Luminescence of ordered silver iodide nanoclusters inside zeolite host

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Abstract

Ordered silver iodide nanoclusters inside zeolite Y host were prepared by using a thermal diffusion method. The Y–AgI samples were characterized with powder X-ray diffraction, differential thermal analysis, X-ray photoelectron spectroscopy, adsorption technique and chemical analysis. The results show that silver iodide nanoclusters were situated in the ordered cages of the zeolite Y host. The results on the luminescence of the nanocomposites Y–AgI suggest that when the sizes of silver iodide nanoclusters are were very small, non-radiation surface recombination exceeds radiation process and the luminescence efficiency increases as the size of the silver iodide nanoclusters increaseds As the sizes of AgI nanoclusters increased, non-radiative surface recombination effect become equal to the radiation effect of the excitons. As the size of the nanoclusters of AgI in zeolite host further increases, the surface recombination of the nanoclusters becomes a major process.
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1. Introduction

Zeolites [1], a group of materials having excellent porous crystalline structures, have found application as ideal hosts [2–8] in recent years for nanomanufacturing due to their perfect periodic nanostructures besides their application to the area of ion exchange, adsorption, and catalysis. Silver-iodide-modified zeolites have applications in some fields such as semiconductor, photoconductor, information storage, and photoelectric conversion materials [8,9]. For the preparation of this kind of materials, most of the methods used are ion-exchange [1] or impregnation [10] of the porous materials with the corresponding material solutions followed by introduction of the anion ions. However, the ion-exchange or impregnation method cannot prepare materials with high loading of the guest and the procedures are very complicated for introducing anion ions. Studies exploring the luminescence of this kind of materials are also very scarce. In this paper, thermal diffusion method was used to prepare ordered silver iodide nanoclusters inside zeolite Y host. The present procedure is very easy to operate and can prepare nanocomposites with high loading of silver iodide nanocluster guests. It can also prepare nanocomposites that the ion-exchange method cannot prepare, such as for the loading of the metal oxide guests not having the ion-exchange ability, etc. In the previous paper [8], we prepared the Y–AgI samples and made the characterization of the samples. In this work, we used powder X-ray diffraction, differential thermal analysis, X-ray photoelectron spectroscopy, adsorption technique and chemical analysis to characterize the prepared samples Y–AgI host–guest nanocomposite materials. The samples with the guest loadings 1.0%, 5.0%, 9.7%, 14.3% and 18.6% (W/W) inside zeolite Y were prepared, respectively. The luminescence of Y–AgI materials was mainly observed. The prepared

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nanocomposites Y–AgI have the potentiality for use as luminescence materials.

2. Experimental

2.1. Sample preparation

Zeolite NaY was synthesized by a hydrothermal synthesis [1,11] with the ratio of SiO_2 to Al_2O_3 of 4.8. The zeolite Y was dehydrated at 673 K for 2 h to remove the water content before use. The mixtures of the zeolite and silver iodide (The First Chemical Plant of Shanghai, A.R.) were heated at 793 K for 48 h to prepare the nanocomposites. The primary amine mixture N-1923 (Changchun Institute of Applied Chemistry) was used [8] to extract the silver iodide adsorbed on the outside surface of the zeolite during the cooling process after the preparation. The prepared nanocomposites were designed as Y–AgI. They were stored without air.

2.2. Characterization

Powder X-ray diffraction was carried out on a Rigaku D/MAX-III A diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) operated at 30 kV and 20 mA. Differential thermal analysis was performed on a DTA-1700 thermal analysis instrument. Adsorption experiments for water were made using a CAHN 200 adsorption instrument. The samples were outgassed at 573 K for 12 h before measurements were made. X-ray photoelectron spectroscopy experiments were performed on a MARK-II energy spectrum instrument with a vacuum of 5×10^{-5} Pa using polluted carbon $C_{1m} = 284.60$ eV as an internal standard. Luminescence spectra were recorded on SPEX-FL-2T-2 spectrofluorimeter. The spectra were fully corrected for the spectral response of the instrument. The contents of the silver iodide nanoclusters in the prepared nanocomposites were measured by atomic absorption spectrometry with a Hitachi Z-8000 atomic absorption spectrophotometer.

3. Results and discussion

The powder X-ray diffraction results for the Y–AgI samples showed that the characteristic peaks of silver iodide disappeared and all diffraction peaks could be attributed to those of the zeolite Y [8]. This suggests that silver iodide was incorporated into the zeolite Y host and it did not exist on the outside surface of the zeolite. For the mechanical mixtures of zeolite Y and silver iodide, the characteristic peaks of AgI could emerge. This illustrates that the preparation condition used in the present work made silver iodide to incorporate into

the zeolite Y host by a thermal diffusion method. The maximum loading of silver iodide nanoclusters in the zeolite Y was 18.6% (wt). The threshold of the silver iodide nanocluster encapsulated in Y zeolite host was 12.4 molecules of AgI per unit cell of the cage [8]. The differential thermal analytical results of the host Y, the guest AgI and the prepared nanocomposite Y–AgI are shown in Fig. 1. It shows that the phase transition of AgI from α to β phase was 169.7°C and the melting point of AgI was 557.0°C. From the DTA curve of Y–AgI it can be seen that the characteristic peaks of the phase transition and melting point, endothermic peak of AgI crystal, disappeared. This also proves that silver iodide was incorporated into the zeolite and did not adhere to the outside surface of the zeolite. The silver iodide nanoclusters encapsulated in the zeolite Y has different properties as compared with those of the AgI bulk. This successfully indicated the incorporation of AgI into zeolite Y host. The adsorption results for water show that for Y–AgI samples the volume of the pore of the zeolite decreased 1.3%, 4.7%, 7.2%, 12.7% and 22.3% compared with that of the Y host when the amounts of silver iodide nanoclusters in the prepared samples were 1.0%, 5.0%, 9.7%, 14.3% and 18.6% (wt), respectively. The decrease in the pore volume of the zeolite Y suggests that silver iodide might be mainly located in the cages of the zeolite. As the zeolite was in the form of NaY, the cage spaces utilized were small and the guest silver iodide might mainly exist in the supercages. The electric binding energies of the bulk AgI, of Ag/Y prepared by an ion-exchange method, and of the Y–AgI nanocomposites prepared by a thermal diffusion method were comparatively studied. The electric binding energy of the Ag/Y prepared by an ion exchange method was found basically identical to the one of the $Ag3d_{5/2}$ of the bulk AgI. But the electric binding energies of the silver and iodine moved to the region of high energy in Y–AgI samples. For the
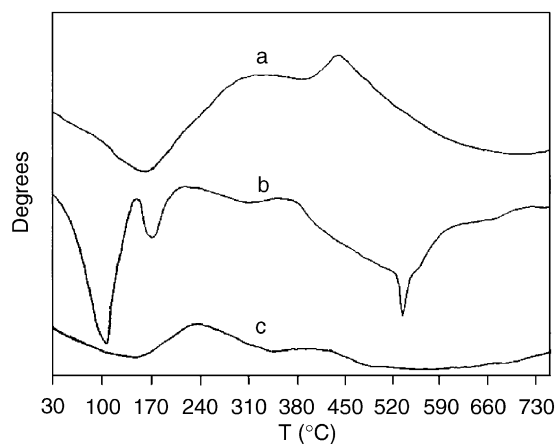

Fig. 1. Differential thermal analytical curves of the Y zeolite, AgI guest and the nanocomposite Y–AgI: (a) Y; (b) AgI; and (c) Y–AgI.

samples with the different loadings of silver iodide nanoclusters, the electric binding energies of $Ag3d_{5/2}$ ($I3d_{5/2}$) were 368.6 (619.9, 5.0% wt), 368.9 (620.0, 9.7% wt), 369.0 (620.1, 18.6% wt) eV, for Y–AgI, respectively. However, those for the bulk AgI and Ag/Y were 368.3 (619.5) and 368.2 eV, respectively. In the Y–AgI sample, $Ag3d_{5/2}$ moved 0.7 eV for the sample with 18.6% (wt) guest to the high region of energy compared with the one of the bulk silver iodide. The electric binding energy of $Ag3d_{5/2}$ and $I3d_{5/2}$ of Ag/Y prepared by the ion-exchange method almost did not change. However, the electric binding energies of $Ag3d_{5/2}$ and $I3d_{5/2}$ of the Y–AgI samples moved to the region of the high energy. This suggests that the locations of the silver in the Y–AgI samples were different from that of Ag/Y prepared by an ion-exchange method. The results show that the tie force of silver ion to the electrons of the inner shells enhanced. Based on the theory that oxidation state with electric binding energy is a direct ratio, it can be considered that apparently silver ion changed to some extent. At the same time, the results show the density of electric cloud of silver decreased and the component of the covalence bond decreased based on the shielding effect. The stereo confinement and the quantum size effect of the nanoscale cages of Y zeolite made the elongation of the bond lengths between silver and ligand in the prepared nanocomposites Y–AgI samples.

The excitation and emission spectra of Y–AgI are shown in Fig. 2. Three excitation peaks appear at 4.75, 4.04, and 3.43 eV, respectively. The smaller the crystal particle, the greater the width of the forbidden band [12]. The excitation at 3.43 eV can be ascribed to that of the AgI nanoclusters in β cage in zeolite Y. The excitation peaks at 4.75 and 4.04 eV originate from AgI nanoclusters in the supercages of zeolite Y, respectively. Since the sizes of the clusters were not homogeneous, there existed large amounts of defects in the nanocomposite materials, Y–AgI. When the silver iodide nanoclusters were lit by the light of excitation, the
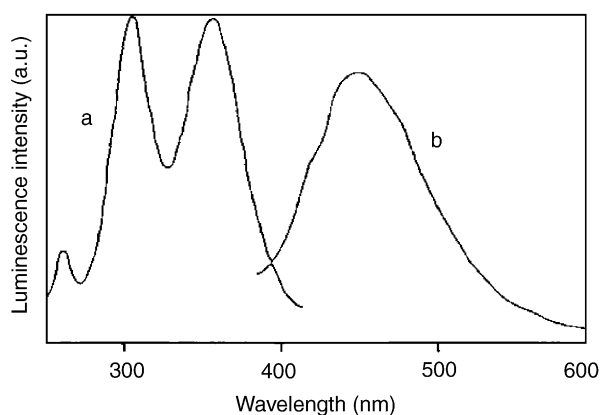
defect levels produced and the luminescence might accompany the transition of $4d \rightarrow 5s$ of silver. We observed the luminescence of the Y–AgI samples with different loadings of the guest nanoclusters. When the content of guest AgI was very low at the level of 1.0% (wt), the luminescence intensity was very weak. As the content of the AgI guest nanocluster gradually increased, the luminescence intensities enhanced and more bands emerged for the Y–AgI sample with 5.0%(wt) AgI. This phenomenon can be ascribed to the excitation–emission of the different forms of the AgI nanoclusters. Furthermore, the emission of the AgI nanoclusters in zeolite Y is related to the size of the guest. As the loading of the clusters decreased, the emission peaks showed blue shift. The emission wavelengths varied from 329 to 321 nm for the samples Y–AgI of the guest loading 18.6% (wt) and 1.0% (wt), respectively, and a blue shift was seen as the guest loading decreased. As the size of AgI got into nanoscales [12], the quantization of the electrons of the conduction bands took place. The relative values of the electric energy between them were the migrating values. The results of the luminescence intensity versus loading of AgI nanoclusters in zeolite Y are shown in Fig. 3. The luminescence efficiency of the nanocomposite Y–AgI increased as the size of the nanocluster guests increased. When the size of the nanocluster guest further increased, the luminescence efficiency was kept stable. If the size or loading of the nanoclusters further increased, the luminescence efficiency dropped. This is because the energy of the incident light was used as the electron excitation in the nanoclusters and the energy did not re-emit, but it made the superlattice vibrate and consume within a very short time. If the AgI nanoclusters in zeolite Y could be arranged in their cages in an ordered way, then the excitation light used could excite the guest
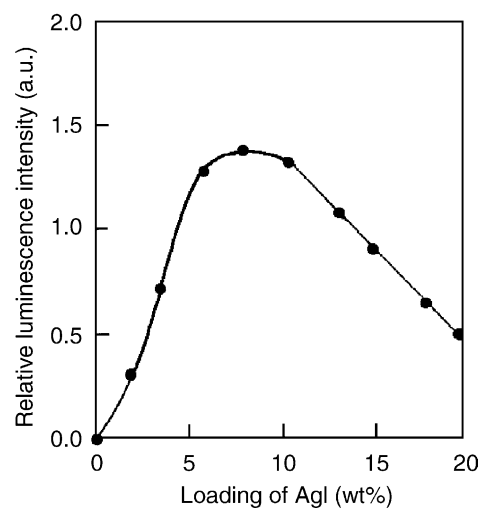

Fig. 2. Excitation–emission spectra of the nanocomposite Y–AgI with 10% (wt) AgI: (a) excitation spectrum ($\lambda_{em} = 451$ nm) and (b) emission spectrum ($\lambda_{ex} = 361$ nm).

Fig. 3. Relationship of the luminescence intensity versus loading of AgI nanoclusters in Y–AgI samples ($\lambda_{ex} = 261$ nm).

nanoclusters and the excitation energy transferred from one cluster to another. The related dropping of the luminescence resulted from the Frenkel excitons and the polariton effect. The clusters could not arrange in an ordered way for the samples where the contents of the guest were very low, so the polariton effect was reduced. The transition rate of the recombination of electrons and holes and the surface states or defect sites were the two major factors that determine the luminescence efficiency. The surface states or defect sites may decrease the quantum yield of luminescence. The competition of the non-radiative surface recombination and exciton radiation influence the luminescence efficiency. When the size of the guest silver iodide is smaller, the non-radiative surface recombination was superior over the radiative process. The luminescence efficiency increased as the cluster size increased. When the size of the AgI further increased, the effect of the non-radiative surface recombination was equal to that of the radiative process, the luminescence intensity was preserved stable. As the loading of the nanoclusters further increased, the radiative recombination became a major process and the non-radiative surface trapping became weaker and the decrease in luminescence intensity took place at this time. The usual case in a cluster is that the electrons and holes could form excitons by Coulomb interaction under the illumination of the appropriate light. The excitons were not free. As soon as the carriers were captured, the carriers might be released to the ground by non-radiative recombination or by recombination transfer of the energy to the near configuration or they recombine and transmit the exciton photon.

4. Conclusions

The silver iodide guest nanocluster was successfully prepared in the ordered cages of the zeolite Y by a thermal diffusion method. The existence of silver iodide nanoclusters in the cages of the zeolite host was proved by powder X-ray diffraction, differential thermal analysis, X-ray photoelectron spectroscopy, adsorption technique and chemical analysis. When the size of silver iodide nanoclusters was smaller, non-radiation surface recombination exceeded radiation process. As the size of AgI nanoclusters increased, non-radiative surface recombination effect equaled the radiation effect of the excitons. If the size of silver iodide nanoclusters further increased, the guest clusters were bigger and the surface recombination became a major process. The prepared host–guest Y–AgI nanocomposites have the potentiality as luminescence materials.

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