Citrate ions and chloride ions involved in the synthesis of anisotropic silver nanostructures

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Anisotropic metal nanoparticles are of considerable interest to researchers because of their unique optical, electronic and catalytic properties compared with spherical nanoparticles. This Letter describes how chloride ions and citrate ions can be added to silver (Ag) nitrate solution to synthesise anisotropic silver nanostructures especially to form the Ag nanowires (AgNWs) without high hydrothermal or solvothermal operating temperatures. The AgCl colloidal precipitates were produced in the initial stage promoting the reduction of free silver ions and helping control silver ions at low concentration for the growth of AgNWs. The synthesis of AgNWs was also temperature and hydroxide radical dependent since the citrate ions could direct the growth of AgNWs at proper temperatures (over 130°C) in the absence of chloride ions. Transmission electron microscopy and UV–vis absorption spectra have been used to investigate the obtained products. The experimental results suggested that the chloride ions played a crucial role in directing the growth of anisotropic Ag nanostructures.

1. Introduction: In the past few decades, silver (Ag) nanostructures have attracted widespread interest because of their unique physicochemical and biological properties [1, 2]. In particular, anisotropic Ag nanostructures such as nanorods [3], nanoplates [4], nanoantennas [5] and nanowires [6] have been extensively explored for surface-enhanced Raman scattering (SERS) and antibacterial compounds [7]. A variety of methods have been exploited to prepare anisotropic Ag nanostructures in the solution phase by using a soft or hard template [8–11]. In addition, templateless approaches have also been achieved by adding seeds and/or shape-directing capping agents [12]. For example, Murphy and co-workers, in 2003, [13] reported for the first time the synthesis of Ag nanowires (AgNWs) in the absence of a surfactant or polymer template and without externally added seed crystallites. Ren *et al.* [14] reported the mass synthesis of Ag dendrites with a templateless wet-chemical method. Recently, Lopez-Miranda *et al.* [15] studied the synthesis of Ag nanostructures using citrate ions and Cu^{2+} ions without the template. Moreover, Liz-Marzan and co-workers [16] emphasised that the halide ions directed the anisotropic growth of metal nanocrystals in seeded growth syntheses.

In the context of these research reports, we have attempted to prepare Ag nanostructures mainly AgNWs using citrate ions and chloride ions without using external templates or seeds and without high reaction temperatures. The mechanism of the synthesis of Ag nanostructures with citrate and chloride ions is discussed in this Letter. Moreover, transmission electron microscopy (TEM) and UV–vis absorption spectra were employed to characterise the obtained Ag nanostructure.

2. Experimental procedures: All chemicals were of analytical reagent grade and used without further purification. E-pure water (18.2 MΩ·cm) was produced by a Millipore Simplicity-185 ultrapure-water purification system. For a typical synthesis of Ag nanostructures, 100 µl of Ag nitrate solution (0.1 M) was added to a tinfoil-masked round bottom flask with 50 ml of deionised H_2O. This solution was immersed into a boiling water bath with rapid stirring for a preheat treatment of 20 min and then 100 µl of sodium citrate solution (0.1 M) and 50 µl of sodium chloride solution (0.1 M) were added into the boiled solution. The boiled mixture solution was continuously stirred for 1 h with a magnetic stirrer. Next, the reactor was cooled down to room temperature. The obtained products were used for further characterisation.

TEM was utilised to characterise the overall morphology of the samples. The TEM images were captured using a PHILIPS TECNAL-10 electron microscope operating at 100 kV. The UV–vis spectra of the colloidal Ag solutions were obtained using a SHIMADZU UV-2550 spectrophotometer with a 1 cm quartz cell at room temperature.

3. Results and discussion: Sodium citrate (Na_3Ct) was both the reducing agent of Ag ions and the capping agent of metallic Ag. Fig. 1 shows the scheme for the formation of Ag nanostructures. First, when sodium citrate and sodium chloride (NaCl) were added to the boiled $AgNO_3$ solution system, Cl^- ions and citrate (Ct^{3-}) would react with Ag^+ to generate AgCl aggregates and Ag/citrate complex in situ (1) and (2), although the solubility product (K_{sp}) of the AgCl in water was 1.2×10^{-6} (100°C) and the solubility of the Ag/citrate complex was 0.0285 g/l (25°C) [12, 17]. The ionisation equilibriums of the AgCl and the Ag/citrate complex were also presented in the solution system (1) and (2). Secondly, the initially generated AgCl precipitation could serve as 'seeds' for the synthesis of Ag nanoparticles. In the boiling solution system, the free Ag^+ ions, AgCl colloidal precipitation and Ag/citrate complex were reduced to Ag nanostructures and the oxidation product of citrate. Thirdly, the dissociative chloride ions played a crucial role in the growth processes and acted as face-specific capping agents to promote the synthesis of anisotropic Ag. Finally, the colourless transparent reaction solution changed to a grey-coloured suspension, indicating the formation of anisotropic Ag nanostructures. The overall chemical reaction can be described by (3)

$$Ag^+ + Cl^- \Leftrightarrow AgCl \tag{1}$$

$$Ag^+ + C_6H_5O_7^{3-} \Leftrightarrow Ag^+/C_6H_5O_7^{3-} \text{ complex} \tag{2}$$

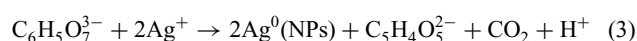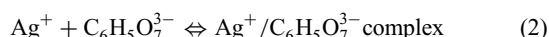$$C_6H_5O_7^{3-} + 2Ag^+ \rightarrow 2Ag^0(NPs) + C_5H_4O_5^{2-} + CO_2 + H^+ \tag{3}$$

Fig. 2 shows the typical TEM images of the obtained samples at different concentrations of NaCl. Increasing the amount of NaCl in the reaction mixture led to increased nanowire yield. There were a lot of quasi-spherical nanoparticles with a diameter of 62–80 nm and a few nanorods with an aspect ratio of about 12 when only 2 µl of
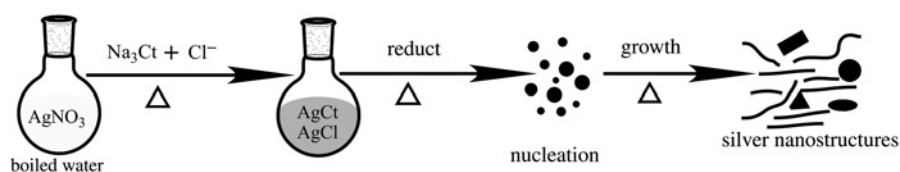
Figure 1 *Schematic illustration of the synthesis of Ag nanostructures with citrate and chloride ions*

NaCl was added (Fig. 2a). In Fig. 2b, it is clearly shown that AgNWs with a diameter of about 22 nm (based on the magnified image) were successfully synthesised by relatively large quantities of NaCl added (10 μl of 0.1 M NaCl). The length of the nanowires grew from about 0.6 to 1.5 μm. For the highest concentration of NaCl (50 μl of 0.1 M NaCl) added, the AgNWs with over 3 μm in length and about 20 nm in width were present (Fig. 2c). The average aspect ratio was about 140. The ratio of AgNWs, nanoparticles and nanorods was estimated to be 65:65:20 based on the measurement of 150 nanostructures. From Fig. 2d, it is seen that the peaks observed at 415, 428 and 442 nm corresponded to the surface plasmon resonance (SPR) band of the Ag nanoparticles synthesised at different amounts of NaCl. Especially, the UV–vis spectra of Ag colloid showed a broad band at 428 nm with over 10 μl of NaCl. A shoulder peak at 350 nm was an optical characteristic of bulk Ag. The plasmon absorption peak at about 370 nm was also observed. According to the previous study, the UV–vis spectra of the AgNWs solution had a sharp peak at 370 nm corresponding to the transverse plasmon band of the wires [13]. The observed multiple peaks in the same spectrum indicated that the final products were mixtures of Ag nanorods or nanowires and spherical particles. These results correlated well with the observed nanostructures in the TEM. This dependence of nanowires on the concentration of chloride can be understood by the following explanation. The addition of Cl$^-$ dramatically reduced the free Ag$^+$ ions in the reaction system by forming AgCl colloidal precipitate. The nano-AgCl precipitate functioned as seeds and accelerated the reduction of Ag$^+$ and the Cl$^-$ ions acted as 'controlling agents' to continuously keep a low Ag$^+$ concentration [18]. Meanwhile, according to the report of Tang *et al.* [19], the AgCl in the reaction system can be reduced to Ag atoms directly to obtain AgNWs. As the reaction progressed, the concentration of chloride was increased, and the chloride ions were thought to adsorb onto the side faces of the seeds and then confine the lateral growth of the nanorods or nanowires. As a result, AgNWs with a smaller diameter and a higher aspect ratio were synthesised.

In the absence of chloride ions, no matter how the molar ratio of Ag ions and citrate ions changed, there were no AgNWs present. Fig. 3 shows the TEM images of the Ag nanostructure samples synthesised with citrate without introducing Cl$^-$ ions, with various concentrations from 10 to 500 μl. The size of the nanoparticles was about 50 nm in all Ag nitrate and sodium citrate mixture solution, and only little short nanorods presented with the molar ratio of 2:1 and 1:1. In spite of this, many research teams have reported the preparation of AgNWs with only citrate ions using the hydrothermal method [12, 18–20]. The different results obtained were because of the different temperatures employed by each team. Our experiment was carried out in a boiling water bath (about 97°C) and the reported results were almost conducted at a temperature range of 130–200°C. Subsequently the reaction temperature was studied to demonstrate the distinction of the reaction.

In general, the system temperature had a significant influence on the reaction process and reaction kinetics. In addition, the result reported by Huang *et al.* [21] demonstrated that the elevated temperature affected the synthesis route and synthesis products. To verify this viewpoint, the influence of reaction temperature on the
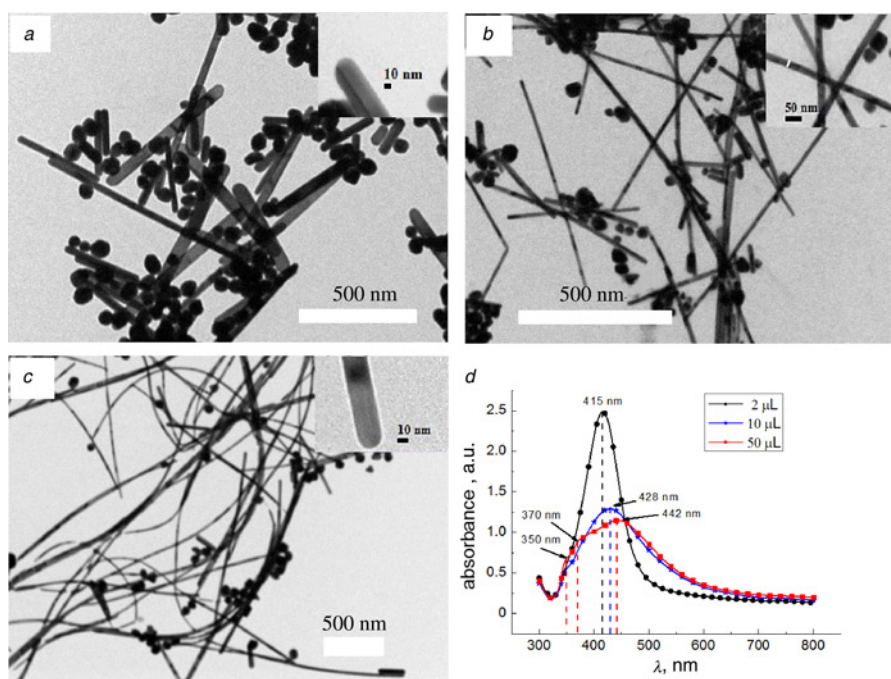

Figure 2 *TEM images of Ag nanostructures prepared at different amounts of NaCl: 2, 10 and 50 μl (Figs. 2a–c) (insets are the magnified images); corresponding UV–vis spectra of Ag nanostructures (Fig. 2d)*
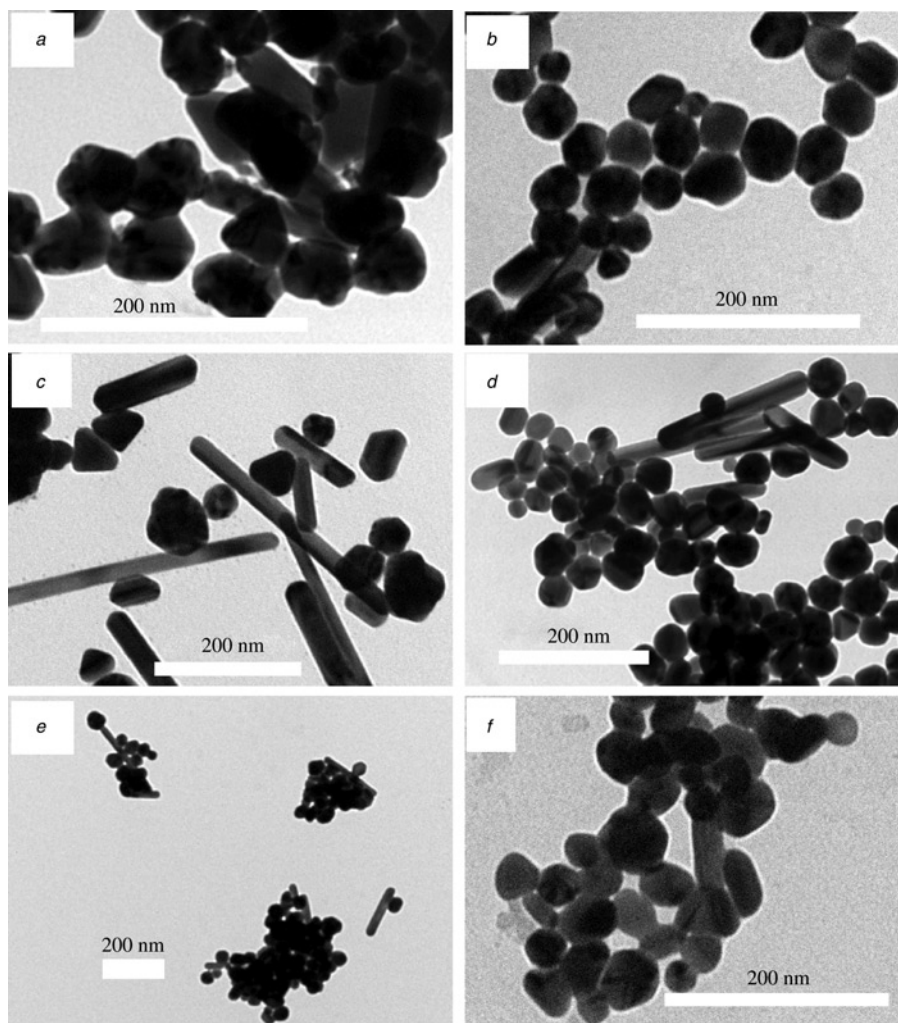
Figure 3 *TEM images of Ag nanostructures at different molar ratios of Ag$^+$ and citrate*
a 10:1
b 5:1
c 2:1
d 1:1
e 1:2
f 1:5

formation of AgNWs without NaCl was investigated. Regarding Fig. 4, the Ag nanostructures were prepared from 110 to 130°C with 100 µl of Ag nitrate and 50 µl of sodium citrate. On increasing the reaction temperature, the number of anisotropic Ag nanostructures increased markedly. Fig. 4a shows that Ag nanoparticles with an average size of 45 nm and a few nanorods with an aspect ratio of 9 were successfully prepared at 110°C. The Ag nanoparticles were gradually enlarged to ~75 nm and with increasing Ag nanorods as presented in Fig. 4b (120°C). The temperature raised up to 130°C led to the generation of appreciable AgNWs (Fig. 4c). Fig. 4d shows the UV–vis spectra of Ag nanostructures prepared at different temperatures. This result suggested that the synthesis temperature had an important role in the formation process of AgNWs.

Murphy and co-workers [13] reported that hydroxide, rather than sodium ion, had an important role in AgNW growth. Increasing the amount of NaOH in the reaction mixture led to a decreased nanowire yield. This phenomenon was also observed by Anker and co-workers [12] utilising the one-pot hydrothermal synthesis of AgNWs by adjusting the pH value of the reaction solution. It was also reported that increasing the pH for the preparation of metal nanoparticles resulted in the initiating and acceleration of the reduction [22, 23]. In addition, the additive of OH$^-$ ions reacted with Ag$^+$ to result in the formation of Ag$_2$O and was responsible for the formation of Ag nanoparticles in high concentrations [24]. In our experiments, the concentration of OH$^-$ ions was introduced by adding NaOH to the reaction solution. As shown in Figs. 5a and b, the reaction with no NaCl added gave products without AgNWs presented. Moreover, a few short nanorods were present by adding 2 µl of 1 M NaOH (Fig. 5a), and almost monodisperse spherical Ag nanoparticles were generated in the system by adding 10 µl of 1 M NaOH (Fig. 5b). At the same time, there was a decrease in the diameter of the formed nanoparticles. This phenomenon was in accordance with the literature which reports the formation of the AgNWs [12, 13]. Fig. 5c shows that the AgNWs were obtained by adding 20 µl of the NaCl and NaOH mixture. The results indicated that the Cl$^-$ ions added to the reaction system played a key role in determining the morphology of the products. Fig. 5d shows the corresponding UV–vis spectra of Ag colloids. The peak observed at 405 nm corresponds to the SPR band of the Ag nanoparticles (Figs. 5a and b). The spectrum with a peak at around 370 nm was observed because of the transverse plasmon band of the AgNWs as mentioned above (Fig. 5d). On the basis of the above results, it was clearly understood that the Cl$^-$ ions played a more crucial role in directing the growth of anisotropic metal nanostructures compared with the OH$^-$ ions at the high anion concentration range.
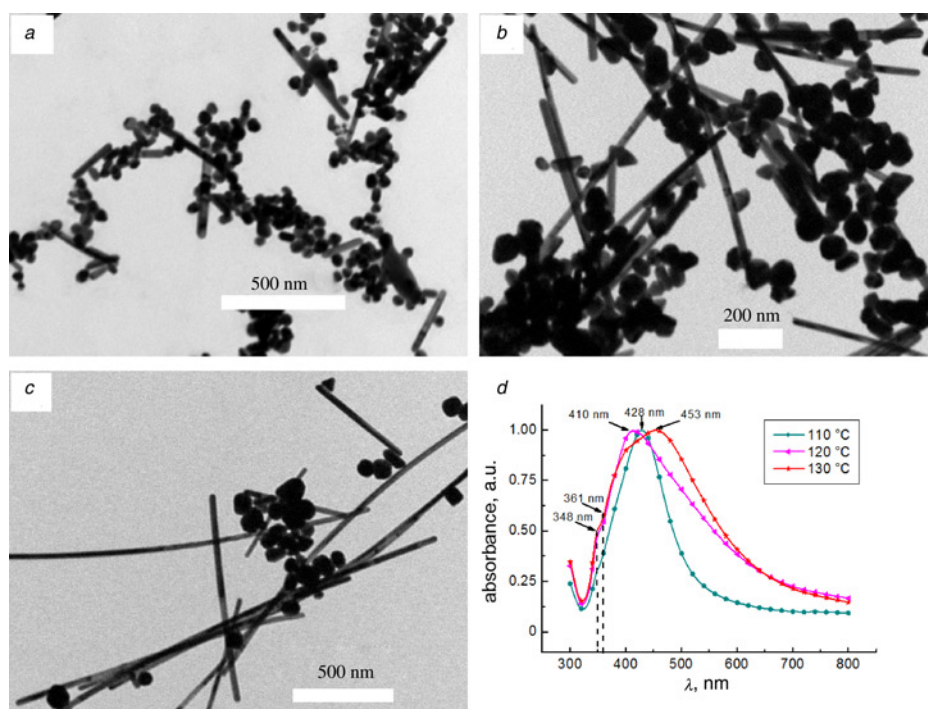
Figure 4 *TEM images of Ag nanostructures synthesis at temperatures of 110, 120 and 130°C, respectively (Figs. 4a–c); corresponding normalised UV–vis spectra of as-prepared Ag nanostructures (Fig. 4d)*
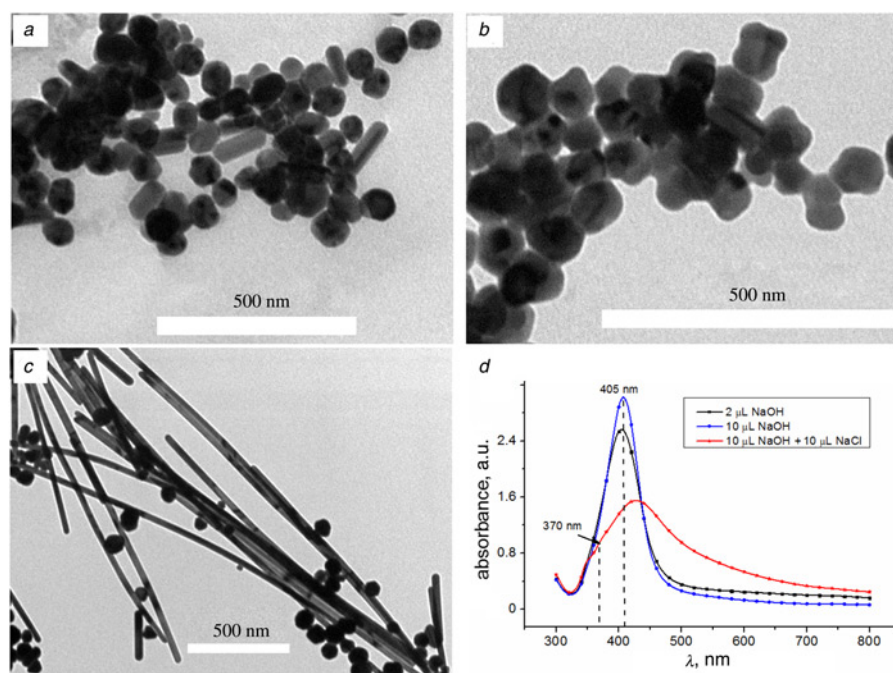

Figure 5 *TEM images of Ag nanostructures with different NaOH, 2 and 10 µl, respectively (Figs. 5a and b); 20 µl of NaCl and NaOH mixture (Fig. 5c); corresponding UV–vis spectra of Ag nanostructures (Fig. 5d)*

4. Conclusion: The citrate ions and chloride ions promoting the synthesis of an anisotropic Ag nanostructure were studied. Cl⁻ ions with a concentration of 0.2–5 µM introduced to the system were beneficial in the formation of AgNWs by controlling the Ag^+ concentration at a low concentration. Moreover, adding Cl⁻ ions rendered the preparation of AgNWs at below 100°C. In the absence of Cl⁻ ions, it was necessary to raise the temperature to more than 130°C to obtain AgNWs. This Letter demonstrates that Cl⁻ ions play an essential role in directing the growth of anisotropic metal nanostructures. We expect that the additive such as the halide ions will help to improve the synthesis of more monodisperse anisotropic Ag nanostructures and the obtained AgNWs can be extensively applied in the SERS, biosensors and photoelectron fields.

6 References

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