Glasses

On the Chemistry of Gold in Silicate Glasses: Studies on a Nonthermally Activated Growth of Gold Nanoparticles**

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The history of gold-ruby glasses goes back to the Roman Empire. However, the first known written report about the manufacturing of these glasses was published in 1689 by the German pharmacist and alchemist Johannes Kunckel.[1] Colorless glasses containing the “magic” noble metal gold become characteristically ruby-colored after annealing because of the formation of gold colloids. The absorption of light is caused by an excitation of a collective oscillation of gold valence electrons. The quantum of this plasma oscillation is called the surface plasmon.[2] The surface plasmon resonance frequency mainly depends on the size, shape, topology, and dielectric environment of metal clusters.[3] By changing these parameters it should be possible to create materials that can be used in nanophotonic devices. A large nonlinear optical response with a fast response time is needed for applications in the field of optical computing. Plasmonic materials are exceptionally promising candidates for ultrafast optical switches and modulators because of their large third-order nonlinear susceptibility $\chi^{(3)}$. A second advantage is a response time in the range of picoseconds, which would therefore enable processors with terahertz frequencies.[4]

Another challenging problem is the chemical and mechanical stability of these materials. Gold clusters in glass matrices exhibit the extended stability required for the fabrication of nanodimensional optoelectronic circuits and optical memory with ultrahigh recording speed and storage density. With synchrotron radiation it is already possible to create very small devices, circuits, and even miniaturized lasers by UV and X-ray lithography. We have now succeeded in the spatial synthesis of gold nanoparticles of defined size and with a sharp size distribution by activation of gold silicate glasses with synchrotron radiation and subsequent heating of the samples. Understanding the chemical and physical processes of cluster formation is fundamental for the directed modification of the size, shape, and topology of gold clusters and hence for the creation of structures with a specific functionality. Therefore we have studied the activation caused by the reduction of gold ions to atoms as well as the nucleation and the growth of the gold nanoparticles in gold silicate glasses by UV/Vis spectroscopy, X-ray absorption near-edge spectroscopy (XANES), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM).

Soda–lime–silicate glasses were doped with 0.02 mol% AuCl₃ by melting the component materials at 1450°C. Selected samples were irradiated with a photon flux density of $10^{12}$ photons mm⁻²s⁻¹ on a defined area with hard X-ray radiation (32 keV) for 300 s in the Berlin electron storage ring (BESSID II).[5] During this irradiation the activated area turned brownish (Figure 1a). Maxima at 315, 440, and 620 nm can be identified in the extinction spectrum of the activated sample (Figure 2, curve b). These peaks can be assigned to defect centers in the SiO₂ framework. In general, the absorption at 315 nm in soda–lime–silicate glasses is caused by holes trapped in oxygen vacancies that neighbor alkali-metal ions ($E'$ centers).[6] This extinction is obviously much stronger in gold-doped samples than in undoped ones (Figure 2, curve a). Antonietti et al. recently reported TD-DFT (time-dependent density functional theory) cluster model calculations of optical transitions in...
gold atoms bound to silicate defect centers. The highest calculated oscillator strength of possible gold–defect bonds is predicted at 4.02 eV (308 nm) for gold atoms bound to E centers. Therefore the peak at 315 nm in the experimental spectrum could be assigned to gold atoms that were generated by activating the glass sample with X-rays.

Peaks at 440 and 620 nm can be attributed to the NBO (nonbridging oxygen) centers HC1 and HC2 (holes trapped in SiO4 tetrahedrons with three or two nonbridging oxygen atoms, respectively). These extinction maxima do not differ very much in doped and undoped samples (Figure 2). The irradiated glasses were subsequently annealed in a muffle furnace. After 10 min of thermal treatment at 450°C the glasses became colorless again. Apparently the color centers consisting of electrons and holes recombine and their absorption vanishes. When the glass samples were annealed at a higher temperature of 550°C, the color of the activated array changed to red within 30 min (Figure 1b).

The red color corresponds to a peak at 540 nm in the extinction spectrum. This extinction can be attributed to the surface plasmon resonance (SPR) of gold nanoparticles. When the activated gold silicate glass was annealed for 45 min at 550°C instead of for 30 min, the extinction peak shifted to 549 nm (Figure 3, curve a). A remarkable red shift of the SPR with increasing duration of thermal treatment was also observed when samples were annealed at 590°C (SPR peak after 10 min at 547 nm and after 45 min at 556 nm) and 630°C (SPR peak after 5 min at 547 nm and after 15 min at 554 nm) (Figure 3, curves b and c, respectively).

The optical properties of spherical metal clusters can be described with the Mie theory using the complex dielectric function \( \varepsilon_{\text{sphere}} = \varepsilon_{\text{bulk}} + i \varepsilon'_{\text{sphere}} \) of the metal and the refraction index of the matrix material \( n_m \). For clusters with radii between 1 and 10 nm the extinction Ext can be formulated within a quasi-static approximation under the exclusive consideration of dipolaric excitations [Eq. (1)].

\[
\text{Ext} = \left( \frac{18}{4 \pi} \frac{\lambda \sigma}{4} \right) \frac{n_m}{\varepsilon_0} \left( \frac{\varepsilon'_{\text{sphere}}}{(\varepsilon'_{\text{sphere}} + 2 n_m)^2} + \frac{\varepsilon''_{\text{sphere}}}{\varepsilon_c} \right)
\]

The dielectric function of a metallic sphere \( \varepsilon_{\text{sphere}} \) can be calculated from the dielectric function of the bulk material \( \varepsilon_{\text{bulk}} \), if one considers its dependence on the sphere radius \( R \) caused by the effect of the limited mean free path of electrons \( \ell_{\infty} \), as described by Equations (2) and (3). Values for \( \varepsilon_{\text{bulk}} \) and \( \varepsilon_{\text{sphere}} \) were taken from ref. [10]. The Drude plasma frequency \( \omega_p \) of gold is \( 1.37 \times 10^16 \text{ s}^{-1} \) and the halfwidth \( \Gamma(R) \) is given by Equation (4) with the Fermi velocity being \( v_{\text{Fermi}} = 1.40 \times \Gamma(R) = \Gamma_{\infty} + \frac{v_{\text{Fermi}}}{R} = \frac{v_{\text{Fermi}}}{\ell_{\infty}} + \frac{v_{\text{Fermi}}}{R} \).

Transmission electron microscopy (TEM) was used to determine the mean cluster radius \( R \) of the gold nanoparticles in two samples to be 3.2 ± 0.9 nm (sample had been activated and annealed for 45 min at 550°C) and 6.2 ± 1.5 nm (sample had been activated and annealed for 15 min at 630°C). The shape of the curve and the halfwidth of SPR in the experimental UV/Vis spectra are very well described by calculating the extinction spectra for gold spheres with radii of 3.2 and 6.2 nm, respectively (Figure 4). The red shift of SPR with increasing cluster size cannot be explained with Mie theory for radii between 1 and 10 nm. Only for remarkably larger nanoparticles should red shifts and broadening of SPR caused by retardation effects be expected.

Equation (1) is valid only for spherical clusters. For the investigation of the shape of the gold particles, HRTEM images of the gold glass samples were made (Figure 5a,b).
Thus it appears that the shape of nanoparticles is approximately spherical. When the glasses were not activated by synchrotron radiation, a violet stain could be observed only after they had been annealed for 60 min at 590°C. The maximum of the observed SPR in the extinction spectrum was shifted from 574 nm (after annealing for 60 min) to 580 nm (after annealing for 240 min) (Figure 3, curve d). TEM images give a mean cluster radius of 27 ± 3 nm, and HRTEM images indicate a distinct deviation of particle shape from an ideal spherical symmetry (Figure 5c).

In 1951 Weyl tried to explain the violet stain of gold-ruby glasses after defined thermal treatment by a nonspherical shape of gold colloids. Thus the typical ruby color would be expected. Experiments conducted by Doremus et al. confirm that the effect of particle size on the SPR frequency is marginal. They examined the cluster growth of gold nanoparticles with radii between 3 and 6 nm in borosilicate glass and found a SPR wavelength of 525 nm. This value, which was independent of cluster size, is also in agreement with our calculations.

As a result of long annealing times of up to 150 h and the low diffusion constant in borosilicate glasses one can assume that the spherical nanoparticles are formed by a very slow growth process. Therefore red shifts of SPR observed in our samples could be explained by an increasing deviation of gold clusters from spherical shape. Studies on noble-metal ellipsoids in glass matrices would also confirm this thesis because of the observation of a red shift of SPR with increasing aspect ratio (and consequently an increasing deviation of spherical shape). This property of our gold silicate glasses is very interesting because a shift of SPR can be achieved in unexpectedly small clusters within a very short period of time only by changing the annealing temperature and thus the optical properties can be modified very easily.

In activated glasses cluster growth occurs at a lower temperature and within a shorter period of time than in nonactivated samples. Light microscopy and TEM images show that the distribution of gold nanoparticles is more homogenous and cluster density is much higher than in exclusively annealed gold glasses. An explanation therefore could be that the activation with synchrotron radiation leads through a reductive process to a very high density of gold atoms, which can diffuse much easier through the glass matrix than bound, oxidized gold species. Thereby an effective cluster growth is facilitated when the samples are annealed at a temperature near the glass transformation temperature.

The chemistry of gold in glass is so far a mystery. The only certainty is that the glass compounds are doped with gold(0) before the melting process starts. Assumptions of the oxidation state in the resulting glass are contradictory. However, recent experiments come to the conclusion that the noble metal is mainly in cationic form before either annealing or activation. Furthermore, one must assume that the gold cations undergo reduction to produce the coloring gold colloids.

We used Au LIII-edge XANES spectroscopy to study the effect of synchrotron radiation on the oxidation state. XANES spectroscopy is a reliable method for determining oxidation states and is also an established method for the qualitative analysis of gold nanoparticles. In our studies a gold film with a thickness of 40 nm on silica glass, gold(iii) cyanide, and gold(0) oxide were used as reference materials. Cationic gold standards show distinct white lines (caused by transitions of 2p electrons into vacant 5d states) at 11922 eV (Au(0)) and 11926 eV (Au(iii)) and can be clearly distinguished from Au samples, whose spectra do not show any white lines. A XANES spectrum was recorded for the activated area of a gold silicate glass. If the oxidation values ±0, ±1, and/or ±III of gold exist in the sample, its spectrum should be composed additively of the reference spectra. Therefore the spectra of the gold film and gold(0) oxide were added in different proportions (Figure 6), and the LIII edges of the gold film and gold silicate glass were found to match up almost exactly. The white line at 11922 eV in the glass spectrum also indicates a minor fraction of gold(iii).

XANES spectra of glass samples were furthermore compared with spectra obtained by combination of oxidation values ±0 and ±1 (Figure 7). It is remarkable that the white line of AuCN at 11926 eV differs clearly from the white line of the activated glass sample. Indeed one cannot exclude a significant influence of ligands in the vicinity of Au(iii) on the XANES spectrum. This effect should be clarified by inves-
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Figure 6. Normalized Au L$_{III}$-edge XANES spectra of different gold samples (solid lines) and spectra composed additively of reference spectra (dashed lines) obtained from a) gold silicate glass activated with synchrotron radiation; b) Au film; c) 0.2Au$_2$O$_3$ + 0.8Au film; d) 0.6Au$_2$O$_3$ + 0.4Au film; e) Au$_2$O$_3$.

Figure 7. Normalized Au L$_{III}$-edge XANES spectra of different gold samples (solid lines) and spectra composed additively of reference spectra (dashed lines) obtained from a) gold silicate glass activated with synchrotron radiation; b) Au film; c) 0.2AuCN + 0.8Au film; d) 0.6AuCN + 0.4Au film; e) AuCN.

Although XANES measurements were conducted with photon flux densities ($10^{10}$ photons mm$^{-2}$s$^{-1}$) well below activating densities ($10^2$ photons mm$^{-2}$s$^{-1}$), occurrence of color centers could be observed in nonactivated samples, too, as a result of long measurement times. Hence it is not possible to get information about the oxidation state before synchrotron irradiation. In future work fast XANES spectroscopy must be used, because this method would provide a determination of oxidation values in a very short period.

In conclusion, activation of gold silicate glasses with synchrotron radiation allows spatial reduction of cationic gold. By subsequent annealing, gold clusters with a sharp size distribution can be synthesized within a short period of time. With increasing cluster size a red shift of surface plasmon resonance can be observed in the extinction spectra. This effect can be explained by the increasing deviation from spherical symmetry with the increase in gold cluster size. Au L$_{III}$-edge XANES spectra of activated gold silicate glasses can be described best by a combination of the spectra of a gold film and an Au$_2$O$_3$ reference. This indicates that cationic gold species were found at least as minor compounds in the glass samples investigated. Because of the short wavelength used it should be possible to create nanostructures in glasses with X-ray lithography. This could provide an opportunity for developing nanophotonic devices in glass matrices for optoelectronic circuits, whose surface plasmon resonance could be tuned over a wide range of wavelengths by changing the size and shape of the gold nanoparticles. [13]

Experimental Section

Glasses composed of 70SiO$_2$·20Na$_2$O·10CaO (values in mol%) were doped with 0.02 mol% AuCl$_3$·2H$_2$O. Reagent-grade SiO$_2$, Na$_2$CO$_3$, CaCO$_3$, and AuCl$_3$·2H$_2$O were used as starting materials. Approximately 35-g batches were mixed and melted at 1450°C for 90 min in an electric furnace. The glass melt was then slowly cooled down to room temperature and cut, and samples were polished to sizes of 10×10×1.00 mm$^3$.

Selected samples were irradiated (“activated”) on an area of approximately 2.0×1.5 mm$^2$ with synchrotron radiation from BESSY II with 32 keV for 300 s. In the subsequent thermal treatment the glass samples were placed into a platinum crucible and annealed in a muffle furnace. XANES spectroscopy was also recorded at BESSY II. Au L$_{III}$-edge XANES spectra were acquired in fluorescence mode (detection at the Au L$_{III}$ line at 9707 eV) between 11900 eV and 11960 eV with an increment of 1 eV. Peak integration was determined with the program QXAS 3.5. The background spectra was corrected by subtracting the absorption value at 11900 eV and normalizing the value at 11960 eV to unity. Extinction spectra were acquired with a StellarNet EPP2000C-50 spectrometer and a Mikropack DH-2000 deuterium/halogen light source. For the activated samples a nonactivated area of the same glass was defined as the reference, and its spectrum was subtracted from the extinction spectrum of the activated area. For exclusively thermally treated samples an untreated glass with the same composition was defined as the reference, and its spectrum was subtracted from the extinction spectrum.

TEM measurements were made at Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin with the microscope Philips CM 200 LaB$_6$ operating at an acceleration voltage of 200 kV.

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References


