

Formation Of ZnS Clusters in Zeolite-Y

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Abstract We report on the formation of ZnS clusters in zeolite-Y prepared by the exchange of Zn^{2+} ions into the zeolite following sulfurization with Na_2S in solution. Blue-shifts in optical absorption spectra from that of the bulk ZnS are obviously observed, exciton absorption and emission are also exhibited by the samples. The absorption edges and excitation peaks shift to the red as the ZnS loading levels increase. These features indicate that the ZnS clusters have been formed successfully. Factors affecting the cluster quality in sample processing are discussed. It is found that sulfurization with Na_2S in solution is a good method to decrease the defects in the clusters.

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Semiconductor clusters with dimensions comparable to the exciton Bohr radius exhibit a host of novel physical properties, such as blue shifts in optical absorption spectra, increased photooxidation potentials and unusual nonlinear optical properties^[1~6]. The study of these advanced materials is a current topic with great interest. Excellent reviews on the preparation, characterization and potential applications of semiconductor clusters have been given by Henglein^[2], Weller^[3], Brus^[4], Stucky *et al.*^[5], Ozin^[6] and Herron^[7]. One attractive method for assembling and maintaining controlled such nanoclusters is to encapsulate them into porous solid host lattices. For example, stable clusters with molecular sizes and uniform size distribution may be formed in zeolites^[8]. The preparation and optical properties of ZnS clusters in zeolites have been reported by Stucky *et al.*^[9]. However the formation and optical properties of ZnS clusters in zeolite-Y have not yet reported. Here we report briefly the synthesis and optical properties of ZnS clusters in zeolite-Y prepared in solution.

The preparation of ZnS clusters in zeolite-Y is as follows. The starting zeolite materials were commercially available from Dalian Institute of Chemical Physics, CAS, and were

used without further purification, because the materials were synthesized according to our requirements. Zinc nitrate and sodium sulfide of chemical pure were purchased from Beijing Chemical Factory of China.

The zeolite powder was slurried in deionized water and the pH of the solution was adjusted to 5 with nitric acid. The zinc nitrate was added and the mixture was stirred at room temperature for 20h. The Zn^{2+} -ion-exchanged zeolite was collected by filtration, washed sufficiently with deionized water until no Zn^{2+} was detected in the filtrate by Na_2S solution, then vacuum dried to a damp powder. The materials were dried and calcined at 220°C in air for 10h. Sulfurization was carried out by the reaction of Zn^{2+} -ion-exchanged zeolite with Na_2S stirring at room temperature for 20h. Then the materials were collected again by filtration and washing. Finally the samples were dried at 150°C in vacuum for 5h.

The UV-VIS absorption spectra were measured by using a Hitachi 340 spectrophotometer. The excitation and emission spectra were recorded by a Hitachi M-850 fluorescence spectrophotometer. All measurements were carried out at room temperature.

The absorption spectra of four samples are shown in Fig. 1. The concentration of ZnS in preparation is 1, 3, 5 and 10wt% (from curve 1 to 4), respectively. As not all ZnS would enter into the zeolite pores, the effective loading levels should be a slightly lower than these values. The absorption spectrum of the bulk ZnS is also given in Fig. 1 ("bulk"). It can be seen from the absorption spectra that the normal band-gap transition of the bulk ZnS (around 334nm) virtually disappears, instead there appear absorption peaks at 290, 296, 298 and 300nm. Blue-shifts of absorption edges of the clusters from that of the bulk ZnS are obviously observed. This indicates that ZnS clusters in zeolite-Y have been formed.

The absorption peak of each sample can be assigned to the transition from the highest occupied molecular orbital (HOMO) in the valence band to the lowest unoccupied molecular orbital (LUMO) in the conduction band (i. e. $1s$ - $1s$ exciton transition^[4]). As the ZnS loading levels increase the absorption peaks and edges shift to the red, meanwhile the absorption intensity becomes stronger. The change of absorption spectra upon ZnS loading levels is caused by the so called quantum size effects, which have been studied extensively^[4,10~14]. The correlation between cluster sizes and absorption peaks could be simulated by models based on an effective-mass approximation^[10~12] and a recent tight-binding approximation^[13], respectively. The former gives a clear concept of the blue-shift of the opti-

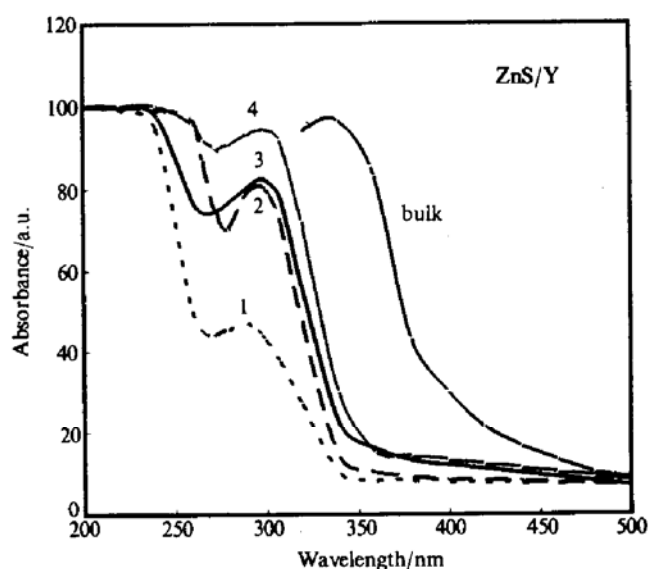


Fig. 1 Reflectance absorption spectra of ZnS clusters in zeolite-Y

cal absorption threshold, while the latter is able to make a better description of band structure^[14]. From tight-bonding model^[13], the sizes of the ZnS clusters estimated by using the absorption peaks in Fig. 1 are within 1.8~2nm, which are a little too big for the clusters in zeolite-Y. Because zeolite-Y contains two cages with different sizes, i. e. sodalite cages with 0.5nm and supercages with 1.3nm the ZnS clusters formed inside the zeolite pores should be smaller than the cages space. It is considered that the clusters were formed in the supercages, because the entry aperture of sodalite cage is too small (only 2.1×10^{-1} ^[15]) for S^{2-} anions ($\sim 3.6 \times 10^{-1}$ ^[16]) to enter to form sulfide. A strong interaction between the clusters and the host (zeolite framework)^[17], which has not been taken into account in any theoretical models, is probably the major factor to cause the difference between the theoretical estimation and the practical sizes of the clusters.

It can be seen from Fig. 1 that as the ZnS loading levels increase, the exciton absorption peaks become stronger and sharper. This indicates that larger and more order clusters were formed. The clusters with high quality in size distribution, low defects and well surface passivation might be formed in zeolites. The sizes and size distribution of the clusters were controlled by the structure of the zeolite. Because the zeolite has a well-defined structure composed of cages, each kind of cage has the same size and shape^[5~8]. So the clusters encapsulated in it may have a uniform size distribution. It was found by us that the sulfurization with Na_2S in solution is better for the cluster formation than the sulfurization with H_2S in gas-solid state reaction. Because in the gas-solid reaction, the sulfurization may only occur at the surface or intersurface of the zeolite, the reaction inside the crystal might not approach to complete. In the samples prepared with gas-solid state reaction, some unreacted ions (Zn^{2+}) always exist in the clusters as defects. But in the solution reaction, these defects may be controlled in a very low content. We also noted that sulfurization in air is helpful to the passivation of the surface states via formation of a very few oxides at the surface^[18]. These are probably the three factors in sample processing that can form the clusters with high quality.

The quality of clusters may be reflected easily from their fluorescence, because it was reported that only the clusters with high quality in narrow size distribution, low defects and well surface passivation can exhibit obvious exciton emission^[19]. All the II-VI semiconductor clusters in zeolites prepared in gas-solid state reaction reported up to now exhibit only the trapped luminescence caused by defects^[20~22], while obvious exciton emission was observed in our samples (see Fig. 2). The data in Fig. 2 are corresponding to sample 3[#] in Fig. 1. The two emission bands are excitonic emission (A) and trapped luminescence (B). The widths of the emission bands (both exciton and trapped luminescence) from our samples are much narrower than that of similar clusters reported before^[19~22]. This demonstrates further that high quality ZnS clusters were formed in our experiments. The excitation spectrum of the sample also shows pronounced structure of excitons. Details about the luminescence of ZnS clusters in zeolite-Y will be reported in a forthcoming pa-

per.

In summary, ZnS clusters have been formed inside zeolite-Y with the ion-exchange method in solution. Pronounced exciton absorption and emission were observed. Our results indicate that the quality of the semiconductor clusters may be improved via sulfurization with Na_2S in solution.

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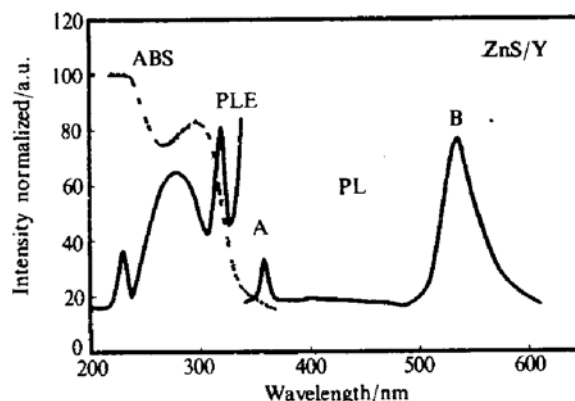


Fig. 2 Reflectance absorption (ABS), PLE and PL spectra of ZnS clusters in zeolite-Y

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