Eur. Phys. J. B **24**, 437–441 (2001)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

A qualitative model for the growth mechanism of silver clusters in polymer solution

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Received 18 July 2001 and Received in final form 3 October 2001

Abstract. A simple and high-reproducible method for the synthesis of polymer-protected silver cluster of controlled size is described. UV-visible spectroscopy has been used for investigating the influence of the aging of the protective poly(vinylpyrrolidone) layer on the cluster growth rate at different reaction temperatures and poly(vinylpyrrolidone)/ethylene glycol weight ratios. The obtained results show that the aging time of the polymeric stabilizer solution plays a fundamental role in the reproducibility of the cluster growth process. A model for the metal cluster formation-grow process is also proposed.

PACS. 78.67.Bf Nanocrystals and nanoparticles – 36.40.Gk Plasma and collective effects in clusters – 82.30.Nr Association, addition, insertion, cluster formation

1 Introduction

Polymers can be modified by special fillers, and the resulting composite materials are used for advanced structural and functional applications in many technological fields. Nano-sized metals are characterized by novel thermodynamic, chemical, catalytic, optical, magnetic, and electronic properties [1], which are produced by surface and confinement effects. Many physical characteristics of mesoscopic matter can be used to provide polymers of special advanced properties. These polymer-based nanocomposites are very promising as functional materials especially in optics, electronics, and photonics [2]. For example, optical plastics (polycarbonate, polystyrene, poly(methyl methacrylate)) filled by metal clusters can be used as optical filters (color filters, UV absorbers, etc.) [3], ultra high/low refractive index materials [4,5], non-linear optical devices [6], etc. However, metal/polymer nanocomposites can be successfully applied as non-porous catalytic membranes [7,8], new recording materials [9], transparent shielding systems [10], antistatic materials [10], and microwave absorbers [11].

Still limited are the methods available for the preparation of polymer-based nanocomposites. An efficient method for the synthesis of these materials should allow for a contact-free dispersion of identical nanoparticles into the polymeric matrix. Contact-free dispersion of nanoparticles in an embedding matrix is very important to control mesoscopic properties in the final product, but just few of the available techniques are really adequate. The reduction in the presence of stabilizers of ionic precursors by light chemical reductants like alcohols, sodium borohydride, hydrazine, etc. represents a very convenient way for preparing polymer-protected metal clusters. The method is interesting because it allows both to control the cluster size from an atomic or molecular level and to produce bulk quantities of nanostructured materials, making possible a simple scaling-up of the process. In particular, alcoholic reduction and polyol process [12–14] represent two simple and very effective techniques for the preparation of polymer-protected clusters of noble metals (Au, Ag, Pd, Pt, Ir, Os, Ru, Rh), light transition metals (Cu, Cd, Co, Ni, Fe), metal alloys, and core/shell bimetallic structures (*e.g.*, Pd/Au, Ag/Co, etc.). The study of the mechanisms involved in the process of nanoparticle formation and growth is of fundamental importance in the understanding of involved chemical processes, and in controlling the development of the nanoparticle microscopic structure. In this framework, the application of reliable spectroscopic techniques for studying the time evolution of metal cluster sizes plays an important role in the chemistry of these materials since they make possible *in situ* real-time monitoring of new reaction schemes for the nanometer cluster synthesis.

Another important point concerns with the reproducibility of both cluster formation and growth process. Since the nanostructured material properties are strictly related to their microscopic structure (*i.e.*, shape, size, and composition), it is very important to know the influence

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of the various experimental conditions on the synthesis in order to allow for reproducibility of the reaction.

In the present work, the growth mechanism of silver clusters produced by alcoholic reduction of ionic silver in the presence of a protective agent (*i.e.*, poly(vinylpyrrolidone)) has been investigated. Optical spectroscopy has been used for an *on-line* monitoring of the time evolution of the silver cluster size, for investigating on the influence of the aging time of the PVP solution in the growth process at different temperatures and concentrations.

2 Experimental part

$AgNO_3$ (Aldrich) was used as precursor salt in the silver cluster synthesis. Ethylene glycol (Aldrich) was used as solvent-reductant and poly(N-vinyl-2-pyrrolidone) (PVP, Aldrich, $M_w = 10\,000$) as stabilizer. The reagents were not purified before their use. PVP was dissolved in ethylene glycol at room temperature and then the required amount of a freshly prepared $AgNO_3$/ethylene glycol/water solution was quickly added at room temperature under vigorous stirring. A little amount of water (2% by weight) was introduced in the Ag^+ solution in order to inhibit the direct reduction of silver ions by ethylene glycol. Optical spectra were recorded at different reaction times by an UV-Visible spectrophotometer (HP-8453 UV-Vis spectrophotometer), equipped with a Peltier apparatus to control the reaction temperature with an accuracy of 0.1 °C. The system employed a magnetic stirring to allow for the homogenization of the reactive mixture. Far UV quartz cuvettes were used as reactor. The temporal size development of clusters was monitored by the automatic recording of spectral data on a personal computer connected to the spectrophotometer.

According to the LaMer's theory [15], and tacking into account the fast nucleation of the silver clusters at room temperature, nucleation and growth are separated stages of the cluster formation process. In this case, the cluster system can be assumed to consist of spherical monodispersed particles, and the extinction of such a colloidal system can be theoretically modeled by the well- known Mie's theory [16,17]. The total extinction (*i.e.*, the integral of plasmon absorption peak), W, can be written in terms of the particle concentration D, and of the particle volume V, in the following form:

$$W = DV \int K_0 \mathrm{d}\omega = \frac{4}{3}\pi D R^3 \int K_0 \mathrm{d}\omega \tag{1}$$

where R is the particle radius and $K_0(\omega)$ is the frequency dependent extinction coefficient referred to the unit concentration. Equation (1) allows to compare colloid extinction measurements obtained at different times during the growth process. We can approximate the integral in equation (1) by the following relation:

$$\int K_0 \mathrm{d}\omega \approx K_{0,\max}\delta \tag{2}$$

where $K_{0,\max}$ is the maximum extinction constant referred to unit concentration and δ is the full width at half-maximum intensity. Since D does not change during the particle grow process, and by assuming the product $K_{0,\max}\delta$ in equation (2) as approximately constant for particle diameters ranging from 2 nm to 25 nm [18], equations (1) and (2) can be combined to determine (qualitatively) the particle radius R in terms of the cubic root of the measured total extinction W, namely

$$R \sim W^{1/3}. \tag{3}$$

This relationship provides a convenient way for following the evolution of the particle radius under different experimental growth conditions by monitoring the UV-visible transmission spectra of the reactive mixture. Calibrated scale of cluster size can be determined from the extinction data by Transmission Electron Microscopy (TEM) measurements performed on colloidal samples growth at well defined time intervals.

3 Results and discussion

UV-Visible spectra recorded at time intervals of 15 min, according to typical reaction conditions (*i.e.*, 22.5 mg of $AgNO_3$, 5 g of PVP, and 26.5 ml of ethylene glycol), are shown in Figure 1. The intensity of the surface plasmon band increases during the particle growth process. The absence of any distortion of the spectra means that in these conditions a contact-free system of clusters is growing during the reaction. The temporal evolution of the cluster radius is obtained from the spectrophotometric data recorded at different reaction time by using equation (3). Figure 2 shows the behavior of the average silver cluster radius, R, as a function of the square root of time for a different aging of the PVP solution employed in the preparation of the reactive mixture. The aging process was performed at isothermal conditions by using a thermostatic bath. The PVP/Ag weight ratio used in the reaction was 350. For a given reaction time aged solutions produce silver clusters larger than that obtained by unaged solution. The growth rate calculated from spectrophotometric data was found to increase linearly with the square root of the time, thus suggesting a diffusion-based mechanism [19] underling the kinetic growth process. Nevertheless, Figure 2 shows that the growth process in stage I proceeds at higher rate compared to that of the subsequent region marked as stage II. The higher slope of the stage I is indicative of a faster diffusion process occurring at the beginning of the reaction. However, the difference between the slopes corresponding to these two stages reduces for higher aging times of the PVP solution, as it can be clearly inferred from Figure 2 by comparing the radial growth rate data of the curves corresponding to 48 h and 12 h. It has also been observed that after 48 h of aging the difference between the two stages is negligible, and a simple diffusion law, linear in the square root of time, can account for the whole evolution process.

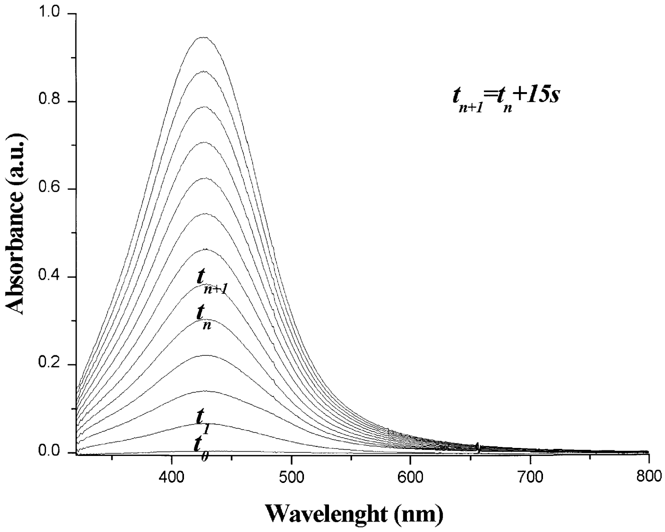


Fig. 1. Evolution of the UV-visible absorption spectra of the reactive mixture with the composition reported in Table 1. The temperature is 25 °C and the spectra are collected at time intervals of 15 min. The absorbance peak values correspond to the plasmon resonance of silver clusters.

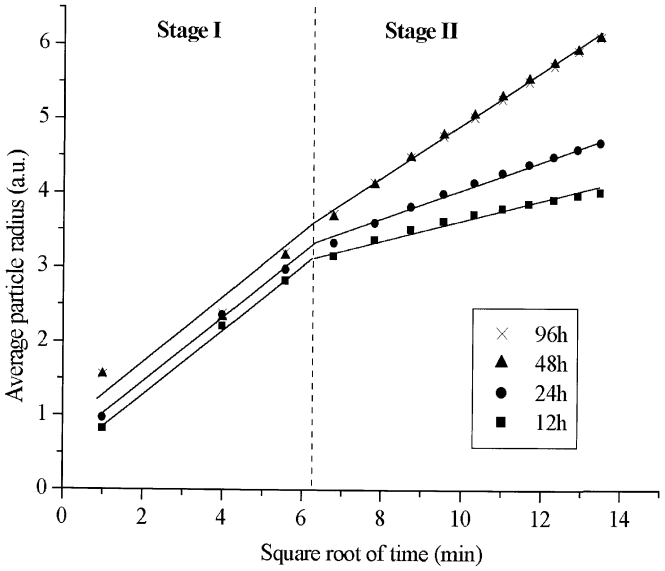


Fig. 2. Behavior of the average cluster radius with time square root for an increasing aging of the PVP solution (PVP/Ag weight ratio of 350). Two different diffusion regimes can be observed during the cluster growth.

High reproducibility of the cluster size measurements was achieved by this method and the corresponding percentage errors were found to be less than 0.5%.

It is well known that one of the main limitations in the metal clusters synthesis by solution chemistry is the poor reproducibility of the nucleation- growth process, owing to the difficulty for controlling accurately the various physical and chemical parameters involved in the reaction (*e.g.*, reagent purity, surface characteristics of the reactor walls, stirring speed, etc.). However, the poor reproducibility of the kinetic data is mainly due to the fact that the protective layer of PVP, which controls the diffusion rate of the silver atoms towards the surface of the growing nucleus, requires some amount of time to reach the thermodynamic equilibrium. The polymeric layer embedding the growing clusters evolves dynamically by solvent absorption during the growth process, until it reaches the thermodynamic equilibrium. Therefore, in order to achieve a high reproducibility of the diffusion process and consequently of the particle growth-rate, the protective layer has to be at thermodynamic equilibrium during the cluster formation-growth process. Consequently, the observed increase of the cluster growth rate with the aging time of the protective PVP solution can be well explained by considering that the larger swelling of the polymer barrier with the aging time enhances the diffusion of the silver atoms through the barrier. After 48 h of aging, the radial growth of clusters has always the same behavior because in these conditions the thermodynamic equilibrium has been finally approached.

In order to show that a diffusion based mechanism can account for the kinetic of silver cluster growth, the reaction has been carried out at different temperatures, ranging from 18 to 30 °C. All measurements were performed using solution aged for more than 48 h and characterized by a Ag/PVP weight ratio of 350. The experimental values of the average cluster radius R, computed from the spectrophotometric data, are shown in Figure 3 as a function of the square root of the reaction time, for increasing values of the reaction temperature. The dependence of the radius *vs.* the square root of time was found to be linear in the considered thermal range. Figure 3 shows that the growth rate increases with increasing the reaction temperature because of linear dependence of the diffusion coefficient on the temperature. Also in this case the diffusion process was found to occur faster at beginning of the growth process. A proposed explanation for the experimental findings can be given according to the following growth model. The polymer chains in solution have a coil structure whose shape is basically a sphere. After the mixing of the PVP solution with the silver ions, the latter are adsorbed on the surface of the polymeric random-coils and slowly diffuse towards the center of the spherical system. Because of the presence of the reductant molecules (alcohol) inside the polymeric structure, the reduction of coordinated silver ions takes place and the diffusing ions are reduced up to the zero-valence state. Since both diffusion and reduction processes takes some time, the atomic silver concentration near the random-coil surface is higher than that in the center. Consequently, the nucleation starts at the point of the random-coil surface where the supersaturation level is higher. The phase separation and the following growth of the cluster proceeds by absorbing silver atoms from the surrounding, thus lowering the local concentration of silver atoms. Therefore, once the cluster is produced it behaves as diffusion center. The cluster will grow by diffusion-deposition of the metallic atoms. Because of the low molecular weight of PVP used (10 000 a.m.u.) only mononuclear structure can

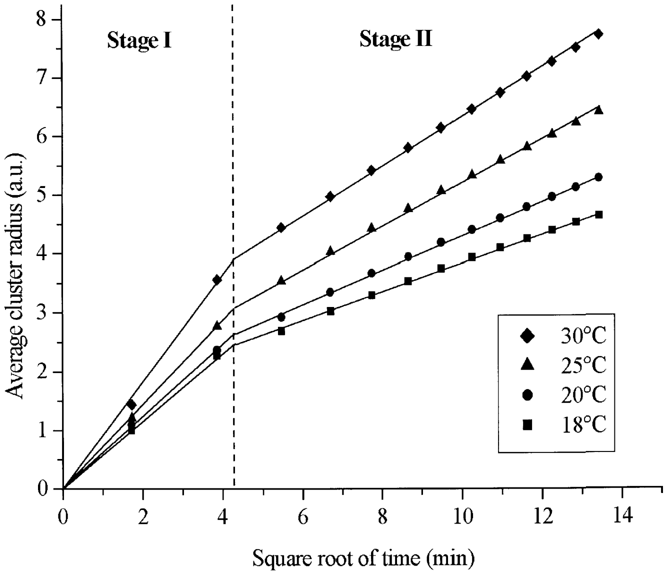
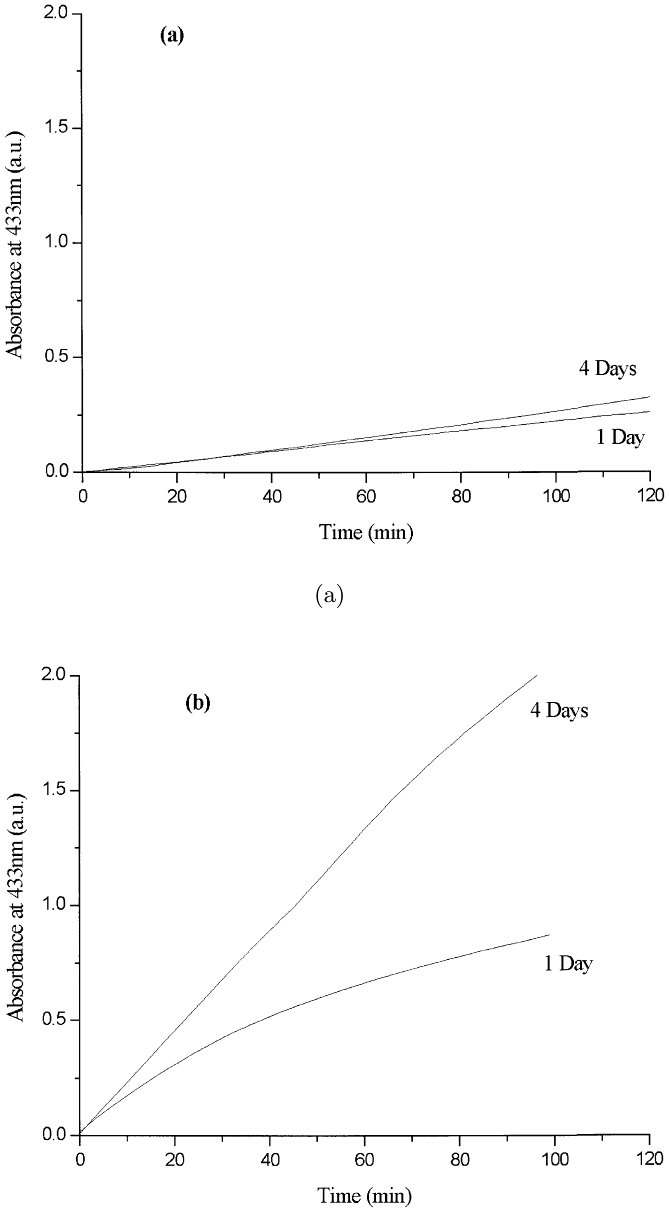


Fig. 3. Behavior of the average cluster radius with time square root at four reaction temperatures (Ag/PVP weight ratio of 350, and aging time >96 h). Two different diffusion regimes can be observed during the cluster growth.

be produced during the process. The plasmon absorption can be observed at the initial instant of formation of the cluster, when it is still located near the surface of the polymeric coil. In these conditions (stage I) the thickness of the diffusion barrier is small and the cluster growth proceeds rapidly. However, owing to the reorganization of the soft polymeric coating layer embedding the cluster, the cluster probably migrates towards the center of the random coil. This cluster migration should be caused by the Brownian collisions between the polymer-coated structures. In fact, due to the symmetry of the system and to the random nature of the Brownian collisions, the center of the spherical random-coil becomes the equilibrium point of the cluster inside the structure. When the cluster has reached the random-coil center (stage II) it grows at a lower rate because of the enlargement of the diffusion layer around it. According to this qualitative model, the less appreciable difference between these two stages can be explained by considering that for longer aged solutions the reaction proceeds in presence of more swollen polymeric random-coils.

Figure 4 shows the time evolution of the absorbance peak values at 433 nm, for different aging of the PVP solution. The plots correspond to a constant ratio PVP/Ag of 350 and different PVP/ethylene glycol weight ratios ranging from the value 0.33, corresponding to a concentrate system to the value 0.15 for a dilute one. The dilute system (Fig. 4a) after an aging time of one day has almost reached the thermodynamic equilibrium; for higher concentration values (Fig. 4b), there is a remarkable difference between the absorbance data obtained after one day of aging as compared with those recorded after four days, when the solution can be safely assumed to be at thermodynamic equilibrium. In fact, in a dilute system the swelling process proceeds at higher rate compared to the concentrated mixture, since a larger amount of ethylene glycol is available for the polymer swelling. Such experimental result is perfectly in accordance with the proposed model for the cluster growth mechanism.



(a)

(b)

Fig. 4. Temporal evolution of the absorbance peak values at two different PVP/ethylene glycol weight ratios ((a): 0.15, (b): 0.33).

Figure 5 shows a diffusion-controlled mechanism of cluster growth for different PVP/Ag weight ratios ranging from 150 to 350. The PVP solutions always were used after an aging period of more then 48 h at 25 °C. In particular, the radial growth rate is higher at lower PVP/Ag weight ratio, meaning that the particle growth rate increases with

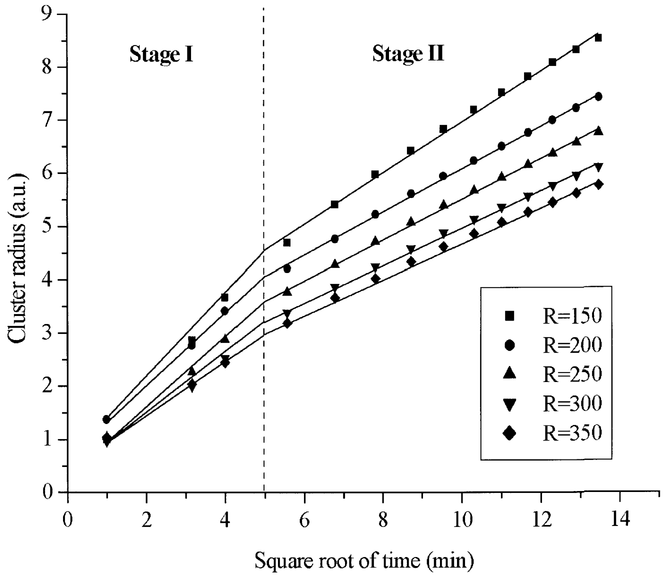


Fig. 5. Average cluster radius as a function of the time square root for different values of the PVP/Ag weight ratios (R) (PVP solution aging time >48 h).

increasing the silver concentration. Data reported in Figure 5 indicate that the increase in the Ag^+ concentration leads to larger clusters for a given reaction time. This effect is very similar to that produced by the solution aging as discussed in Figure 2.

4 Conclusions

A very simple method for the synthesis of polymer-protected silver clusters of controlled size has been described. When the polymeric stabilizer solution has been correctly aged, this technique allows to obtain a high reproducible diffusion growth of silver clusters. In particular, a spectrophotometric monitoring technique has been employed to investigate the influence of the aging of the protective PVP layer on the cluster growth rate, under different reaction temperatures and PVP/ethylene glycol and PVP/Ag weight ratios. Experimental results have shown that the aging time which is required to obtain a reproducible particle growth process is a function of the composition of the reactive mixture. A qualitative model has also been presented and discussed to account for the observed kinetic behavior of the cluster growth process. The model explains on the basis of a simple Brownian theory the diffusion- controlled mechanisms underling the temporal evolution of the UV-visible experimental spectra.

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