

Semiconductor electrodes. 58. The effect of temperature on photo- and electroluminescence in aluminum-doped self-activated zinc sulfide crystals

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and third states, the nonbonding orbital on the NO₂ oxygen atoms lies in the NO₂ plane and, in the fifth state, the nonbonding orbital is perpendicular to the NO₂ plane. The fourth state is an $n \rightarrow p\sigma^*$ excitation on the HO₂ fragment. Our results suggest the second and third states, for which excitation energies of 5.61 and 6.48 eV have been obtained, are responsible for the observed UV absorption spectrum. Because these states involve π^* excitation on the NO₂ fragment, we speculated photolysis results in removal of an oxygen atom or molecule from the NO₂ end of the HO₂NO₂ molecule.

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Semiconductor Electrodes. 58. The Effect of Temperature on Photo- and Electroluminescence in Al-Doped Self-Activated ZnS Crystals

Fu-Ren F. Fan and Allen J. Bard*

Department of Chemistry, The University of Texas, Austin, Texas 78712 (Received: September 14, 1984)

The effect of temperature on the electroluminescence (EL) (in a persulfate-butyronitrile solution) and the time-resolved photoluminescence (PL) of Al-doped self-activated ZnS single crystals has been studied. The PL shows a blue emission with a short-lived exponential-decay component (lifetime, ~ 3.7 ns) followed by a slow-decay component described by a t^{-1} relationship. A model for the PL based on an excited activator generated via electron tunneling between two localized levels (donor and acceptor) is proposed. This model is also consistent with the effect of temperature (T) on the EL behavior. The half-widths of the EL spectra are proportional to $T^{1/2}$, indicating that the transition responsible for the luminescence takes place in simple centers. The EL efficiency decreases exponentially with increasing T , with activation energy of 0.20 eV for the thermal quenching of EL. This value agrees well with the reported thermal ionization energy of a donor level associated with Al in ZnS.

Introduction

Luminescence techniques have recently been employed actively as probes to study photoelectrochemical systems.¹⁻⁹ The luminescence is usually characterized by a short-lived component, which arises from localized electronic excitation at the luminescent centers and usually decays exponentially with time (t). This is followed by a long-lived component, which may show either an exponential decay, or one that conforms to a power law (i.e., luminescence intensity (I_L) is proportional to t^{-m}).¹⁰ In addition to phosphorescence or delayed fluorescence caused by triplet states, several mechanisms have been proposed to explain the long-lived luminescence components. When the rate-determining step of the overall luminescence process involves the diffusion of the charge carriers or excitons, the luminescence intensity is expected to decay as $I_L \propto t^{-m}$ with $m \neq 1$.¹¹ When the rate-determining step involves the thermal activation of electrons from uniformly dis-

tributed (in energy) trap levels, an $I_L \propto t^{-1}$ decay law is observed.¹²

We have reinvestigated the origin of the power law decay of luminescence and report here that the blue emission from an aluminum-doped self-activated ZnS crystal has a short-lived exponential-decay component with a lifetime (τ) of about 3.7 ns, followed by a slow-decay component over a time region longer than 1 μ s; the latter shows decay kinetics described by a t^{-m} relationship, with $m \approx 1.0$. The slope of the (I_L^{-1} vs. t) plot decreases with increasing excitation light intensity.

The EL of a ZnS electrode during reduction of S₂O₈²⁻ in aqueous solutions (arising from hole injection by the intermediate SO₄^{-•}) has previously been described.^{5d} We report here extensions of the studies with a butyronitrile solution of S₂O₈²⁻, which allows investigations over an extended range of temperature. We show that the half-width of the EL spectrum increases remarkably with an increase in temperature, whereas the efficiency of EL increases dramatically with a decrease in temperature; the absolute EL intensity is less dependent on temperature. Those results are not consistent with a model based on the thermal activation of electrons from uniformly distributed trap levels or the other models mentioned above. In this report, we suggest a phenomenological model based on electron tunneling which has long been applied to explain the decay kinetics of ground-state donor/acceptor pair emission in semiconductors¹³ and recombination luminescence in glasses.¹⁴

Experimental Section

Al-doped (100 ppm) ZnS single crystals (Eagle-Picher Industries, Inc., Cincinnati, OH) were cut into slices and were heated

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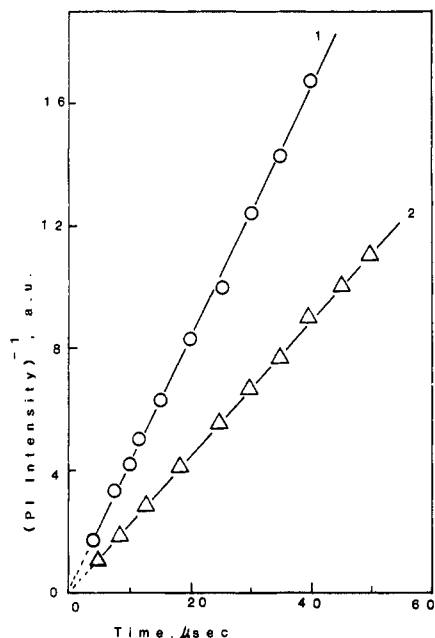


Figure 1. Photoluminescence decay curves at 460 nm of Al-doped self-activated ZnS single crystal after laser pulse (YAG, 266 nm, 1-ns duration) excitation. Line 1 has one-half of excitation intensity of line 2.

in molten zinc (99.9999%, Alfa Products, Danvers, MA) at 900 °C for 15–20 h. The resulting crystals, with low resistivities (10–100 ohm cm), were used in both photoluminescence (PL) and electroluminescence (EL) experiments. The crystals were polished with carborundum (1- μm grit size) and alumina (0.5- μm particle size). In EL experiments, the crystals were provided with ohmic contacts, mounted, and etched by the same procedures as reported previously.^{5d}

Butyronitrile (BN, reagent grade, Alfa Products) was purified by procedures reported previously.¹⁵ Tetra-*n*-butylammonium tetrafluoroborate (TBABF₄, polarographic grade, Southwestern Analytical Chemicals, Austin, TX) was recrystallized twice from methanol and dried in vacuo for 24 h. Neutral alumina (ROC/RIC Chemical Co.) was activated in vacuo at 300 °C for 24 h. Tetra-*n*-butylammonium persulfate was prepared by mixing tetra-*n*-butylammonium hydroxide (Southwestern Analytical Chemicals) and ammonium persulfate (reagent grade, Matheson Coleman and Bell) in a 2:1 mol ratio in MeOH. The methanolic solution was dried on a rotaevaporator. The solid was then recrystallized from methylene chloride. The purified BN was treated with activated alumina and transferred to the electrochemical cell under nitrogen. The cell used for electrochemical and EL studies was a three-electrode type of conventional design, which can be fitted to a Dewar flask for low-temperature experiments. The apparatus and techniques employed in the EL studies are the same as those previously described.^{5d}

The decay curve of the slow photoluminescence component was monitored with a photomultiplier tube (PMT, Hamamatsu R928) equipped with a 460-nm band-pass filter. Signals from the PMT were amplified by a current-to-voltage converter and displayed on a Tektronix 535A oscilloscope. The response time of the whole detecting system was less than 1 μs . Luminescence excitation in this experiment was accomplished with a YAG (266 nm) pulse laser of duration about 1 ns.

The fast-decay component of the photoluminescence was monitored with a single-photon-counting system (PRA 1770 photon counter) with a response time of about 1 ns.

Results

Decay of Photoluminescence. The photoluminescence decay of Al-doped self-activated ZnS crystals at room temperature in air follows an exponential decay law only over a very short time

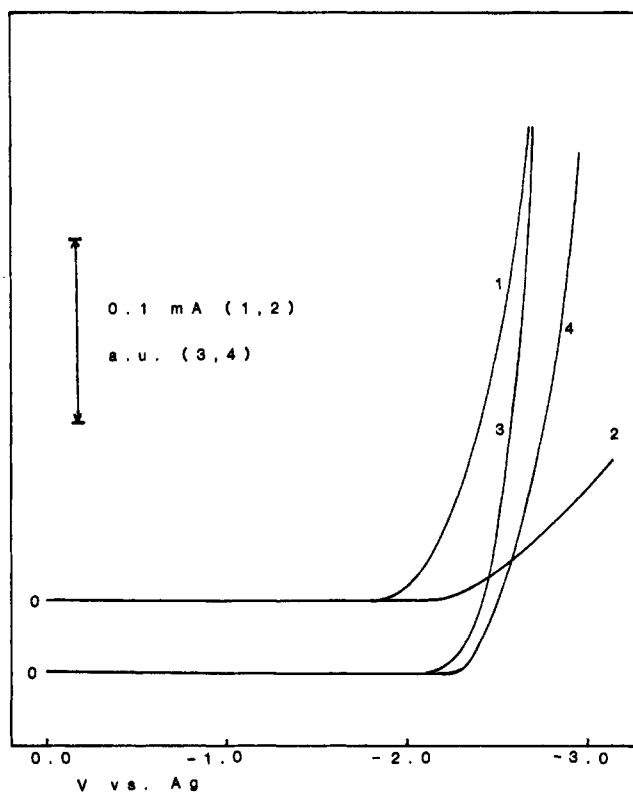


Figure 2. Temperature effect on current-potential and EL intensity-potential behavior of ZnS (Al) in butyronitrile containing 0.2 M of tetrabutylammonium persulfate. Current: curves 1 (23 °C) and 2 (-66 °C). EL: curves 3 (23 °C) and 4 (-66 °C). Scan rate 10 mV/s.

range (about 10 ns). The lifetime of this fast-decay component was about 3.7 ns, which is close to the value for an allowed transition of unit oscillator strength. After this exponential decay, the luminescence decay follows an approximately t^{-1} decay law; this is demonstrated in Figure 1 where a plot of the reciprocal of the photoluminescence intensity (excited at 266 nm at different excitation intensity) vs. time is linear with zero intercept. Note that doubling the excitation intensity decreases the slope of the (I_{PL}^{-1} vs. t) plot by about one-half.

Temperature Effect on the Efficiency of Electroluminescence. Electroluminescence arises when ZnS electrodes immersed in BN containing 0.3 M tetra-*n*-butylammonium persulfate are swept to negative potentials (Figure 2). As shown in Figure 2, both the EL intensity-potential ($I_{\text{EL}}-V$) and, especially, the current-potential ($i-V$) curves were strongly temperature dependent. At low temperature, e.g., at -66 °C, the current increase was very sluggish with respect to the change in potential, whereas the EL response was only slightly less steep than that at higher temperature, e.g., at room temperature. Since the EL efficiency, ϕ , defined as photons emitted per electron passed, is strongly dependent on current density,^{5d} to demonstrate the temperature effect on ϕ , we normalized I_{EL} to a constant current density, 1 mA/cm². The result is shown in Figure 3. Note that ϕ_{EL} increases exponentially with a decrease in temperature and seems to level off at temperatures below about -70 °C. ϕ at 1 mA/cm² is increased a factor of about 50 by decreasing the temperature from room temperature to about -80 °C. For convenience in the following discussion, we also plot the logarithm of ϕ_{EL} as a function of $1/T$ (Figure 3).

Temperature Effect on the Shape of the Electroluminescence Spectrum. EL spectra at several temperatures are shown in Figure 4. In these experiments, the EL spectra were recorded at nearly the same intensity by adjustment of the current. The peak position of the EL spectrum was essentially independent of temperature over the temperature range studied (-85 to 25 °C). The width of the EL spectrum increased significantly with increasing temperature. The width at half-height changed linearly with $T^{1/2}$ at the lower end of the temperature range studied (see Figure 5).

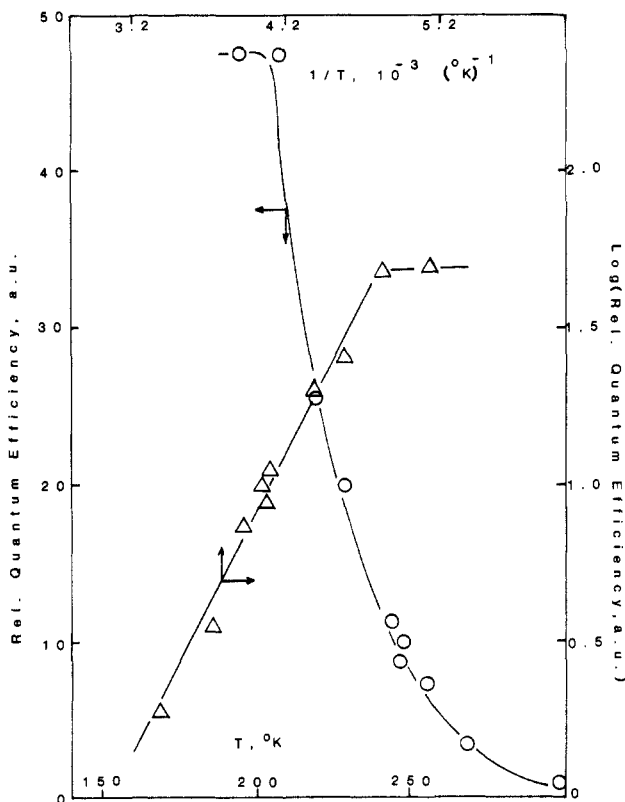


Figure 3. Temperature effect on the EL efficiency of ZnS (Al) in BN containing 0.2 M $(\text{TBA})_2\text{-S}_2\text{O}_8$.

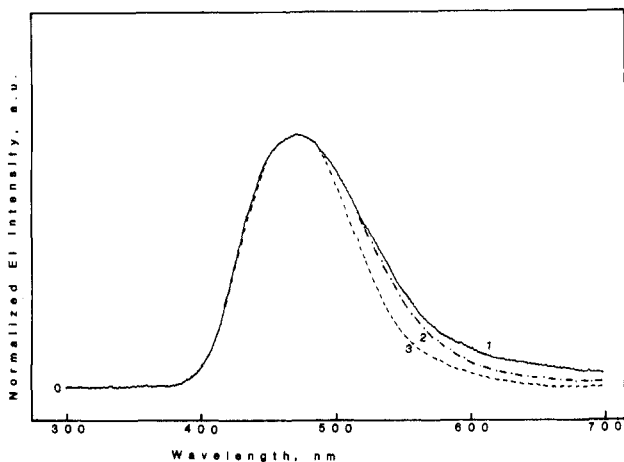


Figure 4. Temperature effect on the EL spectrum of ZnS (Al) in BN containing 0.2 M $(\text{TBA})_2\text{-S}_2\text{O}_8$. Curve 1: 10 °C; curve 2: -30 °C; curve 3: -85 °C.

Discussion

Decay of Photoluminescence. Several mechanisms can be proposed to explain the observed $I_L \propto t^{-1}$ behavior for the luminescence decay: thermal activation of electrons,¹² second-order recombination, and electron tunneling.¹⁴ In the first model, the sub-band-gap luminescence is assumed to be caused by an electronic transition between an energy band and a localized activator level. The rate-determining step of the overall process involves the thermal activation of electrons (or holes) from donors (or acceptors) that are uniformly distributed (in energy). Our results for the temperature effect on the electroluminescence cannot be explained by this model, since it predicts a higher efficiency at higher temperature. However, thermal activation of electrons from donors might be responsible for nonradiative recombination (considered in the following discussion). The $I_L \propto t^{-1}$ decay law can also be derived by assuming that there is a predominant recombination. The former is assumed to be either a nonradiative process or a radiative process which emits photons of a different

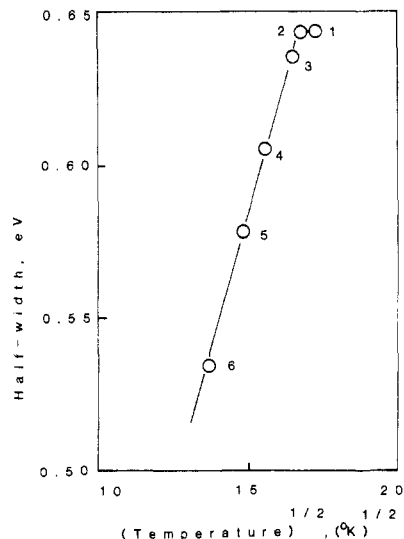
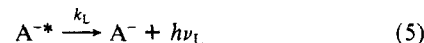
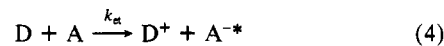
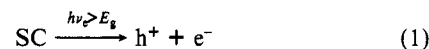


Figure 5. Half-width of the EL spectrum of ZnS (Al) in BN containing 0.2 M $(\text{TBA})_2\text{-S}_2\text{O}_8$ as a function of temperature. 1: 25 °C; 2: 10 °C; 3: -2 °C; 4: -30 °C; 5: -55 °C; 6: -85 °C.

energy. This process would be more important at high intensities of excitation light and at the beginning of a decay curve, where a higher concentration of excited states is available. Thus, one would expect from this model that the luminescence intensity after short-pulse excitation should follow a power decay law at the beginning, followed by an exponential decay law, when first-order processes predominate. This is not observed, however.

The model which can explain the experimental results self-consistently is based on electron tunneling between two localized states (donor and acceptor) to generate an excited state which undergoes radiative recombination along with the thermal deactivation of the excited states by release of electrons from donors to the conduction band or to other nonradiative recombination centers. The reaction scheme can be described as follows:



in which SC is the semiconductor, h^+ and e^- are holes and electrons, D and A are electron donor and acceptor centers in the ZnS; D^+ and A^- are their higher and lower oxidation states, respectively; E_g is the band gap of the semiconductor; A^{-*} is the excited state of A^- ; h is Planck's constant, ν_e and ν_L are the frequencies of the excitation light and the luminescence, and k_{et} and k_L are the rate constants for electron transfer and luminescence, respectively. According to the tunneling model, process 4 is assumed to be the rate-determining step for the overall process. This model is analogous to one used in solution-phase electrogenerated chemiluminescence (ecl).¹⁶ After production of electrons in the conduction band and holes in the valence band (eq 1), a "reduced" state of the ionized donor, D, and an "oxidized" state of the acceptor, A, are formed (eq 2 and 3). Representation of the ionized states as D^+ and A^- is arbitrary. The electron-transfer reaction, eq 4, is sufficiently energetic to generate the excited state of the acceptor species, written A^{-*} (eq 4).

The specific rate k_{et} depends on the distance, R , between D and A and is usually expressed as¹⁷

$$k_{et}(R) = k_0 \exp(-2R/a) \quad (6)$$

where a is the effective radius for overlap of the wave function of D with that of A and k_0 is proportional to the fraction of the D-A pairs in a tunneling state. Let $P(R)$ be the distribution function of D around an A at time, t ; $\bar{P}(R)$ be the total donor species (D^+ and D) around an acceptor species (A or A^-); k_ϕ , the proportionality constant for the generation of the D-A pair; I , the excitation intensity and let us assume that the generation rate of the D-A pair is proportional to I . The rate equation for $P(R)$ during excitation is given by

$$dP(R)/dt = k_\phi I [\bar{P}(R) - P(R)] - k_L k_{et} P(R) \quad (7)$$

After integration with $P(R) = 0$ at $t = 0$

$$P(R) = C \bar{P}(R) [1 - \exp(-C't)] \quad (8)$$

where

$$C = k_\phi I / (k_\phi I + k_L k_{et}) \quad (9)$$

$$C' = k_\phi I + k_L k_{et} \quad (10)$$

Since the excitation duration, δt , is short (~ 1 ns) compared to the time scale of the slow component of the luminescence (> 10 μ s), we can assume that $C' \delta t \approx 0$. Thus, the distribution function of D around an acceptor A right after the laser pulse is

$$P_0(R) = k_\phi I \bar{P}(R) \delta t \quad (11)$$

After excitation, $I = 0$, and the rate equation for $P(R)$ is given by

$$dP(R)/dt = -k_L k_{et} P(R) \quad (12)$$

Integrating $P(R)$ with respect to t , we obtain

$$P(R) = P_0(R) \exp(-k_L k_{et} t) \quad (13)$$

Equations 11 and 13 yield

$$P(R) = k_\phi I \bar{P}(R) \delta t \exp(-k_L k_{et} t) \quad (14)$$

The total luminescence intensity as a function of t is obtained by integrating $P(R) k_{et} k_L$ over all R . Assuming that $\bar{P}(R)$ is a slowly varying function of R as compared to $\exp(-k_L k_{et} t)$, we can replace it by its mean value, \bar{R}_0 ,¹⁸ thus

$$I_L = \int_0^\infty \bar{P}_0 k_\phi I \delta t k_{et} k_L \exp(-k_L k_{et} t) dR \quad (15)$$

or, with eq 6 and $R' = k_L k_{et} t$

$$I_L = (a/2t) k_\phi I \bar{P}_0 \delta t \int_0^{k_L k_{et} t} \exp(-R') dR' \quad (15a)$$

After integration

$$I_L = (a/2t) k_\phi I \bar{P}_0 \delta t [1 - \exp(-k_0 k_L t)] \quad (16)$$

Since k_0 can be of the order of 10^{15} s^{-1} ,^{17a} and if k_L is not too small, the times of interest $k_0 k_L t \gg 1$ and eq 16 reduces to

$$I_L = (a/2t) k_\phi I \bar{P}_0 \delta t \quad (17)$$

As suggested by this equation, the luminescence should follow an $I_L \propto 1/t$ decay law with the slope proportional to the excitation light intensity and the intercepts close to the origin, as shown in Figure 1.

The Temperature Effect on Electroluminescence. As suggested in the reaction scheme described above (eq 2), an electron trapped at a donor site, D^+ , can also be thermally activated back to the conduction band; from here nonradiative processes could take place. Thus, the EL efficiency, ϕ_{EL} , is expected to decrease with increasing temperature, as shown in Figure 2. We can also calculate the thermal ionization energy, E_D , of this donor state. The probability, P_T , of an electron escaping from a donor of depth

E_D at temperature T is of the form¹⁹

$$P_T = s \exp(-E_D/kT) \quad (18)$$

in which s is a constant which varies very slightly with temperature and k is Boltzmann's constant. ϕ can be expressed as

$$\phi_{EL} = P_L / (P_L + P_T) \quad (19)$$

where P_L is the probability that an electron in D takes part in the luminescent process and is a function of k_{et} and k_L , which are both assumed to be temperature insensitive.

Since $\phi_{EL} \ll 1$ over the temperature range studied, this implies that $P_T \gg P_L$, so eq 19 reduces to

$$\phi_{EL} = P_L / P_T \quad (20)$$

Combining eq 18 and 20 yields

$$\phi_{EL} = (P_L/s) \exp(E_D/kT)$$

or

$$\log(\phi_{EL}) = \log(P_L/s) + E_D/2.303kT \quad (21)$$

As indicated by eq 21, the plot of the logarithm of ϕ_{EL} vs. $1/T$ will give a straight line with the slope containing information about E_D . Such a plot for Al-doped ZnS is shown in Figure 3. From its slope, we obtain $E_D = 0.20$ eV.

The thermal quenching of the EL efficiency might also be caused by ionization or other nonradiative processes of the excited states of activator, A^* . The same equations as eq 18-21 are applicable to this case with E_D replaced by the activation energy for thermal quenching of A^* , E_Q . We are unable to differentiate these two mechanisms simply based on the results reported here. However, we can compare the E_D value determined here with the thermal ionization energy, E_{th} , of Al in ZnS, as obtained by thermally stimulated luminescence or conductivity.^{20a,b} Klasens and Hoogenstraten reported $E_{th} = 0.25$ eV, while Shionoya et al. reported $E_{th} = 0.074 \pm 0.02$ eV (obtained by UV-induced infrared absorption or by infrared photoconductivity techniques).^{20c}

Note also that the temperature dependence of the half-width, W_{EL} , of the EL spectrum shown in Figure 4 can be explained by the simplified configurational coordinate model used for the transition in simple centers,²¹ which yield the expression

$$W_{EL} = W_0 [\coth(h\nu/2kT)]^{1/2} \quad (22)$$

in which W_0 is a constant involving force constants of the ground state and the excited state, the displacement of the minimum of the excited state from that of the ground state, and the vibrational frequency, ν , of the excited state. At high temperature, eq 22 reduces to

$$W_{EL} = W_0 (2kT/h\nu)^{1/2} \quad (23)$$

Our results shown in Figure 4 agree fairly well with this relation. This suggests that the blue EL emission from Al-doped self-activated ZnS occurs between two localized levels rather than between an energy band and a localized level.

In conclusion, our results on the blue emission from Al-doped self-activated ZnS are similar to those found with Cl-doped self-activated ZnS,²² which originates from the excited state (A^*) of an acceptor whose energy levels are located within the forbidden gap of ZnS. The slow-decay component of the luminescence is associated with electron tunneling from a shallow donor level to

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an empty acceptor level to generate an excited state (A^{-*}). The thermal quenching of the EL efficiency is probably caused by the thermal activation of electrons from the donor states to the conduction band.

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Incorporation of a Recyclable Surface-Active Electron Donor in Synthetic Vesicles: Application to Photosensitized Hydrogen Formation by Vesicle-Stabilized Rh-Coated Colloidal CdS Particles

Rafael Rafaeloff,¹ Yves-M. Tricot, Faruk Nome,² Pietro Tundo,³ and Janos H. Fendler*

Department of Chemistry and Institute of Colloid and Surface Science, Clarkson University, Potsdam, New York 13676 (Received: October 4, 1984)

Colloidal rhodium-coated CdS particles were in situ generated in thiol-functionalized surfactant/dioctadecyldimethylammonium chloride (DODAC) mixed vesicles. Upon visible light irradiation, the thiol-functionalized surfactant acted as a recyclable electron donor and promoted hydrogen generation. This vesicle-integrated electron donor could be chemically regenerated to resume hydrogen production at the same rate as during its first oxidation. This is a new concept in surfactant stabilized colloidal semiconductor systems, making possible a cyclic process of hydrogen generation.

Introduction

Artificial photosynthesis continues to be an area of intense interest.⁴⁻⁷ One approach involves the utilization of catalyst-coated colloidal semiconductors in photosensitized relayless water reduction.⁸⁻¹⁹ Light absorption (i.e., band-gap excitation) leads to the promotion of an electron from the valence to the conduction band and, hence, to the creation of an electron-hole pair in the semiconductor. Intercepting electron-hole recombinations by appropriate electron donors results, in turn, in water reduction

at the catalyst-water interface. The extremely short electron-hole lifetime (<1 ns)^{20,21} requires the presence of uniform and small (ca. 40 Å diameter) semiconductor particles and high concentrations of electron and/or hole transfer agents in close proximity. This requirement cannot be easily met in homogeneous solutions. It has been difficult to maintain small uniform colloidal semiconductors in homogeneous solutions even in the presence of stabilizers.

Recently, we have demonstrated the feasibility of in situ generation of small (ca. 40 Å diameter) uniform catalyst-coated colloidal CdS particles in ca. 1000-Å-diameter dihexadecyl phosphate (DHP) and dioctadecyldimethylammonium chloride (DODAC) surfactant vesicles.²²⁻²⁴ Surfactant-vesicle-incorporated, Rh-coated, colloidal CdS particles remained stable for several months and have sensitized water photoreduction by a membrane permeable electron donor, thiophenol (PhSH). Accumulation of the oxidized electron donor, PhSSPh, in the vesicle bilayer has precluded, however, the realization of the full potential of vesicle entrapped colloidal semiconductors in artificial photosynthesis.

A new approach is reported in the present work. A surface-active reusable electron donor, $(n-C_{18}H_{37})_2N^+(CH_3)-CH_2CH_2SH, Br^-$ (RSH), has been incorporated into DODAC vesicles. Band-gap excitation of Rh-coated CdS, in DODAC-RSH vesicles, resulted in hydrogen formation at the expense of RSH oxidation to the disulfide RSSR. Reduction by $NaBH_4$ of the disulfide lead to the regeneration of the active electron donor, RSH, which could be reused for additional colloidal semiconductor photosensitized water splitting.

(1) On leave from Israel Atomic Energy Commission, Soreq Nuclear Research Center, Yavne, 70600, Israel.

(2) Permanent Address: Depto. de Quimica, Universidade Federal de Santa Catarina, 88000 Florianopolis, Santa Catarina, Brazil.

(3) Permanent Address: Istituto di Chimica Organica della Universita de Torino, Via Bidone 36, 10125 Torino, Italy.

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