Catalysis and Photocatalysis at Polarized Molecular Interfaces: An Electrochemical Approach to Catalytic Processes Based on Two-Phase Systems, Self-Organized Microheterogeneous Structures, and Unsupported Nanoparticles

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I. INTRODUCTION

The main objective of this chapter is to illustrate how fundamental aspects behind catalytic two-phase processes can be studied at polarizable interfaces between two immiscible electrolyte solutions (ITIES). The impact of electrochemistry at the ITIES is twofold; first, electrochemical control over the Galvani potential difference allows fine-tuning of the organization and reactivity of catalysts and substrates at the liquid|liquid junction. Second, electrochemical, spectroscopic, and photoelectrochemical techniques provide fundamental insights into the mechanistic aspects of catalytic and photocatalytic processes in liquid|liquid systems. We shall describe some fundamental concepts in connection with charge transfer at polarizable ITIES and their relevance to two-phase catalysis. In subsequent sections, we shall review catalytic processes involving phase transfer catalysts, redox mediators, redox-active dyes, and nanoparticles from the optic provided by electrochemical and spectroscopic techniques. This chapter also features a brief overview of the properties of nanoparticles and microheterogeneous systems and their impact in the fields of catalysis and photocatalysis.

II. FUNDAMENTAL ASPECTS OF CHARGE TRANSFER AT THE ITIES

Electrochemical processes at the ITIES involve two basic types of elementary reactions: ion transfer and electron tunneling across the liquid|liquid boundary. Depending on the properties of the ionic species and the solvents, these two processes can be accompanied by a variety of phenomena such as solvent exchange, interfacial complexation, adsorption, photoexcitation, acid–base dissociation, etc. There are conceptual as well as practical
issues concerning charge-transfer phenomena and catalytic processes in two-phase systems. In this section, we shall outline an electrochemical framework in which experimental results may be described and discussed.

A. Ion Transfer Reactions at the ITIES

The difference in the activity of an ionic species in a system with two immiscible electrolytes manifests itself in terms of an electrical potential. This term, in analogy to cell membranes, has profound influence on the reactivity and composition of the system. By convention, we shall define $\Delta_{0w}^o$ as the difference in the Galvani potential of the aqueous electrolyte, $\phi^o$, and the organic phase, $\phi^w$, respectively.

\[
\Delta_{0w}^o \phi = \phi^w - \phi^o
\]  
(1)

Let us consider an ion, $i$, with charge $z_i$ present in both liquid phases at equilibrium:

\[
i^i(w) = i^i(o)
\]  
(2)

At constant temperature and pressure, the equilibrium condition is determined by the equality of the electrochemical potentials in water, $\tilde{\mu}_i^w$, and in the organic phase, $\tilde{\mu}_i^o$:

\[
\tilde{\mu}_i^w = \tilde{\mu}_i^o
\]  
(3)

which can be further developed to obtain the Galvani potential difference as a function of the concentration ratio of the ionic species:

\[
\Delta_{0w}^o \phi = \frac{\mu_i^o - \mu_i^w}{z_iF} + \frac{RT}{z_iF} \ln \frac{a_i^o}{a_i^w}
\]  
(4)

where $a_i$ and $\mu_i$ correspond to the activity and the standard chemical potential of the ion in each electrolyte phase. The standard Gibbs energy of ion transfer from water to oil, $\Delta G_{\text{tr},i}^{\text{w,o}}$, is given by the difference in chemical potentials. This term is determined by the difference in the bulk solvation energies of the ionic species. By defining the standard Galvani potential for the ion transfer from water to oil as

\[
\Delta_{0w}^w \phi_i = \frac{\Delta G_{\text{tr},i}^{\text{w,o}}}{z_iF}
\]  
(5)

the corresponding Nernst expression can be obtained [1]:

\[
\Delta_{0w}^w \phi_i = \Delta_{0w}^w \phi_i^o + \frac{RT}{z_iF} \ln \frac{a_i^o}{a_i^w}
\]  
(6)

From this relatively simple expression, a variety of useful considerations can be developed. First, if we consider an ion that is soluble in both phases, the Galvani potential difference can be tuned by changing the concentration ratio of the ionic species. This condition is commonly referred to as an ideally nonpolarizable interface. On the other hand, if the ionic species is strongly insoluble in one of the electrolyte solutions, the corresponding standard transfer potential [see Eq. (5)] will be rather positive or negative, depending on the sign of the charge $z_i$. Consequently, the Galvani potential difference can be varied over a certain range without affecting the concentration ratio of the ionic species. This condition defines ideally polarizable interfaces. We will be employing this terminology throughout this chapter. It should also be considered that when more than one ionic species is involved in the equilibrium condition, and when the phase volume ratio is
significantly different from unity, estimation of the interfacial potentials can be complex [2,3]. These questions are dealt with in a separate chapter [chapter by Prof. Kakiuchi].

In the case where the ionic species in the aqueous electrolyte are fairly hydrophilic and the organic phase features hydrophobic ions, the liquid|liquid junction behaves similarly to an ideally polarizable metal electrode. Under this condition, the Galvani potential difference can be effectively controlled by a four-electrode potentiostat [4,5]. A schematic representation of a typical electrochemical cell is shown in Fig. 1 [6]. Cyclic voltammograms illustrating the potential window for the water|1,2-dichloroethane (DCE) interface for various electrolytes are also shown in Fig. 1. In the presence of bis(triphenylphosphoranylidene)ammonium hexafluorophosphate (BTPPA$^+$ PF$_6$) as the supporting electrolyte in DCE, the potential window is limited to less than 200 mV due to the hydrophilicity of the anion. Wider polarizable potential ranges are obtained on replacing

![Diagram](https://example.com/diagram.png)

**FIG. 1** Typical electrochemical cell employed for electrochemical studies at the polarizable water|1,2-dichloroethane interface. Cyclic voltammograms in the presence of various supporting electrolytes are also illustrated. Polarizable potential windows close to 1 V can be obtained employing Li$_2$SO$_4$ and BTPPA$^+$ TPFB as supporting electrolytes in the aqueous and organic phase, respectively. (From Ref. 6.)
PF₆⁻ by either tetrakis-(4-chlorophenyl)borate (TPBCl⁻) or tetrakis(pentafluorophenyl)borate (TPFB⁻). Figure 2 exemplifies a voltammetric response for a quasireversible transfer of an ionic species taking place within the polarizable window [7]. The position of the voltammetric signal allows determination of the formal transfer potential, from which valuable information such as the Gibbs energy of transfer [Eq. (6)] can be obtained. In the case of a reversible ion-transfer process, the charge of the crossing ion can be calculated from the peak-to-peak separation (ΔEₚ ≈ 59 mV/zᵢ). In the particular case of Fig. 2, the transferring ion zinc meso-tetrakis-(N-methylpyridyl)porphyrin (ZnTPPS) has charge -4, and the ΔEₚ approaches 15 mV. Furthermore, the concentration ratio of the ion at the interfacial region is readily accessible as a function of the Galvani potential difference, Eq. (5). Dynamic parameters such as diffusion coefficients and the phenomenological rate constant of ion transfer can also be evaluated.

The measured current due to an ion transfer from one phase to the other can be expressed as [8–12]

\[ I = z_i F A \left[k c_i^a - k c_i^b\right] \]  

(7)

where \( k \) and \( \bar{k} \) are the forward and backward local ion transfer rate constants in units of cm s⁻¹. This expression describes the flux of ions across two reaction planes “a” and “b” located at each side of the liquid-liquid boundary. The concentration of the ion at the reaction planes can be expressed in terms of the bulk concentrations, \( c_i^a \) and \( c_i^b \), and the potential drop across the corresponding diffuse layers, \( \Deltaφ^a \) and \( \Deltaφ^b \).

\[ c_i^a = c_i^w e^{-z_i F \Deltaφ^a / RT} \]  

(8)

\[ c_i^b = c_i^o e^{-z_i F \Deltaφ^b / RT} \]  

(9)

Substitution of Eqs (8) and (9) into Eq. (7) yields:

\[ I = z_i F A \left[k c_i^w e^{-z_i F \Deltaφ^a / RT} - k c_i^o e^{-z_i F \Deltaφ^b / RT}\right] \]  

(10)

FIG. 2 Cyclic voltammogram of the water-soluble ZnTPPS⁴⁻ transfer at the water/DCE junction. The composition of the cell is as in Fig. 1, employing Li₂SO₄ and BTPPATPFB as supporting electrolytes. The voltammograms were recorded at 10, 20, 40, 60, and 80 mV s⁻¹. The formal transfer potential as well as the diffusion coefficient in the aqueous phase can be readily extracted from the voltammetric signal. Reprinted with permission from Ref. 7. Copyright (1999) American Chemical Society.
If we consider that the potential drop between the reaction planes is negligible [13–15], i.e., the applied potential is effectively developed within the diffuse layer in each phase, Eq. (10) can be rewritten as

\[
I = z_i FA \frac{\alpha z_i F \Delta^w_0 \phi}{k c^w_0 e RT} - \frac{-(1 - \alpha)z_i F \Delta^o_0 \phi}{RT}
\]

(11)

where the term \(\alpha\) corresponds to the fraction of the applied potential developed in the aqueous phase. In analogy to the classical expression in electrodynamics, the standard rate constant for ion transfer, \(k_i^0\), can be defined from the condition:

\[
\frac{\alpha z_i F \Delta^w_0 \phi}{k c^w_0 e RT} = \frac{-(1 - \alpha)z_i F \Delta^o_0 \phi}{RT} = k_i^0
\]

(12)

allowing Eq. (12) to be expressed as

\[
I = z_i FA k_i^0 \left[ \alpha z_i F (\Delta^w_0 \phi - \Delta^o_0 \phi) \right] - \frac{-(1 - \alpha)z_i F (\Delta^o_0 \phi - \Delta^w_0 \phi)}{RT}
\]

(13)

This general expression has been confirmed experimentally by different groups [8,16–19], although deviations have also been observed [20–23]. Questions remain open concerning the physical meaning behind this phenomenological ion-transfer rate constant. For instance, it is still a matter of debate whether ion transfer can be treated as an activated phenomenon or as a transport process through an inhomogeneous media. We have very little knowledge on what the correlations are between the observed rate constant of ion transfer and properties such as solvation distribution and dynamics, surface tension, specific adsorption, local viscosity, and friction forces [24].

It should also be mentioned that the Gibbs energy of ion transfer can be affected by complexation phenomena at the liquid/liquid boundary. A classical example is given by the work of Koryta [25], who studied the transfer of \(K^+\) from water to nitrobenzene assisted by dibenzo-18-crown-6. The complexation step decreases the energy of solvation of the cation in the organic phase, decreasing the formal transfer potential as defined in Eq. (5). Various mechanisms have been proposed for assisted ion-transfer processes, namely, aqueous complexation followed by transfer, transfer followed by complexation in the organic phase, transfer by interfacial complexation, or transfer by interfacial dissociation [26,27].

Despite the lack of a comprehensive understanding of the physical aspects underlying the phenomenological expressions derived previously, they allow characterization of the dynamics of charge transfer employing electrochemical techniques. Conventional techniques such as cyclic voltammetry, chronamperometry, and a.c. impedance have been complemented by more modern approaches including voltammetry at microinterfaces [28–33] and dynamic spectroelectrochemistry [34–43]. All these methodologies can provide valuable insights into the mechanistic aspects of two-phase catalysis involving charged species. As discussed in Section III, electrochemical techniques can provide information on the transfer rate of a phase transfer catalyst by means of Eq. 13. Furthermore, the partitioning of an ionic catalyst can affect the Galvani potential difference as indicated by the Nernst expression, inducing concentration polarization of ionic reactants and substrates (Eqs. 8 and 9).
B. Electron-Transfer Reactions at the ITIES

In many biological systems, electron transfer takes place between redox couples present in media with different dielectric properties. Electrochemical studies at the ITIES enable one to address systematically the effect of polarization and specific properties of the electrolyte medium on the dynamics of electron transfer. This knowledge has particular relevance in processes involving redox phase transfer catalysis.

Let us consider a heterogeneous electron-transfer reaction of the form:

$$O^+_1 + R^-_2 \xrightarrow{k_{ET}} R^+_1 + O^-_2$$

for which the equilibrium condition can be described by the corresponding Nernst equation:

$$\Delta_w^o \phi = \Delta_o^w \phi_{ET}^o - \frac{RT}{nF} \ln \left( \frac{a_{O_1} a_{R_2}^o}{a_{R_1} a_{O_2}^o} \right)$$

where $$\Delta_o^w \phi_{ET}^o$$ is the standard potential for heterogeneous electron transfer, and $$n$$ is the number of electrons transferred in the redox process. The standard potential for heterogeneous electron transfer is determined by

$$\Delta_o^w \phi_{ET}^o = E_{O_2/R_2}^c - E_{O_1/R_1}^c$$

where the bulk phase standard potentials, $$E_{O_2/R_2}^c$$ and $$E_{O_1/R_1}^c$$, are related to the same reference state.

By employing transition-state theory a phenomenological Butler–Volmer equation can be derived for the heterogeneous electron-transfer rate [12,24,44]:

$$I = I_o \left[ e^\beta F(\Delta_o^w \phi - \Delta_o^w \phi^*)/RT - e^{-(1-\beta)F(\Delta_o^w \phi - \Delta_o^w \phi^*)/RT} \right]$$

where

$$I_o = nFk_{ET} c_{O_1}^o c_{R_2}^c$$

In Eq. (17), $$\beta$$ is the fraction of the applied potential acting at the transition state. The exchange current, $$I_o$$, is determined by the concentrations of the reacting redox species, $$c_{O_1}^o$$ and $$c_{R_2}^c$$, and the standard rate constant for the heterogeneous electron transfer, $$k_{ET}$$. Similarly to electrochemical studies of the ion-transfer process, experimental evidence seems to support the behavior described by Eq. (18) [45–48]. However, the significance of the parameter $$\beta$$ is yet to be clarified, as a simplified model of the electrical double layer suggests that the potential drop developed between the redox species at the interface should be relatively insignificant. However, the basic physics in connection with the phenomenological rate constant of electron transfer are better understood than in the case of ion-transfer phenomena. Contributions by Marcus [49–52], Kharkats and Volkov [53,54], and Schmickler [55] in this area can be highlighted.

From the perspective of two-phase catalysis, the relevance of these concepts can be discussed in similar terms to ion-transfer phenomena. For instance, by introducing ions with the appropriate transfer potential, the Galvani potential difference between two immiscible liquids can be adjusted in order to enhance the driving force for interfacial redox processes. Furthermore, a combination of electrochemical and spectroscopic techniques allows unraveling of the interaction between redox catalysts and substrates in the interfacial region [56].
C. Photoinduced Charge-Transfer Processes

Photocatalytic processes in two-phase systems involve either a homogeneous photoreaction followed by the transfer of intermediate species across the interface, or a heterogeneous electron transfer between the photoactive species and the substrate. At the polarizable ITIES, both processes would manifest themselves by an increase in the current on illumination at constant potential, i.e., a photocurrent response. Indeed, photocurrent measurements have been recorded for the transfer of photogenerated ions at a liquid/liquid boundary, as well as for heterogeneous redox quenching. We shall review some of these studies in this section.

According to the Frank–Condon approximation, light absorption by molecules leads to electronic transitions in which the momentum is essentially preserved. The “hot” excited state readily relaxes to thermally equilibrated excited states within picoseconds. Further relaxation phenomena can involve radiative transitions between states of the same spin multiplicity (fluorescence) or different multiplicity (phosphorescence). Excited states can also undergo intersystem crossing, where the system changes from a state of high to low spin multiplicity. A schematic diagram of the photophysical phenomena and characteristic lifetimes for zinc tetraphenylporphyrin is displayed in Fig. 3 [57]. From the kinetic point of view, all these phenomena are in competition with unimolecular photochemical reactions such as isomerization and bond cleavages, as well as bimolecular processes involving energy and electron transfers.

From Fig. 3, it is clear that the reactivity of molecules in the excited state is directly linked to lifetimes. In general, the redox potentials of an excited state, $E_{S^+/S^-}$ and $E_{S^+/S^-}$, can be expressed in terms of the ground state redox potentials, $E_{S^+/S}$ and $E_{S^+/S^-}$, as

$$E_{S^+/S^-} = E_{S^+/S} - E^*$$

$$E_{S^+/S^-} = E_{S^+/S^-} + E^*$$

FIG. 3 Jablonski energy level diagram for a regular porphyrin, illustrating the photophysical transitions and corresponding time scales for excitation at the Soret ($S_0 \rightarrow S_2$) and Q-bands ($S_0 \rightarrow S_1$).
where $E^*$ is the characteristic energy of the excited state. If electron transfer can effectively compete with vibrational relaxations, leading to thermally equilibrated excited states ("hot" electron transfer), $E^*$ corresponds to the wavelengths of excitation. These phenomena have been observed in dye-sensitized metal oxides [58–63]. However, electron transfer commonly involves relatively long-living excited states such as the first singlet ($S_1$) or triplet states ($T_1$). Figure 4 shows the redox potentials associated with the ground state and $T_1$ for the dye ruthenium (II)-trisbipyridine Ru(bpy)$_3^{2+}$ [57].

As we mentioned previously, photoinduced electron transfer at the polarizable liquid/liquid junction manifests itself by photocurrent responses under potentiostatic conditions. The nature of the photoelectrochemical processes is reflected in the basic features of the photocurrent transient. For instance, a homogeneous photochemical reaction followed by the transfer of the products is characterized by a slow increase in the photocurrent on illumination. A typical example can be extracted from the work of Kotov and Kuzmin shown in Fig. 5(a) [64–66]. In this case, protoporphyrin is located in the organic phase in the presence of benzoquinone. On illumination, the quinone is reduced and the radical anion transfers to the water phase. The increasing photocurrent is connected with the flux of the radical anion from DCE to water.

The rather slow transients observed in the previous case can be contrasted with the relatively fast photocurrent response arising from heterogeneous redox quenching [see Fig. 5(b)] [7,24,56,67–69]. In this case, the ion pair formed by zinc meso-tetrakis-(p-sulfonatophenyl)porphyrin (ZnTPPS$^{4-}$) and zinc meso-tetrakis-(N-methylpyridyl)porphyrin (ZnTMPyP$^{4+}$) located in the aqueous phase is reductively quenched by decamethylferrocene (DCMFe) present in the DCE phase [7]. In this case, the observed photoresponse results from competition between the decay of the excited state and the rate of heterogeneous electron transfer. The magnitude of the photocurrent increases as the Galvani potential difference is shifted to more positive values.

The general mechanism associated with heterogeneous photoinduced electron transfer is highlighted in Fig. 6. Considering the efficiency of intersystem crossing in zinc porphyrins, it is expected that the electron transfer takes place from the excited state $T_1$. The dependence of the photocurrent on the applied potential indicates that the electron transfer step is in competition with the decay of the excited state. The relationship between the phenomenological $k_e$ and the driving force for electron transfer has been described in terms of the Marcus expression for electron transfer between redox species separated by a sharp change in the dielectric medium [70].

Depending on the redox properties of the quencher and the Galvani potential difference, back electron-transfer reactions can occur [56,69–71]. The back electron transfer manifests itself as relaxation after the initial photocurrent. The rather small relaxation

![FIG. 4 Latimer diagram for Ru(bpy)$_3^{2+}$. The excited state corresponds to a triplet metal-to-ligand charge transfer state.](image)
observed in the photocurrent transient of Fig. 5(b) reveals an efficient separation of the photoproducts. Dynamic photoelectrochemical measurements including photocurrent transients and intensity modulated photocurrent spectroscopy (IMPS) have provided valuable insights into the dynamics of photoinduced electron transfer as well as back charge-transfer phenomena [69,71].

Photoelectrochemical studies have also revealed information on the molecular organization of dyes at interfaces. Photoresponses are essentially connected to the heterogeneous quenching of specifically adsorbed dyes at the liquid|liquid boundary [72,73]. For instance, zinc meso-tetracarboxyphenylporphyrin self-assembles at the water|DCE junction via the formation of co-operative hydrogen bonds. The coverage as a function of the applied Galvani potential difference has been estimated from the photocurrent dependence on the concentration [68]. Furthermore, photocurrent measurements employing linearly polarized light in total internal reflection allowed estimation of the average orientation of the transition dipole of the adsorbed photoactive dye.

The detailed information about organization and reactivity of dyes obtained from photoelectrochemical approaches has been complemented by a variety of spectroscopic techniques including second-harmonic generation [74], dynamic fluorescence [42,43], and quasielastic laser scattering [75]. Indeed, one of the most appealing aspects of modeling photocatalytic processes in a system with two liquid phases is the diversity of experimental techniques at hand. These techniques not only allow characterization of the kinetics of charge-transfer phenomena, but also the interfacial organization of photocatalysts.
III. CATALYTIC REACTIONS AT LIQUID|LIQUID INTERFACES

One of the main aspects behind two-phase catalysis is the synergism of homogeneous and heterogeneous catalysts. Homogeneous catalysis has the advantages of high activity and selectivity, mild reaction conditions, low sensitivity to catalyst poisoning, effective mass transfer, and the possibility of varying the steric and electronic properties of the catalyst [76]. Heterogeneous catalysis features long service life of the catalyst and the ease of separating the catalyst from the products. An effective combination of the two approaches consists of separating the catalyst and the substrates by a liquid|liquid boundary [77]. In principle, this configuration can overcome the difficulty often found in homogeneous catalysis of separating and recovering the catalyst after the reaction. A common configuration features the catalyst in the aqueous phase, while the substrate is located in the organic phase. A great deal of recent interest has been directed towards synthesizing water-soluble ligands and metal complexes to transfer the traditional homogeneous catalysts into an aqueous environment [76,78].

The use of a two-phase system can also have some other advantages in addition to the catalyst-separation issues. A liquid|liquid system can be used to catalyze a reaction which would be very unfavorable in a homogeneous medium due to large differences in the solvation energies of substrates and products. Substantial changes in heterogeneous reaction kinetics can be brought about either by an appropriate choice of solvents, tuning the Galvani potential difference along with redox properties of the reactants [79], or by inhibiting undesired processes [80].

A. Catalytic Studies at Polarizable Liquid|Liquid Interfaces

As we described in Section II, control over the Galvani potential difference allows tuning of the distribution, organization, and reactivity of species at the liquid|liquid boundary. This

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**FIG. 6** General mechanism for photoinduced heterogeneous electron transfer at dye-sensitized liquid|liquid interfaces. The electron transfer from the excited state is in competition with the relaxation process. In addition, the intermediate generated after the electron-transfer step can undergo back electron transfer or dissociate at the interface. In the case of water-soluble porphyrins at the water|DCE junction, the orders of magnitude of the phenomenological rate constants are indicated in the figure. The photoinduced electron transfer is denoted as a pseudo-first order process with respect to the excited state (k_e). Reprinted with permission from Ref. 7. Copyright (1999) American Chemical Society.
property is useful in the particular case where the interfacial catalyst is charged. Classical examples of ionic catalysts include phase transfer catalysts, which shall be discussed in more detail in the next section. Another powerful aspect concerning the electrochemical approach to two-phase catalysis is the possibility of real-time monitoring of the rate of the interfacial reaction, employing a variety of techniques such as chronoamperometry, chronopotentiometry, cyclic voltammetry, a.c. impedance, and more recently, scanning electrochemical microscopy (SECM) [81]. Electrocatalysis in this case is defined as a catalytic reaction involving electron or ion transfer, which takes place at the liquid|liquid interface between reagents located in different phases, and which requires an interfacial potential.

Despite the usefulness of the ITIES concepts, only very few studies have been published on mechanistic evaluations of catalytic processes at liquid|liquid interfaces. One of the few was presented by Cheng and Schiffrin [82], who employed cyclic voltammetry for studying the behavior of redox mediators at a polarizable water|DCE junction. This work described the effect of modifying the liquid liquid boundary by an adsorbed monolayer of phospholipids on the electron-transfer rate between a hexacyanoferrate couple in water and tetracyanoquinodimethane (TCNQ), lutetium bisphthalocyanine [Lu(PC)2], and bis(pyridine)-meso-tetraphenylporphyrinato–ruthenium(II) [Ru(TPP)(py)2] in DCE. The electron-transfer rate to TCNQ was noticeably decreased, while the electron transfer to Lu(PC)2 or Ru(TPP)(py)2 appeared totally hindered in the presence of the phospholipid layer. The hindrance effect of the surfactant was rationalized in terms of an increase in the tunneling distance between the redox couples at the interface. However, for a system containing both TCNQ and Ru(TPP)(py)2 in the organic phase, a voltammetric response with two waves was observed. This behavior suggests that the electron transfer between Ru(TPP)(py)2 and the hexacyanoferrate couple is effectively mediated by TCNQ. The redox mediation is connected to the ability of TCNQ to penetrate the phospholipid layer, and act as an electron shuttle between both phases.

Another form of two-phase redox electrocatalysis was discussed by Shao et al. [83], who employed the ITIES as a model system to investigate the mechanism and kinetics of complex catalytic microemulsion reactions. The problem in studying electrochemical kinetics in microemulsions is the lack of a well-defined interfacial area, and this can be circumvented by the use of the ITIES. The SECM technique was used to probe the reaction between the electrochemically generated aqueous Co(I) form of vitamin B12 and trans-1,2-dibromocyclohexane in benzonitrile. The effects of reactant concentration, Galvani potential difference, and surfactant adsorption on the electron-transfer kinetics were investigated. Kong and Kakiuchi [84] studied the nucleophilic substitution reaction of 2,4-dinitrofluorobenzene with hydroxide ions. Previously, this reaction has been studied in homogeneous and micellar systems. They successfully used d.c. polarography and cyclic voltammetry at a polarized water|nitrobenzene interface to obtain mechanistic information on the reaction.

A recent work by Chung and Anson [85] revealed interesting catalytic effects on the oxygen reduction on graphite electrodes modified by thin benzonitrile layers containing meso-tetraphenyl cobalt porphyrin (CoTPP). As depicted in Fig. 7, the current associated with oxygen reduction increases on deposition of a thin layer of benzonitrile on the graphite electrode. This increment of the current is associated with the larger solubility of oxygen in the organic layer. Furthermore, a net enhancement of the four-electron oxygen reduction over the two-electron pathway was observed in the presence of the benzonitrile layer. These results were initially rationalized by postulating that the organic layer effectively protects active sites on the graphite electrode from electroreduction processes that may take place in aqueous media. The results in voltammograms (b) and (c)
indicate that the CoTPP can effectively catalyze the oxygen reduction when dissolved in the benzonitrile thin layer. The CoTPP in the acidic environment is involved in a multi-electron transfer cycle that catalyzes the four-electron process. Although some of these interpretations may require independent experimental verification, the results do open new areas for two-phase redox electrocatalysis.

B. Electrochemical Approach to Phase Transfer Catalysis

Several chapters in this book are devoted to phase transfer catalysis (PTC), highlighting conventional as well as novel approaches to this important process. In this section, we shall look at these phenomena from the viewpoint of electrochemistry in two-phase systems.

A key point to realize is that quaternary ammonium salts commonly employed as PT catalysts exhibit a finite solubility in aqueous as well as in a variety of organic solvents. According to Eq. (5), the partitioning of an ion induces a Galvani potential difference between the electrolyte phases, which is determined by the difference in the solvation energies of the ion. Similar ions have been used for electrochemical studies at the ideally nonpolarizable ITIES [86,87].

Based on these ideas, Cunnane et al. [88] compared the oxidation of tin diphthalocyanine [Sn(PC)₂] in the DCE phase by aqueous ferri/ferrocyanide redox couple under external polarization and in ideally nonpolarizable conditions. Good correlation for the formal redox potential measured in each case was observed. One of the main conclusions of this work is that the role of “PT catalysts” can be simply associated with polarization of the two-phase system, resulting in an enhancement of the interfacial concentration of the

FIG. 7 Cyclic voltammograms of oxygen reduction at modified pyrolitic graphite electrodes. (a) Voltammograms for the naked graphite electrode (curve 1) and in the presence of a thin layer of benzonitrile (BN) (curve 2) are shown for oxygen-saturated HClO₄ electrolyte solution. The dashed line corresponds to Ar-saturated solutions in the presence of the BN layer. (b) Voltammograms obtained for a 6 x 10⁻⁶ mol cm⁻² layer of CoTPP deposited on the graphite electrode, in the presence (full line) and absence (dashed line) of oxygen. Finally, the cathodic current (plotted upwards for all curves) is further increased on depositing a thin layer of BN on the CoTPP-modified graphite electrode. Reprinted from Ref. 85 with permission from Elsevier Science.
reactants or an increase in the driving force for the charge-transfer process. Tan et al. [89] successfully applied the above formalism in the study of the Williamson ether synthesis and concluded that the PT catalyst salt established a Galvani potential difference, which in turn acted as the driving force for transferring the reactive aqueous ions to the organic phase.

Kong et al. [90] applied the electrochemical approach to the study of a two-phase azo coupling facilitated by reverse PTC. Cyclic voltammetry and chronoamperometry were employed to evaluate quantitatively the rate constants for the reaction. The process was interpreted in terms of an EC mechanism, i.e., diffusion-controlled electrochemical charge transfer followed by a homogeneous chemical reaction. The authors highlighted the usefulness of this approach based on the factors that enable the estimation of the contributions of the chemical reaction, mass transfer, partitioning, and the adsorption of reactants at the interface to the overall two-phase reaction.

In a similar line of research, Forssten et al. [91] investigated the formation of 2-hydroxy-3-methylbutyric acid (ROH) from 2-bromo-3-methylbutyric acid (RBr) at a water|DCE interface. This $S_n2$ reaction in two-phase systems can be represented as

$$
(CH_3)_2CHBrCOOH_{(o)} + OH^-_{w} \rightarrow (CH_3)_2CHOHCOOH_{(o)} + Br^-_{w})
$$

which can be catalysed in the presence of $I^-_{w}$ by following the cycle:

$$
(CH_3)_2CHBrCOOH_{(o)} + I^-_{w} \rightarrow (CH_3)_2CHICOOH_{(o)} + Br^-_{w})
$$

$$
(CH_3)_2CHICOOH_{(o)} + OH^-_{w} \rightarrow (CH_3)_2CHOHCOOH_{(o)} + I^-_{w})
$$

Figure 8 illustrates the effect of increasing the concentration of RBr in the organic phase on the cyclic voltammogram responses in the presence of $I^-$ in the aqueous phase. As the concentration of RBr is increased, the voltammetric signal associated with the transfer of $I^-$ is shifted toward more negative potentials. Indeed, in an excess of RBr the transfer signal approaches the transfer potential of Br$^-$ (trace 5). In order to rationalize this behavior, a combination of two ECE mechanisms was postulated. The first sequence involves the transfer of $I^-$ (electrochemical step), followed by the homogeneous

![Figure 8](image-url)

**FIG. 8** Effect of 2-bromo-3-methylbutyric acid concentration (RBr) on $I^-$ transfer at a water|DCE interface. The compositions for the curves were: $[I^-] = 1$ mM, $[RBr] = 0$ (1); $[I^-] = 1$ mM, $[RBr] = 1$ mM (2); $[I^-] = 1$ mM, $[RBr] = 2$ mM (3); $[I^-] = 1$ mM, $[RBr] = 4$ mM (4); $[I^-] = 0$, $[Br^-] = 1$ mM (5); $[I^-] = [RBr] = 0$ (6). It is observed that the ion-transfer signal shifts from the transfer potential of $I^-$ in (1) to the transfer potential of Br$^-$ (5), with increasing concentration of RBr. Reprinted from Ref. 91 with permission from Elsevier Science.
reaction (22) (chemical step) and the second electrochemical step is the transfer of $\text{Br}^-$ to the aqueous phase. The other ECE mechanism corresponds to the assisted transfer of $\text{OH}^-$ to the organic phase, homogeneous substitution of the $\Gamma^-$ [step (23)], and transfer of the last to the aqueous phase. Simulation of this mechanism yielded results compatible with the experimental trends. Furthermore, the reaction was also induced by partitioning of the tetraphenylphosphonium ion, which establishes the appropriate Galvani potential difference for the reaction to take place according to the voltammetric studies, and the formation of the final products was confirmed by NMR spectroscopy.

More recently, Forssten et al. [92] employed a similar approach to study the oxidation of cis-cyclo-octene by permanganate at a water|DCE junction. As in the previous case, the redox species in the aqueous phase is driven in and out of the organic phase by a linear sweep of the Galvani potential difference. However, the homogeneous reaction is rather slow, and the amount of permanganate consumed during the potential cycle appears insignificant. In order to increase the transient time of permanganate in the organic phase, a pre-electrolysis step was applied, in which the potential was held for a fixed period of time in the region where the transfer of permanganate was diffusion controlled. Subsequently, the potential was cycled to positive values, transferring the remaining permanganate back to the aqueous phase. From the current associated with the back transfer of permanganate and the pre-electrolysis time, the rate of the homogeneous reaction was estimated. Indeed, the recent works by Forssten et al. [92,93] and Kong and coworkers [84,90] provide an elegant illustration of how electrochemical analysis can deliver valuable kinetic information on PTC processes.

IV. PHOTOCATALYSIS AT DYE-SENSITIZED MOLECULAR INTERFACES

In Section II.C, we described the reactivity of adsorbed dye species at liquid|liquid junctions in heterogeneous photoredox reactions. The properties of these systems can be used to catalyze electron-transfer processes. The behavior of dyes at interfaces has been vigorously studied in micelles and microemulsion systems, and many excellent reviews and books are available on this subject [94–97]. In this section, we shall consider some basic aspects of photoprocesses in microheterogeneous systems that are relevant to polarizable ITIES. This is not intended to cover comprehensively the recent developments in the active area of photochemistry at organized assemblies, but to highlight how spatial confinement, hydrophilic–hydrophobic forces, and local potentials can affect the course of a photochemical process. We shall also revise some recent developments in photocatalysis and photosynthesis at polarizable liquid|liquid interfaces, highlighting advantages and limitations in relation to two-phase catalysis.

A. Photocatalysis Employing Dyes at Organized Assemblies

Due to the tremendous impact of photocatalysis in the area of environmental chemistry, photocatalysts are mainly associated with colloidal suspensions of metal oxides, in particular $\text{TiO}_2$ [98–101], or with iron chloride solutions in the presence of hydrogen peroxide, also known as Fenton reagent [102–104]. Dye species can also behave as photocatalysts either by generating singlet oxygen via energy transfer to molecular oxygen, or by direct electron transfer involving excited states. For the latter mechanism, the ground state of the dye species must be regenerated after the redox step; therefore, this approach is essentially constrained to single electron-transfer reactions. Semiconducting nanoparticles with high
dielectric permittivity, e.g., TiO₂, are best suited for multielectron transfer processes due to their ability of storing charge within the nanocrystal structure. We shall come back to the catalytic properties of nanoparticles in the next section. However, the possibility of fine-tuning the hydrophilicity of dye species provides an effective tool for designing photocatalytic processes at water/oil systems.

Photoredox reactions at organized assemblies such as micelles and microemulsions provide a convenient approach for modeling life-sustaining processes. Micelles are spontaneously formed in solutions in the presence of surfactants above a certain critical concentration. In aqueous solutions, the hydrophobic tails of the surfactant form aggregates with the polar head facing toward the aqueous environment, as depicted in Fig. 9. The hydrophobic core in micelles is amorphous and exhibits properties similar to a liquid hydrocarbon. The polar heads are also randomly oriented, generating an electrical double layer around the micelle structure. In this respect, surface properties of micelles can be somewhat correlated with the polarized ITIES. The structure of micelles is in dynamic equilibrium, in which monomers are exchanged between bulk solution and the assembly.

The general features of micelles and reversed micelles (polar head buried in, with the hydrophilic tail pointing out to a low dielectric medium) can enhance the separation of photoproducts in different fashions. One of the best known examples is the effect of the surfactant cetyltrimethylammonium chloride (CTAC) on the photoreduction of C₁₄V²⁺⁺ by Ru(bpy)₃⁺⁺ [105]. As schematically depicted in Fig. 10(a), the radical C₁₄V⁺ is extracted into the inner core of the micelle due to its hydrophobic character. The oxidized Ru(bpy)₃⁺⁺ is electrostatically repelled away from the positively charged micelle, decreasing
the probability of back electron transfer. As a result, the product lifetime is increased by a factor of 20 with respect to the bulk homogeneous process.

The viologen reduction by EDTA in reverse micelles in the presence of Ru(bpy)$_2$$^+$ is another example of vectorial photoinduced electron transfer [106]. The accumulation of photoproducts is associated with the catalytic cycles depicted in Fig. 10(b). The oxidative quenching of the ruthenium complex occurs at the micelle outer boundary, while the regeneration of the dye takes place by the oxidation of EDTA in the inner core of the micelle. The reduction of the final product 4-dimethylaminoazobenzene is further mediated by the acceptor 1-benzylnicotinamide (BNA$^+$). In Fig. 10(c), the photocatalytic reduction of methyl benzoyleformate (MBF) by thiosulfate is described in the presence of the porphyrin ZnTPPS and the mediator quinolinium-3-carboxiamide (DCA$^+$) [107]. This sequence of reactions occurs only in micelles such as those formed by hexadecyltrimethylammonium bromide, which contain in the interior the ultimate donor acceptor. Under illumination, ZnTPPS photoreduces DCA$^+$ to DCQ, which is subsequently extracted into the micelle core. Within the microenvironment, DCA$^+$ is regenerated via reduction of MBF, while the oxidized porphyrin is reduced by thiosulfate outside the micelle.

Efficient photocatalytic processes have also been studied in water-in-oil (W/O) and oil-in-water (O/W) microemulsions. W/O microemulsions are readily prepared in C$_5$–C$_8$
$n$-alkanes in the presence of surfactants with a rather hydrophobic character such as sodium bis-(2-ethylhexyl) sulphosuccinate. The basic structure can be regarded as a small water pool entrapped by the surfactant in the alkane solvent. The differentiation between reversed micelles and W/O emulsions could be ambiguous, but in general the radii of the former are of the order of 10–20 Å while for the latter the radii are above 200 Å. Willner and Joselevich [108] have compared the oxidation of tributylamine by Fe(CN)$_6^{3-}$ in the presence of eosin (Eo$^2^-$) and ethyl eosin (EoEt$^-$). The optical transient response at 460 nm, which corresponds to the oxidized form of the dyes, is depicted in Fig. 11(b). It can be observed that the concentration of the oxidized Eo$^2^-$ sharply decreases on illumination, while a steady-state concentration of the EoEt is clearly observed. These observations are rationalized in terms of the mechanism depicted in Fig. 11(a), in which the back electron transfer from Fe(CN)$_6^{4-}$ to the oxidized eosin is in competition with the transfer from the water inner core to the organic phase. In the case of EoEt$^-$, the radical formed after the photoinduced electron transfer is rather hydrophobic and is efficiently extracted from the water pool prior to the back electron-transfer phenomenon. In the organic medium, EoEt$^-$ is regenerated by tributylamine followed by transfer back to the water pool.

Through these well-known examples the effect of three basic features of organized assemblies can be visualized: (1) inhomogeneous solvation properties, (2) interfacial potentials, and (3) spatial confinement. Apart from the last, the other aspects can be finely controlled at the polarizable ITIES. As we have seen in Section II, the Galvani potential difference not only affects the dynamics of photoinduced electron transfer, but also the concentration ratio of ionic species.

**FIG. 11** (a) Schematic representation of electron transfer across a W/O microemulsion based on the “shuttle photosensitizer” mechanism. (b) Transient absorption of the oxidized form of the sensitizer eosin (Eo$^2^-$) and ethyl eosin (EoEt$^-$) after a 9 ns pulse in the presence of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ and tributylamine (Bu$_3$N). The faster decay observed for Eo$^2^-$ is connected to back electron transfer phenomena within the hydrophilic emulsion core. Reprinted with permission from Ref. 108. Copyright (1999) American Chemical Society.
B. Photosynthesis and Photocatalysis at the Polarizable ITIES

The previous example illustrated how microheterogeneous systems can affect the efficiency of charge separation following a photoredox process. These processes cannot be unambiguously defined as photocatalytic or photosynthetic unless the overall change in the Gibbs free energy is dealt with in a quantitative fashion. This can be complex as not only the redox potentials, but also the changes in solvation energy associated with the ionic and neutral species crossing the interfacial boundary have to be accounted for. From an academic point of view, the possibility of tuning the Galvani potential difference and accurate knowledge of the transfer potential of the ionic species provide a unique framework for characterizing the energy balance of photosynthetic and photocatalytic reactions.

![Diagram of photocurrent transient responses associated with the heterogeneous quenching of the dimer ZnTPPS/ZnTMPyP by tetracyanoquinodimethane (TCNQ) at a water/DCE interface. The redox couple Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ was used as supersensitizer in the aqueous phase. The back electron transfer reaction, responsible for the photocurrent decay in the on-transient, is significantly quenched in the presence of the supersensitizer. According to the redox diagram in (b), the overall process at $\Delta\phi = -0.11$ V corresponds to the reduction of TCNQ by the redox couple in the aqueous phase photocatalyzed by the porphyrin complex. Reprinted from Ref. 109 with permission from Elsevier Science.](image)

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The photoinduced reduction of TCNQ by the porphyrin heterodimer ZnTPPS–ZnTMPyP provides a good illustration of these concepts [56,109]. Figure 12(a) displays photocurrent transients at the water|DCE junction in the presence and absence of an equimolar ratio of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$. The photocurrent relaxation in the absence of the aqueous redox couples is associated with the back electron transfer from TCNQ$^-$ to the oxidized porphyrin complex. The substantial decrease in back electron transfer on addition of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ is associated with the supersensitization phenomenon schematically depicted in Fig. 12(b). The back electron transfer from the radical TCNQ$^-$ to the oxidized porphyrin complex is in competition with the regeneration of the dye by ferrocyanide. In the absence of back electron transfer, the overall reaction involves electron transfer from the redox species in the aqueous phase to TCNQ. In this case, the energetic balance is determined by the Galvani potential difference across the interface.

From the redox potentials illustrated in Fig. 12(b), it is clear that, for the photoresponses obtained at potentials more negative than $-0.07 \text{ V}$, the overall reaction can be considered as a photocatalytic process. The heterogeneous reduction of TCNQ by ferrocyanide across the water|DCE interface is a quasireversible process featuring a phenomenological bimolecular electron transfer of the order of $10^{-22}$ cm$^4$ s$^{-1}$ [47,48]. On the other hand, the heterogeneous redox quenching of the porphyrin heterodimer by TCNQ can be estimated to be close to $10^{-20}$ cm$^4$ s$^{-1}$ [7,56,109]. Considering that the rate-determining step is the heterogeneous electron transfer step, the net increase in the reaction rate is due to the larger driving force for the forward electron in the presence of the adsorbed dye.

Despite the simplicity of the electrochemical approaches to photoinduced reactions at the ITIES, very few studies can be found dealing with dye-sensitized interfaces. An interesting point to be revisited is the dynamics and energetics associated with the classical processes exemplified in Fig. 10. As we mentioned earlier, the distribution of ionic species can be tuned by the Galvani potential difference, providing a highly effective tool for manipulating the rate of the overall process.

V. CATALYTIC AND PHOTOCATALYTIC PROPERTIES OF NANOPARTICLES AT THE ITIES

A. Catalytic Properties of Metal Nanoparticles and Colloids in Solution

Decrease in the size of a metal particle below a critical dimension results in dramatic changes in the electronic properties of the bulk metal. Properties like conductivity, magnetism, light absorption, luminescence, electrochemical, and catalytic activity depend on the particle size. Many heterogeneous catalysts are based on finely divided metal particles on various supports. However, this section deals with the catalytic properties of unsupported nanoparticles.

Metal nanoparticles can be prepared in a myriad of ways, e.g., by pulse radiolysis [110], vapor synthesis techniques [111], thermal decomposition of organometallic compounds [112], sonochemical techniques [113,114], electrochemical reduction [115,116], and various chemical reduction techniques. Some of the most frequently used reducing agents include alcohols [117,118], citrate [119,120], H$_2$ [121], borohydrides [122], and, more recently, superhydride [123]. The chosen experimental conditions determine the size, size distribution, shape, and stability of the particles. Because naked metal particles tend to aggregate readily in solution, stabilizing the nanoparticles is the key factor for a successful synthesis. Sometimes the solvent can act as a stabilizer, but usually polymers and surfac-
tants and, more recently, ligands and monolayers, have been used for this purpose. An important point is that the catalytic properties of the nanoparticles, including selectivity and activity, could be affected by the choice of the stabilizer [124]. Also, the solubility of the nanoparticles depends on the nature of the stabilization. Generally, hydrophilic ligands yield water-soluble colloids and hydrophobic ligands yield colloids in organic solvents.

Catalysis involving unsupported colloids has been referred to as “heterogeneous catalysis in solution” [125]. In addition to the size-dependent electronic properties, the fraction of catalytically active surface atoms in nanoparticles is exceptionally large. Furthermore, reactions at the surface of small particles can be surface controlled whereas reactions at a large plane surface may be diffusion limited [126]. Differences between one metal colloid and another arise because of a number of factors: the particular energy and symmetry of orbitals of the surface atoms and the cohesive energy of the particle [127]. In general, colloidal metals can be regarded as convenient pools into, and from, which electrons may be readily transferred. They can be described as nanoelectrodes in solution.

Most of the studied reactions take place in a “one-phase” environment, i.e., the catalyst colloid and other reactants are dissolved in the same solvent or solvent mixture. Hydrogenation reactions are the most extensively investigated organic reactions catalyzed by unsupported metal, especially polymer-stabilized Pt [128–130] or Pd [131–133] colloids. Polymer-stabilized Pt has been found to have more than five times higher activity than a carbon-supported Pt catalyst with increased selectivity for partial hydrogenation of allyl alcohol [134]. The regioselective [135] and enantioselective [136] properties of these catalysts in hydrogenation reactions have gained attention. Very recently, it was shown with para-hydrogen-induced polarization NMR that, in the case of the hydrogenation of phenylacetylene mediated by colloidal Pd catalyst, the reaction follows a homogeneous pathway [137].

In the last few years, a significant amount of research has been carried out on Pd colloids as catalysts for Heck reactions, and the most recent literature is focused on the correlations between the structure of the colloidal catalyst and the catalytic performance [138–141]. Other reactions for which the metal colloids have proven to be useful include hydrosilylations [142], isomerizations [128], and Suzuki reactions [124].

The excellent electron-transfer mediator properties of nanoparticles find special use in the different oxidation [126] and reduction [143,144] reactions catalyzed by noble metal colloids. Recently, Ung et al. [145] showed how Ag particles coated with a thin layer of silica act as redox catalysts, and how the control of the rate of the catalyzed hydrogen evolution reaction was possible by tuning the silica shell thickness. It was concluded that the shell acts as a size-selective membrane, which can be used to alter the chemical yields for competing catalytic reactions. This kind of tailoring of the catalyst properties opens up very interesting prospects in future catalyst planning.

Successful tailoring of the metal nanoparticle catalyst has also been achieved by the use of discrete, well-defined polymers called dendrimers as stabilizers. Dendrimers offer effective stabilization against agglomeration, and due to the steric nature of the stabilization a substantial fraction of the particle surface is unpassivated and available for catalytic reactions. Dendrimer branches can be used as selective gates to control access of substrates to the nanoparticle surface, and the terminal groups on the dendrimer can be modified to control the solubility of the catalyst. The hydrogenation reaction rate could be controlled by using dendrimers with different porosities. The use of different stabilizing dendrimers also makes selective catalysis possible [146].
Bimetallic nanoparticles have interesting scientific and technological properties in relation to catalysis. Bimetallization can improve catalytic properties of monometallic catalysts or create completely new assets. The new effects can often be explained with ensemble or ligand effects in catalyses [147]. The chemical preparation of bimetallic particles can be achieved by two strategies: coreduction or successive reduction of two metal salts. The latter is used for preparing “core–shell” structured bimetallic nanoparticles. Unsupported colloidal bimetallic nanoparticles have been used to study hydrogenation [148,149] and hydration [147] reactions. The activity and selectivity of the catalyst was improved compared to that of a monometallic catalyst.

Colloidal catalysts tend to precipitate in homogeneous processes [150]. This can be observed by the appearance of black metal residues in the system. This causes catalyst losses and decrease in the catalyst activity. Another significant problem in “one-phase” colloid catalysis is the recovery of the catalyst. Although in some cases the nanoparticle catalyst can be recycled several times by membrane filtration [151], most authors do not report on catalyst recycling. One possible solution is the use of two-phase systems. For example, aqueous Rh colloids were shown to be effective hydrogenation catalysts in a two-phase system, where the water immiscible phase was olefin [152]. The colloidal catalyst could be readily separated and recycled. It was shown that surfactants could be used to lower the interfacial tension to improve the efficiency of the two-phase system [153,154].

Another possibility, taking advantage of the biphasic environment, is to use fluorous organic solvents as the catalyst phase instead of water [155]. Crooks and coworkers prepared dendrimer-stabilized colloid catalysts soluble in the fluorous phase and used the catalysts in hydrogenation [156] and in a Heck reaction [157]. In both cases the colloidal catalyst in the fluorous phase was recyclable and showed some interesting selectivities and products unique to the nanoenvironment in the dendrimer interior.

The interface between two immiscible electrolyte solutions offers the means to combine two-phase catalysis, colloid catalysts, and electrocatalysis. In the study of Lahtinen et al. [158] citrate-stabilized palladium and gold colloids were prepared by a traditional chemical reduction method. The voltammetric response of a system with an aqueous colloid and an electron donor in the organic phase revealed an irreversible voltammetric wave as the potential was swept positive. The response was detected only in the presence of both the colloid and the electron-donor DCMFc. The response was concluded to result from heterogeneous charging of the colloid with electrons from DCMFc.

The electrophoretic mobility of the particles was determined to confirm the buildup of negative charge on the colloid. In these measurements, the potential difference across the liquid-liquid interface was controlled by potential-determining ions. It was shown that the charge on the colloid was dependent on the concentration of the electron-donor DCMFc. The results clearly showed that the metal colloid was charged in the two-phase process.

Finally, catalytic experiments were conducted in order to establish whether the charged colloids can be used as an electron source in organic reactions. Dehalogenation of 2-bromoacetophenone (BrAc) was used as the model reaction. The experiments were carried out in a similar fashion to the charging experiments. In addition to the electron-donor DCMFc and the supporting electrolyte, the organic phase contained BrAc. The mixture was stirred for 2 h to achieve a conversion to acetophenone. These results showed the usefulness of this approach as a new type of two-phase catalysis. Figure 13 presents a tentative catalytic cycle where the catalyst can be separately charged, brought in contact with the substrate, stirred effectively, and, after the reaction, the catalyst can be easily separated from the reaction mixture and regenerated for another cycle.
B. Electrochemically Generated Particles as In Situ Catalysts at the ITIES

In the standard chemical preparation methods, the properties, especially the size and size distribution of the nanoparticles, are defined by the choice of the reaction conditions, reactant concentrations, etc. The use of electrochemical techniques to generate nuclei has the advantage that the supersaturation is determined by the applied potential or current density. Thus, the size of the particles can be controlled by electrochemical instrumentation rather than by changing the experimental conditions. Reetz and Helbig [115] demonstrated how electrochemical methods can be used to produce metal colloids of nanometer size and more importantly how particle size can be controlled in a simple manner by adjusting the current density [159]. First, a sacrificial anode was used as the source of the metal ions, which were then reduced at the cathode. Later, a more general approach was introduced, where metal salts were used as the starting material [160]. The particles were stabilized by alkylammonium or betaine salts. With a suitable choice of surfactants, the electrochemical method can be applied in the preparation of different shapes of particles, e.g., nanorods [161].

Metal nanoparticles can also be synthesized at a polarized liquid/liquid interface. As a matter of fact, the first experimental evidence for heterogeneous electron transfer at an externally biased ITIES featured the electrodeposition of copper and silver [162]. More recently, Cheng and Schiffrin [163] demonstrated the formation of gold nanoparticles at the ITIES by reducing tetracyctylammonium tetrachloroaurate dissolved in DCE by aqu-
eous ferrocyanide. Spectroscopic measurements confirmed the generation of gold particles. Unfortunately, the transfer and adsorption of the tetrachloroauroate ions complicated the voltammetric response, and systematic analysis of the nucleation reaction at the ITIES was not possible.

The electrodeposition of palladium at the ITIES has been studied by Johans et al. [164]. The advantage over the gold system is the absence of ion-transfer signals in the polarizable potential window. A model was presented for diffusion-controlled potential-static electrodeposition at the ITIES, taking into account the development of diffusion fields in both phases. It should be emphasized that the experimental system has to be chosen with care. Ammonium tetrachloropalladate was used as the aqueous substrate and butylferrocene as the reducing agent in the organic phase. In a cyclic voltammogram of the system, an irreversible reduction peak was formed at positive potentials, featuring a typical nucleation loop. Comparison of experimental and simulated current transients provided good correlations with classical concepts such as progressive and instantaneous nucleation, and gave information on the number densities of the particles at the interface. Johans et al. [165] have also investigated galvanostatic electrodeposition. The authors developed a general model for three-dimensional nucleation. In this approach they incorporated the effect of kinetics of the growth reaction into the model. The same model was used to investigate the influence of interfacial tension controlled by surfactants on nucleation kinetics by cyclic voltammetry and amperometry [166]. The position of a nanoparticle at a liquid/liquid interface was considered by classical thermodynamics. The theoretical model indicated that while large particles preferentially reside in the interfacial region, small particles are expelled. This introduces a second critical radius in the nucleation experiments. The experiments were in line with that prediction. There still are problems to be solved concerning the use of the ITIES for preparing nanoparticles. In particular, the question of stabilization has to be carefully considered.

The catalytic properties of the deposited particles are yet to be systematically studied. In one rare account, Schiffrin and Cheng [167] reported the catalytic dehalogenation of 2-bromoacetophenone to acetophenone by an organic reductant in the presence of electrogenerated Pd particles. It was observed that the Pd particles exhibited interesting selective properties.

C. Two-Phase Photocatalysis in Presence of Metal and Semiconducting Nanoparticles

As we mentioned in Section IV, current trends in photocatalysis are strongly biased toward photo-oxidation of organic substrates in the presence of semiconducting nanoparticles. The complete or partial mineralization of organic pollutants in aqueous media by TiO$_2$ nanoparticles has proved to be commercially viable, and a significant impact on the multibillion € worth “clean technology” appears imminent. Beyond photo-oxidation processes, other reactions such as dehydrogenation and metal deposition as well as removal of pollutants in the gas phase have been studied for a variety of semiconducting nanoparticles [101,168]. The literature in this area can be traced to numerous disciplines, and a comprehensive review would be outside the scope of this section. We shall concentrate on some basic aspects of photoinduced redox processes involving nanoparticles and their relevance in photocatalysis at liquid/liquid junctions.

One of the outstanding features of TiO$_2$ as a photoactive material is the possibility of water splitting [169]. As indicated in Fig. 14, radiation with energies greater than the band gap (3 eV) generates electron–hole pairs, which subsequently dissociate in the conduction...
and valence bands, respectively. Dynamic photochemical studies indicate that valence band holes are readily captured by adsorbed OH\(^{-}\) groups, generating surface OH\(^{-}\) that behaves as an intermediate in photo-oxidation processes. Hole capture effectively competes with the nonradiative recombination with conduction band electrons. Furthermore, the electron-capture cross-section of the surface radical OH\(^{-}\) is rather small, allowing the possibility of H\(_2\)O\(_2\) formation at the surface or the oxidation of a species in solution. Photogenerated electrons can reduce molecular oxygen, although this reaction is rather slow. The initial steps in photoredox processes can be represented by

\[
\begin{align*}
X \rightarrow h_{VB}^+ + e_{CB}^- & \quad \text{Photoionization of a nanocrystal site} \\
h_{VB}^+ + OH_S \rightarrow OH_S & \quad \text{Hole capture by surface OH}^- \text{ groups} \\
e_{CB}^- + OH_S \rightarrow OH_S & \quad \text{Surface recombination via OH} \\
2OH_S \rightarrow (H_2O_2)_n & \quad \text{Surface OH}^- \text{ coupling}
\end{align*}
\]

FIG. 14  (a) Redox potentials for valence and conduction bands of TiO\(_2\) in comparison with the potentials for hole capture by water and electron capture by oxygen. (b) Schematic diagram of the initial stages of photoinduced water splitting at TiO\(_2\) nanoparticles modified by RuO\(_2\) and Pd clusters.

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\[ e_{CB} + O_2 \rightarrow O_2^- \] Electron capture by oxygen (28)

\[ OH_5 + \text{Red} \rightarrow OH_5^- + \text{ Ox}^+ \] Oxidation step via surface OH (29)

The surface-confined \( \text{H}_2\text{O}_2 \) can further react with \( \text{OH}^- \) ultimately to generate oxygen [170–173]. Recent studies on rutile [174] and anatase [175] single-crystal photoelectrodes demonstrate that surface recombination mainly occurs via step (26). In addition, the recombination step appears strongly inhibited in the presence of organic species such as formic acid and methanol, further confirming that photo-oxidation processes occurs via \( \text{OH}^- \).

In colloidal suspensions, the overall efficiency of photoreactions at the TiO\(_2\) surface is determined by the removal of conduction band electrons. In order to catalyze step (28) or even hydrogen evolution, Pd and Pt clusters have been deposited at the surface of TiO\(_2\) nanoparticles [99,176,177]. The basic principle of catalytic centers on TiO\(_2\) particles is also illustrated in Fig. 14. Photospitting of water has been achieved by further depositing clusters of RuO\(_2\) on TiO\(_2\) particles, which is able to accelerate steps (25), (27), and eventually \( \text{O}_2 \) evolution. However, under certain conditions the metal–semiconductor boundary can also play the role of recombination center.

Metal oxide nanoparticles are usually stabilized in aqueous media by electrostatic interactions. By fixing the pH at values higher or lower than the characteristic pH of zero zeta potential, the particle surface exhibits a net positive or negative charge, respectively. Recent studies have demonstrated that interfacial concentration of TiO\(_2\) nanoparticles at water|DCE junctions can be effectively tuned by the Galvan potential difference [178]. At pH 2, the particles are positively charged and interfacial accumulation is achieved by applying a positive Galvan potential difference with respect to the organic phase. Under these conditions, heterogeneous photo-oxidation of species located in the organic phase can be induced under UV illumination. Photocurrent responses originating from the photo-oxidation of ferrocene (Fc) by TiO\(_2\) at the water|DCE interface have been observed [178]. These photoresponses exhibit features similar to those observed for dye-sensitized liquid|liquid junctions (see Fig. 5), but with negligible back electron transfer. The photo-oxidation of ferrocene can be interpreted in terms of Eqs (24) to (29), considering that the latter step is in competition with the recombination and the radical coupling processes. At basic pH, the accumulation of particles takes place at negative potentials, and the heterogeneous transfer of conduction band electrons toward acceptors in the organic phase is readily observed. This exciting approach opens the possibility of using photoelectrochemical means to study a variety of photocatalytic reactions where the substrate is insoluble in polar media.

Recent results have also shown that the photoreactivity of TiO\(_2\) at liquid|liquid junctions can be extended into the visible region via dye sensitization [178]. Dyes species such as alizarin exhibit a strong affinity for metal oxide surfaces, and ultrafast injection of electrons into the particles has been observed on photoexcitation [58–63]. In the case of heterogenous reactions at water|DCE junctions, the photoinduced electron injection is followed by electron transfer from the donor in DCE to the oxidized dye. The regeneration of the dye, also known as supersensitization, manifests itself as a photocurrent response. The basic principle is illustrated in Fig. 15. These processes are somewhat analogous to the phenomena responsible for the photoeffects in dye-sensitized nanocrystalline solar cells (DSNC) [179,180]. The main difference is that the photoresponses in DSNC arise from the transport of injected electrons across the TiO\(_2\) mesoporous film, while in this case the photocurrents originate from the supersensitization step.

Sensitization phenomena have also been observed in the presence of metallic nanoparticles. In this case, the nanoparticles act as an electron-transfer relay, enhancing the
charge separation due to the favorably situated energy levels [181]. Colloidal noble metal catalysts have been used in the reduction of carbon dioxide [182,183] and decomposition of water [184–187] as well as in various hydrogenations [188]. Bimetallic nanoparticles showed higher catalytic activity in the decomposition of water compared to the monometallic colloids [189]. Figure 16 illustrates the mechanism for visible light-induced hydrogen generation catalyzed by a bimetallic colloid. In this case, the excited state of the ruthenium complex injects an electron into the methyl viologen ion (MV$^{2+}$), which is subsequently transferred to the nanoparticle where hydrogen evolution takes place.

FIG. 15 Schematic diagram of the photoinduced electron transfer reaction at liquid|liquid interfaces featuring dye-sensitized semiconducting nanoparticles.

FIG. 16 Schematic illustration of the mechanism of light-induced hydrogen generation catalyzed by Au–Pt bimetallic nanoparticles. (From Ref. 189.)
We have also demonstrated that metallic nanoparticles can act as redox relays for photoinduced heterogeneous redox processes at water|DCE interfaces [190]. Electro-generated particles prepared by heterogeneous reduction of tetrachloropalladate as described in Section IV.B exhibit catalytic effects toward electron transfer from photoexcited porphyrins to redox species located in the organic phase. This catalytic effect of Pd nanoparticles is illustrated in Fig. 17(a), where photocurrent responses are measured in the presence of the water-soluble porphyrin ZnTPPC and a DCE solution containing the redox donor ferrocene and the acceptor TCNQ [190]. The positive photocurrent in the absence of the palladate salt indicates that the excited state of the dye is more effectively quenched by the donor species, especially at positive potentials. Even in an excess of TCNQ, the negative photoresponses are small and located at rather negative potentials. On addition of the palladate complex, the photocurrent responses became negative over a large range of potentials, indicating a preferential photoreduction process. This sign reversal is only observed in the presence of TCNQ; therefore, it is not directly connected with the nucleation process involving the palladate ion and ferrocene.

![Photocurrent responses originating from the heterogeneous quenching of the watersoluble porphyrin ZnTPPC by TCNQ and Fc at the water|DCE junction. The reductive quenching by Fc (positive photocurrent) is more efficient than the oxidative quenching by TCNQ (negative photocurrent), even for 10 times greater concentration of the latter. On addition of PdCl₂⁺, the sign of the photocurrent is reversed over a wide potential range (a). The in-situ generated Pd nanoparticles act as mediators for the photoinduced electron transfer from the porphyrin excited state to the redox acceptor, as illustrated in (b). Reprinted from Ref. 190 with permission from Elsevier Science.](image-url)
The photocatalytic effect of dye-sensitized Pd nanoparticles is schematically depicted in Fig. 17(b). At positive potentials, the ferrocene reduces the palladate complex in the dark to generate Pd nanoparticles at the liquid|liquid boundary. These nanoparticles act as electron-capture sites at the interface, which are subsequently transferred to the electron acceptor in the organic phase. This behavior is surprising in the sense that injected electrons in metallic particles are expected to have a very short lifetime due to fast back electron transfer to the oxidized dye, or even hydrogen generation at the particle surface. A possible rationale for the mechanism highlighted in Fig. 17(b) is linked to adsorption of \( \text{Cl}^- \) at the particle surface, which competes with the adsorption of \( \text{H}^+ \), decreasing the rate of hydrogen evolution. Furthermore, the \( \text{Cl}^- \) adsorption introduces a negative surface charge that can electrostatically repel the anionic dye.

**VI. CONCLUSIONS**

The various catalytic and photocatalytic processes in two-phase systems highlighted in this chapter allows evaluation of the potential impact of electrochemistry at the ITIES in this area. In a general sense, the possibility of tuning the interfacial concentration of charged species and the reactivity of the whole system by controlling the electrical potential across the interface opens an effective way of controlling reaction mechanisms and rates. Furthermore, electrochemical techniques provide direct access to the rate of charge transfer across the interfacial region. In conjunction with surface-sensitive spectroscopic techniques and modern computational methods [191–194], our understanding of the structure and reactivity at liquid|liquid interfaces at the molecular level has remarkably increased in the last few years. These developments provide the ideal platform for understanding and developing catalytic processes at molecular junctions. In order fully to realize the potential of the electrochemical methods it would be advantageous in the future to see a more multidisciplinary approach, bringing together electrochemists and synthetic chemists.

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