

# Real Time Kinetic Measurements of Silver Nanocluster Growth

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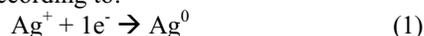
## ABSTRACT

Metallic clusters of noble metals are of tremendous technological importance due to their conduction properties, size, low reactivity and optical properties. Clusters containing as few as two and four silver atoms have been prepared in our laboratory by the reduction of the silver ion ( $\text{Ag}^+$ ) with  $\text{OH}^-$  in basic solution. The UV absorption spectra of  $\text{AgNO}_3$  /  $\text{NaOH}$  solutions are characterized by the appearance of UV absorption peaks at 275 and 310 nm, attributed to the formation of the tetramer di-cation  $\text{Ag}_4^{2+}$  and to  $\text{Ag}_2^+$  or small non metallic clusters ( $\text{Ag}_n$ ), respectively, and at about 380 nm due to the excitation of the silver plasmon in larger clusters. The 275 and 310 nm peak areas were found to be sensitive functions of initial  $\text{AgNO}_3$  and  $\text{NaOH}$  concentrations.

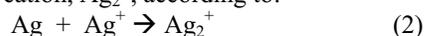
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## INTRODUCTION

There is a tremendous interest in the reactions and chemical intermediates that precede the formation of metallic clusters in solution, due to the possibility of controlling cluster sizes during the early stages of nucleation processes.<sup>2-6</sup> Silver clusters represent an excellent system to work for the development of experimental methodology for particle size growth because the intermediates involved in the synthesis of metallic silver particles from the reduction of the silver cation,  $\text{Ag}^+$ , in basic solution are well known.<sup>1</sup>  $\text{Ag}^+$  cations are reduced in basic solution to form single Ag atoms according to:



Silver atoms react with silver ions to form the silver dimer cation,  $\text{Ag}_2^+$ , according to:



The silver dimer can couple to other dimers to form a double charged tetramer,  $\text{Ag}_4^{2+}$ , according to:



Further reactions of silver metal atoms and the dimer and tetramer cations, result in the formation of small silver clusters ( $\text{Ag}_n$ ). Large, metallic, silver

clusters exhibit peak at 380 nm in UV absorption experiments due to the excitation of a plasmon. The silver dimer and tetramer exhibit UV absorption peaks at 310 and 275 nm, respectively. Small, non-metallic silver clusters have absorption peaks between 350 and 300 nm.

As part of our efforts in developing methods to control silver clusters sizes, we have begun studies aimed to obtain an understanding of the factors that control reactions 1, 2 and 3. We report here on systematic studies on the effect of initial  $\text{Ag}^+$  and  $\text{OH}^-$  concentrations on the amounts of the silver dimer and tetramer.

## EXPERIMENTAL

The  $\text{AgNO}_3$  and  $\text{NaOH}$  solutions used in the experiments were prepared by dissolving different amounts of the salts in gas-free water. For this rapid process we used a stopped-flow reaction analyzer (SFR), from Applied Photophysics Ltd., London, UK. This apparatus allows the study of fast chemical and biochemical reactions in liquid media. A photo diode linear array, with 256 elements, allowing a separation of 2.17 [nm], was used to obtain the complete spectra as a function of time. The equipment has less than 2 [ms] of dead time, and allows us to take ~800 spectra in a 1 [s] period.

## RESULTS

The dependence of the UV-Vis absorption spectra on time for mixtures of  $\text{AgNO}_3$  and  $\text{NaOH}$  are summarized on Figure 1. The bottom trace represents the UV-Visible absorption spectrum of the  $1 \times 10^{-2}$  M  $\text{AgNO}_3$  used in this work is indicated by the trace displayed on figure 1 for 0 seconds. Only a weak absorption peak due to the nitrate is observed in the spectrum. The trace shown for 0.001 seconds is obtained after the addition of a  $5 \times 10^{-3}$   $\text{NaOH}$  solution to the reaction cell. A peak centered at about 275 nm dominates the trace. A high wavelength shoulder at about 300 nm is observed in the trace. This shoulder develops into a peak in the trace obtained 0.03 seconds

after the addition of the NaOH to the AgNO<sub>3</sub> solution. The two peaks are clearly identified in the trace obtained 1.0 second after the mixture has been prepared.

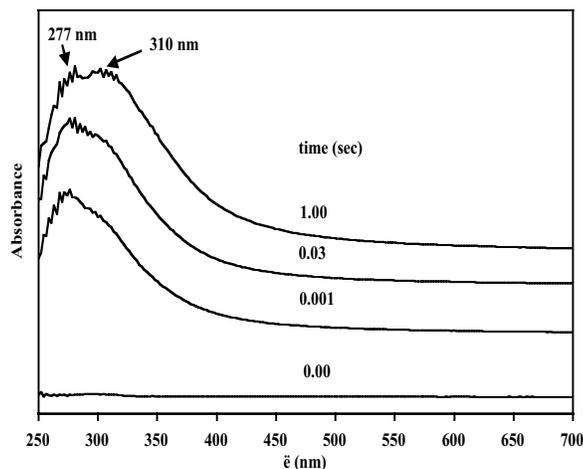


Figure 1: Real time UV absorption spectra following the reaction of  $1 \times 10^{-2}$  M AgNO<sub>3</sub> with  $5 \times 10^{-3}$  NaOH.

The two peaks shown on Figure 1 have been observed in previous studies regarding the reduction of Ag<sup>+</sup> in basic solutions. Peaks at about 280 and 310 nm have been attributed to the formation of the Ag<sub>4</sub><sup>2+</sup> and Ag<sub>2</sub><sup>+</sup> cluster ions in radiolytic studies of Ag<sub>2</sub>SO<sub>4</sub>, respectively. Absorption peaks between 300 and 350 nm can also be attributed to the formation of small silver clusters (Ag<sub>n</sub>). To learn more about the species formed in the reduction of Ag<sup>+</sup> in basic solution, we have carried out the above reaction using a higher initial NaOH concentration.

To gain more information on the conditions that lead to the formation of the species responsible for the absorption peaks at 275 nm and 310 nm, the experimental data between 250 and 350 nm was modeled with two Gaussian curves in a Matlab environment. The width of each Gaussian used in the modeling was 17.8 and 26.0 nm for the 275 and 310 nm absorption peaks, respectively. Representative results from the fitting are summarized on Figure 2. The Gaussians have peaks at 270 and 312 nm. The difference between the sum of the two Gaussians and the experimental data was less than 5 % at the each peak maximum.

We have use modeling like the one displayed on figure 2 to establish the time dependence of the 275 and 310 nm absorption peak areas. Representative results are summarized on figure 3. The 275 and 310 nm peak areas increase with time up to about 0.25 seconds. After that time, the 275 and 310 nm peak areas decreased slowly. The 275 and 310 nm maximum peak areas, and the time required to reach maximum peak areas, were found to be sensitive functions of the initial AgNO<sub>3</sub> and NaOH concentrations.

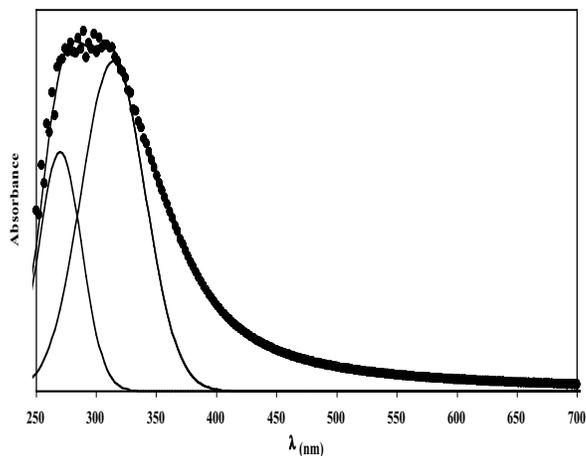


Figure 2: The dense dots show a typical UV trace for the reaction between  $1 \times 10^{-2}$  Ag<sup>+</sup> and  $5 \times 10^{-4}$  OH<sup>-</sup>. The solid lines represent the Gaussian curves used to fit the UV absorption peak to a quantitative model. See text for details.

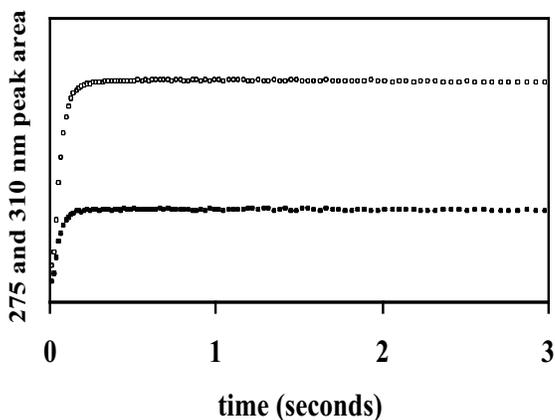


Figure 3: The dependence of the 275 (open circles) and 310 nm (closed circles) absorption peak areas on time following the addition function of initial AgNO<sub>3</sub> concentration. The NaOH concentration is  $5 \times 10^{-4}$  M.

Figure 4 show the dependence of the 275 and 310 nm maximum peak areas on the initial AgNO<sub>3</sub> concentration. The initial NaOH concentration for the experiments described on figure 4 is  $2 \times 10^{-3}$  M. The initial AgNO<sub>3</sub> concentration was varied as indicated on the figure. The maximum peak area corresponding to the 275 and 310 nm peaks were determined using the Gaussian fitting procedure described in the previous paragraphs. The 275 and 310 nm maximum peak areas increase with the of AgNO<sub>3</sub> concentration up to 0.01 M, when it starts to decrease.

A different behavior was observed in the dependence of the 278 and 310 nm maximum peak

areas on NaOH concentration, as illustrated on figure 4. The  $\text{AgNO}_3$  concentration was held fixed at  $1 \times 10^{-2}$  M for all the measurements described on figure 5. The NaOH concentration was varied as indicated on the figure. The 275 and 310 nm maximum peak areas increased with NaOH concentration in the range studied here.

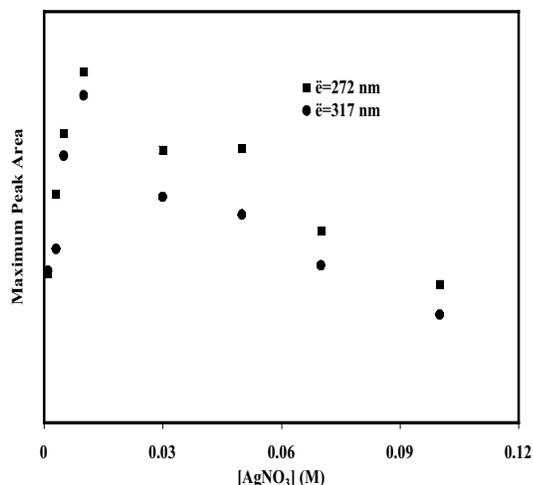


Figure 4: Dependence of the 275 and 310 nm maximum peak areas on initial  $\text{AgNO}_3$  concentration. The initial NaOH concentration is  $2 \times 10^{-3}$  M.

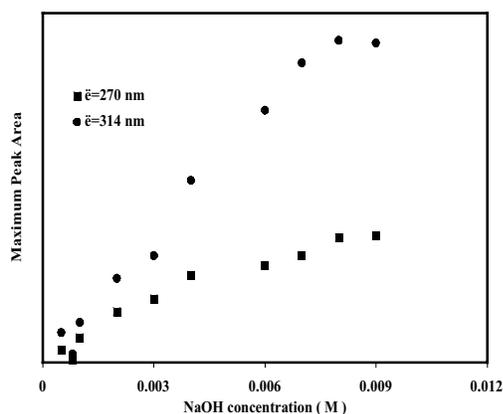


Figure 5: The dependence of the 275 and 310 nm maximum absorption peak areas as a function of NaOH concentration. The initial  $\text{AgNO}_3$  concentration is 0.01 M.

The time required for the 275 and 310 nm absorption peaks to reach a maximum was also found to increase nearly exponentially with initial  $\text{AgNO}_3$  concentration; it showed only a slight dependence on NaOH concentration.

## DISCUSSION

The reduction of  $\text{Ag}^+$  in basic solution has been studied with a stop flow reactor over a range of initial  $\text{AgNO}_3$  and NaOH concentrations. Peaks centered at 275 and 310 nm have been observed, consistent with previous work on  $\text{Ag}^+$  reduction. Belloni and co workers have attributed the 275 and 310 nm absorption peaks to  $\text{Ag}_4^{2+}$  and  $\text{Ag}_2^+$  species.<sup>1</sup> We have observed the 275 nm absorption peak in all our measurements and, frequently, at an earlier stage than the 310 nm absorption peak. In the context of the assignment proposed by Belloni and co workers, one would expect the 310 nm peaks to, at least, appear before the 275 nm absorption peak.<sup>1</sup> One explanation consistent with both results is that the formation of  $\text{Ag}_4^{2+}$  from the reduction of  $\text{Ag}^+$  in basic solution, in the concentration range studied here, may occur in a time scale shorter than a millisecond. Indeed, time scales for  $\text{Ag}^+$  reduction of a few nanoseconds have been reported.<sup>1</sup> If this reasoning is correct, then the 310 nm absorption peak can not be assigned to  $\text{Ag}_2^+$ .

UV absorption and fluorescence measurements of silver clusters, containing as few as eight atoms, have been recently measured in argon matrices.<sup>8</sup> The common feature in the UV absorption spectra of these clusters is the presence of a peak between 350 and 300 nm, well below the 380 nm plasmon peak characteristic of metallic silver. In the case of the  $\text{Ag}_8$  cluster, for instance, the position of the absorption maxima is located at about 320 nm. It is therefore possible that small, non-metallic clusters are responsible for the 310 nm absorption peak observed in our experiments. Further experiments are needed with modern probes to elucidate the details of the reactions involved in the reduction of  $\text{Ag}^+$  and the growth of metallic silver particles. Theoretical work regarding the optical properties of silver cluster ions, in particular the  $\text{Ag}_2^+$  and  $\text{Ag}_4^{2+}$  ion is now underway in our group.

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