Effect of Ag nanoparticles on the luminescence of Tb doped sol-gel silica

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Abstract: Tb doped silica has been synthesized using the sol-gel method and emits green light of wavelength 544 nm. X-ray diffraction (XRD) results show that these samples remain amorphous even after annealing at 1000˚C. In other samples, silver nitrate was added during the synthesis. The presence of Ag nanoparticles (NPs) in the silica matrix was confirmed by XRD and transmission electron microscopy (TEM) analysis and the average crystallite size was found to be 20-30 nm. The TEM results showed that the shape of NPs was changed by thermal treatment and the average NPs size of Ag increased by increasing the temperature in the thermal treatment process. Photoluminescence showed that in the presence of 1 mol% Ag there was a great enhancement in the emission from the Tb ions when excited by a wavelength of 325 nm. The effect of the concentration of the Ag NPs on the excitation and emission of the Tb ions was systematically studied.

1. Introduction

Nanomaterials are of importance for science and technology, due to their small size and large surface areas. Noble metal nanoparticles (NPs) are particularly interesting due to their plasmonic effects [1-2]. The study of the interaction of lanthanide ions with metal NPs has been paid much attention [3-9] because of their unique luminescent behaviours and potential applications. The interaction between Ag NPs and lanthanide ions, both dispersed in a host material, can result in enhanced luminescence from the lanthanide ions. This occurs when the excitation or emission wavelength of the lanthanide ions are close to the LSPR wavelength of the NPs [7]. Ag is known to give more pronounced near-field effects than Au due to less pronounced resonance damping by interband electron transitions, as it is known to have a higher energy separation between localized surface plasmon resonance (LSPR) and interband absorption [10]. Ag NPs can be incorporated into silica using a sol-gel process [11], which is attractive due to its low cost, low temperature operation and environmental friendliness.

Among the lanthanides, the green luminescence of Tb ions finds many uses for light emitting devices and display applications. However, Tb ions have a small cross section due to parity forbidden f-f transitions, which mean that they cannot be efficiently excited directly by long wavelength ultraviolet (UV) light longer than 300 nm. Researchers have used different approaches, particularly exciting the strong f-d transitions of Tb at shorter wavelengths or employing energy transfer from a sensitizer such as Ce, to enhance the excitation efficiency of Tb ions. In the present work, Ag NPs have been incorporated together with Tb ions in silica, with the aim to enhance the f-f absorption of Tb ions due to the strong electric field associated with the LSPR of the metal NPs. The effect of the Ag NPs on the luminescent properties of the Tb ions in amorphous silica is reported.

2. Experimental

All the chemicals were purchased from Sigma Aldrich and used without further purification. The reagents for the sol-gel process to make silica were tetraethoxysilane (TEOS) (99.0%), ethanol (99.7%) and water [12]. The molar ratio of the starting solution was taken as 1:5:10 for TEOS: ethanol: water. For all samples the TEOS was dissolved in the ethanol and stirred for 30 min. Dilute HNO_3 (0.15 M) was then added to the solution instead of the water, to catalyse the reaction, followed by stirring for a further 30 min. To dope the silica samples, $Tb(NO_3)_3$ (99.999%) and/or $AgNO_3$ (99.9%) were dissolved ultrasonically in a small amount of ethanol and added to the mixture, which was stirred for another 5 h. All solutions were then stored in closed containers in a water bath at 50˚C until a gel was formed. For drying, gels were placed in open containers in air for 22 h, ground to fine powder and transferred to a drying oven at 50˚C for a further 20 h. Each sample was divided into two parts, one annealed at 500˚C and the other annealed at 1000˚C for 2 h. Samples were analysed at room temperature. X-ray diffraction (XRD) patterns were recorded with a Bruker D8 diffractometer. Morphology and size of the Ag NPs were obtained from transmission electron microscope (TEM) images recorded with a Philips CM 100. Diffuse reflection spectra were obtained using a PerkinElmer Lambda 950 UV-vis spectrophotometer with spectralon as a standard, while phosphorescence emission and excitation spectra were measured using a Cary Eclipse fluorescence spectrophotometer.

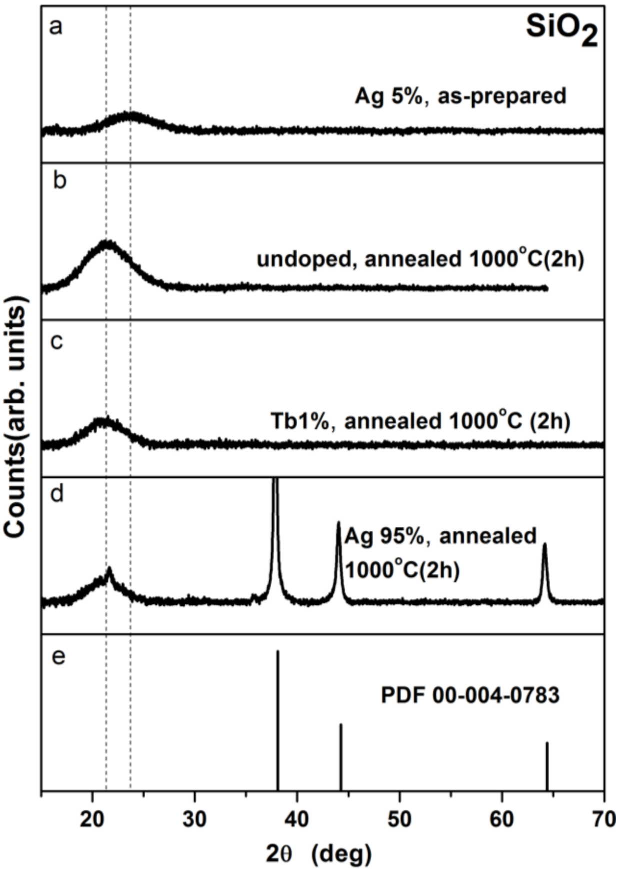

Figure 1. XRD patterns of (a) as-prepared silica with 5 mol% Ag, (b) pure silica annealed at 1000˚C (2h), (c) silica with 1 mol% Tb annealed at 1000˚C (2 h), (d) silica with 5 mol% Ag annealed at 1000˚C (2 h) and (e) PDF 00-004-0783 file for Ag.

3. Results and discussion

3.1 Structural and morphological characterization

Figure 1 shows the XRD patterns of several samples prepared during the study. The as-prepared samples (before annealing) showed only a broad amorphous diffraction band centred at 2θ ~ 23˚, even when doped with 5 mol% Ag (figure 1(a)). In the undoped sample annealed at 1000˚C for 2 h (figure 1(b)) this peak shifted to 2θ ~ 21˚, corresponding to an increase in the structural order of the amorphous silica towards the cristobalite phase, which is one of the crystalline forms of silica [11]. The addition of 1 mol% Tb did not produce any additional peaks in the XRD pattern, even after annealing (figure 1(c)), but when the sample containing 5 mol% Ag was annealed (figure 1(d)) peaks corresponding to crystalline Ag appeared, as confirmed by comparison with the Powder Diffraction File (PDF 00-004-0783, figure 1(e)). In addition, a small peak on the amorphous silica band near 2θ ~ 21˚ indicates that some of the amorphous silica converts to the crystalline phase due to the Ag doping. The average size of Ag NPs was calculated by Scherrer's equation $D = 0.9\lambda/(\beta\ \cos\theta)$ where β is the full width at half maximum of a diffraction peak in radians, θ is the corresponding Bragg angle and λ is the wavelength of the x-rays (154 pm). The average diameter of the NPs obtained using the different Ag diffraction peaks was in the range of 20-30 nm.

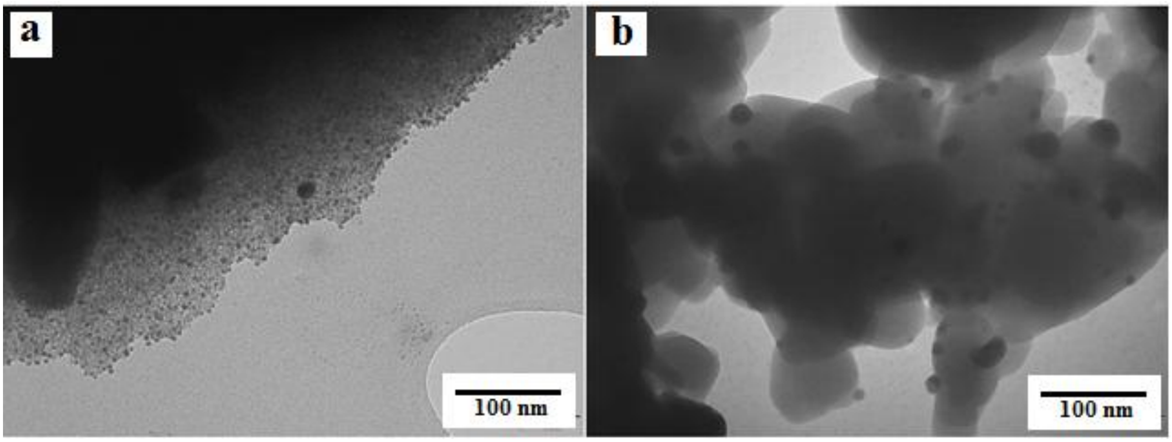

Figure 2. TEM results for two silica samples doped with 5 mol% Ag (a) annealed at 500ºC for 2 h, (b) annealed at 1000ºC for 2 h.

Figure 2 shows TEM images of silica doped with 5 mol% Ag annealed at (a) 500˚C and (b) 1000˚C for 2 h. The sample annealed at 500˚C shows a fine distribution of a large number of Ag NPs in the silica matrix, which appear spherical in shape and about 5-10 nm in diameter. In the sample annealed at 1000˚C the Ag NP density was much lower and the NPs were much larger in size (20-33 nm in diameter, in agreement with the mean size calculated by Scherrer's equation) and not perfectly spherical in shape. This is attributed to aggregation of the Ag NPs during the high temperature treatment. This means that the thermal treatment can affect the size and shape of the Ag NPs. The phenomenon of aggregation is controlled by the Gibbs–Thomson effect, where the chemical potential is inversely proportional to the particle size [13].

3.2 Optical characterization

Figure 3 shows diffuse reflectance spectra of two silica samples annealed at 1000 ºC for 2 h of (a) pure silica (b) 0.1 mol% Ag doped silica. The broad absorption peak in the doped sample near 405 nm corresponds to the LSPR peak of Ag NPs and confirms the formation of Ag NPs in the silica matrix, in agreement with the XRD and TEM measurements.

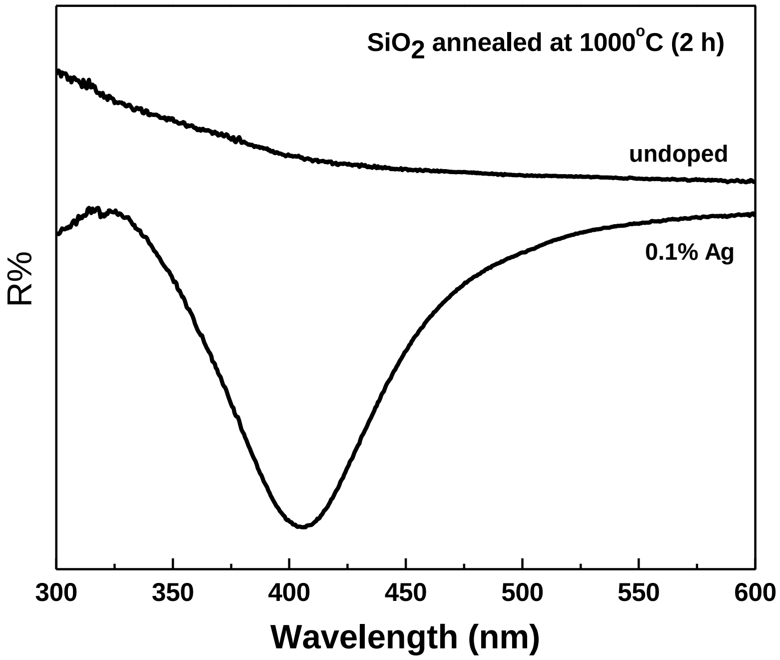

Figure 3. UV–vis diffuse reflectance spectra of (a) pure silica (b) silica doped with 0.1 mol % Ag, both annealed at 1000°C for 2 h.

For silica samples doped only with Tb, the green emission from the Tb^{3+} ions at 544 nm increased in intensity with the doping concentration up to 7 mol%, which was the highest concentration considered. However, due to the high cost of terbium nitrate it was decided to work with further samples doped with 5 mol% Tb. Figure 4(a) shows the excitation spectra for the 544 nm emission of Tb for sol-gel silica samples with 5 mol% Tb in the presence of different amounts of Ag, where the samples have been annealed at 500˚C for 2 h. For the sample with no Ag added, we observed six peaks at 485, 377, 369, 351, 340, and 318 nm and assigned them to the electronic transitions of Tb^{3+} ions from the ground state $^7F_6$ to the $^5D_4$, $^5D_3$, $^5L_{10}$, $^5D_2$, $^5G_4$, and $^5D_1$ excited states, respectively. As the amount of Ag increased, the excitation peaks below 400 nm become less distinct, although the $^7F_6$ to $^5D_4$ transition near 485 nm is little affected. It is clear that the shorter wavelength f-f transitions are highly affected by the addition of Ag. Depending on the excitation wavelength, there can be considerable enhancement of the Tb emission. The emission intensity of all samples at 544 nm excited by 325 nm as the function of Ag load is shown in Figure 4(b). The intensity increases with increasing Ag load from 0 to 1 mol%, whereas further increasing of Ag concentration decreases the intensity. The inset shows the relation between Ag load and enhancement factor (the Tb emission intensity relative to the sample without Ag) and it can be seen that the maximum enhancement factor is 8.8. This enhancement factor is particularly high because the wavelength of 325 nm does not correspond to one of the Tb f-f transition wavelengths. However, even for those wavelengths some enhancement does occur, e.g. for the $^7F_6$ to $^5D_3$ transition near 377 nm the peak height is increased by the addition of some Ag and the maximum occurs for a Ag load of 0.3 mol%. For simple plasmonic enhancement of the Tb f-f levels, it was expected that the excitation bands would retain their positions and that the peaks closest to the LSPR of the Ag NPs would increase in height. Clearly the experimental results are different to this, with the f-f excitation bands becoming less distinct. Stark splitting of the energy levels could be the reason for this, but is not considered to be the case since the 4f levels are well shielded and stark splitting would also result in a broadening of the emission bands, which is not observed. So although we have achieved some enhancement of the green Tb emission by the addition of Ag, the mechanism does not appear to be simple plasmonic enhancement, but is unclear and requires further study. One possibility is the interaction of Tb ions with Ag ions, instead of Ag NPs, and energy transfer from the Ag ions instead of a plasmonic enhancement [14].

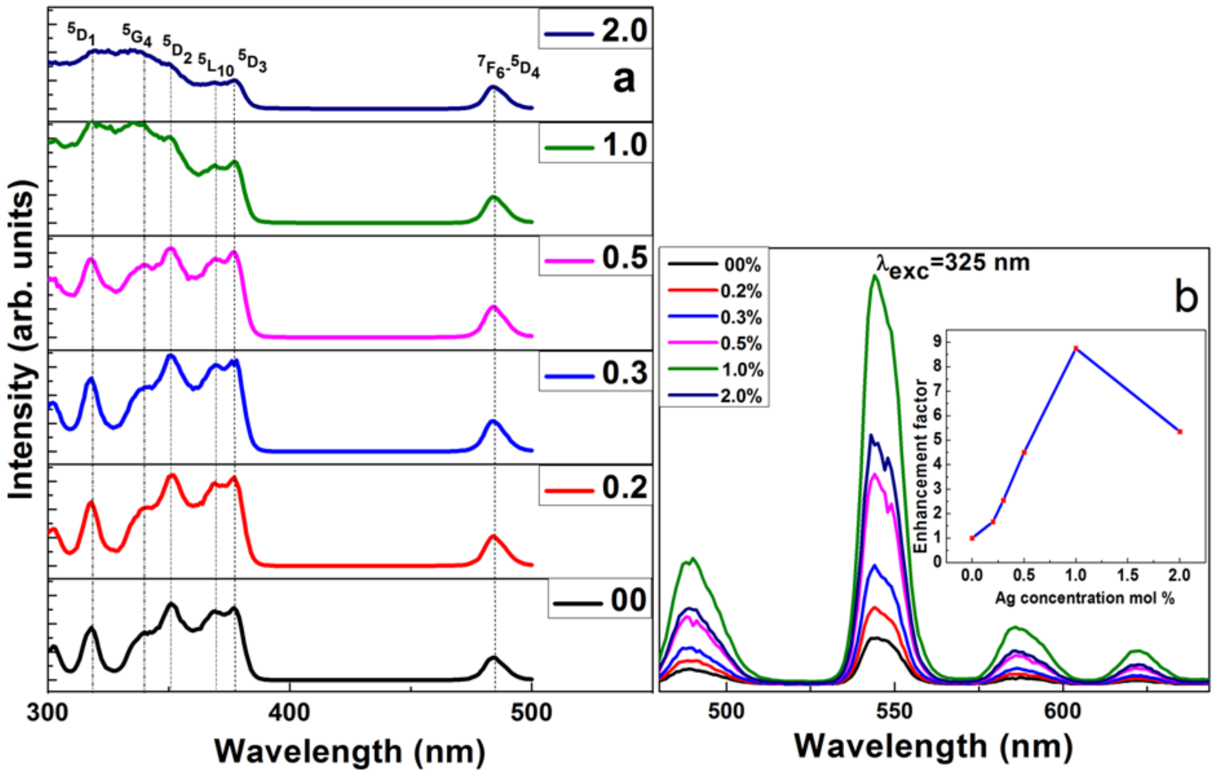

Figure 4. Luminescence spectra of silica samples doped with 5 mol% Tb and various concentrations of Ag (a) excitation (λ_{em} = 544 nm) (b) emission (λ_{exc} = 325 nm), after annealing at 500˚C for 2 h.

4. Conclusion

Tb and Ag co-doped silica samples have been successfully synthesized using the sol-gel method. XRD, TEM and UV-vis diffuse reflectance results confirmed the formation of Ag NPs in the silica matrix. The results showed that the annealing temperature can be used as mechanism to control the shape and size of the Ag NPs in amorphous silica. For an excitation wavelength of 325 nm, the highest intensity of the green emission of Tb ions at 544 nm is obtained when the doping concentration of Ag was 1 mol %. The change in the Tb f-f excitation spectrum is not merely an increase in the f-f excitation peaks closest to the LSPR wavelength of the Ag NPs, as expected for simple plasmonic enhancement, but instead the peaks merge into a broad excitation band. This may be evidence that energy transfer from Ag ions also plays a role in the luminescence enhancement.

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