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Electrogenerated Chemiluminescence

34. Photo-Induced Electrogenerated Chemiluminescence and Up-Conversion at Semiconductor Electrodes

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ABSTRACT

Photosensitized oxidations or reductions at p- and n-type GaAs and InP semiconductor electrodes of aromatic species in aprotic solvents leading to electrogenerated chemiluminescence (ECL) are described. The energy of the irradiating light equal to the bandgap energy of the semiconductor and the electrical energy input couple to produce excited states which eventually produce emission at shorter wavelengths. Intense ECL is observed by alternately generating radical cations and radical anions at an illuminated semiconductor electrode with smaller potential excursions than required on metal (platinum) electrodes.

Photoassisted electrode processes of a number of species (e.g., aromatic hydrocarbons and heterocyclic compounds) at semiconductor electrodes in aprotic solvents have been described (1-5). These studies have demonstrated that electrochemical oxidations at n-type semiconductors occur at less positive potentials (or reductions at p-type semiconductors at less negative potentials) than are required to carry out the same process at an inert metal (e.g., Pt) electrode. These processes thus involve the partial conversion of light energy to chemical energy in the electrogenerated species. When the electrogenerated species (e.g., radi-

cal ions) are capable of undergoing homogeneous electron transfer reactions near the electrode surface to produce excited states, electrogenerated chemiluminescence (ECL) results. Hence the over-all scheme involves coupling of the input light energy and electrical energy to produce an output emission of higher energy (or "up-conversion"). Such a scheme was initially suggested by Nicholson (6), but prior to this report was never reduced to practice. A previous report from this laboratory described a similar experiment where the photoinduced reduction of 9,10-dichloro-9,10-dihydro-9,10-diphenyl-anthracene (DPACl₂) on p-Si irradiated with red light in acetonitrile (7) produced violet emission. There, however, emission is observed only upon reduction of DPACl₂ via a chemical-

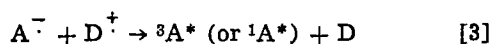
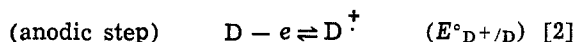
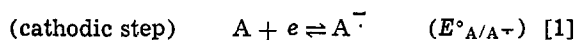
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Key words: photoluminescence, visible, voltammetry, energy conversion.

electrochemical mechanism (8), and much of the energy of the emitting light may be attributed to the chemical energy of DPACl₂ moiety itself, which is not regenerated in the over-all process.

The ECL scheme usually involves production and annihilation of radical ion species at metal electrodes by an electron-transfer mechanism (9, 10)



where A represents an electron acceptor (e.g., an aromatic hydrocarbon) and D represents an electron donor (e.g., an aromatic hydrocarbon or amine). Formation of excited states of D and exciplexes are also possible during the ion-annihilation reaction, Eq. [4], but are omitted, since they are not important in the reactions to be described here. When the ECL reaction is carried out on a semiconductor electrode, two new features emerge. First, the semiconductor/liquid interface behaves like a Schottky junction and shows diode-like behavior. This results in anodic reactions occurring positive of the flatband potential, V_{fb} , being blocked at n-type materials and cathodic reactions occurring negative of V_{fb} being blocked at p-type materials (11). Thus irradiation of the electrode is required to allow

generation of both $A^{\cdot -}$ and $D^{\cdot +}$ and observe emission. Secondly, irradiation of the semiconductor photoassists the electrochemical process, so that oxidations at irradiated n-type electrodes occur at potentials less positive than $E^{\circ}_{D^{\cdot +}/D}$ and reductions at irradiated p-type electrodes occur at potentials less negative than $E^{\circ}_{A/A^{\cdot -}}$. Details of ECL experiments at several semiconductor electrodes incorporating these features are reported here.

Experimental

Acetonitrile (ACN; Spectroquality, Matheson, Coleman and Bell) was refluxed over fresh CaH₂ powder for 8 hr followed by fractional distillation under dry nitrogen. The middle fraction was transferred to a vacuum line and subjected to four freeze-pump-thaw cycles to remove dissolved gases. The solvent was then vacuum distilled into a storage flask containing molecular sieves (Linde 4A) activated by heating under high vacuum at 400°C for 72 hr. Benzene (BZ; Spectroquality, Matheson, Coleman and Bell) was refluxed over potassium for 24 hr under dry nitrogen, distilled, and subjected to four freeze-pump-thaw cycles. The solvent was vacuum distilled into a storage flask containing Na-K alloy.

Tetra-n-butylammonium perchlorate (TBAP; Southwestern Analytical Chemicals) and rubrene (RUB; Aldrich) were purified as previously described (8). Chrysene (CHR; Aldrich) was treated with maleic anhydride, chromatographed on an alumina column, and recrystallized repeatedly from benzene. Fluoranthene (FLU; Zone Refined, Aldrich) and perylene (PER; Gold Label, Aldrich) were used as received. 9,10-Diphenylanthracene (DPA; Gold Label, Aldrich) was sublimed and zone refined. 10-Methylphenothiazine (10-MP; Eastman) and tetracene (TET; Eastman) were purified by multiple recrystallizations from benzene. Pyrene (PYR; Eastman) was recrystallized from ethanol and sublimed twice. N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) was prepared and purified as previously reported (12). p-(9-Anthranlyl)-N,N-dimethylaniline (DMAA), generously provided by Dr. Kingo Itaya, was used as received.

N- and p-type InP and GaAs semiconductor electrodes were prepared as previously reported (13, 14). V_{fb} of the semiconductor electrodes was determined by photocurrent onset measurements and Schottky-Mott plots. GaAs and InP semiconductor electrodes were etched in H₂SO₄-30% H₂O₂-H₂O (3:1:1) for 5-10 sec and then in 6M HCl for 30 sec (GaAs) or 5 sec (InP). The electrodes were then rinsed with H₂O and ethanol, and dried immediately under vacuum at room temperature.

The electrochemical ECL cell was of conventional design (12) and incorporated semiconductor and Pt wire-working electrodes. The Ag wire quasireference electrode was shielded in a Teflon jacket having a porous Vycor plug. The auxiliary electrode consisted of a large Pt foil in the bulk solution. The cell, containing radical ion precursor compounds and supporting electrolyte, was assembled and evacuated 5-18 hr at high vacuum. Solvent was added by vacuum distillation. Solutions typically contained 1-3 mM A and D and 0.1M TBAP as supporting electrolyte. The electrochemical and spectroscopic apparatus and techniques utilized have previously been reported (12, 13). Illumination of the semiconductor electrodes was accomplished with either a 3 mW He-Ne laser or a 650W tungsten-halogen lamp incorporating Ditic Company infrared pass (<1.7 eV) filters. A CuSO₄ solution filter was typically used to eliminate stray infrared light incident on the photomultiplier tube.

Results

The semiconductors studied and their properties are given in Table I, and the spectroscopic and electrochemical properties of the donor and acceptor molecules of the ECL systems are given in Table II.

N-type semiconductors.—Typical electrochemical behavior on n-type semiconductor electrodes is given in Fig. 1 and 2. In the dark, virtually no current flows at potentials positive of V_{fb} . At potentials negative of V_{fb} , however, the semiconductor electrode becomes degenerate (11) and shows cyclic voltammetric (cv) behavior similar to that on a metal electrode. Thus redox couples located negative of V_{fb} (e.g., DPA, FLU) show reversible cv waves. When the n-type semiconductor

Table I. Semiconductor electrode properties

| Electrode | E_g (eV)* | V_{fb} ** | Area (cm ²) |
|-----------|-------------|-------------|-------------------------|
| n-InP | 1.27 | -1.0 ± 0.2 | 0.22 |
| n-GaAs | 1.43 | -1.0 ± 0.2 | 0.12 |
| p-InP | 1.27 | +0.0 ± 0.2 | 0.15 |
| p-GaAs | 1.43 | +0.1 ± 0.2 | 0.11 |

* Bandgap energy.

** Flatband potential, volts vs. SCE in acetonitrile.

Table II. Electrochemical and spectroscopic properties

| Compound | $E_{1/2}$ (R/R ⁺) [*] | $E_{1/2}$ (R/R ⁻) [*] | E_s (eV) | E_T (eV) |
|---|---|---|------------|------------|
| N,N,N',N'-tetramethyl p-phenylenediamine (TMPD) | 0.20, 0.77 | — | 3.1 (15) | 2.38 (15) |
| 10-methylphenothiazine (10-MP) | 0.79 | — | 2.9 (15) | 2.4 (15) |
| 9,10-diphenylanthracene (DPA) | 1.28 | -1.84 | 3.06 (16) | 1.77 (17) |
| fluoranthene (FLU) | — | -1.74 | 3.4 (17) | 2.30 (17) |
| rubrene (RUB) | 0.94** | -1.43** | 2.36 (18) | 1.2 (18) |
| p-(9-anthranlyl)-N,N-dimethylaniline (DMAA) | 0.75 | -2.00 | 2.52 (19) | — |
| perylene (PER) | 1.14 | -1.63 | 2.85 (17) | 1.52 (17) |
| pyrene (PYR) | 1.31 | -2.05 | 3.34 (17) | 2.10 (17) |
| tetracene (TET) | 1.02** | -1.58** | 2.60 (17) | 1.27 (17) |
| chrysene (CHR) | 1.56 | -2.25 | 3.4 (17) | 2.48 (17) |

* Volts vs. SCE in acetonitrile unless otherwise noted.

** Acetonitrile-benzene mixed solvent.

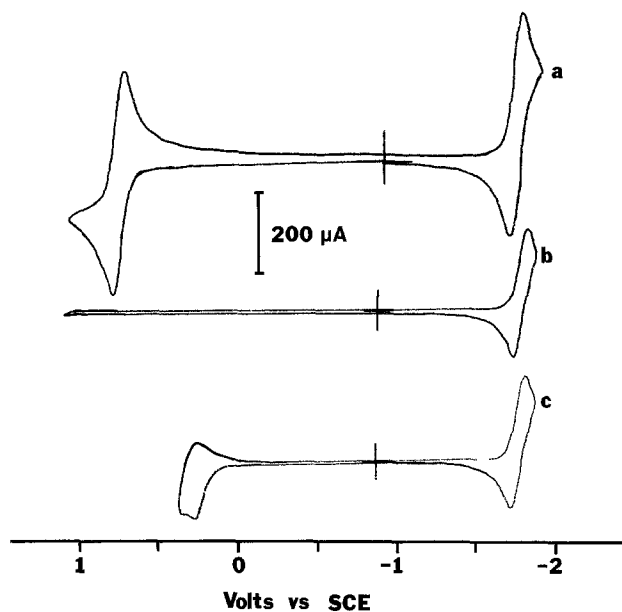


Fig. 1. Cyclic voltammetry of ~ 3 mM 10 MP and 3 mM FLU in 0.1M TBAP/ACN; scan rate, 200 mV/sec. (a) On platinum; (b) on n-InP in the dark; (c) on illuminated (3 mW He-Ne laser) n-InP.

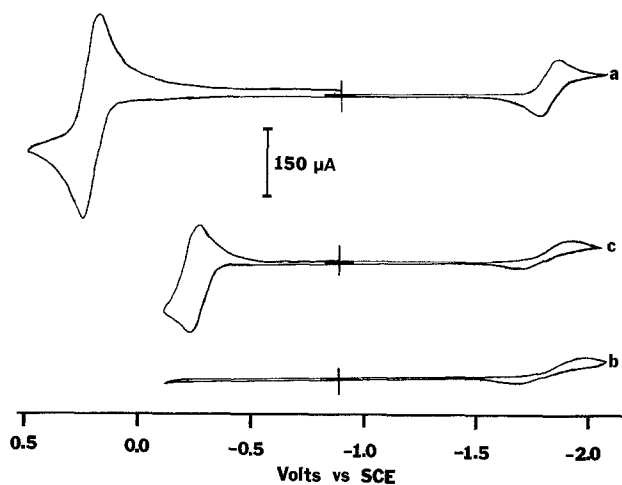


Fig. 2. Cyclic voltammetry of ~ 2.5 mM TMPD and 1 mM DPA in 0.1M TBAP/ACN; scan rate, 200 mV/sec. (a) On platinum; (b) on n-GaAs in the dark; (c) on illuminated (3 mW He-Ne laser) n-GaAs.

electrode is illuminated with light of greater energy than the bandgap energy (E_g), electrons are excited into the conduction band and holes produced in the valence band can be populated by electron transfer from suitable solution species. This process is most efficient at potentials positive of V_{fb} where the photo-produced holes accumulate at the semiconductor-solution interface. The photoinduced oxidation of species with solution energy levels located at potentials more positive than the valence band edge (E_v) is not expected since a hole produced at energy E_v would not be sufficiently energetic. Such a phenomenon was observed here, however. A similar photoeffect on oxidations occurring negative of V_{fb} was found in a previous study at GaAs electrodes (14) and was ascribed to production of a film on the electrode surface upon reduction which effectively formed a solid/solid junction adding a bias under illumination. Such an effect cannot be occurring here, since a photoeffect is found for the D/D^+ wave, but not at the A^-/A one. An alternate explanation rests on a change in the surface of the electrode which shifts the value of V_{fb} toward more positive values (Fig. 3). Effectively then, illumi-

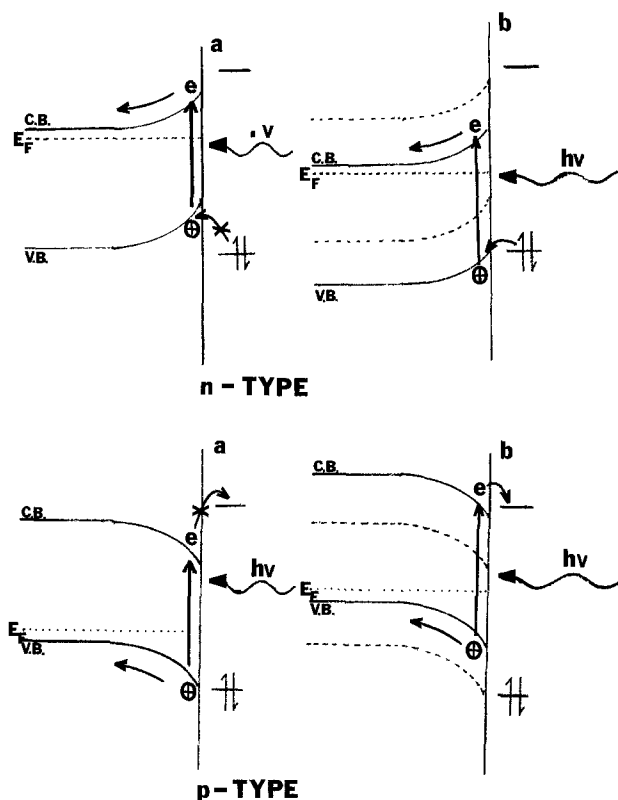


Fig. 3. Shift of conduction and valence band energies upon film formation: (a) prior to film formation; (b) film formation allowing electron transfer upon photoexcitation of the semiconductor electrode.

nation of the n-type semiconductor electrode with bandgap energy light results in the oxidation of the solution species D at less positive potentials than those where this species is reversibly oxidized on metal electrodes. This "negative overpotential" effect (7, 14) is the basis for solar energy conversion utilizing electrochemical systems.

A typical experiment involving photoinduced ECL at an n-type semiconductor electrode is shown in Fig. 4. The initial potential is established where no current flows until the electrode is illuminated, whereupon an anodic current flows and the oxidized species is produced at the electrode. Stepping the potential to negative values to form the reduced species results in in-

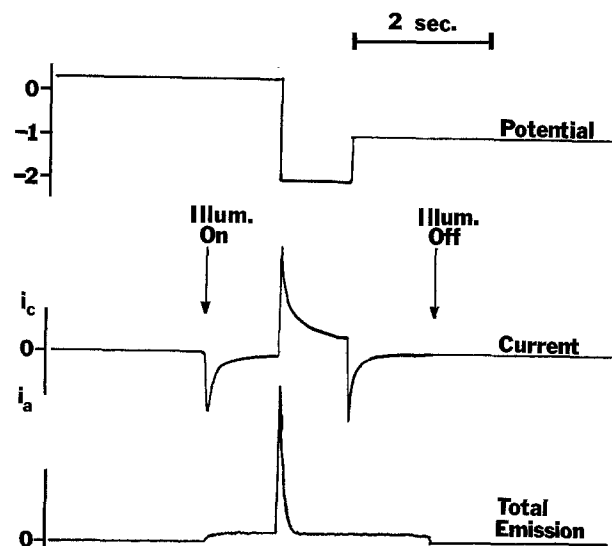


Fig. 4. Potential-, current-, and emission-time profiles illustrating photoinduced oxidation of 10 MP and reduction of FLU on n-InP yielding ECL. Illumination of n-InP with 3 mW He-Ne laser.

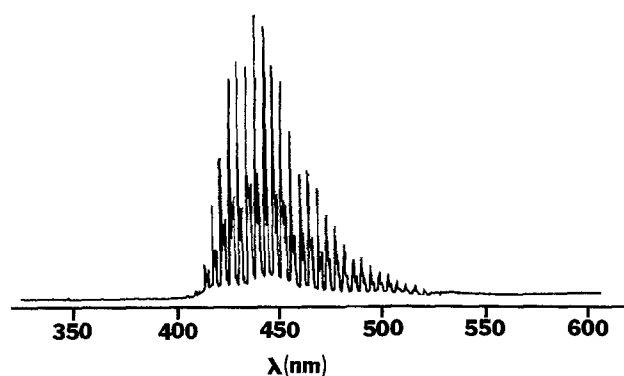


Fig. 5. Uncorrected ECL spectrum of ~ 2 mM TMPD and 1 mM DPA on n-InP illuminated with 3 mW He-Ne laser. Potential pulsed from -0.05 to -2.0 V vs. SCE at 1 Hz.

tense ECL as the radical ions annihilate in the diffusion layer adjacent the electrode. Pulsing the semiconductor electrode potential between these potential limits results in pulses of ECL emission when the electrode was illuminated with bandgap energy light (>1.4 eV). With these same potential excursions, no emission was observed on a platinum electrode, because the potential limits were insufficient to produce D^+ and A^- with photoassistance. A typical ECL spectrum obtained by scanning the emission wavelength during repetitive pulsing under irradiation is shown in Fig. 5.

The potential dependence of the emission was ascertained by employing anodic linear potential sweeps from potentials where the reduced species is formed toward positive values, as previously described (13) (Fig. 6). Under dark conditions, virtually no emission is observed at the semiconductor until the electrode potential reaches very positive potentials. The semiconductor electrode illuminated with bandgap energy light, however, gives emission at potentials less positive than those necessary for emission on platinum.

The ECL emission observed in all of the cases examined (Table III) was quite bright, visible to the eye in a well-illuminated room, and comparable to the emission observed on platinum electrodes when using larger potential excursions. Although the ECL of systems utilizing easily oxidizable species (e.g., TMPD) was quite stable with continuous potentiostatic pulsing and illumination, less stability was found with species oxidized at more positive potentials. For example, although an initial ECL pulse with RUB on n-InP was intense (and easily visible), the intensity rapidly decayed upon further pulsing, probably because of oxida-

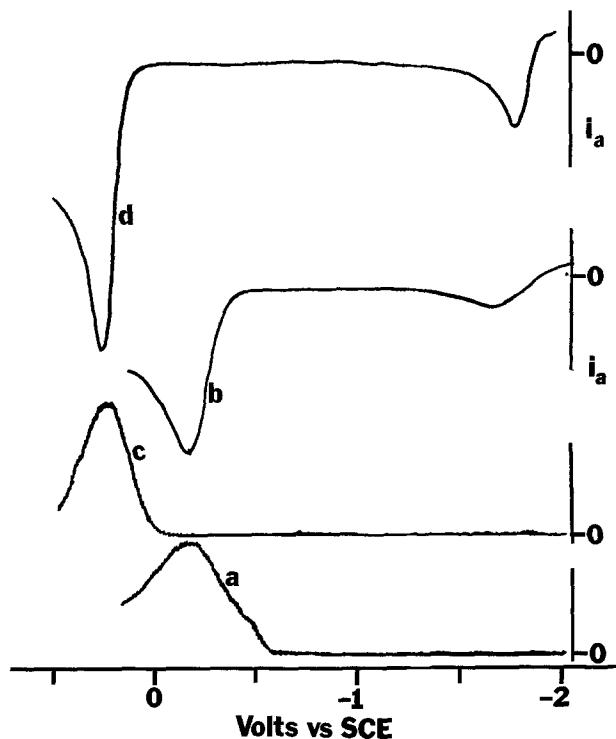


Fig. 6. ECL- and current-potential curves observed by anodic linear potential sweep voltammetry at 2 V/sec with 3 mM TMPD and 1 mM DPA in 0.1M TBAP/ACN. (a) ECL intensity; and (b) current obtained on n-InP illuminated with $h\nu < 1.7$ eV.; (c) ECL; and (d) current obtained on platinum.

tion of the semiconductor lattice (14). Electrode stability was similarly adversely affected by traces of H_2O when less rigorously dehydrated solvent was used. Under these conditions, the photoinduced oxidation of the semiconductor lattice was found to occur at less positive potentials and resulted in the accumulation of an electrically insulating film on the semiconductor electrode surface.

P-type semiconductors.—The electrochemical behavior at p-type semiconductor electrodes was analogous to that found with n-type electrodes. Typical cyclic voltammograms are shown in Fig. 7 and 8. Unlike oxidations at the n-type material, some current attributable to dark reduction of the substrate is observed at the p-type material, but only at potentials negative of where the reduction wave is found at Pt. Oxidations at potentials positive of V_{fb} occur readily and the electrode shows essentially metallic behavior.

Table III. Summary of ECL experiments on the photoinduced up-conversion at p- and n-type InP and GaAs

| Electrode | System | Oxidation** | | Reduction** | | ΔE_{ECL}^{***} | Emission | Comments† |
|-----------|-----------|-------------|-----------|-------------|-----------|------------------------|----------|--|
| | | E_{p_a} | E_{p_c} | E_{p_c} | E_{p_a} | | | |
| n-GaAs | TMPD/DPA | -0.38 | -0.34 | | | 1.5-1.7 | Blue | Stable, bright, $\Delta E_{ECL} < E_T$ |
| | 10-MP/DPA | -0.17 | +0.09 | | | 2.1-2.2 | Blue | Moderately stable, bright emission |
| | DMAA | 0.25 | 0.28 | | | 2.1-2.3 | Yellow | Bright intramolecular exciplex emission, cation unstable |
| n-InP | 10-MP/FLU | 0.29 | 0.29 | | | 2.0-2.1 | Blue | Mod. stable, bright, $\Delta E_{ECL} < E_T$ |
| | RUB | 0.52 | 0.47 | | | 1.9-2.1 | Yellow | Bright, unstable |
| | TMPD/DPA | -0.22 | -0.17 | | | 1.9-2.1 | Blue | Stable, bright |
| p-GaAs | 10-MP/FLU | | 0.29 | -1.45 | -1.48 | 2.2-2.4 | Blue | Stable, bright, $E_{ECL} \leq E_T$ |
| | PER | | 0.30 | -1.18 | -1.31 | 2.2-2.5 | Blue | Bright, mod. stable, cooxidation of electrode |
| | DPA | | | -1.46 | -1.52 | 2.7-2.8 | Blue | Bright, unstable, cooxidation of electrode |
| p-InP | PER | | | -1.30 | -1.06 | 2.3-2.5 | Blue | Bright, mod. stable, some oxidation of InP |
| | DPA | | | -1.37 | -1.14 | 2.6-2.8 | Blue | Bright, unstable, cooxidation of InP |

* 0.1M TBAP/acetonitrile solution.

** Current peak potentials, volts vs. SCE. Electrode illuminated with $h\nu < 1.7$ eV.

*** Potential excursions needed to obtain ECL on illuminated semiconductor electrode.

† Stability refers to semiconductor electrode with respect to degradation.

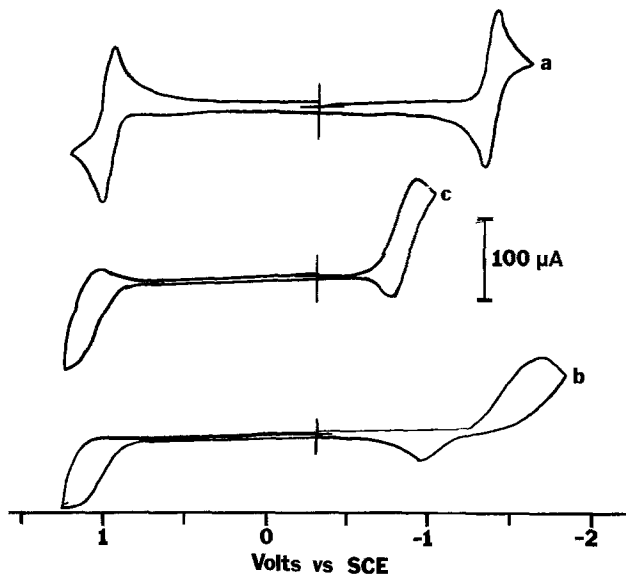


Fig. 7. Cyclic voltammetry of 1 mM RUB in 0.1M TBAP/ACN-BZ(1:1); scan rate, 200 mV/sec. (a) On platinum; (b) on p-InP in the dark; (c) on p-InP illuminated with $h\nu < 1.7$ eV.

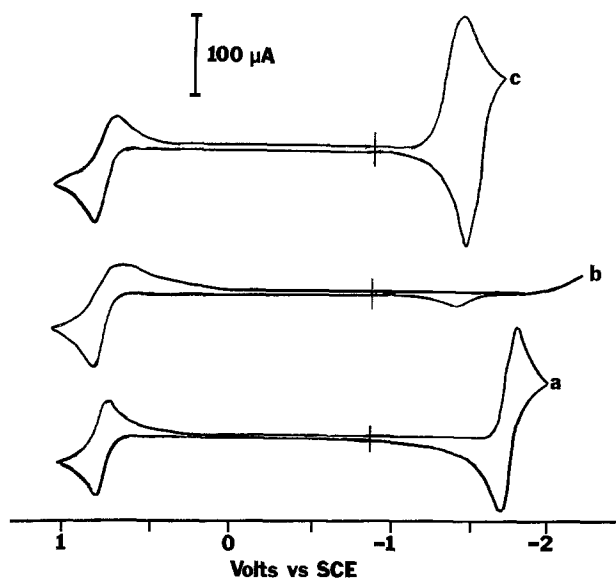


Fig. 8. Cyclic voltammetry of ~ 2.5 mM FLU and 1.5 mM 10-MP in 0.1M TBAP/ACN; scan rate, 200 mV/sec. (a) On platinum; (b) on p-GaAs in the dark; (c) on p-GaAs illuminated with $h\nu < 1.7$ eV.

When the electrode at potentials negative of V_{fb} is illuminated with bandgap energy light, electrons excited into the conduction band can reduce the solution acceptor species. Again, some surface phenomenon which allows the photoinduced reduction of suitable solution species with solution energy levels above the conduction band edge with a considerable "negative overpotential" must be involved (14).

The ECL results with p-type semiconductor electrodes are summarized in Table III; a typical experiment is shown in Fig. 9. Although the reduced species (FLU here) could be generated in the dark at very negative potentials (i.e., beyond ca. -2.5 V), the A^- was typically generated at potentials positive of where it is thermodynamically accessible on platinum by illuminating the semiconductor electrode. As illustrated, no ECL could be observed on platinum under these conditions.

The ECL from the systems examined was quite intense and visible to the eye. Species with rather

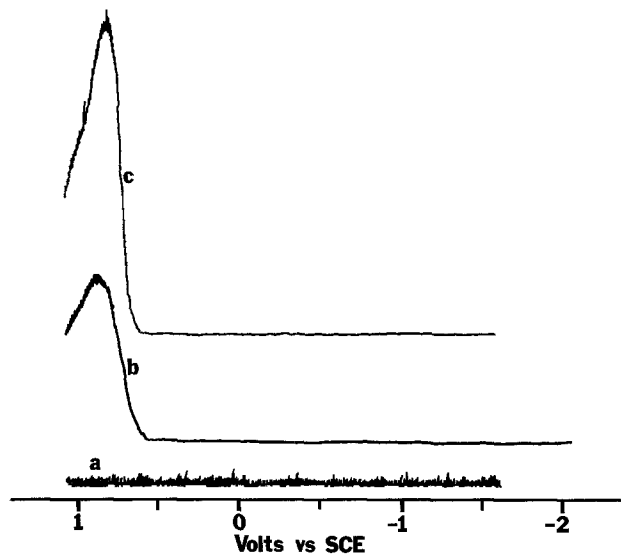


Fig. 9. ECL-potential curve obtained by anodic linear potential sweep voltammetry at 2 V/sec with 2.5 mM FLU and 1.5 mM 10-MP in 0.1M TBAP/ACN. (a) On platinum from -1.60 V vs. SCE (Gain, $\times 100$); (b) on platinum from -2.1 V vs. SCE; (c) on p-GaAs illuminated with 3 mW He-Ne laser from -1.60 V vs. SCE.

positive $E_{1/2}(R/R^+)$ values were oxidized concurrently with the semiconductor electrode lattice and in these systems the ECL intensity tended to degrade with continuous pulsing. For example, the oxidation of DPA occurs at potentials where semiconductor lattice oxidation is observed and the ECL emission with this system was rather short-lived. A system employing 10-MP which has a somewhat less positive

$E_{1/2}(R/R^+)$ value was quite stable with continuous potential pulsing and illumination of the p-type semiconductor electrodes examined however. As observed on the n-type semiconductor electrodes, traces of H_2O had a deleterious effect upon the semiconductor electrode stability, especially when rather positive potentials were applied to the electrode.

Discussion

The results presented here demonstrate that up-conversion by the ECL-semiconductor electrode scheme, in a process where no material is consumed (except perhaps by parasitic side reactions), is possible. Moreover, photoassistance of the electrode process allows a coupling of the light energy and electrical energy input to produce emission at an energy where neither the light nor electrical energy alone would be sufficient. In the systems examined negative overpotentials of 400-600 mV could be attained. While it is true that the triplet-triplet annihilation step, Eq. [4], was responsible for the energy gain, in some of the cases examined neither the potential stimulus nor the energy of the illumination light alone was sufficient to populate the lowest triplet level. For example, for the 10 MP FLU system at n-InP, E_T for FLU is 2.30 eV, while the applied potential to the system was only 2.0-2.1V.

The results reported here suggest that the fabrication of devices employing small bandgap (< 1.5 eV) semiconductor electrodes to up-convert near infrared light to higher energy light in the visible region may be possible. The emitted light was quite intense and the semiconductor electrodes were quite stable under strictly anhydrous conditions upon repeated cycling, although most ECL systems are known to degrade over a very long time period. A device built on these principles would require rather low voltages (~ 3 V) and would have a spacial resolution determined by the narrow width of the radical ion annihilation zone.

Acknowledgment

We gratefully acknowledge the Army Research Office and the National Science Foundation for the support of this research. We are indebted to Paul Kohl for the flatband potential measurements and many helpful discussions concerning this work.

Manuscript submitted May 17, 1978; revised manuscript received July 19, 1978.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1979 JOURNAL. All discussions for the December 1979 Discussion Section should be submitted by Aug. 1, 1979.

Publication costs of this article were assisted by the University of Texas at Austin.

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Semiconductor Properties of Iron Oxide Electrodes

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ABSTRACT

The semiconductor electrode properties of thermally grown iron oxide and anodic oxide films on iron are compared. The bandgaps are 2.1 and 1.9 eV, respectively. Donor densities and flatband potentials are reported. Measurement of the currents produced by chopped illumination ($f \leq 100$ Hz) has allowed evaluation of electrode parameters and determination of reaction pathways.

The recent interest in iron oxide electrodes centers around their potential application to photoassisted electrolysis of water. These materials are promising because of their relatively narrow bandgap and of possible use because of their stability. The n-type polycrystalline $\alpha\text{Fe}_2\text{O}_3$ (1-5) behaves much as does single crystal $\alpha\text{Fe}_2\text{O}_3$ (6) (see Table I, Part A) and has the advantage of being easy to prepare.

The anodic oxide or passive film on iron is also reported to be a semiconductor (7-9) (see Table I, Part B). Photocurrent data, however, has not been reported. In the present investigation, the semiconducting character of thermally grown polycrystalline iron oxide and anodically produced oxide films on iron are compared directly with regard to photocurrent, differential capacitance, and polarization measurements.

Experimental

All measurements were made in a solution 0.075N in H_3BO_3 , 0.075N in $\text{Na}_2\text{B}_4\text{O}_7$, and 1N in NaNO_3 (pH 8.4). The $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ couple was added in certain experiments. All solutions were prepared from

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Key words: passivity, photocurrent, electrolysis, iron oxides.

triply distilled water and were saturated with purified N_2 . All chemicals were reagent grade or better.

A two compartment Pyrex cell containing a platinum gauze counterelectrode and a saturated calomel reference electrode (SCE) was used. All potentials are reported vs. SCE. The working electrode was approximately 0.5 cm from a Pyrex window through which the light was focused on the electrode surface in photocurrent experiments.

Electrodes were constructed from zone-refined iron (99.99% Fe). The thermally grown iron oxide electrodes were prepared as described previously (5). The bare metal electrodes were polished to a mirror finish and cleaned with methanol prior to use. For each working electrode a 0.5-1.0 cm^2 planar surface was exposed to solution by insulating the rest of the electrode with silicone adhesive (Dow Corning). Anodic oxide films were formed by first cathodically reducing any air formed oxide at -0.80V in pH 8.4 buffer solution for 1 hr, replacing with fresh solution under nitrogen and then polarizing at $+0.80\text{V}$ for 12 hr. The film thickness was estimated by galvanostatic reduction (10).

The photocurrent measurements (Fig. 1) employed a 200W tungsten lamp for polychromatic experiments.