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PHOTOELECTROCHEMISTRY OF PLAIN AND DYE-SENSITISED MESOSCOPIC TiO_2 ROTATING DISC ELECTRODES

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ABSTRACT. The photoelectrochemical properties of porous pressed TiO_2 rotating disc electrode was studied and it is sensitive to UV and visible light. The photocurrent in the UV region of aqueous 0.1 M KCl, 0.1 M NaI acetonitrile, and 0.1 M $LiClO_4$ ethanol solutions were examined. The photocurrent in aqueous solution was found to be much lower than in the rest of the solvents. This is because water is poor hole scavenger in the system. Similarly the effect of rotation speed of the disc, in the presence of air, oxygen, and nitrogen was studied. The photo-currents as function of the thickness of the disc membrane were also studied. The photocurrent is substantially decreased in the presence of air and oxygen. For the relatively thick electrodes the photocurrents were fairly independent of the thickness of the disc membrane and quite unexpectedly even very thick porous electrodes gave good quantum yields. The photocurrent depends on rotation speed of the disc up to about 100 rpm. However, significant photocurrent is still obtained if the solution is purged with nitrogen. This was assigned to the fact that on illumination of the disc electrode some heat is evolved in the solution at the electrode-electrolyte interface. This in turn causes convection. Examination of the action spectra of plain and dye sensitised electrodes revealed the importance of the dye in achievement of photo-response in the visible region for even very thick TiO_2 disc electrode.

INTRODUCTION

With the introduction of the dye-sensitised nanoporous-nanocrystalline, the so called nanostructured electrode [1], new interesting features of the photoelectrochemical cell (PEC) was discerned. Quite unexpectedly a very highly disordered porous structure of a semiconductor was shown to be able to efficiently separate charges. Quantum yields close to 100% were reported for example for plain nanostructured [2] as well as dye-sensitised electrodes. The mechanisms of the charge separation and charge transport in the nanostructured electrodes are not fully understood, and nanostructured thin film electrodes are currently under investigation worldwide [1-6] .

The photocurrent in the nanostructured TiO_2 electrodes utilised in the dye-sensitised photovoltaic cells depend on the ability of the nanostructured electrode material to transport electrons efficiently in the conduction band (CB) of the TiO_2 particles. The data obtained from front and backside illumination experiments [5] and the registered photocurrent transient [6] were explained by proposing simple diffusion as the mechanism for transport of the electron in the nanostructured TiO_2. But the transport of charge in the nanostructured electrode may also be limited by the obstructed diffusion of the redox

couple in electrolyte. We have for this reason recently also studied the obstructed diffusion of one of the most commonly used electrolytes, the I_3^- ion, in pressed TiO_2 membranes [7]. In the present study we have extended our work on the same type of pressed TiO_2 membranes now mounted as a porous rotating disc electrode in a three electrode system. The properties of the electrodes are examined. We report the current-voltage characteristics in different electrolytes and solvents, the effects of the rotation speed on the observed photocurrent, the thickness dependency of photocurrent, and the spectral distribution of the quantum efficiency (IPCE) both for plain and dye-sensitised electrodes.

EXPERIMENTAL

Preparation of rotating TiO_2 disc electrodes. The TiO_2 rotating disc working electrode (RDE) having the area of 0.502 cm^2 was prepared following a similar procedure of our earlier work [7], in which Degussa powder (P25 AG, Germany, a mixture of *ca.* 30% rutile and 70% anatase) is pressed and thermally oxidised. A cylindrical titanium metal rod was oxidised at *ca.* 700 °C to get an insulating TiO_2 oxide film over the rod. To fix the TiO_2 disc, on the rod and get a direct disc to metal electrical contact, the circular end surface of the rod was polished. Thereafter the titanium rod with membrane was heated in air to 450 °C for about 30 min. Then the membrane with metal rod was mounted in a PINE instrument rotator (MSRX Speed Control, USA) as a usual electrochemical disc electrode. The thickness of the electrodes was estimated by a digital caliper (Digimatic Caliper, 500-311, Japan). Generally the pressure applied for preparation of the membranes was in the range of 4 to 200 Mpa (Mega Pascal) for 6 to 25 mg of TiO_2. Finally from the estimated thickness and mass of the TiO_2, the porosity of the membrane was estimated following the procedure in [7]. The porosity of the nanostructured disc was within the range of 45-65%.

Illumination of the electrodes. The mounted TiO_2 disc electrode was illuminated through the bottom of the electrochemical cell in which the optically flat quartz window was designed for the passage of the light to the centre of the vessel. The light beam from 1000 W Xe lamp (Spectral energy, LPS255HR, Universal ARC-Lamp Power supply, USA) goes through a lens via a quartz window beam splitter to a mirror where light is vertically reflected directly to the electrode surface. Similar procedures were followed when investigating action spectra except that a monochromator (Kratos, Schoeffel, Instruments) was placed between the light source and the mirror. The intensity of the light (*ca.* 25% solar energy) was determined by Pyranometer (Model Delft/Holland, sensitivity of 4.83 x 10^{-6} V/Wm^{-2}, cm 11 Kipp and zonen) for full light illumination. A photodiode was placed in the focus beam deflected from the quartz window beam splitter. The diode was calibrated with an optical power meter (Photo dyne, 3 M model 66XLA with a silicon diode model No 400 sensor head having an active area of 0.38 cm^2). Corrections were made for the differences in area of the RDE and active area of sensor head of power meter. A shutter and filters to eliminate the second order spectra were also used depending on the nature of measurements. In all measurements, illumination was for practical reasons on to the electrolyte-electrode interface.

Electrolytes and photocurrent measurement. The electrochemical cell was a 20 mL quartz vessel equipped with a RDE disc working electrode, Ag/AgCl reference and a Pt counter electrode. All experiments were performed at room temperature (*ca.* 22 °C). The observed photocurrent (i_{ph}) under illumination was measured by Potentiostat/Galvanostat PAR M273 (EG & G, Princeton Applied Research), using software M270. Electrochemical measurements were performed in open air, after saturation with oxygen and purging with nitrogen gas. The photocurrents were collected at 300 mV. The electrolytes were 0.1 M KCl (proanalysi, E. Merck, Darmstadt, Germany) in deionized Milli-Q water solution, 0.1 M $LiClO_4$ (Fluka, dehydrated) in ethanol (EtOH) (Spectroscopy 99.5%, Kemetyl, Stockholm) and 0.1 M NaI (suprapur, E. Merck, Darmstadt, Germany) in acetonitrile (ACN) (Fluka, HPLC, 99.9%) for both full light and monochromatic measurements. The increase in I_3^- concentration with time during photocurrent measurement of NaI-ACN system was followed by absorbance measurement at 290 and 361 nm with a UV-Vis Hewlett Packard 8453 spectrophotometer. Photocurrent action spectra in the visible region were reasonable in 0.1 M NaI acetonitrile solution with the TiO_2 RDE coated with 0.5 mM cis-$(SCN)_2$bis(2,2'-bipyridyl-4,4-dicarboxylate)-ruthenium(II) complex Dye (N3) (cf. Ref. 2). Dying of the porous TiO_2 disc electrode was carried out by soaking the sintered electrode in an ethanol solution of the dye. The electrode was transferred directly from the sintering procedure at a temperature of *ca.* 90°C to the dye solution. Then it was allowed to stay in the solution for *ca.* 24 h. The dye was adsorbed to the depth of approximately 80 μm.

RESULTS AND DISCUSSION

The preliminary study was in 0.1 M aqueous KCl solution (pH 6.7) for TiO_2 disc electrodes having the porosity of 45 to 65%. In this system the photocurrent was found to be low. Its voltamogramm in Figure 1 shows the typical features of TiO_2 electrodes [8]. More negative applied potential beyond -400 mV destroys the electrode and the electrode appeared to be dark blue, which was suggested to be due to intercalation of protons from the aqueous solutions [9]. Regardless of electrolyte in this solvent, the anodic dark current essentially approaches zero, i.e. independent of the presence of oxidising and reducing agents. On the other hand, the cathodic current increases with an increase of cathodic potential. This suggests that the electrons in the electrode are transferred to chemical species like oxygen and protons at the electrolyte-TiO_2 interface. At anodic potentials the net reaction product of aqueous system under illumination is the generation of the oxygen at the working RDE disc electrode at the anode and hydrogen at the cathode. This has been observed by Honda and Fujshima in their earlier work [8]. Holes in the valence band travels to the surface of the TiO_2 and react with water. The electrons in the conduction band is transferred to counter electrode e.g. Pt where they reacts with the protons. This is known to be photoelectrolysis of water to oxygen and hydrogen:

$$TiO_2 + 4hv \rightarrow 4p^+ + 4e \quad (1)$$

$$4p^+ + 2H_2O \rightarrow O_2 + 4H^+ \quad (2)$$

$$4e + 4H^{+} \rightarrow 2H_2 \quad (3)$$

The overall reaction is

$$TiO_2 + 2H_2O + 4hv \rightarrow O_2 + 2H_2 \quad (4)$$

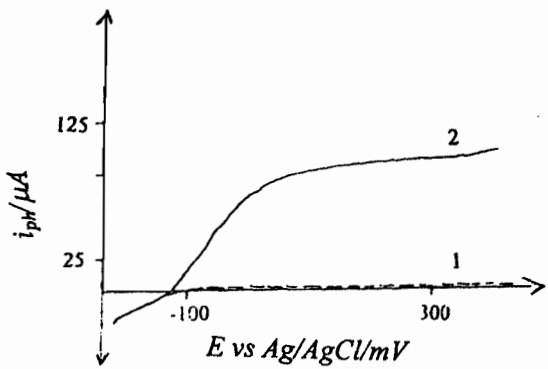

Figure 1. Voltammogram (scan rate 1 mVs^{-1}) in a 0.1 M KCl aqueous solution (pH 6.7), of a TiO_2 RDE having a thickness of *ca.* 230 μm with porosity of 46% at 120 rpm in nitrogen purged solution. (1) in dark, (2) under illumination of white light with power of *ca.* 270 wm^{-2}.

Our investigation was extended to the study of the effects of some parameters. These are, the effect of air and oxygen saturation of the solution, nitrogen purging, rotation speed of RDE and the thickness of the TiO_2 disc. The observed results will be presented and discussed below.

Effect of air and oxygen purging on photocurrent. As mentioned above, when measurement was carried out in open air, the photocurrent was low. This photocurrent decay is explained in terms of the trapped air in the porous TiO_2 membrane. This trapped air can scavenge the travelling electrons from conduction band to back contact where it is going to be detected as photocurrent (see Figure 2). Similarly, saturation of the solution with oxygen almost completely destroys the photocurrent. These observations generally agree with literature [2,5, 10]. The reaction product in the first step is probably superoxide ion, then peroxide ion [10]:

$$O_2 + e \rightarrow O_2 \quad (5)$$

Consequently, the photocurrent response at the back contact in the presence of oxygen is low. As explained above one of the net products of photoelectrolysis of aqueous system is oxygen. Therefore, reaction of oxygen with electrons of the conduction band initiates the indirect recombination of excited electrons with intermediate reduction products at the surface. The final product is water:

$$4e + 4H^{+} + O_2 \rightarrow 2H_2O \quad (6)$$

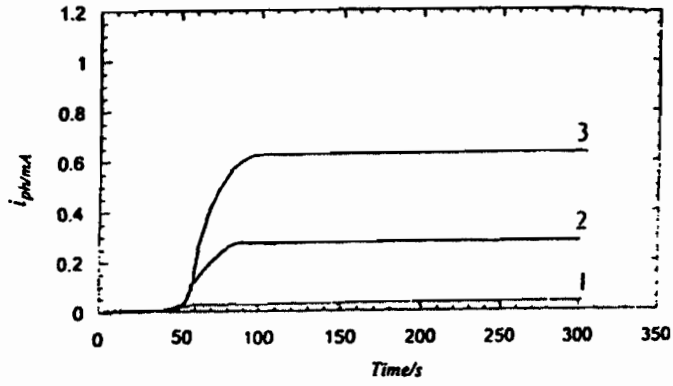

Figure 2. The i-t characteristic of a porous TiO_2 RDE having thickness of 210 μm at 300 mV and rotation speed of 300 rpm for 0.1 M $LiClO_4$ ethanol solution (pH 6.9) and light on after 50 s. The effect of (1) saturated oxygen, (2) air, and (3) nitrogen purging on photocurrent of the system.

Effect of nitrogen purging. The effect of purged nitrogen in the electrolyte solution was pronounced. The photocurrent was found to be high as revealed from chronoamperometric measurements (Figure 2). The high photocurrent is expected and in agreement with literature [2,5,10]. As mentioned above, loss of electrons will take place under aerobic condition and with bubbling of oxygen.

The effect of rotation. To be able to maintain a photoinduced current in an outer circuit it is necessary that the reactant is transferred from the bulk solution into the pores of the nanostructured electrode. Similarly the formed product(s) must be removed from the interior of the electrode. These transport processes in the pores are believed to be effected mainly by diffusion. However, the diffusion is obstructed by the particles in the disc electrode. The diffusing specimens in the electrolyte may also be in an equilibrium with the surface of the semiconductor which further contributes to slow down the flux. The diffusion of the different components in the electrolyte can for this reason not be regarded as free. Nevertheless an effective obstructed diffusion coefficient of I_3^- can be determined [7]. In a homogeneous porous disc, the transport of the different electroactive components to and from a certain interval within the disc will depend on the effective diffusion coefficient and the concentration gradient within the interval. The flux, J, of the component will follow the Fick's 1st law:

$$J = -D\, dc/dx \qquad (7)$$

where D is the effective diffusion coefficient and dc/dx the concentration gradient in the disc. This flux, as we will see further on, may limit the net photoinduced current in the system. If so, it is obvious that for highest photocurrent the concentration gradients perpendicular to the membrane electrode should be as large as possible. That is, the concentration of the products (formed within porous disc) should be kept as low as possible in the bulk solution outside the disc electrode. And for the same reason, the concentration of the reactant should be kept as high as possible. Any concentration gradient outside the disc electrode will necessarily decrease the gradient within the disc

and thus the current. The Levich equation [11] states that for a diffusion controlled system the limiting current is expressed by:

$$i_L = 0.62nFAD^{2/3}\nu^{-1/6}c^b w^{1/2} \quad (8)$$

where ν is the kinematic viscosity of the solution (viscosity/density), w is rotation speed of the disc, c^b is the bulk concentration of electroactive substances, D is the diffusion coefficient of the electroactive species, F is the Faraday constant and n is number of electrons exchanged. Not only a fast reaction of the hole with a oxidizable specimen in the solution is necessary. This oxidised specimen has to leave the matrix of the nanostructured disc electrode.

The plot of i_{ph} *vs* $w^{1/2}$ is shown in Figure 3 in ethanol solution. From the plot a dependence of the photocurrent on the rotation speed was found up to *ca.* 100 rpm. Beyond this limit, it becomes independent of rotation. It is evident from the figure that the photo- current generated at the nanostructured RDE electrode does not follow the Levich equation. The curve is not linear, the intercept is not zero, and the influence of rotation is minor. Furthermore, there is a definite upper limit around 100 rpm, where further increase in the rotation speed does not contribute to an increase in the photocurrent. We can at this stage only give a qualitative explanation to the i_{ph} *vs* $w^{1/2}$ curve that we observe.

The electrode is illuminated with high intensity white light. Heat is evolved at the electrode and convection due to the heat at the electrode electrolyte interface can be expected. This creates a convective flux of solution towards the electrode, so that a fairly undefined diffusion layer is maintained at the nanostructured electrode-bulk solution interface. Further stirring decreases the thickness of this diffusion layer and most probably also makes it more well defined. At a certain rotation speed around 100 rpm, this diffusion layer has decreased to the limit where no further transport of reactants to, and product from, the electrode can contribute to increase the current. At the given light intensity the observed photocurrent is now limited by the inherent properties of the nanostructured disc electrode. This is the desirable situation. This situation can also be achieved by stirring the solution [2].

Effect of RDE thickness. Similarly, the effect of the disc thickness on photocurrent in nitrogen purged system has also been studied. The result has revealed its insignificant role on magnitude of the photocurrent (Figure 4). The thinnest disc electrode is 0.06 mm thick, which is very thick when compared with ones reported in the literature [1-6,12]. It seems that above a certain thickness, the photocurrent is more or less independent of thickness.

From the hydrophilic characteristics of TiO_2, one cannot question whether aqueous solution does penetrate the disc or not. To circumvent such suspicion, the independent measurement for thick TiO_2 membrane has also been carried out following the procedures of our earlier work [7] using the aqueous solution of $K_3[Fe(CN)_6$. From that the fast electrolyte penetration through colloidal TiO_2 membrane has been confirmed. The diffusion experiment of the aqueous solution of $K_3[Fe(CN)_6$ through pressed TiO_2 membrane was detected from time dependent absorbance spectrophotometrically at 420 nm. The observation has verified the affinity of membrane towards water and the penetration ability of aqueous solution through the membrane.

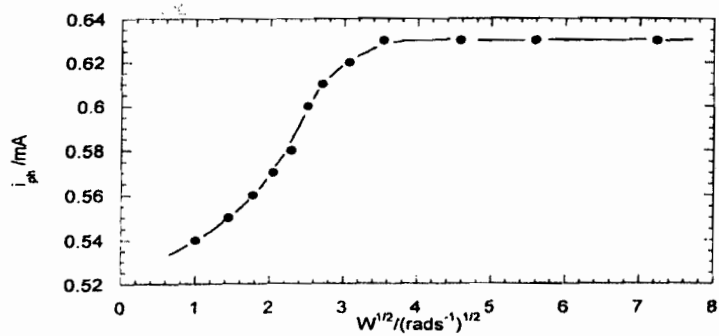

Figure 3. Representative plot for the effect of rotation of TiO_2 RDE i_{ph} vs $w^{1/2}$ for 0.1 M $LiClO_4$ in ethanol (pH 6.9) at 300 mV for thickness of 110 μm 46% porosity in nitrogen purged solution.

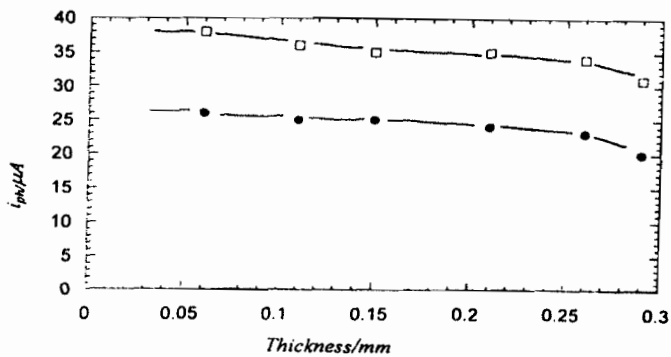

Figure 4. The effect of TiO_2 membrane thickness on photocurrent at 0 (shaded square) and 60 (open square) rotation per minute (rpm) for nitrogen purged 0.1 M KCl aqueous solution.

To obtain high photocurrent, effective electron-hole separation should take place. The hole generated in the valence band must be transported to the semiconductor electrolyte interface (SEI) where it is to be reduced by reduced chemical species in the electrolyte [13,14]. The recombination of electrons in the conduction band and hole in the valence band will be therefore low. To achieve such efficient electron-hole separation, the system must incorporate a good hole scavenger in the electrolyte. As clearly shown in aqueous KCl solution, water is the only expected hole scavenger in the system which is known to be poor in such activity. As result poor charge separation at semiconductor-electrolyte interface (SEI) takes place and becomes kinetically limited which is considered to be one of the responsible reasons for the appearance of the low photocurrent in aqueous solution.

In order to compare the response of TiO_2 in different solvents and electrolytes, $LiClO_4$ in ethyl alcohol and NaI in acetonitrile solutions were also used. These will be presented below.

Ethanol-$LiClO_4$ solution. Similar to aqueous solution the photocurrent of the TiO_2 RDE was measured in 0.1 M $LiClO_4$ ethanol solution using full light of UV and visible region. The photocurrent data were collected from chronoamperometric techniques at 300 mV. This is because to avoid the intercalation of lithium in the TiO_2 disc in normal voltammetric measurements [15]. The photocurrents obtained were much higher than that found in 0.1 M KCl aqueous solution. The separate experiment was performed to confirm that the ethanol penetrates the TiO_2 membrane. This was also evidenced from the dyeing procedure (see the *effect of rotation*).

Ethanol is reported to be a good hole scavenger for nanostructured TiO_2 film electrodes [5,10]. We therefore propose that the ethanol has served as the hole scavenger in our case, because high photocurrent was observed.

The parameters studied in aqueous solutions were also studied in ethanol solutions and the results show similar trends. The monochromatic beam photocurrents for these solutions were also measured in UV region for plain TiO_2 RDE (Figure 5). The action spectrum peaks are high at long wavelengths (around 380 nm) and has modest response

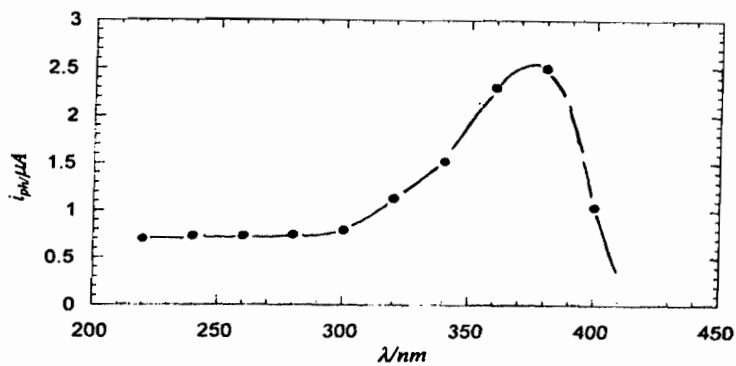

Figure 5. Photocurrent *vs* wavelength in UV region for 0.lM $LiClO_4$ ethanol unstirred solution at 300 mV for thickness of 230 μm of porosity 46% plain TiO_2 RDE.

below 300 nm where the absorption coefficient of the mainly anatase TiO_2 Degussa powder is an extremely high. This action spectral response is typical for nanostructured electrodes illuminated from the EE side [2,5]. The explanation is that the absorption coefficient is small for photons with energies close to the band gap energy, that is at long wavelengths. The electrons are lost on there way to the back contact due to different recombination processes. Thus the probability for electrons promoted to the conduction band deeper in the electrode, to reach the back contact is higher than those promoted to the conduction band close to the bulk electrolyte/disc electrode interface.

Acetonitrile-NaI solution. By following the same procedures mentioned above, the photo- current of the TiO_2 RDE was detected in 0.1 M NaI acetonitrile solutions. The current found was also high compared to aqueous solution. This is may be because iodide ion is also a good hole scavenger in this particular system. In metal solution interface iodide is a good surface active substance and the charge transfer reaction at interface is usually by inner-sphere reaction mechanism, in which iodide is specifically adsorbed on the metal surface, Pt and Au [16,17]. It was also argued that the encounter-complex formation takes place between the excited electron (or hole) and oxidised (or

reduced) chemical species in the solution. This was studied under kinetic treatment of interfacial electron transfer reactions in the colloidal TiO_2 electrode [12]. Similarly in our measurement, iodide is probably adsorbed at Inner Helmholtz Plane (IHP) of the TiO_2 electrolyte interface to form an encounter-complex with the TiO_2. When iodide is specifically adsorbed on the surface of the TiO_2 particles, the process of scavenging the hole is kinetically favoured. While for the electrolytes at Outer Helmholtz Plane (OHP) (the so called outer sphere reaction mechanism) the hole scavenging will be kinetically limited, which is expected to be the case for KCl aqueous solution.

In NaI-ACN solution, however, the full light measurement at both UV and visible region made the colourless NaI solution to become brownish. This coloured solution was checked with spectrophotometry and the absorption peak was found to be at *ca.* 290 and 360 nm which is due to generation of I_3^- ion [18]. Since there is strong absorption bands in UV and visible region this coloured solution interferes the result. However for the measurement of action spectra, monochromatic beam was used which is not intense enough to generate triiodide ion with the given time interval in three electrodes setup. To have insight into the effect of dye in harvesting light by simple pressed TiO_2 disc electrode, 0.1 M NaI-ACN solution was used to run the action spectra. As shown in Figure 6, the action spectra obtained on pressed thick TiO_2 is in agreement with the nanostructured TiO_2 film [3-5]. The incident photon to current conversion efficiency, IPCE was calculated as [3]:

$$\text{IPCE} = \frac{1241 i_{ph}(\mu A)}{p(\mu w)\lambda(nm)} \qquad (9)$$

The IPCE for dye sensitised TiO_2 RDE is *ca.* 25% at 540 nm for 0.1 M NaI ACN solution.

Generally, as reported in the literature [5], the low photocurrent for thicker electrode is due to indirect recombination of electrons and barriers encountered in the net work of the membrane. In this measurement, substrate/electrode (SE) interface illumination was not possible to compare the results with EE illumination. As SE illumination always gives higher IPCE values than EE illumination the observed EE values must be regarded as very high. The more so since the disc electrode used here is very thick (80 μm) and the EE values always decreases with increasing thickness.

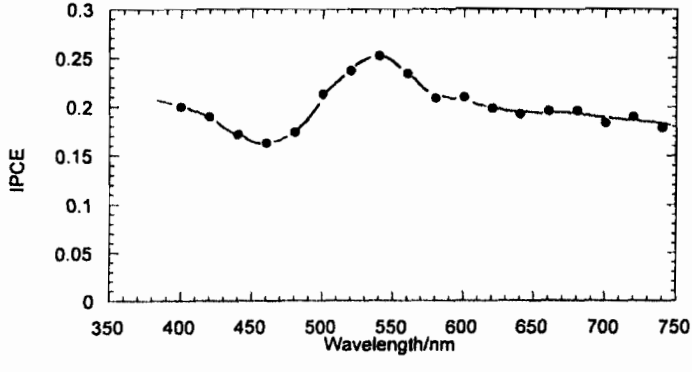

Figure 6. Incident photon to current conversion efficiency, IPCE *vs* wavelength for a dye sensitised TiO_2 RDE (disc thickness 80 μm, 45% porosity) in a 0.1 M NaI acetonitrile solution measured in three electrode system at 300 rpm.

SUMMARY

The results obtained on this simple TiO_2 electrodes made from pressed Degussa powder are informative as the extension of our diffusion coefficient determination of the triiodide electrolyte in similar pressed porous membranes. We learn that reproducible photoelectro- chemical measurements at thick electrodes can only be achieved when the electrode is rotated (or the solution is heavily agitated). We also observe that there is upper limit where further convection does not contribute to the photocurrent. Above this point the photocurrent depends solely on the inherent properties of the porous electrode and diffusion processes within the porous membrane electrode. A major result of the present investigation is that even very thick TiO_2 membrane electrodes can convert photon energy into electric current with the fairly good efficiency. This holds for dye sensitised as well as plain TiO_2 porous electrodes.

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