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Why Gratzel's cell works so well

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Dedicated to Michael Gratzel.

Abstract

In Gratzel's cell, the electrons injected by the photo-excitation of dye molecules, anchored to a mesoporous TiO_2 film, efficiently diffuse to the back contact achieving solar energy conversion at efficiencies exceeding 10%. The mesoporous TiO_2 surface constituted of randomly arranged nanocrystallites with a roughness factor of the order 1000 is heavily populated with traps, defects and adsorbed species which act as recombination centers. Nevertheless, the cell functions, mitigating recombination expected to occur via the interaction electrons at the surface. Evidence based mainly on $1/f$ noise measurements is presented to show that dye bonded to the TiO_2 surface passivates recombination centers. Furthermore the suppression of trapping–detrapping events at the surface increases the diffusion coefficient of the electrons through the nanocrystalline matrix facilitating electron transport to the back contact. The Gratzel cell is also unique, none of the high bandgap oxide materials other than TiO_2 yield energy conversion and quantum efficiencies as high as that of the cells based on TiO_2. $1/f$ noise measurements also reveal a distinct difference between TiO_2 and ZnO mesoporous films suggesting that the films made from the latter material are more intensely populated with surface states that mediate recombination.
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1. Introduction

Gratzel's cell [1–4] is a remarkable innovation rich in new physical and chemical concepts as well as unresolved puzzles. It closely mimics natural photosynthesis in using a pigment for light harvesting and adopting a similar technique for suppression of concentration quenching [5]. This cell is also a prototype example which clearly demonstrates the unique features of a device structured at the nanoscale level. With all these attractive features, Gratzel's cell remains a 'dirty' system in the sense that the functioning unit, the dye coated mesoporous titanium dioxide film, happens to be a highly disorganized structure constituted of nanocrystallites of varying sizes loosely sintered to each other and to the back contact of a conducting tin oxide

glass. Nanocrystallites are heavily populated with traps, defects and impurities. Traps, defects and impurity sites interfere with the diffusive transport of electrons and act as recombination centers [6–8]. Nevertheless, the cell works delivering a short-circuit photocurrent as high as $20\,mA\,cm^{-2}$ and a maximum point efficiency of 10–12% at one sun illumination. In this note, we present evidence to show that in addition to light harvesting, the dye plays a profound role in passivating surface states. Such passivation greatly reduces trapping–detrapping interactions of electrons at the surface. The result is the enhancement of the diffusive transport of electrons along the nanocrystalline matrix and suppression of surface state mediated recombination. Results from $1/f$ noise measurements [9], dark current measurements and diffusion coefficient measurements are discussed to show that the dye surface chelation to the mesoscopic material greatly suppresses dissipative losses. Although the oxide semiconductors

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TiO$_2$, ZnO and SnO$_2$ have similar bandgaps and band positions, efficient dye-sensitized solar cells cannot be made from the nanocrystalline films of ZnO and SnO$_2$ unless barrier layers of other materials are deposited on the surface (highest reported efficiencies for cells based on ZnO, SnO$_2$ sensitized with N3 dye ([2,2′-bipyridyl 4,4′-dicarboxylate] Ru(II)) are 5%, 1%, respectively) [6,10,11]. Noise measurements also show a distinct difference between TiO$_2$ and ZnO nanocrystalline films, suggesting that the latter films are more heavily populated with electron trapping sites. The study shows that the unique features of TiO$_2$ greatly contribute to the success of the Gratzel cell.

2. Discussion

The 1/f noise characteristics are used as a diagnostic technique for assessing the reliability of electronic devices [12–16], because irreversible processes such as trapping and recombination greatly contribute to 1/f noise. Generally surface interactions play a dominant role in generating 1/f noise in the current through semiconductors making nanostructured systems (where the surface-to-bulk ratio is exceptionally high) more susceptible to 1/f noise. The noise is detected as fluctuations in the current (or equivalently voltage) across a component of the device. The spectral power density of noise $S(f)$ in the current generally satisfies Hoog's empirical relation [17],

$$S(f) = \frac{AI_0^2}{f^\delta} \tag{1}$$

where I_0 is the mean value of the fluctuating current $I(t) = I_0 + X(t)$, with $<X(t)> = 0$ and

$$S(f) = \mathrm{Lim}_{T \to 0}\left\{ \frac{1}{2T} \int_{-T}^{T} X(t)\mathrm{e}^{-2\pi f t}\mathrm{d}t \right\} \tag{2}$$

The constant A in (1) which determines the level of noise, usually takes the form $A = \gamma/N$ [17], where N is the total number of free carriers in the sample and the parameter γ is referred to as Hoog's constant.

Because of the high intrinsic resistivity of nanocrystalline oxide materials, the sample thickness needs to be kept small ($\sim$10 μm) to obtain a mean current I_o well above the mean fluctuation $\langle |X| \rangle$ (the average of the modulus of the fluctuation). Thus, to meet the above requirements, nanocrystalline films of TiO$_2$, ZnO used for noise measurements were prepared as follows [9]: The electrical connectivity of a fluorine doped conducting tin oxide glass sheet (1 × 2.5 cm^2) was discontinued by scribing a line on the surface (thickness $\sim$8 μm) with a diamond point glass cutter. A layer of colloidal TiO$_2$ or ZnO (thickness 10–12 μm) was screen printed above the scribe and the film was sintered in air at 430 °C for 30 min (sample geometry indicated in Fig. 1). The circuit used for noise measurement is shown in Fig. 2. The sample with leads secured to the opposite edges of the conducting glass surface was placed in a chamber provided with accessories for heating, evacu-
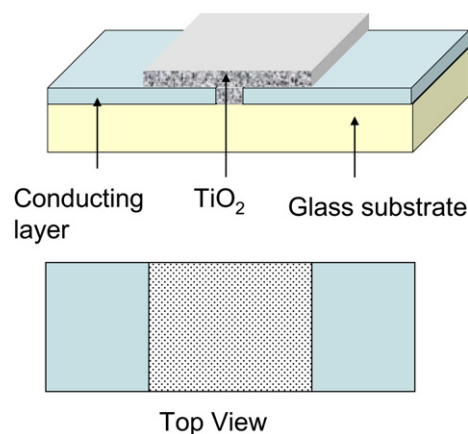

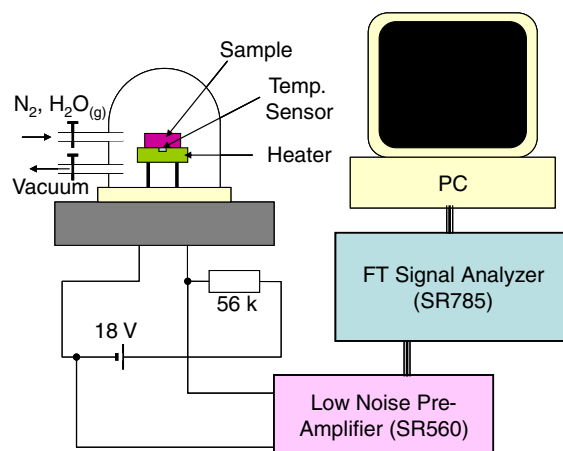Fig. 1. Schematic diagram showing the geometry of the sample used for measurement of noise.

Fig. 2. The circuit used for measurement of noise.

ation and introduction of gases. A resistor R ($\sim$50 kΩ) connected in series with an 18 V Ni–Cd battery and a low noise preamplifier was used to amplify the voltage fluctuation across the sample. A power spectrum analyzer (Stanford Research SR7885 Fourier Transform Dynamic Signal Analyzer) computed $S(f)$ and plotted its variation with frequency.

The noise spectra (log plots of $S(f)$ versus f) of nanocrystalline films of TiO$_2$ under different conditions are presented in Fig. 3. When the sample is in moist air or N$_2$ a high level of 1/f is noticeable (Fig. 3, curve a), the noise level gets reduced but persists even if the chamber is evacuated. However, if the sample is heated to $\sim$90–100 °C for few minutes during evacuation, the 1/f noise becomes barely detectable and no changes were observed on cooling the sample to room temperature (Fig. 3, curve b). Again the 1/f noise was not observed when the evacuated chamber is filled with dry N$_2$ (Fig. 3, curve c) but introduction of trace quantities of water renewed the 1/f noise (Fig. 3, curve a). Clearly the cause of the 1/f noise has been the adsorbed moisture. Similarly, introduction of iodine to the N$_2$ atmosphere generated intense 1/f noise (Fig. 3, curve d). Most amazing to note was that if the nanocrystal-
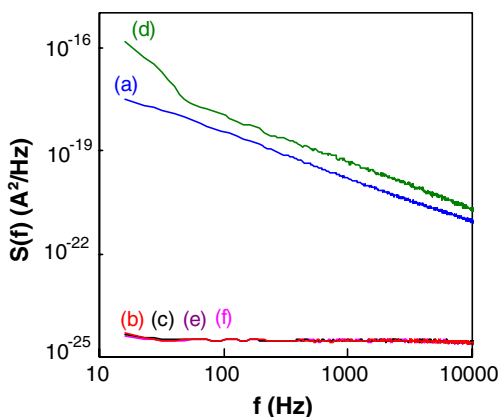
Fig. 3. Noise spectra of TiO_2 films under different conditions: (a) in N_2 (relative humidity 70%), (b) preheated sample in vacuum: (c) in dry nitrogen (preheated in vacuum at 90 °C for 5 min); (d) preheated in dry nitrogen after introduction of a trace amount of iodine; (e) dye coated film in dry nitrogen; and (f) dye coated film in dry nitrogen after introduction of iodine.

line TiO_2 surface is dyed (e.g., N3), introduction of trace quantities of water or iodine did not generate a $1/f$ noise (Fig. 3, curve f) in complete contrast to bare TiO_2. Fig. 4 also indicates noise levels when the dyed samples are in dry N_2 and dry N_2 containing a trace quantity of Iodine vapor. The above observations suggests that the interaction of electrons with acceptor states on the oxide surface causes a $1/f$ noise[9]. Water adsorbs dissociatively on the TiO_2 surface forming H and OH radicals and acceptor OH could act as an electron trapping agent [18]. Again iodine adsorbed on the TiO_2 surface could also readily accept electrons to form I^- [9]. A question that arises is how the adsorbed dye suppresses the noise. There are two possibilities: The first is the dye passivates the absorption sites of the electron acceptors. The uncoordinated Ti^{+4} sites produced by oxygen deficiency in TiO_2 act as sub-bandgap trap sites [19], which may be cured by dye surface chelation. It is known that such traps are detrimental to functioning of the dye-sensitized solar cell. Measurements
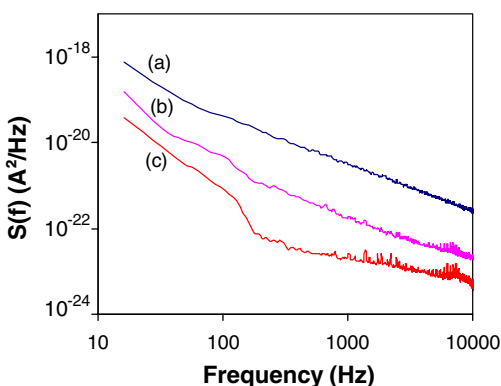

Fig. 4. Noise spectra of a nanocrystalline film of ZnO: (a) in air at a relative humidity of 70%; (b) in vacuum after heating to 110 °C for 10 min; and (c) in vacuum when the preheated sample is kept in the continuously evacuated chamber for 4 h.

also indicate that these sites themselves do not generate a $1/f$ noise. Oxygen vacancies can be created by heating TiO_2 in vacuum. However, prolonged heating of the sample in vacuum did not induce any $1/f$ noise. It seems that adsorbed electron acceptors on the TiO_2 surface are the cause of an intense $1/f$ noise. In this situation, intra-band trap states mediate electron transfer to adsorbed species, i.e.,

$$e^- \text{ (conduction band)} + \Gamma \rightarrow \Gamma(e^-) \tag{3}$$

$$\Gamma(e^-) + \Sigma \rightarrow \Sigma(e^-) \tag{4}$$
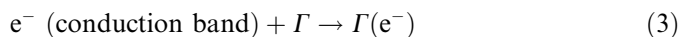
where $\Gamma(e)$ denotes an electron occupied trap Γ and $\Sigma(e)$ a filled acceptor level Σ.

Generally the electron in the reduced acceptor $\Sigma(e^-)$ can be consumed in a recombination reaction (e.g., combination with I_3^- in the cell that uses an I^-/I_3^- redox couple).

Another parameter crucial for the functioning of the dye-sensitized solar cell is the diffusion coefficient of electrons in the nanocrystalline matrix. The maximum permitted value for the thickness of the nanocrystalline film is of the order of the diffusion length $L_D = (D\tau)^{1/2}$ (D = diffusion coefficient, τ = recombination time) of the electrons in the nanocrystalline film. If the film thickness exceeds L_D, a large portion of injected electrons undergo recombination before reaching the back contact. Keeping the film thickness as large as possible enables accommodation of more dye into the film, to enhance the light absorption cross-section and therefore the quantum efficiency of the cell. Measurements indicate that the diffusion coefficient is higher in dye coated TiO_2 films compared to the uncoated ones [4]. The effective electron mobility of mesoporous materials is greatly reduced from the single crystal bulk value owing to trapping–detrapping of carriers at the states located on the surface. Passivation of the TiO_2 surface suppresses trapping–detrapping events at the surface facilitating the transport and increasing the diffusion coefficient.

In trap mediated recombination, the trap Γ captures a conduction band electron and transfers it to an acceptor species Σ. Thus, processes that transit conduction band electrons to trapped states, largely determine the recombination rate. Simple quantum mechanical considerations lead to important conclusions. The wavefunction of an electron trapped in a shallow level depth E below the conduction band edge can be written as [6]

$$|\Gamma\rangle = A e^{-r/a} \tag{5}$$

where $a = h/(2m^*E)^{1/2}$, with m^* = effective electron mass and the radial coordinate r is measured from the trapping site. The trapped state is undoubtedly mixed with conduction band states. For a conduction band state, described by the wavefunction,

$$|C\rangle = B e^{k \cdot r} \tag{6}$$

the quantity $P = |\langle C|T\rangle|^2$ is a measure of the trapping probability of the conduction band electron. Simple calculation

shows that P depends on the factor $Exp(-2R/a)$, where R is the radius of the particle. Thus transition probability is sensitive to the effective mass of the electron; the larger the effective mass, the lesser is the probability of transition of a conduction band electron to a trapped state. Electrons in TiO_2 have a very large effective mass (~ 10 m_e or more) compared to ZnO (~ 0.2 m_e) or SnO_2 (~ 0.1 m_e) [20,21]. It follows that conduction band electrons in TiO_2 are less likely to get trapped and therefore the recombination is better suppressed in TiO_2 based cells. Furthermore the parameter a (Bohr radius of the hydrogenic wavefunction) that determines the spread of the wavefunction of the trapped electron depends on the electron effective mass (Eq. (5)). If the particle size is comparable to or less than a the wave function leaks to the outside of the particle making an entry into a surface state highly probable. Clearly, a smaller effective mass (i.e., $m^* < h^2/2R^2E$) favors trapping as well as transfer of the trapped electron to an acceptor state at the surface of the particle. This is undoubtedly one of the reasons why the efficiencies of dye-sensitized cells made from SnO_2 and ZnO are significantly low compared TiO_2 based cells [6,10,11]. It has been demonstrated that with nanocrystalline films made of low effective mass materials, an ultrathin barrier on the surface greatly improves the efficiency [8,22,23]. Here, the barrier prevents tunneling of the electrons to reach acceptors at the surface. The photo-excited dye molecule anchored to the outer surface of the barrier injects electrons to the conduction band via transmission across the barrier. Once the electron relaxes to the conduction band edge, the barrier prevents back electron transfer. The transmission coefficient through a barrier of height V and width d is given by the expression

$$T = Exp\left[\frac{-2d\sqrt{2m^*V}}{h}\right] \qquad (7)$$

Again a larger effective mass gives a smaller transmission coefficient. The above discussion suggests that a larger effective electron mass in TiO_2 stands favorably for suppression of recombination in dye-sensitized solar cells. A barrier also has some influence in reducing injection probability. For TiO_2 backward transmission is negligible and the net effect of the barrier is the lowering of the photocurrent and generally a drop in the efficiency. Unlike in SnO_2 an increase in efficiency above the optimum has not been seen when insulating barriers are deposited on the nanocrystalline film of TiO_2 cells [10].

Fig. 4 shows the noise spectra of a nanocrystalline film of ZnO. When the sample preheated to 450 °C is transferred to the chamber containing air at a relative humidity of 70% and 23 °C an intense $1/f$ noise was observed (curve a). Any significant decrease in the $1/f$ noise was not observed when a sample heated up to 100 °C for few minutes and the evacuation is continued. On increasing the heating temperature to ~ 110 °C, the intensity of the $1/f$ noise gradually decreased as the chamber is evacuated

but not completely suppressed on prolonged evacuation at 23 °C (Fig. 4, curve b). Here, in contrast to TiO_2, the $1/f$ noise persisted under vacuum conditions (the preheated sample is kept in the chamber and evacuated for 4 h, Fig. 4, curve c). Possibly, the adsorbed species (e.g., water) bonded more strongly to the ZnO surface or intrinsic trapping sites in ZnO act as the sources of $1/f$ noise. This observation correlates well with the inferiority of ZnO for dye-sensitized solar cell application. The ZnO surface seems to be more heavily populated with traps (defects or surface states) compared to the TiO_2 surface. Again the dark currents of dye-sensitized photovoltaic cells made of ZnO films were higher than that of similar cells based on TiO_2 sensitized with the N3 dye, an indication of the higher recombination rate in the former system. It is well known that the rates of injection and recombination depend on the nature of the dye and its mode of anchoring to the oxide semiconductor surface. Passivation of the surface which suppresses the non-geminate recombination (i.e., combination of the relaxed electron with an acceptor species) seems to depend on the mode of bonding of the dye. The N3 dye gives exceptionally high (over 85%) incident photon to photocurrent conversion efficiencies (IPCEs) with TiO_2 and much lower IPCEs with zinc oxide. However, in the case of the dye merbromin (mercurochrome), the highest IPCE (69%) has been obtained for ZnO films [24]. It seems that merbromin acts more effectively in passivating the ZnO than TiO_2. Again indoline dyes give higher IPCEs for SnO_2 compared to TiO_2 [25]. It is very likely that nitrogen in indoline dyes passivate electron accepting Lewis acid sites on the oxide surface.

3. Conclusion

Gratzel's cell has many unique features enabling its functioning under apparently unacceptable circumstances. One of the most puzzling features has been the absence of appreciable germinate and non-geminate recombination. Although a quantitative understanding is still lacking, the former type of recombination is understood to be a result of the ultra-fast injection rate. A more important recombination mode that lowers efficiency is the reaction of electrons with acceptors during transit to the back contact. Traps seem to mediate this recombination and a low effective electron mass favors both trapping and the entry of a trapped electron into a surface state. The present investigation based mainly on the measurement of $1/f$ noise in the current through nanocrystalline films, shows that the dye plays an important secondary role in passivating the semiconductor oxide surface and inhibiting the recombination with acceptors. As passivation suppresses surface interaction of the carriers, the dye is also instrumental in increasing the diffusion coefficient of electrons in the nanocrystalline matrix. Investigation also shows how detrimental the adsorbed moisture on the oxide surface is and gives very important clues as to why efficient cells cannot be made out ZnO films. In addition to the strong bonding

of water molecules to the ZnO surface, the low effective electron mass favors transition of electrons to the hydroxyl radical produced by dissociation of water.

Much effort has been diverted to synthesize dyes that match better the solar spectrum. Dye synthesis should also consider the passivating effect and identify suitable ligands that close the recombination centers. The suitability of a ligand as a passivator seems to depend on the nature of the oxide material.

Acknowledgement

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