in this region). As we increase the [electrolytes], the NO_3^-, SO_4^{2-} and $H_2PO_4^-$ will try to get incorporated into the reaction site through electrostatic interactions, which are the normal behaviors found in the literature [39-41]. Second, Fermi level of particles increases with a rise in the concentrations of nucleopilies (NO_3^-, SO_4^{2-} and $H_2PO_4^-$) due to the adsorption of these anions on to the surface of Ag-NP [23]. Hence, the k_{obs} decrease as the [electrolytes] increases. The difference in the action of NO_3^-, SO_4^{2-} and $H_2PO_4^-$ ion is due to the fact that $H_2PO_4^-$ is specifically, *i.e.*, high polarizability, incorporated into the reaction site [42].

The adsorption of additives on colloidal silver parti-

cles in aqueous solution is accompanied by strong optical changes. The SRP absorption band is damped and its maximum is shifted to shorter or longer wavelengths, depending on the nature of the adsorbed species and its concentrations [21-25, 43, 44]. Stability of the Ag-NP in presence of these salts was also investigated (**Figure 2**). The SRP band remains unaffected in presence of NaNO₃ or NaH₂PO₄ (from 25.0×10^{-3} to 75.0×10^{-3} mol·dm⁻³). The intensity of SRP decreased sharply and the spectrum became broader at low concentrations of Na₂SO₄. The peak intensity was enhanced (hyperchromic-shift) by in-creasing the [Na₂SO₄] from 25.0×10^{-3} to 75.0×10^{-3} mol·dm⁻³. When mono-valent anions (e.g., NO_3^- or $H_2PO_4^-$) are added into the Ag-NP solution, they adsorb onto the surface of silver cluster, Ag_4^{2+}, without affecting the nano-particle dispersivity and no change is observed in SRP band. The bivalent anions such as SO_4^{2-}, causes the interaction of one anion with several Ag-NP at low concentrations, such type of multi-interaction causes the aggregation of free Ag-NP, which in turn, decreases the intensity of SRP band. When the anion concentration is increased, enough anions adsorb onto the surface of Ag-NP and a charge reversal of the shell occurs. As a result, redispersal of the Ag-NP occurs. Consequently, intensity of SRP band increases. Interestingly, no turbid solution of AgCl or AgBr was detected in presence of NaCl or NaBr. This result indicated that essentially all Ag⁺ ions were transformed to the Ag⁰ during the redox process and/or adsorbed on the surface of silver cluster, *i.e.*, Ag_4^{2+}. Thus, we may safely conclude that Cl⁻ or Br⁻ ions could not detach the adsorbed Ag⁺ from the Ag_4^{2+} [37]. In case of NaCl, hyperchromic- and blue-shift of the intensity and SRP band were observed with increasing the [NaCl], respectively. Immediately after addition of NaCl the stronger SRP band centered at ca. 425 nm changed into a broad absorption shoulder at about 400 nm. On the other hand, different behavior was observed for NaBr. No absorption at 425 nm of colloidal silver appeared. It thus seems that the Ag-NP is rather unstable in presence of NaBr under the same [NaCl] and is rapidly converted into larger particles. This red-shift is attributed to the strong interactions between the adsorbed Ag⁺ and Br⁻ ions on the surface of Ag_4^{2+}, the nucleoplilicity of the Br⁻ ion is better than that of Cl⁻ ion [45,46]. The surface neutralization or adsorption slightly induces the particle aggregation, as reflected by the shift of SPB. It should be emphasized that the solutions were non-opalescent before as well after the addition of Br⁻ as viewed by the naked eye.

3.4. Ammonia Effect Results

Ammonia is a mandatory reagent for silver-mirror reac-
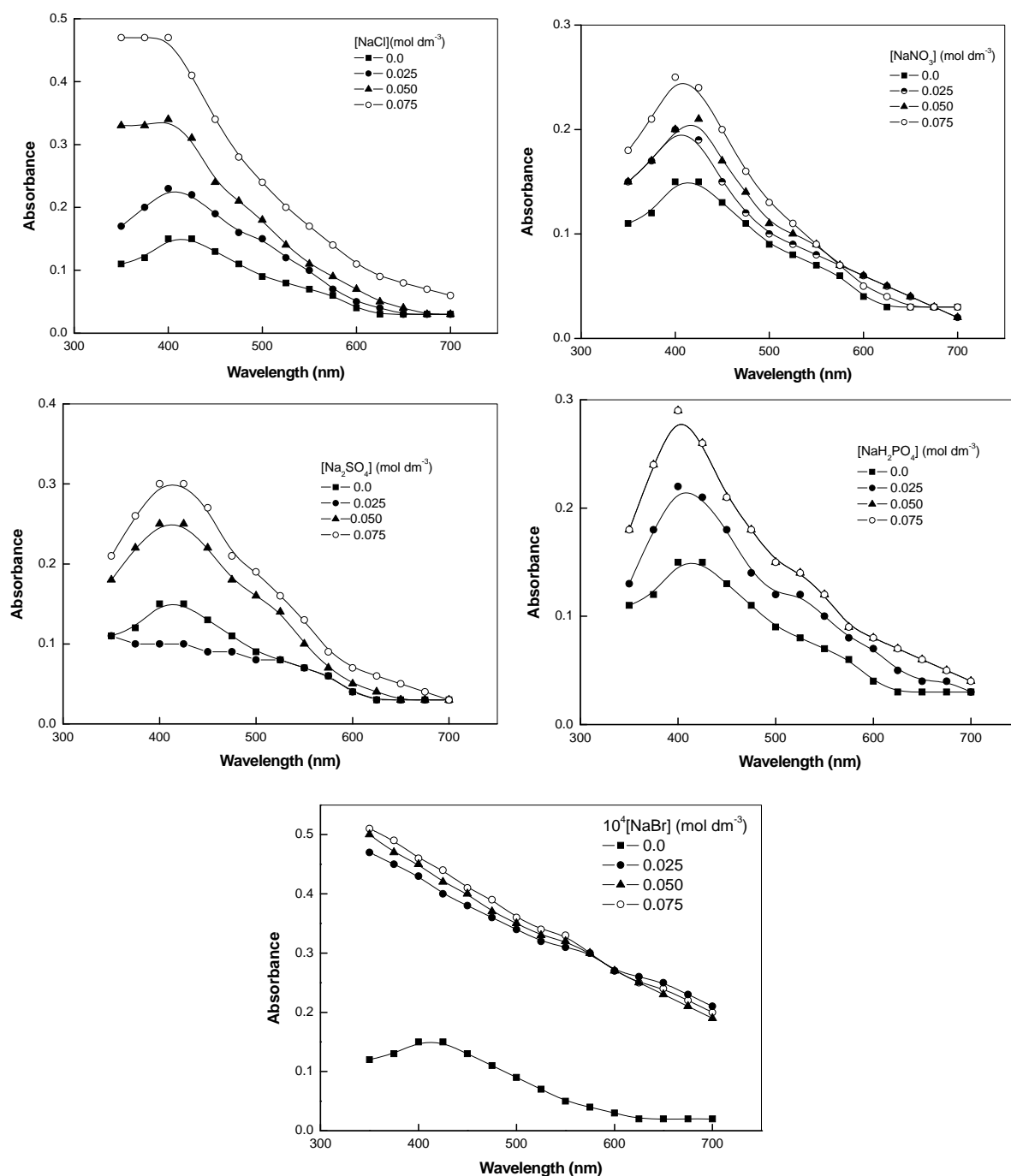
Figure 2. Effect of [electrolytes] on the surface plasma resonance band of Ag-NP. The concentration of Ag-NP was diluted from the original solution by 4 times.
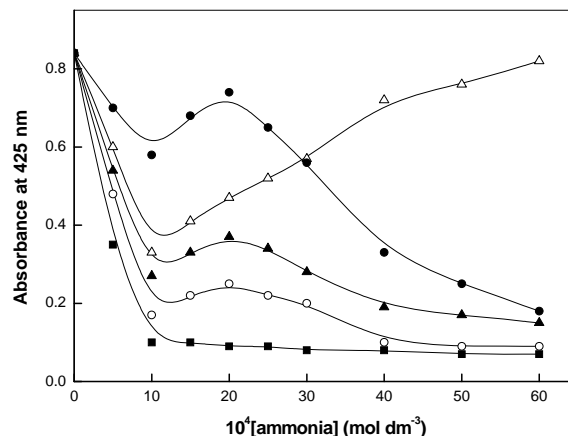
tion and their concentration play a major role in controlling the Ag-NP size and shape [27,47-49]. In order to gain insight into the role of ammonia, the oxalic acid-silver(I) reaction was also studied in presence of [ammonia]. The evolution of the absorption spectra with time is presented in **Figure 3** in an ammonia solution containing 4.0×10^{-4} mol·dm^{-3} oxalic acid, 20.0×10^{-4} mol·dm^{-3}

AgNO$_3$ and 10.0×10^{-4} mol·dm^{-3} CTAB. As shown in **Figure 1** the SRP band centered at about 425 nm decreased in intensity and shifted to shorter wavelengths with increasing time (blue shift of about 15 nm). It seemed possible that the decrease in the intensity was related to the complexation of ammonia with Ag$^+$ ions during the course of reaction. To conform this hypothesis,
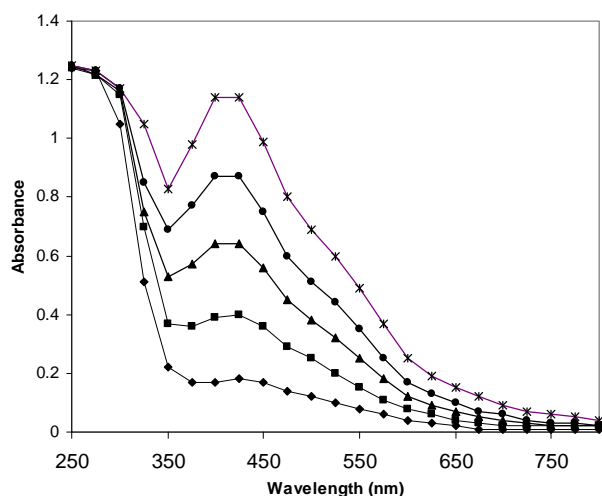
Figure 3. UV-visible spectra of Ag-NP for [oxalic acid] = 4.0 × 10^{-4} mol·dm^{-3}, [Ag$^+$] = 20.0 × 10^{-4} mol·dm^{-3} and CTAB = 10.0 × 10^{-4} mol·dm^{-3} in presence of [ammonia] = 20.0 × 10^{-4} mol·dm^{-3} as a function of time 20 (♦), 40 (■), 60 (▲), 80 (●) and 100 min (*) at 30°C.

Figure 4. Effect of [ammonia] on the surface plasmon resonance absorbance. *Reaction conditions*: [oxalic acid] = 4.0 × 10^{-4} mol·dm^{-3}, [Ag$^+$] = 20.0 × 10^{-4} mol·dm^{-3} and CTAB = 8.0 × 10^{-4} mol·dm^{-3} under different order of ammonia mixing: (1) Ag$^+$, CTAB, oxalic acid and ammonia (time = 20 (▲) and 60 min(●), (2) Ag$^+$, CTAB, ammonia and oxalic acid (time = 20 (○) and 60 min (△) and (3) Ag$^+$, CTAB, ammonia and oxalic acid after 10 min (■).

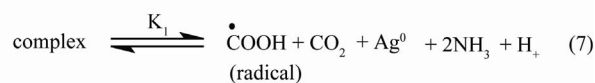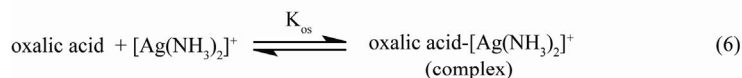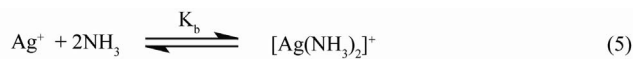the experiments were performed under different conditions: (i) addition of oxalic acid followed by ammonia and vice versa and (ii) allowing ammonia and Ag$^+$ ions reaction to proceed for 10 min, followed by addition of 4.0 × 10^{-4} mol·dm^{-3} oxalic acid. Observations of these experiments are summarized in **Figure 4**, as absorbance- and k$_{obs}$-[ammonia] profiles. At 425 nm, the absorbance first decreased then increased continuously and decreased with [ammonia], respectively, for the certain reaction time *i.e.*, 60 and 20 min, to the experimental condition (i) (**Figure 4**, ○ and ●) whereas the absorbance first decreased until it reached a maximum then decreased with [ammonia] to the addition of ammonia followed oxalic acid (**Figure 4**, ▲). For the reaction conditions (ii), absorbance decreased progressively with [ammonia] (**Figure 4**, ■). The reduction of Ag$^+$ ions by oxalic acid results in a fast formation of Ag-NP. Spectroscopic and kinetic results (**Figures 1**, **3**, **4**) show that in the presence of ammonia the reduction rate is slower and that significant changes in the reactivity of Ag$^+$ ions occur in solutions containing ammonia. It is clear that ammonia play a crucial role in the reduction of Ag$^+$ ions by oxalic acid. In the presence of ammonia the Ag$^+$ ions are expected to form [Ag(NH$_3$)$_2$]$^+$ [50]. The intensity and rate of the Ag-NP decreased after the addition of ammonia, indicating that the formation of [Ag(NH$_3$)$_2$]$^+$ species, which ultimately decreases the reduction potential of Ag$^+$ ions as well as the generation of metallic silver at the early stages of the reaction (separates the Ag$^+$ ions from the oxalic acid). Instant and/or after 10 min addition of oxalic acid into the reaction solution (AgNO$_3$ and ammonia) also decreases the intensity and rate of Ag-NP

formation (● and ▲). At higher [ammonia] ≥ 30.0 × 10^{-4} mol·dm^{-3}, there is no significant changes in the reaction rate. On the basis of these observations, we may safely concluded that oxalic acid is capable to reduce Ag$^+$ to Ag^0. In presence of ammonia there is a competition between oxalic acid and ammonia to react with Ag$^+$. Obviously, ammonia has strong affinity towards Ag$^+$ and small time is enough to form [Ag(NH$_3$)$_2$]$^+$. Complexation lowers the reduction potentials to such an extent that the reactive site (electrons gaining tendency) of Ag$^+$ is partially blocked by the presence ammonia molecules in [Ag(NH$_3$)$_2$]$^+$ [50] but not totally prevent the Ag$^+$ reduction. These results are also in agreement with the idea that once a metal atom which acts as a nucleation center is formed; it acts as a catalyst for the reduction of remaining metal ions present in solution via autocatalysis [51].

In presence of ammonia, **Scheme 1** mechanism can be modified as **Scheme 2**.

The direct oxidation of oxalic acid by [Ag(NH$_3$)$_2$]$^+$ is not possible. Thus, the reaction may generally be expressed by Equation (6) (K$_{os}$ is the rapid equilibrium for the encounter complex formation between the redox couple [52]). By analogy with previous results [52], we assume that complex decomposes in a rate-determining one-step one-electron oxidation-reduction mechanism to give Ag^0 and corresponding radical due to the sacrificial electron donor's property of oxalic acid.

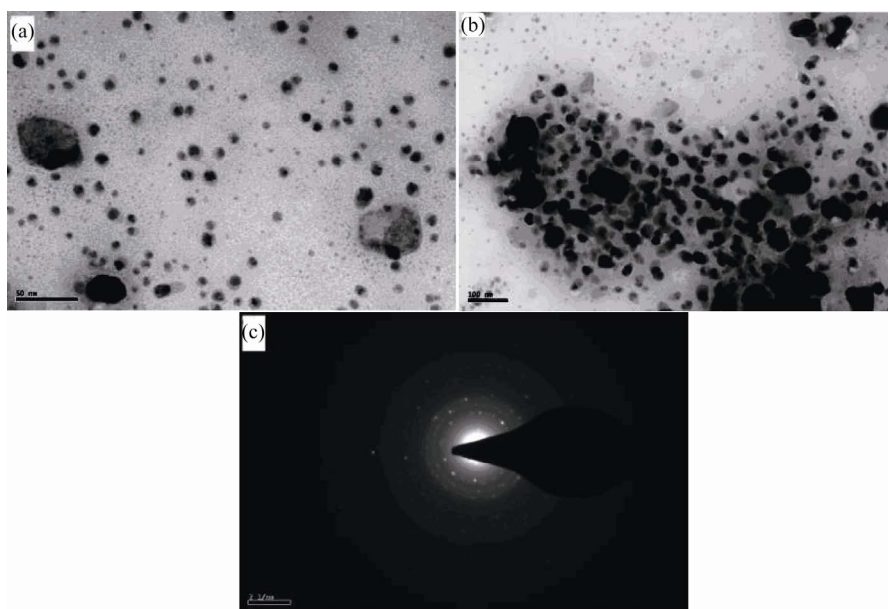### 3.5. TEM Images

Figures 5 and **6** show TEM images of silver sol (or ange-

$$Ag^+ + 2NH_3 \xrightleftharpoons{K_b} [Ag(NH_3)_2]^+ \quad (5)$$

$$oxalic\ acid + [Ag(NH_3)_2]^+ \xrightleftharpoons{K_{os}} oxalic\ acid\text{-}[Ag(NH_3)_2]^+ \quad (6)$$
$$(complex)$$

$$complex \xrightleftharpoons{K_1} \overset{\bullet}{C}OOH + CO_2 + Ag^0 + 2NH_3 + H_+ \quad (7)$$
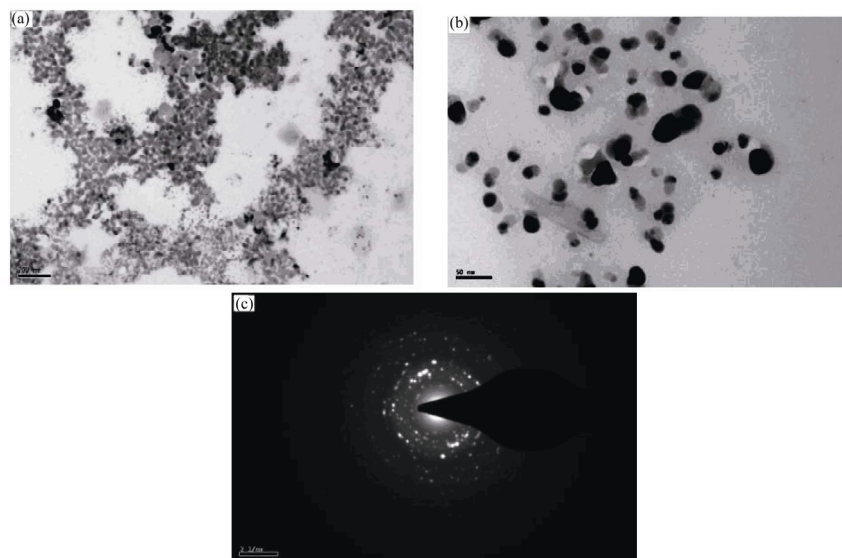$$(radical)$$

(Radical follows the same reaction as shown in Scheme 1)

Scheme 2. Oxidation of oxalic acid by Ag-ammonia complex.

Figure 5. TEM images of Ag-NP. *Reaction conditions*: [oxalic acid] = 4.0×10^{-4} mol·dm^{-3}, [Ag$^+$] = 20.0×10^{-4} mol·dm^{-3} and CTAB = 10.0×10^{-4} mol·dm^{-3}.

Figure 6. TEM images of Ag-NP. *Reaction conditions*: [oxalic acid] = 4.0×10^{-4} mol·dm^{-3}, [Ag$^+$] = 20.0×10^{-4} mol·dm^{-3} and CTAB = 10.0×10^{-4} mol·dm^{-3} in presence of [ammonia] = 20.0×10^{-4} mol·dm^{-3}.

red color prepared by the oxalic acid-Ag$^+$ reaction in absence and presence of ammonia). One can see well-dispersed spherical Ag-NP, with size ranging from 3.5 to 9 nm and a monodisperse size distribution can be easily evidenced from the TEM image of **Figure 5(a)**. The sol is quite polydisperse. The monodispersity is manifested also in the 2D hexagonal colloidal assemblies observed in most of the micrographs we scanned [53]. As can be seen in **Figure 6(a)** and **(b)** (typical example), show that the particles are spherical, polydispersed, and small-sized of diameter *ca.* 16 nm in presence of ammonia. Interestingly, the CTAB stabilized Ag-NP were formed faster than in the CTAB + ammonia containing silver sols. TEM image of **Figure 6(a)** also reveal that these Ag-NP aggregate and/or deposited onto the surface of particles in an unsymmetric manner to form necklace-like structure. Such type of aggregation we did not observed without ammonia. Presence of ammonia, decreased the nucleation rate, because the ammonia present in the reaction mixture reduce the reduction potential of Ag$^+$ ions which inhibit the particle nucleation and growth (**Table 1**). As a result, the size of the particles is higher in presence of ammonia. Comparison of spectroscopic, kinetic and TEM data clearly indicates that the shape, the size distribution, nature of reaction-time curves, mechanism, aggregation, and polydispersity strongly depends on the presence of [ammonia]. The crystalline nature of the Ag-NP was revealed by the electron diffraction patterns. The typical selected-area diffraction pattern are shown in **Figures 5(c)** and **6(c)** and it clearly exhibited diffraction rings with interplanar spacing The rings patterns are consistent with the plane families {110}, {111}, {200}, {220}, {311}, {331} and {422}, of pure face-centred cubic silver structure in absence and presence of ammonia [54, 55].

4. Conclusions

The silver nanoparticles were prepared based on the reduction reaction of silver nitrate and oxalic acid using CTAB as a stabilizing agent. Additives and ammonia plays a major role in this method and their concentrations are an important parameter to determine the growth rate. TEM and selected area electron diffraction confirmed that formation of spherical, aggregated and face-centered-cubic Ag-NP, respectively. The AG-NP is stable in $NaNO_3$ and NaH_2PO_4 solutions but the presence of NaCl, NaBr and Na_2SO_4 causes their aggregation.

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