Investigation of laser induced photocurrent generation experiments†

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Current signals produced by the laser-illumination of bare and non-chromophore containing peptide modified gold electrodes were investigated, and we suggest that these current signals which are due to the interfacial potential drop induced by laser heating, may have been mistakenly assigned to molecular-based photocurrents in several recent publications.

In recent years, photocurrent generation by molecular assemblies has received significant interest because of its potential in understanding the natural photo-systems,[1] which is crucial for developing artificial solar energy converters, and exploring the possibility of using molecules as scaffolds for nano-scaled photovoltaic devices. There are several reports in which natural photo-systems are mimicked by synthetic α-helices functionalized with light-harvesting chromophores.[2] Kimura and co-workers reported a molecular photodiode system composed of chromophore-modified helical peptides on gold surfaces and photocurrent generation by the chromophores upon laser excitation was described.[2a] The influence of dipole-moment was also probed with two peptide systems, making use of two chromophores (*N*-ethylcarbazoyl, laser excitation λ = 351 nm; tris(2,2′-bipyridine)ruthenium(II) complex, laser excitation λ = 459 nm) showing a dependence of the generated photocurrent on the orientation of the peptide. In another work,[2b] the same group reported reversible switching of the photocurrent direction by changing the pH of the solution using a naphthyl-labeled peptide (laser excitation λ = 280 nm).

These results are indeed exciting and they stimulated us to further investigate the feasibility of photocurrent generation in peptide films. In this paper, we report the results of our photo-electrochemical studies of peptide films having opposite dipole orientations on the gold surface. Surprisingly, we observed "photocurrent generation" and "pH switching" in the absence of a chromophore and even by the irradiation of a bare gold electrode with laser light. As a result of our study, we suggest that an important consequence of laser irradiation has been overlooked and that at least in some cases the so-called photocurrent phenomenon is probably a result of the interfacial potential drop induced by laser heating.

Before outlining the results obtained on peptide-modified gold surfaces, we carried out a number of control experiments with unmodified polycrystalline gold electrodes. Fig. 1 shows the experimental current signals for a polycrystalline gold electrode at different potentials (*vs.* Ag/AgCl) under 20 s laser (473 nm) irradiation (the supporting electrolyte is 0.1 M Na_2SO_4 aqueous solution). The directions of the current signals at different potentials are similar to those of the current transients produced by pulsed laser irradiation reported previously by Compton *et al.*[3] The current signal changes its direction from cathodic to anodic on changing the potential of the working electrode from negative to positive.

The illumination of the electrode with a laser pulse has been reported[3,4] to cause a sudden heating of the electrode surface according to the following expression:

$$\Delta T = \frac{I(1-R)}{\sqrt{\pi k\, c\, d}}\left(1+\sqrt{\frac{k_s\, c_s\, d_s}{k\, c\, d}}\right)^{-1}\sqrt{t_0}$$

where *I* is the intensity of the light, *R* the reflectivity of the surface, *k*, *c*, *d*, and k_s, c_s, d_s are the heat conductivity, specific heat, and density of the metal and solution, respectively and t_0 is the duration of the laser pulse. The heat instantaneously increases the temperature of the interfacial region[5–7] and a detailed analysis of the resulting electrochemical response (either the current transients in potentiostatic mode,[3] or the potential transients in coulostatic mode[4,6,8–10]) showed that the transients mainly reflect the response of the double-layer to the increase of the temperature. The thermo-diffusion potential between the hot solution (in contact with the working electrode) and the cold solution (in contact with the

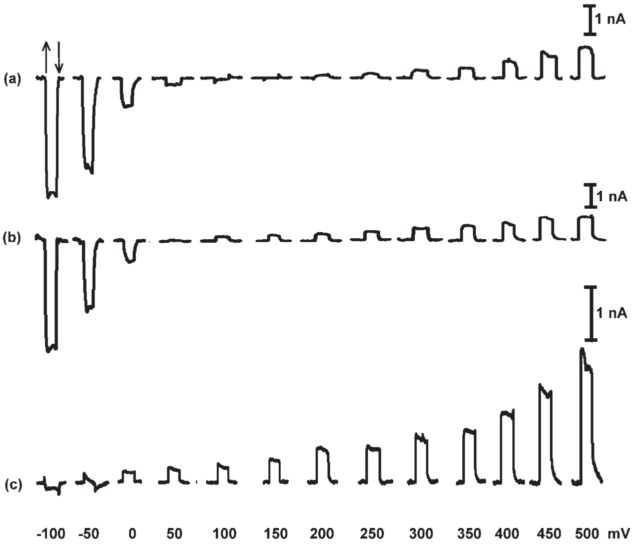

Fig. 1 Current responses from a bare gold electrode at different applied potentials (mV *vs.* Ag/AgCl) in 0.1 M Na_2SO_4 aqueous solution: (a) pH = 3, (b) pH = 7, (c) pH = 10. Up and down arrows denote light on and off, respectively. Irradiation time = 20 s.

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† Electronic supplementary information (ESI) available: Experimental details; current responses from a bare gold electrode in 0.1 M NaF and after addition of 0.1 M NaCl; cyclic voltammograms of bare, **Ac18L**, and **18LAc** modified gold. See DOI: 10.1039/b612617k

reference electrode) has been reported to be very small.[4,7,10] The temperature coefficient of the metal/solution potential drop can be split into three contributions:[9,11]

$$\left(\frac{\partial\phi^{\mathrm{M-S}}}{\partial T}\right)_{\sigma,m} = \frac{1}{e}\left(\frac{\partial\Phi}{\partial T}\right)_{\sigma} + \left(\frac{\partial\phi^{2}}{\partial T}\right)_{\sigma,m} + \left(\frac{\partial\phi^{\mathrm{w}}}{\partial T}\right)_{\sigma,m}$$

where Φ is the work function at the given charge σ, ϕ^2 is the potential drop at the diffuse layer, and ϕ^{w} is the contribution to the potential drop due to solvent structuring. It has been shown[9–13] that the temperature coefficient of the work function and the contributions due to the thermal coefficient of the potential drop through the diffuse layer (estimated from the Gouy–Chapman theory) are negligible, and the potential transients are mainly because of the temperature coefficient of the potential drop across the electrochemical double layer due to the increased disorder (caused by the increase of the temperature) of the oriented solvent molecules in the interphase. The change in sign of the transients is explained as a change in sign of the dipolar contribution to the potential drop in the interphase.[9,10] The negative transients at lower potentials are due to the decrease of the positive contribution from the layer of water dipoles, and the positive transients at higher potentials reflect a decrease in the absolute value of the negative contribution to the potential drop.[9,10] When the electrode is irradiated continuously (as in our experiments) instead of a pulse, a gradual contribution to the potential drop is expected due to the constant temperature rise, resulting in a current response.[14]

The potential at which the current response is zero (the transition potential) has been identified as the potential of maximum entropy (pme) of formation of the double layer,[5,8] and is located in the vicinity of the potential of zero charge (pzc) of the working elelctrode.[8–12,15] The pzc of a gold electrode can vary over a wide range (for example, from −180 to +250 mV *vs.* Ag/AgCl for Na_2SO_4 aqueous solution)[16] depending on the crystallographic orientation of the electrode's surface. In addition, significant discrepancy exists among values determined by different methods.[17] In order to further determine if the transition potential is truly related to the pzc, we recorded current signals in solutions of different pHs. The pzc of gold is known to shift negatively upon increasing the pH of the electrolyte solutions due to the increasing surface concentration and higher electrosorption of OH^-.[14,17b] Fig. 1 shows that the transition potential shifts negatively with the increase of the solution pH. In another set of experiments, the transition potential in 0.1 M NaF aqueous solution was also found to shift negatively when 0.1 M NaCl was added to the solution (Fig. S1†), which is consistent with the greater electrosorption of Cl^- on the gold surface.[17b]

Similar types of laser-induced current signals were obtained for two helical peptide self-assembled monolayers (SAMs) (on polycrystalline gold electrode surfaces) having different dipole directions on the surface and no chromophore. The peptide **Ac18L** ($Ac\text{-}KTAL_{18}NPC\text{-}NH_2$) possesses the thiol-functionalized Cys residue at the C-terminal, whereas, peptide **18LAc** ($Ac\text{-}CTAL_{18}NPK\text{-}NH_2$) has the Cys residue at the N-terminal side of the molecule (Fig. 2), so that when immobilized on the gold surface *via* the thiol linker, the positive end of the helix dipole is on the surface in **Ac18L** SAM and the negative end in **18LAc** SAM. Note that in both cases the amine functionalized Lys residue is facing the solution side.

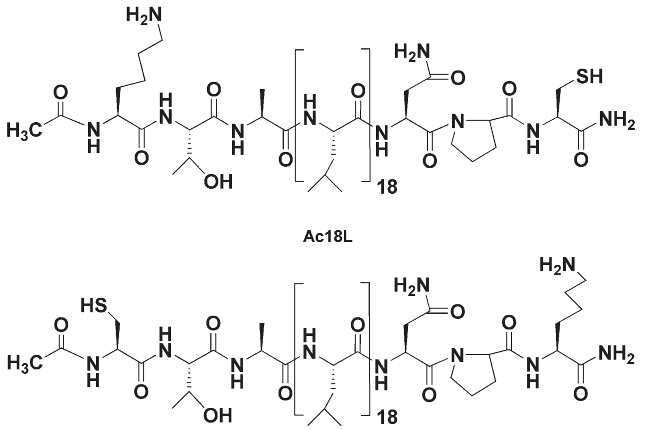

Fig. 2 Molecular structures of the peptides **Ac18L** and **18LAc**.

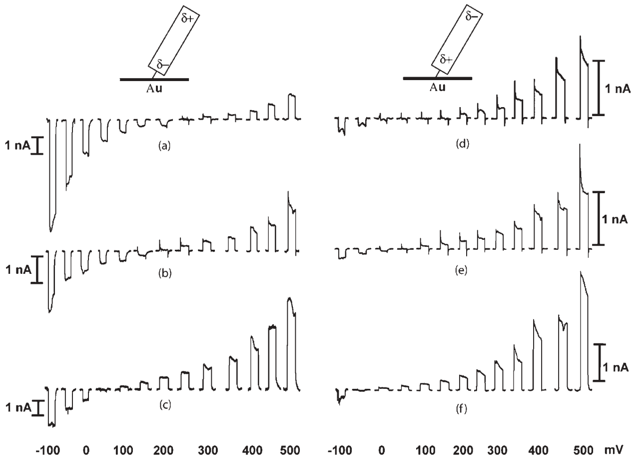

Fig. 3 Current responses from peptide modified gold electrodes at different applied potentials in 0.1 M Na_2SO_4 aqueous solution: **Ac18L**, pH = 3 (a), 7 (b) and 10 (c); **18LAc**, pH = 3 (d), 7 (e) and 10 (f). Schematic diagrams of the orientation of the helix dipole moment on gold surface are also included.

A preliminary account of the syntheses and characterization of the peptides has already been published elsewhere.[18] Both peptides form well packed films on gold from trifluoroethanolic solutions (see ESI†). At all pHs, the transition potentials of **Ac18L** SAM are higher than those of **18LAc** SAM, which can be explained by the nature of the helix dipole on the surface which is positive for **Ac18L** SAM and negative for **18LAc** SAM. Also for both SAMs, the transition potential shifts to the positive with the decrease of the pH of the solution due to the protonation of the amine group of the terminal Lys residue (Fig. 3).

At this point some features of the current signals at different potentials can be discussed. The intensity of the current signal is zero only near the pzc of the working electrode and for a particular type of electrode the position of the pzc is dependent on the pH, concentration and the nature of the supporting electrolyte of the solution,[17a,b] and also on the nature of the molecules in the SAM.[19] If the pzc is not at 0 V (*vs.* Ag/AgCl), laser irradiation produces a steady current signal at this potential (at which laser-irradiated photocurrent generation experiments are usually performed[2]) and depending on the position of the pzc, the direction of the current signal can be cathodic (Fig. 1a) or anodic (Fig. 1c). Note that upon changing the pH of the solution from acidic to basic, the current signal (at 0 V) from bare gold switches from the cathodic to the anodic direction. In photocurrent generation experiments, action spectra of photocurrents at various wavelengths are sometimes reported[2] and compared to the absorption spectra of the chromophores. The similarity between the two types of spectra is claimed to be the proof for the generation of photocurrent from the chromophore. But our observation of similar photocurrents from bare gold and non-chromophore containing peptide modified electrodes, lead us to conclude that the phenomenon is probably correlated to the increase of temperature due to UV-absorption of the chromophores.[20] UV absorption is the highest at the $\lambda_{\max}$ of a particular chromophore and the associated increment in temperature is also highest at that particular wavelength giving the most intense current signal. In addition, the binding energy of a singlet exciton, *i.e.* the energy needed to split an exciton to coulumbically unbound charges, is no less than 0.5 eV.[21] So the commencement of photoconductivity right at the onset of optical absorption has been suggested not to be unambiguous proof for photocurrent generation from a chromophore.[22] Furthermore, the photoemission threshold for gold is around 200 nm (the work function of gold is around 5 eV)[23] and we do not think that photoemission from the gold electrode is occurring due to the laser (473 nm). To date, photocurrent generation has been reported for various systems and, since the current signal from bare and non-chromophore containing modified electrodes is similar to the so-called photocurrent response, at least some reports about photocurrent generation should be revisited.

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