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Supporting Information

Comprehensive resistive switching behavior of hybrid polyvinyl alcohol and TiO_2 nanotube nanocomposites from combining experimental and density functional theory studies

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Table S1. Calculated lattice parameters and band gaps of TiO_2 anatase, PVA monoclinic and isolated PVA monomer of this work together with the reference experimental data. The values in parentheses were calculated using the optB88-vdW functional.

Lattice parameters	TiO_2 anatase		PVA monoclinic		PVA monomer
	This work	Expt [a]	This work	Expt [b]	
a (Å)	3.800 (3.819)	3.782	7.856 (7.563)	7.81	2.47 (2.57)
b (Å)	3.800 (3.819)	3.782	2.55 (2.569)	2.52	
c (Å)	9.727(9.710)	9.502	5.37 (5.1636)	5.51	
β (°)			92°88' (93°60')	91°42'	
Band gap					
E_g (eV)	2.58 (2.0)	3.2	5.32 (5.53)	5.02 (This work)	4.83 (4.80)

a [1]

b [2]

Table S2. Comparision of FTIR vibrations of PVA-TiO_2 nanocomposites by using theoretical calculations and experiments

	Calculations			**Experiments**		**Assignments**
	PVA bulk	**Isolated PVA**	**PVA-TiO_2**	**PVA bulk**	**PVA-TiO_2**	
Wavenumber (cm^{-1})	3287 (vs)	3301 (vs)	3683 (m) 3583 (s)	3363 (vs)	3378 (w)	OH stretching
	-	-	3073 (vs)	-	-	OH stretching
	2967 (w)	2996 (w)	2996 (w)	2939 (s)	2945 (w)	CH_2 stretching
	2882 (w)	2880 (w)	-	2878 (w)	-	CH_2 stretching
	-	-	-	1735 (s)	1739 (w)	C=O group stretching
	1473 (s)	1464 (s)	1565 (m) 1464 (m)	1450 (m)	1460 (w)	CH_2 bending
	1226 (vw)	1224 (vw)	-	1257 (m)	1265 (w)	CH wagging
	1130 (w)	1133 (w)	-	1103 (s)	1109 (m)	CH_2 bending
	563 (m)	594 (m)	-	609 (s)	715 (m)	OH bending

vs: very strong, s: strong, m: medium, w: weak, vw: very weak in intensity

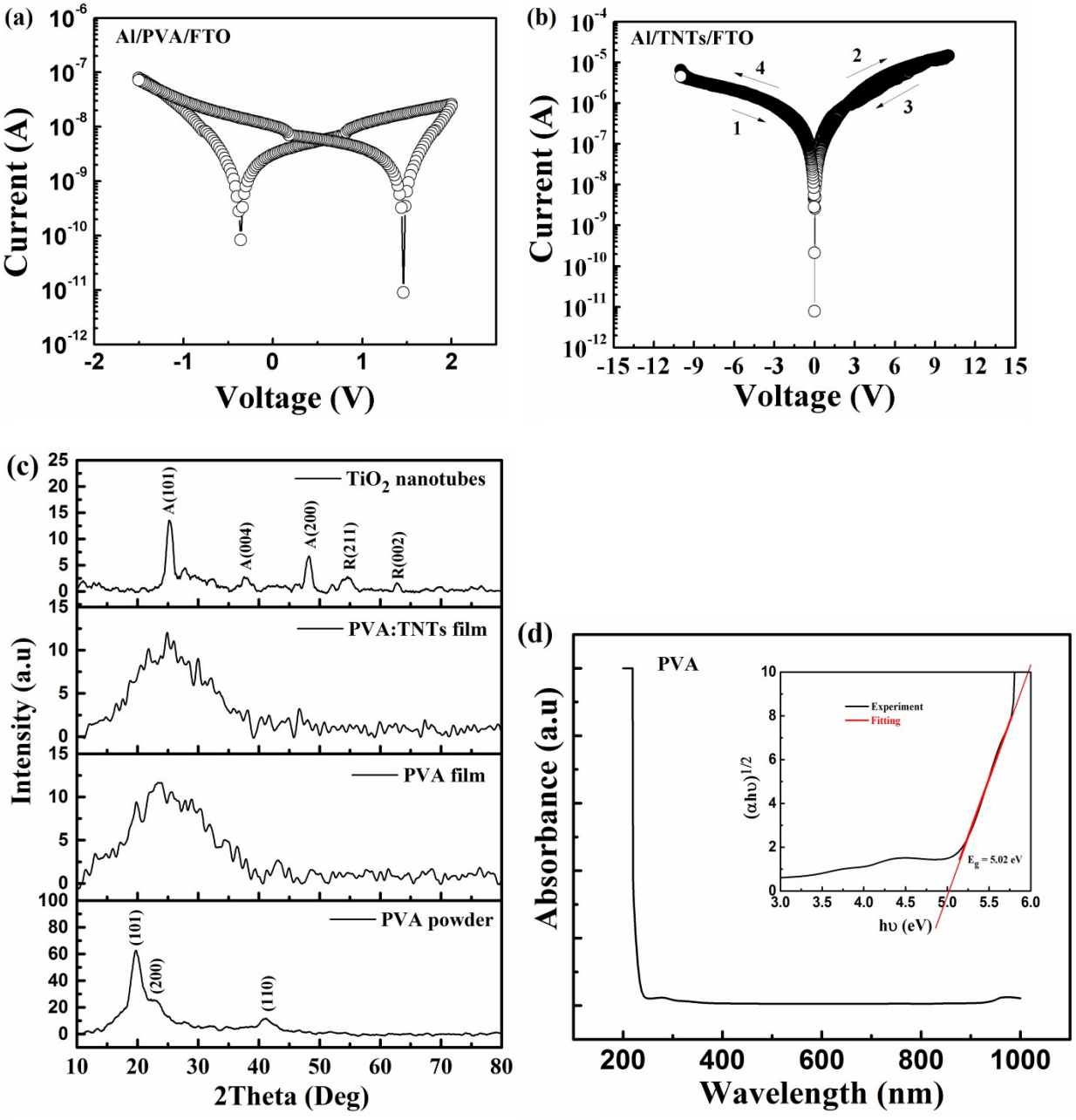

Figure S1. The current – voltage curve of Al/PVA/FTO (a) and Al/TNTs /FTO (b) device. XRD pattern of PVA, TNTs and nanocomposite thin films (c). Absorption spectra and band gap calculation from Tauc's plot of PVA inserted (d).

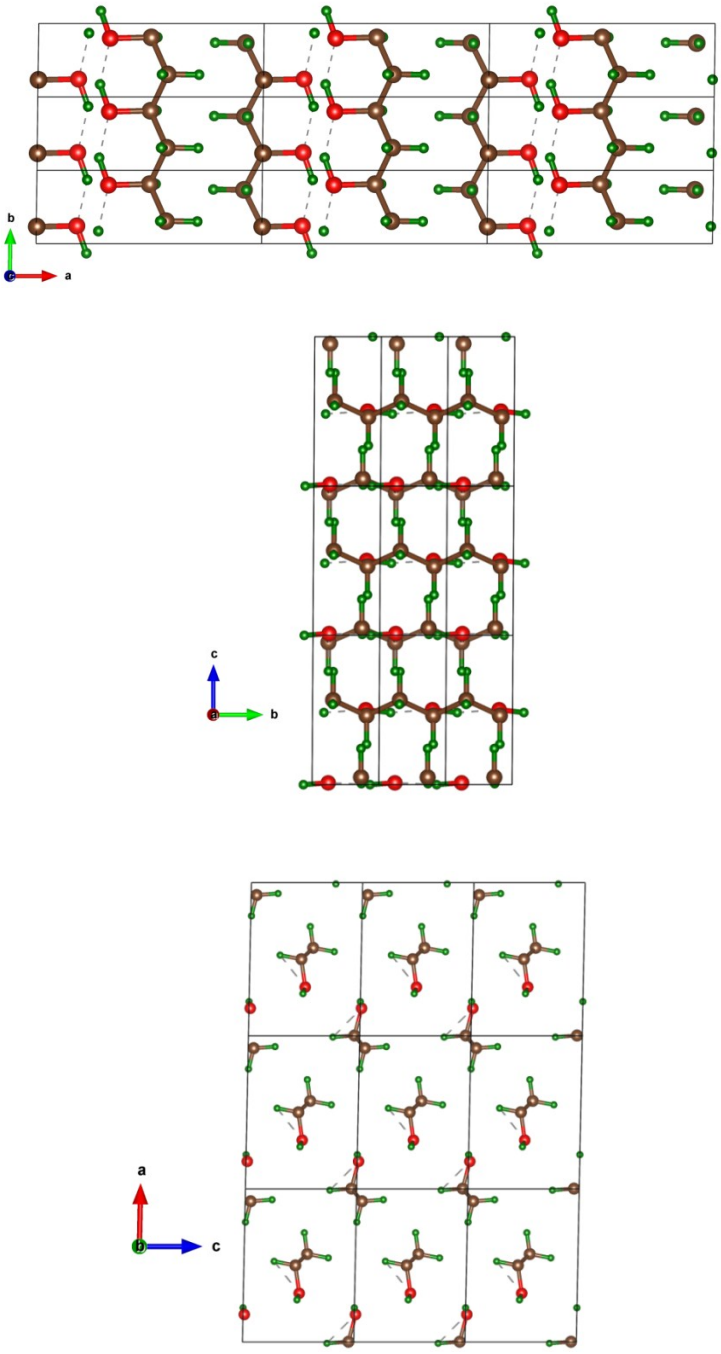

Figure S2. The atom structure of PVA monoclinic in (a) a, (b) b and (c) c direction of the lattice parameters. The one unit cell of PVA monoclinic is depicted by black lines.

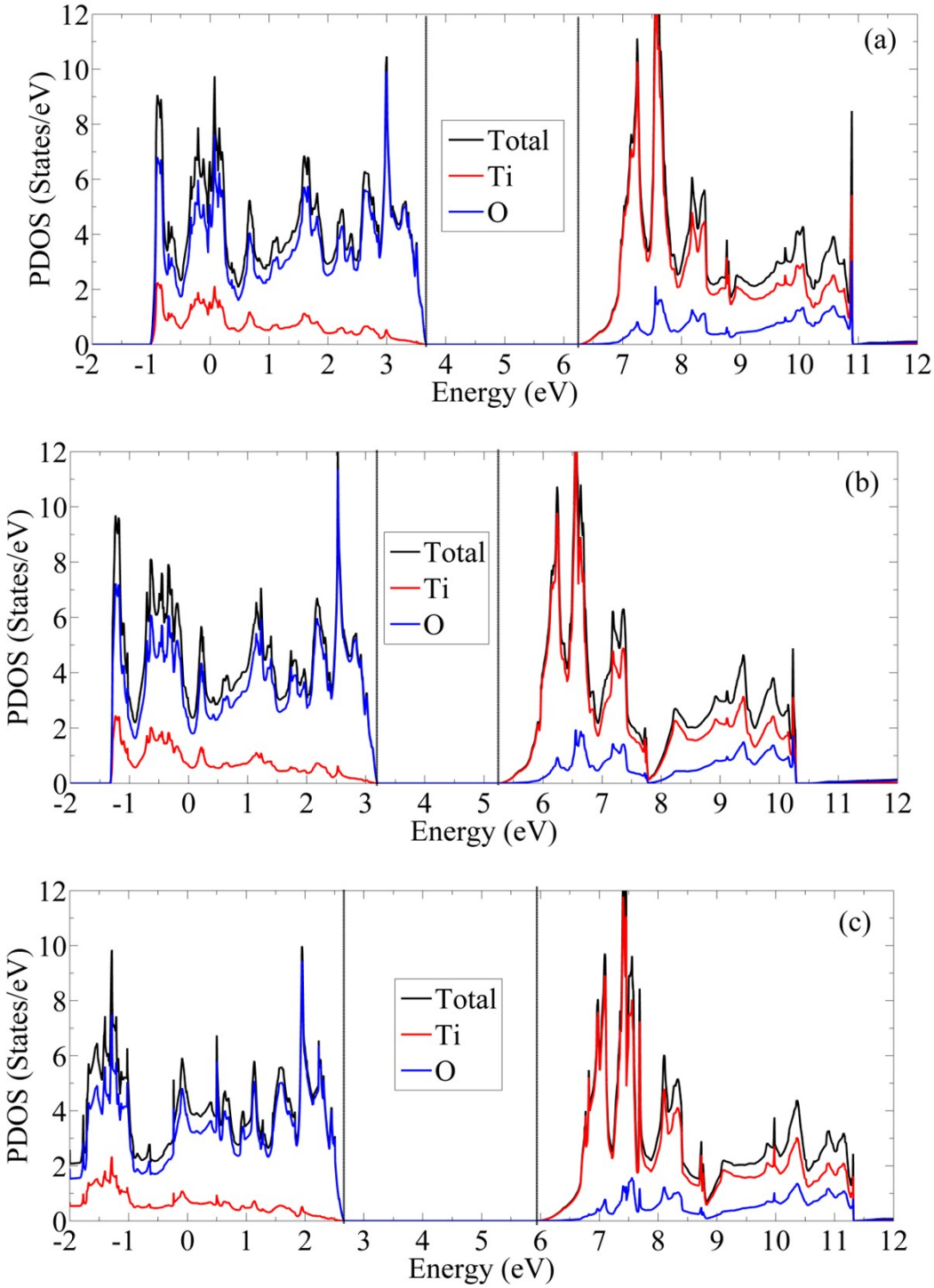

Figure S3. The partial DOS (PDOS) of TiO_2 anatase were calculated from the functionals of (a) PBE+U, (b) optB88-vdW and (c) HSE06. The VBM and CBM levels were indicated by the dashed line. The Fermi level is at the VBM level.

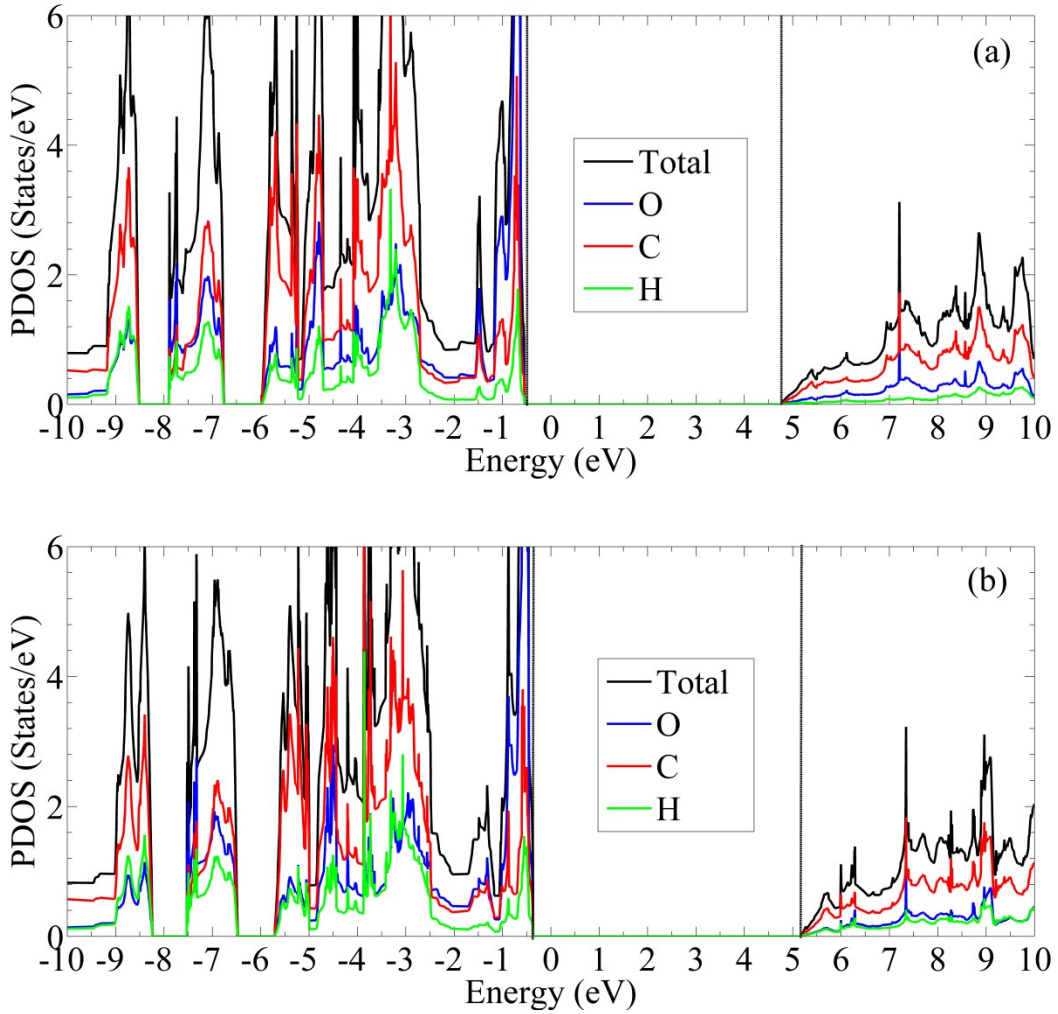

Figure S4. PDOS of PVA monoclinic in case of (a) the PBE functional and (b) optB88-vdW functional. The VBM and CBM levels were indicated by the dashed line. The Fermi level is at the VBM level.

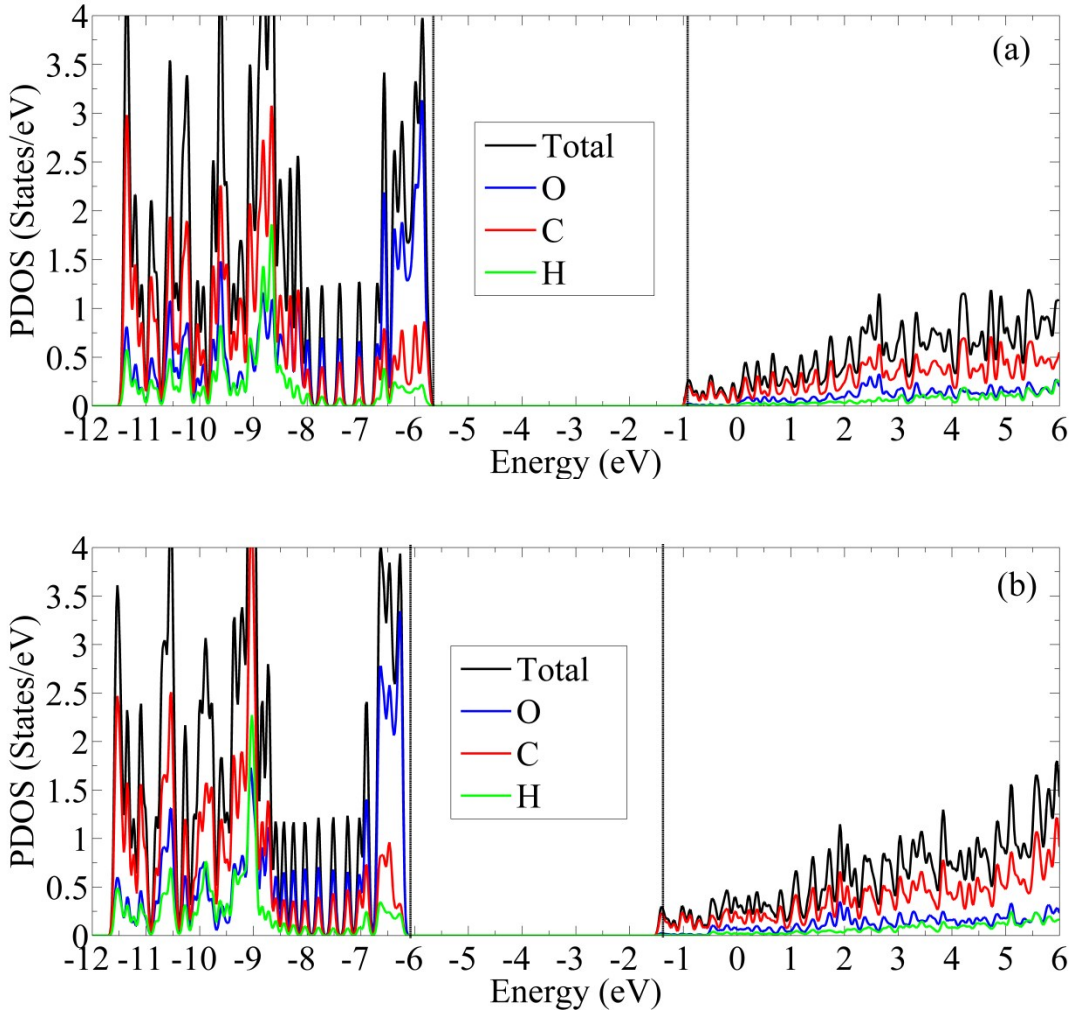

Figure S5. PDOS of isolated PVA monomer in case of the (a) PBE functional and (b) optB88-vdW functional. The HOMO and LUMO levels were indicated by the dashed line. The Fermi level is at the HOMO level.

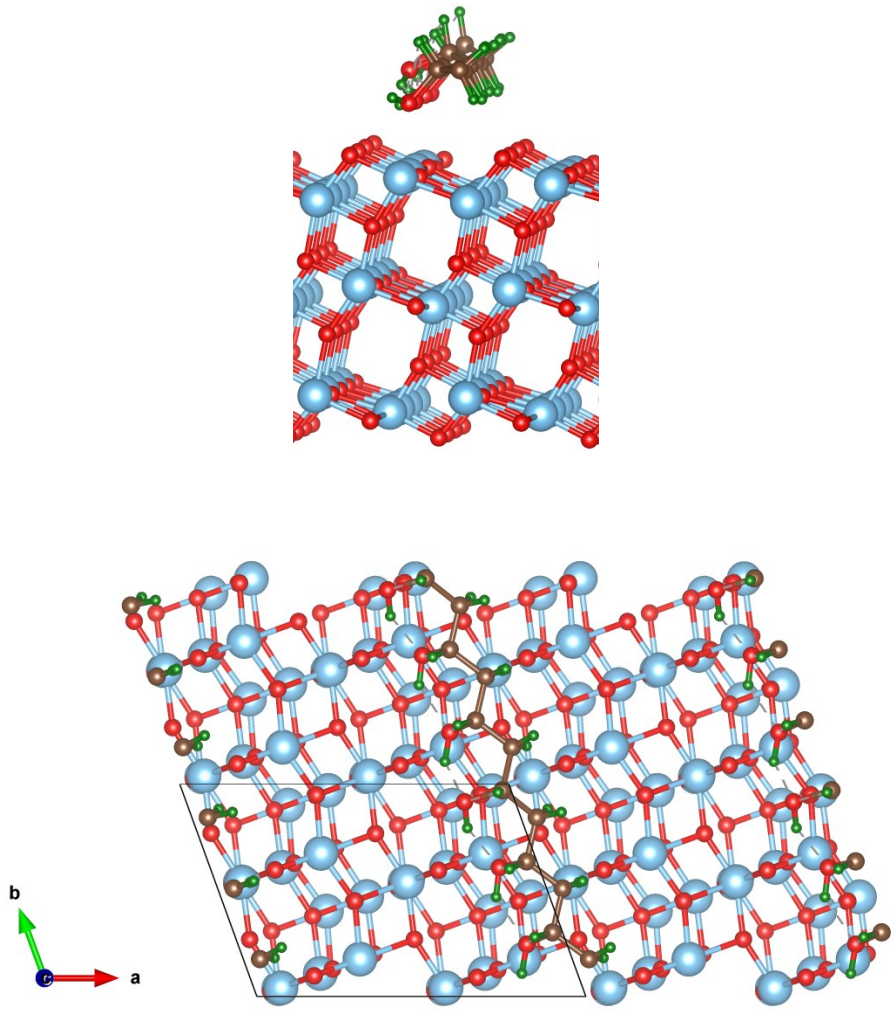

Figure S6. The atom model for the interface structure between anatase TiO_2(101) surface and PVA monomer with the binding energy of -0.69 eV. (a) side view and (b) top view. The 2×2 supercell of anatase TiO_2 (101) surface is depicted by black lines.

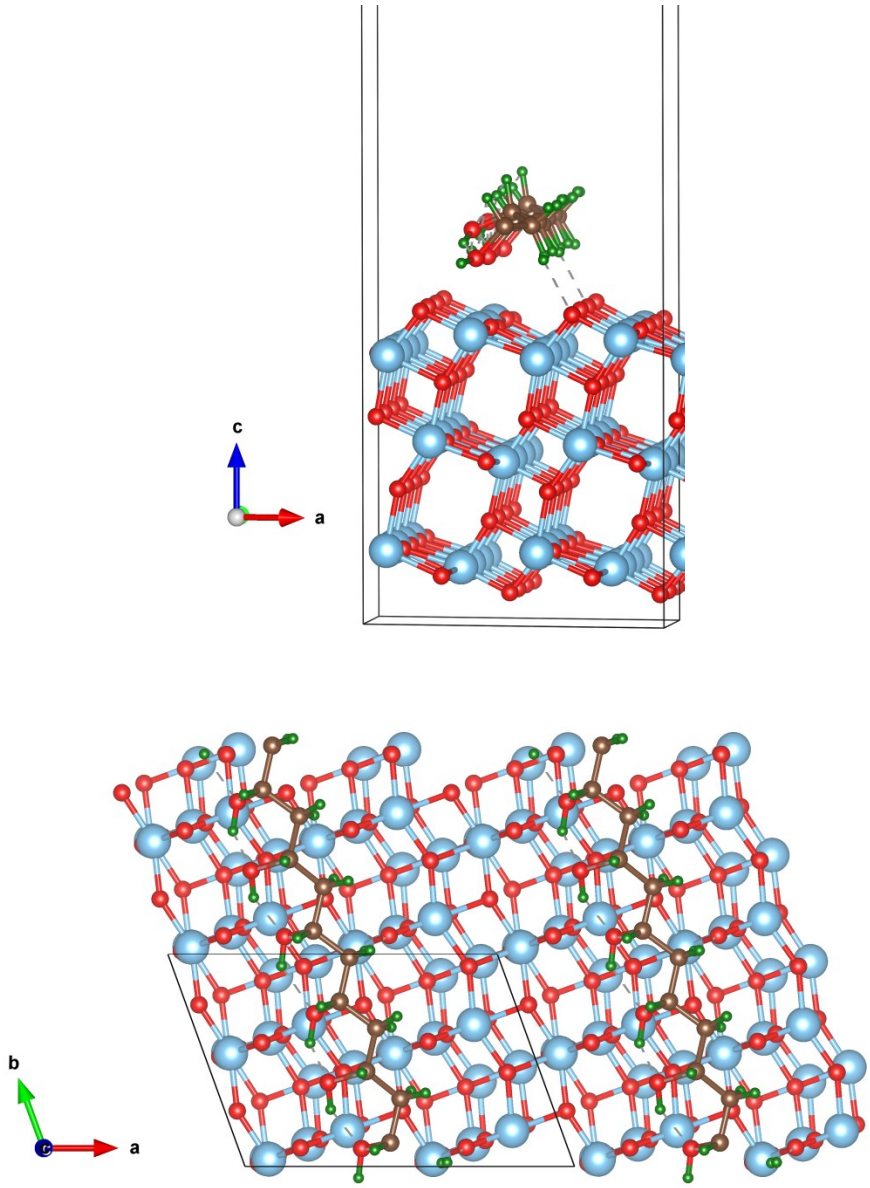

Figure S7. The atom model for the interface structure between anatase TiO_2(101) surface and PVA monomer with the binding energy of -0.68 eV. (a) side view and (b) top view. The 2×2 supercell of anatase TiO_2(101) surface is depicted by black lines.

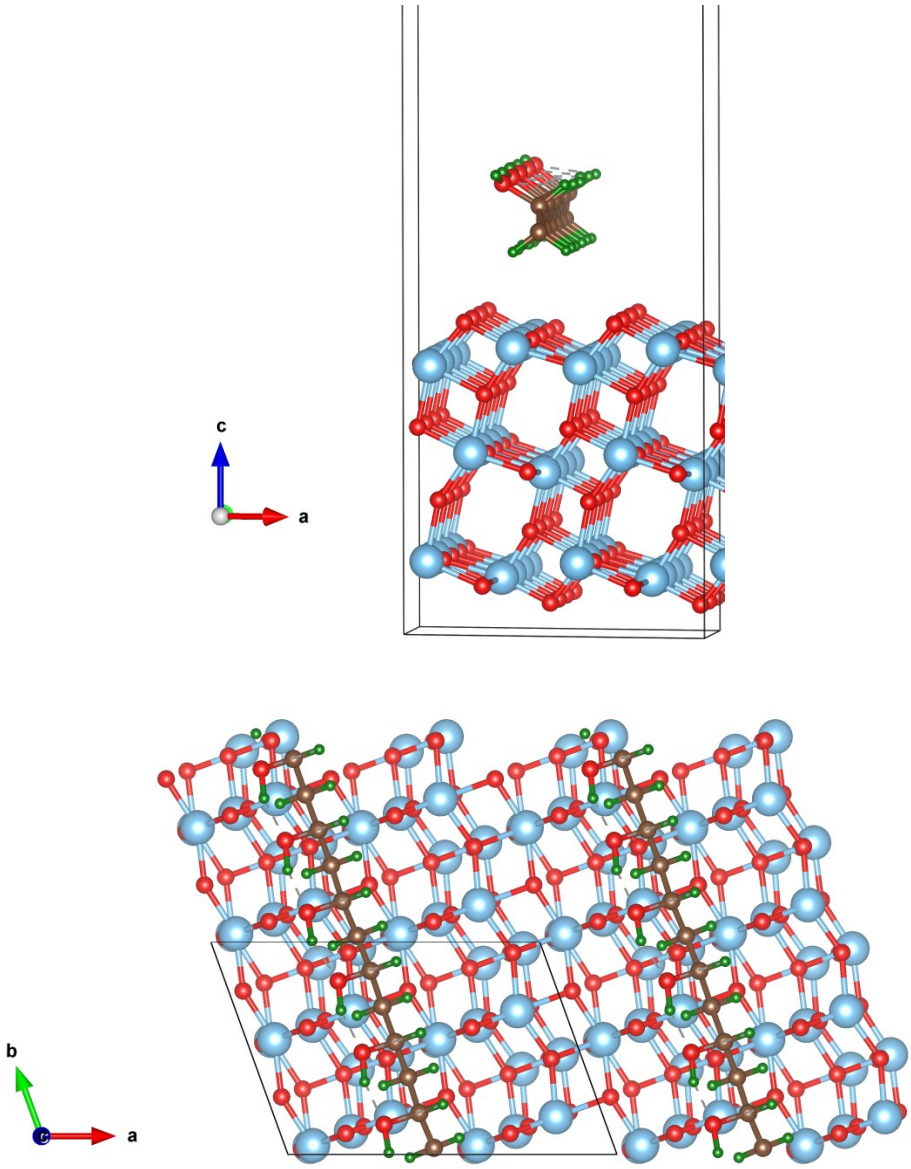

Figure S8. The atom model for the interface structure between anatase TiO_2(101) surface and PVA monomer with the binding energy of -0.26 eV. (a) side view and (b) top view. The 2×2 supercell of anatase TiO_2(101) surface is depicted by black lines.

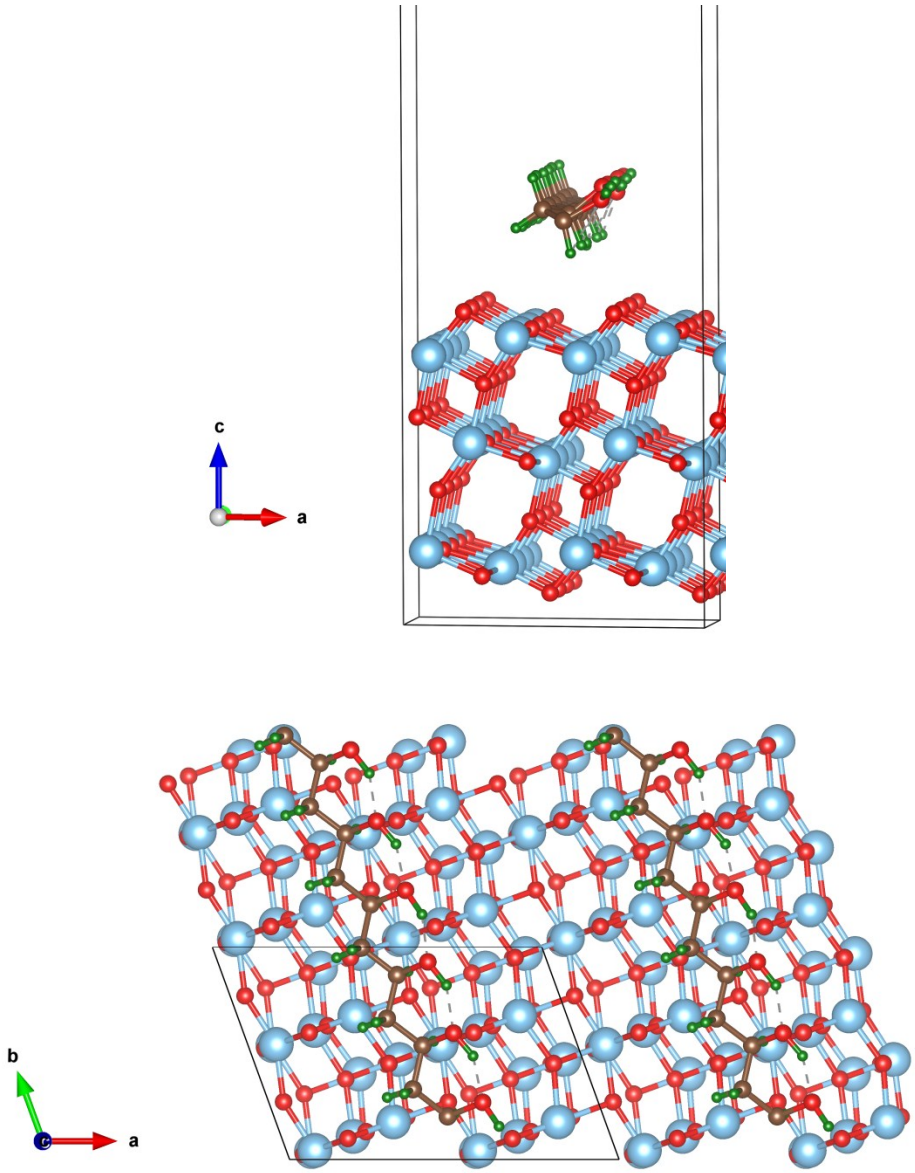

Figure S9. The atom model for the interface structure between anatase TiO_2(101) surface and PVA monomer with the binding energy of -0.25 eV. (a) side view and (b) top view. The 2×2 supercell of anatase TiO_2(101) surface is depicted by black lines.

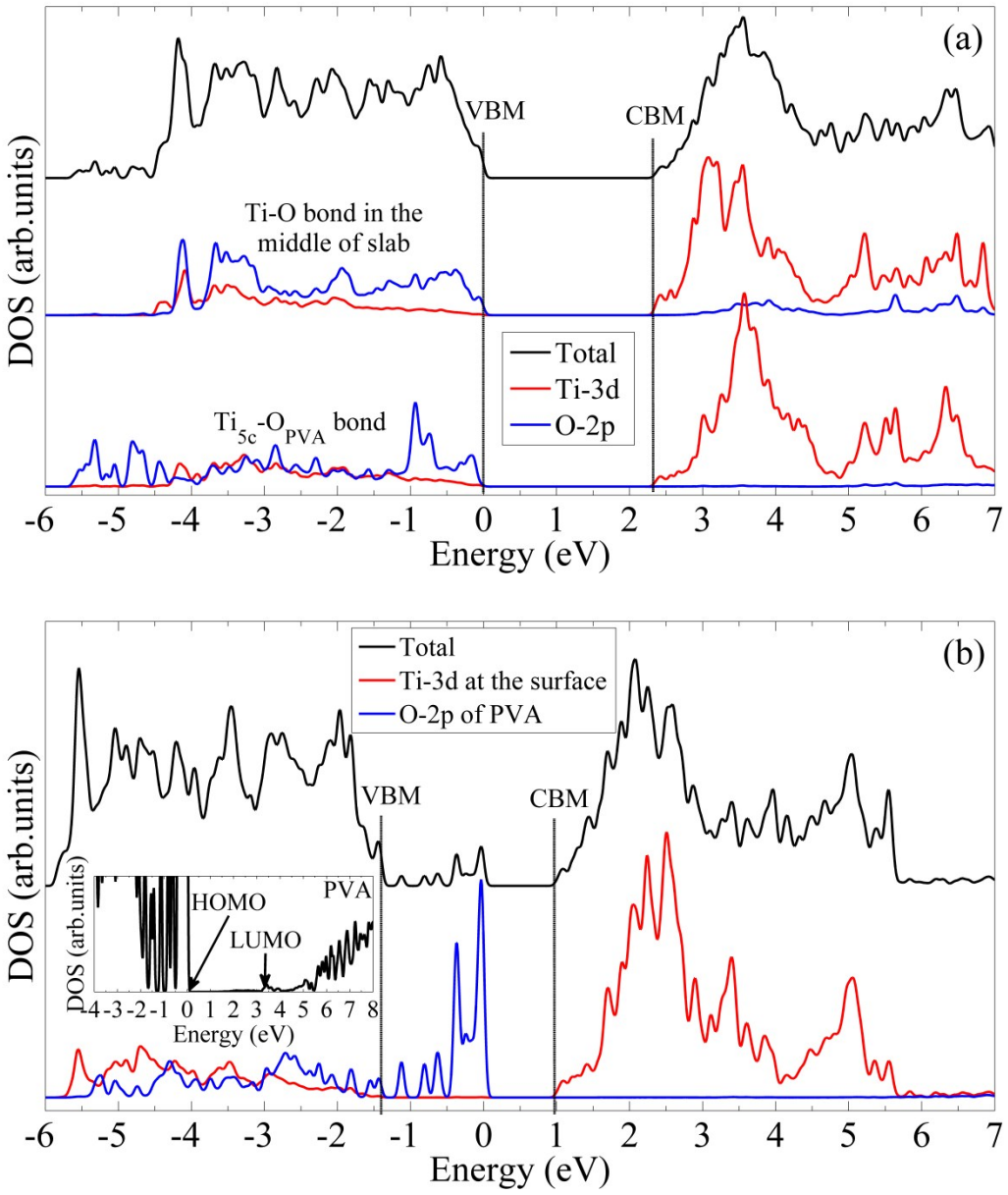

Figure S10. Project DOS on the d orbitals of the Ti atom (Ti-3d) and p orbitals of O atom (O-2p) calculated using the optB88-vdW functional for (a) the most stable structure in the middle of slab and at the interface region; and (b) the least stable structure at the interface region and the figure inset shows DOS of absorbed PVA with its HOMO and LUMO levels. The VBM and CBM levels were indicated by the dashed line. The Fermi level is at 0 eV.

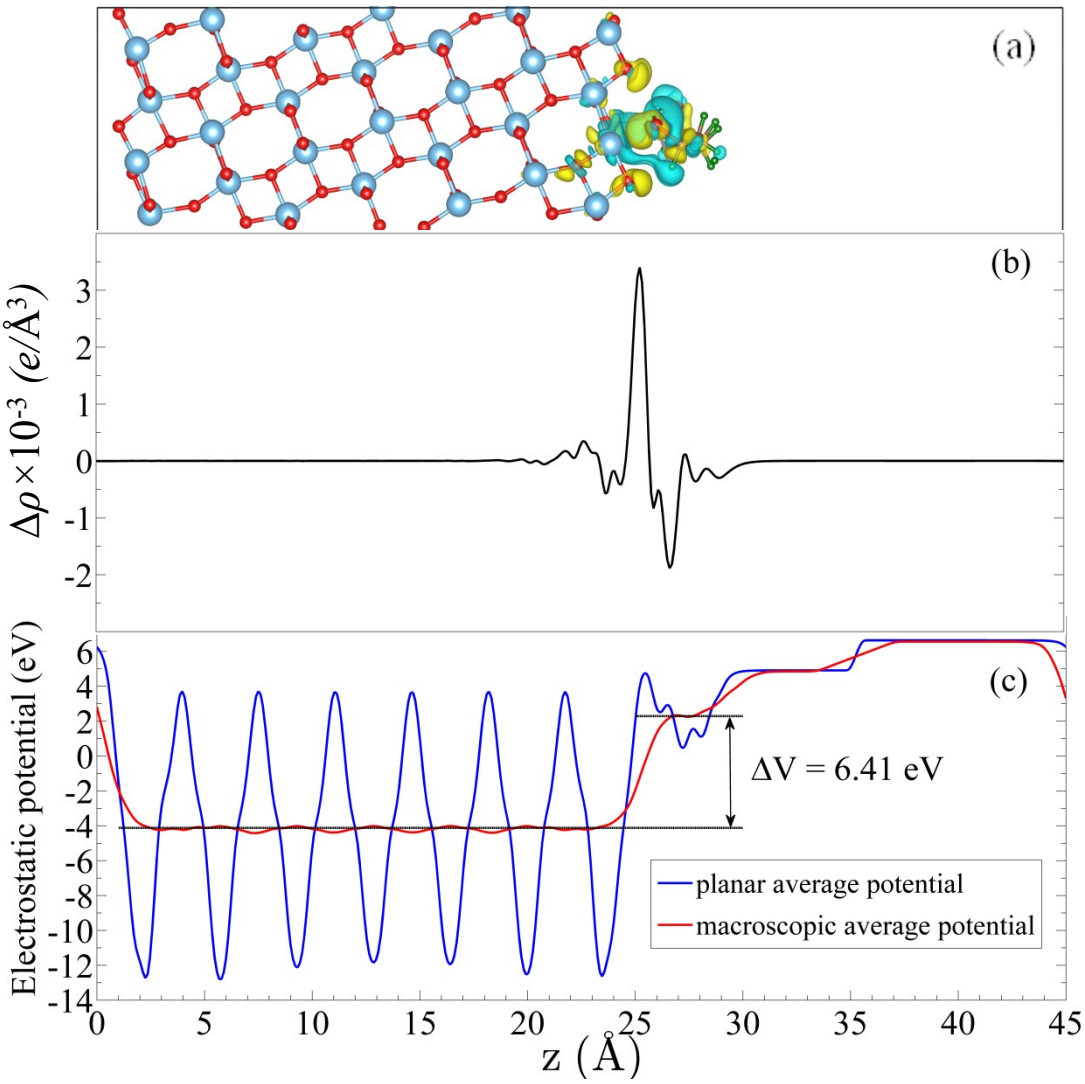

Figure S11. (a) The charge density difference of PVA on TiO_2(101) surface in an isosurface value of ± 0.001 e/Å^{-3} (+: yellow; – : cyan), (b) plane-averaged charge density difference in z-direction and (c) the planar average potential, macroscopic average potential and the built-in potential, $\Delta\overline{\overline{V}}_{bi}$, of the most stable interface structure deriving from the optB88-vdW functional**.**

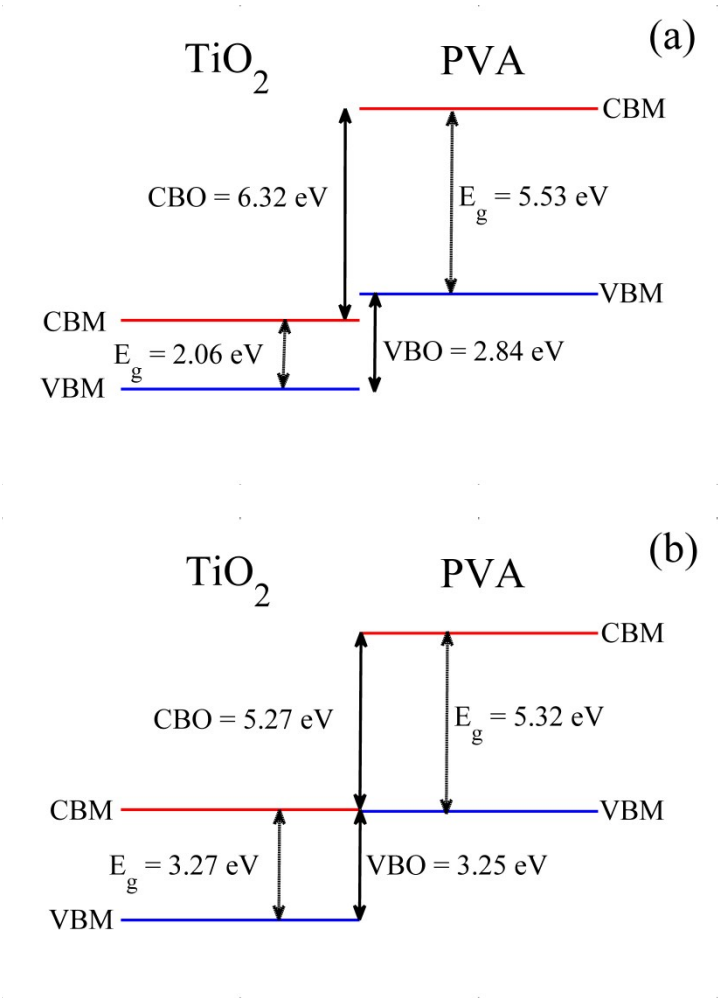

Figure S12. The schematic diagram of the band offsets of TiO_2/PVA composite deriving from (a) the optB88-vdW functional and (b) the mixed schema of the PBE+U and HSE06 functional.

References

1. Burdett, J.K., Hughbanks, T., Miller, G.J., Richardson, J.W. & Smith, J.V. Structural-electronic relationships in inorganic solids: powder neutron diffraction studies of the rutile and anatase polymorphs of titanium dioxide at 15 and 295 K. *Journal of the American Chemical Society* **109**, 3639-3646 (1987).
2. Colvin, B.G. Crystal structure of polyvinyl alcohol. *Nature* **248**, 756-759 (1974).