Surface Functionalization of Zinc Oxide by CarboxyAlkylphosphonic Acid Self-Assembled Monolayers

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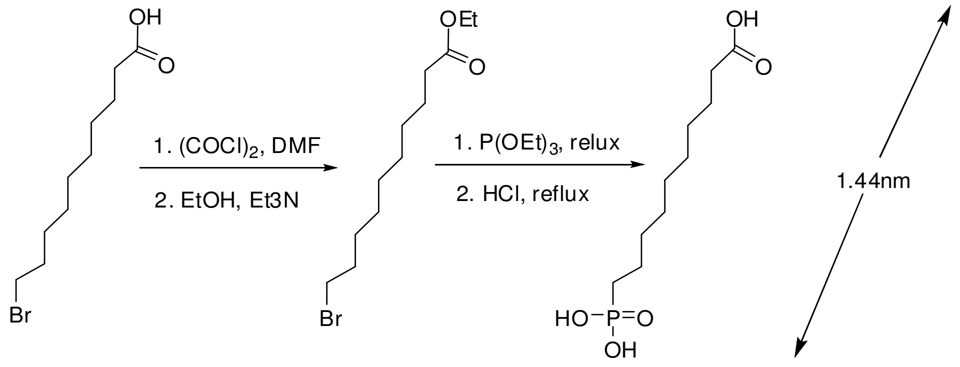
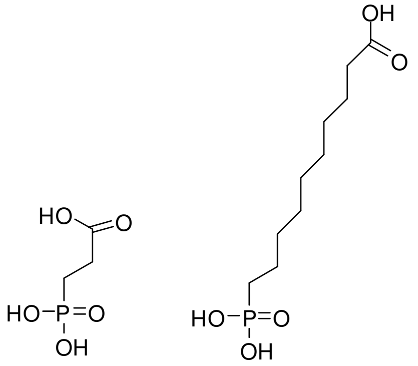
Synthesis and NMR analysis of 10-phosphonodecanoic acid (10-PDA)

10-Phosphonodecanoic acid ($HOOC(CH_2)_9P(O)(OH)_2$, 10-PDA) was synthesized as follows (Scheme S1) : Bromodecanoic acid ($HOOC(CH_2)_9Br$, Sigma) was first stirred in oxalyl chloride and then reacted with ethanol under a nitrogen atmosphere at room temperature to protect its carboxylic acid group by forming an ethyl ester. Afterwards, the resulting ester was phosphonated with triethyl phosphite via Michaelis-Arbuzov reaction.[s1, s2] The product was then refluxed in a concentrated HCl for 16 hours and cooled to room temperature, followed by filtration, rinsed in deionized water (DI water, R ≥ 18.2 MΩ· cm, Millipore Milli-Q system) and vacuum dried.



Scheme S1. Synthesis of 10-PDA.



3-PPA 10-PDA

Chart S1. Structure of 3-PPA and 10-PDA.

The 10-PDA was analyzed by nuclear magnetic resonance spectroscopy (NMR) and mass spectrometry (MS) with the following results: ^{1}H NMR

(CD_3SOCD_3, 400M): 1.21 (br.s, 10H), 1.44 (br.s, 6H), 2.15 (t, J = 9.6 Hz, 2H), 10.77 (br.s, 2H) ppm; ^{13}C NMR (CD_3SOCD_3, 400M) 174.9, 34.1, 30.5, 29.2, 29.1, 29.0, 28.4, 27.1, 24.9, 23.0 ppm; ^{31}P NMR (CD_3SOCD_3, 400M): 33.71 (s) ppm; MS: m/z 253 ($[M+1]^+$).

As shown below, based on molecular mechanics calculations (MM2), the total length of the 10-PDA molecules (from O atom (P=O) of PO_3H_2 groups to the O atom (C=O) of CO_2H group) is ~1.44 nm.

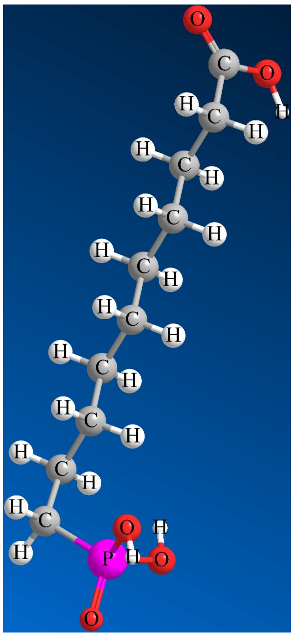


Figure S1. Molecular structure of 10-PDA.

Synthesis, morphology and composition characterizations of ZnO nanowires

ZnO nanowires were synthesized using hydrothermal methods. Briefly, the reaction solution was prepared by adding the appropriate quantity of ammonia (25%) into 200 mL zinc chloride solution ($ZnCl_2$, 0.15 M) to adjust the pH value to 10.0. The solution was transferred into bottles with autoclavable screw caps. Glass slides, cleaned with acetone and DI water in an ultrasonic cleaner, were vertically immersed into the reaction solution. The bottles were then heated up to 95 °C in an oven for 60 min. Finally, the nanowires were sonicated from the slides into DI water and dried in air for further characterization.

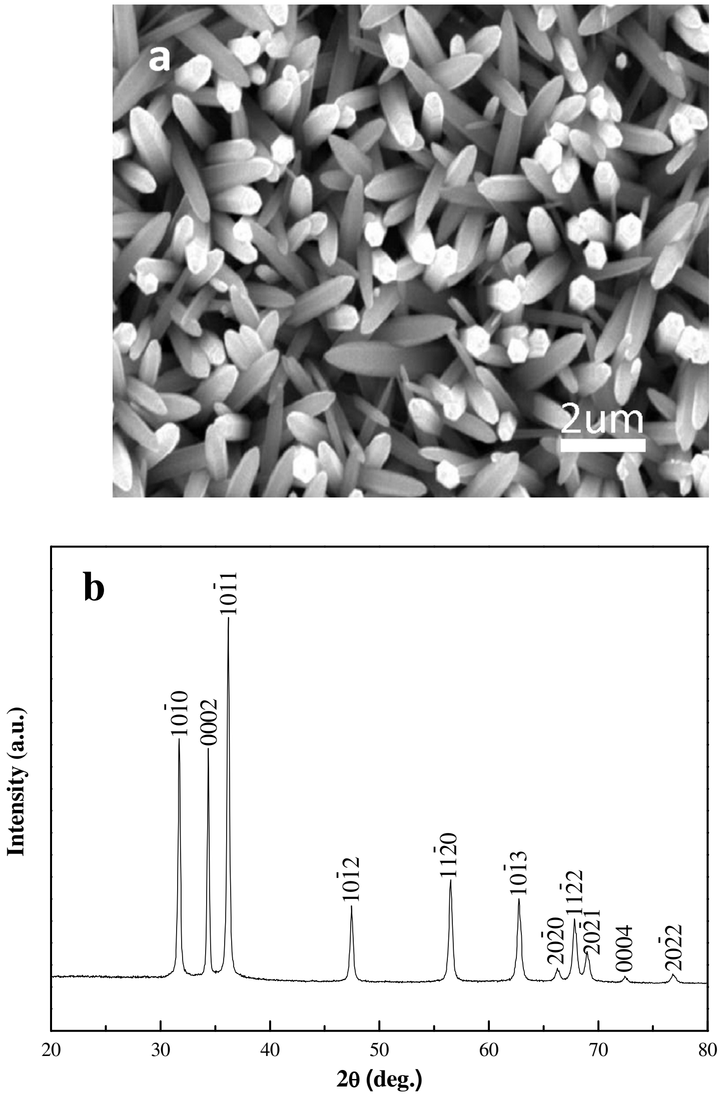


Figure S2. SEM image (a) and XRD pattern (b) of the as-obtained ZnO nanowires.

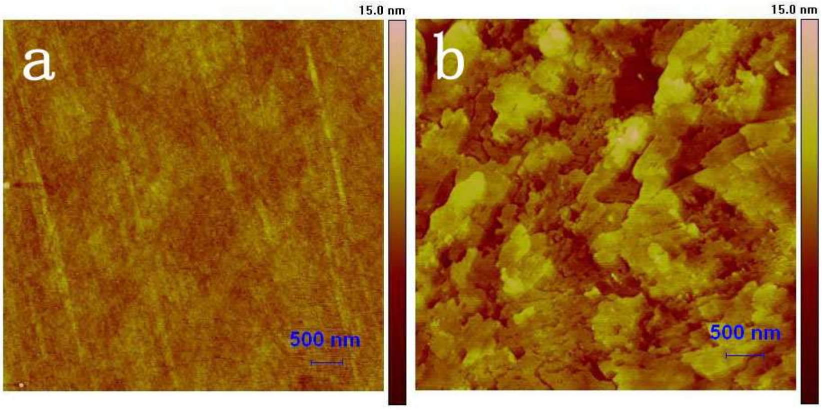


Figure S3. AFM images of SiO_2 before (a) and after (b) functionalized by 10-PDA.

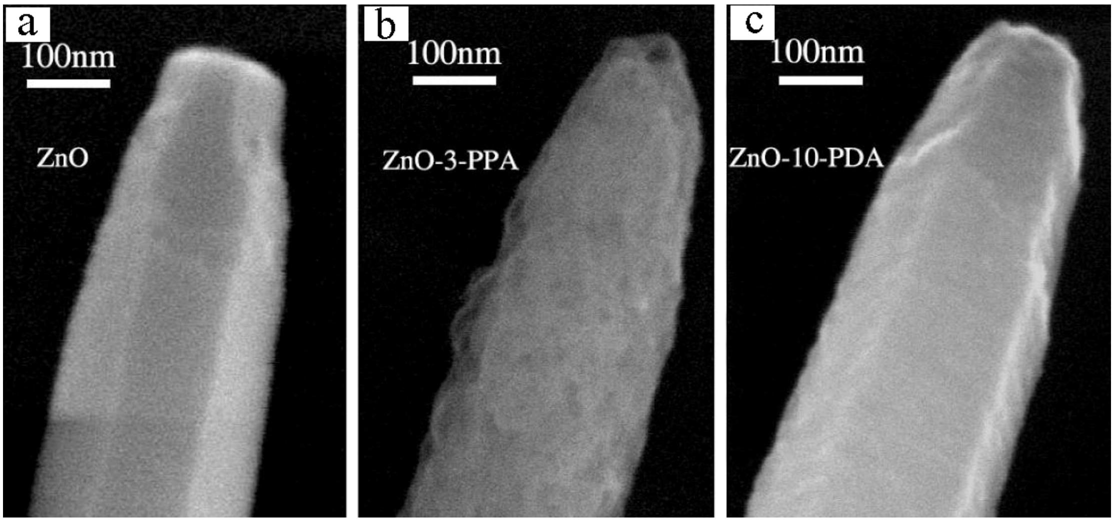


Figure S4. SEM micrographs of pre-functionalization (a), 3-PPA functionalized (b) and 10-PDA functionalized (c) ZnO nanowires.

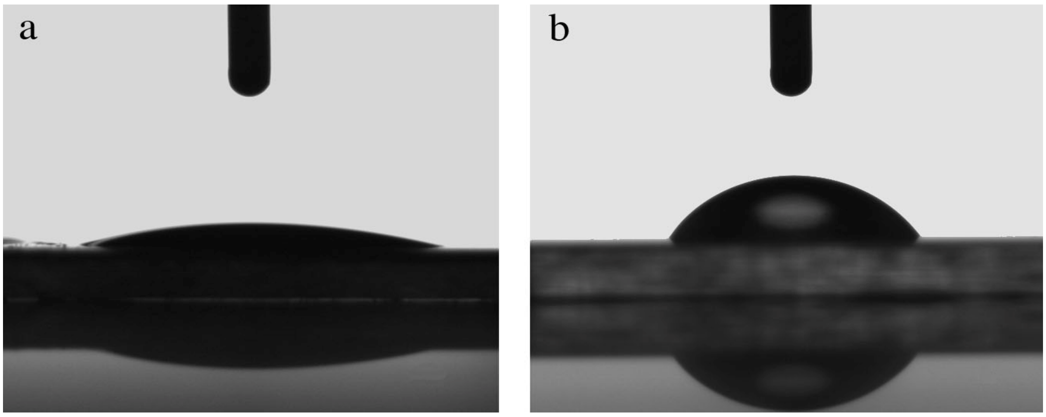


Figure S5. Water contact angle images of ZnO wafer pre-functionalized (a) and post-functionalized (b) by 10-PDA.

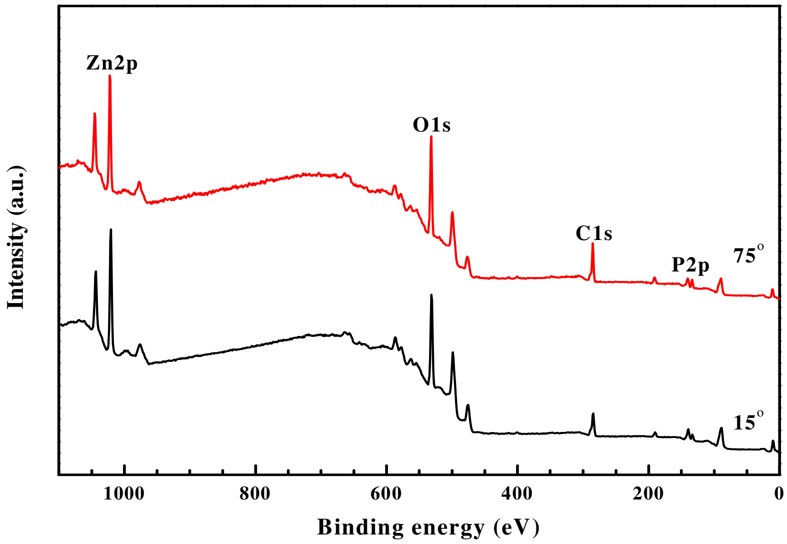


Figure S6. XPS spectra of 10-PDA functionalized ZnO at different take-off angles (15° and 75°).

Table S1. XPS binding energies ($E_B \pm 0.1$eV) of the 10-PDA SAM modified ZnO wafers

element	assignment	Energy [eV]	ΔE [eV]

C (1s) (1)	**C**-H/**C**-C	284.75	—
C (1s) (2)	O-**C**=O	288.75	-0.40
C (1s) (3)	-**C**-P(O)(OH)$_2$	286.25	0.10
O (1s) (1)	Zn**O**	530.32	—
O (1s) (2)	Zn-**O**-P, P=**O**	531.42	0.22
O (1s) (3)	P-**O**-H	532.12	-0.19
O (1s) (4)	-C-**O**OH	532.92	-0.39
O (1s) (5)	-C-**O**-H	533.82	-0.59
P(2p)	C-**P**-(O)(OH)$_2$	133.05	-0.40
Zn (2p3/2)	**Zn**O	1021.90	0.40

Table S2. Atomic Concentration (%) and Elemental Ratio of Self-Assembled 10-PDA on ZnO wafers

	Atomic concentration (%) and C/P ratio at emission angle	
	15°	75°
C	30.98	38.67
O	49.99	45.28
P	3.59	4.28
Zn	15.44	11.77
C/P	8.63	9.04

References

(s1) Kosolapoff, G. M. *J. Am. Chem. Soc.* **1945**, *67*, 1180.

(s2) Bhattacharya, A. K; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415.