EFFECTS OF TEMPERATURE ON EXCITED-STATE DESCRIPTIONS OF LUMINESCENT MATERIALS

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by

Arthur B. Ellis* and Bradley R. Karas

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Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

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To whom all correspondence should be addressed.
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Arthur B. Ellis and Bradley R. Karas

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Office of Naval Research/Chemistry Program
Arlington, Virginia 22217

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Photoelectrochemistry; luminescence; doped cadmium sulfide electrodes

The effect of temperature on excited-state deactivation processes in a single-crystal, n-type, 100 ppm CdS:Te-based photoelectrochemical cell (PEC) employing aqueous polychalcogenide electrolytes is discussed. While serving as electrodes these materials emit (λ<sub>max</sub> ~600 nm). Photocurrent (quantum yield φ<sub>p</sub>) from ultraband gap (≥2.4 eV; X ≤ 500 nm) 501.7 nm excitation increases modestly by ≤20% between 20° and 100°C; photocurrent from band
gap edge 514.5 nm excitation increases by about an order of magnitude, reaching 50-100% of the room temperature 501.7 nm value. Highlighting the competitive nature of emission and photocurrent as excited-state decay processes, luminescence (quantum yield \( \phi_r \)) declines over the same temperature regime by factors of between 10 and 30. At most, modest red shifts of \( \lambda_{max} \) (<10 nm) are observed in the spectral distribution of emission with temperature. These effects are discussed in terms of optical penetration depth, band bending, and the known red shift of the CdS absorption edge with temperature. Correlations involving \( \phi_x \) and \( \phi_r \) suggested by the data are discussed.
The need for alternate energy sources has led to the rapid development of photoelectrochemical cells (PECs). A PEC consisting of an n-type semiconductor, a counterelectrode, and a suitably chosen electrolyte can convert optical energy directly into chemical fuels and/or electricity (1,2,3,4). We recently reported that tellurium-doped CdS (CdS:Te) mimics undoped CdS in its ability to sustain the conversion of monochromatic ultraband gap light (\(\lambda \leq 500 \text{ nm} \)) into electricity at \(\approx 7\%\) efficiency in PECs employing aqueous polychalcogenide electrolytes (6,7,8,9). A novel feature of the CdS:Te photoanodes is that they emit \(\lambda_{\text{max}} \approx 600 \text{ nm}\) for 100 ppm CdS:Te with \(\approx 0.1\%\) efficiency while effecting the oxidation of polychalcogenide species.

Luminescence results from the introduction of intraband gap states by the substitution of Te for S in the CdS lattice. Because of its lower electron affinity, Te sites trap holes which can then coulombically bind an electron in or near the conduction band to form an exciton. Subsequent radiative collapse of this exciton leads to emission (10,11,12,13). In the context of the PEC, emission thus serves as a probe of electron-hole (\(e^- - h^+\)) pair recombination which competes with \(e^- - h^+\) pair separation leading to photocurrent. Except for intensity, the emitted spectral distribution is found to be independent of the presence and/or composition of polychalcogenide electrolyte, excitation wavelength (Ar ion laser lines, 457.9-514.5 nm) and intensity (\(\leq 30 \text{ mW/cm}^2\)), and applied potential (\(-0.3\text{ V vs. SCE to open circuit}) (6,7,8,9).

Optical penetration depth plays a significant role in the PEC properties we observe. The absorptivity of 100 ppm CdS:Te for 514.5 nm light is \(\approx 10^3 \text{ cm}^{-1}\) (5,10,11,12,13). Since the depletion region in which \(e^- - h^+\) pairs are efficiently separated by band bending to yield photocurrent is \(\approx 10^{-4} - 10^{-5} \text{ cm}\) thick (14), a significant fraction of 514.5 nm light is absorbed beyond this region. We therefore expect and observe greater emission intensity and smaller photocurrent with 514.5 nm excitation than with ultraband gap wavelengths (8) for which the CdS:Te...
absorptivity is \(\approx 10^4\) to \(10^5\) cm\(^{-1}\) (5, 10, 11, 12, 13). Additionally, whereas there is little potential dependence of emission intensity with 514.5 nm excitation, a strong dependence is observed with ultraband gap irradiation: in passing from \(-0.3\) V vs. SCE to open circuit in aqueous polychalcogenide electrolytes, increases in emission intensity of \(\approx 15\) to \(1400\)% obtain (6, 7, 8, 9). This is in accord with the premise that variations of potential correspond to alterations in the degree of band bending (14).

Temperature is another PEC parameter which can potentially modify the efficiencies of photocurrent and luminescence. Among the materials whose temperature dependent PEC properties have been studied are SnO\(_2\) (15), TiO\(_2\) (16) and CuInS\(_2\) (17). Undoped CdS has a known optical band gap temperature dependence of \(-5.2\times10^{-4}\) eV/°K between 90 and 400 K (18). Owing to the general similarity of CdS:Te to CdS, we anticipated a comparable red shift in the onset of absorption. In this paper we summarize the results of temperature studies on CdS:Te-based PECs employing aqueous polyselenide (9) and sulfide electrolytes.

**Experimental**

Single-crystal plates of vapor-grown, 100 ppm CdS:Te were purchased from Cleveland Crystals, Inc., Cleveland, Ohio. Emissive spectral features were consistent with those previously reported for CdS:Te (6-13) and confirmed (Roessler's correlation, (12)) that the Te concentration was \(\leq 100\) ppm. The \(\approx 5\times5\times1\) mm samples had resistivities of \(\approx 2\) ohm·cm (four point probe method) and were oriented with the 5x5 mm face perpendicular to the c-axis. Samples were first etched with 1:10 (v/v) Br\(_2\)/MeOH and then placed in an ultrasonic cleaner to remove residual Br\(_2\). The electrolyte was either sulfide, 1M OH\(^-\)/1M S\(_2^2^-\), or polyselenide, typically 5M OH\(^-\)/0.1M Se\(_2^2^-\)/0.001M Se\(_2^2\)\(^2^-\); short optical pathlengths (\(\leq 0.1\) cm) were used to make the latter essentially transparent for \(\lambda > 500\) nm. Electrode and electrolyte preparation as well as electrochemical and optical instrumentation employed have been described previously (8). Electrolytes were magnetically stirred and blanketed under N\(_2\) during use.

Assembling the PEC inside the sample compartment of a spectrophotofluorometer permitted measurement of emission spectral data (200-800 nm; \(\approx 5\) nm bandwidth). Front-surface emissive properties were recorded by inclining the photoelectrode at \(\approx 45^\circ\) to both the incident Coherent Radiation CR-12 Ar ion laser beam (501.7 or 514.5 nm) and the emission detection optics. In all experiments the \(\approx 3\) mm dia. beam was 10X expanded and masked to fill the electrode surface; incident intensities were generally \(\approx 10\) mW/cm\(^2\). Temperature of the PEC was adjusted as previously described (9).
Results and Discussion

Emissive and Photocurrent Properties. Three characteristics of emissive PECs which might display thermal effects are the emissive spectral distribution, emission intensity, and photocurrent. We observed the emission spectrum of 100 ppm CdS:Te in both polyselenide and sulfide electrolytes from 20-100°C. Low-resolution spectra of the various samples revealed red-shifts of $\lambda_{\text{max}}$ with increasing temperature of at most 5-10 nm; the displacement of $\lambda_{\text{max}}$ for many samples, however, was within the bandwidth of the spectrometer (~5 nm). These results are in the range of an extrapolation of Roessler's data (12) from which we would predict a red-shift in $\lambda_{\text{max}}$ of ~7-11 nm between 20 and 100°C. Parallel shifts have also been reported for CdS:Te absorption and excitation spectra over subambient temperature ranges (13). These spectra incorporate a low-energy band which distinguishes CdS:Te from CdS and, in fact, masks the exact position of the CdS:Te band gap (7,8,11,12,13). Several other features of the CdS:Te emission spectrum are particularly relevant in the context of PEC experiments. For a given temperature the spectral distribution is independent of whether 501.7 or 514.5 nm excitation is used and of electrode potential between +0.7 V vs. Ag (pseudoreference electrode, PRE) and the onset of cathodic current. Such an insensitivity to potential indicates that the energies of the intraband gap Te states are affected by potential in the same manner as the conduction and valence band energies.

A very profound temperature effect was observed for the emission intensity. Figure 1 presents an emission-temperature profile at open circuit in sulfide electrolyte; the relative invariance of the sample's spectral distribution with temperature allowed us to monitor emission intensity at the band maximum. Emission intensity was matched for 501.7 and 514.5 nm excitation at 20°C using ~17 times as much 501.7 nm intensity. Over the 20-100°C excursion emission intensity is seen to drop by factors of ~8 and 30 for 501.7 and 514.5 nm excitation, respectively. These factors are consistent with the 10- to 20-fold decline observed in polyselenide electrolyte; in those experiments there also appeared to be little potential dependence of the results (9). Similar thermal quenching data has been reported for dry CdS:Te samples irradiated with UV light (10,12,13), electron beams (11), and a particles (19). The temperature dependence of the decline in emission intensity has been linked to the ionization energy of the Te-bound hole, ~0.2 eV (10,11,12,13,19).

Given the inherently competitive nature of emission and photocurrent, it should not be surprising that photocurrent was generally observed to increase with temperature. Figure 2 is a photocurrent-temperature profile obtained at +0.7 V vs. Ag (PRE) in sulfide electrolyte; the light intensity and sulfide concentration employed ensured that photocurrents were limited by excitation rate and not by mass transport, i.e., photocurrents
were not saturated with respect to light intensity and were not
affected by stirring. At 20°C for matching intensities (ein/sec)
\( \times 15 \) times the photocurrent is observed with ultraband gap
501.7 nm excitation as with band gap edge 514.5 nm light. As
the temperature is increased to 100°C, a modest increase in
501.7 nm photocurrent is observed, while about an order of
magnitude growth is obtained for 514.5 nm excitation. In fact,
at 100°C the 514.5 nm photocurrent has reached \( \sim 60\% \) of the
ultraband gap photocurrent. Similar effects were observed in
polyseleide electrolyte for both CdS:Te and undoped CdS (9).

The photocurrent enhancement for 514.5 nm excitation is a
predictable consequence of an absorption edge which red shifts
with temperature: As the absorptivity for 514.5 nm light
increases with temperature, progressively larger fractions of
light will be absorbed in the depletion region. In this sense
the accelerated decline in emission intensity observed for
514.5 nm relative to 501.7 nm excitation (Figure 1) may include
a contribution reflecting decreasing optical penetration depth;
weaker emission would be expected as 514.5 nm light acquires
status as an ultraband gap wavelength, since near-surface
nonradiative recombination sites could play a more significant
role in excited-state deactivation (7,8). Although the rate
at which 514.5 nm photocurrent increases with temperature is
in reasonable accord with the CdS optical band gap temperature
coefficient, the effect of potential-dependent absorptivity must
be considered.

Electroabsorption measurements have been made on undoped CdS
at room temperature. They reveal that for electric fields of
\( \sim 10^5 \) V/cm, the change in absorptivity, \( \Delta \alpha \), is \( \sim +1x10^3 \) and \( -4x10^3 \)
cm\(^{-1}\) at 515 and 500 nm, respectively (20). While this effect
helps to blur the discrepancy in 514.5 and 501.7 nm optical
penetration depths, the resultant absorptivities are still
sufficiently disparate relative to the width of the depletion
region to yield very different photocurrents at 295 K. To our
knowledge electroabsorption data are not presently available
for CdS:Te. A crude attempt to gauge the magnitude of this
effect at 295 K for 514.5 nm light suggests it is small (8). In
the absence of electroabsorption data over the 20-100°C range,
however, the electric field and thermal effects are not completely
decoupled and the results presented here should be so treated.

We should point out that the temperature effects on emission
intensity and photocurrent are completely reversible. Although
this result suggests that electrode stability obtains over the
duration of the experiments, the properties measured may not be
very sensitive to variations in surface or near-surface
composition. There is now considerable evidence, in fact, that
surface reorganization processes do occur in CdS- and CdSe- based
PECs in polychalcogenide electrolytes (17, 21-26). In particular,
the occurrence of such an exchange reaction for CdS:Te in poly-
seleide electrolyte would yield CdSe to whose lower band gap
(1.7 eV (27)) some of the observed properties could be attributed. The reversibility of the temperature effects as well as the similar behavior seen in sulfide electrolyte argue against such an explanation. Additionally, we have employed low light intensities (≤10 mW/cm²) and current densities (≤2 mA/cm² with a total charge of generally ≤1 C/cm²) to further minimize exchange processes. But we do recognize that our techniques by no means rule out the possibility of surface reorganization processes at some level.

Simultaneous measurement of current, luminescence and voltage can be presented in iLV curves which summarize much of our data. We find that the ratio of open-circuit to in-circuit luminescence intensity (Φ₀/O) is a useful expression of the emission’s potential dependence, with the in-circuit value taken at a potential where the photocurrent is saturated. Low values of photocurrent quantum yield, Φx ≤ 0.1, occur with band gap edge excitation and yield Φ₀/O values close to unity. Ultraband gap excitation generally yields 0.5 ≤ Φx ≤ 1.0. Pulsing the electrode between open circuit and the potential corresponding to saturated photocurrent easily demonstrates the non-unity value of Φ₀/O. Since photocurrent quantum yield increases markedly with temperature for band gap edge illumination, we predict that Φ₀/O will exceed unity at elevated temperatures. Figure 3 presents full iLV curves for a CdS:Te-based PEC employing polyselenide electrolyte. Equivalent intensities (ein/sec) of 501.7 and 514.5 nm light were employed at both room and elevated temperatures (49°C for 501.7 nm; 86°C for 514.5 nm). These iLV curves may be summarized as follows: Photocurrent at 23°C is ≈18 times greater for 501.7 nm excitation (curve A vs. curve B) and open-circuit emission intensity is ≈5 times smaller (curve A' vs. curve B') than for 514.5 nm light. The ratio of Φ₀/Φx is 1.0 for 514.5 nm (curve B') and 3.5 (curve A') for 501.7 nm illumination. Increasing the temperature to 49°C increases the photocurrent from 501.7 nm light by ≈15% (curve C) and diminishes the luminescence intensity by a factor of 2. However, a similar Φ₀/Φx ratio of 3.4 obtains (curve C'). At 86°C the 514.5 nm photocurrent increases by a factor of almost 8 (curve D). Despite its approximately 10-fold drop in intensity, emission from 514.5 nm excitation now exhibits a potential dependence with a Φ₀/Φx value of 1.27 (curve D' - note 10X scale expansion). Similar non-unity Φ₀/Φx values were observed in sulfide electrolytes at temperatures exceeding ~80°C.

Interrelationships of Excited-State Decay Routes. The iLV curves conveniently display the competitive nature of photocurrent and luminescence intensity as excited-state deactivation pathways. Our analysis is limited in the sense that we have obtained absolute numbers for Φx but have had to content ourselves with relative Φx measurements. We lack measures of nonradiative recombination efficiency (Φnr), although they now appear to be
obtainable by the technique of photothermal spectroscopy (28,29). Treating these as the only possible decay routes yields eq. 1

$$\phi_x + \phi_T + \phi_{nr} = 1$$

At open circuit $\phi = 0$ and photogenerated $e^-\text{--}h^+$ pairs are forced to recombine. The ratio of $\phi_T$ to $\phi_{nr}$ is shown to be wavelength dependent by comparing the open-circuit emission intensities of curve A' and curve B' in Figure 3. This ratio is also temperature dependent, as shown in Figure 1.

Correlation of $\phi_x$, $\phi_T$, and $\phi_{nr}$ involves knowing the relative extent to which nonradiatively and radiatively recombining $e^-\text{--}h^+$ pairs are prevented from recombining, i.e., their relative contribution to photocurrent. Three possible schemes are: photocurrent, $\phi_T$, interconverts (1) exclusively with $\phi_{nr}$; (2) exclusively with $\phi_{nr}$; (3) with both $\phi_T$ and $\phi_{nr}$ such that $\phi_{nr} = k\phi_T$ for any $\phi_x$.

Scheme 1 is unlikely because of the relative magnitudes of $\phi_T$ and $\phi_x$. Measured values of $\phi_T$ and $\phi_x$ are $10^{-3}$ and $10^{-1}$, respectively, for band gap edge excitation (8). In passing from $+0.7$ V vs. Ag (PRE) to open circuit, a $\sim$100-fold increase in emission intensity is predicted. This is inconsistent with the insensitivity displayed in curve B', Figure 3. Scheme 2 argues that $\phi_T$ will be independent of potential. While it appears that curve B' (Figure 3) agrees with this, it is contradicted by curves A', C', and D'. Although not perfect, Scheme 3 is most compatible with our data. This assumption when combined with eq. 1 leads to a simple relationship for monochromatic excitation between $\phi_x$ and $\phi_T$:

$$\frac{\phi_T}{\phi_x} = \frac{1}{1 - \phi_x}$$

Table 1 consists of a compilation of $\phi_T/\phi_x$ ratios as a function of $\phi_x$. Our results and those presented for p-GaP and n-ZnO are in rough agreement with this simple model (8,9,30,31,32). Construction of a more refined model awaits incorporation of other data (nonexponential lifetimes, electroabsorption, carrier properties, intensity effects, quantitative evaluation of $\phi_{nr}$ by photothermal spectroscopy, e.g.) and examination of other systems.

Acknowledgment

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Table I. Relationship Between $\phi_x$ and $\phi_{r_0}/\phi_r^a$

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$^a$Calculated from eq.2 where $\phi_x$ is the photocurrent quantum yield, and $\phi_{r_0}/\phi_r$ is the ratio of emission quantum yields between open circuit and the potential where $\phi_x$ is measured.

Abstract

The effect of temperature on excited-state deactivation processes in a single-crystal, n-type, 100 ppm CdS:Te-based photoelectrochemical cell (PEC) employing aqueous polychalcogenide electrolytes is discussed. While serving as electrodes these materials emit ($\lambda_{max} \approx 600$ nm). Photocurrent (quantum yield $\phi_x$) from ultraband gap ($\geq 2.4$ eV; $\lambda < 500$ nm) 501.7 nm excitation increases modestly by $\leq 20\%$ between 20°C and 100°C; photocurrent from band gap edge 514.5 nm excitation increases by about an order of magnitude, reaching $\approx 50-100\%$ of the room temperature 501.7 nm value. Highlighting the competitive nature of emission and photocurrent as excited-state decay processes, luminescence (quantum yield $\phi_r$) declines over the same temperature regime by factors of between 10 and 30. At most, modest red shifts of $\lambda_{max}$ ($<10$ nm) are observed in the spectral distribution of emission with temperature. These effects are discussed in terms of optical penetration depth, band bending, and the known red shift of the CdS absorption edge with temperature. Correlations involving $\phi_x$ and $\phi_r$ suggested by the data are discussed.

Literature Cited

Figure Legends

Figure 1. Relative emission intensity monitored at 600 nm vs. temperature in 1M OH-/1M S²⁻ electrolyte of CdS:Te excited at open circuit with 514.5 (squares) and 501.7 nm (circles) light in identical geometries. The excitation intensity at 501.7 nm is ~17X that at 514.5 nm in order to approximately match room temperature emission intensities.

Figure 2. Relative photocurrent vs. temperature for the CdS:Te photoelectrode of Fig. 1 in 1M OH⁻/1M S²⁻ electrolyte excited in identical geometries with equivalent intensities (ein/sec) of 514.5 nm (filled circles) and 501.7 nm (open circles) light at +0.7 V vs. Ag (PRE). The scale is such that the 25°C, 501.7 nm photocurrent has been arbitrarily set to 100 and corresponds to a current density of ~0.38 mA/cm² and a photocurrent quantum yield of ~0.66.

Figure 3. Current-luminescence-voltage (iLV) curves for a 100 ppm CdS:Te electrode in polyselenide electrolyte. Unprimed, solid-line curves are photocurrent (left-hand scale) and primed, dotted-line curves are emission intensity (right-hand scale) monitored at λmax ~600 nm. Curves A and A' result from excitation at 501.7 nm, 23°C; curves B and B' from 514.5 nm, 23°C; curves C and C', 49°C and 501.7 nm excitation; curves D and D', 86°C, 514.5 nm irradiation. Note that the ordinate of curve D' has been expanded by a factor of 10. Equivalent numbers of 501.7 and 514.5 nm photons were used to excite the photoelectrode in identical geometric configurations. The exposed electrode area is ~0.41 cm², corresponding to an estimated φe for 501.7 nm excitation at 23°C and +0.7 V vs. Ag (PRE) of ~0.50, uncorrected for solution absorbance and reflectance losses (9).
Fig. 1

RELATIVE EMISSION INTENSITY, a.u.

TEMPERATURE, °C

CdS:Te
100 ppm

○ 501.7 nm
□ 514.5 nm
Fig. 2

CdS:Te
100 ppm

TEMPERATURE, °C

RELATIVE PHOTOCURRENT

20 30 40 50 60 70 80 90 100

10 20 30 40 50 60 70 80 90 100