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Optical properties of nanometre AgI–silica composite synthesized by a simple quenching method

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Abstract

Optical absorption and room temperature photoluminescence (PL) properties of nanometre AgI–silica composite synthesized by a simple heating–quenching method were investigated. The absorption of quenched AgI–silica was enhanced markedly. Three absorption bands at 440 (2.8 eV), 260 (4.8 eV) and 220 nm (5.6 eV) were observed. The excitonic absorption of AgI showed a red shift of ~ 0.11 eV, in contrast to the usually observed blue shift in AgI nanocrystals. Besides two UV emissions from a non-bridging hole centre and E' centre defects formed in silica, the composite exhibited two PL emissions at 2.62 and 2.40 eV. The 2.62 eV PL was ascribed to donor–acceptor recombination of AgI, while the 2.40 eV one may correlate with energy levels induced by the interaction between silica and AgI. The role of silica in improving the PL for nanometre AgI is discussed.

1. Introduction

Recently, there has been increasing interest in silver iodide (AgI) due to its superionic properties and its use as a sensitive detector in the visible range. Investigations of AgI have prompted progress in the fields of solid state ionics and photography, and applications of relevant devices. In the past decade, substantial progress has been made in nanotechnology. Several approaches have been developed to synthesize AgI nanoparticles [1–4] which show optical and electrical properties different from bulk AgI. It has been reported [5] that AgI clusters may find applications as photocatalysts for solar energy conversion and as a medium for optical information or image storage.

The optical properties of semiconductor micro- and nanocrystals are of much current interest, as they provide information about the evolution of physical characteristics from atom to bulk and about the three-dimensional confinement of carriers and excitons [6]. Among those

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optical analyses, optical absorption and photoluminescence (PL) are two useful tools for monitoring electronic changes at the nanoparticle surface. For the bulk case, Cardona [7] studied the absorption of thin AgI film in wurtzite and zincblende phases, defining bands at ~ 420 nm (2.95 eV) and 326 nm (3.8 eV) described as direct excitonic absorption associated with the Γ_8 and Γ_6 valence bands (VBs), respectively. At low temperature, generally two PL emissions are reported [8, 9] arising from radiative excitonic recombination and donor–acceptor (D–A) recombination, at about 425 (2.91 eV) and 450 nm (2.76 eV), respectively. For nanometre AgI, the excitonic absorption undergoes a blue shift [10–12] due to the quantum confinement effect and the PL property is altered by the introduction of D–A states or lattice imperfections. For example, in gelatin- and polymer-stabilized AgI colloids (>30 nm), the radiative excitonic recombination is dramatically reduced and D–A recombination is favoured [13, 14]. Although several results have been reported [14–17], data about PL properties of AgI at room temperature (RT) are rather poor.

Sol–gel derived porous silica has been extensively used as a matrix for synthesizing various nanoparticles. The pore size can be tuned from several nanometres to several tens of nanometres by varying preparation parameters. Although a AgI–SiO₂ composite was intensively investigated for its enhanced ionic conductivity [18], AgI nanoparticles embedded in silica as well as their optical properties were seldom reported. On the other hand, a quenching method has been used to deposit amorphous AgI [19] and CuI [20] films, which showed strongly enhanced optical absorption. In this paper, we report optical absorption and RT PL properties of nanometre AgI–silica composite synthesized by liquid nitrogen (LN) quenching. A decrease in band gap energy and a broad PL around 2.5 eV for AgI were observed. The present investigation may throw light upon the application of AgI nanoparticles.

2. Experiment

Tetraethoxysilane (TEOS), ethanol (EtOH), and acid water (HNO₃) were mixed slowly in a 1:3:2 mol ratio at 25 °C. The mixture was stirred for 30 min and the clear liquid was allowed to gel at 60 °C. After 2 days, the container was opened to the air and the excess liquid was decanted. The remaining glass was then air dried at 25 °C for at least 2 days before being heated at 400 °C for 2 h at a 2 °C min⁻¹ ramp to form porous silica.

AgI powders and porous silica were mixed in a 1:4 mol ratio and ground in darkness. The powders were then sealed and heated to 580–730 °C (the melting point of AgI is 558 °C) with intervals of 50 °C for 15 min before being quenched in LN. This procedure produced a composite that underwent blue–green PL.

X-ray diffraction (XRD) patterns, optical absorption spectra, PL and PL excitation spectra were measured to characterize the quenched AgI–silica composite. The PL spectra were measured using a Hitachi 850 fluorescence spectrophotometer. The spectra were excited with 230 nm (5.4 eV) light, utilizing a 290 nm short- λ cutoff filter. The excitation light was produced by a xenon lamp equipped with a grating monochromator. All of the measurements were performed at RT.

3. Results and discussion

Figure 1 illustrates the XRD patterns of AgI–silica composite quenched at 630 °C and virgin AgI. It is well known [21, 22] that AgI crystals consist of hexagonal wurtzite-type β -AgI and cubic zincblende-type γ -AgI under ambient conditions, as seen in the diffractogram of virgin AgI. However, β -AgI disappears after quenching, evidenced by the disappearance of

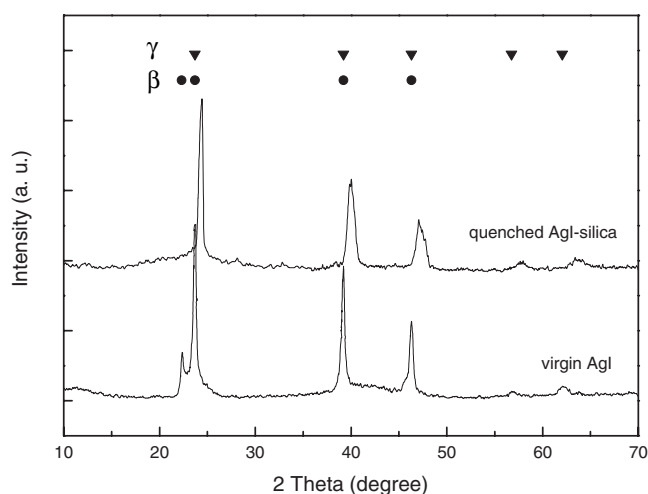


Figure 1. XRD patterns for AgI–silica composite synthesized by quenching at 630 °C. The pattern of virgin AgI and the standard diffraction position for β - (circle) and γ -AgI (triangle) are also plotted as references.

the peak at 22.4° which corresponds to the (100) plane of β -AgI. This agrees with Burley's conclusion [23] that quenched AgI tends to present in the γ -phase. It was also found that the position of all diffraction peaks shifts to higher degrees and the FWHM (full width at half maximum) increases. An average lattice deformation of about -2% was obtained from the shifts. The large deformation results from the transition of body-centred cubic (bcc) α -AgI ($a = 5.09 \text{ \AA}$) to face-centred cubic (fcc) γ -AgI ($a = 6.49 \text{ \AA}$) at 147 °C. In an AgI system, a martensitic mechanism for the α - γ transition has been proposed [24], during which a shear deformation is produced when the bcc (100) planes transform into the fcc close-packed layers. This shear deformation cannot be fully relaxed due to the fast quenching process. The increase of FWHM is evidence of a decrease in AgI grain size. According to the Scherrer formula, the grain size was estimated to be about 15 nm after quenching.

The absorption spectra for AgI and AgI–silica are shown in figure 2, both being quenched at 630 °C, as well as bulk AgI spectrum as a reference. A sharp peak at 424 nm (2.92 eV), ascribed to the $Z_{1,2}$ excitonic absorption of AgI [22], and a faint band at about 260 nm (4.8 eV) were observed in the bulk spectrum. The two spectra for quenched samples are alike; both have several prominent features different from the bulk one:

- (1) the $Z_{1,2}$ peak shifts to about 440 nm (2.82 eV), with a broad tail on the long wavelength side being formed;
- (2) the absorption increases steadily (but more rapidly for AgI–silica) with the wavelength decreasing before the drop at 260 nm;
- (3) the absorption at 260 nm is greatly enhanced, as well as the appearance of a new absorption at about 220 nm (5.6 eV).

When molten AgI is quenched, a number of intrinsic defects should be expected to be formed in the grains, at the grain boundaries, on the surface, and/or at the AgI/silica interface, invariably leading to energy levels within the energetically forbidden gap. These separate defect levels can extend to form an energy band and overlap with the conduction band (CB) or VB of AgI, thus giving rise to band tail states. From the figure it can also be concluded that the red shift of the $Z_{1,2}$ absorption is caused only by quenching, and has nothing to do with

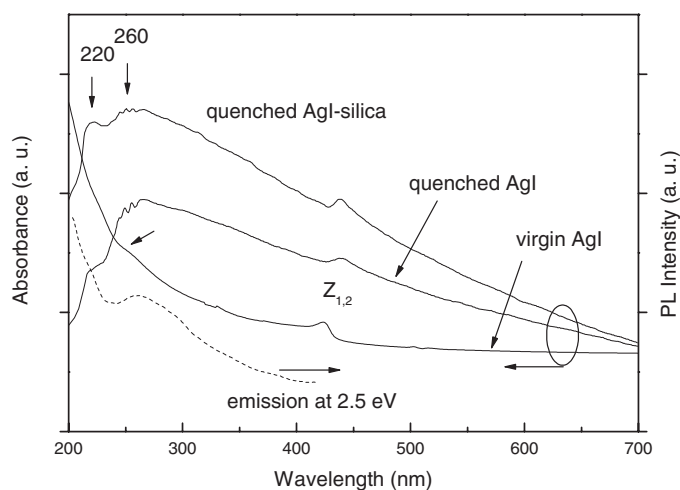


Figure 2. Absorption spectra of quenched AgI, quenched AgI-silica, and bulk AgI. The PLE spectrum for quenched AgI-silica monitored at 2.5 eV (500 nm) is also plotted (dashed curve).

silica. It is well known [10] that a decrease in particle size generally results in the blue shift of this peak due to enhanced quantum confinement. However the red shift is not too surprising when the effect of lattice compression (see figure 1) is taken into account. According to the bonding orbital theory [25] of band structure for covalent semiconductors, such as AgI (its band structure is characterized by a strong p-d hybridization), energy bands are derived from the extension of molecular orbitals (MOs) in unit cells. As the lattice parameter decreases, the overlap between the MOs in adjacent cells increases, leading to broadening of the band width. The broadening of band width generally results in a decrease of band gap, as observed in many semiconductors and insulators. Moreover, a decrease in lattice parameter results in a reduction of electron-hole distance in the exciton, leading to stronger electron-hole interaction and a larger binding energy of the exciton. In these ways the excitonic energy is reduced.

The band around 260 nm (4.8 eV) can be assigned to the E_1 peak as observed in most zincblende-like semiconductors. The transition occurs for k in the [111] direction somewhere inside the Brillouin zone (between the A point and the L point) [7]. It can be expected that quenching in LN will induce lack of long-range order in the local lattice of AgI, leading to relaxation of the k -conserving and/or symmetry-imposed selection rule. Such a relaxation contributes to the enhanced absorption within the range 700–260 nm. Similar enhancement has been achieved in many amorphous materials, particularly in indirect-band-gap semiconductors such as Si. For quenched AgI-silica, the absorption within the whole range enhances more quickly. We suggest that the interaction of AgI with the silica network produces various interfaces and defects, which also contribute to the absorption.

The absorption shows a drop at wavelengths lower than 260 nm (4.8 eV) in the two quenched samples. A similar decrease was observed in quenched amorphous AgI film at low temperatures [19] and AgI-loaded zeolite LTA [12]. Kondo *et al* [19] ascribed it to fewer Ag 4d and I 5p electrons contributing to the absorption at higher energy. However, their spectra became similar to that of bulk AgI at temperatures above 220 K. In our experiment, this decrease may correlate with the new chemical bonding configuration produced by the lattice deformation and the decrease of grain size, which leads to modification of the band structure of AgI. The actual mechanism is not fully understood so far and needs further investigation.

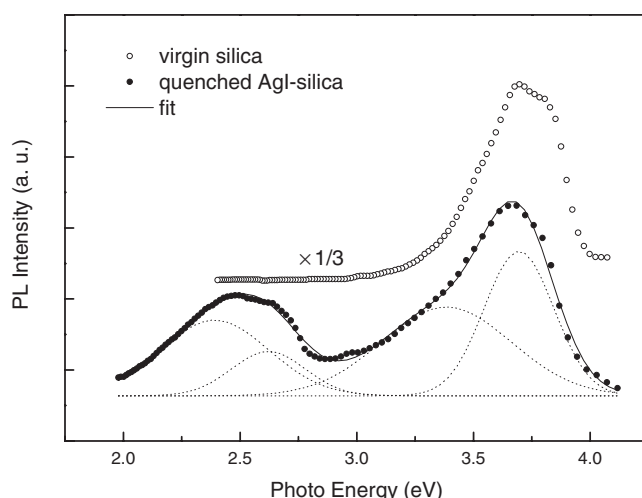


Figure 3. PL spectra for AgI–silica composite quenched at 630 °C and virgin silica. The spectrum for the composite is fitted by four Gaussian peaks. The intensity of the spectrum for virgin silica is multiplied by 1/3.

The newly observed peak at 220 nm (5.6 eV) in quenched samples is reminiscent of the spin-orbital splitting of the VB maximum. The splitting at $k = 0$ found from the exciton spectrum of AgI is 0.84 eV. Since the E_1 peak is produced by transitions occurring for some k points in the [111] direction, the splitting should be 2/3 of that at $k = 0$, 0.56 eV [7]. Generally this splitting cannot be discriminated at RT for bulk AgI, as seen in figure 2. The energy splitting found from quenched AgI (~ 0.8 eV) is larger than that for the E_1 peak. The appearance and increase of the splitting in the present experiment may be due to relaxation of the k -conserving and symmetry-imposed selection rule.

Figure 3 shows the PL spectrum for quenched AgI–silica composite, with that of virgin silica as a reference. The spectrum for virgin AgI (either quenched or not) was not plotted due to the absence of any PL emission at RT. The spectrum for quenched AgI–silica can be fitted by four Gaussian peaks at 3.70, 3.35, 2.62 and 2.40 eV, respectively. The 3.70 eV emission is actually a doublet with a slightly weaker shoulder at an energy of 0.11 eV higher. It has been observed frequently in sol–gel silica and was ascribed to non-bridging oxygen hole centres (NBOHC, $\equiv\text{Si}-\text{O}\uparrow$, \uparrow represents an unpaired electron) [26, 27]. The emission at 3.35 eV is most likely associated with E' centres [28] defects in silica based on the discussion in a previous work [29]. There are many E' variants in SiO_2 material [30]. In amorphous SiO_2 , as in the present case, E' centres ($\equiv\text{Si}\uparrow^+\text{Si}\equiv$) can be formed by an intrinsic process which involves the displacement of oxygen from an otherwise perfect Si–O–Si network [31]:



Before discussing the origin of the emission around 2.5 eV, we first draw attention to the fact that defects or impurities in sol–gel silica, such as neutral oxygen vacancy [31] and carbon-related species [27], are known to photoluminesce in the blue–green spectral range. Although the virgin silica in our experiment did not exhibit such PL emissions, the things in AgI–silica still need careful investigation. Figure 2 shows the PLE spectrum monitored at 2.5 eV (dashed curve). The PLE spectrum is very similar to the absorption spectrum of AgI, with a peak at 260 nm (4.8 eV). The excitation peak at about 260 nm for AgI PL has been reported by several groups [15, 17]. It was also found that the absorption at 220 nm (5.6 eV)

contributes to the luminescence more predominantly. It is well accepted that γ -AgI has a PL emission at about 450 nm (2.76 eV) due to D–A recombination [9]. The peak at 2.62 eV agrees well with the reported value when the decrease in band gap energy (~ 0.11 eV obtained from the red shift of $Z_{1,2}$ peak) is taken into account. Other authors have reported PL from nanometre AgI at close energies. Kumar and Sunandana [16] reported five prominent peaks at about 440, 450, 470, 485 and 495 nm in the PL spectrum of vapour quenched AgI films. Chen *et al* [15] observed a PL emission at 474 nm (2.62 eV) from AgI nanoclusters in zeolites. Based on the above results, we concluded that the PL emission around 2.5 eV originated from nanometre AgI.

At RT, the quantum yield associated with the D–A recombination in bulk AgI is very low. After being excited, the vast majority of charge carriers, i.e. electron–hole pairs, decay primarily via non-radiative pathways [16]. Therefore RT PL from AgI was seldom reported. For quenched AgI, a large concentration of donor–acceptor states or lattice imperfections may be introduced causing the excitons to be trapped more quickly in the smaller samples [13, 14] and recombine radiatively. However, quenched pure AgI did not show any PL emission at RT. This can be understood by considering the effect of a large surface-to-volume ratio. As for quenched AgI, unsaturated dangling bonds [32] and substantial reconstructions [6] should be expected to be created in the surface region, which trap electrons or holes and degrade the optical properties of the material. In a quenched AgI–silica system, however, a passivation process [6] occurs by which these surface trap states are bonded to silica, a material with much larger band gap than AgI, eliminating the deleterious energy levels inside the AgI band gap. On the other hand, the presence of silica results in the substantial enhancement of the absorption intensity at 260 (4.8 eV) and 220 nm (5.6 eV), as mentioned earlier, which is responsible for the AgI PL. In these ways silica improves the PL property of AgI.

The foregoing discussion is based on interaction between AgI particles and silica. This is supported by the decrease in intensity of the emission at 3.70 eV compared with that of quenched virgin silica (see figure 3). It is obvious that NBOHC will bond with silver dangling bonds at the AgI/silica interface to create a $\equiv\text{Si}-\text{O}-\text{Ag}$ structure. The formation of this structure has also been reported in silver ion-exchanged silica [33]. When AgI is melted above 560 °C, this reaction is expected to take place easier. On the other hand, interaction between AgI and silica may facilitate the displacement of oxygen atoms, leaving E' centres behind, as evidenced by the appearance of the 3.35 eV PL in figure 3. As a result, shallow levels related to interactive states were induced into the gap of AgI. The electron transition from the CB of AgI to these shallow levels may give rise to the PL emission at 2.40 eV. Note that other species may also give rise to luminescence in this range. For example, Ehrlich and Edwards [34] observed PL emissions of 2.3–2.5 eV in iodide-doped AgCl systems and ascribe them to I_m^{n-} clusters. Chen *et al* [15] reported PL emission at 510 nm (2.43 eV) from Ag clusters coexisting with AgI nanoparticles. The actual mechanism of this emission needs to be further investigated.

The intensity of the PL around 2.5 eV as a function of quenching temperature was also investigated (figure 4). The intensity maximizes at 630 °C. We note that a higher quenching temperature results in smaller AgI particle size [4], leading to a larger concentration of D–A states. However, the surface trap states are also expected to increase with the quenching temperature. Therefore the decrease in PL intensity at temperatures above 630 °C can be understood by considering that the surface traps increase more quickly with temperature and cannot be effectively bonded by silica.

4. Conclusion

In summary, AgI–silica composite was synthesized by heating the mixture to temperatures above 580 °C and then quenching it in LN. The quenched AgI is in the γ -phase with a grain

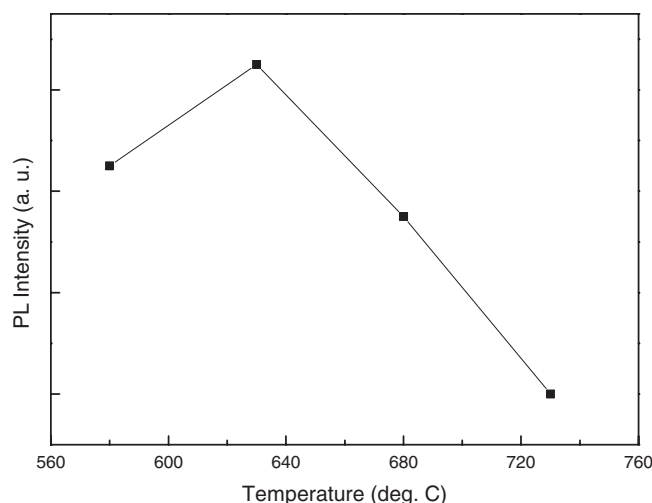


Figure 4. PL intensity of AgI–silica composite as a function of quenching temperature.

size of about 15 nm and shows a lattice deformation of about -2% . The band structure of AgI is altered by quenching as evidenced by its optical properties. The absorption of the composite was enhanced and three peaks were observed around 220 (5.6 eV), 260 (4.8 eV) and 440 nm (2.82 eV). The band at 440 nm was ascribed to $Z_{1,2}$ excitonic absorption of AgI, which showed a red shift from the bulk value and formation of a band tail. The composite exhibits four PL emissions at 3.70, 3.35, 2.62 and 2.40 eV. The former two were attributed to NBOHC and E' centres in silica, respectively, while the latter two correspond to D–A recombination and defect levels within the band gap of nanometre AgI. We suggested that silica serves as a passivant to eliminate deleterious trap states, resulting in enhancement of PL intensity.

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