Energetics of Nanoparticle Semiconductor Electrodes Determined by Spectroelectrochemical Measurements of Free Electrons

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Figure S1a shows the change of %T when reductive potential was applied. %T shown here is the transmittance of the electrochemical cell which includes mesoporous TiO_2 film, FTO glass substrate, cuvette and electrolyte in the optical path. In the absence of a TiO_2 film, the transmittance (%T) of the other components in the optical path did not change in response to the applied potential range of interest herein. Therefore, we attribute the absorbance difference (ΔA) shown in Figure S1b exclusively to the TiO_2 film.
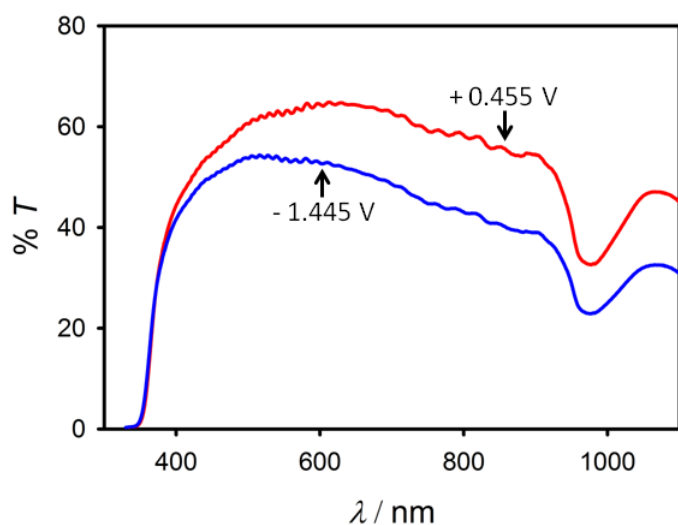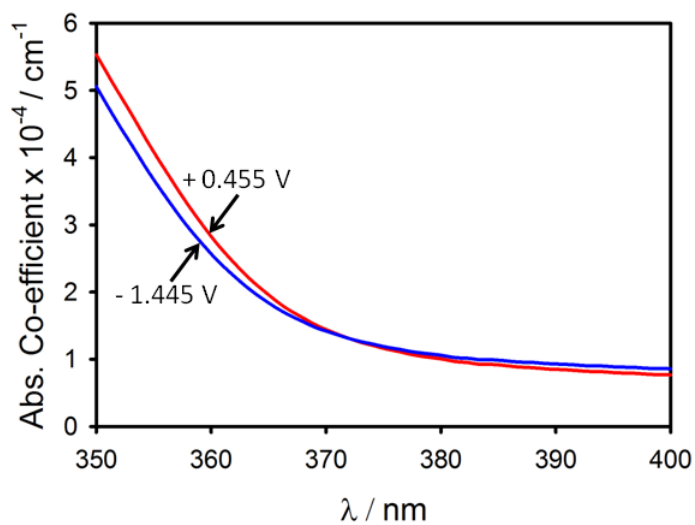

(a)
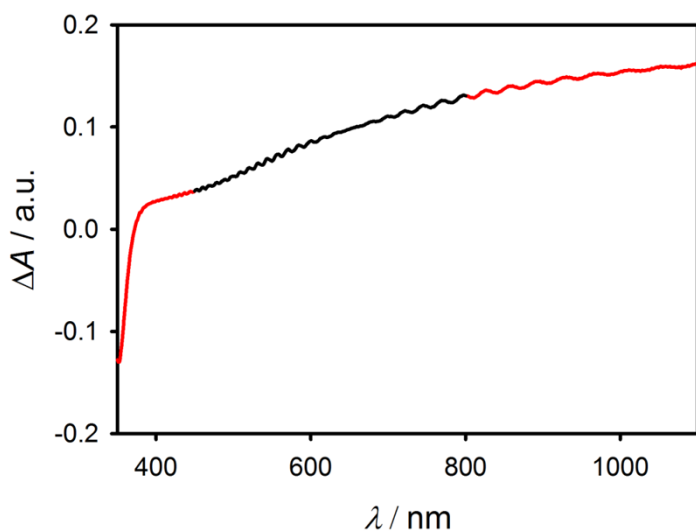
(b)

Figure S1. (a) Transmittance (%*T*) spectra of TiO$_2$ photoanode in contact with aqueous 0.2 M KCl solution at pH 12.8. Potentials were given against SCE. (b) Change in absorbance of TiO$_2$ film. $\Delta A= A(-1.445\ V) - A(+0.455\ V)$.

While applying reductive potential, the absorption edge of the TiO$_2$ film moved towards higher energy suggesting an apparent widening of the band gap.


Figure S2. Absorbance spectra of a nanostructured TiO$_2$ film in response to applied potentials. Electrolyte was 0.2 M aq. KCl solution at pH 12.8. Potentials were given against SCE.

In addition to the conduction band states, porous TiO_2 films are well-known to contain a large number of sub-bandgap trap states.[2] The concentration of both trapped electrons and free electrons in the film increases exponentially while raising the Fermi level. The total concentration of electrons, n_{Total}, is therefore the sum of free conduction band electrons, n_{CB}, and electrons contained in localized trap states, $n_{Trapped}$. Charge extraction method was used to determine the total electron concentration (n_{Total}) at various potentials.[3–5] In this method a three-electrode set-up was used. The photoanode was sealed to an opening of the electrochemical cell with a Viton O-ring and a high surface area platinum mesh was used as the counter electrode. N_2 gas was purged into the aqueous electrolytes for 30 minutes, prior to any measurement. TiO_2 photoanode was charged for 5 minutes followed by applying a positive bias to extract all the charges stored during charging. The current was measured against time and the total charge was calculated by integrating the area under the current vs. time curve. Figure S3a shows a comparison of the n_{Total}, measured by charge extraction data, with the absorbance at 780 nm, ΔA. This mismatch is not very large under these conditions, which can be misleading regarding that all the electrons, both free and trapped, are contributing to the absorbance observed in Visible region. However, n_{CB} and ΔA are well matched (Figure S3b) which supports our argument that the free electrons have the major contribution to the absorbance measured at visible region.
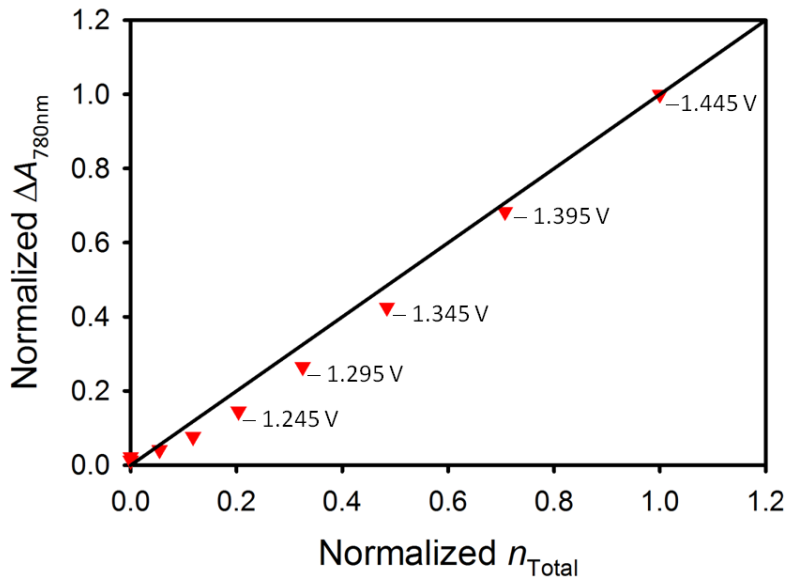

(a)
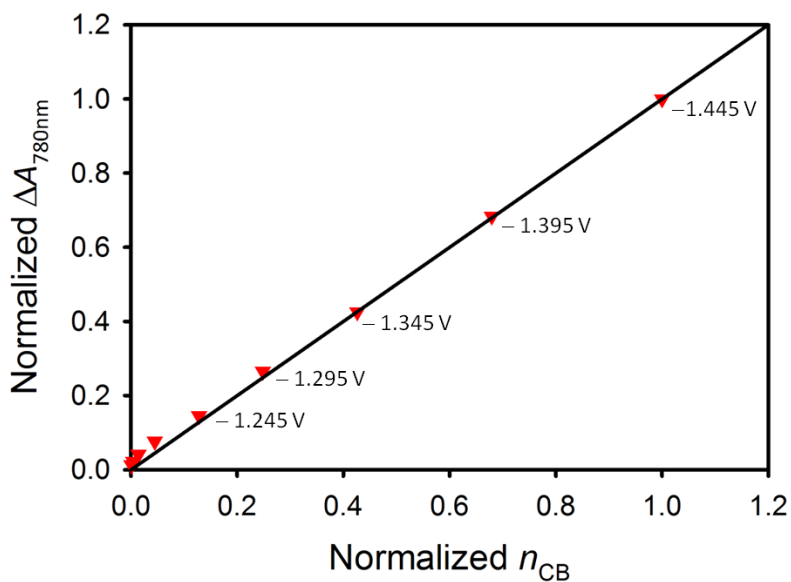
(b)

Figure S3. Plot of absorbance *vs.* electron concentration measured at a potential range from -1.045 to -1.445 V *vs.* SCE. n_{Total} (a) is the total electron concentration determined from the charge extraction method and n_{CB} (b) is the electron concentration calculated from the band gap broadening and is assigned to be the free electrons in the conduction band. The straight line represents slope = 1 and deviation from this line shows the mismatch between electron concentration and the corresponding absorbance. This mismatch is significant in case of ΔA *vs.* n_{Total} whereas ΔA *vs.* n_{CB} is well matched.
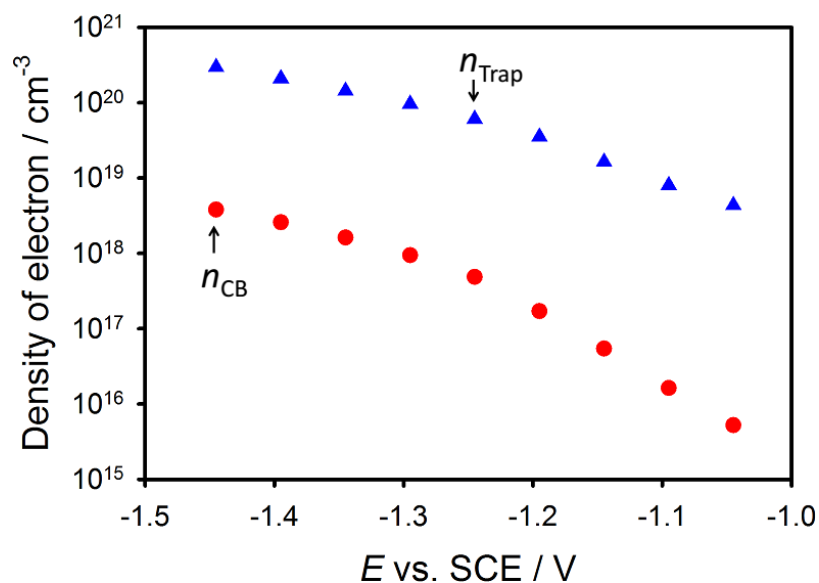
Figure S4. Plot of the density of free and trapped e^- as a function of applied potential. n_{CB} is the free e^- in the conduction band determined from the Burstein shift (ΔE_G). n_{Trap} is the density of trapped e^- calculated by subtracting n_{CB} from n_{Total}.

Table S1. Calculations of E_{CB}/q and ε_{780nm} using a range of values for effective mass of electrons (m_e^*) and holes (m_h^*) found in literature, where m_0 is the mass of a free electron.

E vs. SCE / V	E_{CB}/q / V			
	$m_e^* = 1.0\,m_0$ $m_h^* = 1.0\,m_0$	$m_e^* = 1.0\,m_0$ $m_h^* = 0.8\,m_0$	$m_e^* = 10.0\,m_0$ $m_h^* = 1.0\,m_0$	$m_e^* = 10.0\,m_0$ $m_h^* = 0.8\,m_0$
-1.045	-1.261	-1.265	-1.326	-1.334
-1.095	-1.282	-1.286	-1.346	-1.355
-1.145	-1.301	-1.305	-1.366	-1.374
-1.195	-1.322	-1.326	-1.387	-1.395
-1.245	-1.345	-1.349	-1.410	-1.418
-1.295	-1.378	-1.383	-1.443	-1.451
-1.345	-1.414	-1.419	-1.480	-1.487
-1.395	-1.452	-1.457	-1.518	-1.525
-1.445	-1.493	-1.497	-1.558	-1.566

	$m_e^* = 1.0\,m_0$ $m_h^* = 1.0\,m_0$	$m_e^* = 1.0\,m_0$ $m_h^* = 0.8\,m_0$	$m_e^* = 10.0\,m_0$ $m_h^* = 1.0\,m_0$	$m_e^* = 10.0\,m_0$ $m_h^* = 0.8\,m_0$
ε ($M^{-1}\,cm^{-1}$) at 780 nm	9.9×10^4	1.2×10^5	4.1×10^4	5.5×10^4

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