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EXAFS study of changes in atomic structure of silver nanoparticles in soda-lime glass caused by annealing

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ABSTRACT

Atomic structure of silver nanoparticles in soda-lime glass at T = 10 K before and after annealing was studied by Ag K-edge EXAFS. To overcome ambiguities in the structure determination by the Fourier-transform analysis of these spectra, caused by the presence of various species of the absorbing silver atoms in the sample, the refinements of the fitting technique of the Fourier transforms F(R) have been implemented. The F(R) of Ag K-edge EXAFS in as prepared and annealed glasses were analyzed in the extended range of interatomic distances (R) up to ~6.5 Å using Ag K-edge EXAFS in Ag-foil at the same temperature as the reference. The proposed technique of the fit enabled to go beyond the averaged description of silver nanoparticles structure in glass and to reveal the atomic structure of the core region of nanoparticles, the structural characteristics of their near-surface region, parameters of Ag – O bonds inside the glass matrix and the percentage of Ag atoms in each of these species before and after the annealing process. The mean size of silver nanoparticles in as prepared and annealed glasses was estimated and the mechanism of nanoparticles growth after the thermal treatment was suggested.

1. Introduction

Silver nanoparticles are extensively used as catalysts, bactericidal agents, in the production of anti-reflective optical coatings [1–3]. The size of nanoparticles, structure and composition of their interior and the near-surface regions determine the exhibited properties. Therefore silver nanoparticles have been studied by different experimental and theoretical techniques including X-ray absorption spectroscopy (XAS), to establish the dependence of size and atomic structure on the treatment conditions, kind of the stabilizing matrix or the support [4–9]. The XAS method is especially promising for such a structural analysis since experimental spectra of nanoparticles, differently prepared or existed in different surroundings, differ essentially from each other and from the spectra of corresponding bulk compounds. Interpretation of the observed differences in spectra and their numerical analysis enables to get the required structural information. However, the obtained information dominantly has an averaged character because the absorbing Ag atoms in the studied material are often existed in a several species, differed by the type of Ag local structure. Therefore, determination of atomic structure in metallic silver nanoparticles, including the type of point symmetry in the interior (core) region of small nanoparticles, the nearest-neighbor Ag–Ag distances and the structure of the near-surface region still remain a challenging problem.

In this paper XAS is applied to determine the atomic structure of silver nanoparticles in soda-lime glasses at temperature $T = 10$ K and the structural changes, caused by the thermal treatment (annealing) during 8 h at $T = 823$ K [10]. To get structural information of the core and near-surface regions of silver nanoparticles the Fourier-transform (FT) analysis of experimental Ag K-edge extended X-ray absorption fine structure (EXAFS) in “as prepared” and “annealed” glasses was performed. The application of this technique to materials with various local structures of the absorbing atom requires a large number of variables, which are often strongly correlated. The fit results depend also upon the wave numbers interval $\Delta k = k_{max} - k_{min}$, used for the Fourier-transformation of the oscillatory part $\chi(k)$ of experimental EXAFS, and hence Δk must be considered as one of the factors, which affects the outcome. As a result, the fitting procedure becomes unstable and normally gives only the average values of the limited number of structural parameters. To overcome these difficulties and limitations in the structural analysis of nanoparticles by EXAFS we propose in Section 3 the refinements of the fitting procedure which enabled to perform the structural analysis of silver nanoparticles under the presence of different species of Ag atoms in glass. In Section 4 this fitting procedure is applied to Ag K-edge EXAFS in as prepared and annealed samples to determine the atomic structure of the core region in silver nanoparticles, the average values of structural Ag–Ag parameters for

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their near-surface region, as well as to determine the percentage of Ag atoms in the core, near-surface regions of nanoparticle and of Ag ions bonded with two oxygen atoms in glass matrix. The obtained structural parameters were used to estimate the change of silver nanoparticles mean size and to propose the mechanism of nanoparticle growth after the thermal treatment.

2. Experimental

Soda-lime-silica glasses containing (in wt.%) 70.95% SiO_2, 14.1% Na_2O, 8.4% CaO, 3.69% MgO, 1.8% Fe_2O_3, 0.6% Al_2O_3, 0.18% K_2O and 0.22% SO_3 have been used as base glass material. Ag ions were introduced into by an Ag/Na ion exchange of several slices (15 mm × 15 mm in square and about 150 μm thick) of the base glass in a $NaNO_3$/0.05% $AgNO_3$ melt at 603 K for 195 h. Experiments of energy-dispersive X-ray spectroscopy (EDXS) of cross-section specimens showed a silver/sodium of approximately 10% at the glass surface immediately after the ion exchange (as-prepared). EDXS results demonstrated that the silver content decreases continuously from each surface side down to a depth of about 50 μm. In the glass interior no Ag could be detected, while upon annealing at 603 K a constant amount of silver was found throughout the whole sample as a result of interdiffusion processes.

Transmission electron microscope (TEM) investigations were carried out in addition to evaluate the size of silver particles by means of a Philips CM 20 FEG at 200 kV. Typical TEM bright-field images taken from different deep regions of the as-prepared sample and the annealed one, respectively, can be seen in Fig. 1. Obviously, compared to the initial state after annealing an increased number of Ag particles is present (Fig. 1c,d). For both charges of samples similar values of the particle size were measured in surface-near regions (as prepared: 1.5–6.5 nm, annealed: 1.5–5 nm). However, significant differences in the area density of nanoparticles can be observed. Presumably, the thermal treatment predominantly promoted nucleation processes, thus leading to an increase of the number of particles. Generally, for both samples the average particle size increases as a function of depth. In addition, in the case of the as-prepared state the number of Ag particles drops down drastically in regions deeper than about 50 μm. In the middle of this sample nearly no particles are present (see Fig. 1b). This is in contrast to the annealed sample, exhibiting a few particles with sizes up to 30–40 nm besides smaller ones in interior zones (cf. Fig. 1d). These TEM images do not demonstrated the existence of core–shell structures reflecting different densities of silver atoms within the silver particles. Some high-resolution TEM investigations showed similar results representing the structure of monocrystalline or polycrystalline Ag particles.

In HASYLAB (Hamburg, Germany) at beamline X1 Ag K-spectra (25.514 keV) were recorded in transmission mode at 10 K by means of a liquid-helium vapor flow cryostat. In each case a stack of several glass slices was used as sample in order to get a sufficient high signal. Experimental Ag K-edge EXAFS spectra of silver metallic foil as reference and of as prepared and annealed ion-exchanged soda-lime glasses for 8 h at 823 K were recorded [10].

3. Theory. Data analysis method

To study atomic structure of as prepared and annealed soda-lime glasses by experimental Ag K-edge EXAFS spectra one must consider at least two Ag species (states), contributing into oscillatory parts $\chi(k)$ of these spectra: i) Ag atoms in silver nanoparticles and ii) Ag ions inside the glass matrix, connected with two oxygen atoms, similar to that in AgO [11]. In Fig. 2 $\chi(k)$ of experimental Ag K-edge EXAFS and their Fourier-transforms F(R) in as prepared and annealed samples at $T =$ 10 K are compared to those of Ag K-edge EXAFS in Ag foil at the same temperature. Fig. 2(a) shows that the amplitudes of $\chi(k)$ oscillations in the spectra of glasses are lowered in comparison to foil, reducing the k-interval of the useful signal to $k_{max} \sim 14\,Å^{-1}$ for as prepared sample. Moreover, there are no significant changes in the frequencies of $\chi(k)$ oscillations beginning from $k \sim 4\,Å^{-1}$ to k_{max}. Fig. 2(b) shows that in the extended R-range of interatomic distances, all the peaks in $F(R)$ of Ag foil are retained in $F(R)$ of glasses. For Ag foil these peaks are reproduced below in Fig. 4(b) by the fit, taking into account the first five coordination shells of Ag in *fcc* structure of Ag foil and therefore, the comparison of Fig. 2(b) indicates that at least part of Ag atoms in nanoparticles, existing in as prepared and annealed glasses, have a local structure similar to that of *fcc* in Ag foil.

The simplest model of nanoparticles atomic structure, that provides such a behavior of $F(R)$ in the extended R-range, could be the atomic cluster of a chosen size, with undistorted *fcc* structure up to the cluster's surface. However, on the real surface and in the few following atomic layers the concentration of defects increases [12] and as the next approximation it is reasonable to assume that the model of silver nanoparticle atomic structure should consist of the *fcc* core and the near-surface region, which includes the atoms of the surface and subsurface layers. The last one should be a more or less distorted *fcc* structure with regard to atom positions and lattice vibrations. According to this model one must consider the following species (states) of the absorbing Ag atoms in glass, schematically illustrated in Fig. 3: Ag(1)—atoms in the core region of nanoparticle, which have the local structure similar to *fcc* structure of Ag foil; Ag(2)—atoms in the near-surface region of nanoparticle; Ag(3)—ions in glass bonded with two oxygen atoms.

Such a treatment permits to perform more detailed study of Ag nanoparticles atomic structure in soda-lime glasses using the fit of $F(R)$ of experimental Ag K-edge EXAFS, based on the function $\chi_{model}(k)$ compiled of the different terms $\chi_{Ag(i)}(k)$:

$$\chi_{\text{model}}(k) = C_1\chi_{Ag(1)}(k) + C_2\chi_{Ag(2)}(k) + C_3\chi_{Ag(3)}(k) \quad (1)$$

where each term $\chi_{Ag(i)}(k)$ represents the possible local structure of Ag(i) atom in glass. In this equation C_1, C_2, and C_3 are the percentages of Ag(1), Ag(2) and Ag(3) atoms respectively, from the total number of Ag atoms in glass, contributing to the $\chi(k)$ extracted from the experimental spectrum, so that:

$$C_1 + C_2 + C_3 = 1. \quad (2)$$

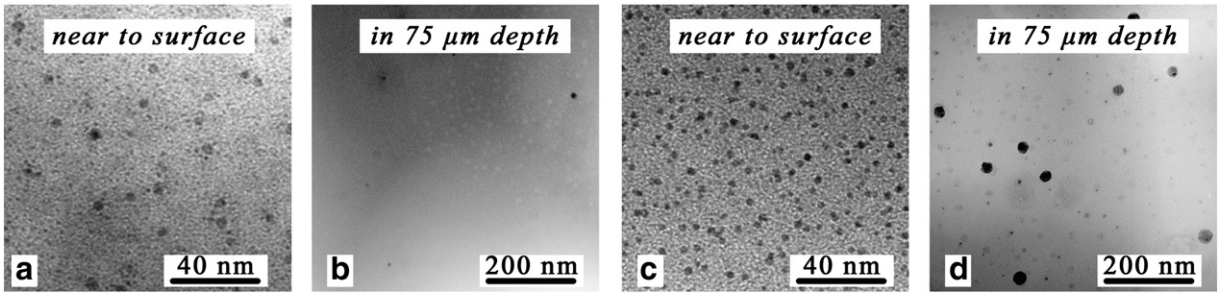

Fig. 1. TEM bright-field images of glasses with embedded Ag nanoparticles, microstructural peculiarities as found in different depths of a), b) the as-prepared sample, and c), d) the annealed one.