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# Oxygen-induced enhancement of surface plasmon resonance of silver nanoparticles for silver-coated soda-lime glass

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## Abstract

The optical properties of a silver film on soda-lime glass substrate were studied after treatment in different atmospheres at different temperatures. It has been shown that pre-treatment in air (at about 500 °C for 1 h) can induce the enhancement of the surface plasmon resonance (SPR) of silver nanoparticles after subsequent treatment in H<sub>2</sub>. This enhancement effect decreases with decrease in the pre-treatment temperature in air up to 500 °C. Alternately heat-treating the as-prepared sample in air and then H<sub>2</sub> results in a continuous increase of the SPR. If the treatment temperature is at or above 600 °C, the SPR absorption can drastically be increased only by treatment in air without subsequent treatment in H<sub>2</sub>. We can thus control the SPR intensity of the sample. A further experiment has revealed that the SPR is from the silver nanoparticles formed in the sublayer of the glass substrate. Pre-treatment in air is crucial to the formation of silver nanoparticles in the sublayer after subsequent treatment in H<sub>2</sub>, which enhances the SPR.

## 1. Introduction

Metallic nanoparticles embedded in soda-lime glass have attracted much attention owing to their application in integrated optical devices [1–4]. Among nanoparticles of metals, silver nanoparticles are of great interest due to their large third-order optical nonlinearity and pronounced surface plasmon resonance (SPR) absorption which have potential applications in many aspects, such as optical waveguides and optical switches [2–4]. The SPR absorption depends on the dielectric properties of the surrounding host matrix, or the environmental atmosphere, in addition to the particle size and shape [2]. As we know, silver is very sensitive to some atmospheres, especially to oxygen [5, 6]. Study of the optical change with annealing

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atmospheres is thus of great significance. However, research on the effect of the atmosphere on the optical properties of silver nanoparticle-containing samples is very limited [7]. Our previous work [8, 9] showed that there is a big difference in optical absorption for silver nanoparticles located within the pores of mesoporous SiO<sub>2</sub> annealed in oxidizing and reducing atmospheres. It had been found that air annealing at 500 °C or higher temperature results in the disappearance of the SPR absorption, and that subsequent H<sub>2</sub> (or N<sub>2</sub>) annealing induces the reappearance of such SPR absorption. Alternately annealing in air and H<sub>2</sub> (or N<sub>2</sub>) induces alternating disappearance and appearance of the SPR absorption, showing the reversibility of the optical changes.

Recently, we have investigated the effect of the atmosphere on the optical properties of silver on soda-lime glass substrate. It has been found that a pre-heat treatment in air at about 500 °C can remarkably enhance the SPR absorption after subsequent heat treatment in H<sub>2</sub>. On pre-heating in air at higher temperature ( $\geq 600$  °C), however, the SPR absorption also drastically increases but without the need for treatment in H<sub>2</sub>. We can thus control the SPR of silver nanoparticles in glass in a very simple way. The details are reported in this paper.

## 2. Experiments

Soda-lime glass slides (main constituents: 72 mol% SiO<sub>2</sub> and 13.8 mol% Na<sub>2</sub>O) were washed with ethanol and then distilled water in an ultrasonic bath. A drop of 0.2 M AgNO<sub>3</sub> solution (about 0.05 ml) from a quantitative pipette was placed on the surface of the cleaned glass substrate, and a uniform liquid film with about 2 cm<sup>2</sup> area was formed by spin-coating, followed by drying at 80 °C for 20 min and annealing at 600 °C in H<sub>2</sub> for 2 h. The as-prepared samples were subsequently treated in different atmospheres at different temperatures for further optical characterization.

The surface morphology of the as-prepared samples was observed by a scanning electron microscopy (SEM, Sirion 200). X-ray diffraction (XRD) spectra were recorded on an X'Pert Pro MPD diffractometer and optical absorption was measured on a Cary-5E UV-Vis-NIR spectrophotometer at room temperature after each treatment.

## 3. Results

For the as-prepared sample, the XRD spectrum is shown in figure 1(a), indicating that silver has been formed on the glass substrate. Figure 1(b) illustrates the corresponding morphology of the film, which is mainly composed of discrete and micro-sized islands on the soda-lime glass substrate. Its optical absorption measurement demonstrates that there is an absorption peak around 400 nm, as shown in curve (a) of figure 2, which is the well known SPR absorption peak of silver nanoparticles or a fingerprint feature of silver nanoparticles, indicating the formation of silver nanoparticles [2].

If we remove the silver film on the substrate by immersion of the as-prepared sample in a concentrated nitric acid solution, the background absorption decreases but the SPR peak is almost unchanged, as illustrated in curve (b) of figure 2. This means that the measured SPR is mainly from the silver nanoparticles embedded in the soda-lime glass matrix. Subsequent treatment in air or H<sub>2</sub> leads to unchanged spectra (see curves (c) and (d) in figure 2).

After heat treatment of the as-prepared sample in air at 500 °C for 1 h (without removal of the silver film on the substrate), the SPR absorption peak shifts about 12 nm to longer wavelength, together with a slight decrease of whole spectrum (see curve (b) in figure 3). However, if we subsequently treat the sample in H<sub>2</sub> at 500 °C for 1 h, the SPR increases significantly and the peak position blue-shifts back, as shown in curve (c) of figure 3. Further

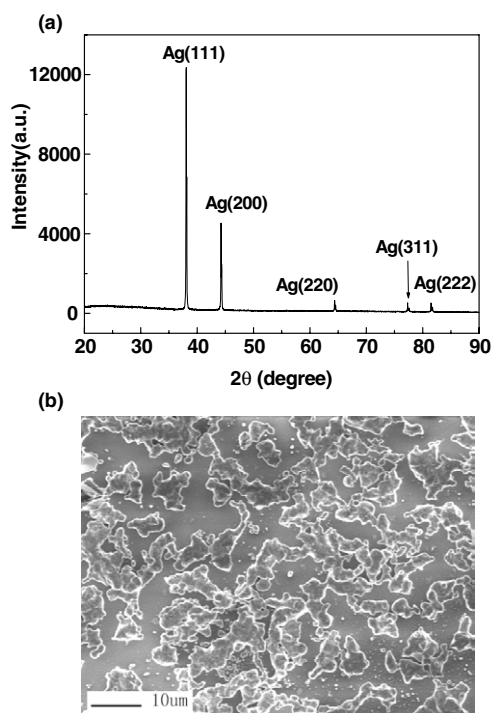


Figure 1. XRD spectrum (a) and the SEM image (b) of the as-prepared sample.

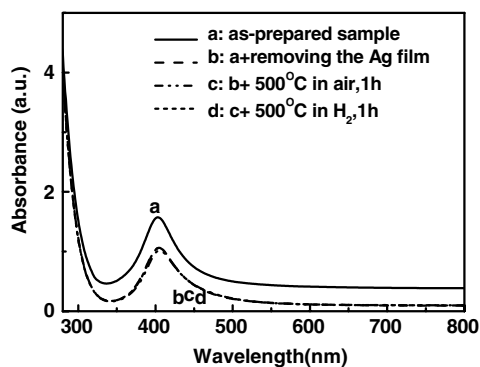
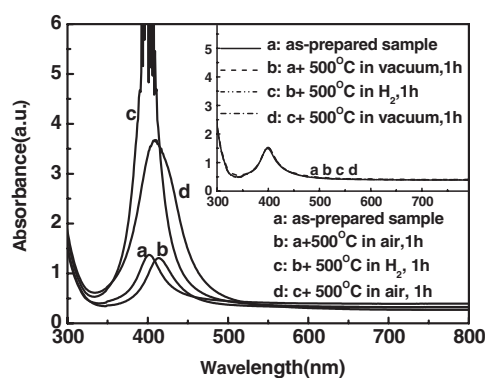
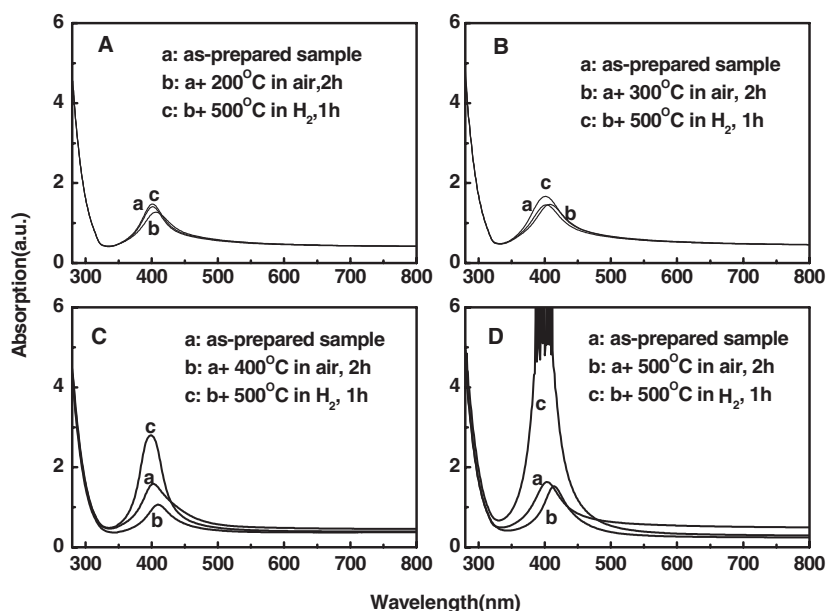


Figure 2. Optical absorption spectrum of the as-prepared sample, and its spectral evolution after removal of silver film on the substrate and subsequent treatment in different atmospheres at 500 °C for 1 h.

heat treatment in air (at 500 °C for 1 h) once more induces a slight decrease and red-shift of the SPR (see curve (d) in figure 3). On alternately heat-treating the as-prepared sample in air and then H<sub>2</sub>, the SPR absorption can be continuously enhanced, and the peak position alternately red- and blue-shifts. In contrast, if the as-prepared sample is alternately treated at 500 °C in vacuum ( $\sim 10^{-5}$  Pa) instead of air, and then H<sub>2</sub>, no change is observed for the optical spectrum, as shown in the inset of figure 3. Obviously, it is air and not any thermal effect that induces the enhancement of the SPR adsorption after subsequent treatment in H<sub>2</sub>.



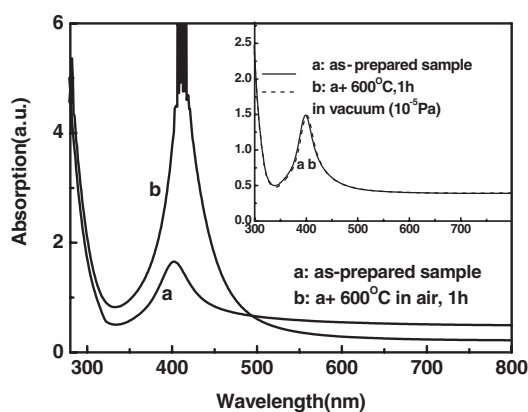
**Figure 3.** Optical absorption spectral evolution of the as-prepared sample after alternately heating in air and  $H_2$  at  $500\text{ }^\circ\text{C}$  for 1 h. Inset: optical absorption spectra of the as-prepared sample after alternately heating in vacuum ( $10^{-5}$  Pa) and  $H_2$  at  $500\text{ }^\circ\text{C}$  for 1 h.



**Figure 4.** Optical absorption spectra of the as-prepared sample after pre-heat treatment at different temperatures in air for 2 h and subsequent annealing in  $H_2$  at  $500\text{ }^\circ\text{C}$  for 1 h. (A)–(D): pre-heat treatment in air at 200, 300, 400, and  $500\text{ }^\circ\text{C}$ , respectively.

However, if the pre-treatment of the as-prepared sample in air is below  $500\text{ }^\circ\text{C}$ , enhancement of the SPR is not significant after subsequent treatment in  $H_2$  at  $500\text{ }^\circ\text{C}$ , as shown in figure 4. The lower the temperature of pre-treatment in air is, the more insignificant is the enhancement of the SPR after subsequent treatment in  $H_2$  at  $500\text{ }^\circ\text{C}$ .

If the air-heating temperature is higher than  $500\text{ }^\circ\text{C}$ , say  $600\text{ }^\circ\text{C}$ , the result is quite different. Figure 5 shows the optical absorption spectra for the as-prepared sample after heat-treatment in air at  $600\text{ }^\circ\text{C}$  for 1 h without subsequent heat-treatment in  $H_2$ . The SPR also drastically increases, but the peak position still shifts to the longer wavelength. However, if the as-prepared



**Figure 5.** Optical absorption spectra of the as-prepared sample heated in air at 600 °C for 1 h. Inset: absorption spectra of the as-prepared sample heated in vacuum at 600 °C for 1 h.

sample is heat-treated in vacuum at 600 °C for 1 h, no change can be detected for the optical absorption spectrum, as seen in the inset of figure 5.

#### 4. Discussion

Now let us give a brief discussion about the effect of air-pretreatment at different temperatures on the SPR of silver nanoparticles after subsequent treatment in H<sub>2</sub> for the silver-coated glass. It is well known that AgNO<sub>3</sub> can decompose into Ag by heating in ambient air according to the reaction [10]



Thus it is expected that the AgNO<sub>3</sub> film on the glass is completely decomposed into Ag after annealing in H<sub>2</sub> at 600 °C for 2 h, which has been confirmed by XRD measurement (shown in figure 1(a)). Ion exchange between partial Ag<sup>+</sup> ions in the solution film and Na<sup>+</sup> ions in the sublayer near surface region of soda-lime glass could occur during drying before heating in H<sub>2</sub> [7, 11–13]. Subsequent H<sub>2</sub>-treatment leads to the reduction of silver ions and formation of silver nanoparticles in the sublayer of the glass, due to the hydrogen permeability in glass [7], which induces the SPR, in addition to the formation of the silver film on the substrate, which causes the background absorption in the wavelength region studied.

Sears *et al* [14–16] reported that on the surface of some metal oxides or soda-glass, silver ions and charged oxygen gas (O<sub>2</sub><sup>-</sup>) would be produced from polycrystalline silver metal in oxygen at a high temperature (about 500 °C). In our experiment, there inevitably exist Ag<sup>0</sup> atoms on the substrate for the as-prepared sample. Heat treatment in air 500 °C for 1 h will lead to the formation of Ag<sup>+</sup> ions on the substrate due to oxygen, and the occurrence of ion exchange between the Ag<sup>+</sup> ions on the substrate and Na<sup>+</sup> ions in the sublayer of the glass. Subsequent treatment in H<sub>2</sub> gives rise to reduction of the silver ions and formation or growth of silver nanoparticles in the sublayer, which causes enhancement of the SPR. Obviously, alternately treating in air and then in H<sub>2</sub> will continuously enhance the SPR due to the formation of more and more silver nanoparticles in the sublayer. Also, due to the dependence of atomic activity on temperature, the enhancement effect of the SPR after subsequent treatment in H<sub>2</sub> increases with the increase in the pre-treatment temperature of the as-prepared sample in air up to 500 °C (see figure 4).

Furthermore, pre-treatment in vacuum or removal of the film on the substrate for the as-prepared sample will not produce silver ions, and hence subsequent treatment in H<sub>2</sub> leads to the unchanged SPR (see figure 2 and the inset of figure 3). As regards the significant enhancement of the SPR induced only by pre-treatment in air at 600 °C without subsequent treatment in H<sub>2</sub>, it seems that reduction of Ag<sup>+</sup> ions in the sublayer (from substrate surface) occurred at 600 °C in air, which is still unclear in mechanism and needs further study. But it should be associated with treatment in air because no enhancement is observed if the pre-treatment is in vacuum at 600 °C (see figure 5). In addition, a red-shift and decrease of the SPR for the silver nanoparticles in the glass matrix after treatment in air could be associated with oxygen adsorption (or bondage) on silver nanoparticles in the sublayer by oxygen atomic diffusion. Such oxygen bondage on silver nanoparticles will involve charge-transferring or surface localization of some free electrons in the silver nanoparticles, and hence result in red-shift and decrease of the SPR, as previously reported in detail [2, 17, 18]. However, the oxygen bondage on silver nanoparticles in the sublayer, after treatment in air, is to be confirmed in future work.

## 5. Conclusions

In summary, we have studied the optical properties of a silver film on soda-lime glass substrate after treatment in different atmospheres at different temperatures. Pre-treatment of the as-prepared sample in air leads to production of Ag<sup>+</sup> ions on the substrate surface and the occurrence of ion exchange between the Ag<sup>+</sup> ions and the Na<sup>+</sup> ions in the sublayer of the glass. Subsequent treatment in H<sub>2</sub> induces a reduction of the exchanged Ag<sup>+</sup> ions and formation or growth of silver nanoparticles in the sublayer, leading to enhancement of the SPR. Alternate treatment in air and in H<sub>2</sub> will lead to more and more silver nanoparticles in the sublayer and hence continuous enhancement of the SPR. We can thus control the enhancement effect of the SPR in a very simple way.

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