Substrate dependent surface plasmon resonance evolution of Ag nanoparticles treated in atmospheres

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Abstract

The evolution of surface plasmon resonance (SPR) with alternate air and H_2 treatment was investigated for silver nanoparticles on different SiO_2-based substrates (soda-lime glass, quartz glass and mesoporous SiO_2). It has been shown that evolution behaviours on the three substrates are very different. For silver nanoparticles on the mesoporous SiO_2 substrate, alternate air and H_2 heat treatment led to the alternate disappearance and appearance of the SPR, showing the reversibility of optical changes. For a soda-lime glass substrate, the SPR absorption also disappeared after the first run heat treatment in air and re-appeared after subsequent H_2 heat treatment, but the second run heat treatment in air could not induce the re-disappearance of the SPR. After alternate heating of the sample in air and H_2 for four or more cycles, the SPR stayed almost unchanged. For a quartz glass substrate, however, the SPR absorption became negligible after alternate air and H_2 heat treatment. Such effects of the substrate on the SPR are explained in terms of the subtle difference of the three SiO_2-based substrates in micro-structure or chemical composition, and the redox of silver in the treatment atmospheres. This study could be important for the design and architectonics of new optical devices based on SiO_2 materials and could also promote the understanding of the interaction of silver nanoparticles with the environment.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

SiO_2-based composite materials containing metal nanoparticles have attracted much attention owing to their applications in integrated optical devices [1–4]. Among metal nanoparticles, Ag is of great interest due to its large third-order optical nonlinearity and pronounced surface

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plasmon resonance (SPR), which have potential applications in many aspects, such as optical waveguides and optical switches [2]. In addition to particle size and shape [2, 5], the SPR absorption of silver nanoparticles is also very sensitive to the atmosphere (especially to oxygen [6, 7]) and the supporting substrates or surrounding host matrix. However, the study of the effects of the atmosphere and substrate on the optical properties of silver-containing samples is very limited [8].

In our previous work [9, 10], it had been reported that there was a big difference in optical absorption for small Ag nanoparticles located within pores of mesoporous SiO_2 annealed in reducing and oxidizing atmospheres. H_2 (or N_2) annealing ($\geqslant 500\,°C$) resulted in strong SPR absorption, as is usually expected, but subsequent air annealing induced the disappearance of such SPR absorption. Alternate annealing in air and H_2 (or N_2) induced the alternate disappearance and appearance of the SPR, showing the reversibility of optical changes. The air-annealing-induced disappearance of the SPR was attributed to the oxidation of Ag, since the SPR is usually a fingerprint feature of metallic silver nanoparticles. Further thermodynamic analysis [10] showed that it is possible for silver nanoparticles to be oxidized to Ag_2O even at high temperature when the particle size is small enough (smaller than a critical size). However, we did not find direct experimental evidence of Ag_2O formation after air annealing at $\geqslant 500\,°C$. Some questions remain. Is the oxidation product Ag_2O or Ag^+ ions which enter the mesoporous silica skeleton or adsorb on the pore wall? Are the redox process and corresponding SPR evolution related to the surrounding host matrix or the supporting substrates? Therefore, research on the effects of the substrate on the SPR in different atmospheres should be of significance for addressing such issues.

In this paper, we investigate the effects of the substrate on the optical evolution of silver nanoparticles on three different SiO_2-based substrates (soda-lime glass, quartz glass, and mesoporous SiO_2) after alternate air and H_2 heat treatments. It has been found that samples on the three different substrates exhibit great differences in optical evolution with the treating atmospheres, indicating that the redox process and corresponding SPR evolution are related to the substrates. This study could be important for the design and architectonics of new optical devices based on SiO_2 composite materials, and could promote understanding of the interaction of silver nanoparticles with the environment. The details are reported in this paper.

2. Experimental details

Mesoporous SiO_2 (planar-like, about 1.5 mm in thickness) was first prepared by a sol–gel technique with precursors: tetraethylorthosilicate, water, alcohol (catalyzed by HNO_3), followed by drying, and finally annealing at $700\,°C$ for 1 h, as previously described in [11, 12]. The mesoporous silica prepared in this way, whose pores are interconnected and open to ambient air, had a porosity of about 50%, a specific surface area of $560\ m^2\ g^{-1}$, and pore diameters mainly distributed in the range below 20 nm, determined by isothermal N_2 adsorption measurement, as described previously in [13]. Commercially available soda-lime glass slides (main constituents: 72 mol% SiO_2 and 13.8 mol% Na_2O) and quartz slides (pure SiO_2 glass) were washed with ethanol and then distilled water in an ultrasonic bath.

High-quality bulk Ag with a purity of 99.999% was deposited on the surface of the three kinds of substrates up to an equivalent thickness of about 20 nm by thermal evaporation under a vacuum of 1×10^{-5} Pa at room temperature. The deposition rate was about $0.3\ nm\ min^{-1}$, controlled by a film thickness monitor (FTM-V, Shanghai).

The as-prepared samples were alternately treated in air and H_2 at $500\,°C$ for 1 h. Optical absorption spectra were measured on a Cary 5E UV–vis–NIR (ultraviolet–visible–near-infrared) spectrophotometer at room temperature after each heat treatment.
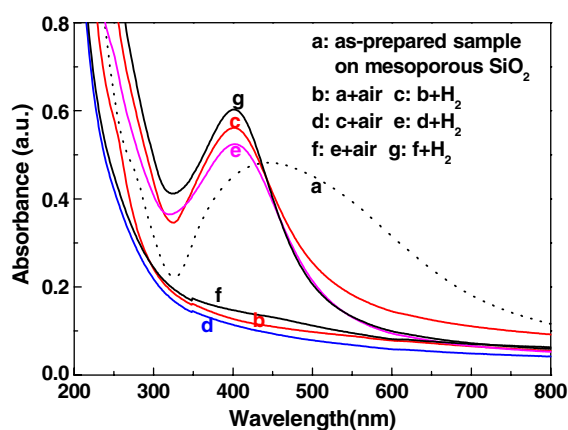
Figure 1. Optical absorption spectra of the sample on a mesoporous SiO_2 substrate after treatment at $500\,°C$ for 1 h in air or H_2: (a) as-prepared without treatment; (b)–(g) sample (a) after alternate treatment in air and H_2, respectively (see the text).

Figure 2. Optical absorption spectra of the sample on a soda-lime glass substrate after treatment at $500\,°C$ for 1 h in air or H_2: (a) as-prepared without treatment; (b)–(i) sample (a) after alternate treatment in air and H_2, respectively (see the text).
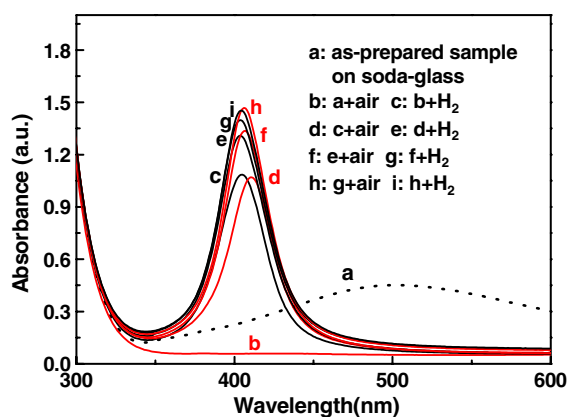
3. Results

3.1. Initial heat treatment in air

The optical absorption spectra for the sample on the mesoporous SiO_2 substrate are shown in figure 1. The as-prepared sample shows a broad peak at around 450 nm (see curve (a) in figure 1), which should originate from the well-known SPR of Ag nanoparticles. After treatment in air at $500\,°C$ for 1 h, however, the SPR absorption disappears (see curve b of figure 1). The following H_2 heat treatment induces the appearance of the SPR again, with a peak at around 400 nm (shown in curve (c) of figure 1). If we subsequently treated this sample alternately in air and H_2 atmospheres, the disappearance and appearance of the SPR of silver nanoparticles occurred alternately with an unchanged peak position (at about 400 nm) (see curves (d)–(g) of figure 1), showing reversible optical changes.

For the sample on the soda-lime glass substrate, however, the optical evolution is quite different, as shown in figure 2. The as-prepared sample showed a broad SPR of silver
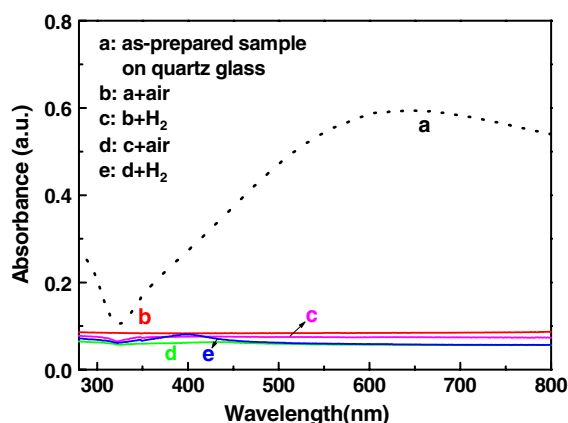
Figure 3. Optical absorption spectra of the sample on a quartz glass substrate after treatment at 500 °C for 1h in air or H_2: (a) as-prepared without treatment; (b)–(e) sample (a) after alternate treatment in air and H_2, respectively (see the text).

nanoparticles at around 500 nm (see curve (a) in figure 2). Initial heat treatment in air led to the disappearance of the SPR, and subsequent H_2 heat treatment induced its appearance at around 405 nm (see curves (b) and (c) in figure 2), which is similar to the sample on mesoporous SiO_2. However, the following air–heat treatment could not induce the disappearance of such SPR, and only led to a small red-shift (to about 410 nm), as illustrated in curve (d) of figure 2, which was completely different from that on the mesoporous SiO_2 substrate. After experiencing H_2 heat treatment once more, the SPR increased slightly and the peak shifted back to a shorter wavelength (about 405 nm) (see curve (e) of figure 2). After subsequent alternate heat treatment of the sample in air and H_2 for four or more cycles, the SPR stayed almost unchanged.

In contrast, the optical spectra for the sample on the quartz glass substrate were much different from those of the samples on both substrates mentioned above, as illustrated in figure 3. The as-prepared sample showed a very broad absorption peak at around 630 nm (curve (a) in figure 3). After heat treatment in air, the absorption peak disappeared (see curve (b) of figure 3). Subsequent heat treatment in H_2 only led to very weak absorption (see curve (c) of figure 3). The following heat treatment in air and H_2 also resulted in the disappearance of SPR and a very weak optical absorption (which is negligible) (see curves (d) and (e) of figure 3).

An x-ray diffraction (XRD) spectral study was conducted. Ag diffraction was observed for the as-prepared samples on the three substrates, but no diffraction peak appeared after the initial air–heat treatment.

3.2. Initial heat treatment in H_2

If the as-prepared samples were initially treated in H_2 instead of air, the optical spectra exhibited different evolutions.

For the as-prepared sample on mesoporous SiO_2, the SPR was narrowed and blue-shifted to 375 nm after initial H_2 treatment, as illustrated in curve (b) of figure 4. Subsequent alternate air and H_2 heat treatment induced similar results to those shown in figure 1, namely the alternate disappearance and appearance of the SPR with an unchanged peak position at 400 nm (see curves (c)–(h) in figure 4).

If the sample on the soda-lime glass substrate was initially heated in H_2, the SPR blue-shifted to 415 nm (shown in curve (b) of figure 5). Subsequent air–heat treatment induced
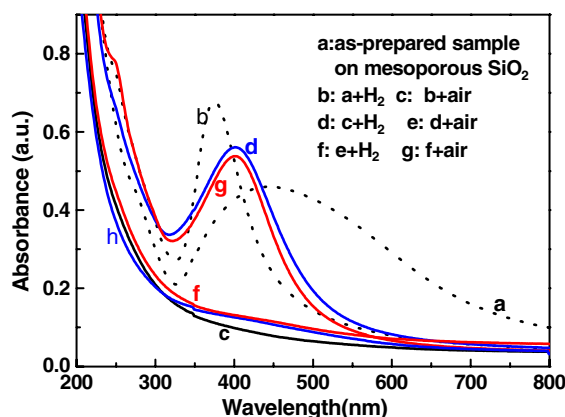
Figure 4. Optical absorption spectra of the sample on a mesoporous SiO_2 substrate after treatment at $500\,°C$ for 1 h in H_2 or air: (a) as-prepared without treatment; (b)–(g) sample (a) after alternate treatment in H_2 and air, respectively (see the text).

Figure 5. Optical absorption spectra of the sample on a soda-lime glass substrate after treatment at $500\,°C$ for 1 h in H_2 or air: (a) as-prepared without treatment; (b)–(j) sample (a) after alternate treatment in H_2 and air, respectively (see the text).
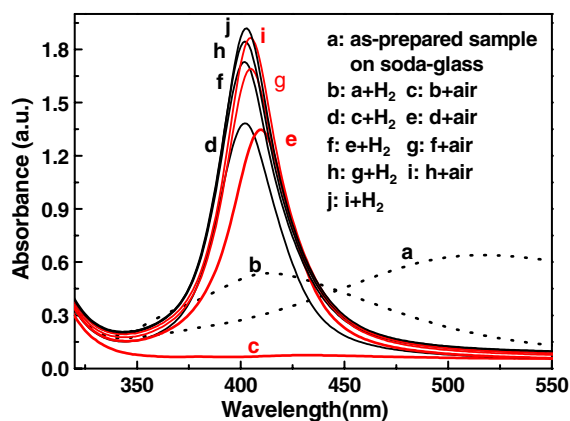
the disappearance of such SPR absorption (see curve (c) of figure 5). The results induced by following alternate heat treatments were similar to those shown in figure 2.

After initial H_2 heat treatment of the as-prepared sample on the quartz substrate, the SPR blue-shifted to 400 nm, with a shoulder absorption at about 360 nm (shown in curve (b) of figure 6). Subsequent air–heat treatment led to a very weak SPR absorption (shown in curve (c) of figure 6). Subsequent heat treatment in H_2 produced a very small increase in SPR (see curve (d) of figure 6). Final alternate heat treatment in air and H_2 only induced negligible optical absorption (see curves (e) and (f) of figure 6).

4. Discussion

As mentioned above, initial treatment in air leads to the disappearance of the SPR for the as-prepared samples on the three substrates, while initial treatment in H_2 instead of air induced
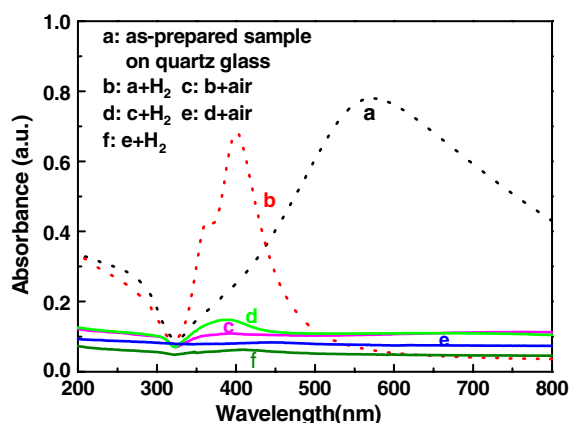
Figure 6. Optical absorption spectra of the sample on a quartz glass substrate after treatment at 500 °C for 1 h in H_2 or air: (a) as-prepared without treatment; (b)–(f) sample (a) after alternate treatment in H_2 and air, respectively.

a blue-shift and a narrowing of the SPR. In subsequent alternate treatment in air and H_2, the samples on the three different SiO_2-based substrates exhibited very different optical evolution. Mesoporous silica substrate leads to the reversible disappearance and appearance of the SPR. Soda-lime glass substrate induces a small change in the SPR, which was relative strong and an alternate red/blue-shift. Quartz glass substrate results in negligible SPR optical absorption.

Generally, H_2 heat treatment only produces a reducing effect, while the effect of oxygen is more complicated. It has been reported that, when silver was exposed to an air or oxygen atmosphere at high temperature, faceting behaviour [14, 15] occured and striations [16–18] were formed on the surface of silver, due to oxygen modifying the surface energies of the silver crystal planes. Rhead *et al* [15, 19] found that diffusion, the evaporation rate and thermal etching would be much greater when bulk silver is exposed to oxygen or air than to H_2/N_2. Sharma *et al* [20] observed an agglomeration phenomenon for silver films on quartz substrate in oxygen, which was induced by the quick diffusion of silver atoms on the substrate. Bao *et al* [6] pointed out that oxygen can dissolve into, adsorb on, or bind to bulk Ag(110) and (111) planes at the high temperature of ($\geqslant$500 °C). For the nanometre-sized Ag, some special reactions, which do not easily happen in a bulk system, could occur. In this study, after initial air–heat treatment of the as-prepared samples on the mesoporous SiO_2 and soda-lime glass, the SPR absorption all disappeared, which can be attributed to oxidation of Ag nanoparticles. Such oxidation induces the formation of Ag^+ ions, i.e. the reaction [21],

$$Ag^0 + O_2 \rightarrow Ag^+ + O_2^- \tag{1}$$

would occur.

For mesoporous SiO_2, there are a great deal of dangling bonds on the pore wall [22], which could combine with other active ions. Air–heat treatment at high temperature led to the formation of Ag^+ ions, which can be trapped by dangling bonds on the pore walls, i.e.

$$-O-\underset{|}{\overset{|}{Si}}-O\cdots Ag$$
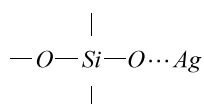
In fact, previous research on photoluminescence spectra [23, 24] also suggested that there are Ag^+ ions diluted in the SiO_2 matrix for the sol–gel SiO_2 containing silver after

air annealing. Hence the initial air–heat treatment led to the disappearance of the SPR absorption (see curve (b) of figure 1). Subsequent H_2 treatment would induce the reduction of such oxidized silver species and the formation of Ag nanoparticles again, leading to the re-appearance of the SPR (see curve (c) of figure 1). Subsequent alternate treatment in air and H_2 gives rise to alternate redox and hence a reversible optical change (see curves (d)–(g) of figure 1).

For the as-prepared sample on the soda-lime glass, similar to that on the mesoporous silica, initial air–heat treatment led to oxidation of Ag nanoparticles and hence the disappearance of the SPR (see curve (b) of figure 2). It is well known that silver ions (in melting $AgNO_3$ or $AgNO_3$ solution) can be readily exchanged by alkalis in soda-lime glass [2–5]. The Ag^+ ions resulted from the oxidation of silver during air–heat treatment and could also exchange with Na^+ in glass, leading to the diffusion of Ag^+ ions into the sublayer of the substrate. Due to hydrogen permeability in soda-lime glass [8], subsequent H_2 treatment induced the reduction of Ag^+ ions in the sublayer and the formation of Ag nanoparticles in the sublayer, leading to the re-appearance of the Ag SPR at 400 nm (see curve (c) of figure 2). Obviously, subsequent treatment in air could not induce re-oxidization of the Ag nanoparticles formed in the sublayer and hence kept the SPR (see curve (d) of figure 2). A small red-shift of the SPR peak position could be associated with the adsorption of oxygen during treatment in air [25]. Subsequent alternate treatments in H_2 and air led to an alternate shift with a small increase for the SPR due to more Ag nanoparticles being formed in the sublayer by ion exchange (see curves (e)–(i) of figure 2). After experiencing four cycles of alternate heat treatments in air and H_2, the SPR absorption stayed almost unchanged, because the silver on the substrate had been exhausted and no more silver ions diffused from the surface into the sublayer.

For the as-prepared sample on quartz, however, there are no surface dangling bonds for Ag^+ ion adsorption or Na^+ ions in the substrate for ion exchange. In this case, the evaporation of Ag, and the agglomeration of small particles into larger ones, could be dominant, leading to many blank areas on the substrate and hence a big decrease in the SPR absorption (which was negligible, see figure 3). Figure 7 shows the morphology of the as-prepared sample before and after initial treatment in air at 500 °C. For the latter, we can see that isolated large particles of micrometre size are formed and most areas on the substrate are blank without silver, which induces high optical transmittance and hence very low absorption.

Finally, initial treatment in H_2 instead of air for the as-prepared samples on the three substrates would induce the formation of spherical isolated silver nanoparticles, leading to narrower SPR and its blue-shift (see curves (b) of figures 4–6) due to the dependence of the SPR on size and shape [2, 5].

5. Summary and remarks

Silver nanparticles on different substrates (soda-lime glass, quartz glass, and mesoporous SiO_2) show different optical evolution with treatment atmospheres at high temperature. The interaction of Ag with oxygen in air leads to the oxidation of Ag and the formation of Ag^+ ions. For silver nanoparticles on the mesoporous SiO_2 substrate, the Ag^+ ions can adsorb on the pore walls due to the dangling bonds during air treatment. H_2 treatment leads to the reduction of Ag^+ ions and the formation of Ag nanoparticles. Alternate air and H_2 heat treatments induce the alternate redox of Ag and hence the alternate appearance and disappearance of the SPR. For soda-lime glass substrate, Ag^+ ions can exchange with Na^+ ions and enter the sublayer of the substrate during air treatment. Subsequent H_2 treatment can lead to the reduction of the Ag^+ ions and the formation of Ag nanoparticles in the sublayer. Subsequent alternate treatment in air and H_2 only induces a small change in the SPR, which was relatively strong.
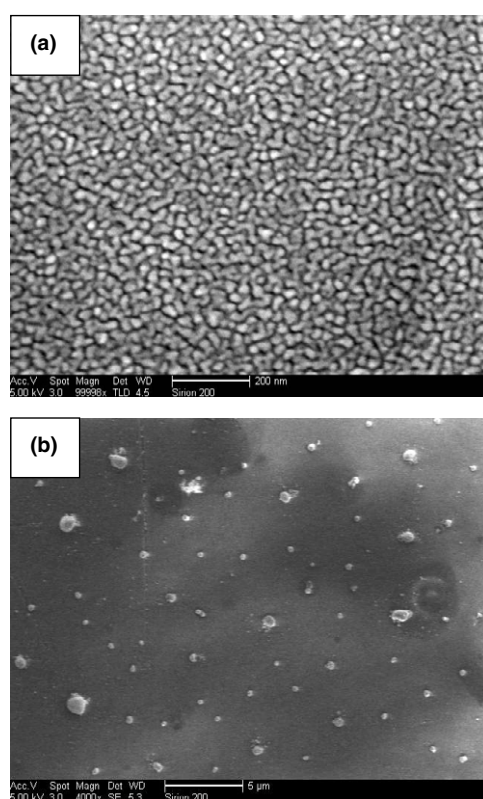
Figure 7. Field emission scanning electron microscopic images of the as-prepared sample on quartz glass (a) and after heating in air at 500 °C for 1 h (b).

For the quartz glass substrate, the evaporation of Ag and the agglomeration of small particles into larger ones would be dominant during treatment at high temperature due to the absence of surface dangling bonds for Ag^+ ion adsorption or Na^+ ions in the substrate for ion exchange, leading to negligible SPR absorption after alternate air and H_2 heat treatment.

This study has revealed that the substrate has a significant effect on Ag SPR in different atmospheres, which could be important for the design and architectonics of new optical devices based on SiO_2 materials and could promote the understanding of the interaction of silver nanoparticles with the environment. Also, the study of the substrate dependence of Ag SPR on different atmospheres in this paper has clarified the oxidation product of the supported Ag nanoparticles, induced by air or oxygen at high temperature, i.e. the product should be Ag^+ ions, which will adsorb on the pore walls for a mesoporous SiO_2 support or enter the sublayer for a soda-lime glass substrate, instead of Ag_2O, as previously reported.

Acknowledgments

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