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Photoelectrochemically driven processes at the *N,N,N',N'*-tetrahexylphenylenediamine microdroplet|electrode|aqueous electrolyte triple interface

Abstract Novel photoelectrochemical processes are observed upon irradiation of the liquid|liquid|solid triple interface at microdroplets of *N,N,N',N'*-tetrahexyl-*para*-phenylenediamine (THPD) deposited onto a basal plane pyrolytic graphite electrode and immersed in aqueous electrolyte solution. In the presence of neutral THPD, cathodic photo responses, and in the presence of THPD$^+$, anodic photo responses with anion-dependent characteristics, are observed. A maximum in the photocurrents observed at intermediate coverage of the electrode surface suggests that the triple interface THPD|electrode|aqueous electrolyte is the reaction zone. This is the first report of photoelectrochemical processes at this type of interface.

Keywords Photoelectrochemistry · Triple interface junction · Voltammetry · Modified electrodes · Energy conversion

Introduction

Photoelectrochemical processes at conventional liquid|liquid interfaces are of considerable fundamental interest, e.g. for "light harvesting systems" and synthesis, and have been studied extensively (for example, see [1]). Usually, high-photon-flux laser excitation has to be used to achieve sufficient adsorption of energy into the reactive interface and dye sensitization has been employed to control the process [2]. Alternatively, energy adsorbed in the bulk phase has to be transported towards the interface in a way similar to processes observed at semiconductor|liquid interfaces (for example, see [3]) to result in efficient light adsorption and conversion. In recent work in liquid|liquid redox chemistry it has been demonstrated [4] that triple interface processes offer an interesting alternative and versatile new approach to the detection of interfacial redox processes. In order to detect these processes the extent of the three-phase junction organic liquid|aqueous electrolyte|electrode surface has to be maximized, for example by employing an array of microdroplets deposited onto a suitable substrate.

It has been demonstrated that processes at the triple interface α|electrode|aqueous electrolyte, where α denotes a solid [5, 6] or liquid [7] redox-active material, may be studied by voltammetric techniques. The reactive triple interface zone becomes considerable when the redox-active liquid is deposited in the form of microdroplets onto an electrode surface and then immersed into aqueous electrolyte. In the present study, *N,N,N',N'*-tetrahexyl-*para*-phenylenediamine (THPD) deposited in the form of microdroplets onto a graphite electrode is shown to give characteristic photoelectrochemical responses. Although photoelectrochemical processes at triple interface systems are of considerable importance and the use of voltammetric techniques for the study of light-induced processes at the solid|electrode|aqueous electrolyte has been reported recently [8], the processes described in this study are the first examples of triple interface photoelectrochemical reactions at a liquid|liquid|solid triple interface.

N,N,N',N'-Tetramethyl-*para*-phenylenediamine (TMPD) and its derivatives are known to undergo facile photoexcitation coupled to redox conversion when exposed to light of ca. 300 nm wavelength [9, 10]. Based on the literature on photo-redox processes of radical cations [11], it is not unexpected that also phenylenediamine derivatives in the mono-oxidized state undergo photoelectrochemical processes. For the solid derivative tetrabenzylphenylenediamine, conductivity induced by photons has been reported (for example, see [12]) and exploited in several patents.

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In the preliminary work presented here, a first attempt is made (1) to characterize the photoelectrochemical behaviour of a THPD microdroplet-modified graphite electrode, (2) to establish the triple interface characteristics of the process by studying the coverage dependence, and (3) to identify new effects introduced by the anion insertion process associated with the liquid|liquid interfacial redox process.

Experimental

A gravity flow system (see Fig. 1) with a working electrode located in a rectangular channel cell was used. In this experimental configuration, thermal effects due to light absorption can be minimized [11]. The channel electrode employed consists of a 3×3 mm basal plane pyrolytic graphite electrode (Pyrocarbon, Le Carbone, Sussex, UK) embedded in a Delrin base. The channel duct is 9 mm wide and ∼1 mm high with an optically transparent silica cover plate. All solutions were thoroughly degassed with argon (Pureshield, BOC Gases) prior to and during experiments. The 1000 W model LX/1000-1 xenon lamp and monochromator have been described previously [13]. All electrochemical measurements were carried out using an Oxford Electrodes potentiostat (Oxford, England), connected to a Lloyd PL3 chart recorder (Lloyd Instruments, Southampton, UK). NaClO$_4$ (Aldrich), KSCN (Fisons), NaOH (BDH) and Ph$_3$CCOOH (Aldrich) were of analytical or the highest commercially available purity. THPD was prepared following a literature procedure [7]. Water was taken from an Elgastat filter system (Elga, High Wycombe, Buckinghamshire, UK) with a resistivity of not less than 18 MΩ cm. The basal plane pyrolytic graphite working electrode was polished with silicon carbide paper (Waterproof Abrasive Paper, P1000, Acton & Borman, Stevenage, UK) with grit size of 18.3 μm prior to deposition of THPD via acetonitrile evaporation [7].
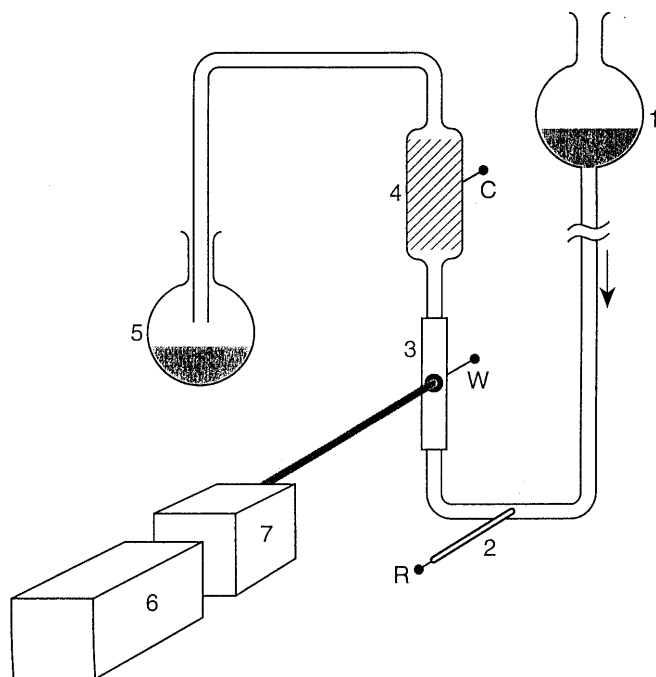
Results and discussion

Both the neutral and oxidized forms of THPD [7] are water-insoluble, viscous liquids. The oxidation of THPD deposited in the form of liquid droplets onto the surface of a basal plane pyrolytic graphite electrode and immersed in aqueous 0.1 M NaClO$_4$ proceeds in two consecutive steps [7, 14], of which only the first chemically reversible one-electron step (Eq. 1) is considered here:

$$THPD(oil) + ClO_4^-(aq) \rightleftharpoons [THPD^+ \cdot ClO_4^-](oil) + e^-$$
(1)
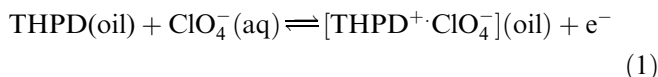
The oil droplet deposit, THPD(oil), on electro-oxidation leads to anion insertion to form [THPD$^+$·ClO$_4^-$](oil) [15, 16]. In Fig. 2a are shown three consecutive cyclic voltammograms obtained for the oxidation of 19 nmol (8.6 μg) THPD deposited in form of microdroplets onto a basal plane pyrolytic graphite electrode of 3×3 mm size, and immersed in aqueous 0.1 M NaClO$_4$. A chemically reversible process consistent with the stoichiometry given in Eq. 1 is detected [14]. The topography of the basal plane pyrolytic graphite electrode surface has been shown to result in a mirodroplet deposit with an average droplet size of the order of 1 μm [16]. The droplet size is crucial in determining the extent of the "reaction zone", the triple interface THPD|electrode|aqueous electrolyte. The voltammetry conducted in a channel flow cell system [17] was unchanged in stationary solution and under flowing conditions, indicating that, as expected [7], transport of ions in the aqueous phase is not a limiting factor in the overall electrochemical process.
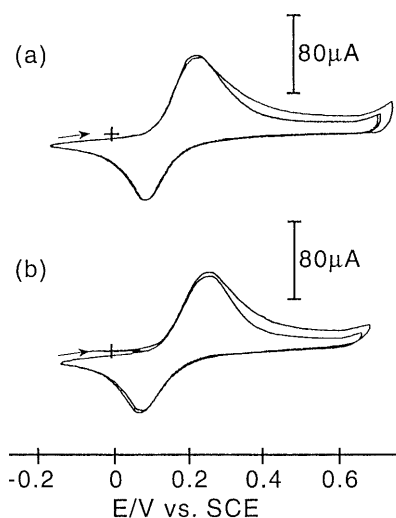

Fig. 1 Schematic drawing of the gravity flow system with (1) the solution reservoir, (2) the reference electrode, (3) the working electrode, (4) the counter electrode, (5) the collection vessel, (6) the lamp and (7) the monochromator

Fig. 2 Cyclic voltammograms (scan rate 0.1 V s^{-1}) for the oxidation of 19 nmol (8.6 μg) THPD deposited on a surface of a basal plane pyrolytic graphite electrode and immersed in **a** aqueous 0.1 M NaClO$_4$ at pH 5.7 and **b** in aqueous 0.8 mM Ph$_3$CCOO$^-$, 0.1 M NaClO$_4$ at pH 10.0

In the presence of light (chopped with ca. 2 s intervals, ca. 10 mW cm^{-2}, 280 nm, 0.1 M NaClO$_4$, solution flow rate 0.02 cm^3 s^{-1}), significant photocurrent responses were detected for both photo-oxidation at an applied potential of 0.4 V vs. SCE (oxidized form THPD$^+$·ClO$_4^-$ present) and photoreduction at 0.0 V vs. SCE (reduced form THPD present). In Fig. 3 the photo responses for photo-oxidation (a) and photoreduction (b) can be seen to reach a steady-state limit, indicative for a well-defined light-driven electrochemical process. However, the magnitude of the anodic and cathodic photoelectrochemical responses are very different and small compared to the current response associated with the bulk conversion of THPD (see Fig. 2). Figure 4a shows the effect of THPD coverage on the anodic and the cathodic photo responses. Perhaps surprisingly, a maximum photo response is detected at ca. 80 nmol (35 μg) deposit independent of the type of process. This observation is characteristic for a triple interface process and can be rationalized based on two factors: (1) the need for a triple phase boundary for the electrochemical process to occur and (2) the increase in light absorption with THPD coverage and droplet size. These two factors have opposite effects on the magnitude of the photocurrent. Increasing the amount of THPD covering the electrode surface causes a better absorption of light but at the same time decreases the reactive triple phase boundary. In Fig. 5a schematic representation of the reaction zone is shown.

In Fig. 4b are given action spectra showing the wavelength dependence of the photo responses. Photo responses exhibit maximum intensity at ca. 280 nm with a decrease towards a shorter wavelength owing to the characteristics of the light source and a decrease at ca. 400 nm due to the lack of light absorption by THPD at longer wavelength. THPD deposited onto a quartz plate shows a strong light absorption at wavelengths < 370 nm (see Fig. 6a) consistent with this interpretation.
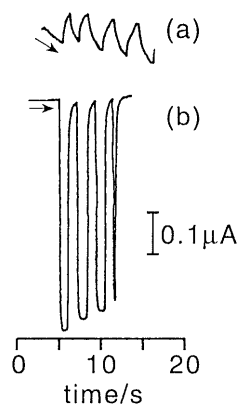

Fig. 3 Photocurrents observed for the photo-oxidation at 0.4 V vs. SCE (a) and for the photoreduction at 0.0 V vs. SCE (b) of 80 nmol THPD (35 μg) deposited onto a 3×3 mm basal plane pyrolytic graphite electrode immersed in 0.1 M NaClO$_4$ (10 mW cm^{-2}, 280 nm, solution flow rate 0.02 cm^3 s^{-1}). The *arrows* indicate the initial part of the trace with the light switched off

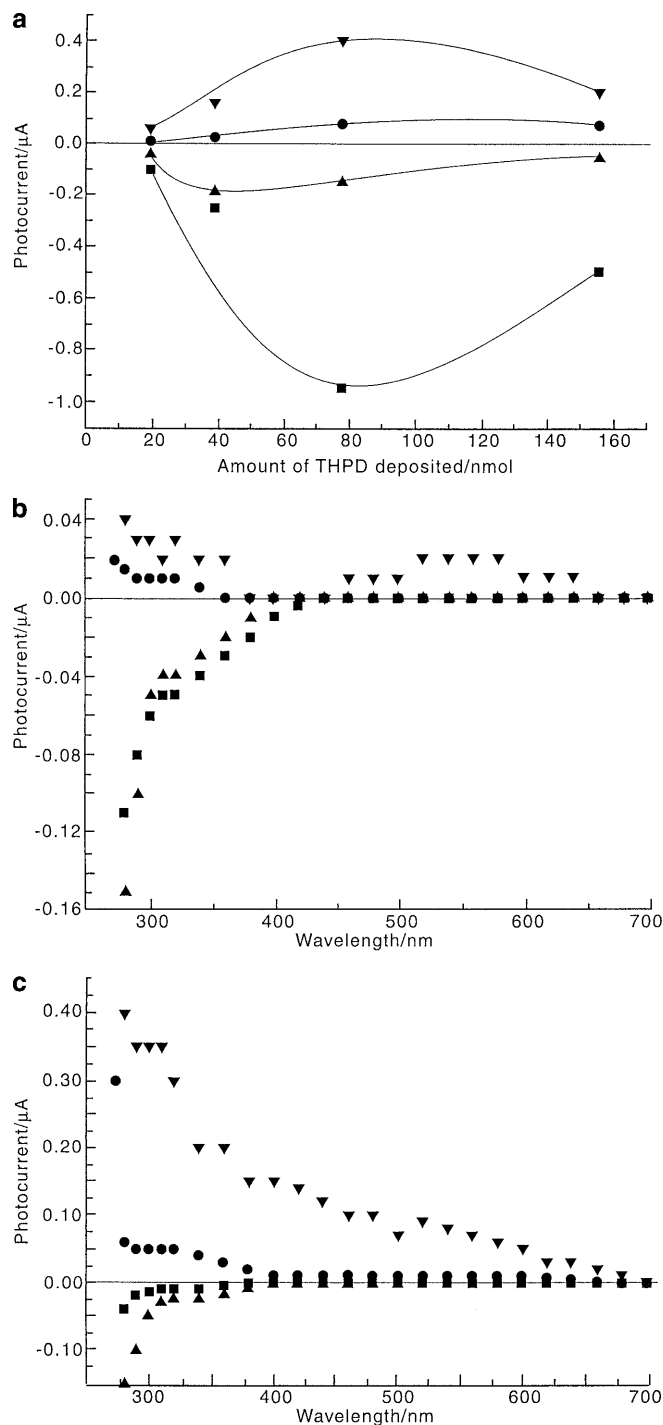**Fig. 4** **a** Graph showing the dependence of the observed photocurrents on the coverage of THPD deposited on the electrode surface: ■ 0.1 M NaClO$_4$, 0.0 V vs. SCE; ● 0.1 M NaClO$_4$, 0.4 V vs. SCE; ▲ 0.1 M NaClO$_4$ and 0.4 mM TPA$^-$ at pH 11.2, 0.0 V vs. SCE; ▼ 0.1 M NaClO$_4$ and 0.4 mM TPA$^-$ at pH 11.2, 0.4 V vs. SCE. **b** Action spectra for the photocurrents observed in the presence of 19.4 nmol THPD in aqueous electrolyte solution: ■ 0.1 M NaClO$_4$, 0.0 V vs. SCE; ● 0.1 M NaClO$_4$, 0.4 V vs. SCE; ▲ 0.1 M KSCN, 0.0 V vs. SCE; ▼ 0.1 M KSCN, 0.4 V vs. SCE. **c** Action spectra for the photocurrents observed for THPD deposited on basal plane pyrolytic graphite in aqueous 0.1 M NaClO$_4$ containing 0.4 mM TPA$^-$ (pH 11): ■ 19 nmol deposit, 0.0 V vs. SCE; ● 19 nmol deposit, 0.4 V vs. SCE; ▲ 77 nmol deposit, 0.0 V vs. SCE; ▼ 77 nmol deposit, 0.4 V vs. SCE
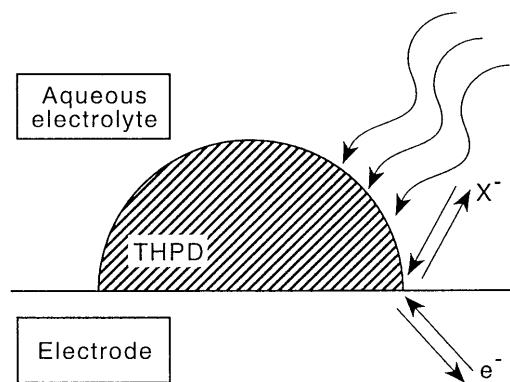
Fig. 5 Schematic drawing of the THPD|electrode|aqueous electrolyte triple interface reaction zone
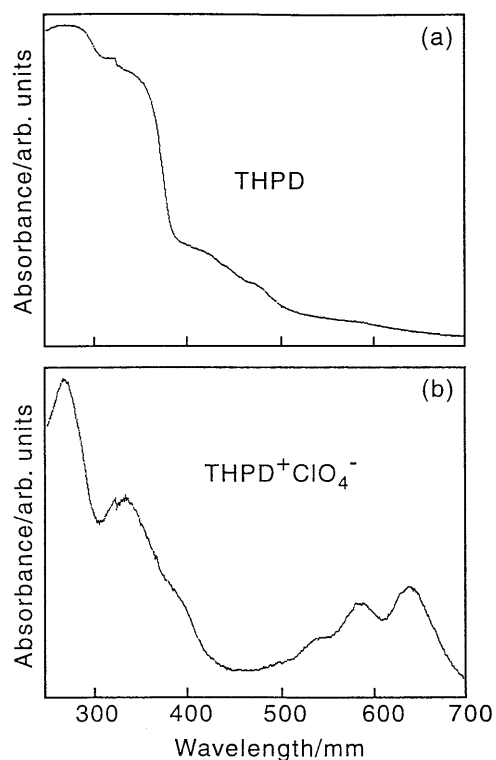

Fig. 6 UV/vis absorbance data for **a** THPD deposited in the form of microdroplets onto a quartz plate and **b** $THPD^+ClO_4^-$ formed as a microdroplet deposit on a quartz plate by immersing the THPD deposit into an aqueous solution of 10 mM $Fe(CN)_6^{3-}$/ 0.1 M $NaClO_4$

For comparison, the light absorption and photochemical reactions for the compound TMPD occurs between 280 and 350 nm [18].

The photo response at an applied potential of 0.4 V vs. SCE (Fig. 4a) corresponds to a photo-oxidation and proceeds at low efficiency in the absence and considerably higher efficiency in the presence of added triphenylacetate (TPA^-). Interestingly, a change in electrolyte anion from ClO_4^- to SCN^-, which is known to cause only a small potential shift in the voltammetric

response [14], causes an additional photo response in the action spectrum, peaking at 570 nm (see Fig. 4b), consistent with the blue $THPD^{+\cdot}$ radical cation absorbing the light. Clearly the anion plays an important role in "tuning" the overall reaction pathway for the photo-electrochemical process. The cation radical $THPD^{+\cdot}$ deposited in the form of microdroplets of $THPD^{+\cdot}$ ClO_4^- onto a quartz plate absorbs at a wavelength < 400 nm and at 550–660 nm (see Fig. 6), consistent with the absorption bands of $TMPD^{+\cdot}$ at 520–640 nm and at 350 nm [18].

Triphenylacetic acid is a model system for the study of Kolbe electro-oxidation processes [19] and has been employed for the in situ generation of trityl radicals [20, 21] (Eq. 2):

$$Ph_3CCOO^- \longrightarrow Ph_3C^{\cdot} + CO_2 + e^- \qquad (2)$$
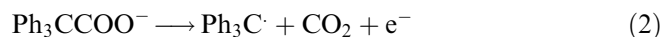
In the presence of 0.4 mM triphenylacetate (TPA^-) at pH 10–11 the voltammetric response attributed to the electroinsertion of ClO_4^- into the oil phase remains, although the hydrophobicity of the organic anion should result in a substantially reduced Gibbs free energy of transfer at the liquid|liquid interface compared to that of ClO_4^-. The slightly wider peak-to-peak separation (see Fig. 2b) indicates interaction of the TPA^- anions with the surface of the droplet. However, the mid potential, $E_{mid} = 0.5(E_p^{ox} + E_p^{red}) = 0.16$ V vs. SCE, is not significantly different from and consistent with the perchlorate insertion process (Eq. 1). It is interesting to note that also the electroinsertion of acetate anions into THPD deposits has not been observed [14].

Photo responses at a wavelength of 280 nm and in the presence of 0.4 mM TPA^- and at 0.4 V vs. SCE applied potential (oxidized form $THPD^{+\cdot}ClO_4^-$ present) are considerably stronger compared to those observed in the absence of TPA^-. Furthermore, a change of the TPA^- concentration from 0.4 to 0.8 mM does not affect the magnitude of the observed photocurrents. Both effects are proposed to be associated with TPA^- being adsorbed to the oil droplet|aqueous electrolyte interface and, based on independent experiments, cannot be explained by the effect of the pH on the process. In Fig. 4c it can be seen that the photo-oxidation in the presence of TPA^- extends over a wider range of wavelength, indicating that both the short wavelength absorption and the 550–660 nm absorption of $THPD^{+\cdot}$ are active. The increase in the photo-oxidation response in the presence of TPA^- must be attributed to an additional process, which under the experimental conditions used here is very likely to be the $THPD^{+\cdot}$ sensitized oxidation of TPA^- to the trityl radical and CO_2 (Eq. 2). Furthermore, the photochemical process in the presence of TPA^- adsorbed at the droplet|water interface causes an irreversible change in the voltammetric response of THPD. In contrast to the case in the absence of TPA^-, gradually the peak currents for the electrochemical response (Fig. 2a) decrease, likely due to an insoluble product being formed at the oil droplet|electrode|aqueous electrolyte interface.

We propose that the photo-oxidation response (at 0.4 V vs. SCE) is due to the formation of the excited state radical cation, $THPD^{+\cdot}*$, followed in the presence of TPA^- by a Kolbe photo-oxidation. In the absence of TPA^- the dication, $THPD^{2+}$, is formed and at the oil droplet|water interface undergoes further irreversible chemical reactions [7]. This photo-DISP-type reaction (Eqs. 3, 4, 5) has been proposed previously for radical ions [17]:

$$THPD \xrightarrow{-e^-} THPD^{+\cdot} \qquad (3)$$

$$THPD^{+\cdot} \xrightarrow{h\nu} THPD^{+\cdot}* \qquad (4)$$

$$THPD^{+\cdot}* + THPD^{+\cdot} \rightarrow THPD + THPD^{2+} \qquad (5)$$

A more detailed analysis of the mechanistic features associated with both cathodic and anodic photoelectrochemical processes observed for THPD and for $THPD^{+\cdot}$ in the form of microdroplet deposits, and of the importance of photoconduction effects, require new experimental approaches and the detection of reaction intermediates and/or products.

Conclusions

Novel condensed phase photoelectrochemical processes have been demonstrated to occur for the case of THPD microdroplets deposited onto graphite electrodes and, although mechanistic details for the observed process are presently not fully understood, interesting effects of the anion present in the ionic liquid phase, the coverage of the electrode, and the redox state of the THPD deposit have been demonstrated. All experimental evidence indicates a photoelectrochemical reaction zone located at the triple interface THPD|electrode|aqueous electrolyte. This novel type of interface for photoelectrochemistry may offer diverse possibilities for new photoelectrosynthetic processes, solar energy conversion (for example, see [22]), and in the design of artificial energy conversion systems (for example, see [23]).

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