Electronic Supplementary Material (ESI) for RSC Advances.

Air-Based Photoelectrochemical Cell Capturing Water Molecules from Ambient Air for Hydrogen Production

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Supporting Information

Methods

Materials: MilliQ water with a resistivity of 18.2 MΩ.cm was used. Nitrogen gas (99.999%) was from Air Liquide (Brussels, Belgium). A stream of N_2 was bubbled through a vessel with MilliQ water at 20 °C to generate a water saturated gas stream. Hydrogen peroxide (50 wt%) and tetraethyl orthosilicate (TEOS; 98%) were obtained from Acros Organics (Geel, Belgium). Sulfuric acid (95–97%), water-^{18}O (97 atom%), tetrakis-dimethylamido titanium (TDMAT; 99.999%) and methylcyclopentadienyl trimethylplatinum ($MeCpPtMe_3$) were obtained from Sigma Aldrich (St. Louis, MO). Tetrapropylammonium hydroxide (TPAOH) was obtained from Alfa (Karlsruhe, Germany). Toray 030 carbon fiber electrode material (thickness 110 μm) was obtained from Fuel Cell Earth (Stoneham, MA). Nafion® solution (5% in ethanol) and Nafion® XL proton exchange membrane were obtained from Quintech (Göppingen, Germany); Multi-walled carbon nanotubes (NC7000) from Nanocyl (Sambreville, Belgium).

High-Resolution Scanning Electron Microscopy: HR-SEM images were obtained with a Nova NanoSEM 450 (FEI, Hillsboro, OR). Samples were mounted on aluminum stubs using carbon tape and observed. For STEM, the sample was prepared by crushing electrode in a mortar and suspending the obtained material in isopropanol, followed by ultrasonication for 30 minutes. After settling of large particles, a few drops of supernatant were drop-casted on a lacy carbon mesh and observed.

Thermogravimetric Analysis: TGA was performed on a Q500 (TA Instruments, New Castle, DE). A disk of 8 mm diameter was cut from the electrode and analyzed under pure oxygen stream at a heating rate of 10 °C/min. For water sorption experiments, electrodes were first dried for 1 h at 60 °C in air, followed by equilibration under ambient conditions overnight. Subsequently, a disk of 8 mm diameter was cut from the electrode and measured under a nitrogen flow that was either dry or saturated by bubbling it through a water bath containing MilliQ water at 25 °C.

X-Ray Diffraction: XRD characterization of the TiO_2/MWCNT/carbon fiber electrode was carried out in a Bruker D8 diffractometry system with Cu Kα X-ray source.

X-Ray Fluorescence: XRF characterization of the Pt/MWCNT/carbon fiber electrode was carried out using the Artax tool in a Bruker D8 system. The equivalent thickness of Pt in Pt/MWCNT/carbon fiber electrode was estimated by comparing the XRF signal intensities of the electrode with 100 nm thick Pt layer sputtered on a planar silicon wafer.

Raman spectroscopy: The Raman measurements were performed on a home-built Raman microscope (Nikon Eclipse Ti-U) equipped with a 532 nm continuous wave diode pumped solid state laser (Cobolt Samba). The laser power at the sample was adjusted to 13 mW and the Raman signals were collected in epi-direction via the same air objective lens (Nikon 60X 0.95NA APO) and directed to the electron multiplying CCD (Model Newton 920, Andor) via a spectrograph (iHR320, Horiba) with 1200 grooves mm^{-1}. The backscattered excitation beam was blocked with a low pass filter (540LP, Chroma). Calibration of the Raman set up was performed via collection of pure toluene spectra.

Zeolite synthesis: The zeolite powder was prepared according to an established procedure.[1] TEOS (37.32 g) was hydrolyzed in aqueous TPAOH solution (40 wt%; 32.13 g) under stirring. The emulsion thus formed under vigorous stirring was gradually transformed into a clear sol as the TEOS was hydrolyzed. Then water was added (30.55 g) and the stirring continued for another 24 h. The clear precursor sol was refluxed at 95°C for three days. After cooling it to room temperature, the colloidal zeolite particles were separated by centrifugation (15 000 rpm, 15 min) and dispersed in water. The zeolite was washed until the pH of the supernatant was lower than pH 9. The dried powder material was calcined at 550 °C. The particle size was about 150 nm.

MWCNT deposition: The carbon fiber electrodes were decorated with MWCNT forests by dip-coating in a MWCNT suspension containing 0.3 wt% MWCNTs. Final MWCNT loading, determined by TGA, was about 15 wt% (0.49 mg cm^{-2}).

Atomic Layer Deposition of TiO_2 and Pt. The MWCNT decorated carbon fiber electrode was loaded into a home-made ALD system with base pressure below 10^{-4} Pa . The sample was heated to 100 °C and exposed to a TDMAT pulse at a pressure of 50 Pa. After 20 s pulse time, the chamber was evacuated for 20 s. An ozone pulse supplied by an ozone generator (Yanco industries, Burton, Canada) was introduced into the chamber for another 20 s. The concentration and the pulse pressure of the ozone were 145 µg mL^{-1} and 50 Pa, respectively. After the ozone pulse, 20 s pumping was used to evacuate the residual ozone and by-products again. The TiO_2 loading determined by TGA in oxidative atmosphere amounted to ~98 µg cm^{-2}.

For the Pt ALD process, $MeCpPtMe_3$ and ozone were used. The pulse time and evacuation time were the same as in the TiO_2 ALD process. The pulse pressures of the $MeCpPtMe_3$ and ozone were 80 Pa and 70 Pa, respectively, and the temperature of the sample for deposition was 200 °C. The Pt content of the cathode used in our experiments was determined to be $\leq$ 16 µg/cm^2 using TGA analysis in oxygen atmosphere until 1000 °C. XRF analysis of the Pt ALD-treated electrode revealed an equivalent flat surface thickness of 7.8 nm Pt. Assuming a Pt density of 21.45 g cm^{-3}, a Pt loading of 13.1 ± 1.3 µg/cm^3 was calculated, in good agreement with the TGA data.

Electrode processing: The as-deposited amorphous TiO_2 on the MWCNTs was crystallized to anatase by heating for 3 h at 550 °C under air atmosphere. A few drops of zeolite suspended in Nafion® solution (1 g L^{-1}) were drop-casted on both electrodes and excess material was blotted on a dust-free tissue. The electrodes were allowed to dry at room temperature for 30 minutes before further processing.

Solar membrane assembly: Nafion® membrane was preconditioned by boiling in a bath of 5 wt% H_2O_2 for 1 h and then in alternating baths of MilliQ water and 1 M H_2SO_4 for 3 h and 2 h, respectively. Treated Nafion® was blotted dry and fixed in an aluminum holder for spin-coating. On both sides of the membrane, a few drops of zeolite/Nafion® solution were deposited while spinning for 1 min at 800 rpm on a Specialty Coating Systems 6800 (Indianapolis, IN). Assemblies were prepared by positioning the anode and cathode carbon fiber electrodes on opposite sides of pre-treated Nafion® membrane, and hot-pressing between Teflon liners at 5 MPa pressure and at 130 °C for 3 min. In between experiments, the assemblies were stored under ambient conditions between dust-free cloth.

Photoelectrochemical experiments: The assembly was fixed in the PEC cell. A mask covering the photoanode with a circular opening of 10 mm diameter ensured an illuminated surface area of 0.785 cm^2. The total cathode surface area was also 0.785 cm^2. The anode in- and outlet were left open to the air, or contacted with a gas stream at 12.5 mL min^{-1}. The cathode was flushed with dry nitrogen for 30 minutes prior to an experiment and sealed. Illumination was done by means of a Xe lamp with IR filter (Oriel 66984, Newport, Irvine, CA) adjusted such that the incident intensity equaled either 50 mW cm^{-2} or 100 mW cm^{-2} and the lamp was fitted either with a UV band pass filter or Air Mass 1.5 solar simulation filter (Newport, Irvine, CA). The currents were recorded at short circuit (zero applied voltage) in a two-electrode measurement using a potentiostat (Versastat 4, Princeton Applied Research, Oak Ridge, TN) and Versastudio electrochemical analysis software. The products were analyzed with a Quantitative Gas Analyzer (Hiden Analytical, Warrington, UK; detection limit 0.1 ppm). A correction was made for interference by water fragments and the nitrogen signal was used as an internal standard.

Additional Figures

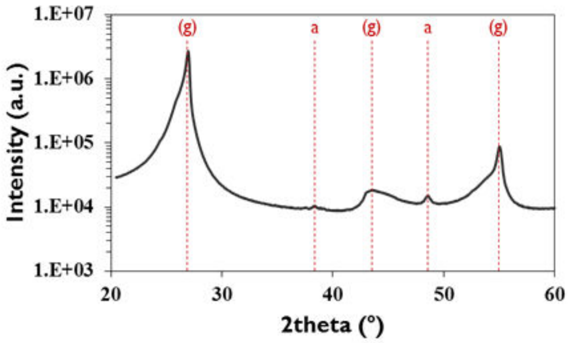

Figure S1. X-ray diffraction pattern of the anode. Diffractions originating from carbon fiber substrate (g) and anatase (a) are indicated.

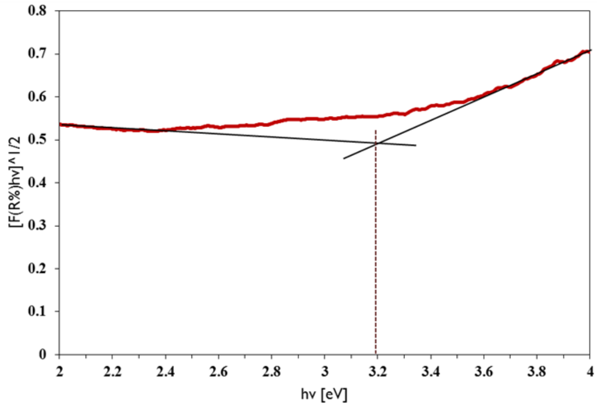

Figure S2. Tauc plot of photoanode. Linear fits indicate anatase band gap of *ca.* 3.2 eV.

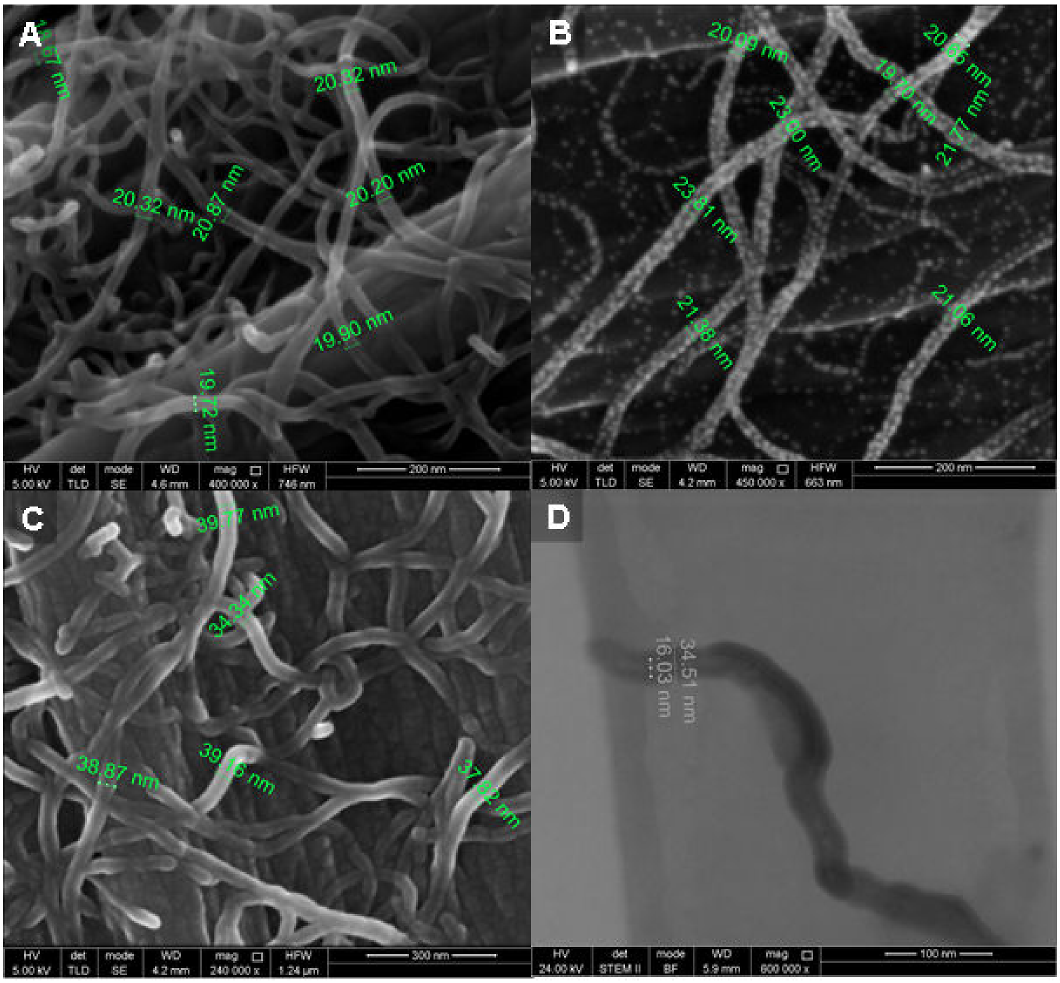

Figure S3. HR-SEM images of the electrodes. (A) MWCNT/carbon fiber parent material, (B) Pt/MWCNTs of the cathode and (C) TiO_2/MWCNTs at the anode with indicated dimensions. MWCNT diameters are ~20 nm and the TiO_2 film thickness ~7-10 nm. (D) Scanning Transmission Electron Microscopy (STEM) of TiO_2/MWCNT confirms the core-shell dimensions.

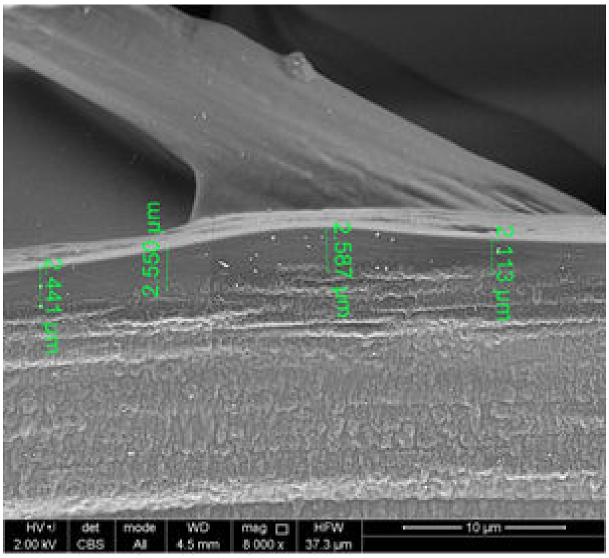

Figure S4. HR-SEM image of carbon fiber cross-section showing ~2.5 µm thick Nafion® coating.

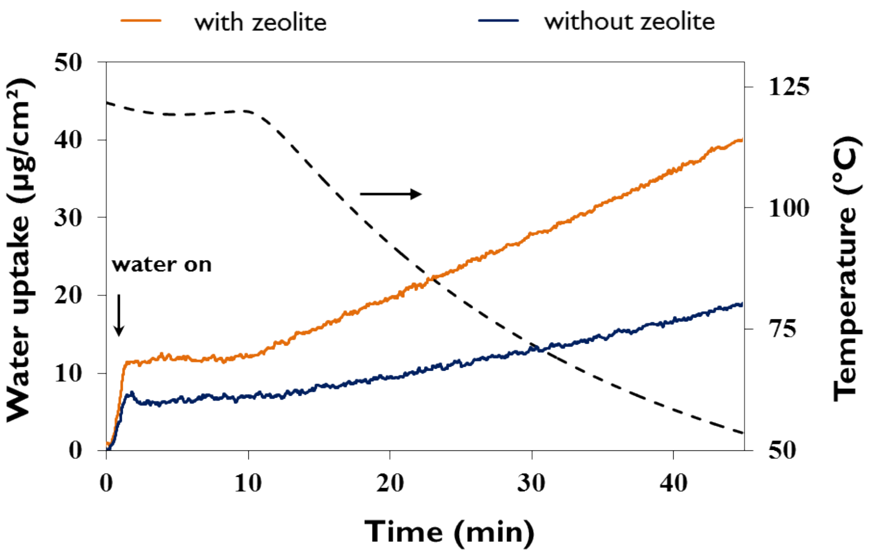

Figure S5. Water uptake of electrodes covered with Nafion® or Nafion®/zeolite composite. Electrodes, dried at 120 °C under N_2 flow, were exposed to humidified N_2 with a water content of 24 g m^{-3}. Chamber temperature was decreased from 120 °C to 50 °C.

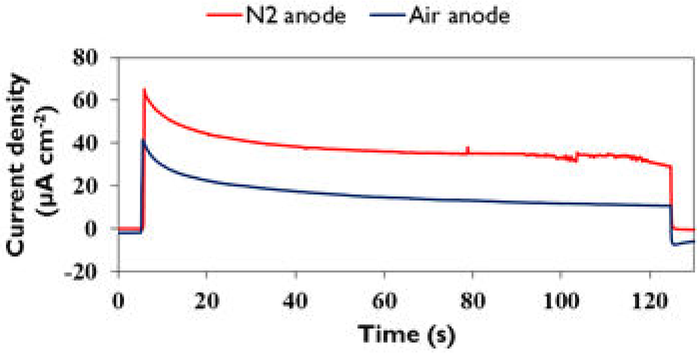

Figure S6. Photocurrent profiles obtained using a non-optimal photoanode with electrophoretically deposited TiO_2 nanoparticles. The cell was illuminated with UV light (50 mW cm^{-2}) for 2 minutes. The cathode compartment was filled with dry nitrogen and the anode compartment fed with humidified nitrogen (red trace) or humidified air (blue trace). In both cases, photocurrent decayed strongly during the 120 s experiment. When humidified air is used as a feed, photocurrent is lower and the decay more pronounced due to the presence of molecular oxygen.

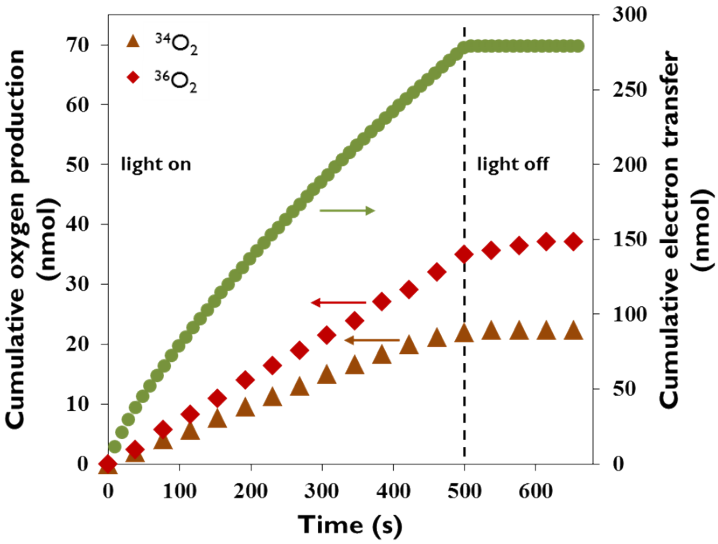

Figure S7. $^{36}O_2$ and $^{34}O_2$ production and electron transfer during a $H_2{}^{18}O$ splitting experiment under UV illumination (100 mW cm^{-2}) in N_2 atmosphere. Illumination was shut off after 500 s. The system contained residual $H_2{}^{16}O$, which causes concurrent $^{34}O_2$ formation.

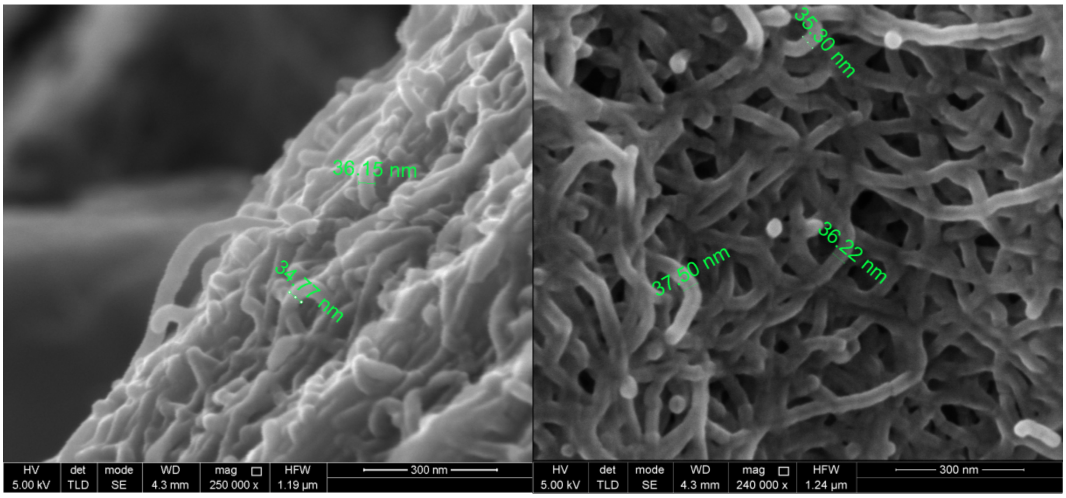

Figure S8. HR-SEM images of TiO_2/MWCNT photoanode after 15 h of UV illumination showing no signs of degradation.

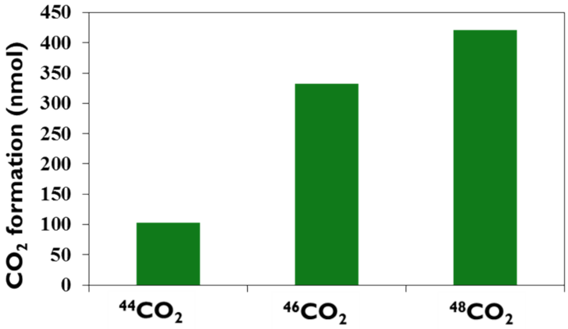

Figure S9. CO_2 isotopes formed at the photoanode during 500 s of simulated solar illumination in the PEC cell fed with $H_2{}^{18}O$ saturated N_2. Non-photoelectrochemical CO_2

formation is to be expected in the presence of TiO_2 semiconductor, which is a very effective photocatalyst for the oxidation of organics. Presumably, the carbon fiber electrode substrate is being oxidized, as the MWCNTs are protected from oxidation by the TiO_2 shell, and because cell performance shows no degradation after extended use. The CO_2 mass distribution shows predominant $^{48}CO_2$ formation in presence of $H_2{}^{18}O$, so it is clear that water is the source of oxygen atoms.

References

1. R. Ravishankar, C. Kirschhock, B. J. Schoeman, P. Vanoppen, P. J. Grobet, S. Storck, W. F. Maier, J. A. Martens, F. C. De Schryver, and P. A. Jacobs, *J. Phys. Chem. B*, 1998, **5647**, 2633–2639.