Supporting Information

Decoupling the Charge Collecting and Screening Effects in Piezotronics-Regulated Photoelectrochemical Systems by Using Graphene as the Charge Collector

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Calculation Details

The basis for the calculations on the PMN-PT/Au/TiO$_2$ and the PMN-PT/graphene/TiO$_2$ heterojunctions is the 1D Poisson Equation—a relationship between the spatially dependent charge density $\rho(x)$ and the second spatial derivative of electric potential $\varphi(x)$.

$$\rho(x) = -\varepsilon_r \varepsilon_0 \frac{\mathrm{d}^2 \varphi(x)}{\mathrm{d}x^2} \tag{1}$$

For semiconductors, the left-hand side of Equation 1 becomes the following:

$$\rho(x) = z_n n + z_p p + z_{N_D} N_D + z_{N_A} N_A \tag{2}$$

Where n, p, N_D and N_A are the electron, electron hole, donor dopant, and acceptor dopant number densities, respectively, and z_i is the charge for species i ($i = n, p, N_D, N_A$). We assume that $N_A \approx 0$ for n-type TiO$_2$. With typical mathematical descriptions for semiconductors, we may combine Equation 1 and 2 to construct the differential equation:

$$\frac{d^2\varphi(x)}{dx^2} = \left(-\frac{1}{\varepsilon_r \varepsilon_0}\right)\left(z_n n_b exp[\frac{-z_n e\varphi(x)}{kT}] + z_p p_b exp[\frac{-z_p e\varphi(x)}{kT}] + z_{N_D} N_D\right) \tag{3}$$

Equation 3 relates the potential profile in the semiconductor to its properties and parameters: the electrical permittivity $\varepsilon_r \varepsilon_0$, bulk electron and hole concentrations (n_b and p_b, respectively), and dopant concentration N_D.

We assume that TiO$_2$ is primarily doped by electronically compensated oxygen vacancies ($null \rightarrow V_O^{\cdot\cdot} + 2e^-$) where $n_b \approx 2\,N_D$. We use the charges $z_n = -1, z_p = +1$, and $z_{N_D} = z_{V_O^{\cdot\cdot}} = +2$. For an operational temperature of 22°C we assume that these oxygen vacancies are uniformly distributed and are stationary. In other words, oxygen vacancies—the charged dopant cores—are not permitted to diffuse in this model despite their being subject to an electric field.

With the law of mass action ($n_i^2 = n_b p_b$), we may rewrite Equation 3 as the following:

$$\frac{d^2\varphi(x)}{dx^2} = \frac{-2N_D exp\left[\frac{e\varphi(x)}{kT}\right] + \frac{\left(N_C exp\left[-\frac{E_g}{2kT}\right]\right)^2}{2N_D} exp\left[\frac{-e\varphi(x)}{kT}\right] + 2N_D}{-\varepsilon_{Semi}\varepsilon_0} \tag{4}$$

Where N_C and E_g are the density of states in the conduction band and the band gap of TiO$_2$, respectively. We treat our PEC system and Equation 4 as a semi-infinite case such that $\frac{d\varphi(x=\infty)}{dx} = 0$ and $\varphi(x = \infty) = 0$ and we reach a special case where $\frac{d^2\varphi}{dx^2} = \frac{1}{2}\frac{d}{d\varphi}\left(\frac{d\varphi}{dx}\right)^2$ may be applied to Equation 4:

$$\frac{d\varphi(x)}{dx} = -\left\{\frac{2kT}{\varepsilon_{Semi}\varepsilon_0}\left[2N_D\left(\exp\left[\frac{e\varphi(x)}{kT}\right]-1\right) + \frac{N_C^2\exp\left[-\frac{E_g}{kT}\right]}{2N_D}\left(\exp\left[\frac{-e\varphi(x)}{kT}\right]-1\right) - \frac{2eN_D z_{N_D}\varphi(x)}{kT}\right]\right\}^{\frac{1}{2}}$$ (5)

Equation 5 sets up a differential equation between electrical potential $\varphi(x)$ and electric field $\frac{d\varphi(x)}{dx}$.

When presented with a ferroelectric polarization D_{Ferro} [C m m^{-3}] from the PMN-PT, the electrode (Au or graphene) and/or the semiconductor (TiO$_2$) must supply the appropriate charges (q_{Int} and q_{Semi} [C m^{-2}], respectively) to maintain charge neutrality.

$$D_{Ferro} + q_{Int} + q_{Semi} = 0$$ (6)

Using Gauss' Law, q_{Semi} may be expressed as:

$$q_{Semi} = \varepsilon_{Semi}\varepsilon_0\frac{d\varphi(x=0)}{dx}$$ (7)

Where $x = 0$ represents the electrode/semiconductor interface, and $\varphi(x = 0)$ is the potential difference between the interface and the bulk of the TiO$_2$; $\varphi(x = 0)$ serves as a boundary condition for solving Equation 5. Combining Equation 6 and 7, we may solve for the value $\varphi(x = 0)$ which satisfies charge neutrality, and numerically solve Equation 5 to construct a potential profile in TiO$_2$.

Since the Au or graphene may contribute some charge density to compensate D_{Ferro}, it is important to look at the magnitude of charge that is *available* within the electrode. We begin with Au which has a high free-carrier density ($\sim 10^{23}$ cm^{-3}) that translates to ~ 100 C m^{-2} for a standard 10-nm thick Au film—over two orders of magnitudes large than that of the measured $D_{Ferro} = 0.3$ C m^{-2} for our poled PMN-PT. We make a similar observation for TiO$_2$ by looking at an isolated system of Au and TiO$_2$ in equilibrium.

Au and TiO$_2$ equilibrate by exchanging charge across the Au/TiO$_2$ interface until their Fermi energies are equal. The resultant space charge region in TiO$_2$ may be compensated by Au on an Å scale, effectively making the potential change between bulk TiO$_2$ and the Au/TiO$_2$ interface equal to the difference between the Fermi energies ($\varphi(x = 0) = E_{F,TiO_2} - E_{F,Au}$). This potential difference corresponds to a charge density on the order of 10^{-3} C m^{-2}; five orders of magnitude smaller than the charge density available in Au.

A 10-nm Au layer has enough available charge to screen the PMN-PT ferroelectric polarization and compensate the charge in TiO$_2$ when the metal and semiconductor equilibrate separately. Even a hypothetical 1-nm Au layer would have 10 and 10^3 times more charges than the charges presented at PMN-PT/Au and Au/TiO$_2$ interfaces, respectively. Thus, Au would fully screen D_{Ferro} and there would be no ferroelectric tuning of band bending in TiO$_2$ when an Au electrode is used.

A single layer of graphene has ~10^{12} cm^{-2} free charge carriers available to compensate for a ferroelectric polarization.[1] This translates to an available charge density on the order of 10^{-3} C m^{-2} —two orders of magnitude lower than that required to fully screen D_{Ferro}. As such, graphene can compensate for only a small fraction of D_{Ferro}, the remainder of which must be compensated by TiO$_2$ to maintain charge neutrality. We describe our system mathematically by assuming that the sign for the charges supplied by graphene is opposite to that of the sign for D_{Ferro}(i.e. $|D_{Ferro} + q_{int}| < |D_{Ferro}|$). This condition is then used to solve Equation 6 and 7 for our boundary condition $\varphi(x = 0)$, and ultimately construct the potential profile in TiO$_2$ by numerically solving Equation 5.

With appropriate poling direction, the ferroelectric charge of PMN-PT can be shown to effectively enhance the band bending in TiO₂. The graphene system requires that TiO₂ supply a charge density about five orders of magnitude larger than that for the Au/TiO₂ junction in equilibrium. This larger charge corresponds to a greater potential change (band bending) in TiO₂, thus showing that the PMN-PT/graphene/TiO₂ heterojunction may be subject to ferroelectric tuning.

Constructing the potential profile within the PMN-PT is fairly simple. PMN-PT is taken to be an ideal insulator (i.e. carries no charge) in which the potential change is linear. The thickness d was arbitrarily chosen and the potential across the PMN-PT was calculated using the parallel plate capacitor equation $\frac{Q}{\Delta V} = \frac{\varepsilon_{PMN-PT}\varepsilon_0 A}{d}$ under different charge $\frac{Q}{A} = D_{Ferro}$.

For the equilibration between the TiO₂ and the electrolyte (1 M NaOH(aq)), we must consider the initial interactions that happen at the TiO₂/electrolyte interface. A surface dipole forms when the two media first come into contact which is the cause for the flat-band potential shift that coincides with a change in the pH of electrolyte. In general, the flat-band potential shift with pH (and thus the work function difference as a function of pH) is approximately 59 meV per unit of pH change. Therefore, if the Fermi level ($E_{Fermi\ at\ iso}$) of the semiconductor relative to solution at the isoelectric point (pH_{iso}) is known, then the Fermi level (E_{Fermi}) at any pH can be approximated by:[2,3]

$$E_{Fermi} = E_{Fermi\ at\ iso} - (0.059) * (pH - pH_{iso}) \tag{8}$$

We remind the reader that energies levels are given relative to vacuum potential; E_{Fermi} and $E_{Fermi\ at\ iso} < 0$. Equation 8 gives a shift of the Fermi energy of E_{F,TiO_2} relative to the Nernst potential for the oxidation evolution reaction $E(O_2/H_2O)$.

The electrolyte equivalent of Equation 5 is given by:

$$\frac{d\varphi(x)}{dx}\bigg|_{Sol} = -\left\{\frac{2kT}{\varepsilon_{Sol}\varepsilon_0}\sum_i n_i\left(\exp\left[-\frac{z_i e\varphi_{Sol}(x)}{kT}\right]-1\right)\right\}^{\frac{1}{2}} \tag{9}$$

Where $i=$ OH⁻, Na⁺, H⁺ and ε_{Sol} is taken to be the relative electrical permittivity of water

(ε_{Sol}=80). Again, we invoke the semi-infinite boundary conditions implemented for PMN-

PT/electrode/TiO₂ multijunction when solving for the equilibration between TiO₂ and the

electrolyte. I.e. far away from the TiO₂/electrolyte interface, the potential in the electrolyte is

$E(O_2/H_2O)$ vs. vacuum and the potential in TiO₂ is the shifted bulk Fermi energy calculated

from Equation (8). This sets up the boundary conditions for the bulk of each of media.

We assume that there is intimate contact between the TiO₂ and the electrolyte which sets

up a boundary condition at the interface: $\varphi_{TiO_2}(x=0) = \varphi_{Electrolyte}(x=0)$. This boundary

condition can be determined by solving for charge neutrality $q_{Semi} + q_{Sol} = 0$ where $q_{Sol} =$

$\varepsilon_{Sol}\varepsilon_0\frac{d\varphi_{Sol}(x=0)}{dx}$, from which the solutions to Equation 5 and 9 may be determined for the TiO₂/electrolyte

interface.

Explicit values used in the calculation:

Temperature:

22°C (295.15 K)

Bandgap of TiO₂ (taken for Rutile):

3.02 eV[4]

Relative Electrical Permittivity of TiO₂:

160[5]

Donor (Oxygen Vacancy) Concentration in TiO_2:

Chosen: 10^{17} cm^{-3}

Density of States in the Conduction Band of TiO_2:

10^{20} cm^{-3}[6]

Electron Concentration in TiO_2:

Two times that of the donor (oxygen vacancy) concentration in TiO_2

Hole Concentration in TiO_2:

Mass action with intrinsic electrons

Fermi Energy of TiO_2:

-4.3 eV[5,7]

Fermi Energy of Au:

-5.1 eV[6]

Free Charge Carrier Density in Graphene:

10^{13} cm^{-3} [1]

Remnant Polarization of PMN-PT:

Measured from experiment: 30μC cm^{-2}

Relative Electrical Permittivity PMN-PT:

5650[8]

Thickness of PMN-PT:

Arbitrarily chosen to be 1.8μm

<u>References</u>

[1] H. Miyazaki, S. Odaka, T. Sato, S. Tanaka, H. Goto, A. Kanda, Kazuhito Tsukagoshi, Y. Ootuka, Y. Aoyagi, *Appl. Phys. Express* **2008**, *1*, 034007.

[2] G. A. Parks, *Chem. Rev.* **1965**, *65*, 177.

[3] C. F. Zinola, *Electrocatalysis: Computational, Experimental, and Industrial Aspects*, CRC Press, **2010**.

[4] D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh, A. A. Sokol, *Nat Mater* **2013**, *12*, 798.

[5] L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, H. J. Scheel, *J. Am. Chem. Soc.* **1996**, *118*, 6716.

[6] Y. Nagao, A. Yoshikawa, K. Koumoto, T. Kato, Y. Ikuhara, H. Ohta, *Appl. Phys. Lett.* **2010**, *97*, 172112.

[7] K. Hu, F.-R. F. Fan, A. J. Bard, A. C. Hillier, *J. Phys. Chem. B* **1997**, *101*, 8298.

[8] "Piezoelectric single crystal," can be found under https://www.jfe-mineral.co.jp/e_mineral/seihin/eseihin034.html, **n.d.**