Long-Term Stable Silver Subsurface Ion-Exchanged Glasses for SERS Applications

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We report on the formation of silver subsurface ion-exchanged metal oxide (silver SIMO) glasses and their surface-enhanced Raman scattering (SERS) activity. The samples were prepared by a combined thermal and chemical three-step methodology and characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), environmental electron scanning microscopy (ESEM), and UV/Vis spectroscopy. This unique method provides SERS substrates with protection against contamination and strong, reliable and reproducible SERS enhancement. The Raman enhancement factors of the long-term stable SIMO glasses were estimated to approximately $10^7$.

1. Introduction

Noble metal nanoparticles play an important role in modern analytics and bioanalytics. Their most outstanding optical property, surface plasmon resonance, dramatically enhances the sensitivity of effects such as Raman scattering and fluorescence. Surface-enhanced Raman scattering (SERS) is based on local optical fields in the immediate proximity of metallic surfaces. It is exceptionally suitable for the simultaneous detection of many analytes and enables to overcome the low Raman scattering cross sections $(10^{-30} - 10^{-25})$ of the Raman effect. Usually, in normal Raman experiments, high concentrations and high laser intensities are required to detect Raman scattering signals. Noble metals such as gold, silver and copper are often used for SERS because they have favorable plasmonic properties, leading to efficient Raman enhancement in the visible and near-infrared spectral range. Often, SERS experiments are carried out in freshly prepared colloidal solutions. However, for many applications, planar substrates would be advantageous and easier to handle. There is a great interest in constructing long-term stable SERS-substrates that offer high reproducibility, especially in the field of bio-analytics. Specifcity of the surface for specific compounds such as DNA or proteins can be achieved by modifying such planar substrates with, for example, biomolecules based on established protocols. In the past years, much effort has been expended on an advance in SERS detection. A great variety of planar SERS substrates such as colloidal crystal films or nanoparticle arrays, adaptive silver films or sol-gel films have been proposed. However, these substrates lack long-term stability. Recently published studies of silver nanoparticle stability in a silica matrix under ambient conditions demonstrated that the prepared clusters are stable on a timescale of days to weeks. Similarly, silver nanoparticles deposited on a quartz surface remained SERS active for 90 days. It is still challenging to produce long-term stable SERS substrates with a high degree of reproducibility. Herein, we describe the formation of new subsurface ion-exchanged metal oxide (SIMO) substrates with long-term stability as well as persistent enhancement activity.

2. Results and Discussion

2.1. Sample Preparation and Characterization

We developed an optimised technique for the synthesis of silver nanoparticles (NPs) in soda-lime silicate glass through a combined thermal and chemical three-step methodology. The complex nucleation and growth of the nanoparticles is separated into three different fundamental physicochemical processes—ion transfer, reduction and growth by diffusion. A large amount of metal ions can be efficiently introduced in a short time (30 s) into the surface layer of glass via ion exchange, which leads to high cluster concentrations spatially localized in a thin subsurface layer. The ion exchange was carried out under isothermal and isochronal conditions. Silver ions were introduced into the glass by immersing the glass slides in a bath of a molten salt mixture of AgNO₃/NaNO₃ (1:2) for 30 s. Sodium ions from the surface and the subsurface region of the glass are substituted by silver ions. After the incorporation of silver ions, reduction was carried out by a subsequent reactive diffusion process in a hydrogen atmosphere. The subsequent reduction of the metal ions in the hydrogen atmosphere also contributed to the localisation of metal atoms in the immediate proximity of the glass surface. Penetration of hydrogen...
into the glass for reduction of noble metal ions is accompanied by diffusion of metal ions in the opposite direction, which leads to further concentration of metal atoms and smaller clusters in the vicinity of the glass surface. The obtained ion-exchanged glass samples were heat-treated (500 °C) in pure hydrogen flux inside a quartz tube. Hydrogen treatment was carried out with a hydrogen flux slightly above the atmospheric pressure, which was also maintained during the cooling stage. Before each experiment the quartz tube was flushed with pure nitrogen. The annealing time was five minutes. Additional thermal treatment in air leads to further growth of the metal particles. Finally, the hydrogen pretreated glass samples were annealed at 600 °C in air for 1 h to promote particle growth. TEM images of the as-prepared Ag SIMO glasses (Figure 1) show that the silver NPs are located in the immediate vicinity of the glass surface.

The NPs are concentrated in the subsurface in a 200 nm thick layer, Area 1 (Figure 1b) and a few particles can also be found down to a depth of 2 μm. The particles are spherical and show high crystallinity, as single atomic planes can be clearly observed (Figure 1c). The high-area fraction given in Figure 1a probably results from the projection of all particles within the sample cross section. The electron-transparent glass sample typically has a thickness of 20–60 nm. The NPs have a mean diameter of 10±3 nm, corresponding to 30% polydispersity. In principle, the very high particle density (62% area fraction) would favour the formation of so-called “hot spots”, which can result in much enhancement of the Raman signal. As it appears from the particle-size distribution histogram, also included in Figure 1a, predominantly small NPs (~6 nm) and only few very large particles are present. The reproducibility of the SERS enhancement is still given because Raman scattering probes the sample on the micron-scale (spot diameter on the sample is 1.6 μm). Therefore the resulting Raman signal intensity is always an average over several nanostructures on the surface, which can provide very high enhancement.

Figure 2 shows the UV/Vis spectra with a strong plasmon band occurring at approximately 415 nm for annealed silver SIMO glasses prepared with different ion-exchange durations (30 s–60 min).

Extending the ion-exchange duration leads to higher initial Ag ion concentrations, and therefore the intensity of the plasmon band is increased. We found a distinct blue-shift of the plasmon peak with increasing Ag concentration, which is usually associated with decreasing interparticle distance. From our observations, the resulting particle size is increased with increasing the initial Ag ion concentration and consequently the interparticle distance decreases. The plasmon peak shifts slightly with increasing concentration (Figures 2a–f) from 415 nm to 404 nm and as the full width at half maximum (FWHM) increases from about 63 nm to 88 nm. The intensity of the plasmon band for all samples remained unchanged over an observation period of one year, confirming that the particles are stable in the glassy matrix. Already for an ion exchange lasting only 30 s, the Ag concentration and therefore the optical density of the glass samples exceeds the linear range of the Lambert–Beer law.

Since the nanoparticles are located in the subsurface in the immediate vicinity of the glass surface they are well stabilized.
because they are covered by a protective glass layer (Figure 1b). For SERS investigations, the particles have to be accessible for the analyte molecules. As a consequence, the particles need to be uncovered, which is possible in principle mechanically by slight scratching or chemically by etching the glass surface.

Chemical etching is easy to perform, well controllable and reliable. The glass samples were etched in a dilute HF (4%) solution for 20 s to obtain substrates with uncovered particles.

Atomic force microscope (AFM) images were taken of an area of approximately 1.6 m². From the AFM image (Figure 3a) of the unetched glass, the intact glass surface without any particles can be observed. The circular structures belong to the glass surface structure, which according to the line-scan (Figure 3c) has a regular surface roughness of approximately 2–3 nm. On the etched sample (Figure 3b) the silver nanoparticles, visible as white spots, can be clearly observed regularly distributed over the entire surface and are also located at different levels.

A line scan across the etched sample surface displays particles protruding from the surface in the range from 20–25 nm (Figure 3d). The observation is also supported by environmental scanning electron microscope (ESEM) measurements of an unetched and etched Ag SIMO glass (Figure 4). Here the unetched glass surface again exhibits only very few particles randomly appearing at the surface (Figure 4a). With the help of an energy-dispersive X-ray spectroscopy (EDX) scan the silver concentration could be determined to 0.4 at%. In contrast, the etched surface (Figure 4b) shows homogeneously distributed silver nanoparticles at a high concentration (4.1 at%) throughout the imaged area of 336 μm².

2.2. Surface-Enhanced Raman Scattering

The silver nanoparticles are embedded in and covered by the glassy matrix. Therefore, they are well protected from contamination. Similarly, the covering of nanoparticles can also be achieved in functionalized sol–gel supports.[10] Nevertheless, problematic regarding the application of sol–gels is the limited durability of these substrates due to the instability of the nanoparticles.[11, 16] In contrast, the subsurface silver particles embedded into a surface layer of soda–lime silicate glass are well protected mechanically and chemically. Furthermore, the covering glass layer ensures consistent surface properties of the particles. The glass slides were etched in dilute HF (4%) for approximately 20 seconds. After pretreatment with dilute HF, the samples were repeatedly rinsed with deionized water and finally with methanol. Raman measurements were carried out with an aqueous solution of adenine as typical sample molecule.[16] Adenine (10⁻⁴ M) was dropped onto the glass substrates after etching of the surface. The experiments were repeated several times, on more than ten equally prepared samples and were found reproducible. The experiments were repeated after one year using the same samples with the same outcome (Figure 5).

From this replication, substrate stability and constant enhancement can be inferred. The silver nanoparticle substrates had sample dimensions of 2 cm². In order to determine homogeneous enhancement activity throughout a larger, microscaled area, selected samples were mapped over an area of 100 μm². Raman mapping experiments were performed at a step width of 10 μm, using an automated X–Y stage and repeated in each case at distinct positions on the same sample. The result of the mappings shows that the substrates display significant enhancement activity throughout the overall area (Figure 6).

In order to determine an enhancement factor of the new substrates, we have used methanol as an internal standard.[17] The SERS enhancement factors can be estimated by the comparison of the normal
3. Conclusions

The prepared Ag SIMO glasses have been shown to be efficient substrates for SERS with enhancement factors above $10^7$. The silver particles embedded in the surface layer of the glass are remarkably well stabilized. In principle, for real applications, such stable glass composites can be safely shipped and stored for long periods of time, before they are used in an analytical laboratory. The particles in the subsurface area can be exposed on demand, which works very well by chemical etching using an aqueous HF solution. The latter fact eliminates any additional potential signals in SERS spectra, which could occur from residual reagents in other preparation methods. With appropriate automated tools, the particles could also be exposed with mechanical methods and at the same time a microstructuring in terms of a patterning could be envisioned.

In contrast to other SERS devices our method stands out with its embedding and thus stabilizing properties. The stability of the particles can be examined and verified by the temporary evolution of the surface plasmon resonance. Over the course of the investigations (two years) no changes in the optical properties could be observed.

Experimental Section

Silver SIMO glass samples were prepared from commercial soda–lime silicate glass slides of 1 mm thickness (composition, wt %, SiO$_2$ 71.72, Al$_2$O$_3$ 1.23, Fe$_2$O$_3$ 0.19, TiO$_2$ 0.14, SO$_3$ 0.44, CaO 4.18, Na$_2$O 14.95, K$_2$O 0.34). AgNO$_3$ and NaNO$_3$ were purchased from Carl Roth. All reagents used were of analytical reagent grade. The glass slides were cleaned with ethanol and stored in ethanol followed by rinsing with deionized water prior to use. Particles embedded in soda–lime silicate glasses were prepared in a modified ion-exchange process under isothermal, isonconcentrated and isochronic conditions. The implemented ion-exchange technique is a three-step methodology composed of ion substitution, reduction and thermal treatment. Silver ion exchange was performed from a AgNO$_3$/NaNO$_3$ (1:2) salt bath at 350–8 °C and post-treated in a hydrogen atmosphere (5.0) for reduction of silver ions and subsequently annealed in air at 600 °C for 1 h.

The samples were investigated by UV/Vis spectroscopy in the 200–1100 nm region [HR2000, Ocean Optics, Sony ILX511 CCD-detector, resolution (FWHM): 0.065 nm] with a deuterium/tungsten lamp as light source. Evaluation of the experimental data was done using Spectra Suite software (Ocean Optics). Graphical evaluation was done with OriginPro 8.0.
The transmission electron microscope (TEM) measurements were carried out with a TITAN 80–300 (FEI) with an acceleration voltage of 300 kV. Image plotting was done with Digitath Micrograph. Statistical evaluation was done with ImageJ.

The atomic force microscope (AFM) measurements were carried out with a “Nanosurf Mobile S” (Nanoscience Instruments, Inc.). For eliminating actively acoustic noise the AFM was operated on a vibrationally isolated experimental board (Halcyonics, Inc.). The multimode AFM, equipped with two different scan head types, a large and a high resolution scan head, allows for maximum intermittend contact mode.

Environmental scanning electron microscopy (ESEM) and energy-dispersive X-ray spectroscopy (EDX) experiments were carried out on a tabletop microscope TM-1000 (Hitachi High-Technologies Europe GmbH) using a pre-centered cartridge filament electron gun and a high-sensitive semiconductor BSE (solid-state backscattered electron) detector. The acceleration voltage was 15 kV and the obtained magnification was between 20–10,000 x.

Raman spectra were acquired using a Raman spectrometer LabRam HR (Horiba Jobin–Yvon, Bensheim) equipped with a LN2-cooled CCD-camera (Horiba) and connected to a microscope (Olympus). The 632.8 nm line of a helium–neon laser was used as excitation source. The excitation light was directed onto the sample and the scattered light was collected with a 60 x water-immersion objective. The spot diameter on the sample was about 1.6 μm. A notch filter served for suppression of Rayleigh-scattered light and a single monochromator (grating 300 gr/mm−1) was used for dispersion of the scattered light. The irradiance on the sample was set to ~20 kW cm−2 and the integration time was 1 s. The line at 520.7 cm−1 in the Raman spectrum of silicon was used for frequency calibration. All data were recorded with LabSpec (Horiba) and analysed with Matlab-based software. The SERS enhancement factor was estimated by the comparison of the normal Raman band of methanol and the surface-enhanced Raman bands of adenine as described by Eichelbaum et al.[22]

The comparison takes into account the difference in the number of molecules of methanol and adenine within the scattering volume. Methanol was added to the aqueous solution of adenine (10−4 m) in a mixing ratio of 1:1. The signal intensity of the adeny ring breathing mode (740 cm−1) was about 10–15 times higher compared to the methanol signal (1030 cm−1).

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