Electronic Supplementary Information

Layer-by-layer assembly of titania nanoparticles based ionic networks

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Experimental details.

1. Chemicals

Materials unless otherwise stated, were used without further purification., Titanium isopropoxide ($Ti(O^iPr)_4$), 1,3-dibromopropane, bromotrimethylsilane, potassium tert-butoxide, dimethylphosphite, 1-bromo-3-chloropropane, sodiumhydride and tetrahydrofuran (THF) were obtained from Sigma-Aldrich, hydrochloric acid (37 %) from VWR, imidazole from Fluka and ethanol, nitric acid (53 %) and dichloromethane from Merck.

2. Instrumentation

Ellipsometric measurements were performed with the alpha-SE® system from J.A.Woolam Co, Inc, under an angle of 70°. Ellipsometric spectra between 380 and 900 nm wavelengths were recorded and fitted using a simple two layer model with silicon substrate and a layer with a refractive index of 1.45; which has been shown to yield suitable results for thin films.[1]

Atomic force microscopy (AFM) measurements were performed using a NanoMan V system from Veeco. For topographic measurements, PPP-NCHR cantilevers (Nano and More) were used in tapping mode®. Tune parameters for the system were 0.5 V target amplitude and the measurement frequency set to 5% off-resonance. The measurement was performed at a damping of approximately 25% and scan rates of 1Hz for 1x1 μm² to 5x5 μm² images.

Lateral force microscopy (LFM) measurements were undertaken using a PPP-CONTR cantilever (Nano and more) with a spring constant of 0.179 N/m. Approach was performed with a deflection setpoint of 1 V to ensure engaging of the system. After contact, the setpoint was changed to the value of interest, covering a range between 0.2 to 5 V (12-300 nN tip force). In-situ control of LFM induced surface modification was undertaken with the same tip at a deflection setpoint of 0.1 V (6 nN tip force). High resolution images of the modified surfaces were obtained in tapping mode as described above.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a system from SPECS Surface Nano Analysis GmbH with a XR-1000 X-ray source and a PHOIBOS-3500 hemispherical analyser. The spectra were recorded using the Mg source. For overview scans (0-600 eV), a resolution of 0.1 eV and a dwell time of 0.1s were chosen and the average of 3 scans was recorded. Peaks for the individual elements were recorded at 0.02 eV resolution averaging 5 scans.

Dynamic light Scattering (DLS) measurements were carried out on an ALV/CGS-3 compact goniometer system, equipped with an ALV/LSE-5003 light scattering electronics and multiple τ digital correlator, and a 632.8 nm JDSU laser 1145P. For the measurement the solid was dissolved in water. The run time of one measurement cycle is 10 seconds. Every size distribution curve is obtained by averaging 10 measurements.

Nuclear magnetic resonance (NMR) in liquid state for ^1H, ^{13}C and ^{31}P nucleus were recorded on a Bruker AVANCE 250 (^1H at 250.13 MHz, ^{13}C at 62.86 MHz, ^{31}P at 101.26 MHz) equipped with a 5 mm inverse-broadband probe head with a z-gradient unit.

3. Syntheses

Synthesis of N-(3-propyltrimethoxysilane) imidazole (1)

Synthesis of 3-iodopropyltrimethoxysilane

Under argon atmosphere 36.9 g (0.246 mol) of sodium iodide were dissolved in 150 mL dry acetone and 48.9 g (0.246 mol) 3-chloropropyltrimethoxysilane were added drop wise under stirring. The mixture was heated to reflux under stirring overnight. Afterwards, the formed precipitate (sodium

chloride) was filtered off and the product distilled under vacuum (3 mbar at 80 °C). A yellowish liquid was obtained. Yield: 37.12 g (53 %, 127.92 mmol)
^{1}H NMR (250 MHz, $CDCl_3$): 0.69 (t, 2H, Si-*CH_2*), 1.89 (q, 2H, I-CH_2-*CH_2*), 3.15 (t, 2H, I-*CH_2*), 3.52 (s, 9H, Si-O-*CH_3*) ppm.

Synthesis of N-(3-propyltrimethoxysilane)imidazole
Under argon atmosphere 2.9 g (0.120 mol) sodium hydride were suspended in 150 mL dry THF, the mixture was cooled to 4°C with an ice bath and 8.2 g (0.120 mol) imidazole were added over a period of 30 minutes. The suspension was stirred for 2 hours until no release of hydrogen were observed. Then 26.12 g (0.090 mol) of 3-iodopropyltrimethoxysilane were added and the mixture was heated to reflux overnight. The orange suspension was filtered and the solvent removed under reduced pressure. Afterwards 150 mL dry dichloromethane was added and the formed precipitate was filtered off. The product, a transparent liquid, was gained by distillation (1 mbar at 150 °C). Yield: 11.6 g (55.7 %, 50.2 mmol)
^{1}H NMR (250 MHz, $CDCl_3$): 0.54 (t, 2H, Si-*CH_2*), 1.83 (q, 2H, N-CH_2-*CH_2*), 3.53 (s, 9H, Si-O-*CH_3*), 3.88 (t, 2H, N-*CH_2*), 6.88 (s, 1H, N-CH-*CH*-N), 7.01 (s, 1H, N-*CH*-CH-N), 7.54 (s, 1H, N-*CH*-N) ppm.
^{13}C NMR (250 MHz, $CDCl_3$): 7.4 (s, 1C, Si- *C*H_2), 25.1 (s, 1C, N-CH_2-*C*H_2), 55.7 (s, 1C, N-*C*H_2), 56.2 (s, 3C, Si-O-*C*H_3), 120.7 (s, 1C, N-CH-*C*H-N), 128.1 (s, 1C, N-*C*H-CH-N), 136.8 (s, 1C, N-*C*H-N) ppm.

Synthesis of 3-chloropropylphosphonic acid (2)[2]
Synthesis of dimethyl-3-chloropropylphosphonate
18 g (160.41 mmol) potassium tert-butoxide were suspended in 150 ml THF. Afterwards 22.01 g (200 mmol) dimethylphosphite were slowly added under vigorous stirring. After 2 hours of stirring the whole suspension was slowly added to a stirred suspension of 47.23 g (300 mmol) 1-bromo-3-chloropropane in 120 ml THF in a 500 mL round bottom flask. A white suspension was formed immediately. The mixture was heated to reflux for 20 minutes. After cooling to room temperature the formed precipitate, potassium bromide, was filtered off and washed twice with 100 mL diethylether. Then the solvents and by-products were removed under vacuum (20 mbar at 170 °C). A slightly coloured liquid was obtained. Yield: 17.9 g (60 %, 96.25 mmol).
^{1}H NMR (250 MHz, $CDCl_3$): 1.82-1.92 (m, 2H, P-CH_2-*CH_2*), 1.93-2.10 (m, 2H, P-*CH_2*), 3.58 (t, 2H, Cl-*CH_2*), 3.72 (d, 6H, P-O-*CH_3*) ppm.
^{31}P NMR (250 MHz, $CDCl_3$): 45.99 ppm.

Synthesis of 3-chloropropylphosphonic acid
6.169 g (33.07 mmol) dimethyl-3-chloropropylphosphonate were mixed with 40 ml hydrochloric acid (37%) and heated to reflux for 24 hours. Afterwards the solvent was removed under reduced pressure and residues of water were removed through azeotropic distillation by adding 20 ml of toluene. The yellowish liquid residue was crystallized from 50 ml chloroform and filtered. The colourless crystalline product was dried in a desiccator over P_2O_5 under vacuum. Yield: 3.73 g (70 %, 23.53 mmol).
^{1}H NMR (250 MHz, DMSO-*d6*): 1.63-1.69 (m, 2H, P-CH_2-*CH_2*), 1.83-1.90 (m, 2H, P-*CH_2*), 3.67 (t, 2H, Cl-*CH_2*), 7.29 (s, 2H, P-O*H*) ppm.
^{31}P NMR (250 MHz, DMSO-*d6*): 37.85 ppm.
^{13}C-NMR (DMSO-*d6*): 24.2 (P-CH2-*C*H2), 26.4 (P-*C*H2), 46.1 (Cl-*C*H2) ppm.

Synthesis of N-imidazolylpropyl phosphonic acid (3)[3]
Synthesis of diethyl-3-bromopropylphosphonate
30 g (180.55 mmol) triethylphosphite and 150 g (722.20 mmol) 1,3-dibromopropane were heated under vigorous stirring to 160 °C for 30 minutes. Unreacted 1,3-dibromopropane was removed under reduced pressure and diethyl-3-bromopropylphosphonate distilled under vacuum (2 mbar at 165 °C). A colorless liquid was obtained. Yield: 23.45 g (50 %, 90.5 mmol).
^{1}H NMR (250 MHz, $CDCl_3$): 1.20 (t, 6H, P-O-CH_2-*CH_3*), 1.80 (m, 2H, P-CH_2-*CH_2*), 1.99 (m, 2H, Br-*CH_2*), 3.35 (t, 2H, P-*CH_2*), 3.97 (m, 4H, P-O-*CH_2*) ppm.
^{31}P NMR (250 MHz, $CDCl_3$): 30.48 ppm.

^{13}C NMR (250 MHz, $CDCl_3$): 16.3 (P-O-CH_2-*C*H_3), 23.1 (P-CH_2-*C*H_2), 25.8 (P-*C*H_2), 33.5 (Br-CH2), 61.5 (P-O-CH2-CH3) ppm.

Synthesis of sodium imidazolide
Under argon 1,2 g (50 mmol) sodiumhydride were suspended in 150 mL dry THF. This suspension was cooled to 4 °C with an ice bath and 3.404 g (50 mmol) imidazole were added over a period of 30 minutes. The suspension was further stirred for 2 hours until no evolution of hydrogen is visible. Afterwards the white product was filtered off and dried in a desiccator over P_2O_5 under vacuum. Yield: 4.41 g (98 %, 49 mmol).

Synthesis of dimethyl-N-imidazolpropylphosphonate
Under argon, in an 25 mL round bottom flask, 0.9 g (10 mmol) of sodium imidazolide were dissolved in 5 mL dry DMF. The solution was cooled to 4 °C with an ice bath and 2.59 g (10 mmol) diethyl-3-bromopropylphosphonate were added at once. Afterwards the ice bath is removed and the suspension is heated to 55 °C for 8 hours under vigorous stirring. The solvent was removed under reduced pressure at 40 °C. The liquid residue was extracted with chloroform and water, 3 times, with 10 mL respectively. The collected organic phases were dried over $MgSO_4$ and the solvent evaporated under vacuum. A colorless liquid was obtained. Yield: 0.78 g (26 %, 3.16 mmol).
^{1}H NMR (250 MHz, $CDCl_3$): 1.26 (t, 6H, P-O-CH_2-*CH_3*), 1.61 (m, 2H, P-CH_2-*CH_2*), 1.99 (m, 2H, P-CH_2-CH_2-*CH_2*), 3.98 (m, 4H, P-*CH_2*, P-O-*CH_2*), 6.91 (d, 2H, N-*CH*-*CH*-N), 7.43 (s, 1H, N-*CH*-N) ppm.
^{31}P NMR (250 MHz, $CDCl_3$): 30.21 ppm.
^{13}C NMR (250 MHz, $CDCl_3$): 16.3 (P-O-CH_2-*C*H_3), 21.1 (P-CH_2-*C*H_2), 24.4 (P-*C*H_2), 46.7 (N-*C*H_2), 61.7 (P-O-*C*H_2-CH_3), 118.7 (N-*C*H-CH-N), 129.5 (N-CH-*C*H-N), 137.1 (N-*C*H-N) ppm.

Synthesis of N-imidazolylpropylphosphonic acid
Under argon, in a 10 mL round bottom flask, 0.43 g (1,75 mmol) of dimethyl-N-imidazolpropylphosphonate were dissolved in 5 mL dry dichloromethane and stirred for 5 minutes. Afterwards 0.80 g (5.24 mmol) bromotrimethylsilane were added and stirred for 24 hours. Then the solvent was removed under reduced pressure and the brownish viscous liquid dissolved in 5 mL dry methanol. Afterwards the excessive methanol was removed under reduced pressure. A viscous brown liquid was obtained. Yield: 0.213 g (64 %, 1,12 mmol).
^{1}H NMR (250 MHz, D_2O): 1.58 (m, 2H, P-CH_2-*CH_2*), 1.98 (m, 2H, P-CH_2-CH_2-*CH_2*), 4.20 (t, 2H, P-*CH_2*), 7.38 (d, 2H, P-*CH_2*, N-*CH*-*CH*-N), 8.63 (s, 1H, N-*CH*-N) ppm.
^{31}P NMR (250 MHz, D_2O): 27.19 ppm.
^{13}C NMR (250 MHz, D_2O): 22.2 (P-CH_2-*C*H_2), 24.3 (P-*C*H_2), 49.4 (N-*C*H_2), 119.8 (N-*C*H-CH-N), 121.9 (N-CH-*C*H-N), 135.5 (N-*C*H-N) ppm.

Synthesis of titania nanoparticles[4]
10 mL (33.96 mmol) of Ti(O^iPr)$_4$ were dissolved in 25 mL dry ethanol. This mixture was added drop wise under vigorous stirring to 250 mL water, adjusted to a pH of 1.7 with 1 mL nitric acid (53 %). During the addition, the reaction mixture was cooled to 4 °C using an ice bath. After complete addition the ice bath was removed and the mixture stirred for 3 days at room temperature. Then, the solvent was removed under reduced pressure and the white crystalline product was dried in a desiccator over P_2O_5 under vacuum.

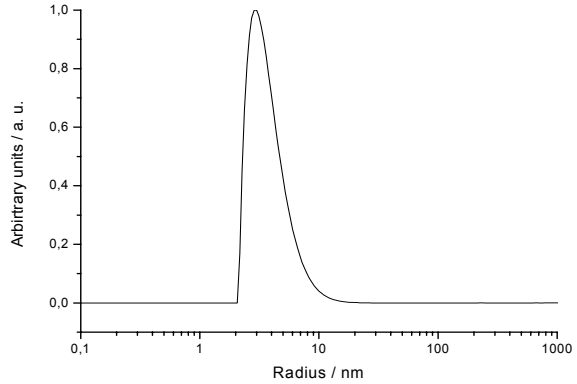

Fig. 1 ESI DLS size distribution of the titania nanoparticles.

Modification of TiO_2 nanoparticles with 3-chloropropylphosphonic acid
0.466 g (2.94 mmol) of 3-chloropropyl phosphonic acid was dissolved in 200 mL water. Afterwards 1 g of previously synthesized TiO_2 nanoparticles, dissolved in 100 mL water, was added. The white suspension was stirred at room temperature for 24 hours. The modified particles were isolated by centrifugation, washed several times with ethanol and water and finally dried in a desiccator over P_2O_5 under vacuum.

Preparation of silicon wafers
Silicon wafers with a native oxide layer are cut into small pieces (about 0.5x1 cm²), washed, and activated using UV/ozone treatment. These substrates are immersed into a 100 mmolar solution of N-(3-propyltrimethoxysilane) imidazole in ethanol for varying times. Cleaning of the samples is performed by sonicating at low power for 1 minute in dry isopropanol and subsequent blow-drying of the substrates.

Deposition of titania nanoparticles onto silica wafers
Deposition of the titania nanoparticles onto the N-(3-propyltrimethoxysilane) imidazole-modified silicon wafers is undertaken by immersion of the slides into a 0.01 mg/ml solution of titania nanoparticles capped with 3-chloropropylphosphonic acid in ethanol for 21 hours, followed by the same cleaning procedure used for the first step (sonication in isopropanol and blow-drying).

Multilayer deposition of titania nanoparticles on silica wafers
For the formation of multilayers on nanoparticles modified silica substrate the samples described above are repeatedly immersed into the linker, N-(3-propyltrimethoxysilane) imidazole or N-imidazolylpropyl phosphonic acid, and nanoparticle, 3-chloropropylphosphonic acid, solutions, respectively.

Results.

XPS spectrum of the titania nanoparticles modified with 3-chloropropylphosphonic acid ligands
The nanoparticles were deposited on a carbon pad and transferred into the spectrometer. As can be seen, the spectrum exhibits strong peaks for oxygen, titanium, chlorine and phosphor. A carbon peak is present but it is mainly caused by the remnant gas within the chamber, masking the signal of the hydrocarbon chain of the particle coating.

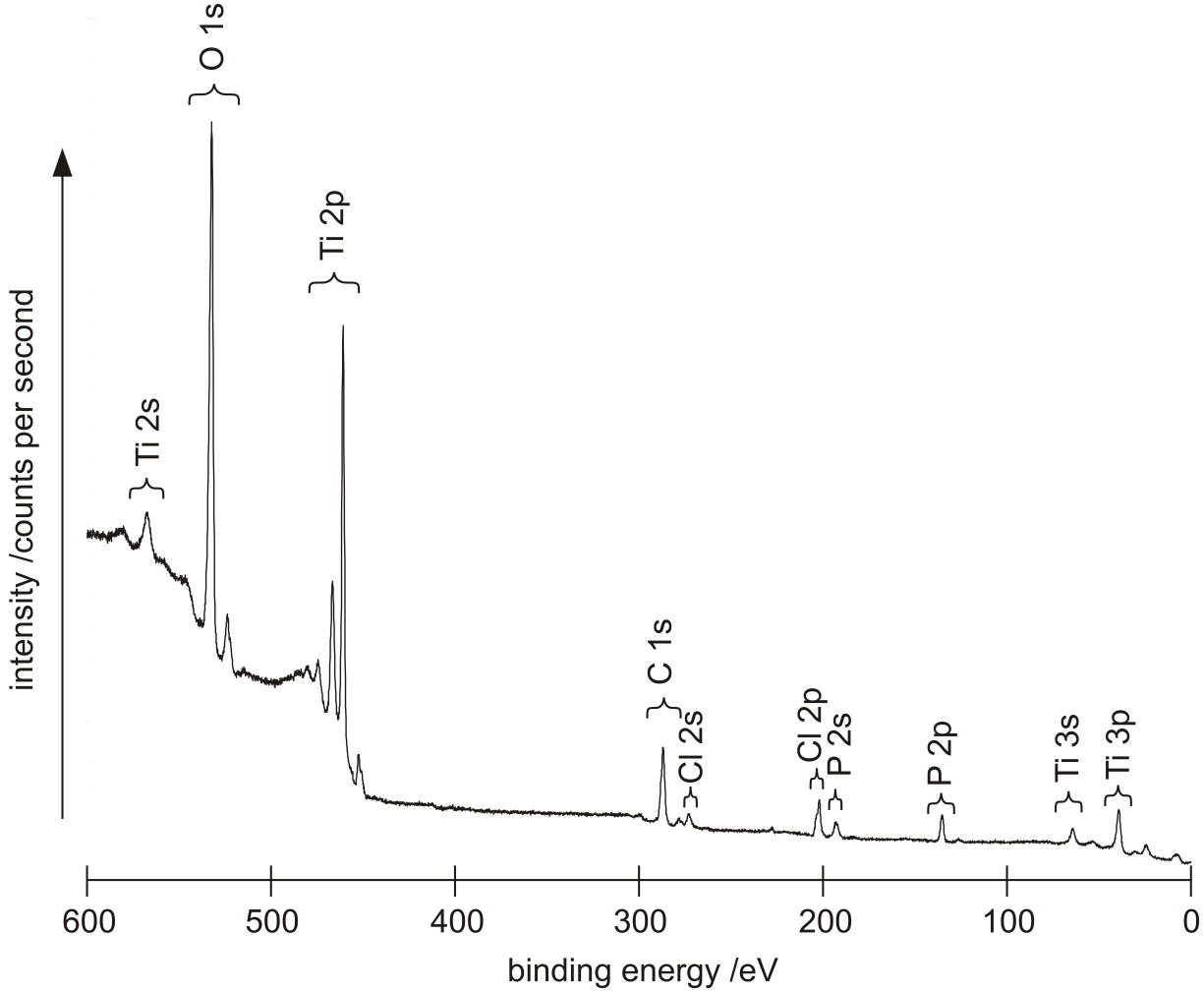

Fig. 2 ESI XPS spectrum for titania nanoparticles modified with 3-chloropropylphosphonic acid.

XPS spectrum of a nanoparticle monolayer

A silicon slide with thick native oxide was first coated with the trimethoxysilylpropyl imidazole linker. After sonication and blow-drying a layer of titania nanoparticles modified with 3-chloropropylphosphonic acid was deposited over night. The XPS spectrum shows the peaks that can be unambiguously attributed to the linker (nitrogen) and the modified nanoparticles (titanium, chlorine, and phosphor). The oxygen peak is very tall and dominated by the silicon oxide from the substrate, although a low energy shoulder is visible which is due to the Ti-O bond. The carbon peak is mainly due to the remnant gas in the analysis chamber. The high energy peaks in both the 2s and 2p silicon signal are related to the Si-O bond whilst the smaller peak at lower binding energies is probably due to the Si-C bond of the linker.

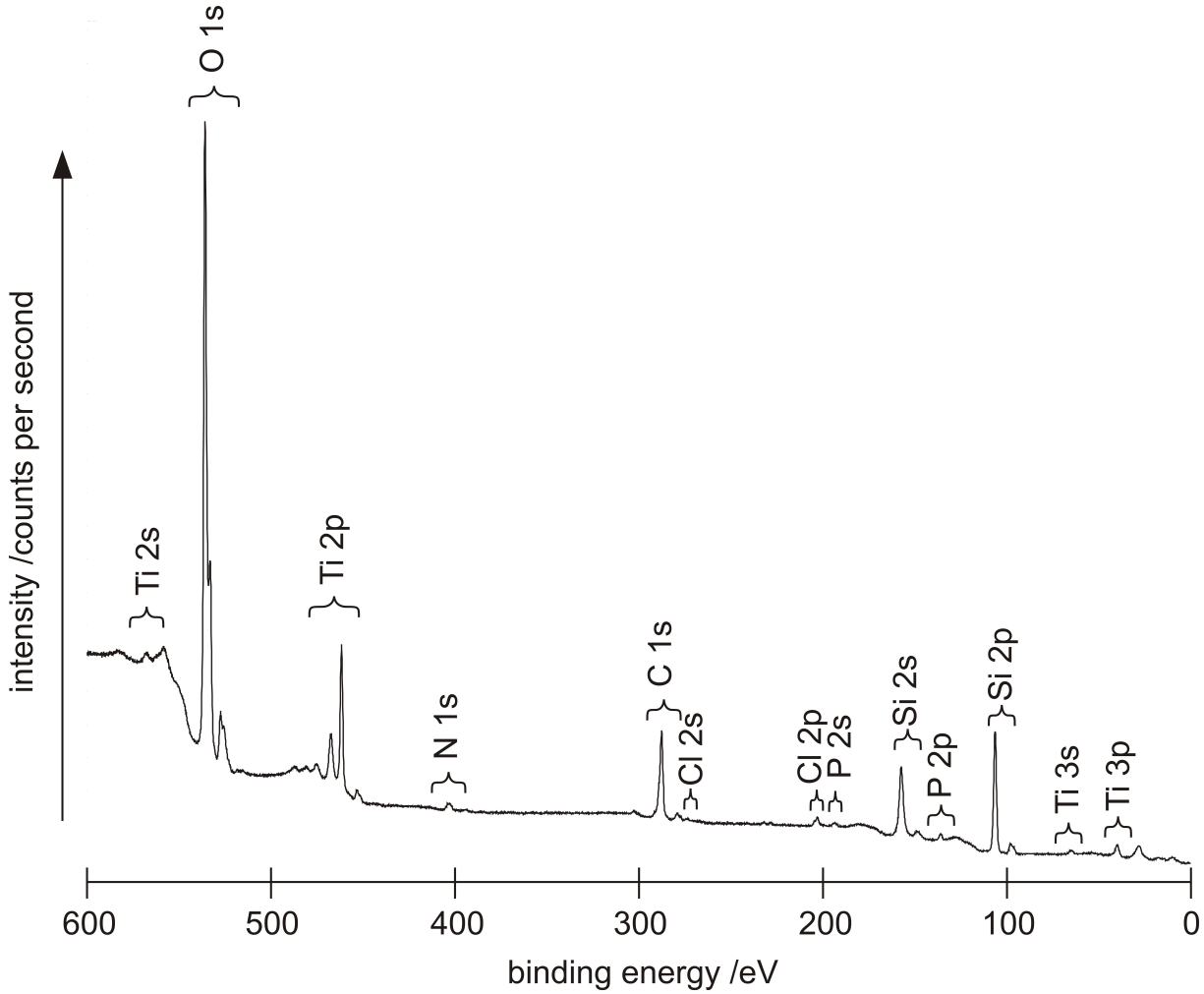

Fig. 3 ESI XPS spectrum for titania nanoparticles monolayer on a silicon support with thick oxide.

Photocatalytic degradation of the organic linker

A sample was irradiated for 100 min in a UV chamber (12 mW cm^{-2}). The spectral changes due to this treatment are depicted in Figure 4 (ESI). As can be seen, the chlorine peaks disappear completely and the nitrogen peak is greatly decreased. For carbon the high energy shoulder (285 eV) is removed. The phosphor peaks are shifted by 1 eV to higher energies. For oxygen, an increase at the higher energy peak at 531 eV occurred.

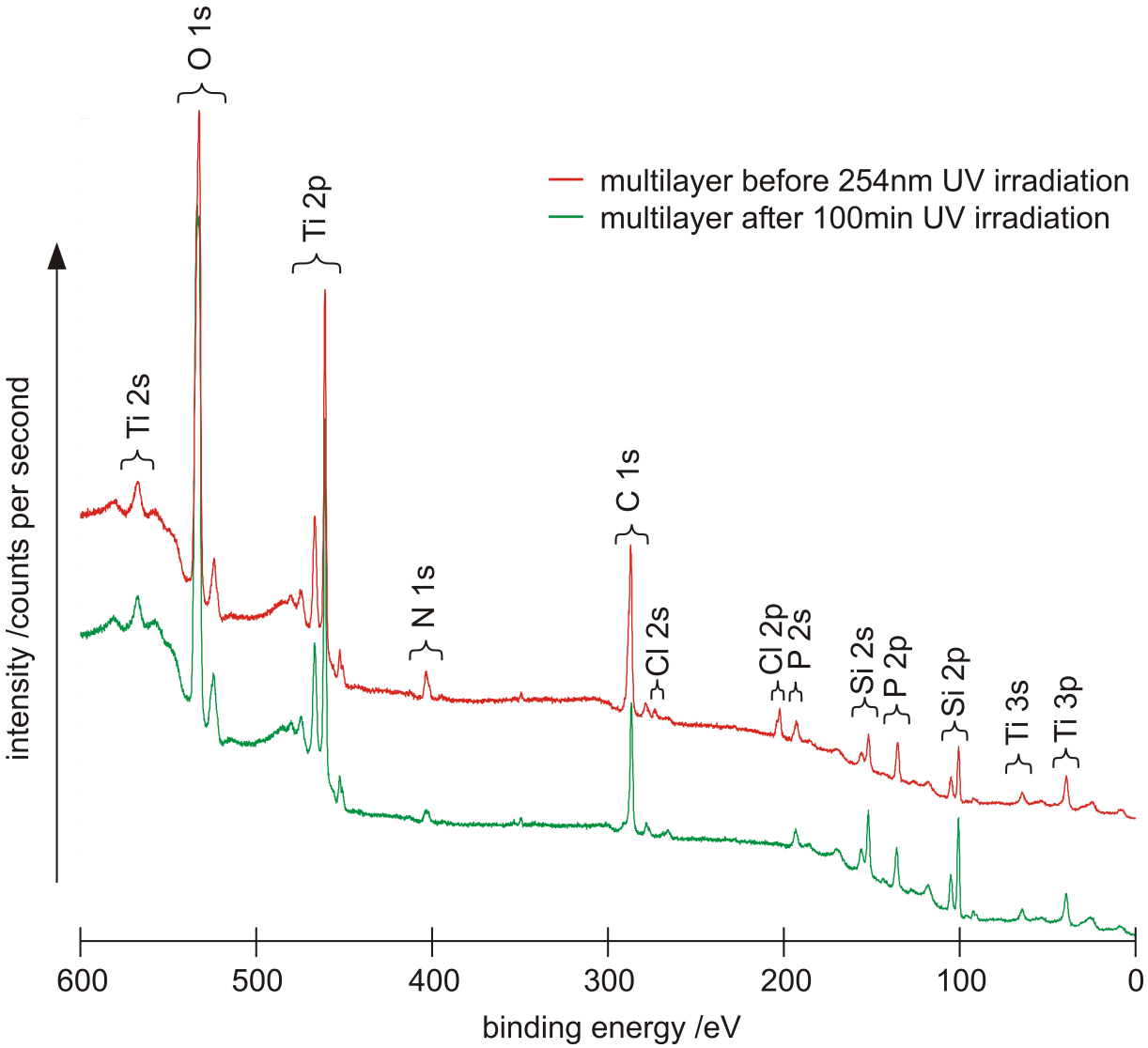

Fig. 4 ESI XPS spectra of a multilayer sample with phosphonic acid-based linkers between the particle layers. The spectra are off-set for clarity reasons.

References

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