PHOTOELECTROMOTIVE FORCE (PEMF) STUDIES OF [Fe(CN)$_5$SCN]$^{3-}$ COMPLEX IONS ADSORBED ON Pb(SCN)$_2$ SEMICONDUCTOR SURFACES

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Dedicated to the memory of the late Professor Antonín A. Vlček.

Adsorbates of [Fe(CN)$_5$SCN]$^{3-}$ complex ions on semiconducting Pb(SCN)$_2$ surfaces were subject to photoelectromotive force (PEMF) investigations. Laser flash excitation of the adsorbates at 560 nm yields a weak PEMF signal due to spectral sensitization of the semiconductor Pb(SCN)$_2$, not absorbing in the visible region. PEMF signals observed with laser flash excitation at 337 nm are explained by hole trapping accompanied with photoinduced redox reactions of the complex, when the number of flashes is increased.
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Photoelectromotive force (PEMF) investigations, described for the first time by Dember in 1934 (ref.[1]), are a powerful tool for detection of charge transfer processes from adsorbates into semiconductors[2]. The method was used to characterize charge injections in the course of photochemical reactions of various transition metal complexes adsorbed on selected semiconductor surfaces. In this paper, PEMF studies of (NMe$_3$Bn)$_3$[Fe(CN)$_5$(SCN)] (Bn = PhCH$_2$–) are reported, showing photoinjection of defect electrons, when adsorbed on semiconducting Pb(SCN)$_2$. Both spectral sensitization of charge injection and photochemical changes of the reactant complex could be established by repeated irradiation of a given sample.

PEMF can be observed when charge carriers in semiconductors are mobilized by light. Charge carriers generated photochemically diffuse through the sample, usually giving rise to two unlike potential peaks at electrodes that are inductively coupled to the sample. PEMF measurements can also be used to distinguish charge injection from energy transfer into solids.

In PEMF experiments, band gap excitation of semiconductors leads to different potential peaks due to mobilization of both electrons and defect electrons, with subsequent separation of charge carriers owing to their different diffusion rates. The driving force is due to an initial concentration gradient in electron/hole pairs resulting from inhomogeneous light absorption. The sequence of positive and negative potential peaks depends on the corresponding carrier mobility. A typical arrangement for PEMF measurements is shown in Scheme 1. The signal $U(t)$ obtained after pulse irradiation of pure uncovered semiconductor material usually shows biexponential decay (Eq. (*1*)), see also Fig. 2.

$$U(t) = U_1^0 \exp(-k_1 t) + U_2^0 \exp(-k_2 t); \quad U_{\text{max}} = U_1^0 + U_2^0 \tag{1}$$

This behaviour may be explained by two independent partial PEMF signals arising from the bulk and the subsurface of the semiconductor. The maximum value U_{max} and the sign of the PEMF signal as well as the set of kinetic parameters $U_1^0/k_1 + U_2^0/k_2$ can be used to characterize any photoconductor[2]. U_{max} is proportional to the concentration of e^-/h^+ pairs. If electrons diffuse
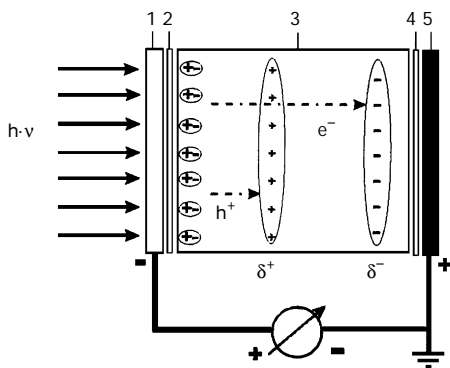
SCHEME 1

Sketch of the PEMF apparatus (1 NESA glass electrode, 2 insulating layer, 3 semiconductor pellet, 4 insulating layer, 5 metal electrode)

faster than holes, the sign of U_{max} will be positive (n-type semiconductor) and *vice versa* (see Scheme 1). Therefore, the type of photoconductivity (n- or p-type) or any chemical treatment concerning surface modification, carrier saturation, *etc.*, can be easily detected.

Recently we have shown[3–5] that photochemical reactions of transition metal complexes can be enhanced, modified, and controlled by excitation of low-energy LMCT states, when the latter complexes are adsorbed on surfaces of such semiconductors that are distinguished by band gap energies higher than λ_{LMCT}^{exc}. As implied by $\lambda_{LMCT}^{exc} > \lambda_{band\ gap}$, the semiconductor does not undergo band gap excitation under these conditions.

Based on these results, questions arise concerning the mode and direction of the charge transfer observed in the presence of a semiconductor support. Direct photophysical measurements should enable assignment of the mechanism of charge injection and the pathway used (*i.e.*, energy and hole or electron transfer) when the adlayer gets photoexcited. This approach seems to be more reliable than inferring reaction channels from chemical results only.

When charge transfer takes place between photoexcited transition metal complexes and semiconductor supports, the process should be accessible to PEMF measurements. The results of the latter measurements differ from those of band gap excitation because only one kind of charge carriers (*i.e.*, defect electrons) is passed into the support. Moreover, selective exchange of a single kind of charge carriers provides better control of secondary processes involving both the adsorbed complex and redox-active solutes.

EXPERIMENTAL

Scheme 1 shows a sketch of the apparatus used for PEMF measurements. A more detailed description is given elsewhere[2]. A nitrogen laser combined with a tunable dye laser ($t_{1/2}$ = 0.5 ns) was used as light source. Transient PEMF is studied at the illuminated transparent electrode and stored by means of a digital oscilloscope.

Pellets (diameter 1 cm, thickness 1 mm) of pure or modified semiconductor $Pb(SCN)_2$ were prepared with a power press as normally used in IR spectroscopy. Light absorption was near 100%.

$(NMe_3Bn)_3[Fe(CN)_5(SCN)]$ was prepared from the corresponding pentacyanonitrosyl-ferrate(III), $Na_2[Fe(CN)_5(NO)]$, according to the literature[6]. The identity of the proper linkage isomer of the thiocyanate ligand was inferred from UV/VIS spectra according to Burmeister[7].

Semiconducting lead thiocyanate was prepared by precipitation using aqueous solutions of lead(II) nitrate and $(NH_4)SCN$. The product was washed and dried *in vacuo* but not recrystallized.

The specific surface was estimated at 1 m^2/g by using BET experiments, working at the lower limit of this procedure. The specific coverages ϑ of the pellets used for the PEMF ex-

periments (1 or 10 monolayers) were calculated according to the above consideration. The sorbate systems were prepared in the dark by dissolving the complex in 2–4 ml of dichloromethane and addition of 1 g of semiconductor powder suspended in 5 ml toluene. Under constant stirring, another 90 ml of toluene was added dropwise and stirred overnight until the adsorption is complete. The adsorbate is filtered off, dried and pressed to get a sample suitable for handling in PEMF studies.

RESULTS AND DISCUSSION

PEMF measurements were performed with dried neat and complex-charged $Pb(SCN)_2$ powders in a Dember apparatus[2]. Flash irradiation is accomplished with a dye or nitrogen laser, depending on the required wavelengths. The sample is coupled to the sensor by inductive means. Electron transfer between electronically excited transition metal complexes and semiconductors leads to a spectral sensitization of the semiconductor. This implies that free charge carriers (dissociated excitons) form without light absorption by the semiconductor used. Charge carriers generated by light absorption can be detected using transient PEMF measurements. The sign of the PEMF at the beginning of the decay process provides information on the kind of majority charge carriers (electrons or defect electrons). The maximum value U_{max} of the PEMF behaves proportionally to the number of charge carriers generated by laser flash excitation. Therefore, electronic excitation of a transition metal complex absorbing in the visible region and adsorbed on a semiconductor should lead to transient PEMF signals when charge injection into the semiconductor occurs.

Thus, electronic excitation of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ adsorbed on semiconducting $Pb(SCN)_2$ by laser flashes of 560 nm leads to a weak PEMF signal, as shown in Fig. 1. Light of that wavelength is only absorbed by the iron(III) complex ($\lambda^{max} = 535$ nm). Actually, as shown in Fig. 1, the PEMF signal is only weak ($U < 0.1$ mV), but fully reproducible. This means, that the iron(III) complex causes a spectral sensitization of the semiconductor $Pb(SCN)_2$. However, the efficiency of the sensitization is rather low.

Based on PEMF studies upon UV excitation (N_2 laser, $\lambda^{exc} = 337$ nm), we have been able to confirm that interactions take place between the iron(III) complex and the surface of the semiconductor $Pb(SCN)_2$. Light of this wavelength is absorbed by both $[N(Me)_3Bn]_3[Fe(CN)_5SCN]$ and $Pb(SCN)_2$.

UV excitation ($\lambda^{exc} = 337$ nm) of pure $Pb(SCN)_2$ yields PEMF signals distinguished by a zero passage starting with negative sign (Fig. 2). This means, that $Pb(SCN)_2$ behaves as a p-type photoconductor.

Adsorption of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$ leads to a sign reversal of the PEMF signal, as shown in Fig. 2. This means, that the adsorbate

behaves as a n-type photoconductor, *i.e.*, an "umpolung" is observed owing to the sorbate coverage. The magnitude of the PEMF signal of the adsorbed iron(III) complex increases depending on the covering degree ϑ (Fig. 2, Ta-
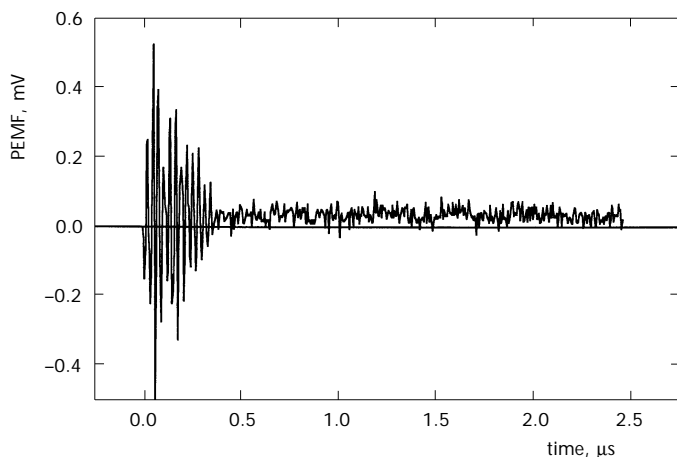

FIG. 1
PEMF signal of a pellet of adsorbate of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$ (λ_{flash} = 560 nm; *ca* $2.7 \cdot 10^{13}$ quanta/flash)
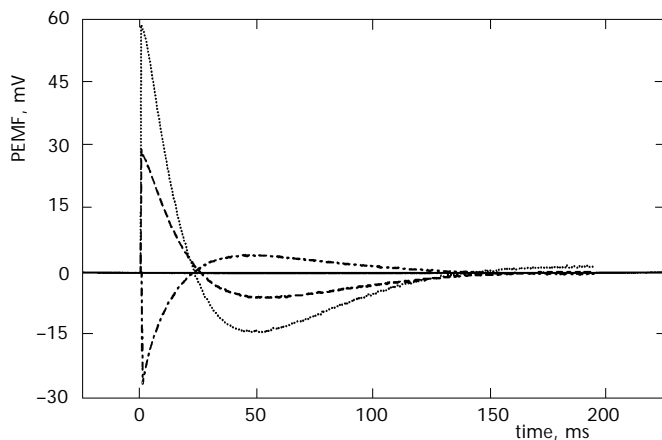
FIG. 2
PEMF signals of pellets of pure $Pb(SCN)_2$ ($- \cdot - \cdot -$), and of adsorbates of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$ with $\vartheta = 1$ ($- - - -$) and $\vartheta = 10$ ($\cdot \cdot \cdot \cdot \cdot$) ($\lambda_{flash}$ = 337 nm; *ca* $2.7 \cdot 10^{13}$ quanta/flash)

ble I). The sign reversal of the PEMF signal due to the adsorption of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$ can be explained by assuming that the iron(III) complex acts as a hole trap. The adsorption of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ leads to an uphill bending of the energy bands of $Pb(SCN)_2$ near the surface. Electrons generated by laser irradiation migrate into the bulk of the semiconductor $Pb(SCN)_2$ because the electron energy level decreases with the distance from the crystal surface. On the other hand, defect electrons generated photochemically remain near the surface

TABLE I
Maximum values and kinetic parameters of the PEMF of pure $Pb(SCN)_2$ and of adsorbates of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$ ($\vartheta = 1, 10$; $\lambda_{flash} = 337$ nm; *ca* $2.7 \cdot 10^{13}$ quanta/flash)

Material	U_{max}, mV	U_1^0, V	U_2^0, V	k_1, s^{-1}	k_2, s^{-1}
$Pb(SCN)_2$	−26.2±5.2	−0.065±0.030	0.039±0.026	56.1±6.1	29.6±4.2
$NMe_3Br)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$; $\vartheta = 1$	29.2±6.1	1.621±0.310	−1.592±0.304	35.1±0.8	34.4±0.7
$NMe_3Br)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$; $\vartheta = 10$	58.7±12.2	4.449±0.851	−4.390±0.839	37.7±0.8	37.1±0.7
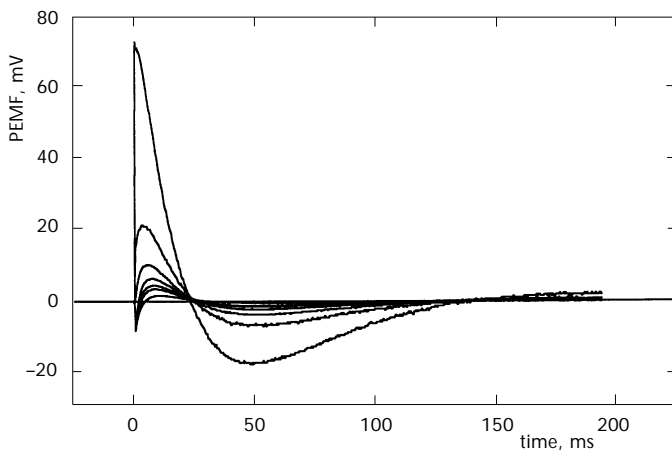
FIG. 3
PEMF signals of a pellet of adsorbate of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$ ($\vartheta = 1$) in dependence on the number of flashes (flash 1, upper curve; flashes 2, 3, 4, 6, and 10, lower curves; $\lambda_{flash} = 337$ nm; *ca* $2.7 \cdot 10^{13}$ quanta/flash)

of the crystal for energy reasons. The differences of the energy levels near the surface and in the bulk of the semiconductor lead to higher mobility of electrons, when compared with the defect electrons. The adsorbate behaves, therefore, as an n-type photoconductor.

However, adsorbates of the iron complex on $Pb(SCN)_2$ show strong positive PEMF signals only during the first flash (Fig. 3, Table II). Independently of the covering degree ϑ, the photovoltage (U_{max}) caused by the second flash decreases to one third, when compared with U_{max} of the first flash. The positive signal further decreases with increasing flash number. The fourth flash already leads to PEMF signals with negative sign. The behaviour of the adsorbate changes with increasing number of flashes from n- to p-type photoconductors.

The change of the PEMF signals depending on the flash number is due to the different mobility of electrons and defect electrons near the surface of the semiconductor. Defect electrons generated by the first flash remain near the surface. Although every flash generates the same number of electrons and defect electrons, electrons may recombine with defect electrons remaining near the surface. Therefore, defect electrons increasingly predominate as charge carriers.

The change in the type of conductivity can also be explained when the photoreactions of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ are considered. Electronic excitation of the iron(III) complex leads to electron transfer from the SCN^- ligand to the Fe^{3+} centre. The $SCN^\bullet$ radical formed injects a defect electron

TABLE II
Maximum values and kinetic parameters of the PEMF of a pill of adsorbates of $(NMe_3Bn)_3[Fe(CN)_5SCN]$ on $Pb(SCN)_2$ in dependence on the number of flashes ($\vartheta = 1$, $\lambda_{flash} = 337$ nm, ca $2.7 \cdot 10^{13}$ quanta/flash, flash interval 60 s)

Flash No.	U_{max}, mV	U_1^0, V	U_2^0, V	k_1, s^{-1}	k_2, s^{-1}
1	29.2	1.621	–1.592	35.1	34.4
2	8.0	0.487	–0.479	33.5	32.9
3	3.4	0.188	–0.185	33.5	32.9
4	–1.6	[a]	[a]	[a]	[a]
6	–4.2	$-5.4 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	245	46.7
10	–5.5	$-6.3 \cdot 10^{-3}$	$0.8 \cdot 10^{-3}$	179	16.7

[a] The signal shows two zero passages and, therefore, cannot be treated with respect to biexponential time dependence.

into the valence band of $Pb(SCN)_2$. With increasing number of flashes, the photoreaction of the iron(III) complex proceeds, associated with progressive injection of defect electrons into the valence band. This, again, leads to a majority of defect electrons as charge carriers.

The change in the PEMF signal with increasing flash number is irreversible, because the reason for band bending near the surface of the semiconductor is removed, due to the proceeding photoreaction of the iron complex.

Summarizing, it can be concluded that PEMF results confirm the general usability of suitable semiconductors as electron (or defect electron) traps to overcome fast back electron transfer that may diminish considerably the photosensitivity of transition metal complexes, as shown for $(NMe_3Bn)_3[Fe(CN)_5SCN]$ in the presence of semiconducting $Pb(SCN)_2$.

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