LUMINESCENCE OF MIXED ZnS · CdS SEMICONDUCTOR CATALYSTS IN NAFION POLYMER FILMS

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The luminescence of CdS and mixed ZnS·CdS semiconductor particles supported in Nafion polymer films has been studied to elucidate the previously reported synergism in the ZnS·CdS system for photoredox H_2 production. (J. Phys. Chem. 89 (1985) 723). The luminescence of these systems is complex, depending on the history of the particular sample, the intensity and wavelength of the exciting light, and the presence of ions that can quench specific emitting states (e.g. S^{2-} or methylviologen). For the mixed ZnS·CdS system the two semiconductors do not alloy but there is intimate contact between the ZnS and CdS phases, indicated by the complete quenching of ZnS luminescence. Prolonged irradiation produces a luminescent ZnS phase. The emission features agree reasonably well with sub-bandgap states deduced from earlier photoconductivity studies on CdS crystals. These results help explain why the reported emission features of CdS are as varied as the laboratories reporting them.

1. Introduction

Small particle semiconductors are much studied as catalysts for photoinduced electron transfer reactions. Although excited state lifetimes are short (< ns), the diffusional path length for conduction band electrons is often greater than the particle size and a large fraction of the excited electrons reach the surface. Photochemical or photophysical processes of the excited semiconductor involve adsorbed species and may be modified by reaction-specific catalysts which are easily placed on the semiconductor surface [1]. Many different approaches to the study and utilization of semiconductor-based systems are currently being pursued, e.g., single and polycrystalline electrodes [2], powders [3], colloids [4], particle suspensions [5] and large particles [6] physically embedded in polymer membranes.

We are interested in approaches which involve semiconductor fabrication in polymeric membranes and small particles on solid supports. The membranes are ionically conductive polymers (Nafion 117) and the advantages of this strategy have previously been expounded [7]. While colloidal systems offer high efficiencies, flocculation often limits sustained operation. In Nafion, however, the semiconductor particles are presumably immobilized and aggregation is not observed. To date, membrane encapsulated CdS, ZnS and TiO_2 have been prepared. The semiconductor particles apparently reside in hydrophobic pockets of the polymer while hydrophilic regions lie close by. Several studies of mobility [8], reactivity [9] and luminescence [10] of various species within Nafion have already appeared. Recent work from this laboratory has explored visible-light-induced water reduction with Nafion encapsulated CdS [7]. In such studies, Pt is required to catalyze proton reduction. The efficiency of such systems is comparable with the best reported for other CdS based systems. ZnS/Nafion is also active for H_2 genera-

tion but requires UV excitation [11]. Recently we observed a remarkable catalytic effect on the hydrogen-producing reaction with films and solid supports containing coprecipitated ZnS and CdS in the absence of a noble metal catalyst [12]. The free Nafion and CdS/Nafion films have been probed by surface-sensitive techniques [13] as have coprecipitated and sequentially precipitated ZnS, CdS/Nafion films [14]. Several basic phenomena resulting from irradiation have been observed [14]: (1) Cd^0 is formed following either visible or UV irradiation of the mixed semiconductor/Nafion system; (2) Cd^0 is not detected after excitation of CdS/Nafion by UV or visible light; (3) metallic zinc is not observed following irradiation of any system.

To gain insight into the important photochemical mechanisms of these films, we have studied the emissive properties of the membrane-encapsulated semiconductors. Since emission is sensitive probe for the location of electron trapping centers in semiconductors, we hoped to address the following questions:

1) Does the local Nafion environment substantially alter the emission energy levels of CdS or ZnS relative to single crystals, colloids or powders?

2) What is the nature of the ZnS · CdS interaction in the coprecipitated semiconductor/Nafion system, i.e. is this situation best described as a solid solution or an intimate mixture of ZnS and Cds.

We show in this work that the energy levels (as revealed by luminescence) of the various sub-bandgap states are almost identical with literature values for single crystals. Absorption and emission spectra of the mixed system are essentially a superposition of those for ZnS/Nafion and CdS/Nafion. The emission results for CdS are quite compatible with earlier photoconductivity studies of CdS crystals at low temperature, and also with recent electrochemical measurements [15]. The latter showed that treatment of CdS with Zn^{2+} serves to block surface states which act as electron/hole recombination centers [15] such that electron transfer to solution species from states within the bandgap is enhanced.

2. Experimental

2.1. Semiconductor fabrication

Prior to semiconductor incorporation, Nafion-117 membranes were cleaned as described earlier [7]. Single-component systems were prepared by soaking in either $Cd(NO_3)_2$ or $Zn(NO_3)_2$ solution (0.5M) followed by treatment with H_2S. Mixed semiconductor (ZnS · CdS/Nafion) systems were prepared by soaking in an equimolar (0.5M each) solution of $Zn(NO_3)_2/Cd(NO_3)_2$, followed by a rinse with distilled water to remove unbound ions. In all cases, soaking times of longer than 5 min saturated the films. The films were then immersed for 10 min in a H_2S saturated aqueous solution through which H_2S was bubbling. Following sulfide precipitation the films were thoroughly washed with water. Films designated ZnS/CdS/Nafion entail a CdS fabrication as above, followed by a water wash and then ZnS formation also as above. This order was reversed for CdS/ZnS/Nafion. In the case of ZnS · CdS films, the 1 : 1 ratio was confirmed by atomic absorption spectrometry. The crystal structure of CdS was controlled by pH; acidic conditions during H_2S treatment resulted in cubic (β) crystals while neutral conditions yielded hexagonal (α) crystals. All of these films were opaque. Transparent films of hexagonal (α) CdS were produced by exposing the Cd^{2+} saturated membrane to Na_2S instead of H_2S. Transparency is presumably the result of smaller particles. The concentration of CdS in the Nafion and the luminescent properties are independent of the method of preparation.

Crystal structure was determined by X-ray powder diffraction (XRD). No XRD signals were observed for ZnS either alone or in the mixture. Relatively strong XRD signals were obtained with CdS/Nafion, but only weak CdS peaks appeared in the mixture. We conclude that ZnS is predominantly amorphous and that CdS crystal growth is strongly influenced by coprecipitation of ZnS.

2.2. Spectral measurements

Spectra were recorded with a variety of instruments and under a variety of conditions. As will be discussed in the Results section, spectra were

very dependent on the excitation conditions. Four excitation methods were used: (1) high intensity pulsed laser excitation, (2) low intensity pulsed laser excitation (for lifetime studies), (3) variable intensity CW laser excitation, and (4) low intensity CW Xe lamp (with monochromator) excitation. A more detailed description follows:

(1) High-intensity pulsed laser: either the third (355 nm) or fourth (266 nm) harmonic of a Quantel YG406 mode-locked Nd : YAG laser was used. The pulse width was 200 ps with a total energy of 20–30 mJ/pulse so that peak fluxes were $\sim 10^8$ W cm^{-2}. Emission was detected by a Hamamatsu R928 photomultiplier (PMT) and data acquisition and reduction was accomplished according to Foyt [16].

(2) Low-intensity pulsed laser: excitation at 320 nm was obtained by cavity-dumped pumping of a Spectra-Physics 375B dye laser by a Spectra-Physics model 3000 mode-locked Nd : YAG laser. Peak fluxes were of the order of 10^3 W cm^{-2}. Single photon counting techniques were employed with a Hamamatsu R928 PMT wired for fast response [17]. Output PMT pulses were amplified with an ORTEC 574 amplifier and passed to an ORTEC CFD583 discriminator. Discriminator output pulses are used as start pulses for an ORTEC 457 time-to-amplitude converter (TAC). TAC output pulses are processed by a Tracor-Northern TN7200 multichannel analyzer. Stop pulses are generated by the output of a specially wired 1P28 PMT [17] and amplified as above. This apparatus is capable of better than 100 ps resolution [18].

(3) Variable-intensity CW laser: an argon ion laser (Coherent R6-UV) was employed (488 and 515 nm) with vidicon detection in a PAR OMA-2 system.

(4) Low-intensity CW Xe lamp: the lowest power excitation studies utilized a 150 W Xe lamp for excitation in a SPEX Fluorolog photon counting fluorometer equipped with an RCA C31034 PMT. For quenching experiments a Spex Fluorolog 2 spectrofluorimeter equipped with a 450 W Xe lamp, double monochromators and Hamamatsu R928 PMT was used. Typical monochromatized fluxes in these instruments were < 10 mW cm^{-2}.

One experimental difficulty with these Nafion-supported semiconductor systems is the heterogeneity in the distribution of semiconductor within the film, which is evident even by visual inspection. The relative intensity of the various emission peaks to be discussed in the Results section can vary significantly depending on the precise region of a given Nafion film that is irradiated. However, if case is taken to support the film precisely such that the same portion of the films is excited, the spectra are completely reproducible over time. In addition, the luminescence is strongly quenched by S^{2-} ion (see Results), which is inevitably present in excess after the film preparation. Consequently the films were thoroughly washed with distilled water before the luminescence was measured.

3. Results

3.1. Luminescence of CdS / Nafion

Absorption spectra of CdS/Nafion films show an onset of absorption at about 520 nm which agrees well with the known bandgap of CdS (2.4 eV). Despite the nitric acid cleaning treatment which produced clear colorless transparent Nafion films, emission attributed to an impurity was detected at about 440 nm in the high-intensity excitation emission spectra of the films prior to and after semiconductor incorporation. The intensity of CdS emission was at least an order of magnitude greater than that of the impurity.

CdS/Nafion luminescence at both high- and low light intensity is shown in fig. 1. At low power densities a number of emission maxima are observed (fig. 1, curves A, B and C) at 530, 550, 600, 680 and ~ 715 nm. These energy levels appear to be independent of the state of CdS [19,20]. As was mentioned in the Experimental section the relative intensities of the peak maxima are dependent on film alignment with respect to the exciting beam and reflect the subtle difference in CdS environments due to inhomogeneous deposition within the film.

Under the influence of high-powered pulsed laser irradiation (355 nM) only a single emission
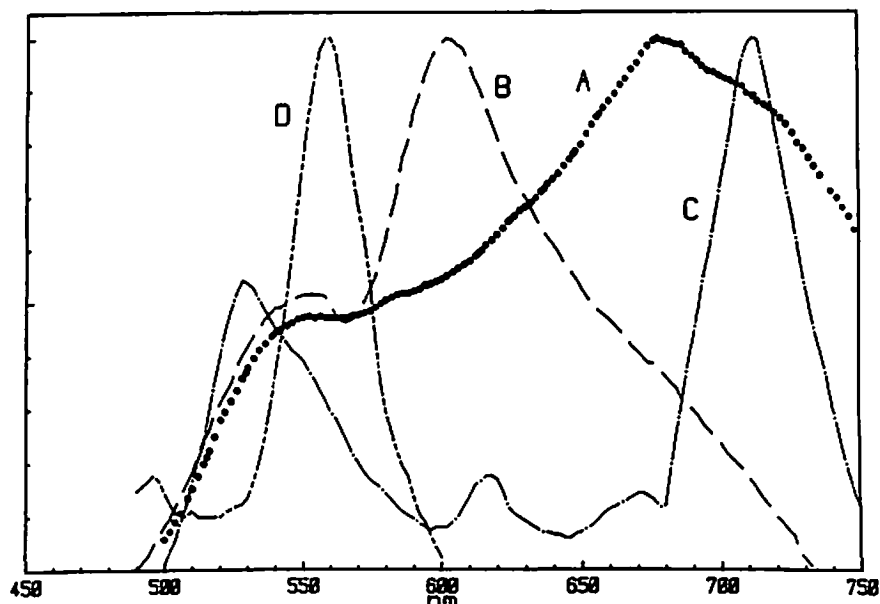
Fig. 1. CdS/Nafion emission under (A) low-power CW laser (488 nm excitation); (B) 150 W Xe lamp excitation (at 450 nm); (C) 450 W Xe lamp excitation (at 450 nm); (D) high-power pulsed laser (355 nm excitation) (all spectra normalized to the same value at maximum).

peak is observed at 550 nm (fig. 1, curve D). The peak positions are independent of crystal structure (hexagonal, α, or cubic, β) and within the limitations imposed by our experimental setup, we did not observe any major differences in luminescence intensity from either crystal form. CdS/Nafion-125 films were also prepared according to the methods reported by Thomas et al. [21]. Emission spectra of these CdS/Nafion systems showed the same bands as those of the 117 films.

The emission lifetime at 550 nm was determined by the single-photon counting method to be ca. 25 ns, with a minor component with a lifetime of ca. 1 ns. Since the 1 ns component is also observed in the undoped Nafion film we ascribe it to an impurity in Nafion. Exposure of the CdS to Na_2S 0.1M solution reduces this lifetime to ca. 0.4 ns and it remains unchanged after high-intensity irradiation to produce H_2. These latter values are similar to those reported previously for CdS colloids [22], but are much shorter than the Ca. 1 μs value at 600 nm reported recently by Thomas et. al. [21] for CdS in Nafion. We note that the 550 and 600 nm emissions originate from different traps (see fig. 7), so this

large difference in lifetimes does not represent any fundamental disagreement between our observations and those of Thomas et al. [21]. These traps are presumably in different physical locations and thus do not communicate electronically. We were not able to measure the emission decay at 600 nm because of the photomultiplier response of our system.

The spectra in fig. 2 demonstrate the quenching effects of ions such as Cd^{2+}, Zn^{2+} and MV^{2+} (~ 1 mM). As on colloids [23] the red (715 nm) emission of CdS (fig. 2A) is completely quenched by methylviologen (MV^{2+}), but a strong emission is observed at 530 nm (fig. 2C) which is distinctly different from the emission of CdS/Nafion in 0.1M Cd^{2+} (fig. 2D). This state-specific quenching by MV^{2+} has been found also in electrochemical measurements [15] and is attribute to strongly adsorbed MV^2 on the surface of CdS. Following ca. 75% quenching of the red emission by a 2 × 10^{-6}M MV^{2+} solution, CdS/Nafion was washed thoroughly with water and soaked overnight in 0.1M $Cd(NO_3)_2$ solution. The emission spectrum was unaltered, indicating the irreversible surface state changes induced by MV^{2+}. As previously

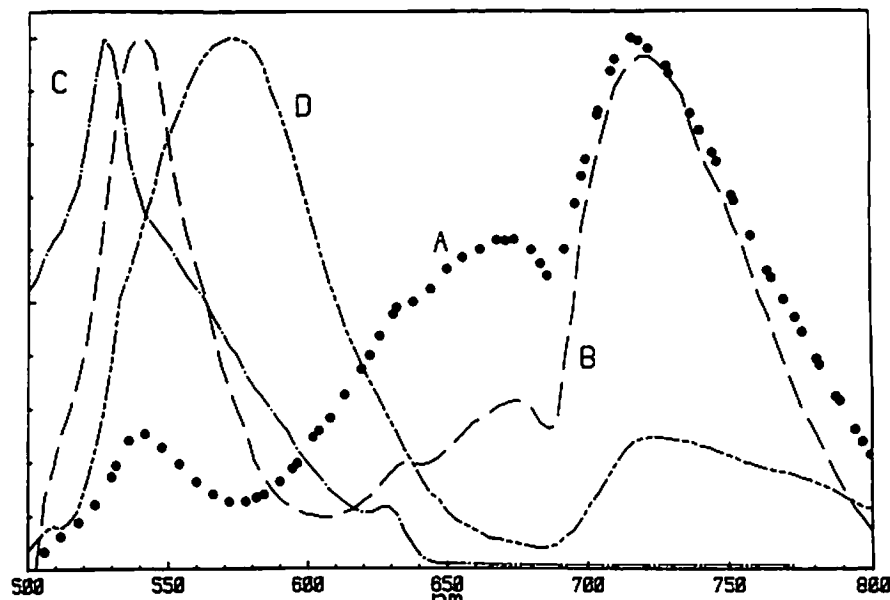Fig. 2. CdS/Nafion (curve A); CdS/Nafion+0.1M Zn(NO₃)₂ (curve B); CdS/Nafion+ MV²⁺ (curve C); CdS/Nafion+0.1 MCd(NO₃)₂ (curve D) (normalized as in fig. 1; all spectra obtained on a SPEX fluorimeter with 450 W Xe lamp).

observed for colloids [24], excess S^{2-} also strongly quenches the CdS emission but because S^{2-} diffuses only slowly into Nafion there is a significant time lag between S^{2-} addition and quenching.

Since one of our objectives is to understand the synergism of the CdS · ZnS/Nafion system for H_2 production, we exposed a CdS/Nafion film to 0.1 M $Zn(NO_3)_2$. The emission spectrum (fig. 2B) shows an increase in intensity of the 530 nm region relative to the 715 nm band which is consistent with the electrochemical observation [15] that Zn^{2+} acts to block or partially remove states that are associated with the 715 nm luminescence band.

No unambiguous assignment of the various luminescence peaks is possible based on these observations, but it is clear that the radiative properties of the various CdS/Nafion surface states can be significantly modified by contact with various solution species. These effects, plus the very strong effect of excitation intensity noted in fig. 1 clarifies why the reported luminescence properties of CdS colloids have been so varied

from different laboratories around the world [15,19,20,26].

3.2. Luminescence of ZnS

Absorption spectra of ZnS/Nafion films show an onset of absorption at about 330 nm which agrees well with the known bandgap of ZnS (3.7 eV).

Figure 3 shows the excitation intensity dependence of ZnS/Nafion emission. Low-power CW excitation yields an emission peaked at 450 nm. High-power-pulsed irradiation of the same sample produces luminescence with λ_{max} near 400 nm. The ZnS/Nafion system was much more spatially and spectrally homogeneous than the CdS/Nafion system. Thus while the general appearance of the ZnS/Nafion luminescence is less complicated than CdS/Nafion, the observation of an intensity-induced blue-shift in the emission is common to both systems. As will be discussed later, we believe this is the result of trap saturation at high photon flux.
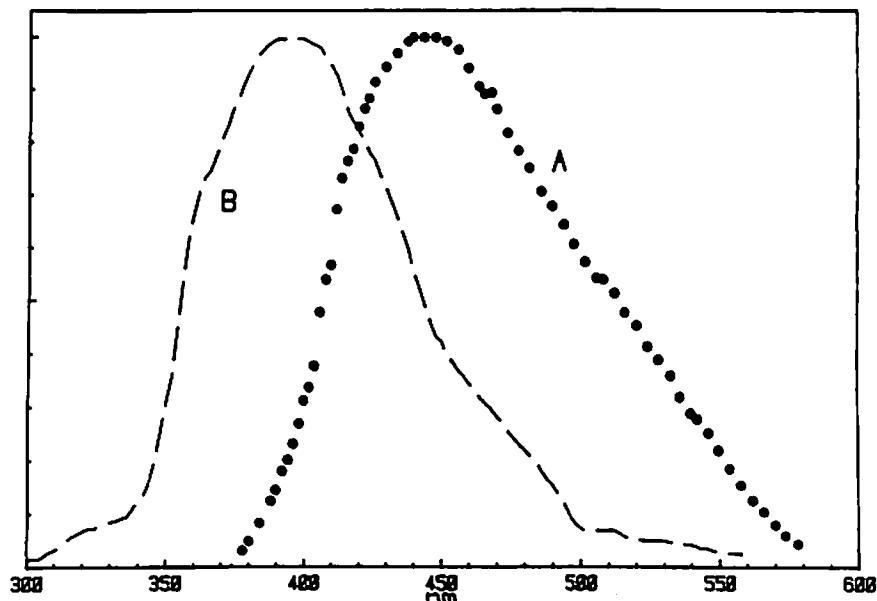
Fig. 3. ZnS/Nafion emission spectra at low power CW excitation (351 nm, curve A) and high power pulsed (266 nm, curve B) laser excitation (normalized as in fig. 1).

The lifetime of the ZnS/Nafion emission near 400 nm was ca. 10 ns. A 30 ns lifetime for 90% decay was previously reported for ZnS colloids in degassed solutions [25]. This yields a $1/e$ lifetime of ca. 13 ns, reasonable agreement with our value.

3.3. ZnS · CdS / Nafion

The absorption spectrum of a typical ZnS · CdS/Nafion film is presented in fig. 4. The CdS spectrum is clearly distinguishable from 520 to 350 nm, followed by the onset of ZnS absorption. The emission of these films induced by visible light excitation is identical to that presented in fig. 1. The absorption and luminescence properties of either ZnS/CdS/Nafion (CdS preparation followed by ZnS preparation) or CdS/ZnS/Nafion (the reverse order of preparation) are identical to ZnS · CdS/ Nafion. These absorption and luminescence properties indicate separate ZnS and CdS particles. CdS microcrystals, but not ZnS, were found by XRD (see above). To test for the presence of distinct ZnS microcrystals by attempting to observe ZnS emission the emission spectra were obtained using UV excitation (fig. 5). Similar

to the result for CdS/Nafion (fig. 1) the observed spectra were highly dependent on excitation intensity. CW laser excitation at 351 nm at different powers produced a series of spectra similar to those produced with CW laser excitation at 488 nm for CdS/Nafion. Increasing the power at 351 nm steadily enhances the intensity of the 520–620 portion of the spectrum, once again implying trap saturation. Pulsed laser excitation at 266 nm produces a single emission peak at 500 nm, blue-shifted by ca. 20–30 nm from the pulsed laser excitation at 355 nm of CdS/Nafion. This emission is in the bandgap region of CdS and it is reasonable to assign it to CdS bandgap emission. Since no emission feature is observed in the ZnS region (350–480 nm, see fig. 3) we conclude that ZnS excited states are quenched by the CdS. This result, and the observation that spectra from ZnS · CdS/Nafion and CdS/Nafion are identical, imply an intimate mixture of CdS and ZnS phases, such that efficient energy transfer from ZnS to CdS can occur.

Remarkable changes in the ZnS · CdS/Nafion emission spectrum occur upon extended irradiation. The emission spectrum of a ZnS · CdS/
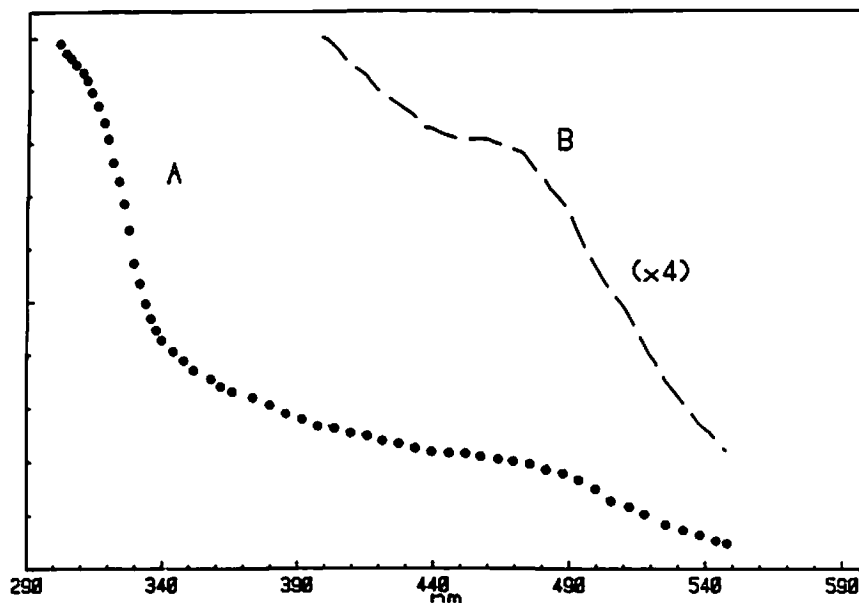
Fig. 4. Absorption spectrum of ZnS·CdS/Nafion film, showing two onsets of absorption. The maximum OD for curve A is ca. 0.73 relative to the scattering losses at long wavelengths.

Nafion film excited by a pulsed laser at 266 nm before and after extensive irradiation at 266 nm (15 min at 10 Hz) are shown in fig. 6A and B, respectively. The ratio of Zn : Cd was 10 : 1 in this sample to enhance the probability of observing emission from ZnS. The first spectrum contains
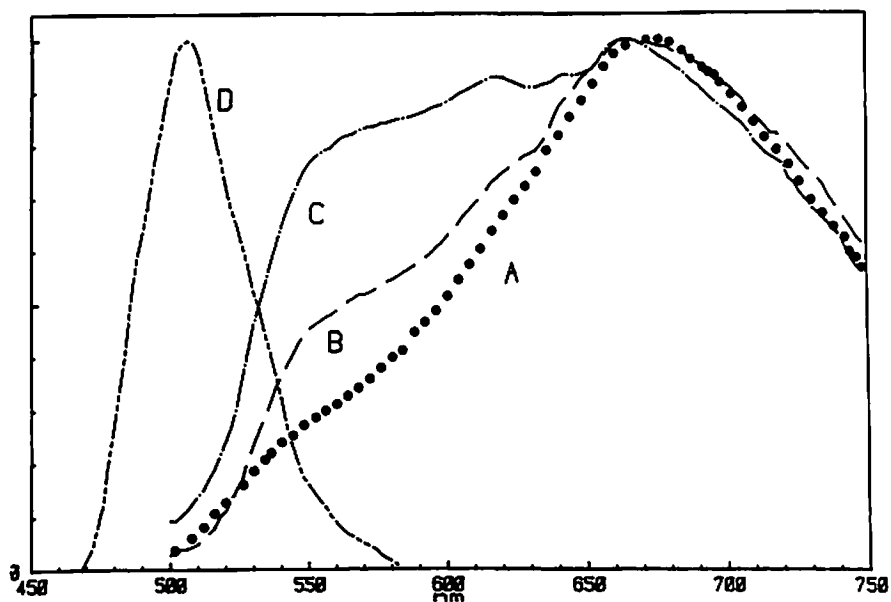

Fig. 5. Variation of ZnS·CdS/Nafion emission spectrum with increasing excitation intensity. Curves A–C employ 351 nm CW laser excitation, curve D utilizes 266 nm pulsed excitation. Curve A = 100 mW cm^{-2}, B = 1.0 W cm^{-2}, C = 2.0 W cm^{-2}, D = 10^5 W cm^{-1}. No emission was observed at wavelengths shorter than 470 nm (normalized as in fig. 1).
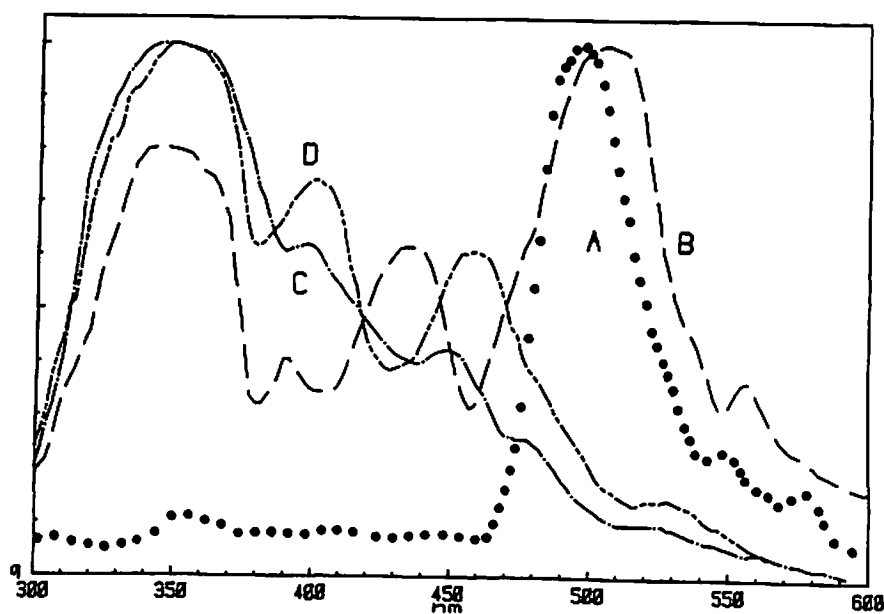
Fig. 6. Curve A, emission of ZnS·CdS/Nafion pre-photolysis; B, following 15 min pulsed laser (266 nm) photolysis, Zn : Cd = 10 : 1; C and D, emission of two different H_2 producing ZnS·CdS/Nafion films. Other than the UV illumination required to measure the spectra, these latter samples had only been exposed to visible irradiation. For all spectra the excitation is pulsed 266 nm laser radiation (normalized as in fig. 1).

only a hint of a ZnS component, while the second has significant intensity in the 300–480 nm region (which, however, is not identical to the pure ZnS spectrum presented in fig. 3). In figs. 6C and D two ZnS · CdS/Nafion films (1 : 1 mol ratio of Zn : Cd) are compared after extensive H_2 production. Despite nominally identical methods of preparation these two films were significantly different (an order of magnitude) in their H_2 production rates. Prior to UV laser irradiation to obtain emission spectra, these two films were exposed to visible light only for purposes of assisting the H_2 production reaction:

$$(ZnS \cdot CdS)^* + 2H^+ + 2S^{2-}$$

$$\rightarrow ZnS \cdot CdS + H_2 + S_2^{2-}. \qquad (1)$$
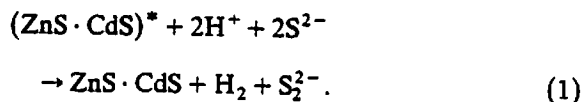
Pulsed laser excitation at 266 nm produced an emission primarily in the ZnS region (300–400 nm) but once again not identical to pure ZnS (fig. 3). The CdS features are either very weak or absent, but this was expected since exposure to S^{2-} quenches the emission of CdS. Additionally

Cd^0 is produced during H_2 production [14] which is also expected to quench CdS emission.

Exposure of ZnS · CdS/Nafion to UV (pulsed laser) or visible radiation (as for H_2 photogeneration) dramatically changes the luminescence of the ZnS in a way that suggests at least part of the ZnS phase has separated from contact with the CdS phase. While CdS is known to photodecompose in the absence of excess S^{2-} ion, prolonged irradiation of these films did not produce any detectable Cd^{2+} ion in the aqueous phase nor were the CdS powder X-ray scattering peaks diminished. On the other hand surface analysis of these films [14]

Table 1
Compilation of CdS trapping levels

Depth of trap relative to CB (eV)	Ref.
0.05, 0.14, 0.25, 0.41, 0.63, (0.83) [a]	[19(c, d)]
0.41, 0.63	[26]
0.76	[19(a)]
0.5, 0.9	[15]

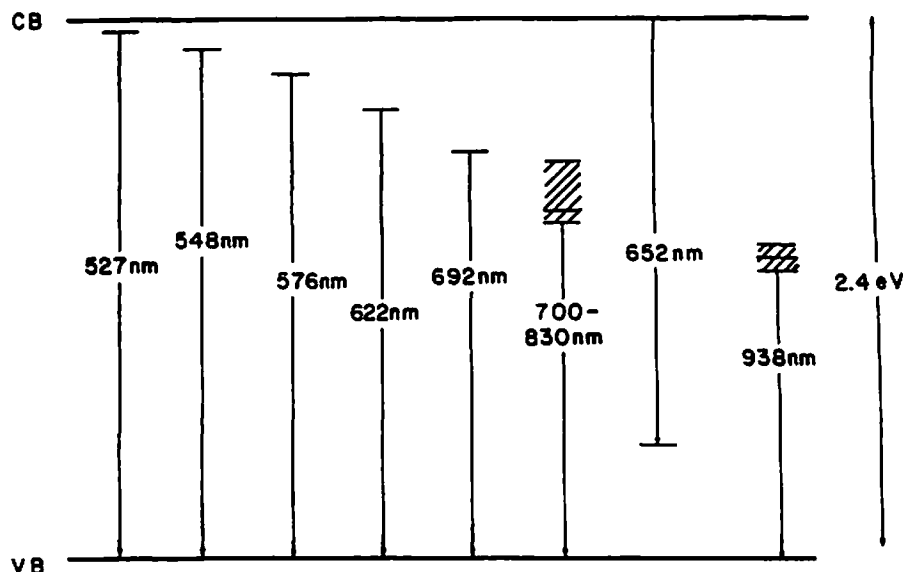[a] This state is considered to be created by a trapped electron.

Fig. 7. Proposed energy level diagram of CdS for CdS alone or ZnS·CdS. All downward arrows represent emissions observed in our experiments except for the 938 nm feature which is outside our range of spectral sensitivity.

demonstrated that visible light irradiation of ZnS · CdS/Nafion drastically decreases the Cd/Zn ratio (from 3 to 0.2) near the surface. Thus some form of "photoannealing" of these particles must occur, which results in ZnS phases that are not electronically coupled to the CdS phase. Also, since the emission spectrum is not identical to that of pure ZnS, it may be a perturbed ZnS phase. While an induction period for H_2 production is observed for these mixed colloid systems (typical of most other semiconductor particulate systems) we have no evidence that "photoannealing" contributes to this induction process.

Our spectroscopic and electrochemical measurements agree closely with the existing literature on CdS sub-bandgap states. These are summarized in table 1. The energy level diagram deduced from these data is presented in fig. 7. The transitions indicated correspond to emission features observed herein. While these assignments must be regarded as speculative, because of the complexity of the energy levels in this system, table 1 and fig. 7 demonstrate that the observed emission features can be put into good correspondence with past work on CdS sub-bandgap states.

4. Summary

As was stated in the Introduction, the present study was undertaken to elucidate the nature of the ZnS · CdS/Nafion system using fluorescence spectroscopy. We found that for the systems composed of a single-metal sulfide in Nafion the relative intensity of the various emission bands was intensity-dependent, suggesting the existence of a number of energy traps that can be saturated at higher excitation powers. In the initially prepared ZnS · CdS/Nafion system the fluorescence of the ZnS was quenched, leaving only CdS emission for all excitation wavelengths. This is what would be expected for an intimate mixture of these two sulfides. Upon extended visible irradiation the ZnS fluorescence developed, implying the creation of an independent ZnS phase. We do not know if this photoannealing process is necessary for the success of this system in assisting the photodecomposition of H_2S.

Finally, the emission spectra reported herein and elsewhere in combination with our electrochemical measurements [15] permits an energy level scheme to be derived that includes a number

of subband states. These are summarized in table 1 and fig. 7. It does not appear that ZnS induces any new subband states in CdS that provide an explanation for the efficiency of the ZnS · CdS/ Nafion system in reaction (1). We have argued that ZnS blocks CdS surface states that are detrimental to the efficiency of CdS as a photocatalyst.

Acknowledgement

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