

## Evolution of the optical spectra of an Ag/mesoporous SiO<sub>2</sub> nanostructure heat-treated in air and H<sub>2</sub> atmospheres

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 Nanotechnology 18 185710

(<http://iopscience.iop.org/0957-4484/18/18/185710>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 202.127.206.107

The article was downloaded on 25/06/2010 at 02:44

Please note that [terms and conditions apply](#).

# Evolution of the optical spectra of an Ag/mesoporous SiO<sub>2</sub> nanostructure heat-treated in air and H<sub>2</sub> atmospheres

Jinlian Hu<sup>1,2,3,4</sup>, Woong Lee<sup>2</sup>, Weiping Cai<sup>3</sup>, Liuniu Tong<sup>1</sup> and Haibo Zeng<sup>3</sup>

<sup>1</sup> School of Materials Science and Engineering, Anhui Key Laboratory of Metal Materials and Processing, Anhui University of Technology, Ma-An-Shan, 243002 Anhui, People's Republic of China

<sup>2</sup> School of Nano and Advanced Materials Engineering, Changwon National University, Changwon, Gyoungnam 641-773, Republic of Korea

<sup>3</sup> Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031 Anhui, People's Republic of China

E-mail: [jlhu@issp.ac.cn](mailto:jlhu@issp.ac.cn)

Received 5 January 2007, in final form 23 February 2007

Published 11 April 2007

Online at [stacks.iop.org/Nano/18/185710](http://stacks.iop.org/Nano/18/185710)

## Abstract

Evolution of the various optical spectra of Ag nanoparticles dispersed in mesoporous SiO<sub>2</sub> after heating alternately in H<sub>2</sub> and air atmospheres has been investigated. It has been observed that, in accordance with alternate heat treatment in H<sub>2</sub> and air, surface plasmon resonance (SPR) absorption of the Ag/mesoporous SiO<sub>2</sub> nanostructure alternately appeared and disappeared and its Raman scattering spectra reversibly increased and decreased. In contrast, its photoluminescence (PL) spectra alternately disappeared and appeared, whereas the infrared (IR) spectra did not change. Such novel optical sensitivities of silver nanoparticles are discussed on the basis of the changes in chemical states of silver induced by the interaction of silver nanoparticles with the atmospheres and the hosting medium. It is suggested that the chemical state of silver in mesoporous SiO<sub>2</sub> changes reversibly between Ag and the Ag<sup>+</sup> ion by the redox process.

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

## 1. Introduction

Metallic nanoparticles dispersed in SiO<sub>2</sub> have drawn much attention due to their potential applications in catalysis and nano-optics [1, 2]. Among metallic nanoparticles, silver (Ag) nanoparticles are of great interest, as they show large third-order optical nonlinearity and pronounced surface plasmon resonance (SPR), which enables potential applications in many fields such as optical waveguides and optical switches [2], surface-enhanced Raman scattering (SERS) [3], optical data storage devices [4], biochemical sensors [5], etc. Besides, since Ag is very sensitive to the

environmental atmosphere, especially to oxygen [1], study of the effect of the environmental atmosphere on the optical characteristics of Ag nanoparticle-containing structures would be of great theoretical and practical significance. For instance, the pores of mesoporous SiO<sub>2</sub> are interconnected with each other and open to the environmental atmosphere, and therefore use of such a mesoporous medium yields an interesting nanostructure in which Ag nanoparticles are highly dispersed and well in contact with the environmental atmosphere. Such nanoparticle-dispersed nanostructures can then be used to study atmosphere-related changes in optical properties of the Ag nanoparticles.

While there has been broad interest in the gaseous reactions of silver nanoparticle-dispersed mesoporous SiO<sub>2</sub> for

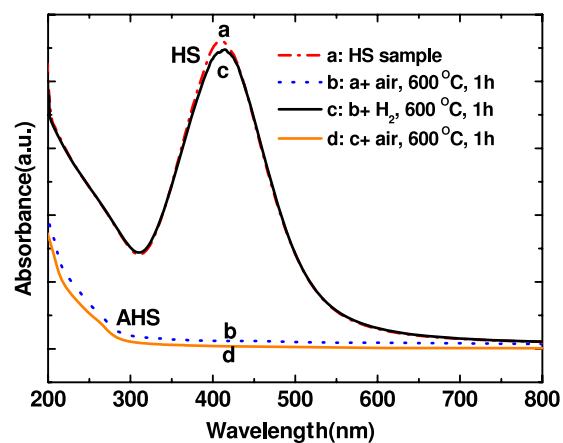
<sup>4</sup> Author to whom any correspondence should be addressed.

catalysis [6–9], research on the effect of the environmental atmosphere on the optical properties of Ag nanoparticle-containing structures is somewhat limited. De *et al* [10] found the changes in peak position and intensity of the SPR absorption spectra when a Ag/mesoporous SiO<sub>2</sub> nanostructure was heat-treated in different annealing atmospheres (air, argon and 5% H<sub>2</sub>–95% N<sub>2</sub>) and Yáñezlimón *et al* [11] observed luminescence in a similar system when annealed in air. However, in these works, no significant atmosphere-sensitive effects on the optical properties has been reported. In the previous works of the current authors [12, 13], it has been reported that there was a great difference in the atmosphere-dependent optical absorption of a Ag/mesoporous SiO<sub>2</sub> structure with low Ag content. Heat treatment in H<sub>2</sub> atmosphere above 500 °C resulted in a strong SPR absorption, whereas subsequent air annealing caused the disappearance of the SPR absorption. The air-annealing-induced disappearance of the SPR absorption was attributed to the oxidation of Ag, since the SPR is usually a fingerprint feature of metallic Ag nanoparticles. Further thermodynamic analysis showed that it would be possible for Ag nanoparticles to be oxidized into Ag<sub>2</sub>O even at high temperature when the particle size is smaller than a certain critical size [13]. Despite this corollary, direct experimental evidence of the formation of Ag<sub>2</sub>O was not found in the samples air-annealed above 500 °C.

Although there are some views that Ag<sub>2</sub>O could exist in SiO<sub>2</sub> glasses containing Ag [14, 15], some questions still remain. It is not clear whether the oxidation product is Ag<sub>2</sub>O or Ag<sup>+</sup> ions which enter the mesoporous silica skeleton and are subsequently adsorbed on the pore wall. Further, physical and chemical states of Ag are not fully understood. Since optical properties are hypersensitive to physical and chemical states of the matter and their surrounding environments, research on optical properties should be important in clarifying such issues. Thus, in the current study, optical properties of Ag/mesoporous SiO<sub>2</sub> (with low Ag content) were investigated to clarify the physical and chemical states of Ag after heating in H<sub>2</sub> and air. Changes in the optical characteristics of the Ag nanoparticles dispersed in mesoporous SiO<sub>2</sub> were investigated by analysing the evolution of the various optical spectra of the nanostructure after alternate heat treatment in H<sub>2</sub> and air atmosphere. Atmosphere-related optical sensitivities of Ag nanoparticles were attributed to the reversible changes in chemical states of silver between Ag and Ag<sup>+</sup> ions in the redox process induced by the interaction of Ag nanoparticles with the atmosphere and the hosting medium. This study should reveal the atmospheric and interfacial reaction and the special optical sensitivity of Ag nanoparticles dispersed in mesoporous SiO<sub>2</sub>, thus contributing to nano-optics.

## 2. Experimental details

Planar-shaped mesoporous SiO<sub>2</sub> (about 1.5 mm thick) was prepared by a sol–gel technique with precursors containing tetraethylorthosilicate, water and alcohol (catalysed by HNO<sub>3</sub>), followed by drying and finally annealing at 700 °C for 3 h, as described previously [16, 17]. The mesoporous silica prepared in this way, the pores of which are interconnected and open to ambient air, had a porosity of about 50%, a specific surface area of 560 m<sup>2</sup> g<sup>-1</sup> and pore diameters mainly



**Figure 1.** SPR optical absorption spectra of the HS sample after alternate heat treatments in air and H<sub>2</sub> atmospheres.

distributed in the range 1–8 nm, determined by isothermal N<sub>2</sub> adsorption measurement, as described previously [18]. This hosting medium was then soaked in AgNO<sub>3</sub> aqueous solution (0.025 M) for 5 days and then taken out for heat treatment in H<sub>2</sub> at 600 °C for 1 h in a quartz tube. The Ag nanoparticles were thus formed *in situ* within the pores of silica mesoporous solid (samples prepared this way are hereafter denoted by HS). The amount of Ag loaded in the mesoporous SiO<sub>2</sub> host was estimated to be 0.125% in weight from the host porosity and concentration of the soaking solution, without considering the loss of Ag during its preparation. For investigation of the oxidized states of the Ag nanoparticles, HS samples were heat-treated in air at 600 °C for 1 h (the air-treated sample is hereafter denoted by AHS). Optical characteristics of the HS and the AHS samples were investigated by absorption spectroscopy using an ultraviolet–visible (UV–vis) spectrometer (Cary 5E), Raman scattering spectroscopy with a 488 nm laser source (Renishaw 1000 Raman spectroscope), infrared (IR) spectroscopy using an FT-IR spectrometer (NEXUS) and photoluminescence (PL) spectroscopy using a spectrophotometer with a Xe lamp (FLS920,  $\lambda = 260$  nm). All spectroscopy was carried out at room temperature immediately after each heat treatment.

## 3. Results and discussion

Figure 1 shows the UV–vis optical absorption spectra of the as-prepared HS sample (curve *a*) and the heat-treated samples (curves *b*, *c*, and *d*). It can be seen that the as-prepared HS sample exhibited a strong absorption peak at about 410 nm, which is a well-known SPR absorption characteristic of Ag nanoparticles [2]. However, subsequent annealing of the sample in air at 600 °C resulted in the complete disappearance of the SPR peak, as reflected in curve *b*, and the optical absorption spectra thus became identical to those of mesoporous SiO<sub>2</sub> (not shown). These are in agreement with the previously reported behaviours elsewhere [13]. Additional alternate heat treatments in H<sub>2</sub> and in air caused the corresponding appearance (curve *c*) and disappearance (curve *d*) of the 410 nm peak again. The alternate appearance and disappearance of the SPR absorption

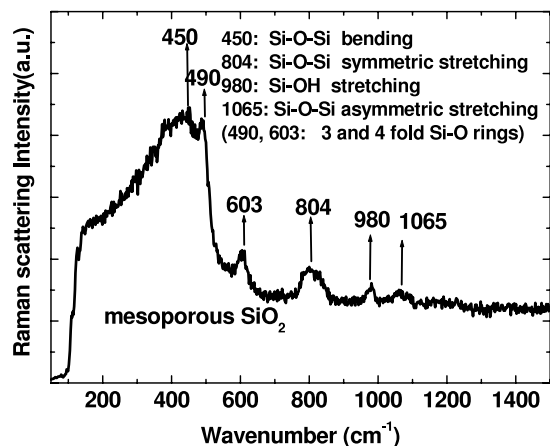


Figure 2. Raman spectra of the mesoporous SiO<sub>2</sub> hosting medium.

peak in accordance with the alternate heat treatment in H<sub>2</sub> and air atmospheres indicates reversibility of the changes in the optical characteristics. In the temperature range between 500 and 1000 °C, the higher the air-treatment temperature was, the more rapidly the SPR absorption peak disappeared. For instance, at 700 °C, the SPR peak of the HS sample would disappear completely after air heat treatment for just 0.5 s.

From the observation that the 410 nm peak appears only in the UV-vis absorption spectra of the as-prepared and the H<sub>2</sub>-treated samples, it is inferred that air heat treatment of the HS sample led to oxidation of Ag, resulting in the disappearance of the SPR peak, since the SPR is usually regarded as a fingerprint feature of metallic Ag nanoparticles [2]. Regarding the 410 nm SPR peak, it has been reported that SPR peaks in the wavelength range between 380 and 450 nm appear from the spherical Ag nanoparticles (diameters from 1 to 50 nm) dispersed in SiO<sub>2</sub> matrix [2, 13]. Therefore, it is believed that the 410 nm SPR peak is an indication of the metallic properties of the nanoparticles, originating from the collective electron resonance of metallic nanoparticles [2], and at the same time showing the reduction effect of H<sub>2</sub>.

Figure 2 shows the Raman spectra of the mesoporous SiO<sub>2</sub> recorded as a reference state, in which all the expected characteristic bands of SiO<sub>2</sub> appeared. The 450 cm<sup>-1</sup> band is assigned to a Si-O-Si bending mode; the small signals at 804 and 1065 cm<sup>-1</sup> to Si-O-Si symmetric and asymmetric stretching modes respectively, and the 980 cm<sup>-1</sup> peak to a Si-OH stretching vibration mode [19]. In addition, two peaks at 490 and 603 cm<sup>-1</sup> are assigned to four- and three-fold Si-O rings. Raman spectra of the HS and the AHS samples are shown in figure 3 as curves *a* and *b*, respectively, together with those of mesoporous SiO<sub>2</sub> (curve *c*). Compared with mesoporous SiO<sub>2</sub>, the Raman scattering background of the HS sample was obviously increased, especially the 450 and the 980 cm<sup>-1</sup> peaks and, at the same time, a strong peak in the wavenumber range 140–150 cm<sup>-1</sup> was noticed. On the other hand, after the HS sample was heated in air at 600 °C for 1 h (AHS sample), no characteristic Raman peak of Ag<sub>2</sub>O appeared at about 545 cm<sup>-1</sup> [20] (see curve *b*), and the Raman scattering spectra obviously decreased, having no noticeable difference from those of mesoporous SiO<sub>2</sub>. Similarly to the changes of SPR absorption spectra in figure 1, Raman

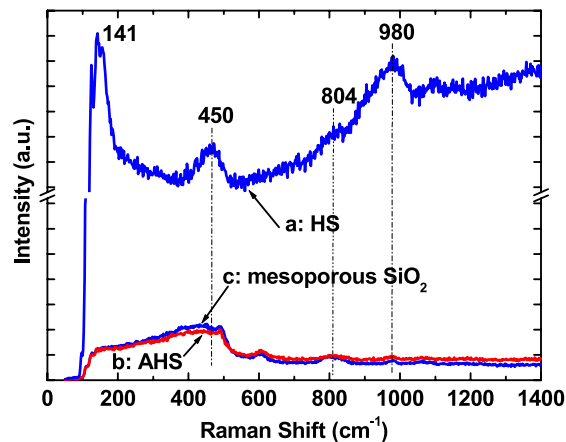
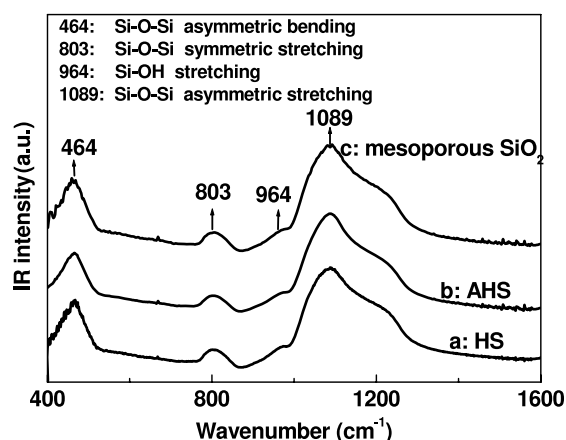


Figure 3. Comparison of the Raman spectra of (a) the HS sample, (b) the AHS sample and (c) the mesoporous SiO<sub>2</sub>.

spectra also exhibited an alternate increase and decrease in the intensities corresponding to the alternate heat treatment in H<sub>2</sub> and in air.

In the Raman spectra of the HS sample, two Raman peaks at 450 and 980 cm<sup>-1</sup> intensified noticeably, in addition to the increased background intensity. It is supposed that the two intensified peaks originate from the surface-enhanced Raman scattering (SERS) effect of metallic silver nanoparticles on the Si-O-Si bending and Si-OH stretching modes, since it is widely accepted that collective electron oscillations of metal nanoparticles can resonate with both exciting and scattered photons [3, 21]. This coupling would concentrate and strengthen the local electromagnetic field, resulting in the SERS effect. In other words, the existence of Ag nanoparticles in the HS sample does not cause structural modification in the mesoporous SiO<sub>2</sub>, but it could change the local electromagnetic field, thereby influencing the Raman scattering spectra of the Ag/SiO<sub>2</sub> nano-assembly. The noticeably increased background intensity, compared to the Raman spectra of the mesoporous SiO<sub>2</sub>, can be associated with electron-hole excitation in Ag nanoparticles [22–25]. One interesting feature in the Raman spectra of the HS sample shown in figure 3 is that there exists strong scattering at 140–150 cm<sup>-1</sup>, the origin of which is not clear. Only low-frequency Raman shifts in the 10–20 cm<sup>-1</sup> wavenumber range have been observed for Ag nanoparticles [26, 27]. As this peak does not appear in both the mesoporous SiO<sub>2</sub> host and the AHS sample, it is tentatively ascribed to some metallic characteristics. But, to confirm this, further investigation will be necessary.

Unlike the above SPR and Raman spectra, as shown in figure 4, IR absorption spectra of the HS (curve *a*) and the AHS (curve *b*) samples did not exhibit any significant differences compared to those of the mesoporous SiO<sub>2</sub> (curve *c*), while the mesoporous SiO<sub>2</sub> showed the expected characteristic IR spectra. The 464 cm<sup>-1</sup> peak of the curve *c* is attributed to Si-O-Si asymmetric bending, while the 803 cm<sup>-1</sup> and the 1089 cm<sup>-1</sup> peaks are assigned to Si-O-Si symmetric and asymmetric stretching vibrating modes, respectively. The band at 964 cm<sup>-1</sup> is due to Si-OH stretching [19]. Further, in the IR spectra of the AHS sample obtained by heat treatment of the



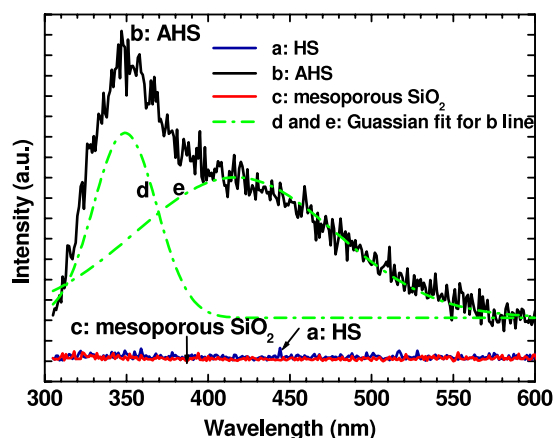
**Figure 4.** Comparison of the IR absorption spectra of (a) the HS sample, (b) the AHS sample and (c) the mesoporous SiO<sub>2</sub>. Note: the plots have been displaced vertically for clarity.

HS sample in air at 600 °C for 1 h, no characteristic IR band of Ag<sub>2</sub>O at 535 cm<sup>-1</sup> [28] was recorded.

In the SPR and Raman spectra in figures 1 and 3, the loss of metallic characteristics of Ag nanoparticles due to oxidation is obvious after heat treatment in air, which is represented as the disappearance or decrease of the peaks specific to the HS sample corresponding to the metallic nature of Ag. In the meantime, in the Raman and the IR spectra in figures 3 and 4, respectively, there is no indication of the presence of Ag<sub>2</sub>O. It is inferred from these observations that, while the loss of the metallic characteristics of Ag nanoparticles due to oxidation is obvious, the oxidation process caused neither a change in the basic structure of mesoporous SiO<sub>2</sub> nor the formation of any oxidation products of Ag such as Ag<sub>2</sub>O. Then it is of interest how the physical and chemical states of the Ag nanoparticles undergo changes during the oxidation process, which is clarified below from the analysis of PL spectra.

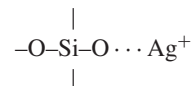
Upon excitation by a 260 nm light source, the HS sample exhibited no luminescence, as shown in figure 5 (curves *a*). However, heat treatment of the HS sample in air at 600 °C for 1 h yielded an emission centred at 350 nm and another emission centred at 420 nm, as shown in figure 5 (curve *b*). Further heat treatment of the AHS sample in H<sub>2</sub> at 600 °C for 1 h caused the disappearance of such luminescence, resulting in PL spectra indistinguishable from those of the mesoporous SiO<sub>2</sub> shown as curve *c* in figure 5. Following heat treatment in air once more, the luminescence emissions appeared again (not shown). Interestingly, in contrast to the changes of SPR and Raman spectra upon alternate heat treatments, PL spectra reversibly disappeared and appeared by alternate heat treatments in H<sub>2</sub> and air, showing optical reversibility.

PL spectra of the AHS sample herein are not similar to those of Ag<sub>2</sub>O reported elsewhere [4]. Considering that the bandgap of Ag<sub>2</sub>O is about 1.20 eV, which corresponds to possible emission at a wavelength of 1033 nm, PL peaks at 350 and 420 nm seem to have other origins and therefore these peaks should provide more information about the oxidation of Ag nanoparticles dispersed in mesoporous SiO<sub>2</sub>. As for the photoluminescence of Ag, it has been reported [29, 30] that there exists fluorescence of Ag<sup>+</sup> due to the 4d<sup>9</sup>5s →



**Figure 5.** Comparison of the photoluminescence spectra of (a) the HS sample, (b) the AHS sample and (c) the mesoporous SiO<sub>2</sub>.

4d<sup>10</sup> transition, strictly forbidden for the free ion but partially allowed in crystals or glasses. From recent studies of the substrate effect on the oxidation of Ag [31, 32], it is deduced that Ag<sup>+</sup> could be produced in air at high temperature in the Ag/mesoporous SiO<sub>2</sub> structure. Although SiO<sub>2</sub> is usually regarded as a chemically inert medium for noble metals, in the case of mesoporous SiO<sub>2</sub>, there exists a substantial number of dangling bonds on the pore wall [33], which could combine with active ions. In such a case, the Ag<sup>+</sup> ions, produced by air heat treatment at high temperature, can be trapped by the dangling bonds on the pore walls of mesoporous SiO<sub>2</sub> [31], i.e.,



where the dangling bonds of mesoporous SiO<sub>2</sub> acted as the carrier for the Ag<sup>+</sup> ion. At the same time, interaction of the dangling bond with an Ag<sup>+</sup> ion would provide suitable local conditions for the transition between energy levels in Ag<sup>+</sup> that is originally forbidden. Thus, the emission band centred at 350 nm is attributed to the 4d<sup>9</sup>5s → 4d<sup>10</sup> parity forbidden transition in Ag<sup>+</sup> ions diluted in the SiO<sub>2</sub> matrix [11] and the other emission centred at 420 nm is attributed to the Ag<sup>+</sup>-Ag<sup>+</sup> pair [29, 34] which can be stabilized by the local electric field due to the dangling bonds. Heat treatment of the AHS sample in H<sub>2</sub> again led to the reduction of Ag<sup>+</sup> ions to metallic Ag nanoparticles, resulting in the disappearance of the PL emission.

In brief, upon heat treatment of the HS sample in air at high temperature, the metallic characteristic is lost and the Ag<sup>+</sup> ions produced during the heat treatment couple weakly with the dangling bonds of mesoporous SiO<sub>2</sub>, resulting in the fluorescence. Reduction and oxidation between Ag and Ag<sup>+</sup> by the alternate heat treatment in H<sub>2</sub> and air is a reversible process. It is the reversible conversion between metallic and non-metallic properties that resulted in the alternate appearance and disappearance of the SPR and the alternate increase and decrease of the Raman scattering spectra, but the alternate disappearance and appearance of the PL spectra. Such optical reversibility could endow the Ag/mesoporous SiO<sub>2</sub> nanostructure with the potential for sensor applications.

#### 4. Summary and conclusions

The various optical spectra of an Ag/mesoporous SiO<sub>2</sub> nanostructure heat-treated in air and H<sub>2</sub> were considered to investigate changes in physical and chemical properties during the oxidation–reduction process. As-prepared and H<sub>2</sub>-reduced samples (HS samples) showed optical characteristics representing the metallic nature of silver nanoparticles, as reflected in their optical spectra such as a strong SPR absorption peak and an enhanced Raman scattering effect. On the other hand, oxidized samples (AHS samples) exhibited optical characteristics corresponding to the loss of metallic nature, as reflected in the disappearance of SPR and the decrease in Raman spectra, which were almost indistinguishable from those of the mesoporous SiO<sub>2</sub> host. Oxidation of the Ag nanoparticles did not result in the formation of Ag<sub>2</sub>O, as there was no spectral band related to Ag<sub>2</sub>O in the IR and PL spectra. Instead, PL spectra of the oxidized samples, together with recent work on the substrate effect on the oxidation of Ag [31, 32], suggested that high-temperature oxidation products of Ag nanoparticles dispersed in mesoporous SiO<sub>2</sub> are Ag<sup>+</sup> ions adsorbed on the pore walls of mesoporous SiO<sub>2</sub> through dangling bonds. This study should promote understanding of the reaction of silver nanoparticles with the environment and the corresponding optical sensitivity, and should be of importance for nano-optics.

#### Acknowledgments

This work was carried out with support from the Natural Science Foundation of Education Commission of Anhui Province, China (grant no. 2005KJ037ZD) and the Brain Korea 21 Project of the Ministry of Education, Korea.

#### References

- [1] Bao X, Muhler M, Schedel-Niedrig T and Schlogl R 1996 *Phys. Rev. B* **54** 2249
- [2] Kreibitz U and Vollmer M 1995 *Optical Properties of Metal Clusters* (New York: Springer)
- [3] Muniz-Miranda M 2004 *J. Raman Spectrosc.* **35** 839
- [4] Peyser L A, Vinson A E, Bartko A P and Dickson R M 2001 *Science* **291** 103
- [5] Iga M, Seki A and Watanabe K 2004 *Sensors Actuators B* **101** 368
- [6] Kumar N, Konova P, Naydenov A, Salmi T, Murzin D Yu, Heikillä T and Lehto V-P 2007 *Catal. Today* **119** 342
- [7] Ai M 2006 *Catal. Today* **111** 398
- [8] Qu Z, Huang W, Cheng M and Bao X 2005 *J. Phys. Chem. B* **109** 15842
- [9] Qu Z, Cheng M, Dong X and Bao X 2004 *Catal. Today* **93–95** 247
- [10] De G, Gusso M, Tapfer L, Catalano M, Gonella F, Mattei G, Mazzoldi P and Battaglin G 1996 *J. Appl. Phys.* **80** 6734
- [11] Garnica-romo M G, Yáñezlimón J M, González-hernández J, Ramírez-bon R, Ramírez-rosales D, Zamorano-ulloa R and Tirado-guerra S 2002 *J. Sol–Gel Sci. Technol.* **24** 105
- [12] Bi H, Cai W, Kan C and Zhang L 2002 *J. Appl. Phys.* **92** 7491
- [13] Bi H, Cai W, Zhang L, Martin D and Träger F 2002 *Appl. Phys. Lett.* **81** 5222
- [14] Gangopadhyay P, Kesavamoorthy R, Bera S, Magudapathy P, Nair K G M, Panigrahi B K and Narasimhan S V 2005 *Phys. Rev. Lett.* **94** 047403
- [15] Chakrabarti K and Whang C M 2001 *J. Appl. Phys.* **90** 6493
- [16] Cai W and Zhang L 1996 *J. Phys.: Condens. Matter* **8** L591
- [17] Cai W and Zhang L 1997 *J. Phys.: Condens. Matter* **9** 7257
- [18] Cai W, Zhang L, Zhong H and He G 1998 *J. Mater. Res.* **13** 2888
- [19] Nakamoto K 1986 *Infrared and Raman Spectra of Inorganic and Coordination Compounds* 4th edn (New York: Wiley–Interscience)
- [20] Wang C-B, Deo G and Wachs I E 1999 *J. Phys. Chem. B* **103** 5645
- [21] Otto A, Mrozek I, Grabhorn H and Akemann W 1992 *J. Phys.: Condens. Matter* **4** 1143
- [22] Portales H, Duval E, Saviot L, Fujii M, Sumitomo M and Hayashi S 2001 *Phys. Rev. B* **63** 233402
- [23] Akemann W and Otto A 1994 *Surf. Sci.* **307** 1071
- [24] Akemann W, Otto A and Schober H R 1997 *Phys. Rev. Lett.* **79** 5050
- [25] Akemann W and Otto A 1994 *Phil. Mag. B* **70** 747
- [26] Fujii M, Nagareda T, Hayashi S and Yamamoto K 1991 *Phys. Rev. B* **44** 6243
- [27] Courty A, Mermet A, Albouy P A, Duval E and Pileni M P 2005 *Nat. Mater.* **4** 395
- [28] Slager T L, Lindgren B J, Mallmann A J and Greenler R G 1972 *J. Phys. Chem.* **76** 940
- [29] Meijerink A, van Heek M M E and Blasse G 1993 *J. Phys. Chem. Solids* **54** 901
- [30] Belharouak I, Parent C, Tanguy B, Le Flem G and Couzi M 1999 *J. Non-Cryst. Solids* **244** 238
- [31] Hu J, Cai W, Zeng H, Li C and Sun F 2006 *J. Phys.: Condens. Matter* **18** 5415
- [32] Hu J, Cai W, Li Y and Zeng H 2005 *J. Phys.: Condens. Matter* **17** 5349
- [33] Glinka Y D, Lin S-H and Chen Y-T 1999 *Appl. Phys. Lett.* **75** 778
- [34] Melnikov N I, Peregood D P and Zhitnikov R A 1974 *J. Non-Cryst. Solids* **16** 195