**Electronic Supplementary Information**

# Band edge engineering of $TiO_2$@DNA nanohybrids and implications for capacitive energy storage devices

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The HRTEM side view image of a single $TiO_2$ nanocrystal in Fig. S1a shows a lattice spacing d = 0.17 nm for the (105) plane of the anatase $TiO_2$ phase. In Fig. S1b, the HRTEM image shows a layered lattice structure with an interplanar spacing of 0.236 nm and 0.189 nm, in agreement with the observed d values of the (004) and (200) planes of anatase $TiO_2$ crystal. In Fig. S1c the lattice spacing of d = 0.148 nm in another mesoporous $TiO_2$ microbead nanocrystal corresponds to the (204) plane of the anatase phase. In Fig. S1d it can be observed that two sets of lattices are oriented perpendicular to each other, with an equal inter-fringe spacing of 0.19 nm and 0.35 nm, corresponding to $TiO_2$ anatase (200) and (101) lattice planes. Fig. S1e shows a side view of another $TiO_2$ nanocrystal with alattice spacing of d = 0.134 nm corresponding to the (220) plane of theanatase phase of $TiO_2$.

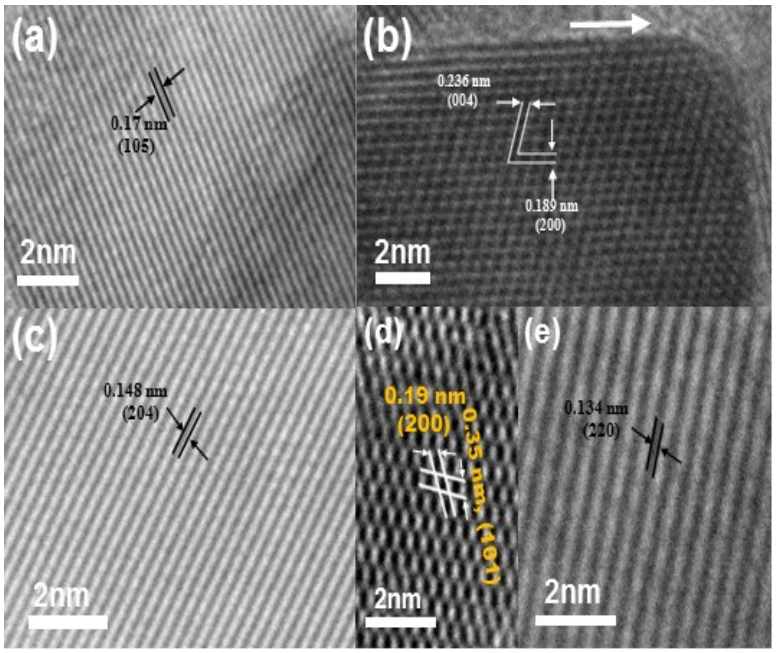


**Fig. S1.** HRTEM images of single $TiO_2$ nanocrystals with different sizes, orientations and shapes, (a, c, e) side view HRTEM images, (b, d) perpendicular HRTEM images recorded in $TiO_2$ nanocrystals.

Fig. S2(a) shows the XPS spectra of the Ti 2p valence band of the bare $TiO_2$ surface and after adsorption of dopamine and DNA on the bare $TiO_2$ surface. For three samples, the spin-orbit-splitting between $2p_{3/2}$ and $2p_{1/2}$ components can be clearly seen in the Ti 2p spectrum, corresponding to binding energies of 458 and 464 eV. It can be seen that the $2p_{3/2}$ component has a shoulder at a lower binding energy. The energy splitting between the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ core levels is 5.7 eV, indicating the normal state of $Ti^{4+}$ in anatase $TiO_2$.[1] Fig. S2(b) shows that the O 1s spectrum is decomposed into two Gaussian curves; note that for all three samples the intense peak at 529.5 eV arises from oxygen atoms on the $TiO_2$ surface. The binding energy of the O 1s peak at 529.85 eV shows that oxygen, through the formation of direct bonds with Ti, acquires a negative charge compared to the neutral oxygen molecules (with a peak binding energy of 531.0 eV).[2] The small peak at 531 eV could be attributed to hydroxyl groups on the surface of $TiO_2$ and $TiO_2$/DA. The peak at 532 eV for $TiO_2$/DA/OGN can be assigned to oxygen atoms bound to carbon atoms as C-O or C=O (532.8 eV).[3]

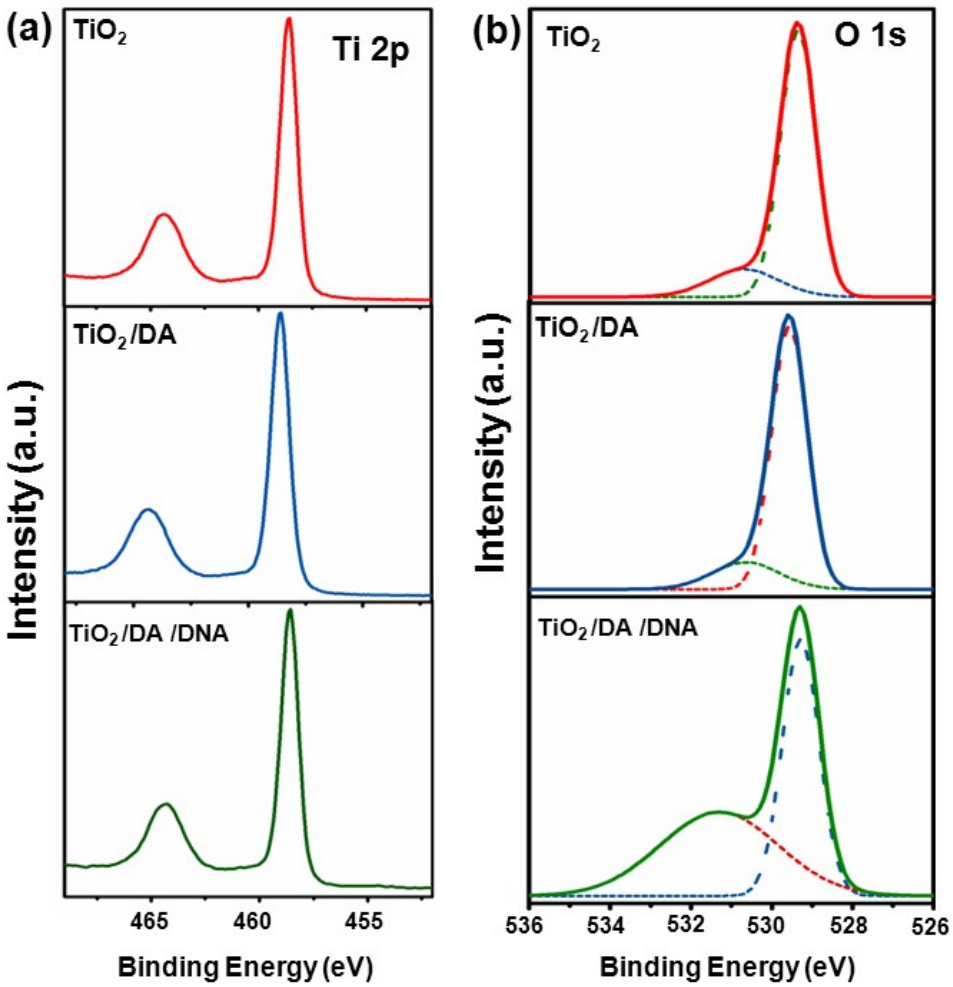


**Fig. S2** XPS spectra for the principal elements of $TiO_2$: experimental data (solid line) and fitting results (dashed line), (a) Ti 2p, (b) O 1s

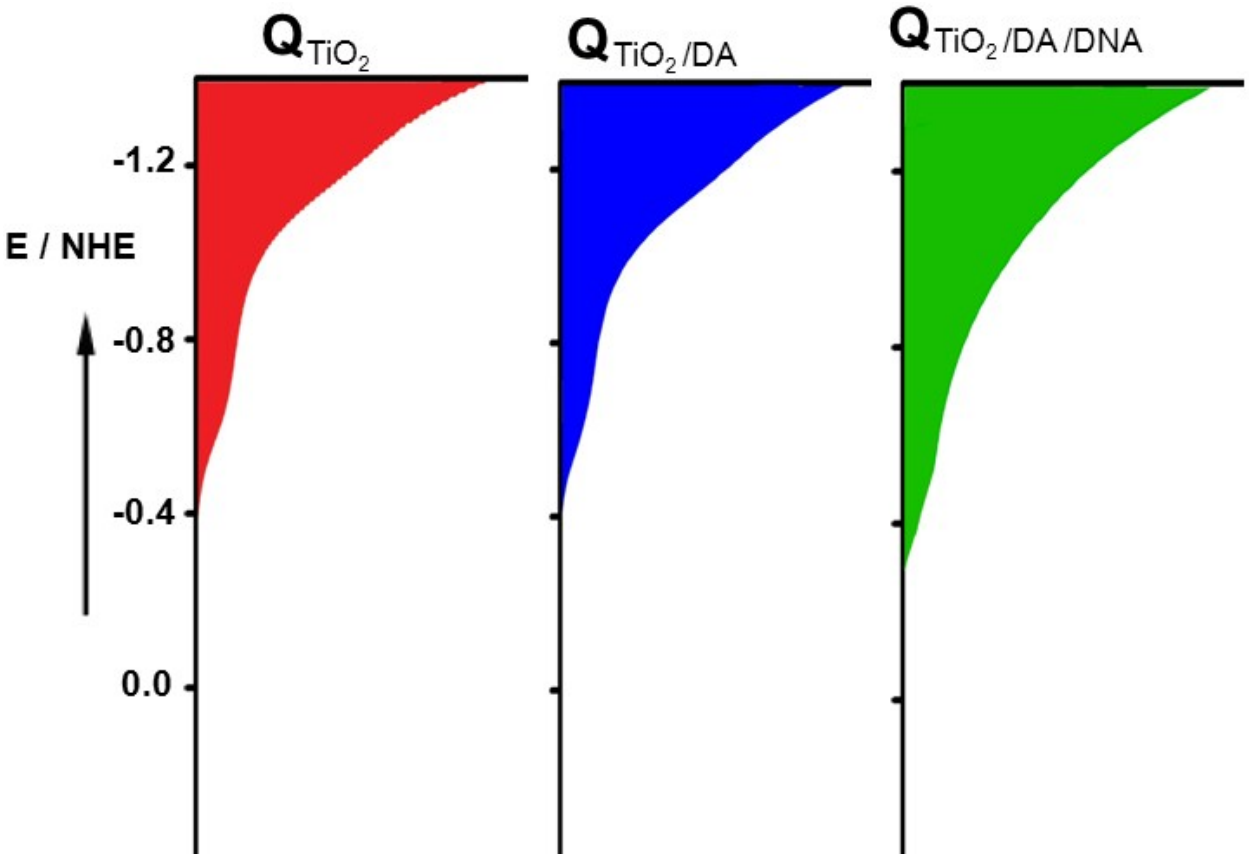


**Fig. S3** calculated DOS (total number of surface states vs applied potential) of modified electrodes: FTO/$TiO_2$, FTO/$TiO_2$/DA, FTO/$TiO_2$/DA/DNA

In a nanostructured semiconductor electrode permeated with electrolyte, when a voltage variation d$V$ is applied to the substrate, the Fermi level is displaced homogeneously as d$E_{Fn}$ = -qd$V$ (where q is the elementary charge). Consequently the electron density changes by a quantity of dn. The chemical capacitance ($C_\mu$) is associated with a change of the number density of electrons, n, and has crucial importance for device performance: [4]

$$C_\mu = q\frac{dn}{dE_{Fn}} \qquad (1)$$

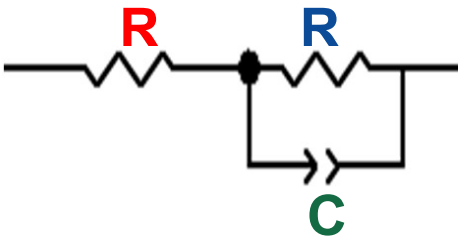


**Fig. S4** circuit used for EIS data fitting with Zview software.

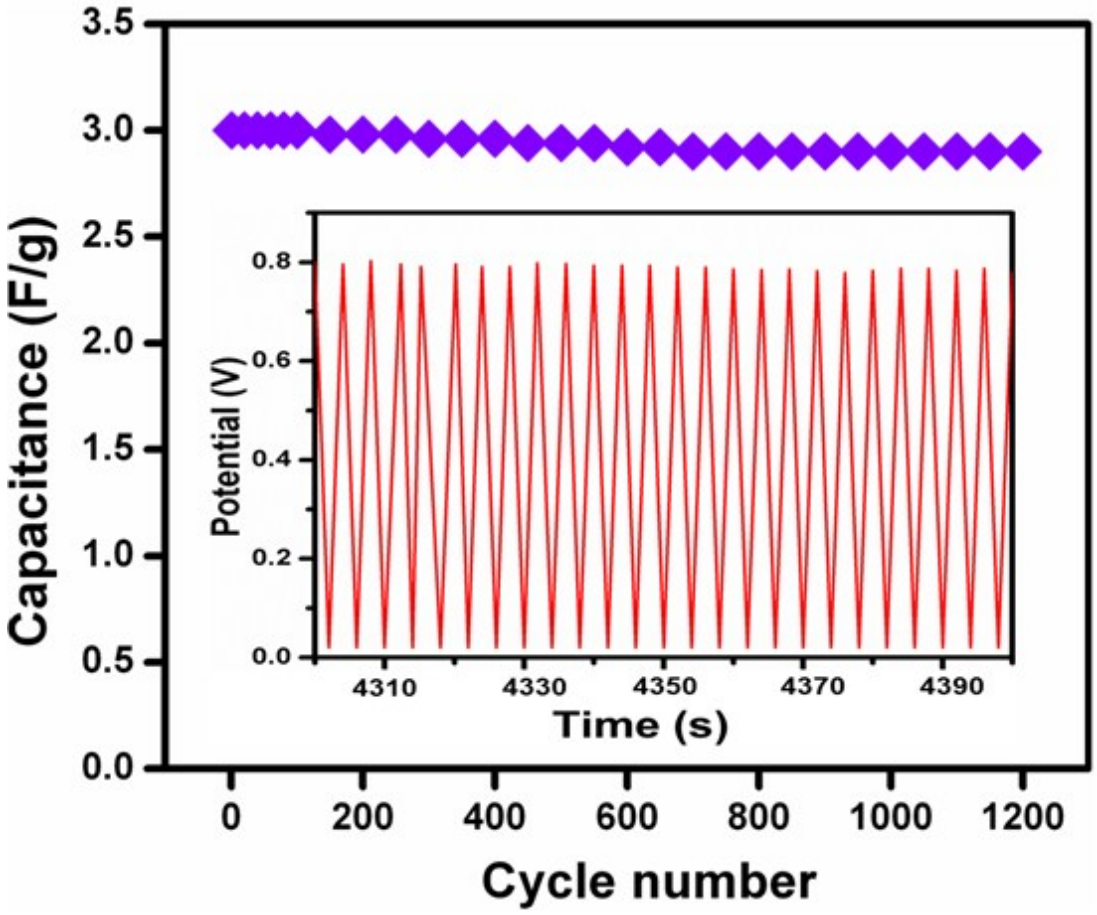


**Fig. S5** Specific capacitance of FTO/$TiO_2$/DA/DNA calculated from Galvanostatic charge–discharge test versus cycle number, along with latest charge and discharge cycles as insets at a current density of 0.6 A/g.

## References


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