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# LETTERS

## Quantum-Sized Silver Sulfide Clusters in Zeolite A

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The reaction of $H_2S$ with activated $Ag^+$-loaded zeolite A leads to silver sulfide zeolite A composites. The optical absorption spectra of samples with different loading densities of silver sulfide suggest the formation of small silver sulfide clusters which are stable under ambient conditions. To our knowledge, this is the first report on the preparation and the optical absorption and emission spectra of silver sulfide clusters in the cavities of a zeolite in the size regime below 15 Å. The loading densities of the investigated silver sulfide zeolite A composites are 0.05, 0.10, 0.25, 0.50, 1.00, 1.25, 1.50, 1.75, and 2.00 silver ions per pseudo unit cell of zeolite A. The samples are colorless (low loading density) or yellow-green (high loading density). The luminescence is blue-green for samples with low silver sulfide content, yellow or orange at medium silver sulfide content, and red at high silver sulfide content.

### Introduction

The synthesis and the properties of semiconductor clusters in the size regime of a few to hundreds of angstroms have recently attracted much interest. A large percentage of the presently available studies focus on II−VI and IV−VI systems such as CdS and PbS, respectively.[1] The well-defined cavities of zeolites provide a convenient environment for preparing clusters with a narrow size distribution or even cluster arrays.[2] In this study we report the synthesis and the optical absorption and emission spectra of silver sulfide zeolite A composites. The preparation method is based on the recent observation that $Ag^+$-loaded zeolite A can be reversibly activated at room temperature.[3]

The low-temperature phase of bulk silver sulfide ($\alpha$-$Ag_2S$ or acanthite, stable up to 177 °C) is a semiconductor with a monoclinic structure and a band gap of approximately 1 eV at room temperature.[4] Figure 1 shows the calculated density of states (DOS) of bulk $\alpha$-$Ag_2S$. The electronic transition from valence band to conduction band is essentially a charge transfer from 3p(S) to 5s(Ag). This property is also observed in a hypothetical $Ag_2S$ molecule. The HOMO−LUMO region of such a molecule, and presumably also of larger silver sulfide clusters, fits well into the gap between the oxygen lone pairs of zeolite A and the zeolite A LUMO region (see right side of

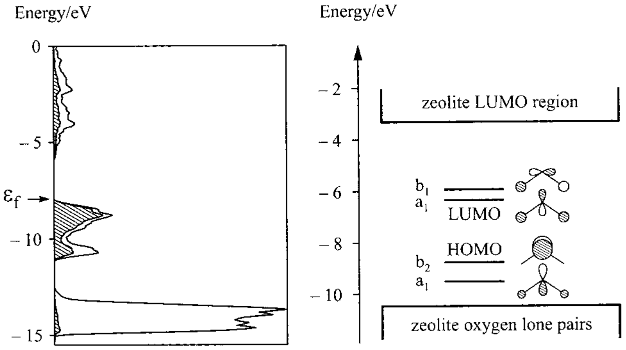

**Figure 1.** Left: Density of states (DOS) plot of $\alpha$-$Ag_2S$. The hatched region indicates the contribution of sulfur 3p-states (BICON−CEDiT[5] calculation). The Fermi level $\epsilon_f$ is marked by an arrow. Right: HOMO−LUMO region of a hypothetical $Ag_2S$ molecule in comparison to the HOMO−LUMO region of zeolite A (ICON-EDiT[6] calculation).

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Figure 1), therefore giving rise to a variety of electronic transitions.

It has been shown that brown-colored nanocrystallites of $Ag_2S$ with diameters of 2.3−7.6 nm can be synthesized in reverse micelles.[7] In this communication we present a preparation method which leads to even smaller silver sulfide species stabilized by the framework of zeolite A. $Ag_2S$ particles in this size regime are believed to play an important role in the photographic process.[8]

## Experimental Section

**Synthesis.** Sodium zeolite A ($Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$) was synthesized and characterized according to ref 9. Hydrogen sulfide gas was obtained from Messer Griesheim and used as received. Silver sulfide−zeolite A composites were prepared by the following procedure: A 120 mg amount of sodium zeolite A (NaA) was finely dispersed in 10 mL of bidistilled water. A calculated volume of a 0.1 M silver nitrate solution (Merck, Titrisol) was added to obtain the desired silver loading (a quantitative exchange of silver ions can be assumed).[10] After shaking the suspension for 30 min at room temperature, the silver exchanged zeolite was centrifuged off, washed two times with 15 mL of bidistilled water, and activated at room temperature under high vacuum for 40−60 h (final pressure $4-7 \times 10^{-7}$ mbar). The color changes observed during this process, which simply corresponds to the dehydration of the silver ions inside the zeolite cages, and the optical absorption spectra of activated silver-containing zeolite A have been reinvestigated recently.[3] The activated sample was then exposed to approximately 80 mbar of $H_2S$ for 1 h and subsequently evacuated overnight to remove excess $H_2S$.

**Nomenclature.** The theoretical stoichiometry of the silver sulfide−zeolite A composites is $Ag_xS_{x/2}Na_{12-x}H_xSi_{12}Al_{12}O_{48}\cdot nH_2O$ (pseudo unit cell contents). In the following we will use the abbreviation $Ag_2S$−NaA-*x* for the differently loaded samples, where *x* denotes the number of silver ions per pseudo unit cell of zeolite A.

**Physical Measurements.** The samples were analyzed by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). Diffuse reflectance spectra were recorded at room temperature using a Perkin-Elmer Lambda 14 spectrophotometer equipped with an integrating sphere (Labsphere RSA-PE-20). The data were converted using the Kubelka−Munk formula. Since the scattering coefficient of zeolite is gradual in the wavelength region of interest, the Kubelka−Munk function is a good representation of the absorption spectrum. Photoluminescence spectra were taken on a Perkin-Elmer LS 50B spectrofluorometer. The samples were cooled in a nitrogen cryostat (Oxford Instruments PE 1704).

## Results and Discussion

**Stability of Silver Sulfide−Zeolite A Composites under Ambient Conditions.** The loading densities of the investigated silver sulfide zeolite A composites are 0.05, 0.10, 0.25, 0.50, 1.00, 1.25, 1.50, 1.75, and 2.00 silver ions per pseudo unit cell of zeolite A. Examination of the samples by XRD and SEM revealed that no disintegration of the zeolite framework had occurred during the synthesis. Figure 2 shows the UV/vis absorption spectra of freshly prepared $Ag_2S$−NaA-0.05, $Ag_2S$−NaA-0.10, and $Ag_2S$−NaA-0.50 under inert atmosphere. An interesting change in the spectral features is observed during the exposure of the samples to ambient conditions. Most striking is the evolution of a band around 320 nm (see inset of Figure 2). This phenomenon seems to be caused by the adsorption of water and the thereby initiated migration of small clusters or silver ions, which leads to the formation of larger and energetically more favorable silver sulfide species. It has to be noted that samples with loadings of one or more silver ions per pseudo unit cell of zeolite A already feature a band around 320 nm before exposure to ambient conditions. The decrease of the band at 225 nm can be attributed to the removal of dissociated $H_2S$. It is known that $H_2S$ adsorbed on sodium zeolite X dissociates to $S^{2-}$ and to $SH^-$. These species are indicated by an absorption band at 235−250 nm.[11] We observed a similar behavior in the case of sodium zeolite A. Adsorption of $H_2S$ leads to a band at 225 nm, which decreases upon exposure to ambient conditions. Furthermore, the maximum of this band is shifted to 205 nm during this process. For silver sulfide−zeolite A composites with loading densities of more than 0.1 silver ions per pseudo unit cell, the variation of the absorption spectrum during the course of the preparation is apparent as essentially three distinctive color changes (samples with lower loading densities, as for example $Ag_2S$−NaA-0.05, remain colorless throughout the synthesis): The colorless $Ag^+$-loaded zeolite A turns yellow upon activation at room temperature.[3] Reaction with $H_2S$ gives colorless ($Ag_2S$−NaA-0.25 and $Ag_2S$−NaA-0.50) or yellow-green colored samples ($Ag_2S$−NaA-1.00 to $Ag_2S$−NaA-2.00). Exposure to ambient conditions renders the colorless samples

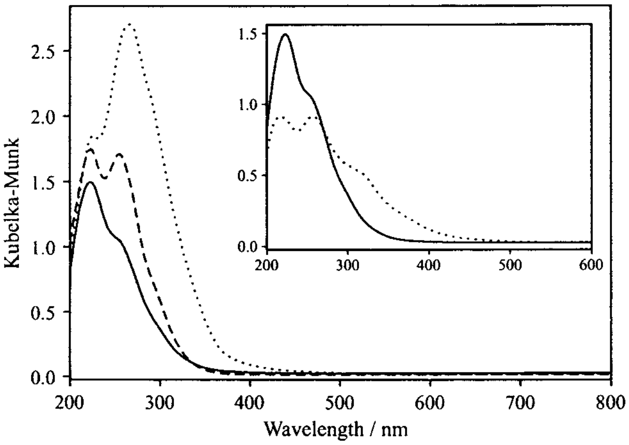

**Figure 2.** UV/vis absorption spectra of $Ag_2S$−NaA-0.05 (solid line), $Ag_2S$−NaA-0.10 (dashed line), and $Ag_2S$−NaA-0.50 (dotted line) before exposure to ambient conditions. The inset shows the spectrum of freshly synthesized $Ag_2S$−NaA-0.05 under inert atmosphere (solid line) and after 3 h under ambient conditions (dotted line).

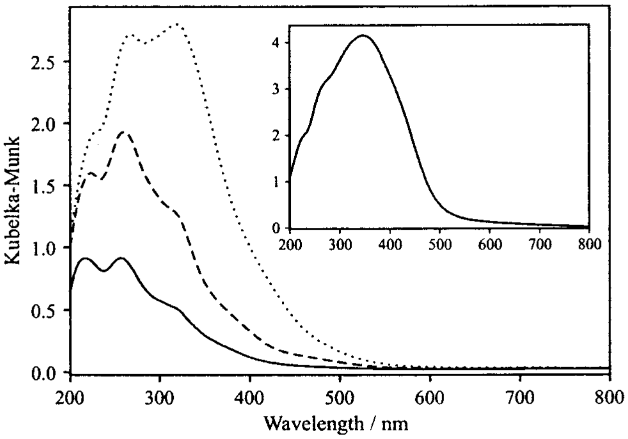

**Figure 3.** UV/vis absorption spectra of $Ag_2S$−NaA-0.05 (solid line), $Ag_2S$−NaA-0.10 (dashed line), and $Ag_2S$−NaA-0.50 (dotted line) after completion of the cluster growth process described in the text. The inset shows the spectrum of $Ag_2S$−NaA-2.00. In this case the low energy band is already observed before exposure to ambient conditions.

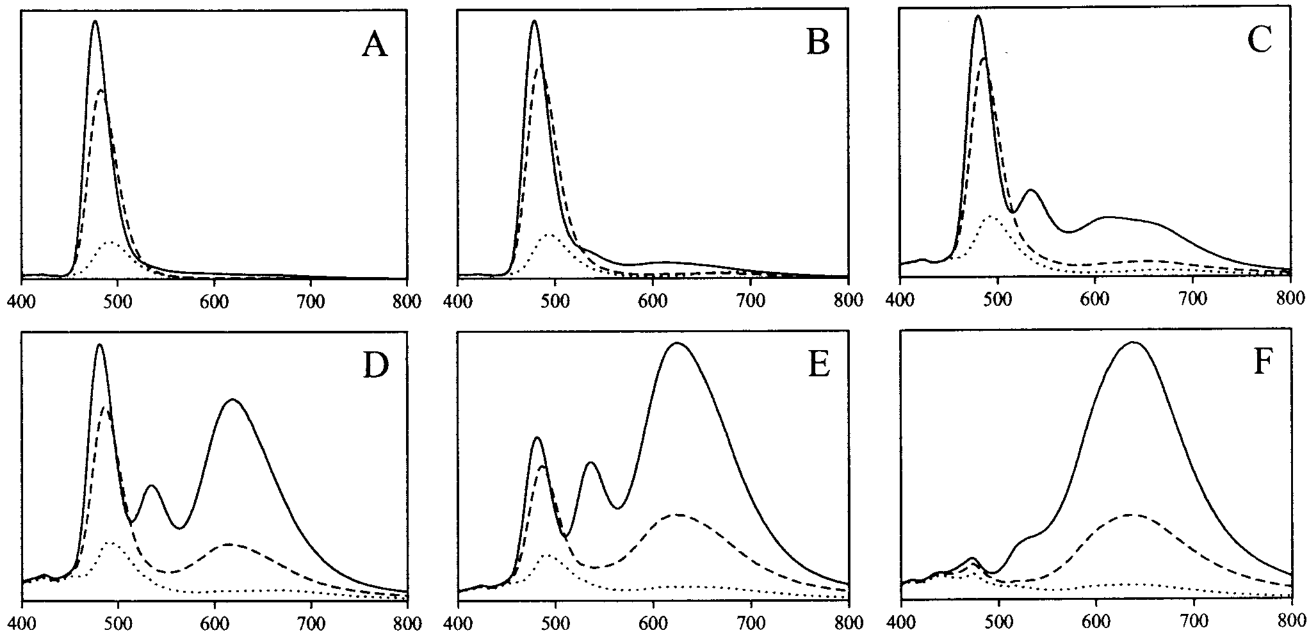

**Figure 4.** Emission spectra of $Ag_2S$−NaA-0.05 (A), $Ag_2S$−NaA-0.10 (B), $Ag_2S$−NaA-0.25 (C), $Ag_2S$−NaA-0.50 (D), $Ag_2S$−NaA-1.00 (E), and $Ag_2S$−NaA-1.25 (F) at −195 °C (solid lines), −100 °C (dashed lines), and −50 °C (dotted lines). The abscissa and the ordinate give the wavelength in nanometers and the emission intensity, respectively. Excitation was performed at 280 nm. No luminescence could be detected at 0 °C.

($Ag_2S$−NaA-0.25 and $Ag_2S$−NaA-0.50) slightly yellow-green as well, while for samples with higher loading densities ($Ag_2S$−NaA-1.00 to $Ag_2S$−NaA-2.00), an intensification of the already visible color can be observed.

No further changes in the chemical or physical properties have been found once the process of water adsorption and cluster growth has been completed. All of the following investigations have therefore been carried out after the exposure of the samples to ambient conditions. For those samples, the low energy band becomes increasingly dominant with higher loading density of silver sulfide (see Figure 3).

**Luminescence Spectra.** Silver sulfide−zeolite A composites exhibit a variety of luminescence properties. Figure 4 shows the development of the emission spectra with increasing loading density of silver sulfide. The observed color of the emission is blue-green for samples with low silver sulfide content ($Ag_2S$−NaA-0.05 and $Ag_2S$−NaA-0.10), yellow or orange at medium silver sulfide content ($Ag_2S$−NaA-0.25 and $Ag_2S$−NaA-0.50, respectively), and red at high silver sulfide content ($Ag_2S$−NaA-1.00 to $Ag_2S$−NaA-2.00) when excited at 350 nm. No luminescence could be detected for pure sodium zeolite A. There are only minor changes in the emission spectra when increasing the loading density from 1.25 to 2.00 silver ions per pseudo unit cell of zeolite A. The shoulder at 520 nm disappears and the intensity of the prominent band at 630 nm decreases. A slight broadening of this band can be observed as well.

## Conclusions

Silver sulfide−zeolite A composites can be prepared in three steps (all of them are carried out at room temperature): (i) intercalation of $Ag^+$ into zeolite A by means of ion exchange, (ii) activation of the $Ag^+$-loaded zeolite, and (iii) reaction of the activated $Ag^+$-loaded zeolite with $H_2S$. The optical absorption and emission spectra of samples with different loading densities of silver sulfide strongly suggest the presence of small silver sulfide clusters. The effect of the variation of the silver sulfide content on the emission spectra is remarkable. It is obvious that the variety of these spectra offers challenging possibilities to obtain information about the electronic structure of the involved silver sulfide species.

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