

## LETTER TO THE EDITOR

**1/f noise and dye-sensitized solar cells**

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**Abstract**

The adsorbed molecular species, such as H<sub>2</sub>O and I<sub>2</sub>, that produce electron acceptor states on the TiO<sub>2</sub> surface are found to generate 1/f noise in the electric current through nanocrystalline films of TiO<sub>2</sub>. It is suggested that the trapping and detrapping of electrons at the surface states is the cause of this noise. When the TiO<sub>2</sub> film surface is coated with dyes, the passivation of the active surface sites suppresses 1/f noise. Implications of 1/f noise on the functioning of the dye-sensitized solar cell, notably the effect of adsorbed iodine in inducing recombinations, are discussed.

The electric current through a conductor at a constant bias voltage and temperature undergoes fluctuations around a mean [1–5]. In addition to the frequency ( $f$ ) independent thermal and shot noises, conducting materials and electrical devices also display a noise whose spectral power density exhibits 1/f dependence [1–5] (more generally 1/f<sup>δ</sup> variation where δ is a positive index, generally close to unity). In many instances, the spectral power density  $S(f)$  of this noise can be described by Hooge's empirical relation [6]

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

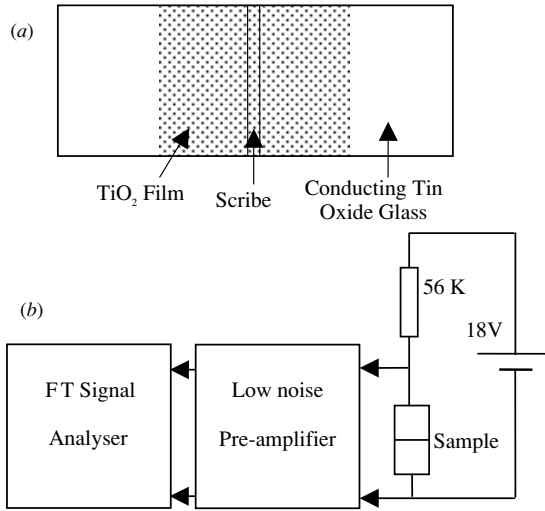
where  $I_0$  is the mean value of the fluctuating current  $I(t) = I_0 + X(t)$ , with  $\langle X(t) \rangle = 0$  and

$$S(f) = \lim_{T \rightarrow \infty} \left( \frac{1}{2T} \left| \int_{-T}^T X(t) e^{-2\pi i f t} dt \right|^2 \right). \quad (2)$$

The constant  $A$  in (1) which measures the level of noise generally takes the form [6]  $A = \Upsilon/N$ , where  $N$  is the total number of free charge carriers in the sample and the parameter  $\Upsilon$  is referred to as Hooge's constant. The interactions of carriers with defects, surface states and associated events such as recombination and trapping–detrapping are believed to be the major causes of 1/f noise in semiconductors [1–7]. Consequently, 1/f noise measurements receive considerable attention as a tool for characterization and understanding the nature of carrier relaxation processes in semiconductors [2, 3]. In electronic measuring devices, the lowest possible level of

1/f noise is desired to improve the detectivity. Also, a high 1/f noise level usually indicates an underlying dissipative process [8]. Both bulk [1, 2, 7] and surface [1, 2, 9] interactions of carriers contribute to 1/f noise in semiconductors. Because of the large surface to volume ratio, surface effects are expected to be a major cause of 1/f noise in nanocrystalline semiconductors. Furthermore, the slow charge transport in nanostructured materials has been attributed to the trapping and detrapping of electrons in intraband-gap surface states [10–12]. In this letter, we describe our observations on 1/f noise in bare and dye-coated nanocrystalline films of TiO<sub>2</sub>. It is found that in bare nanocrystalline TiO<sub>2</sub> films, the adsorbed molecular species that produce electron acceptor surface states (e.g., water vapour, iodine) induce 1/f noise, whereas in dye-coated TiO<sub>2</sub> films, the passivation of active sites on the TiO<sub>2</sub> surface by the dye suppresses the generation of 1/f noise. The implications of these observations on the functioning of the dye-sensitized solar cells are discussed.

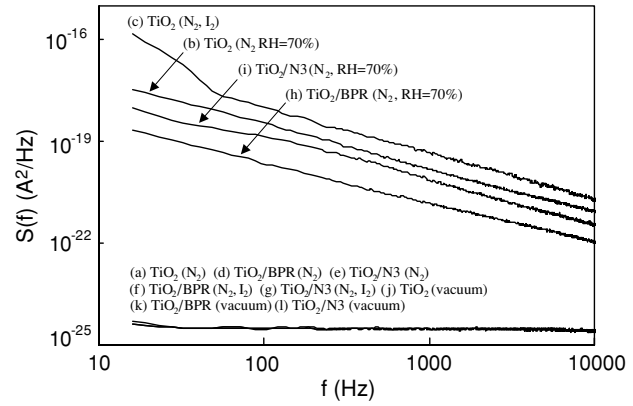
TiO<sub>2</sub> nanocrystalline films used for noise measurements were prepared as follows. The electrical connectivity of a conducting tin oxide glass sheet (1.5 × 2 cm<sup>2</sup>, sheet resistance 12 Ω sq<sup>-1</sup>) was broken by scribing a line (~8 μm thick) with a diamond point glass cutter. A layer of colloidal TiO<sub>2</sub> (thickness ~12 μm) was screen printed above the scribe by the procedure used for the fabrication of dye-sensitized solar cells and sintered at 430 °C for 30 min to form the sample geometry [13] represented in figure 1(a). In some experiments, films were coated with bromopyrogallol



**Figure 1.** (a) A schematic diagram, illustrating sample geometry used for the noise measurement. (b) The circuit used for the noise measurement.

red (BPR) or cis-dithiocyanatobis (4–4'-dicarboxylic acid-2, 2'-Ru[II]) (N3) by soaking them in alcoholic solutions of these dyes ( $\sim 2.5 \times 10^{-3}$  M). Figure 1(b) shows the circuit used for the noise measurements. The sample placed in a chamber with facilities for evacuation and heating was connected in series with a resistor  $R = 56 \text{ k}\Omega$  ( $R \ll$  the resistance of the sample) and an 18 V Ni–Cd battery. A low noise preamplifier (Stanford Research SR560) amplified the voltage fluctuation across the sample and a power spectrum analyser (Stanford Research SR785 Fourier Transform Dynamic Signal Analyser) computed  $S(f)$  and plotted its variation with  $f$ .

When the chamber is filled with air at atmospheric pressure and relative humidity (RH) 27% (23 °C), the noise power spectrum (i.e., plot of  $S(f)$  versus  $f$ ) clearly displayed frequency-dependent noise (FDN). On evacuation of the chamber, FDN persisted but at lower intensity. However, if the film is heated to  $\sim 90$  °C during evacuation, FDN disappeared completely even after cooling the sample to room temperature under vacuum ( $10^{-6}$  Torr) and did not reappear when the chamber was filled with dry  $\text{N}_2$  or  $\text{O}_2$  (figure 2(a)). As the current through the sample is  $\sim 2 \mu\text{A}$ , the thermal noise expected (the Nyquist formula [4]) is of the order of  $10^{-25} \text{ A}^2 \text{ Hz}^{-1}$  and agrees with the observed



**Figure 2.** Noise spectra at 23 °C of (a) bare  $\text{TiO}_2$  film in  $\text{N}_2$ , (b) bare  $\text{TiO}_2$  film in  $\text{N}_2$  at RH  $\sim 70\%$ , (c) bare  $\text{TiO}_2$  in a  $\text{N}_2$  saturated with  $\text{I}_2$  vapour, (d)  $\text{TiO}_2/\text{BPR}$  in  $\text{N}_2$ , (e)  $\text{TiO}_2/\text{N3}$  in  $\text{N}_2$ , (f)  $\text{TiO}_2/\text{BPR}$  in  $\text{N}_2$  saturated with  $\text{I}_2$ , (g)  $\text{TiO}_2/\text{N3}$  in  $\text{N}_2$  saturated with  $\text{I}_2$ , (h)  $\text{TiO}_2/\text{BPR}$  in  $\text{N}_2$  at RH  $\sim 70\%$ , (i)  $\text{TiO}_2/\text{N3}$  in  $\text{N}_2$  at RH  $\sim 70\%$ , (j)  $\text{TiO}_2$  (vacuum), (k)  $\text{TiO}_2/\text{BPR}$  (vacuum) and (l)  $\text{TiO}_2/\text{N3}$  (vacuum).

level of frequency-independent noise. The generation of FDN resumed when water vapour was introduced into the chamber. Figure 2(b) shows the noise spectrum of the sample in a nitrogen atmosphere at RH  $\sim 70\%$ . The above observations show the factor which contributed to FDN when the sample in air was also moisture. When the experiment was repeated replacing water with acetonitrile, FDN was not detected. We once again observed FDN on the introduction of iodine into the chamber filled with  $\text{N}_2$  (figure 2(c)). It was amazing to note the difference in behaviour of bare and dye-coated  $\text{TiO}_2$  films. Here, iodine was ineffective in creating FDN and the noise power density ( $f$ -independent) remained unaltered in the presence of iodine vapour in the chamber (figures 2(d), (e), (f) and (g)). Again the influence of moisture in generating FDN is lesser in dye-coated  $\text{TiO}_2$  films as measured noise levels here are smaller compared to that of the bare  $\text{TiO}_2$  films. Table 1 gives the values of the parameters  $A$ ,  $\delta$  and  $\Upsilon$  when the noise spectra of different systems are fitted to formula (1). The magnitude of the parameter  $A$  for a sample of given geometry (i.e., film thickness, length and breadth of the scribe) measures the level of  $1/f$  noise. In the absence of FDN, the background noise (figures 2(a), (d) and (e)) originates from thermal and environmental influences and does not follow formula (1). Nevertheless, for comparison, table 1 gives the values of  $A$

**Table 1.** The values of parameters  $A$ ,  $\delta$  and  $\Upsilon$  for different systems obtained by fitting noise data to formula (1), biasing voltage = 18 V,  $I_0 = 3.2 \times 10^{-4}$  A.

Sample	$\delta$	A	$\Upsilon$
$\text{TiO}_2$ (vacuum)	0	$4.4 \times 10^{-18}$	$3.2 \times 10^{-7}$
$\text{TiO}_2$ ( $\text{N}_2$ )	0	$4.4 \times 10^{-18}$	$3.2 \times 10^{-7}$
$\text{TiO}_2/\text{BPR}$ (vacuum)	0	$4.4 \times 10^{-18}$	$3.2 \times 10^{-7}$
$\text{TiO}_2/\text{N3}$ (vacuum)	0	$4.4 \times 10^{-18}$	$3.2 \times 10^{-7}$
$\text{TiO}_2/\text{BPR}$ ( $\text{N}_2$ )	0	$4.4 \times 10^{-18}$	$3.2 \times 10^{-7}$
$\text{TiO}_2/\text{N3}$ ( $\text{N}_2$ )	0	$4.4 \times 10^{-18}$	$3.2 \times 10^{-7}$
$\text{TiO}_2$ ( $\text{N}_2$ , RH = 70%)	1.25	$8.8 \times 10^{-10}$	$6.3 \times 10^1$
$\text{TiO}_2/\text{BPR}$ ( $\text{N}_2$ , RH = 70%)	1.15	$4.4 \times 10^{-11}$	$3.2 \times 10^0$
$\text{TiO}_2/\text{N3}$ ( $\text{N}_2$ , RH = 70%)	1.30	$5.7 \times 10^{-10}$	$4.1 \times 10^1$
$\text{TiO}_2$ ( $\text{N}_2$ , saturated $\text{I}_2$ vapour)	1.37	$5.8 \times 10^{-9}$	$4.2 \times 10^2$
$\text{TiO}_2/\text{BPR}$ ( $\text{N}_2$ , saturated $\text{I}_2$ vapour)	0	$4.3 \times 10^{-18}$	$3.1 \times 10^{-7}$
$\text{TiO}_2/\text{N3}$ ( $\text{N}_2$ , saturated $\text{I}_2$ vapour)	0	$4.4 \times 10^{-18}$	$3.2 \times 10^{-7}$

and  $\Upsilon$  for the frequency-independent situations as well, setting  $\delta = 0$  in (1). Hooge's constant  $\Upsilon$  is estimated using the literature value [14] for the carrier density of  $\text{TiO}_2$  ( $\sim 1 \times 10^{17} \text{ cm}^{-3}$ ) and volume of  $\text{TiO}_2$  in the scribe =  $7.2 \times 10^{-3} \text{ cm}^3$  (estimated from the knowledge of the volume of  $\text{TiO}_2$  in a large size film). The resistance of samples in the absence of moisture was of the order of  $10 \text{ M}\Omega$  and reduced to  $4 \text{ M}\Omega$  in the presence of moisture (RH 70%).

The above experiments indicate that the electron acceptor states produced by adsorbed species generate  $1/f$  noise in nanocrystalline  $\text{TiO}_2$  films. Water is known to dissociatively adsorb on the  $\text{TiO}_2$  surface forming H and OH fragments [15]. The acceptor OH radicals act as electron trapping sites. Similarly, iodine adsorbed on the  $\text{TiO}_2$  surface would also trap electrons forming  $\text{I}^-$ . The trapping and detrapping of electrons at the surface states is known to be a cause of  $1/f$  noise in semiconductor materials [1]. This process becomes exceedingly important for nanostructured films because of their large surface to volume ratio. In a dyed  $\text{TiO}_2$  film, water and iodine absorption sites get passivated by surface chelation of the dye molecules and therefore  $1/f$  noise is suppressed. When the RH in the chamber is high ( $\geq 40\%$ ), dye bonded to the  $\text{TiO}_2$  surface seems to desorb partly, allowing water adsorption. This explains the observation that in an environment of high  $\text{H}_2\text{O}$  vapour pressure, dyed  $\text{TiO}_2$  films also exhibit  $1/f$  noise.

The observations presented above have profound implications on the action of the Gratzel-type dye-sensitized photoelectrochemical cell [16]. In fact, they explain why the Gratzel cell works so well. Although the substrate through which the electrons move is highly populated with defects, the adsorbed dye passivates these surface recombination centres. As the trapping–detrapping process at surface states is relieved by dye chelation, the dye absorption also facilitates transport of electrons across the nanocrystalline matrix. In fact, it has been noted that the diffusion coefficient of electrons in dyed nanocrystalline films is higher than that in bare films [17]. If there are voids in the dye monolayer on the  $\text{TiO}_2$  surface, the interaction of iodine at the points of exposure of  $\text{TiO}_2$  would be detrimental to the functioning of the cell. The trapping of electrons by iodine adsorbed at the voids in the dye layer will cause recombination. Partial desorption of the dye, followed by iodine adsorption seems to be a major cause of the recombination loss in the dye-sensitized solar cell. Thus, finding ways of preventing iodine adsorption is important for the improvement of the efficiency of the cell. It is interesting to note that successful attempts have been made to synthesize dyes that resist desorption to the electrolyte [18].

Our experiments also indicate the importance of hydrophobic [19] and water-free electrolytes. Noise measurement also offers a way of characterizing dye adsorbed nanostructured semiconductor films. In this study, we used N3 and BPR as examples of dyes that are strongly complex to the  $\text{TiO}_2$  via carboxylate and hydroxyl ligands respectively, eliminating the surface hydroxyl groups [20]. We believe that  $1/f$  noise studies would be of value in understanding other modes of interactions of molecules with nanocrystalline semiconductor materials.

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