Supporting Information

Highly Transparent and UV-Resistant Superhydrophobic SiO$_2$-Coated ZnO Nanorod Arrays

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EXPERIMENTAL:

Preparation of the SiO₂-coated ZnO Nanorod Arrays

**Materials:** Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%) was purchased from Fisher Chemicals. Hexamethylenetetramine ((CH₂)₆N₄, 99%) and ammonium hydroxide (NH₄OH, 20% in water) were purchased from Acros. Acetone, isopropanol, chloroform, chlorobenzene, 1-chloronaphthalene, tetraethyl orthosilicate (Si(OC₂H₅)₄, 98%), and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PTES) (98%) were purchased from Aldrich. (6,6)-phenyl-C71-butyric acid methyl ester (PC₇₁BM) was purchased from SOLENNE. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) PEDOT:PSS (Clevios™ P VP Al 4083) was purchased from Heraeus. Extran 300 detergent was purchased from EMD. All of the chemicals were used as received without any purification. Milli-Q water with a resistivity >18.0 MΩ·cm was used in the preparation of aqueous solutions. The glass slides were purchased from VWR (Vistavision™) and the flexible sheets of polyethylene terephthalate (PET; thickness: 0.1 mm) were purchased from Goodfellow (ES301400). The adhesion tape used for the “scotch tape” experiment was purchased from 3M (Scotch (3M) Permanent Double Sided tape #34-8507-8235-9 1/2 wide).

**Deposition of the ZnO Seed Layer:** Bare glass slides and tin-doped indium oxide (ITO, 15 Ω sq⁻¹) patterned glass substrates were first scrubbed with a diluted Extran 300 detergent solution to remove organic residues, and then immersed in a sonication bath of diluted Extran 300 for 15 min (Branson 5510). Next, the substrates were rinsed under flowing deionized water for 5 min and sonicated for 15 min each in baths of acetone and isopropanol. After a final last 5 min rinse in flowing deionized water, the substrates were dried under nitrogen. Regarding the ITO-coated glass: the ITO side was covered with a thin layer of PMMA drop-cast from a chloroform solution (0.25g/ml) in order to protect the conducting oxide during the sequential steps used for the preparation of the ZnO nanorod arrays. The substrates were placed in the sputtering chamber (Equipment Support Co., Cambridge, England) at a distance of 15 cm from the ZnO target, and the chamber was evacuated to 6*10⁻⁸ Torr and refilled with Argon to 5 mTorr, the pressure at which the deposition of the seed layer was achieved (room temperature, RF power of 50W).
thickness of the seed layer was adjusted by controlling the deposition time and monitored by ellipsometry (M-2000, J.A. Woollam Co.).

**Hydrothermal Growth of the ZnO Nanorods:** The substrates layered with ZnO were suspended upside down in a container filled with an aqueous solution of zinc nitrate hexahydrate (0.025 M) and hexamethylenetetramine (0.025 M) at 90°C. The time of ZnO nanocrystal growth was varied from 0 to 1h in order to yield nanorod arrays of various lengths. Next, the substrates were removed from the hydrothermal bath and thoroughly rinsed under flowing DI water. Regarding the ITO-coated glass: the drop-cast thin layer of PMMA protecting ITO was carefully peeled off. Finally, the substrates were dried under nitrogen and finally heated to 100°C in a vacuum-oven (3h) to remove residual water.

**Deposition of the SiO\textsubscript{2} Scaffold:** Samples with ZnO nanorod sizes optimized for transparency (growth time: 25min), either on bare glass slides or on ITO-coated glass, were used for the next steps. Regarding the ITO-coated glass: the ITO side was covered with a thin layer of PMMA drop-cast from a chloroform solution (0.25g/ml) to protect the conducting oxide during SiO\textsubscript{2} deposition and treatment with PTES. Next, the nanostructured substrates were subjected to UV-ozone for 15 min to activate the SiO\textsubscript{2} surface, and were then placed in a glass chamber, between 2 vessels containing 1 mL of tetraethoxysilane (TEOS) and 1 mL of ammonia, respectively. The glass chamber was slowly evacuated to 160 Torr and maintained at room temperature. The SiO\textsubscript{2} deposition time was varied between 1h and 12h to yield SiO\textsubscript{2} scaffolds of various thicknesses.

**Passivation of ZnO/SiO\textsubscript{2} with PTES:** The ZnO-nanostructured substrates (with or without SiO\textsubscript{2}) were placed at the center of a petri dish with 2 mL of PTES in ethanol (1%, v/v) drop-cast on the edge. Two mL of water was carefully drop-cast around the samples, avoiding contact with the PTES drops while providing a moist atmosphere. The petri dish was then covered and heated to 140°C (1h) in an oven in order to achieve the PTES surface passivation. Finally, the nanostructured substrates were carefully rinsed with acetone and further sonicated in acetone for 5 min to remove (i) unreacted PTES and (ii) the PMMA layer on the ITO-coated glass substrates.
Characterization Procedures and Supporting Analyses

Equipment and Experimental Methods: Optical transmittance measurements were performed with a Cary 6000i UV-Vis-NIR spectrophotometer under normal incidence (ZnO nanostructured side). The reflectance measurements were performed with a Lambda 950 UV-Vis spectrophotometer (PerkinElmer) equipped with an integration sphere. The static contact angle was measured with a DSA100 from KRUSS, using DI water droplets of 2 µL. Note: when water droplets could not readily be transferred to the surface of the nanostructured substrate due to the superhydrophobicity of the surface, tweezers were used to gently tap the tip of the needle producing the droplets and to allow droplet deposition. As the droplets immobilized on the surface, the static contact angle was measured. The sliding angles were measured on 2 µL water droplets that were placed on the flat surface that was progressively tilted at a rate of 0.2°/s, and the angle at which the first of several droplets started to slide on the surface was recorded as the sliding angle (results averaged over a minimum of 3 measurements). Atomic force microscopy (AFM) was performed with a Dimension Icon scanning probe microscope (BRUKER) in the tapping mode, and a high aspect ratio antimony-doped Si cantilever with a spring constant of 42 N/m (TESPA-HAR, Veeco) was used for the analyses; the radius of the tip was less than 10 nm. Scanning electron microscopy (SEM) was performed with a FEI Nova Nano 630 equipped with a through-lens detector; the acceleration voltage was tuned to 1-5 kV, spot size: 0.5-1.5, working distance: 1-3 mm. In the cross-section SEM characterizations, Pt was sputtered on the sample to compress the charging effects (deposition time: 20 s; current intensity: 5mA). X-ray diffraction (XRD) experiments were carried out on a high-resolution D8 Discover from BRUKER with a Cu Kα radiation point source (k = 1.5406 Å); the scan range was set between 25 and 90 and a scanning rate of 1s/step was used for the measurements. A focused ion beam (FIB, Helios 400s, FEI) was used to prepare the samples for cross-sectional TEM by a “lift-out” protocol. Prior to FIB milling, samples were coated with a polymer photoresist (PMMA) to protect the SiO2-coated ZnO nanorod surface. The lamellae were thinned with a Ga ion-beam (30 kV, 0.28 nA) and cleaned at an accelerating voltage of 2 kV and a current intensity of 47 pA. High-resolution transmission electron microscopy was performed on a Titan ST, working at an accelerating voltage of 300 kV.
Figure S1. Enlarged transmittance spectra of ZnO nanorod arrays (non PTES-treated) grown on a 5 nm seed layer with different growth times.

Figure S2. Effect of the volume of water droplets on the sliding angle (PTES-treated ZnO nanorods, grown for 25 min, on a 5 nm seed layer).

Note on sliding angle measurements: As shown in Figure S2, it is critical to note that the measures of sliding angle are greatly dependent on the volume of the droplets formed on the substrate. More specifically, the sliding angle increases as the droplet volume decreases according to \( \sin\alpha \approx kV^{-2/3} \), where \( \alpha \) is the sliding angle and \( k \) is related to the interaction energy.
between the solid and the liquid, and shows a dependence on the density of the liquid.\textsuperscript{1} Examination of both the experimental and the theoretical\textsuperscript{1} plot variations of the sliding angle with droplet volume indicates that the sliding angle value for a water droplet of 2 µL (8°) can be more than twice as large as that of a 6 µL droplet (3°), before leveling off for 10 µL droplets and beyond. We note that this parameter is not systematically emphasized across the literature, making comparisons between works generally difficult. Here, we note that, in order to improve the accuracy of our experimental measures, all reported sliding angle values throughout the study were estimated from 2 µL water droplets (\textit{i.e.}, significantly smaller than those used in most prior reports).

\textsuperscript{1} M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto and T. Watanabe, \textit{Langmuir}, 2000, \textbf{16}, 5754.
Figure S3. a) AFM image (1x1 µm) of a 5nm-ZnO seed layer sputtered on glass. b) AFM image (5x5 µm) of ZnO nanorods grown on a 5nm seed layer with a growth time of 25 min (non PTES-treated). Note: the aspect ratio of the AFM tip can be expected to limit the accuracy of the height profiles and surface roughness (RMS) measurements performed on densely nanostructured surfaces such as the ones shown in Fig. S3b.
Figure S4. Cross-section SEM image of ZnO nanorod arrays grown on a 5 nm seed layer with a growth time of 25 min.

Figure S5. X-ray diffraction patterns of ZnO nanorods (grown for 25 min on a 5 nm seed layer) with various SiO₂ deposition times (non-PTES-treated).
Figure S6. TEM image of ZnO nanorods (grown for 25 min, on a 5 nm seed layer) with SiO2 deposition times of a) 3h, b) 6h, c) Energy-dispersive X-ray spectroscopy (EDX) spectrum of ZnO nanorods obtained after a SiO2 deposition time of 6h.

Figure S7. Reflectance spectra of SiO2-coated ZnO nanorods (grown for 25 min on a 5 nm ZnO seed layer) for various SiO2 deposition times (non-PTES-treated).
Figure S8. a) SEM image (top-view) of ZnO nanorods (grown for 25 min, on a 5 nm seed layer) obtained after a SiO$_2$ deposition time of 3h. b) Cross-section SEM image of ZnO nanorods (grown for 25 min, on a 5 nm seed layer) with SiO$_2$ deposition time of 3h, and c) 9h.

“Scotch Tape” Experiment: A glass slide covered with double-sided adhesion tape was placed on top of the superhydrophobic substrate, and a load of steel of 0.350 kg producing a pressure of approximately 10 kPa was applied for approximately 1 min. The two glass slides were then separated and the integrity of the superhydrophobic surface of the SiO$_2$/ZnO nanostructured substrate was examined by SEM.

Solar Cell Device Fabrication and Characterization: The solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, 15 Ω sq$^{-1}$) patterned on the surface. Reference device: the substrates were first scrubbed with diluted Extran 300 detergent solution to remove organic residues and then immersed in an ultrasonic bath of diluted Extran 300 for 15 min. Next,
the samples were rinsed in flowing deionized water for 5 min and sonicated (Branson 5510) for 15 min each in successive baths of acetone and isopropanol. After a final 5 min rinse in flowing deionized water, the samples were dried with pressurized nitrogen before being exposed to a UV-ozone plasma for 15 min. Superhydrophobic device: the substrates covered with SiO$_2$/ZnO nanorod arrays were sonicated for 15 min each in successive baths of acetone and isopropanol, and the samples were then dried with pressurized nitrogen before being exposed to a UV-ozone plasma for 15 min. We note that the cleaning step with Extran 300 can be performed prior to the preparation of the SiO$_2$/ZnO nanocomposite on the glass side. An aqueous solution of PEDOT:PSS (Clevios P VP AI 4083) was spin-cast at 4,000 rpm onto the substrates and baked at 140°C for 15 min. Immediately after baking the substrates, the samples were then transferred into a dry nitrogen glovebox (<3 ppm O$_2$) for active layer deposition.

The blend solution was prepared in the glovebox using the PBDTTPD polymer donor synthesized in our laboratories and the PC$_{71}$BM acceptor purchased from SOLENNE. The polymer and PC$_{71}$BM were dissolved in chlorobenzene containing 5% (by volume) of 1-chloronaphthalene (CN) additive, and the solutions were stirred overnight at 115°C. Optimized devices were prepared using a polymer:PC$_{71}$BM ratio of 1:1.5 (by weight), with a concentration of 20 mg mL$^{-1}$.

The active layers were spin-cast from the solutions at 115°C at an optimized speed for 45 s, using a programmable spin coater from Specialty Coating Systems (Model G3P-8), resulting in a film of 100 to 120 nm in thickness. The samples were then dried at room temperature for 1 hour. Next, the samples were placed in a thermal evaporator for evaporation of a 7 nm layer of calcium evaporated at 1 Å s$^{-1}$ and 150 nm of aluminum electrodes evaporated at 5 Å s$^{-1}$, at a pressure less than 1x10$^{-7}$ Torr. Following electrode deposition, samples underwent $J$--$V$ testing.

$J$--$V$ measurements of solar cells were performed in the glovebox with a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5 G, with a KG-5 silicon reference cell certified by Newport. The external quantum efficiency (EQE) measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by NIST.