Tuning the Fermi Level and the Kinetics of Surface States of TiO$_2$ Nanorods by Means of Ammonia Treatments.

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Supporting Information

X-Ray Diffraction Spectroscopy

X-ray diffraction (XRD) measurements (Figure S1) revealed that nanorods were grown with a rutile crystalline structure (JCPDS No. 21-1276) with small traces of the anatase polymorph (JCPDS No. 21-1272). It is worthwhile to note, that there are some missing crystallographic plane diffractions from the rutile pattern in our XRD spectra confirming that these nanorods grew following a preferential orientation. Furthermore, several SnO_2 peaks corresponding to the FTO in the glass substrate (JCPDS No. 41-1445) were also detected in the form of rutile phase, suggesting that the FTO layer acted as a seed for the TiO_2 nanorod growth that ensured an almost perfect interphase thanks to the matching of both rutile structures. As a matter of fact, a peculiar and interesting unidentified peak appeared between SnO_2 and TiO_2 (101) peaks that can be attributed to a solid solution of Sn and Ti oxides formed in the FTO/nanorods interphase.
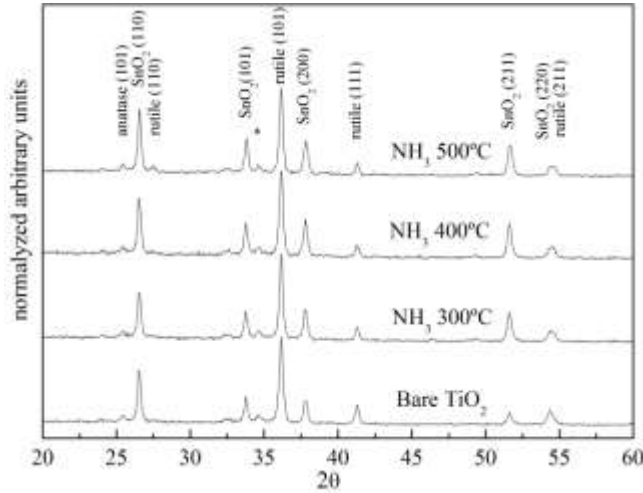

Figure S1. X-ray diffraction spectra of samples treated at different temperatures in ammonia atmosphere.

Mott-Schottky and EIS measurements.

Mott-Schottky plots from all samples were extracted from the fitting of the data obtained with EIS measurements in the dark and at different voltages (Figure S2). EIS were fitted using two ZARC's elements connected in serial, one corresponding to the depletion region (highlighted with the black square in the Bode phase plots) and to other surface contributions (red square), which are beyond the scope of this article and will be not further discussed. From the Mott-Schottky relationship (eq. S1):

$$\frac{1}{C_{SC}{}^2} = \frac{2}{N_D \varepsilon_0 \varepsilon_r}\left[\left(E - E_{fb}\right) - \frac{kT}{e}\right] \quad \rightarrow \quad N_D = \frac{1.41 \times 10^{32}}{\varepsilon_r A^2 (slope)} \qquad (S1)$$
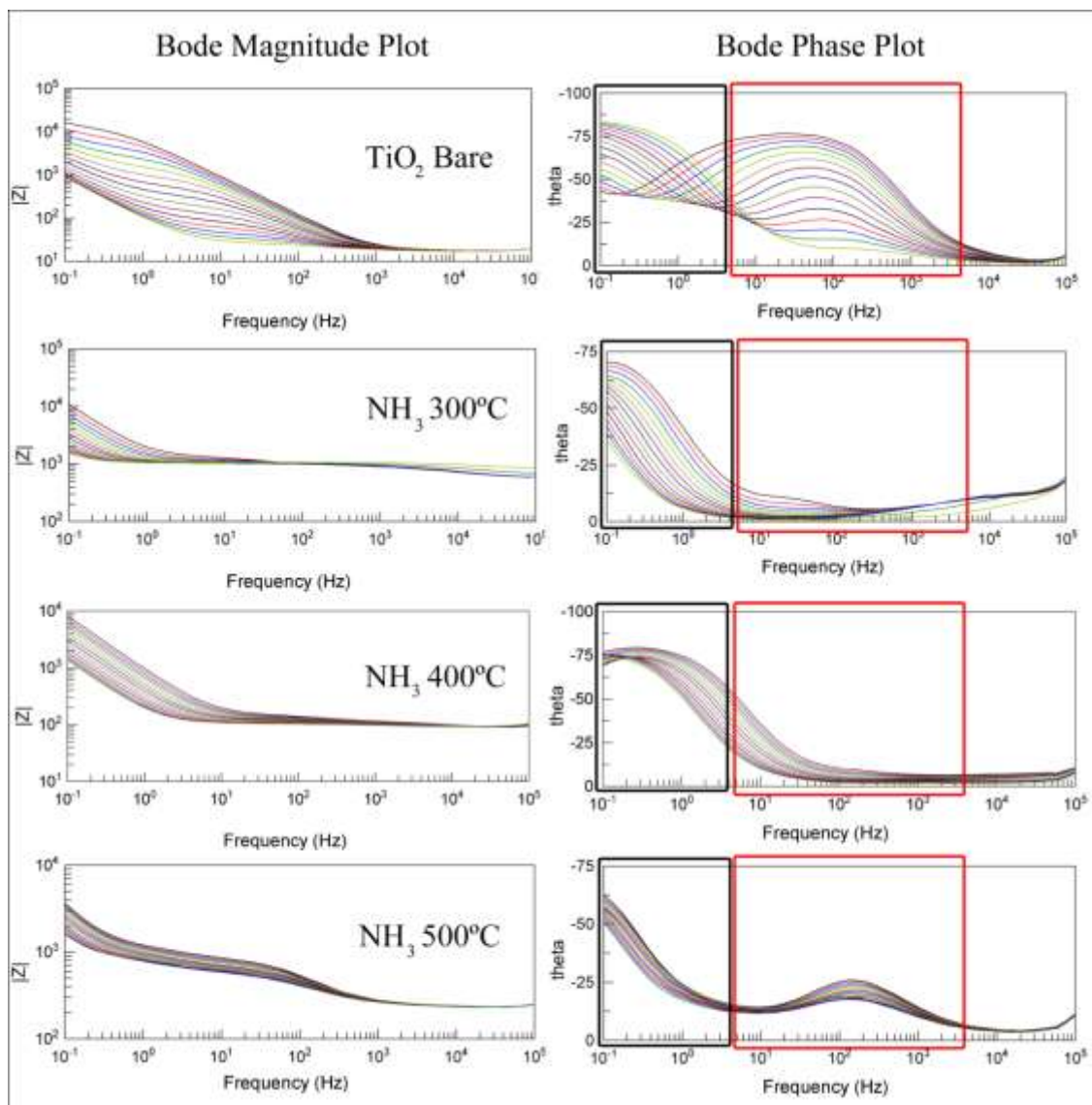
we can obtain the donor density.

Figure S2. Bode plots (Magnitude, Z, and Phase, θ) of all treated samples within a range of voltages between -950 mV and -600 mV (vs. Ag/AgCl).

Space Charge Region in Semiconductors: Potential Distribution

Debye Length

Assuming that both donors and acceptors are fully ionized, the potential ($\phi(x)$) distribution across the semiconductor follows the self-consistent Poisson-Boltzmann equation (eq. S2):

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\varepsilon_r \varepsilon_0}(p_0 exp(-e\phi(x)/kT) - n_0 exp(e\phi(x)/kT) + N_D - N_A) \qquad (S2)$$

where n_0 and p_0 are the intrinsic concentrations of electrons and holes, respectively; N_D and N_A are the concentrations of ionized electron donor and acceptors, respectively; ε_r and ε_0 are the relative dielectric constant of the semiconductor (100 for rutile TiO_2) and the vacuum permettivity (8.85×10^{-12} N^{-1}C^{2}m^{-2}), respectively; e is the fundamental electric charge (1.602×10^{-19} C); k is the Boltzmann constant (1.38×10^{-23} J·K^{-1}); and T is the absolute temperature (K). From the electro-neutrality condition in the bulk of the semiconductor (i.e. at $x \rightarrow \infty$) (eq. S3):

$$p_0 + N_D - n_0 - N_A = 0 \qquad (S3)$$

Thus, the boundary conditions are (eq. S4):

$$\phi(0) = \phi_{SC} \equiv E - E_{fb}, \qquad \left.\frac{d\phi}{dx}\right|_{x\to\infty} = 0 \qquad (S4)$$

If the potential drop at the surface (ϕ_{SC}) is sufficiently small so that $|e\phi_{SC}/kT| \ll 1$, the exponential terms on the right side of Eq. S2 can be expanded as a series and taking into account Eq. S3, the Poisson-Boltzmann equation reduces to (Eq. S5):

$$\frac{d^2\phi}{dx^2} = \frac{e^2}{\varepsilon_r \varepsilon_0 kT}(p_0 + n_0)\phi(x) \qquad (S5)$$

Its analytical solution is easily found (eq. S6):

$$\phi(x) = \phi_{SC} \exp\left(-\frac{x}{L_D}\right) \qquad (S6)$$

where L_D is known as the Debye length and is given by (eq. S7):

$$L_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{e^2(n_0 + p_0)}} \qquad (S7)$$

In our particular case, as $N_D \approx n_0 + p_0$, eq. S7 can be finally written as (eq. S8):

$$\boxed{L_D \approx \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{e^2 N_D}}} \qquad (S8)$$

Depletion Layer Width

Another important case for which eq. S2 can be solved analytically is that of a relatively heavily doped *n*-type semiconductor with a negative surface potential so that a significant depletion layer is formed. In this case, the N_D term on the right-hand side of the eq. S2 dominates, reducing to (eq. S9):

$$\frac{d^2\phi}{dx^2} = -\frac{eN_D}{\varepsilon_r\varepsilon_0} \qquad (S9)$$

Assuming that out from the depletion region (i.e. $x > W$) the electric field is negligible, the boundary conditions are (eq. S10):

$$\phi(W) = 0, \quad \left.\frac{d\phi}{dx}\right|_{x=W} = 0 \qquad (S10)$$

In addition, also considering that $\phi(0) = \phi_{SC}$, we can solve the above differential equation, yielding (eq. S11):

$$\phi(x) = \begin{cases} -\dfrac{eN_D}{\varepsilon_r\varepsilon_0}(x-W)^2, & 0 \le x \le W \\ 0, & x \ge W \end{cases} \qquad (S11)$$

where the depletion layer thickness (w) is given by (eq. S12):

$$W = \sqrt{\frac{2\varepsilon_r\varepsilon_0|\phi_{SC}|}{e^2N_D}} \qquad (S12)$$