

Supporting information

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Experimental

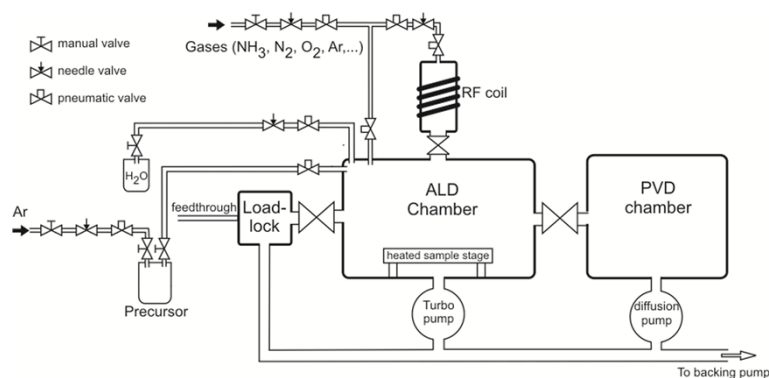


Figure S1: schematic of the home built atomic layer deposition tool used for TiO₂ deposition on MWCNTs.

X-ray diffraction. In situ XRD measurements were carried out in a dedicated Bruker D8 system.^[1] The sample was annealed from 20°C to 850°C in air while being illuminated by Cu K α radiation (wavelength 0.154nm). Diffracted x-rays were captured by a linear detector covering a range of 20° in 2 θ . The collection time of the linear detector was 5 seconds. The temperature of the sample was increased at 1°C per minute and monitored by a K-type thermocouple.

Photocatalytic testing. The reactor employed is a rectangular single-pass, slit-shaped, flow through photoreactor. The dimensions of the slit-shaped reactor chamber are 150 mm x 20 mm x 2.75 mm. The chamber is sealed from the top with a 5 mm thick polished quartz plate. Illumination is provided from above by means of a Philips Cleo UV-A lamp with a peak wavelength at 365 nm (25W) placed parallel to and 25 mm above the long side of the slit. The emitted light intensity was measured at the lamp wall using an Avantes Avespec-3648 spectrometer, and determined to be approximately 205 $\mu\text{W}\cdot\text{cm}^{-2}$ at the peak wavelength of 365 nm. For the photocatalytic test, a sample wafer of 50 mm by 15 mm consisting of 100 ALD cycles on MWCNTs

and then annealed at 500°C for 3 hours, was placed in the middle of the reaction chamber.

A simplified scheme of the reaction set-up can be found in Figure S2. Compressed air (Air Liquide Alphagaz) spiked with acetaldehyde (Air Liquide, 1% in N₂) is provided to the system by means of mass flow controllers (Brooks 5850E). Part of the pure air stream is sent through a gas wash bottle and is mixed with the polluted stream so that the relative humidity in the polluted air stream is 5%. It was verified that 5% humidity was sufficient in order to maintain steady photocatalytic degradation and obtain reproducible results over independent experimental runs. The exact administered acetaldehyde concentration is verified using a calibrated organic vapor sensor (Dräger Polytron). In our experiments, the resulting acetaldehyde concentrations were 25, 52 and 80 ppmv in air. Detection of the reactor outlet is performed by means of online-FTIR monitoring of peak heights of reaction species of interest in time using the Macros Basic software (Thermo Fisher Scientific). The detector is a Nicolet™ 380 FTIR spectrometer (Thermo Fisher Scientific) with ZnSe windows and a 2 m heated gas cell. Spectra were recorded in a range of 4000 - 400 cm⁻¹ at a resolution of 1 cm⁻¹. In particular, the acetaldehyde concentration was monitored based on the FTIR peaks corresponding to $\nu(\text{C-H})$ and $\nu(\text{C=O})$ located at 2728 cm⁻¹ and 1761 cm⁻¹ respectively. The CO₂ concentration is monitored through the $\nu_{\text{as}}(\text{C=O})$ vibration at 2360 cm⁻¹ and calibrated using a CO₂ sensor (Vaisala).

Each measurement consisted of several phases. In the first phase (10 minutes) the polluted gas flow is bypassed around the reactor and led directly to the FTIR detector. This way a reference signal is established corresponding to the inlet concentration. Then, a switch valve sends the flow through the reactor under dark conditions (15 minutes). When the adsorption/desorption equilibrium is established; i.e. when the FTIR signal of acetaldehyde equals the reference value obtained during the bypass phase, the UV lamp is turned on (20 minutes). When photocatalytic degradation occurs, this becomes obvious from a decrease in acetaldehyde concentration and a simultaneous increase in CO₂ formation in the outlet gas stream. The measurements were repeated three times. The error involved was observed not to exceed 2%. This measurement protocol has already been validated in our previous work.^[3,4]

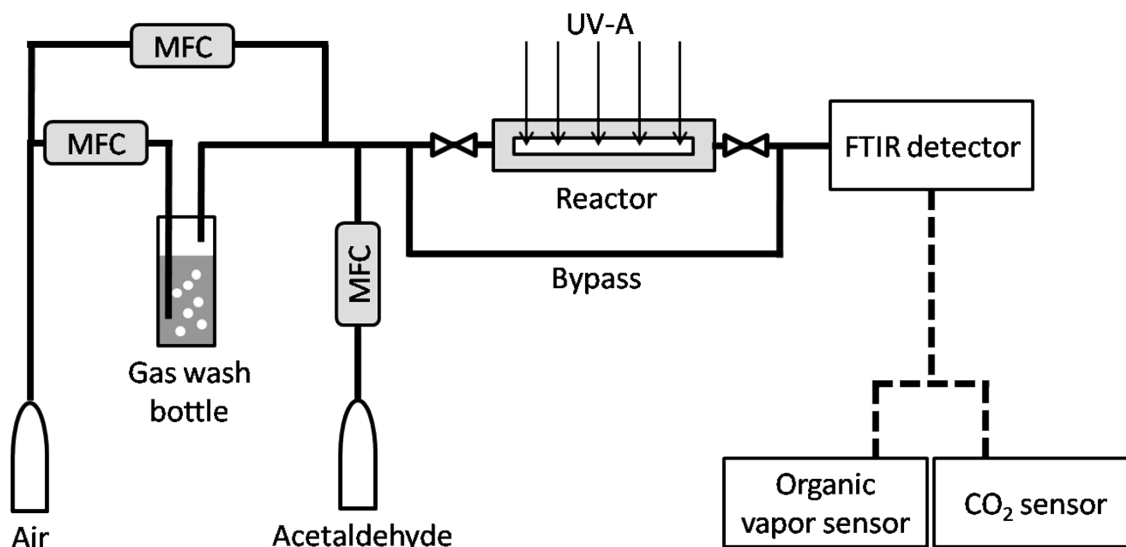


Figure S2: Simplified scheme of the reactor set-up. MFC stands for Mass Flow Controller. Automated valves are symbolized by ▶ ◀. The ducts represented by dashed lines are optional extensions behind the FTIR detector that can be used for relating the FTIR peak heights to the actual acetaldehyde and CO₂ concentrations.

Uniformity of the TiO₂ coating

For a more detailed investigation of the uniformity of the ALD coating on the MWCNTs, EDX was employed. The Ti and C signals were measured every micrometer by scanning a coated wafer from the bottom to the top of the tube bed. Figure S3 shows the results of these measurements on two samples. One sample is the one discussed in the manuscript, involving 100 ALD cycles and 20 s pulse time during the ALD process. The other sample involves 100 ALD cycles, but 90 s pulse time, which allows the precursor molecules more time to interact with the MWCNTs. The inconspicuous fluctuation of the ratio between Ti and C from the bottom to the top of the MWCNTs indicates a uniform coating of TiO₂ over the entire length of the MWCNT bed. Furthermore, the similar Ti/C ratios of the 20 s and 90 s pulse time samples proves that 20 s pulse time is sufficiently long for obtaining a conformal coating.

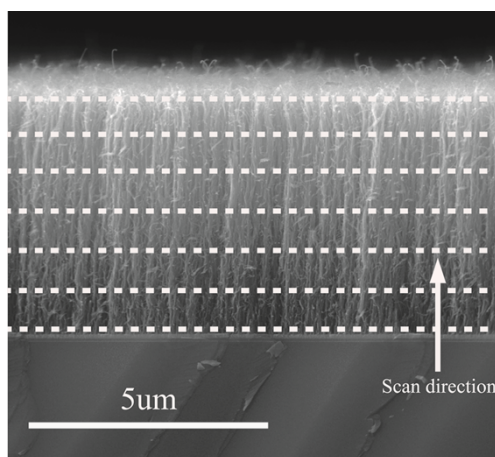
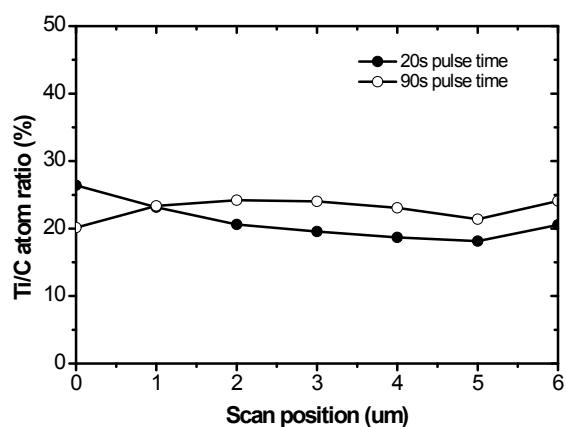


Figure S3: Ti/C ratio measured by EDX every μm along the tube bed as indicated in the SEM picture on the right. Results are given for MWCNTs coated with TiO_2 by 100 ALD cycles with 20 s pulse time (\bullet) and 90 s pulse time (\circ). The background Ti signal from the TiN beneath the MWCNTs has been subtracted.

Particle Size Distribution

Based on high resolution TEM pictures of a sample annealed at 500°C for 3 h, the main particle diameter of 50 randomly selected particles was measured and plotted in a histogram (Figure S4). The obtained particle size distribution shows that most of the particles are between 10 and 14 nm wide. The mean diameter of the particles is 12 nm. This narrow particle size distribution can be attributed to the high conformality of the ALD coating.

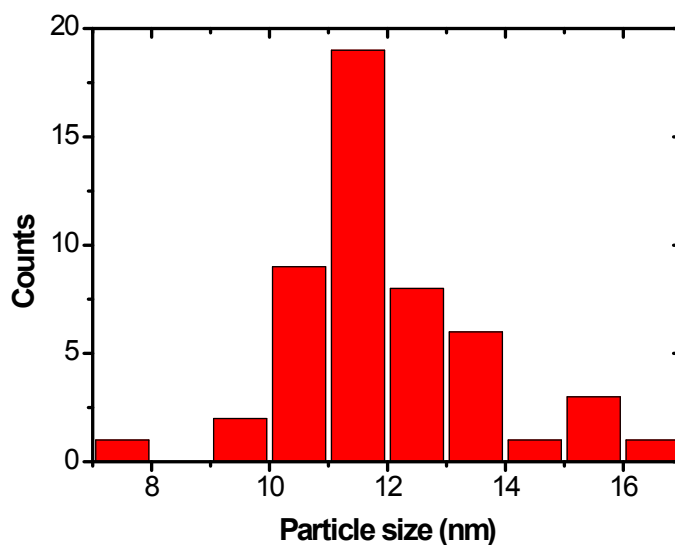


Figure S4: Size distribution of TiO₂ particles obtained after annealing of MWCNTs coated with TiO₂ by 100 ALD cycles.

Sonication treatment on TiO₂ nanoparticle chains.

The sample of TiO₂ nanoparticle chains was put into a beaker which contained isopropanol solution (Sigma Aldrich, >99.5%). Sonication experiment was carried on in a sonicator (SONOMATIC 150B, 75w) for 1 hour at room temperature. After the sonication treatment, the sample still had the same color and don't show any visible collapse or wrinkle, as shown in the pictures below.

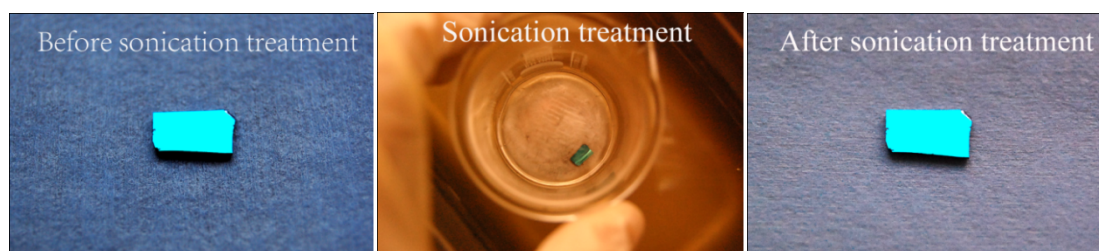


Figure S5: optical pictures of TiO₂ nanoparticle chains before, during and after the sonication treatment.

References

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[2] S. W. Verbruggen, S. Ribbens, T. Tytgat, B. Hauchecorne, M. Smits, V. Meynen, P. Cool, J. A. Martens, S. Lenaerts, *Chem. Eng. J.*, **2011**, *174*, 318.

[3] J. Jammaer, C. Aprile, S. W. Verbruggen, S. Lenaerts, P. P. Pescarmona, J. A. Martens, *ChemSusChem*, **2011**, *4*, 1457.