

KINETIC STUDY OF Ag₂S FLUORESCENT NANOPARTICLES SYNTHESIS

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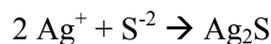
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Introduction

The synthesis of metal and semiconductor nanoparticles has received widespread attention by the scientific community due to the large number of technological applications they find in nanoscaled systems. The mechanism of nanoparticle growth is, in general, still an open question. Studies based on light absorption associated to silver, gold and ruthenium particle growth have been published. A few studies have relied on the fluorescence of semiconductor nanoparticles to monitor particle growth. These previous works have contributed significantly to the current body of knowledge related to the mechanism of nanoparticle growth.

The purpose of this work is to explore on the use real time-conductivity measurements as tool to measure the kinetics of nanoparticle growth. Conductivity measurements can be combined with optical measurements to estimate induction times. For this purpose, we have focused in the synthesis of Ag₂S from the reaction of silver cations, Ag⁺, with sulfide anions, S⁻². Ag₂S semiconductor nanoparticles absorb light deep in the UV (about 230-240 nm) and exhibit a strong fluorescence in the visible at low temperatures. Conductivity measurements on this synthesis are an attractive approach to study the mechanism of nucleation since the reaction:



results in the formation of an insoluble solid with a K_{SP} of the order of 10⁻⁵⁰. Thus a decrease in conductivity is expected to be observed in reaction mixtures of Ag⁺ and S⁻² as they form Ag₂S.

Experimental

Silver solutions were prepared by dissolving silver nitrite (ACS grade Fisher) in deionized water, obtained from a Culligam system. Sulfide solutions were prepared using ammonium sulfide solutions (Alfa Aesar) in deionized water. The concentration ranges of both solutions were from 8.0 x 10⁻²M to 1.0 x 10⁻³M. Reaction mixtures were studied in a Biologic Stop flow reactor model SFM 400. The reactor is equipped with cell suitable for UV-Visible light absorption measurements and two electrodes for conductivity measurements. UV-visible absorption measurements were performed with an Ocean Optic spectrometer coupled to the stop flow reactor with two UV grade fiber optics.

Results

The right and left hand side of figure 1 illustrates the dependence of conductivity, κ , on Ag^+ and S^{2-} concentration, respectively. The conductivity increases with ion concentration due to the increase in charge carriers in solution. Typically, the conductivity depends on concentration according to:

$$\kappa = \kappa_0 + \alpha c^{1/2} \quad \text{equation 1}$$

Where k is the conductivity, C is the ion concentration and κ_0 represents the limiting conductivity. The linear dependence of the silver and sulfide ion conductivity on the square root of the corresponding ion concentration was verified experimentally in this work. Limiting conductivities of about 1.0 and 1.6 mS/cm are found for the silver and sulfide ion, respectively

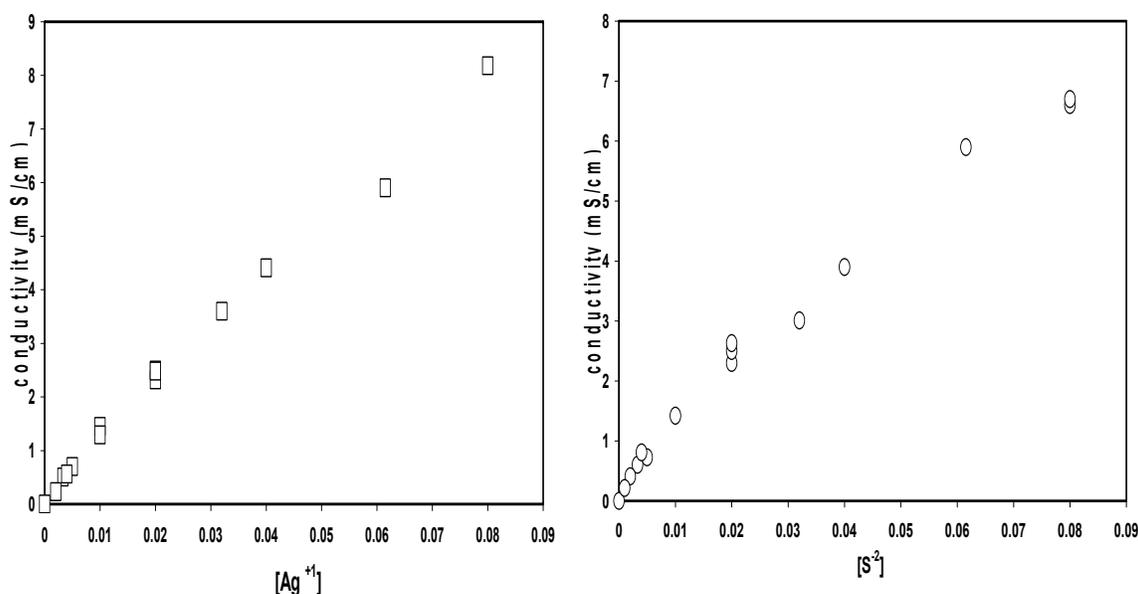


Figure 1. The right and left hand side illustrates the dependence of conductivity, κ , on Ag^+ and S^{2-} concentration, respectively.

The dependence of conductivity on time for a stoichiometric mixture of Ag^+ and S^{2-} is displayed on figure 2. A flow mixture is prepared in the reactor and at time $t = 0$ seconds the flow is brought to a stop. The optical absorption spectra the reaction mixture is also displayed on figure 2. The optical absorption spectra were measured at the times indicated by the arrows. There is no significant absorption of light at times $t \leq 0$ seconds. Independent experiments on Ag^+ and S^{2-} ions exhibit absorption bands at 228 and 237 nm, respectively. The 240 nm band dominates the optical absorption spectrum about 5 seconds after the flow is stopped. This is the only band observed for reaction times as long as 135 seconds, indicating that it represents the final product of the reaction between Ag^+ and S^{2-} . We attribute this band to the formation of Ag_2S , which is the thermodynamically

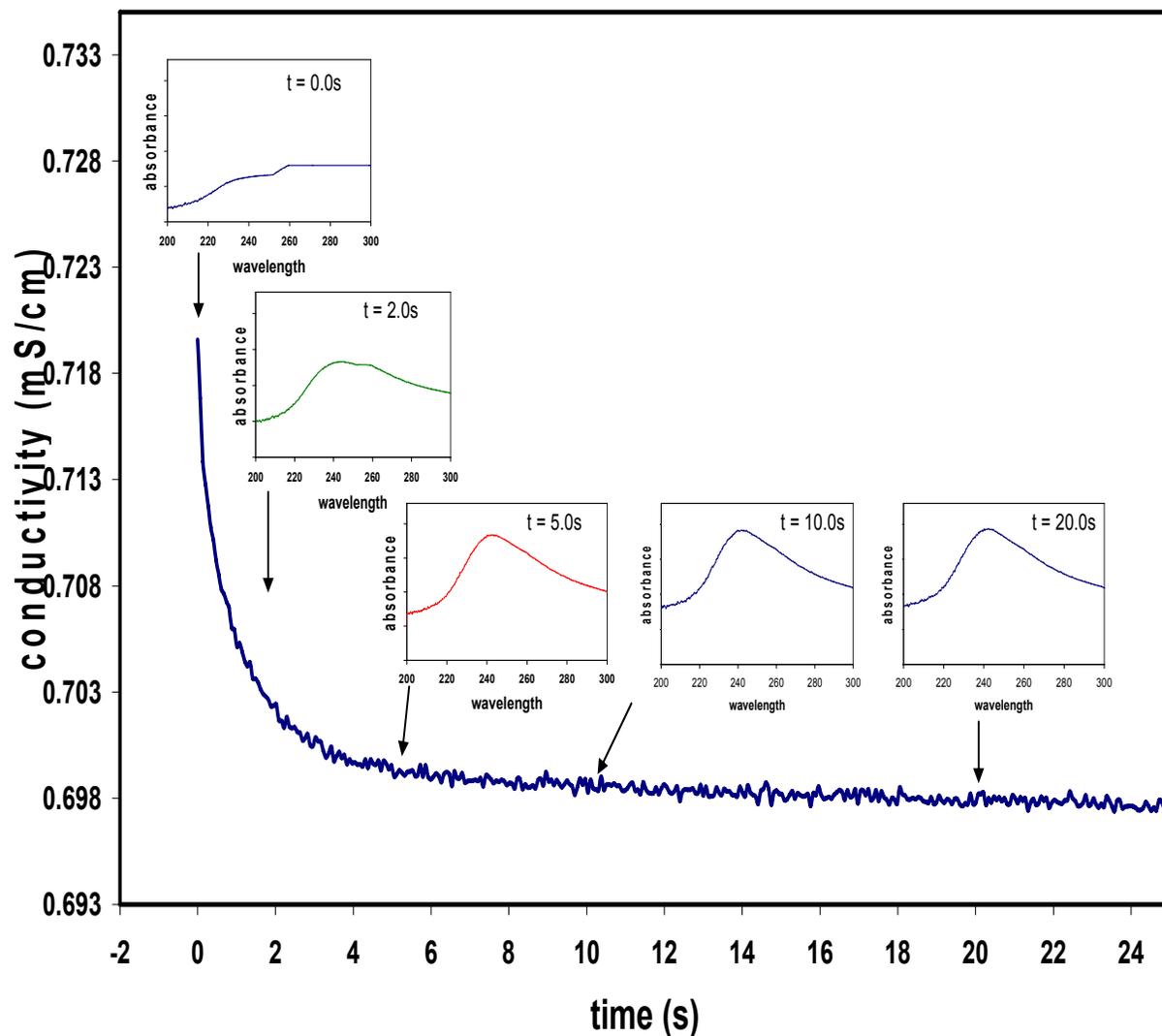


Figure 2. Dependence of conductivity on time for the reaction mixture of Ag^+ and S^{2-} . The insets represent the optical absorption spectra of the same reaction mixture obtained at the times indicated by the arrows. See text for details.

stable form of silver sulfide. In bulk Ag_2S , this band appears around 230 nm. In the reaction mixture prepared under the experimental conditions described previously, Ag_2S formed is likely to be present in colloidal form and therefore to exhibit a shift in absorption wavelength as compared to solid Ag_2S .

The conductivity of the equimolar reaction mixture displayed on figure 2 exhibits an interesting dependence on time. There is a sharp decrease in the conductivity with time after the flow is brought to a stop at time $t = 0$ seconds and extends to about 4 seconds. There is a slow decrease in the conductivity with time after $t = 4$ seconds. The dependence of the conductivity on time is consistent

with the observations discussed on the previous paragraphs regarding the optical absorption spectra of the reaction mixture. Accordingly, the sharp decrease in the conductivity results from the reduction in the number of Ag^+ and S^{2-} ions which forms neutral Ag_2S according to:



Under the conditions of our experiment, the Ag_2S is in colloidal form, i.e., it does not precipitate as a solid in the reaction cell. The absence of a solid precipitate in the cell was verified by visual observation in the optical microscope with a magnification factor of 50 X, consistent with the formation of colloidal Ag_2S . Since the solubility product of Ag_2S is of the order of 10^{-50} , equation 2 may be regarded as irreversible. Thus the decrease in conductivity with time is proportional to the rate of formation of Ag_2S :

$$r \propto -d\kappa/dt \quad \text{equation 3}$$

where r is the reaction rate. The dependence of the reaction rate, as determined from conductivity measurements like the one displayed on figure 2, on initial Ag^+ and S^{2-} concentration were further studied in this work with the purpose of establishing the form of the rate law or the reaction described by equation 2. Graphs of the $\ln(r)$ as a function of $\ln(\text{Ag}^+)$ and $\ln(\text{S}^{2-})$ are displayed at the left and right hand side of figure 3. From the slope of the plots displayed on figure 3, we estimate that the reaction has a -1 order on Ag^+ and a +5 order in S^{2-} . The fact that these reaction orders are markedly different from the stoichiometric numbers described in equation 2 indicates that the reaction mechanism involves multiple steps or that the square root dependence of k on concentration must be taken into account in the quantitative analysis of the data.

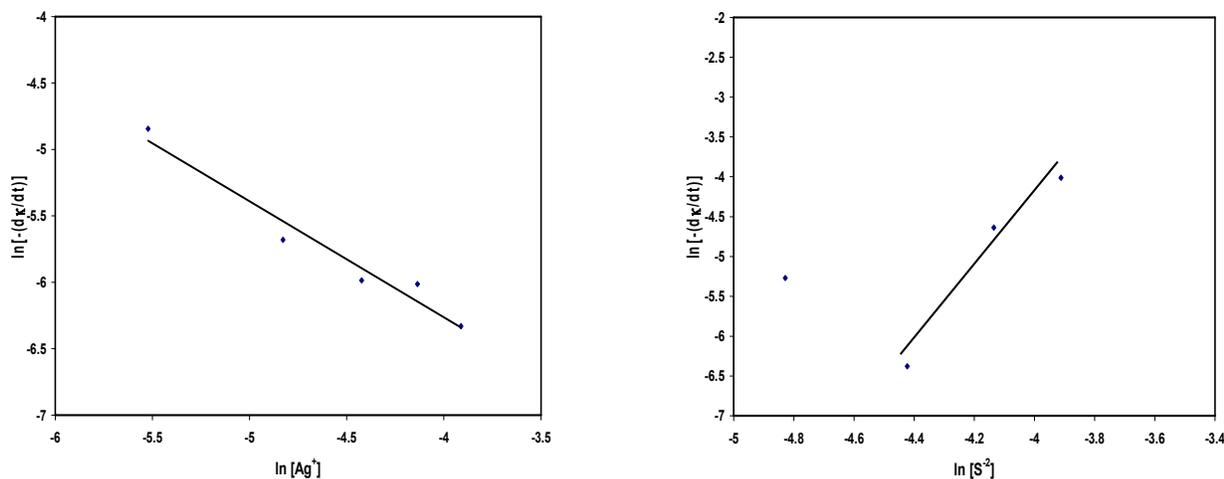


Figure 3: $\ln(r)$ as a function of the $\ln(\text{Ag}^+)$ (left hand side) and $\ln(\text{S}^{2-})$ (right hand side).

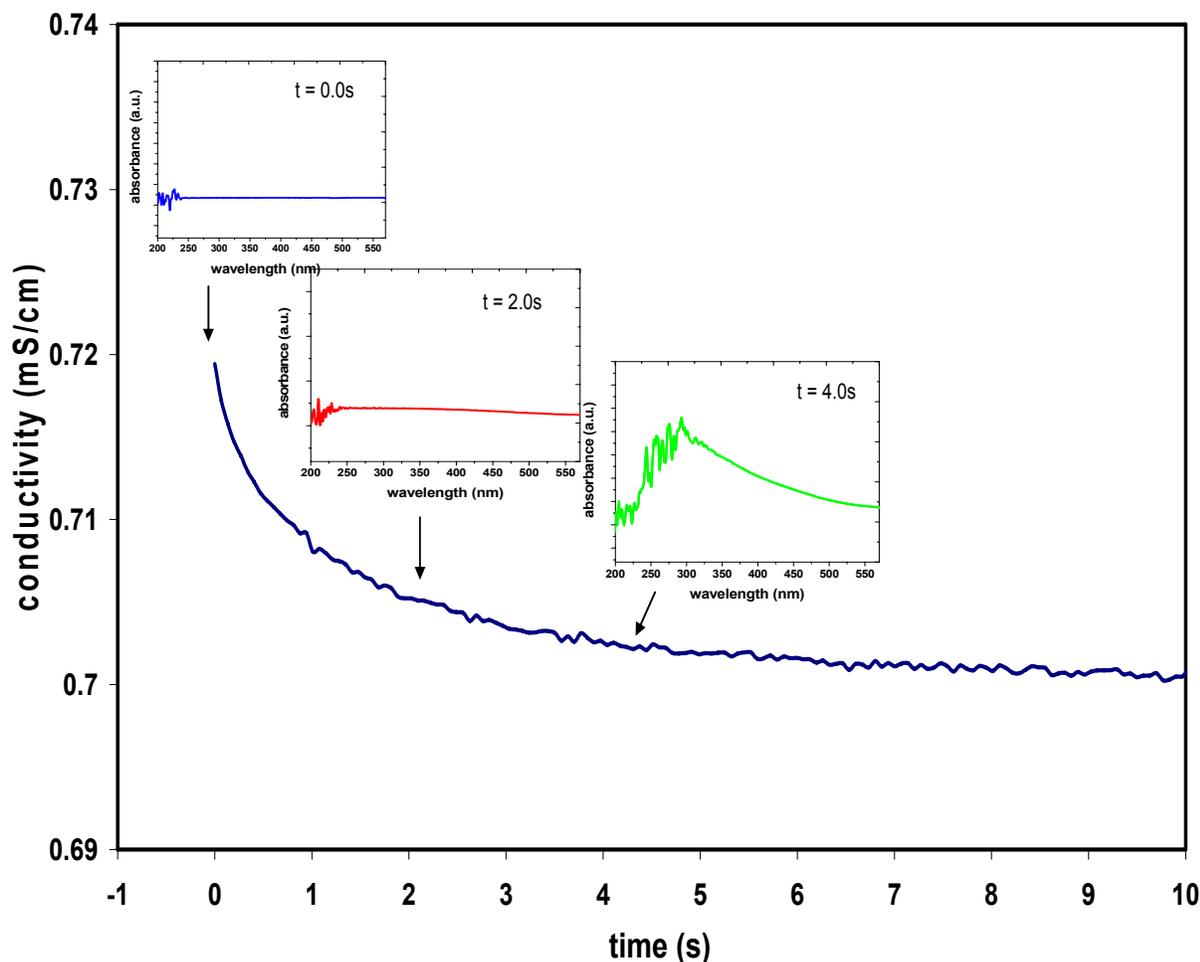


Figure 4. Dependence of conductivity on time for the reaction mixture of Ag^+ and S^{2-} for the excess of Ag^+ . The inserts represent the optical absorption spectra of the same reaction mixture obtained at the times indicated by the arrows.

The dependence of conductivity on time for an excess of Ag^+ on the Ag^+ and S^{2-} reaction mixture is displayed on figure 4. The optical absorption spectra of the reaction mixture are also displayed on figure 4. The optical absorption spectra were measured at the times indicated by the arrows. At times $t \leq 0$ seconds no significant light absorption is observed. A broad absorption band between 200 and 260 nm emerge at about 2 seconds following the stop of the flow. The appearance of these features in the optical absorption spectrum is accompanied with an increase in the baseline absorbance intensity, likely resulting from light scattering processes. An additional high wavelength band is well developed about 4 seconds following the stop of the flow. The structure of the optical absorption spectrum does not change significantly for times above 4 seconds. The high wavelength band appears above 280 nm with a peak near 300 nm. The structure and wavelength of the band is similar to the one observed in the reduction of silver in basic solution. Since $(\text{NH}_4)_2\text{S}$ is used in the reaction mixture, the solution pH is expected to be smaller than 7.0. In the absence of a reducing agent, the Ag_2S colloidal particle surface likely serves as a center for the reduction of silver, as depicted in figure 5 below. In the context of this model, absorption of light above 300 nm results from the

excitation of the silver plasmon. Further experiments with transmission electron microscopy measurements are underway to confirm the heterogeneous mechanism proposed here.

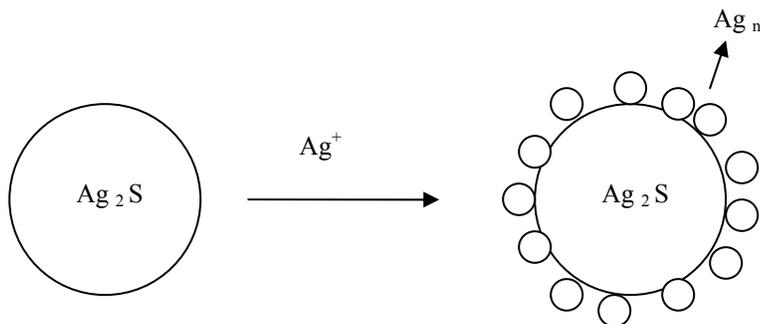


Figure 5. Diagrams of the proposed nucleation of silver on silver sulfide nuclei.

Summary

In summary, we have employed optical absorption and conductivity measurements to study the formation of Ag_2S semiconductor nanoparticles. The kinetic data obtained indicates that the reaction mechanism involves multiple steps or a square root dependence of k on concentration must be taken into account in the quantitative analysis of the data formation. Conductivity and optical absorption measurements indicate that the semiconductor, nucleation and coalescence of particles occur in a time scale shorter than 5 seconds after the flow is brought to a stop.

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