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LETTER TO THE EDITOR

**A primary study on the synthesis and characterization of ZnS clusters in chitosan film**

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**Abstract.** A novel process using chitosan containing ligand groups as a medium for forming ZnS clusters by an ion-coordination method is investigated for the first time. The ZnS clusters in the chitosan film have been identified by x-ray diffraction, ultraviolet–visible absorption and photoluminescence spectra. The ZnS cluster size was estimated to be about 2–6 nm, depending on the processing conditions. Blue luminescence for the undoped ZnS clusters was observed and its mechanism is briefly discussed.

Small metal and semiconductor clusters, having hybrid molecular and bulk properties, represent a new class of materials. This kind of material usually possesses novel optoelectronic properties and can exhibit new phenomena, such as the quantum-size effect, the nonlinear optical effect and 'the giant oscillator strength' effect, and has potential application prospects in the fields of display optical switches, optical fibre communication and nonlinear optics, etc. There is increasing interest in the synthesis and characterization of nanometre-sized semiconductors. Many approaches have been explored for the preparation of small clusters [1], including the use of colloids [2], micellae [3], polymers [4–6], glasses [7] and zeolites [8].

However, at present the clusters obtained, to our knowledge, are not single size and often the surface is not well defined. Therefore, how to develop methods for the preparation of monodisperse clusters and the control of their surface are most important issues. In the following, we will present a novel process using well-distributed chitosan containing ligand groups as a medium for forming ZnS clusters by a so-called ion-coordination method. Since each unit in the chains of chitosan molecules has groups that permit a metal-coordination complexation, and has a similar capability of complexing, the semiconductor clusters formed by this method should be of similar size and be homogeneously dispersed in the medium.

We now discuss the experimental procedure.

Chitin was dissolved in 2% CH<sub>3</sub>COOH solution which was then dropped slowly into 47% (by weight) NaOH solution and allowed to react for 3 h at a temperature of about 60 °C under nitrogen. Afterwards, HCl solution was added to the solution until it became

neutral. Later, the sample was washed and filtered using deionized water, and finally vacuum dried. The chitosan obtained by this method had a 78% deacyl degree identified by infrared absorption spectra. The treated chitosan, redissolved in 2% CH<sub>3</sub>COOH solution, was cast onto the smooth surface of polyflon or quartz plates, becoming a film with a thickness of 0.1 mm, after solidification in air for about 24 h. The chitosan film was submerged in 0.1 M ZnCl<sub>2</sub> solution for 24 h, then washed using deionized water and finally vacuum dried. The ZnCl<sub>2</sub>-treated, dried film was then submerged in 0.2 M Na<sub>2</sub>S solution for an appropriate period, and finally washed and dried as mentioned above.

The characterization of the film obtained was performed using an Infrared Spectrophotometer, a DMS 100S Ultraviolet Spectrophotometer, a Scanning Electron Microscope (SEM), a D/Max-III C X-ray Diffractometer and a Hitachi 850 Fluorescence Spectrophotometer for photoemission spectrum measurements.

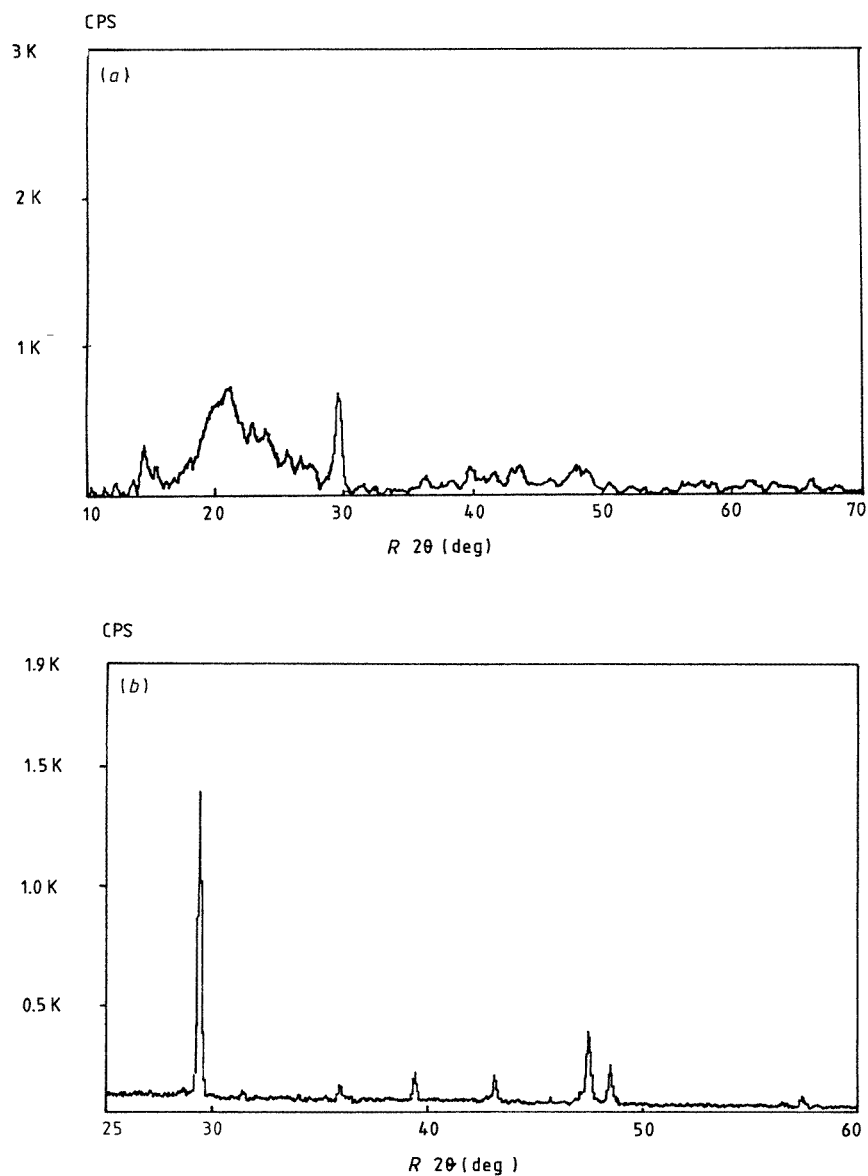
We now go on to give and discuss the results. First we deal with the growth mechanism of ZnS clusters in the chitosan film.

The infrared (IR) absorption spectra of chitosan show that the characteristic peaks representing CO and NH<sub>2</sub> have been obviously shifted, after the groups in chitosan complexed with Zn<sup>2+</sup>. For the C=O group, the wave number has shifted from 1636 to 1718 cm<sup>-1</sup>, and for the NH<sub>2</sub> group, it has shifted from 1559 to 1542 cm<sup>-1</sup>. This means that coordinate bonds between CO or NH<sub>2</sub> and Zn<sup>2+</sup> have been formed, with their vibration frequency changed. In addition, it is also quite possible that a large number of Zn<sup>2+</sup> ions agglomerated around the Zn<sup>2+</sup> complexed with C=O or NH<sub>2</sub> groups in an absorbed state to form so-called metal-ion groups. Thus it could be considered that some of the Zn<sup>2+</sup> ions in ZnCl<sub>2</sub> solution have formed rather strong complexed bonds with NH<sub>2</sub> and CO groups in chitosan, and a large number of Zn<sup>2+</sup> ions in the solution have agglomerated around the complexed Zn<sup>2+</sup> ions with the groups on the chitosan molecules via a so-called absorbing force to form metal-ion groups.

The coordinated Zn<sup>2+</sup> or agglomerated Zn<sup>2+</sup> ions in the chitosan film might react with sulphur ions, S<sup>2-</sup>, in Na<sub>2</sub>S solution to form ZnS clusters which stick to the chitosan film. The IR spectra indicate that the wave number representing the C=O group in the film submerged both in ZnCl<sub>2</sub> and subsequently in Na<sub>2</sub>S solution has risen by 64 cm<sup>-1</sup>, compared to that in the film only submerged in ZnCl<sub>2</sub> solution. Thus, it might be considered that the S<sup>2-</sup> in Na<sub>2</sub>S solution reacts not only with the agglomerated Zn<sup>2+</sup> to form ZnS clusters, but also with the Zn<sup>2+</sup> bonded to the C=O group in chitosan to form coordinate bonds in the form of CO → Zn ← S.

Now we move on to discussing the characterization of ZnS clusters in chitosan film.

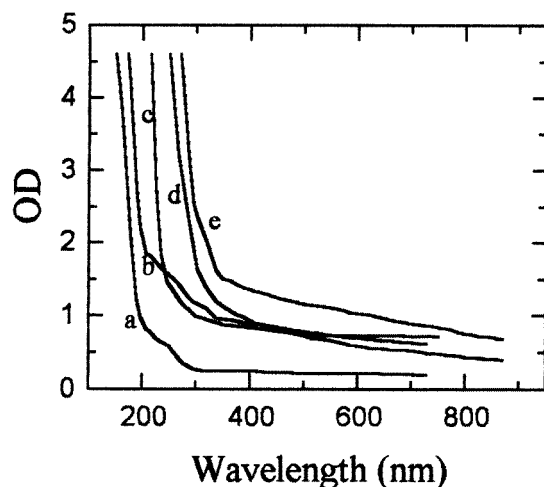
The composition of the ZnS clusters in chitosan was first investigated by EDX, then with a micro-electron probe. The Zn/S atom ratio was estimated to be in the range of 0.9–1.0. A small amount of the elements Na or/and Cl for some samples was also detected, which might be introduced during the processing of the sample preparation. Typical results from x-ray diffraction for the chitosan films treated in ZnCl<sub>2</sub> and Na<sub>2</sub>S solution are shown in figure 1. The main peaks are situated at 29°, 32°, 48° and 57° respectively; these values are roughly consistent with those obtained from the JCPDC card, which are 28.58°, 33.12°, 47.61° and 56.45° corresponding to {111}, {200}, {220} and {311} planes respectively in the β-ZnS crystal. Therefore, it might be considered that the crystallites of the ZnS clusters in chitosan have a finite bulk-like cubic structure. The deviation from the standard data might be caused by non-stoichiometry of the CdS clusters. This would distort the crystal lattice and thus slightly change the *d*-spacings. Comparing figure 1(a) with figure 1(b), it can be seen that the diffraction lines have obviously widened with the decrease of the ZnS cluster growth time and thus with the decrease of the ZnS cluster size. Based on Scherrer's equation [9,



**Figure 1.** The results of x-ray diffraction for ZnS clusters in the chitosan film: (a) shows the data for  $\text{Zn}^{2+}$ /chitosan treated in a  $\text{Na}_2\text{S}$  solution for 30 s; and (b) those for 20 h under the same conditions as in (a).

10] after the removal of errors caused by non-stoichiometry of the clusters, the ZnS cluster size in chitosan was estimated to be about 2–6 nm in diameter. Certainly broadening might also be the result of the defects on the cluster surface or within the clusters. Further work will be needed to explore the defects of the clusters in the chitosan film.

Quantum-size effects are mainly determined by the cluster size, with the cluster size depending on the cluster growth conditions, such as the distribution of groups in the polymer

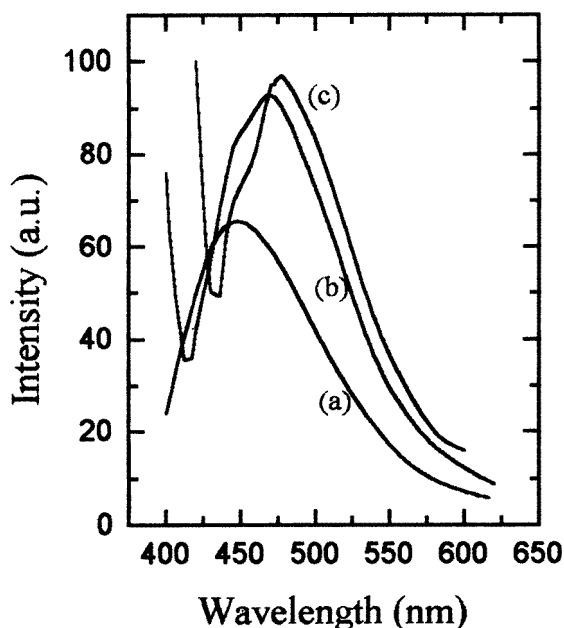


**Figure 2.** The dependence of the optical absorption band edge of the ZnS clusters in the chitosan film on the time of  $\text{Zn}^{2+}$ /chitosan submergence in  $\text{Na}_2\text{S}$  solution: (a) 30 s; (b) 30 min; (c) 1 h; (d) 5 h; (e) 20 h.

molecules, the reaction time between  $\text{ZnCl}_2$  and  $\text{Na}_2\text{S}$ , the concentration of the  $\text{ZnCl}_2$  and  $\text{Na}_2\text{S}$  solution, and the reaction temperature. The dependence of the optical absorption spectra of the ZnS clusters in the chitosan film on the time of submergence in  $\text{Na}_2\text{S}$  solution is shown in figure 2, while the concentration of  $\text{Zn}^{2+}$  in the film and  $\text{Na}_2\text{S}$  solution is kept constant. It can be seen that the absorption band edge is blue-shifted from about 350 to 230 nm with the decrease of the time of  $\text{Zn}^{2+}$ /chitosan submergence in  $\text{Na}_2\text{S}$  solution, and thus with the decrease the ZnS cluster size. This can be attributed to a so-called quantum-size effect at room temperature.

Figure 3 shows the photoemission spectra obtained with the excitation wavelength of 270 nm at room temperature. It indicates that the emission peaks are in the range of 440–480 nm and are blue-shifted with the decrease of the ZnS cluster size, whereas the magnitude of the emission peak shift is smaller than that of the absorption band edge (figure 2). As is well known, the emission spectra caused by an electron band-to-band transition are in the ultraviolet region, and the blue luminescence for ZnS should be normally due to excitation agents doped in ZnS, such as  $\text{Cu}^+$ , and  $\text{Mn}^{2+}$  ions. Since our samples were not intentionally doped with any foreign impurity, it might be reasonably inferred that the blue luminescence observed for ZnS clusters in chitosan is caused by self-activated centres, probably  $\text{Zn}^{2+}$  vacancies  $V_{\text{Zn}}$  [11]; furthermore,  $\text{Cl}^-$  ions present in ZnS clusters act according to the charge compensation effect so as to create  $\text{Zn}^{2+}$  vacancies in the clusters. The  $\text{Cl}^-$  ions might be introduced during the film processing in  $\text{ZnCl}_2$  solution, and not totally removed in the successive procedures, as has been identified using the micro-electron probe as mentioned above. Certainly we cannot entirely rule out the possibility that the blue luminescence might also be attributed to the presence of  $\text{Na}^+$  or other impurity ions, although it has not been identified by our measurements yet.

In fact, from the width of the x-ray diffraction lines we can deduce the mean size of the coherency domains, but there is a lack of information on the nanostructural morphology related to the concentration of ZnS in the films. Roughly, under the 3D percolation threshold we can imagine a system of isolated ZnS nanoparticles, while above this threshold more



**Figure 3.** The dependence of the photoemission spectra for the ZnS clusters in the chitosan film, obtained with the excitation wavelength of 270 nm at room temperature, on the time of  $\text{Zn}^{2+}$ /chitosan submergence in  $\text{Na}_2\text{S}$  solution: (a) 30 min; (b) 5 h; (c) 20 h.

complex particle shapes (agglomerated clusters and chains) could be formed. Of course, these morphologies would considerably influence the quantum-size effects and consequently the optical absorption and luminescence properties. Further research is under way with the aim of directly observing the individual cluster agglomerates or chains by TEM, and to explore the relationships between the morphologies and the optical absorption and luminescence properties.

In conclusion, we have successfully prepared nanometre-sized ZnS clusters in a chitosan medium by an ion-coordination method. A possible growth mechanism of the ZnS clusters in the chitosan film has been proposed. Each stage of the sample preparation was investigated by IR and UV–visible absorption spectra respectively.

The results of x-ray diffraction show that the crystallites of the clusters have a finite bulk-like cubic structure. The number of Zn atoms is slightly less than that of S atoms in the clusters. The cause for this might be due to the presence of  $\text{V}_{\text{Zn}}$ ,  $\text{Cl}^-$  or  $\text{Na}^+$  in the clusters, which were introduced during the sample preparation.

The size of the ZnS clusters prepared by this method depends on the time of  $\text{Zn}^{2+}$ /chitosan submergence in  $\text{Na}_2\text{S}$  solution, while other factors are kept constant, and is estimated to be about 2–6 nm in diameter, based on Scherrer's equation. Quantum-size effects have been demonstrated using ultraviolet–visible absorption spectra.

Photoemission peaks in the range 440–480 nm for the undoped ZnS clusters in the chitosan film were observed at room temperature. This might be caused by the presence of self-activated centres, like zinc vacancies, in the clusters.

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