
D. Tatchev,1,* A. Hoell,2 M. Eichelbaum,3,† and K. Rademann3

1Helmholtz-Zentrum Berlin, Institut fuer Angewandte Materialforschung, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany and Institute of Physical Chemistry – Bulgarian Academy of Sciences, Acad. G. Bonchev Ste. Bl. 11, 1113 Sofia, Bulgaria
2Helmholtz-Zentrum Berlin, Institut fuer Angewandte Materialforschung, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany
3Institute of Chemistry, Humboldt-Universitaet zu Berlin, Brook-Taylor-Strasse 2, D-12489 Berlin, Germany (Received 26 March 2010; revised manuscript received 27 January 2011; published 23 February 2011)

The in situ formation of gold nanoparticles in soda lime silicate glass under constant x-ray irradiation is compared with the ex situ formation in preirradiated glasses. The ASAXS measurements confirm that pure Au particles are formed. The comparison shows that the number of particles nucleated under irradiation is about an order of magnitude higher than of those nucleated with preirradiation. The radius, \( R \), remains slightly below 1 nm under in situ conditions and the Ostwald ripening stage is slowed down. Under ex situ conditions Ostwald ripening is clearly observed and \( R \) grows up to 3 nm.

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Metallic nanoparticles and nanostructures have exceptional magnetic, optical or catalytic size dependent properties that promise wide industrial applications [1–3]. Nanoparticles can be produced by various chemical [1] and physical [4] methods on surfaces or in a great variety of matrices. Nanoclusters grown in solution need a kind of charge or steric stabilization to avoid coalescence or agglomeration, for which, e.g., microemulsions, inverse micelles or organic layers are used. Current research is focusing on exploring the mechanisms of nanoparticle formation in solution [5–8] and in glassy matrices [9]. Glass is generally the perfect matrix for many optical devices. Outstanding future applications like cloaking devices as well as other photonic applications require precise control of the position, size and shape of metallic nanoparticles, for example, of gold in glass [10,11]. Especially gold nanoparticles encapsulated in glass can be produced by doping the glass with Au ions first, reducing the ions to atoms and subsequent precipitation at elevated temperature. Such a procedure has been used to produce colorful glass since antiquity [10,12]. However, it is generally not straightforward to control the size and spatial arrangement of nanoparticles in glassy matrices. The classic process of gold particle formation in glass requires elevated temperatures and annealing times of 20 or more hours. Very recently it was reported, that x-ray irradiation of the glass at room temperature prior to the annealing step significantly shortens the time (to 20 minutes or less) necessary for the precipitation and leads to a larger number density of particles with much smaller sizes [13] down to dimers or even neutral atoms [14]. This provides a unique opportunity for additional control over the precipitation process. Applying also lithographic techniques, even patterns of areas of nanoparticles can be produced [15].

An initially supersaturated solution is unstable and separates a phase containing the solute whenever the kinetic conditions allow it. The separation proceeds by nucleation and growth processes that normally occur simultaneously at the beginning. If the growth is diffusion limited, then the average radius of the particles grows proportionally to \( t^{1/2} \), with \( t \) being the time. Both, the number density of nuclei and the volume fraction increase. Usually, the nucleation rate drops fast with decreasing supersaturation, but the growth continues until the critical particle size becomes comparable with the largest clusters in the system.

The equilibrium solubility of the solute with a curved surface of the newly formed phase depends on the radius of curvature; the higher the curvature the higher the solubility. This difference makes the smaller, compared to some critical cluster size, particles dissolve and the larger one’s grow. The volume fraction of the precipitating phase remains constant; the average radius continues to increase while the number of nuclei decreases. This process is called Ostwald ripening. In its asymptotic stage, the average radii of the particles will increase proportionally to \( t^{1/3} \) (diffusional limitation). Depending on the kinetic parameters a transition period between the nucleation-growth regime and the 1/3 power law may exist during which the average radius does not increase significantly and reshaping of the size distribution occurs, see Figs. 4 and 6 in Ref. [16].

Here we show that the number and size of gold nanoparticles in soda lime silicate glass can be controlled by x-ray irradiation and annealing. We compare two types of glass sample irradiation treatments; preliminary x-ray irradiation and subsequent annealing (ex situ) and x-ray irradiation during annealing (in situ). As a result we show that the in situ annealing process affects the growth mechanism in the ripening stage of gold cluster formation. Mobile gold atoms, generated by irradiation, are needed for both faster initial growth of the particles and for delay of the Ostwald ripening [17,18], both of which are observed in the in situ experiments.

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The glass samples were prepared from reagent grade materials doped with small amounts of AuCl₃ by melting at 1450 °C and rapid quenching to room temperature. The resulting glass has a composition of 70SiO₂-20CaO-10Na₂O (values in mol%, as confirmed by EDX). It is doped with 50 ppm Au as measured by x-ray fluorescence. Polished glass slides with a thickness of typically 1 mm were irradiated by a polychromatic x-ray beam [14] and subsequently annealed at 550 °C for different annealing times. Transmission optical microscopy shows, that the so obtained particles strongly absorb green light due to the gold plasmon excitations [13]. Transmission electron microscopy revealed particles with a nearly perfect spherical shape [13]. Additionally, samples with a thickness of typically 0.3 mm were measured by means of small-angle x-ray scattering (SAXS) at room temperature to determine the average particle radii, the number density of nuclei, and the volume fraction after different annealing times. These experiments will be referred to as ex situ measurements. For comparison, non-irradiated samples were annealed at temperatures between 500 °C and 590 °C during the SAXS measurements at the 7T-MPW-SAXS beam line at the BESSY II synchrotron in Berlin. Here, samples were exposed to x rays at elevated temperatures by the SAXS measurement itself. These experiments will be referred to as in situ measurements.

As for ex situ measurements, anomalous SAXS confirmed that the particles are homogeneous and composed of pure Au. Figure 1 shows the Guinier plots of one specific sample containing Au particles grown up to an average radius of about 3 nm. The slope of the linear fits of these curves does not change with the energy. Hence, the Guinier radius does not depend on the x-ray energy. Consequently, the system consists of two phases, i.e., the particles and the matrix are homogeneous. For more complex systems such as photochromic soda lime silicate glasses containing AgBr or AgCl particles, diffusion zones or particle inhomogeneities are clearly detected by anomalous SAXS [19,20]. The diffusion zone usually requires the assumption of a three phase core-shell structure for explanation, which complicates the SAXS data analysis. In our case, the amount of gold in the glass is so small that its variation around the growing particle cannot be detected as a third phase and the diffusion zone remains invisible for SAXS.

An important feature of the glasses studied is the very small Au particle radius, typically below 3 nm, and their small volume fraction, less than $3 \times 10^{-3}$. Thus, their scattering superimposes on the scattering of the glass itself. The glass matrix scattering is described by a $q^2$ or logarithmic law [21–23] and Porod-like scattering that appears at the smallest scattering angles. Therefore the scattering from the sample can be described by

$$I(q, \varepsilon) = \int_0^{\infty} \Delta \rho(\varepsilon)^2 f(R)V(R)^2\Phi(q, R^2)\,dR + (A + Bq^2) + Cq^{-4}. \quad (1)$$

The integral represents the scattering contribution of the system of Au particles while the two other addends describe the scattering from the glass matrix [21]. Here, $\Delta \rho$ is the electron density difference between glass and gold, $f(R)$ is the particle number density size distribution, which is assumed to be log-normal, $V(R)$ is the particle volume, and $\Phi(q, R)$ is the normalized scattering amplitude of a spherical particle, $q$ is the magnitude of the scattering vector, $R$ is the particle radius, $\varepsilon$ the x-ray energy, and $A$, $B$ and $C$ are constants.

The results of the so analyzed SAXS scattering curves of the ex situ irradiated and in situ annealed samples at 550 °C are shown in Fig. 2. The average size of the particles in the ex situ sample increases to about 2.3 nm, the volume fraction rises to about $10^{-3}$ after 45 minutes. The margin of the maximum possible volume fraction is shown as a hatched rectangle in Fig. 1 (and also in Fig. 2). The margin is calculated from the amount of Au added initially to the glass. The gold amount was confirmed by x-ray fluorescence analysis. As can be deduced from Fig. 2, the experimentally determined volume fraction stays within this margin for annealing times longer than 45 minutes. The particle number density increases first, peaks after 30 minutes, and decreases for longer annealing times. Since the average particle number density drops significantly after 30 minutes, while the average radius increases with the volume fraction remaining constant, we can conclude that Ostwald ripening starts in the ex situ sample after 30–40 minutes annealing time, i.e., the larger particles grow at the expense of the smaller ones.

The in situ data were fit also with Eq. (1). The fit results are shown in Figs. 2 and 3. The number of Au particles per unit volume is of the order of $2.5 \times 10^{15}$ cm$^{-3}$ which is an order of magnitude higher than the values observed in the ex situ experiments. The overall separation of the
excess gold is however faster in the in situ case, as manifested in Fig. 2(a). The nucleation period for the samples annealed ex situ and in situ at the same temperature, 550 °C, is nearly the same; approximately 30–40 min—Figs. 2(c) and 3(c). The nucleation rate under continuous irradiation is therefore higher. In addition, particles do not grow larger than 1 nm in radius and the particle number densities do not show maxima either. This is in strong contrast to the ex situ samples as seen in Fig. 2. As Fig. 3 shows, within the time span of the annealing up to 4 hours under in situ irradiation, the Ostwald ripening is very slow [proportional to \( t^{0.03} \) — Fig. 3(b)] even at higher temperatures of 570 and 590 °C.

Two main observations following the comparison of the in situ and the ex situ transformations as shown in Fig. 2 can be summarized. First, the in situ grown particles are about 1 order of magnitude more in number, and consequently, their size remains smaller due to the constant volume fraction. The in situ irradiation assists the conversion of Au ions to mobile Au atoms [14] and simultaneously creates defects that obviously serve as nucleation sites. Thus the increased nucleation caused by the in situ or ex situ irradiation is of inhomogeneous character. Naturally, a larger number of defects (nucleation centers) is created under continuous irradiation despite the high temperature. This way, the irradiation accelerates the nucleation and growth rates. Second, typical asymptotic Ostwald ripening is not detected for the in situ studied samples for the duration of the annealing process. Obviously, the gold particle growth process is influenced by the in situ SAXS measurements.

The suppressed Ostwald ripening can be understood qualitatively if one bears in mind that the diffusion flow during ripening is proportional to the concentration gradient that depends on the particle size difference. Hence, the narrower the size distribution is, the slower is the ripening. At a hypothetical extreme case, a monodisperse ensemble of particles should not undergo ripening. Thus, the higher nucleation rate during the continuous irradiation of the sample leads to a narrower particle size distribution which slows down the Ostwald ripening. In fact a similar phenomenon has been observed in a liquid solution. It was shown that irradiation by an electron beam initiates nucleation and growth of nearly monodisperse Pt nanoparticles [8].

This hypothesis can also be supported by exploiting the characteristic laws of the growth process. If the particles grow independently under diffusion limitation, the mean particle radius, \( \langle R \rangle \), increases with the time as \( \langle R \rangle = K_D t^{1/2} \) as seen in Fig. 3. In the ripening mode, the mean particle radius increases as \( \langle R \rangle = K_O t^{1/3} \). \( K_D \) and \( K_O \) are time independent constants referring to diffusional growth
and asymptotic ripening modes, respectively. If $K_D / K_O < 1 \text{s}^{-1/6}$, the diffusional growth mode transforms smoothly into the ripening mode following a $t^{1/3}$ law. On the contrary, if $K_D / K_O \gg 1 \text{s}^{-1/6}$ the $t^{1/3}$ ripening mode is delayed and separated from the diffusion growth mode by a period in which $R(t)$ remains nearly constant \cite{16,24}. The ratio $K_D / K_O$ is given by

$$Z = \frac{K_D}{K_O} = \frac{3^{2/3}}{\sqrt{2}} \frac{\alpha_c^{1/6}}{c_{eq}^{1/3}} \sqrt{\Delta \mu D^{1/6}} \sigma^{1/3} (kT)^{1/6}. \quad (2)$$

If we assume that $Z \leq 1 \text{s}^{-1/6}$ in \textit{ex situ} conditions then $Z$ must increase much over $1 \text{s}^{-1/6}$ under irradiation and the same annealing temperature. In our case the atom number density in Au, $c_{eq}$, and $kT$ are constant. As discussed above, there are strong indications of a possible increase of the diffusion coefficient, $D$ in our case. According to Eq. (2) a higher value of $D$ favors a delay of the asymptotic ripening mode. As can be seen in Fig. 2, not only the number of nuclei is larger, but also the growth rate is higher during the first 30 minutes of the transformation, as compared to the \textit{ex situ} case. Such an increase of the diffusion coefficient can be explained by the radiation induced reduction of Au$^+$ ions in the glass to Au$^0$ atoms \cite{14} and the interaction of these atoms with the silica network \cite{25}. Gold atoms have a higher mobility, which would give a higher effective diffusion coefficient.

The nucleation rate is obviously higher during irradiation and it depends on the chemical potential difference, $\Delta \mu$, between the phases and the interfacial energy, $\sigma$. Thus, under irradiation, the ratio $\Delta \mu / \sigma$ should increase in favor of making $Z$ larger. One can expect the x rays to act stronger on the Au particle surface then in its bulk, and therefore $\sigma$ is most probably reduced by the irradiation leading also to the higher nucleation rate. The other two parameters in Eq. (2), the Au concentration close to a flat Au surface, $c_{eq}$, and the Au concentration far from any particle, $c_{eq}$, are not expected to be strongly influenced by the radiation. Thus, the generation of mobile neutral Au atoms and the possible decrease in the Au particle surface energy, both caused by the continuous x-ray irradiation, accelerate the Au separation and slow down the Ostwald ripening. Another possible, but less probable explanation would be a drastic change of the properties (e.g., elastic) of the glass under x-ray irradiation.

We should also mention that the phenomenon of particle growth retarded and even reversed by irradiation has been already treated theoretically and models for its explanation are available \cite{26}. However, to the best of our knowledge the present work is the first experimental evidence for such an interesting influence of the x rays on the growth process.

In conclusion we have shown that the x-ray irradiation creates nucleation centers in the glass on which particles develop. Particularly, the size and number of gold nanoparticles in glass can be precisely controlled by simultaneous x-ray irradiation and annealing. In addition, this method bears the potential to even control the particle position by developing an advanced lithographic process. The delayed Ostwald ripening, when the annealing is carried out under constant x-ray irradiation, is not only an interesting phenomenon as such, but enables the precise control of the size, density, and volume fraction of exceptionally small particles for applications such as the production of linear and nonlinear optical devices.

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*dtachev@ipc.bas.bg

†Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany.