Water vapour-induced enhancement of the surface plasmon resonance for Ag nanoparticles

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LETTER TO THE EDITOR

Water vapour-induced enhancement of the surface plasmon resonance for Ag nanoparticles dispersed within pores of mesoporous silica

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Abstract
The optical evolution for monolithic mesoporous silica soaked in Ag^+ ion solution (0.01–0.06 M) and annealed in air or water vapour is investigated. Heat treatment in air results in the absence of the surface plasmon resonance (SPR) peak of Ag nanoparticles. However, water vapour annealing induces a strong Ag SPR peak, exhibiting a strong reduction effect on Ag^+ ions and an enhancement effect on the SPR absorption. The enhancement and weakening of the SPR can be controlled through annealing in water vapour and air alternately. This finding indicates the possibility that Ag nanoparticles dispersed in silica may be useful in optical sensors for humid environment use at high temperature.

It is well known that bulk metal silver is very stable and insensitive to atmosphere, even at high temperature, because bulk silver oxide (Ag_2O) will decompose in air at above $200\,°C$ according to the reaction [1]

$$Ag_2O \xrightarrow{>200\,°C} 2Ag + \tfrac{1}{2}O_2.$$
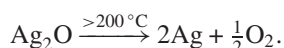
However, very small particles exhibit different physical and chemical behaviours from the bulk. A spherical Ag nanoparticle is characterized by surface plasmon resonance (SPR) absorption in the visible region [2]. The SPR, varying not only with the size and shape of the particles [2–9] but also with the chemical environment [2, 10–12], has been extensively studied due to its potential application in many areas such as non-linear optics and optical devices [2, 13]. Although there are many reports about the SPR absorption of Ag nanoparticles, only a few concern the optical change with annealing atmosphere, involving the small difference in absorption when heat treating Ag-containing samples in different gases, which is generally attributed to the gas chemisorption [11, 14–16]. However, our previous work [17, 18] showed

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that there is a great difference in the optical absorption for Ag nanoparticles located within pores of mesoporous silica annealed in oxidizing and reducing atmospheres. Heat treatment in a reducing atmosphere (H_2 or N_2) induces a strong Ag SPR peak, but air annealing results in the disappearance of the SPR peak. Nevertheless, transmission electronic microscopic (TEM) observation indicated the existence of Ag nanoparticles in the silica in both cases [18]. The absence and appearance of the SPR absorption can be controlled through alternating annealing in air and H_2 (or N_2). Recently, by soaking monolithic mesoporous silica in Ag^+ ion solution and then annealing in water vapour or air, we found that the sample is very sensitive to water vapour. The water vapour can result in reduction of Ag^+ ions and enhancement of the Ag SPR, which is in contrast to the previous report that water vapour can induce oxidation of Pt-group metals in oxygen atmosphere [19, 20]. This finding indicates the possibility that Ag nanoparticles dispersed in silica may be useful for optical sensor use in humid environments at high temperature. The details are reported in this letter.

The monolithic mesoporous silica host (planar-like, about 1.5 mm in thickness) was first prepared by a sol–gel process, drying, and finally annealing at $700\,^\circ$C for 1 h, as described in detail elsewhere [21, 22]. The mesoporous silica prepared in this way, whose pores are interconnected and open to ambient air, had a specific surface area of 600 $m^2\,g^{-1}$ and pore diameters mainly distributed in the range below 20 nm, determined by isothermal N_2 adsorption measurement, as previously described [23]. The host was then soaked into silver nitrate ($AgNO_3$) aqueous solution for five days, and taken out for heat treatment in air or water vapour in a quartz tube in an oven (ambient pressure), at a desired temperature (500 or $700\,^\circ$C); this was followed by cooling down to room temperature in air. Here, the concentrations of $AgNO_3$ solution used were from 0.01 M up to 0.06 M. Correspondingly, the loading amount of Ag in the host was estimated to be from 0.074% up to 0.44% in weight, respectively, from the host porosity and concentration of the soaking solution, without considering the loss of Ag during its preparation [22]. For reference, a silica host without doping is subjected to the same treatment.

Optical absorption spectra were measured on a Cary 5E UV–VisNir spectrophotometer at room temperature immediately after the heat treatment. TEM observation was conducted on a JEOL JEM 2010 operating at an accelerating voltage of 200 kV.

Figure 1 shows the optical absorption spectra for the samples with different loadings, annealed at $500\,^\circ$C for 1 h in air and water vapour respectively. It can be seen that, for the sample annealed in air, no peak appears and the absorption edge red-shifts with increasing Ag loading in the solid sample, which is in agreement with the previous reports [14, 18]. For the sample annealed in water vapour, however, the spectra are completely different. A strong optical absorption peak appears around 390 nm (or 400 nm for the sample with the smallest Ag loading), which is the well known SPR of Ag nanoparticles [2]. The SPR increases with increase of Ag loading up to 0.22% in weight (corresponding to the concentration of soaking solution 0.03 M); this is accompanied by a rise of the absorption in low energy region (showing a long tail). But when the concentration of the soaking solution is 0.04 M, the peak decreases suddenly. Interestingly, further rise of the concentration leads to an increase of the SPR peak again. In addition, Ag loading in silica does not have a significant effect on the SPR position, except for the sample with the smallest loading, in which the position is red-shifted. Further experiments revealed that these results are of good reproducibility. TEM examinations show approximately spherical Ag particles uniformly dispersed in silica for not only the sample treated in water vapour but also that annealed in air (although there is no SPR detected), which is in agreement with our previous results obtained with annealing in H_2 (or N_2) and air respectively, as illustrated in figure 2 in [18]. Figure 2 shows the optical absorption spectra for the samples annealed at a higher temperature ($700\,^\circ$C). For the samples annealed in air,
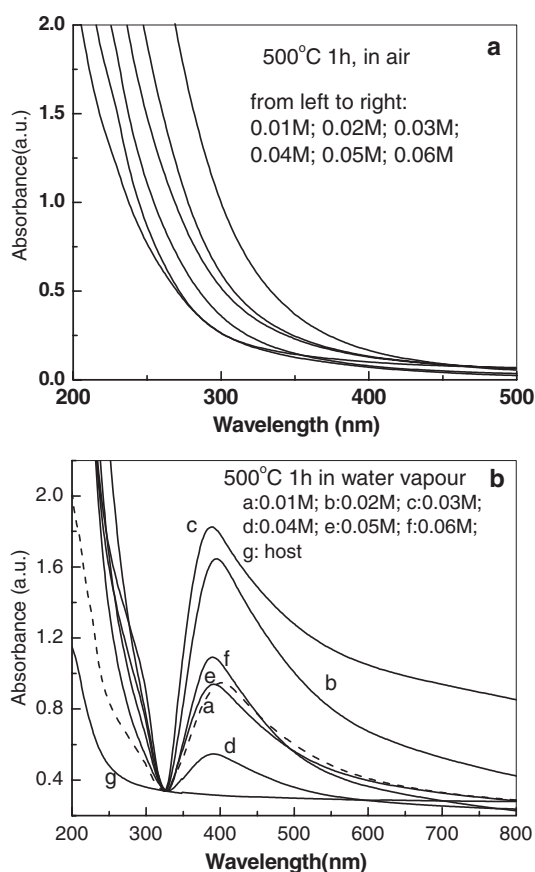
Figure 1. Optical absorption spectra for the meosoporous silica soaked in different concentrations of Ag$^+$ ions, annealed at 500 °C for 1 h in air (a) and water vapour (b).

the spectra are similar to those for samples annealed at 500 °C (not shown here). But for the sample treated in water vapour, the Ag SPR peak increases monotonically with increase of the concentration. The peak intensity is much higher than that shown in figure 1(b) for the sample with the same loading, and the peak shape is approximately of Lorentz type, in contrast to those obtained after annealing at 500 °C. Obviously, water vapour has a strong reduction effect on Ag$^+$ ions at high temperature and an enhancement effect on Ag SPR.

Further, alternating treatment in water vapour/air was also conducted. Figure 3 illustrates typical results for the sample annealed starting with water vapour. For the sample treated at 500 °C, initial water vapour treatment leads to a strong Ag SPR peak (the same as curve f in figure 1(b)). Subsequent treatment in air induces a significant decrease of the peak. On annealing in water vapour once more, an obvious rise of the SPR peak occurs again, but much lower than that with initial treatment in water vapour. Finally, a following annealing in air again gives rise to almost complete disappearance of the peak. The optical evolution for the sample annealed at 700 °C in water vapour first and then in air alternately is similar to the situation for treatment at 500 °C. The difference is that the SPR peak, after final heat treatment in air, does not disappear but is stronger than that after the first heat treatment in air. If we treat the soaked samples in the opposite order to that shown in figure 3, i.e. in air first and then in vapour alternately, the optical evolution appears quite different; a typical illustration
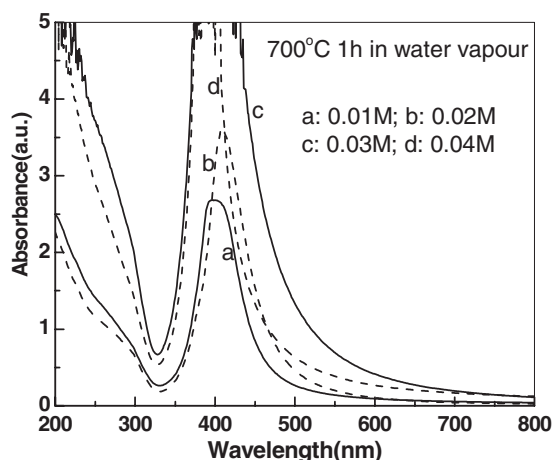
Figure 2. Optical absorption spectra for the soaked mesoporous silica annealed at 700 °C for 1 h in water vapour.

appears in figure 4. After the sample is annealed at 700 °C in air, no peak appears. Subsequent annealing in water vapour gives rise to an obvious SPR peak. The peak decreases significantly after the sample is heated in air again. But the final treatment in water vapour leads to a sharp and strong SPR of Ag nanoparticles, nearly four times as high as that after the previous run of treatment in water vapour (see curves b and d in figure 4(b)). For the sample annealed at 500 °C, it is very much unexpected that no absorption peak appears in the spectra during the first three heat treatment steps (air → water vapour → air). Only the final run of annealing in water vapour results in an obvious Ag SPR peak. We have repeated this experiment for the other parallel samples. The results show good reproducibility. It should be mentioned that the samples with other loadings used in this letter show similar optical evolution with treatment environments to those in figures 3 and 4.

Now let us give a brief discussion. When the sample with very low loading is heat treated in air at 500 °C or above, there is no detectable Ag SPR peak, which is in agreement with previous reports [14, 17, 18, 24, 25], and here this will not be discussed in depth (high enough Ag loading ($> \sim 1\%$ in weight) in silica will usually lead to obvious SPR [16, 23, 26]). Absence of the SPR after original treatment in air was mainly attributed to the chemisorption of O_2 on the Ag particle surface during cooling in air after treatment [14], or oxidation for most particles which are smaller than a critical size (only some larger Ag particles were observed in TEM), as previously systematically studied [14, 17, 18, 27]. The red-shift of the absorption edge with increasing concentration could be associated with optical scattering and/or rise of silver oxide nanoparticle size [14, 18].

Heat treatment in water vapour induces reduction of Ag ions and enhancement of the Ag SPR peak, which exhibits similar effects to those of H_2 and N_2 atmospheres [18]. Although exposure of Ag/SiO_2 samples to a humid ambient at room temperature increases the SPR of Ag nanoparticles [24, 25, 28], to the best of our knowledge it has not been reported so far that treatment in water vapour at high temperature induces reduction of Ag^+ ions and enhancement of Ag SPR. Nevertheless, Weaver *et al* [19, 20] reported that water vapour can trigger surface oxidation of platinum-group transition metals in oxygen atmosphere, instead of reduction of metal ions. Here we suggest that the partial pyrolysis of H_2O into H_2 and O_2 may occur within the nanosized pores (nanoreactors) induced by pore walls in silica [29]. So there exist
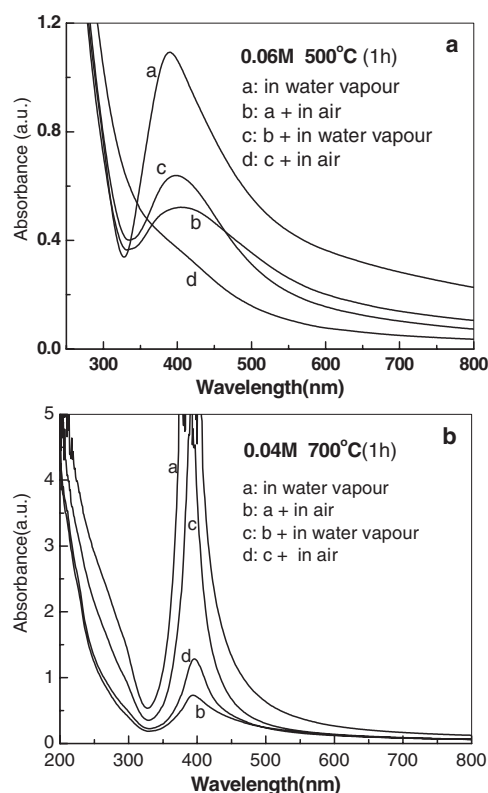
Figure 3. Optical absorption spectra for the soaked mesoporous silica after annealing at 500 °C (a) and 700 °C (b) in water vapour/air for 1 h alternately (see the text).
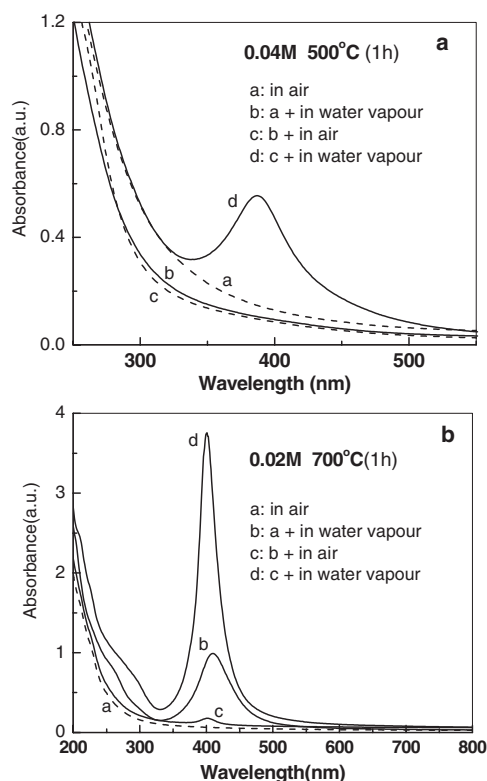
Figure 4. Optical absorption spectra for the soaked mesoporous silica after annealing at 500 °C (a) and 700 °C (b) in air/water vapour for 1 h alternately (see the text).

competing reactions: oxidation and reduction processes. Such reactions should be temperature and particle size (or loading) dependent. Obviously, according to the optical measurements above, when annealing at 700 °C in water vapour, the reduction reaction dominates. If annealing at 500 °C, however, it seems that the reactions are comparable, which might also lead to the special behaviours of the sample prepared with 0.4 M $AgNO_3$ (see figures 1(b) and 4). In addition, in the water vapour atmosphere, the pore wall of silica might be more active and possibly charge transfer will occur between Ag and silica, which may even form a new phase of silver silicate leading to a rise in optical absorption in the low energy region (see figure 1(b)), as previously reported [28]. It is clear that much additional work will be required for a complete understanding of such optical evolution mechanisms in water vapour. Further experiments and analysis are now in progress.

Concerning the SPR position, it is known that it is insensitive to Ag nanoparticle size in the range from 2 to 10 nm [2, 26]. But when the size is smaller (<2 nm), an obvious red-shift will appear because of the free path effect [2, 30] and chemisorption of O_2 on particles [14, 26]. The red-shift for the sample of curve a in figure 1(b) could be attributed to too small a size of Ag particles (smaller loading should correspond to smaller particles in silica).

In conclusion, the optical evolution for Ag-doped silica is dependent on the features of the treatment environment, such as temperature and atmosphere. Water vapour exhibits a strong

reduction effect on Ag^+ ions located within pores of silica and thus causes an enhancement of the Ag SPR. Alternate annealing in water vapour/air at $700\,°C$ results in reversible enhancement and weakening of the SPR peak. These findings indicate the possibility that Ag nanoparticles dispersed in silica may be useful for optical sensor use in humid environments at high temperature.

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