Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Amphiphobic surfaces from functionalized TiO_2 nanotube arrays

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Supplementary Table S1: Identification and assignment of XPS peaks obtained from from TiO_2 thin films and nanotubes coated by PFNA and PDPFA monolayers

Samples	Elements (Region)	Peak Positions (eV)	Chemical entities
TiO_2 –PFNA (thin films and nanotubes)	Ti	458.7 ± 0.2 eV ($2p_{3/2}$) 464.5 ± 0.3 eV ($2p_{1/2}$)	TiO_2
	O	530.2 eV (O1s)	-O-
	C(1s)	284.6 eV ± 0.3 eV (C1s)	graphitic carbon
	C	285.0 ± 0.5 eV	(C-H), sp^3 carbon
	C	286.4 ± 0.5 eV	(C=O), >C=O
	C	288.5 ± 0.5 eV	COOH + C(O)-OC
	F	689 ± 0.5 eV	C-F
	N	400 eV – 402 eV	-CN, N=O, $-CONH_2$
TiO_2 –PFDPA (thin films and nanotubes)	Ti	458.7 ± 0.2 eV ($2p_{3/2}$) 464.5 ± 0.3 eV ($2p_{1/2}$)	TiO_2
	O	530.2 eV (O1s)	-O-
	C(1s)	284.6 eV ± 0.3 eV (C1s)	graphitic carbon
	C	286.4 ± 0.5 eV	(C=O), >C=O
	C	292 ± 0.5 eV	CF_2
	C	294 ± 0.5 eV	CF_3
	F	689 ± 0.5 eV	C-F
	P	132.4 to 135.8 eV (as a function of oxygen environment)	P-C, P-O
	N	400 eV – 402 eV	-CN, N=O, $-CONH_2$

Supplementary Table S2: Contact angle (in degrees) for six different liquids on nine different substrates with the standard deviation determined from the average static contact angle. Also listed are the dispersive, polar and hydrogen-bonding components of the surface energy for each surface studied, calculating by the extended Fowkes method using the average contact angles for diiodomethane, ethylene glycol and water; $\gamma_S = \gamma_S^d + \gamma_S^p + \gamma_S^h$.

	TFF	TFF^{PFNA}	TFF^{PFDPA}	TNA_{Large}	TNA_{Small}	TNA_{Large}^{PFNA}	TNA_{Small}^{PFNA}	TNA_{Large}^{PFDPA}	TNA_{Small}^{PFDPA}
Water	23.5 ±4.5	103.9 ±15.5	110.0 ±5.91	< 5	< 5	> 170	> 170	> 170	> 170
Ethylene Glycol	< 10	90.0 ±2.4	77.8 ±4.99	< 5	< 5	141.18±5.5	140.9±4.5	142.2 ±1.32	149.7 ± 0.22
Dimethylformamide	< 10	42.8 ±0.92	69.9 ±2.58	< 5	< 5	114.5 ±5.9	110.7 ±2.5	132.2 ±0.53	140.0 ±4.92
Dimethyl sulfoxide	32 ±2.2	42. 5±4.22	68.7 ±4.93	< 5	< 5	125.7 ±3.5	87.8 ±23.3	139.3 ±1.44	145.2 ±2.61
Toluene	< 5	64.13±1.29	75.7 ±2.46	< 5	< 5	105.2 ±0.8	110.8 ±3.44	110.5 ±0.91	120.8 ±2.17
Diiodomethane	31.3±2.42	110.1 ±3.31	100.3 ±1.38	< 5	< 5	134.5±1.59	140.4 ±3.39	144.6 ±0.38	143.5 ±0.88
Dispersive component of solid surface energy - γ_S^d (mN m^{-1})	33.27	1.65	2.92	> 43.12	> 43.12	1.40	0.59	0.30	0.64
Polar component of solid surface energy - γ_S^p (mN m^{-1})	14.60	15.56	21.05	> 8.36	> 8.36	0.06	0.08	0.24	0.06
Hydrogen-bonding component of solid surface energy - γ_S^h (mN m^{-1})	27.76	6.22	2.13	> 27.17	> 27.17	< 0.88	< 0.36	< 0.20	< 0.38
Total solid surface energy- γ_S (mN m^{-1})	75.63	23.42	26.10	> 78.65	> 78.65	< 2.35	< 1.03	< 0.74	< 1.07

Supplementary Table S3: Geometric parameters of nanotube-configurations studied here. The geometrical parameters of individual nanotube are obtained from SEM images.

	TNA^{PFNA}_{Large}	TNA^{PFNA}_{Small}	TNA^{PFDPA}_{Large}	TNA^{PFDPA}_{Small}
d (thickness of wall) nm	12	15	12	15
R (outer radius) nm	75	37.5	75	37.5
H (height) □m	17.5	6	17.5	6

Supplementary Table S4: Theoretically predicted contact angles (θ) and the difference between the theory and the experimentally observed contact angle$(\Delta\theta)$. Here it is assumed that the nanotubes behave like a nanorod and there is finite gap between them.

Liquid	TNA^{PFNA}_{Large}		TNA^{PFNA}_{Small}		TNA^{PFDPA}_{Large}		TNA^{PFDPA}_{Small}	
	θ	$\Delta\theta$	θ	$\Delta\theta$	θ	$\Delta\theta$	θ	$\Delta\theta$
Ethylene Glycol	100.95	40.23	102.52	38.38	88.62	53.58	90.57	59.13
Dimethylformamide	62.24	52.26	65.35	45.35	82.19	50.01	84.36	55.64
Dimethyl sulfoxide	62.05	63.65	65.16	22.64	81.23	58.07	83.44	61.76
Toluene	77.62	27.38	79.98	30.82	86.89	28.61	88.90	31.90
Diiodomethane	116.43	18.07	117.61	22.79	107.80	37.20	109.19	34.31
Hexane	62.11	10.69	65.22	28.02	69.83	38.83	72.53	67.53

Derivation of Equation (6):

TiO_2 nanotubes formed by anodization in ethylene glycol-based electrolytes pack in a triangular lattice, whose unit cell is the shaded area shown below in Fig. S1a, which is an equilateral triangle with each side of length $2R_0+s$ where R_0 is the radius of the nanotubes and s is the inter-tubular gap. In Fig. S1b, the shaded area indicates the geometric area fraction occupied by TiO_2 nanotubes. From symmetry considerations, each nanotube contributes $1/6^{th}$ of an annulus. The average value of all the above geometrical parameters, as estimated from scanning electron micrographs, were used to calculate the area fraction parameter f_{sl}.

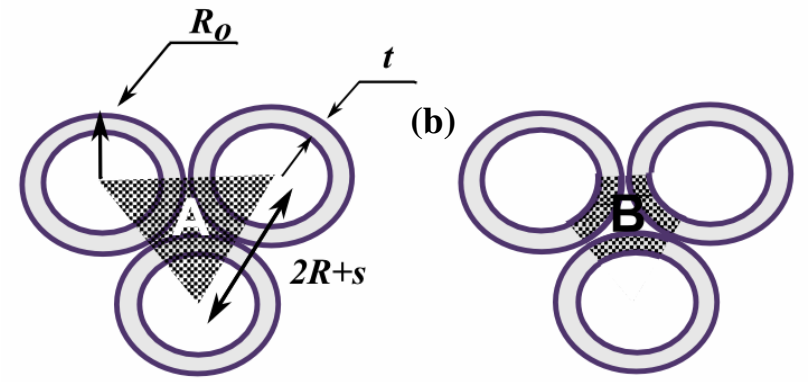

Figure S1: First scenario considered for the analysis: the unit cell consists of three hollow nanotubes with radius R_0, wall-thickness t and inter-tube spacing s

$$f_{sl} = \frac{Area\,(B)}{Area\,(A)} = \frac{\frac{\pi}{2}[R_o^2 - (R_o - t)^2]}{\frac{\sqrt{3}}{4}(2R_0 + S)^2} \tag{6a}$$

$$f_{sl} = \frac{\frac{\pi}{2}[R_o^2 - R_o^2 + 2tR_o - t^2]}{\sqrt{3} \times R_o^2\left(1 + \left(\frac{s}{2R_0}\right)\right)^2} = \frac{\frac{\pi}{2}R_o^2\left[\frac{2t}{R_0} - \left(\frac{t}{R_0}\right)^2\right]}{\sqrt{3} \times R_o^2\left(1 + \left(\frac{s}{2R_0}\right)\right)^2} \tag{6b}$$

$$f_{sl} = \frac{\frac{2t}{R_0} - \left(\frac{t}{R_0}\right)^2}{\frac{2\sqrt{3}}{\pi}\left[1 + \left(\frac{s}{2R_0}\right)^2\right]} \tag{6c}$$

Derivation of Equation (8):

Here, the area fraction parameter of nanorods arranged in a triangular lattice is sought.

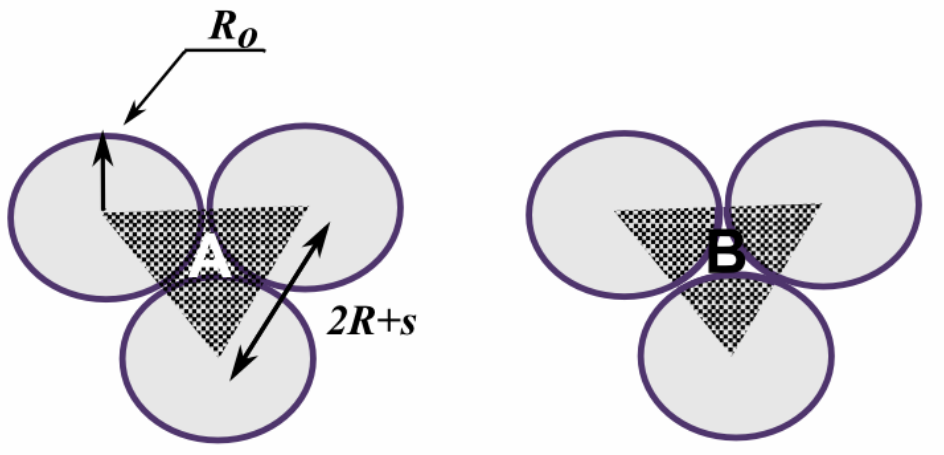

Figure S2: Second scenario considered for the analysis: The nanotubes are considered as solid nanorods of outer radius R_0 and there is a finite gap s in between them.

$$f_{sl} = \frac{Area\,(B)}{Area\,(A)} = \frac{\frac{\pi}{2}[R_o^2]}{\frac{\sqrt{3}}{4}(2R_0 + S)^2} \tag{8a}$$

$$f_{sl} = \frac{\frac{\pi}{2}[R_o^2]}{\sqrt{3} \times R_o^2\left(1 + \left(\frac{S}{2R_0}\right)\right)^2} = \frac{\frac{\pi}{2}[R_o^2]}{\sqrt{3} \times R_o^2\left(1 + \left(\frac{S}{2R_0}\right)\right)^2} \tag{8b}$$

$$f_{sl}^{rod} = \frac{\pi}{2\sqrt{3}}\left(1 + \frac{S}{2R_0}\right)^{-2} \tag{8c}$$

Pre- and Post- Immersion in other solvents – Contact Angle Sustainability

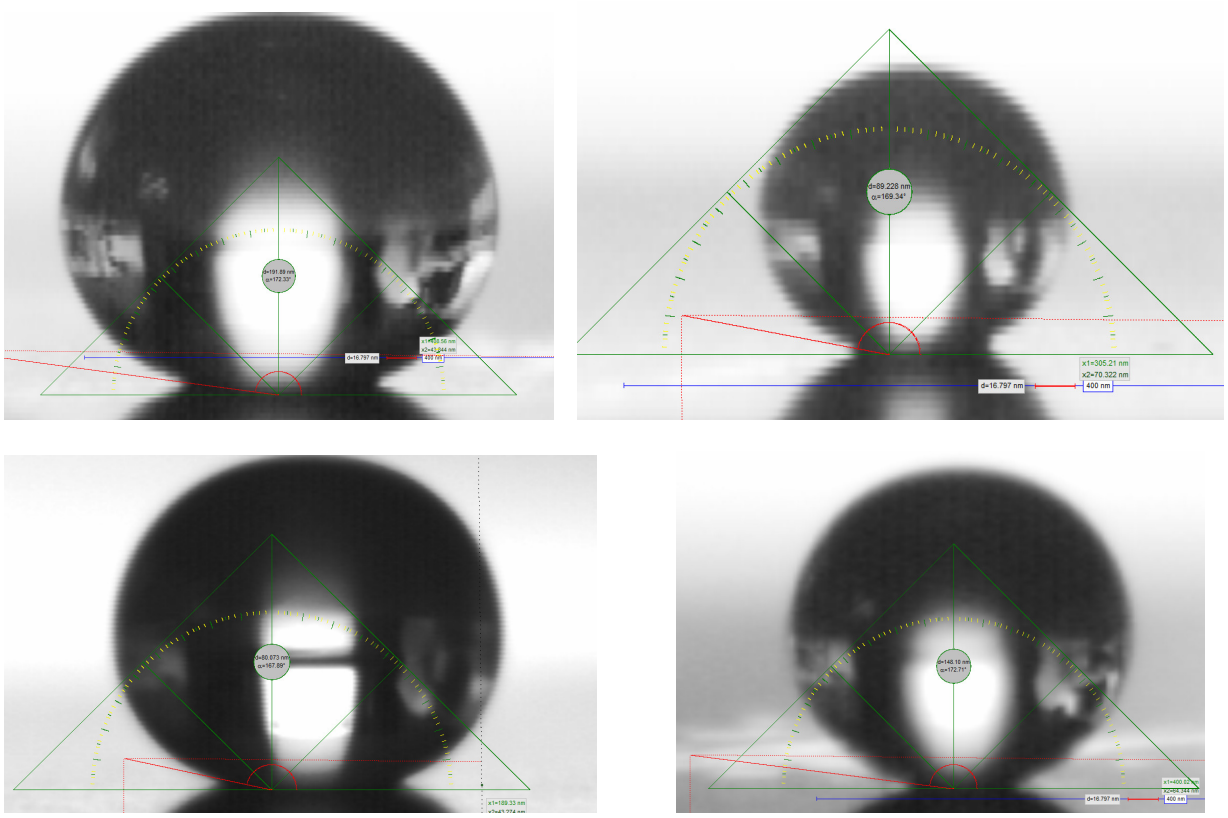

Figure S3: Static contact angles of water on PFDPA-coated (a) large diameter nanotube arrays and (b) small diameter nanotube arrays. Images on left are pre-immersion treatment, on the right are post-immersion treatment in water. The contact angle is unchanged.

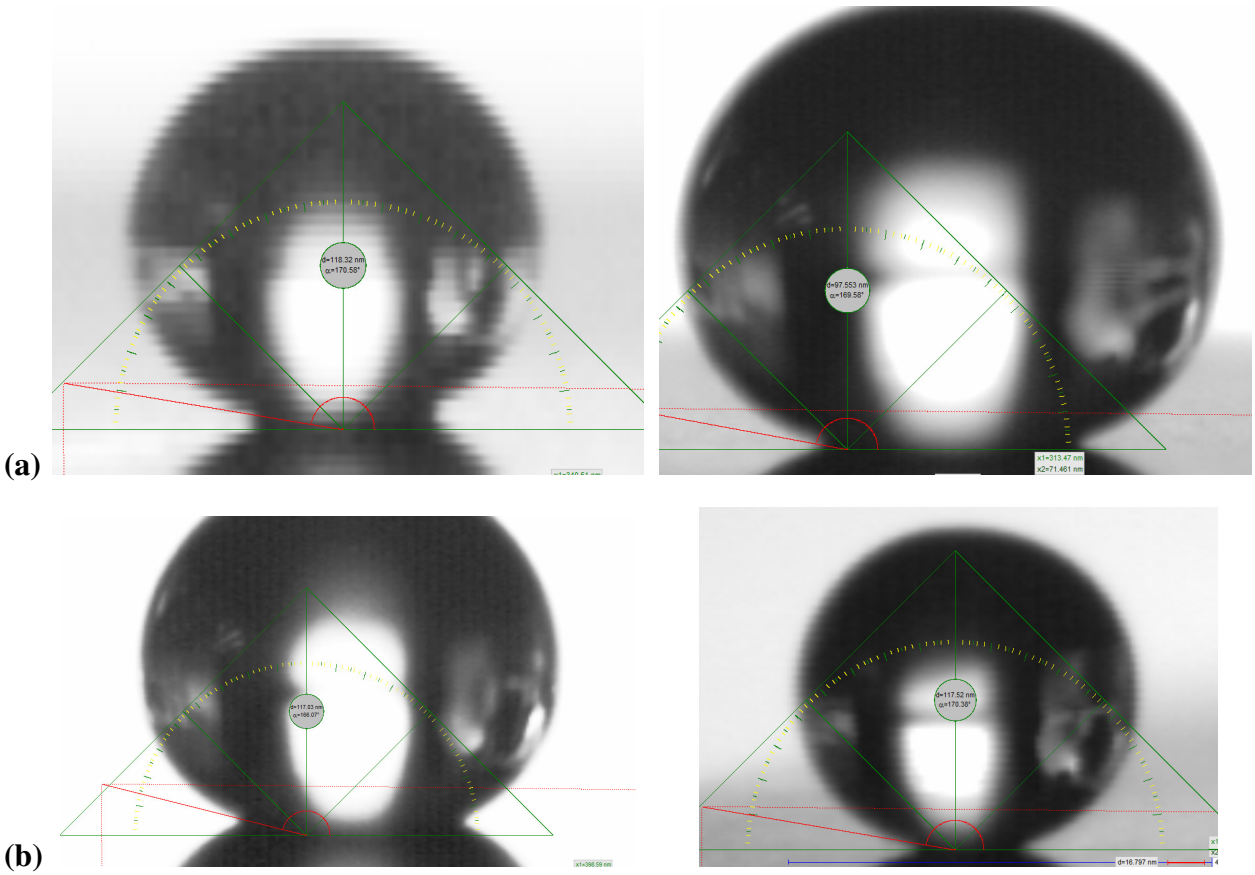

Figure S4: Static contact angles of water on PFDPA-coated (a) large diameter nanotube arrays and (b) small diameter nanotube arrays. Images on left are pre-immersion treatment, on the right are post-immersion treatment in ethylene glycol. The contact angle is unchanged.