Scanning electrochemical microscopy under illumination: an elegant tool to directly determine the mobility of charge carriers within dye-sensitized nanostructured semiconductors

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The diffusion constant of the ferrocenium ion in dye-sensitized nanostructured materials has been determined by time-of-flight experiments under working solar cell conditions with scanning electrochemical microscopy.

Nano-crystalline materials on solid substrates have found a wide range of applications including dye-sensitized nanostructured solar cells (DNSCs) and photocatalysis.[1,2] For those applications the transport of charge and material within the nanosized pores are of crucial importance for the functioning and for the sensitization of the surface in the production process. Furthermore, for future applications in photocatalysis and photosynthesis, the flux of starting materials and products will be decisive for the performance. In the past, a few studies of the mobility of I_3^- within nanocrystalline TiO_2 were published and diffusion coefficients ranging from 3.4×10^{-6} to 4.4×10^{-6} cm^2 s^{-1} were reported.[3–5] Lately, a study of the mobility of ruthenium(II) complexes, which are regularly used as dyes, has been published. For these compounds diffusion coefficients as low as 4×10^{-9} cm^2 s^{-1} have been measured in nanocrystalline networks for the red dye $[Bu_4N]_2$[*cis*-$Ru(NCS)_2(4,4'-(O_2C)_2bipy)_2$] ($4,4'-(HO_2C)_2bipy$ = 2,2′-bipyridine-4,4′-dicarboxylic acid).[6]

Here we present a method to directly determine mobilities of redox mediators in dye-sensitized nanocrystalline substrates by time-of-flight experiments using a scanning electrochemical microscope (SECM) in combination with a light pulse. SECM has lately been successfully applied to photocatalytical systems.[7–10] At the same time a number of contributions have been published describing the determination of charge mobilities as well as molecular transport in thin films.[11–13] These studies demonstrated that with SECM reliable values as well as mechanisms of charge propagation can be measured. In this context it is apparent that SECM coupled with a light source is a valuable tool to study dye-sensitized nanocrystalline films. In a conventional three-electrode setup with a Pt-counter electrode and a $Ag/AgNO_3$ reference electrode, the ultramicroelectrode (UME; r = 12.5 μm) was placed with a positioner (CHInstruments 900 B) close to an illuminated dye-sensitized (N719, Solaronix) nanocrystalline TiO_2 film (Solaronix: 2.5 μm thickness) on a glass substrate.† The electrolyte consisted of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in 3-methoxypropionitrile (3-MPN) with ferrocene as redox mediator (0.1 M). According to the energy scheme in Fig. 1(B), the illumination should trigger electron injection from the dye into TiO_2 leading to the oxidized state of N719. The redox mediator (Fc in our case) regenerates the oxidized dye accompanied by the production of Fc^+, which then is detected at the UME at negative potentials relative to Fc/Fc^+ (Fig. 1(A)). In Fig. 2 the result of such an experiment is plotted. With a potential of −0.5 *vs.* Fc/Fc^+, a current can be observed at the UME at a distance of 30 μm when illuminating the surface, proving the working principle of the experiment.

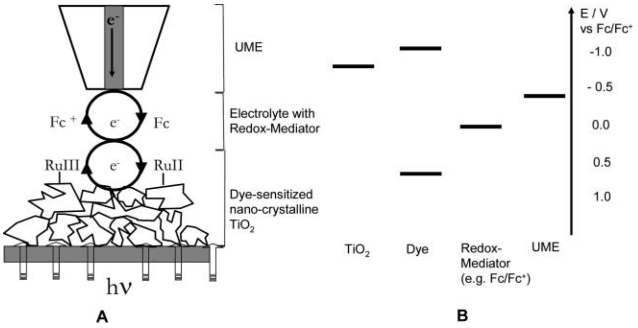

Fig. 1 Working principle (A) and energy levels (B) in the photo-electrochemical SECM experiment.

As the theoretical description of SECM experiments has made great progress over the last 15 years, a variety of experiments can be envisaged based on the concept described above to determine photoelectrochemical parameters including conductivity under illumination or heterogeneous kinetics.[14]

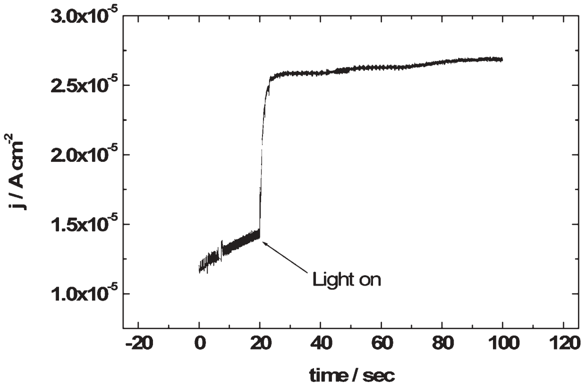

Fig. 2 Current density as a function of time measured with an UME (E = −0.5 V *vs.* ferrocene–ferrocenium) placed 30 μm above an illuminated dye-sensitized nanocrystalline TiO_2 film.

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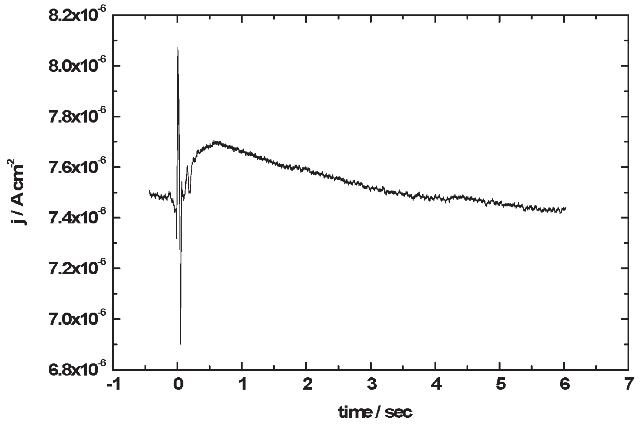

Fig. 3 Current density as a function of time after applying a light pulse of 4 ms and a UME–substrate distance of 30 μm.

A particularly straightforward and attractive experiment is the determination of diffusion coefficients within the nanostructured material by time-of-flight experiments as demonstrated by Murray and Bard.[15,16] In the original experiments, products of a potential pulse from the substrate electrode were measured as a function of time at the UME of known distance to the substrate. In our system we instead applied a light pulse to the nanostructured dye-sensitized material and detected the wave of the oxidized redox mediator according to the above principle. The result of this experiment is the expected increase of the current followed by a slow decay after the light pulse at $t = 0$. An example is shown in Fig. 3. Besides the photoelectrochemical effect related to the dye-sensitized film, a sharp spike at $t = 0$ was observed. A possible explanation is a tip–substrate coupling due to a sudden change in capacitance as it has been described previously.[16] Nevertheless, in a control experiment with only the electrolyte and ferrocene present (0.1 M $TBAPF_6$ in 3-MPN), but without a dye-sensitized film or any other substrate, a similar peak was seen. Therefore a capacitance effect is rather unlikely and we suggest that this effect might be explained by a photoresponse of the reference electrode, but which does not effect the outcome of the experiments.

In order to calculate the diffusion coefficient from time-of-flight experiments, eqn (1) can be applied:[16,17]

$$t_{\max} = \theta d^2/D \tag{1}$$

with $t_{\max}$ the time of the maximum current, d the distance between the electrode and the substrate and D the diffusion coefficient. The constant (θ) in eqn (1) depends mainly on the ratio of d and the radius of the UME (r).[17] The time $t_{\max}$ in our experiment with the UME above a nanocrystalline film has to be the sum of the time for the diffusing material in the solution above the film (t_{sol}) and within the film (t_{film}), giving access to an apparent diffusion coefficient (D_{film}) of the oxidized species within the nanoporous material. Applying this assumption to eqn (1) results in a linear relation between $t_{\max}$ and d^2 (eqn (2)).

$$t_{\max} = t_{\mathrm{film}} + \theta d_{\mathrm{sol}}^{2}/D_{\mathrm{sol}} \tag{2}$$

In order to determine both the magnitude of the constant, θ and D_{film}, we measured $t_{\max}$ as the function of d_{sol}. The results in Fig. 4 confirm a linear relationship between d_{sol}^2 and t.

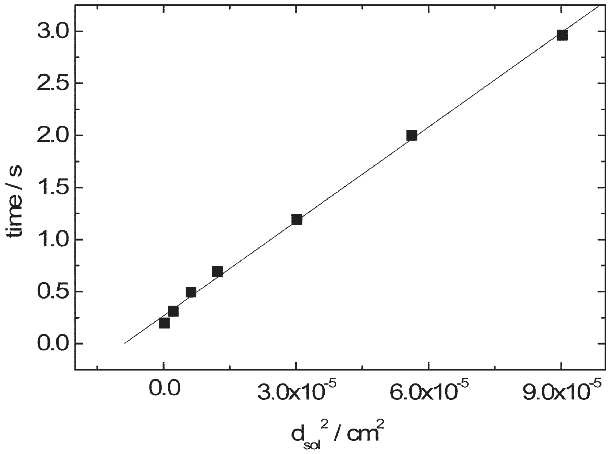

Fig. 4 Value of $t_{\max}$ as a function of the squared distance between the substrate and the UME.

From the slope of the function, D_{sol} has been determined to 3.6×10^{-6} cm^2 s^{-1} using 0.11 for θ in eqn (2). This number was measured by Bard *et al.* for the geometry we used in our experiments.[16]

The validity of the assumptions can be checked by comparing this value with that determined independently by *e.g.* steady-state voltammetry.[17] A value of 3.1×10^{-6} cm^2 s^{-1} has been measured, which compares well to D_{sol} determined by the time-of-flight experiment and therefore confirms both, the principle of the method and that the constant used in this contribution provides correct results.

Taking the function as plotted in Fig. 4 and determining t_{film} from eqn (2), a value of 2.56×10^{-8} cm^2 s^{-1} has been calculated for the diffusion of Fc^+ in nanocrystalline TiO_2 taking the film thickness (d_{film}) as 2.5 μm. The value of d corresponding to the diffusion within the nanocrystalline film according to the method proposed is somewhat uncertain, since Fc^+ evolves throughout the film when illuminating from the bottom of the substrate. Therefore D_{film} contains an uncertainty related to the concentration profile of Fc^+ within the film during illumination. This will be considered in greater detail in future studies. It should be stressed that D_{film} was determined under working conditions of the dye-sensitized nanocrystalline solar cell. Moreover, the mobility of the actual charge carrier is measured, which also implies that not necessarily the physical diffusion of Fc^+ in the nanoporous network is observed. Alternatively, the charge could be transferred through charge hopping along the surface. In a similar system this mechanism shows comparable transfer rates in the order of 10^{-8} cm^2 s^{-1},[18] which suggests that a mixture of surface confined charge hopping and Fc^+ diffusion might be at work. In this respect, the one order of magnitude higher mobility of the charge carrier in our system in comparison to the physical diffusion of the red dye could be due to the smaller size of Fc^+ or due to the different transfer mechanism. Further experiments need to be performed to reach final conclusions.

In summary, the method seems to be ideally suited to optimize the mobility of redox mediators, which is an important factor for the development of alternative electrolytes for the DNSC. Moreover, the improvement of nanocrystalline networks in terms of charge mobility and exchange is a straightforward application of the suggested method.

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Notes and references

† The Pt microelectrodes were polished with alumina, sonicated and electrochemically cleaned in sulfuric acid prior to use. The electroactive surface area was determined by integrating the oxide peak of the UME in sulfuric acid (0.5 M).

The TiO_2 nanocrystalline films were made by "doctor blading" a paste of TiO_2 (Solaronix, Switzerland) onto a microscope slide followed by drying and heating the film at 450 °C for 30 min. This method is regularly applied to produce nanocrystalline TiO_2 films for DNSCs.[19]

The sample was irradiated from the bottom with a 300 W projector lamp (GE ELH/MR16). The light intensity at the sample was 4 mW cm^{-2} and was determined with a photodiode (BPW21R), which has an absorption spectrum comparable to N719. The light pulse was applied with a mechanical shutter, had a width of 4 ms and was monitored during the experiment by a photodiode.

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