Enhanced performance of surface-modified TiO₂ photocatalysts prepared via a visible-light photosynthetic route

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Supporting Information

Experimental details

Materials
TiO₂ powder (Hombikat UV 100, anatase, Sachtleben, Germany, specific surface area (BET) ~ 300 m²/g, crystallite size < 10 nm), benzene (J.T. Baker), 4-chlorophenol (Fluka), and barium sulfate (Sigma-Aldrich) were used as received.

Preparation of TiO₂-B-VIS

1 g of TiO₂ (Hombikat UV 100) was added to 20 ml of benzene in a borosilicate glass reactor and sonicated for 15 min at RT. Then the suspension was irradiated under visible light for 15 h by a 150 W Xenon lamp (LOT Oriel) equipped with a KG-3 (Schott) heat-absorbing filter and a cut-off filter λ > 455 nm (GG455, Schott). During the irradiation process the suspension was stirred magnetically and the powder turned slightly brownish. After irradiation the powder was filtered and dried at 80°C for 3h.

Photocatalytic activity tests

The degradation of 4-chlorophenol and diethyl phthalate was carried out in a cylindrical borosilicate glass reactor attached to an optical train. In the experiment, aqueous solution of the pollutant (25 mL, 2.5 × 10⁻⁴ M) and photocatalyst (25 mg, i.e. 1.0 g/l) were added to the glass reactor. The resulting suspension was sonicated for 5 min and then irradiated under visible light for 3 h by a 150 W Xenon lamp (LOT Oriel) equipped with a KG-3 (Schott) heat-absorbing filter (UV + VIS irradiation, λ > 320 nm) and a corresponding cut-off filter: GG455 (Schott) cut-off filter for VIS-only irradiation (λ > 455 nm); short-wave-pass filter 400FL07 (Schott) for UV-only irradiation (λ < 400 nm). The suspension was stirred magnetically.

Samples were taken at regular intervals, collected in the dark, and – after finishing the degradation experiment – filtered through a micropore filter (Sartorius, 0.20µm) and analyzed by UV-Vis spectroscopy (Cary 50 spectrometer).

Standard deviation (σ) was calculated from more than three degradation experiments. The error bars were constructed using 2σ values (confidence interval of ~95%).

Diffuse reflectance spectroscopy

UV-Vis diffuse reflectance spectra were recorded on samples diluted in BaSO₄ using a Harrick praying mantis diffuse reflectance accessory mounted in a Perkin Elmer Lambda 650 UV–Vis spectrophotometer. 25 mg of each photocatalyst powder was well ground with 0.5 g of BaSO₄ and spread onto the sampling plate prior to the measurement. The background reflectance of BaSO₄ (reference) was measured before. The Kubelka-Munk function \( F(R_s) = \frac{(1-R_s)^2}{2R_s} \), where \( R_s \) is diffuse reflectance of the sample relative to the reflectance of a standard according to the Kubelka-Munk theory.

Photocurrent measurements

For the preparation of the photoelectrode, a suspension containing 200 mg of TiO₂ in 1 ml of ethanol was sonicated for 15 minutes and then smeared onto the ITO glass by doctor blading using a scotch tape as frame and spacer. The electrode was then dried at 100 °C, pressed for 3 minutes at a pressure of 200 kg/cm², and
heated in air at 450 °C for 30 minutes in order to sinter the particles and ensure good electrical contact. The photoelectrochemical setup consisted of a Gamry 600 Reference potentiostat and a three-electrode cell using a platinum counter electrode and an Ag/AgCl reference electrode. The photoelectrodes were pressed against an O-ring of the cell leaving an irradiated area of 0.5 cm2. The electrodes were irradiated from the backside (through the ITO glass) by a 150 W Xenon lamp (LOT Oriel) equipped with a KG-3 (Schott) heat-absorbing filter a cut-off filter $\lambda > 455$ nm (GG455, Schott).

**XPS measurements**

XPS was performed in a UHV set-up equipped with a Gammadata-Scienta SES 2002 analyzer. The base pressure in the measurement chamber was $5 \times 10^{-10}$ mbar. Monochromatic Al Kα (1486.6 eV; 13.5 kV; 37 mA) was used as incident radiation. High resolution region spectra were measured with a pass energy of 200 eV resulting in an effective instrument resolution higher than 0.6 eV. Charging effects were compensated using a flood gun, and binding energies were calibrated based on positioning the main C 1s peak at 285 eV. Measured data were fitted using Shirley-type backgrounds and a combination of Gaussian-Lorentzian functions with the CasaXPS software. Atomic concentration ratios were obtained by determining the integral area of the Gaussian-Lorentzian functions and correcting the values by the specific atomic sensitivity factors proposed by Wagner [S1].

**Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)**

Infrared spectra of the powdered samples were measured in diffuse reflectance using a Thermo Nicolet Protégé 460 spectrometer. The samples were diluted with KBr (sample-to-KBr ratio = 1:100), thoroughly ground in a mortar and placed inside a Harrick HVC-DRP-2 *in situ* cell with a Praying Mantis mirror construction. The samples were measured against a KBr background in dry synthetic air without further pretreatment. 500 scans were averaged for each spectrum.

**Zeta potential measurements**

The zeta potential pH-titrations of photocatalyst suspensions were carried out using a Zetasizer Nano ZS equipped with He–Ne Laser (633 nm) at 25 °C connected with MPT-2 autotitrator (Malvern). Measurements were performed in range of 2.5 to 11 pH-values at temperature 25 °C by sequential addition of 0.1 M HCl (1 pH Unit/step, in 10 steps). The samples were dispersed in HPLC grade water and then placed into the ultrasonic bath for 5 minutes. For the data analysis, the viscosity and refractive index of pure dispersant at 25 °C were used. The refractive index of samples was assumed to be 2.400.

**Quasi-Fermi level measurements**

For heavily doped n-type metal oxides like TiO$_2$, the lower conduction band edge, $E_C$, practically merges with the quasi-Fermi level for electrons, $^*E_{Fn}$, ($|E_C – ^*E_{Fn}| < 0.1$ V). The values of $^*E_{Fn}$ were determined by the method of Roy [S2,3]. In short, we recorded the pH dependence of the potential of a Pt electrode immersed in an irradiated (LOT Oriel 150 W Xenon arc lamp; KG3 filter) suspension of a semiconductor in the presence of an electron acceptor with pH-independent reduction potential (MV$^{2+}$; methyl viologen; 1,1'-dimethyl-4,4'-bipyridinium dichloride; $E_{MV^{2+/+}} = -0.45$ V vs. NHE). The inflection point (pH$_0$) of the potential-pH curve (Fig. S4) determines the pH value at which $^*E_{Fn}$ coincides with $E_{MV^{2+/+}}$. Assuming Nernstian shift of band edges the values of $^*E_{Fn}$ at pH = 7 can be then obtained from equation: $^*E_{Fn} = E_{MV^{2+/+}} + 0.059$ (pH$_0$ – 7).

**References:**


Figure S1. High-resolution C1s XP spectra of pristine TiO2 and TiO2-B-VIS. For comparison, an XP spectrum of TiO2 modified in benzene under UV light (λ > 320 nm) irradiation (2 hours) is shown (TiO2-B-UV).

Figure S2. Diffuse reflectance infrared spectra of the TiO2 and TiO2-B-VIS. Spectra were obtained from an average of 500 scans and converted into log(1/R). The inset shows a difference spectrum in which the spectrum of the TiO2 support has been subtracted from the TiO2-B-VIS sample spectrum to show more clearly the vibration bands originating from the carbonaceous deposits.
**Figure S3.** 4-CP concentration changes in suspensions of TiO$_2$ and TiO$_2$-B-VIS stirred in the dark.

**Figure S4.** pH dependence of the potential of a Pt electrode immersed in an irradiated suspension of pristine TiO$_2$ and TiO$_2$-B-VIS in the presence of (MV)Cl$_2$. $E_{\text{pH}} = E_{\text{MV}^{2+/+}} + 0.059 \ (\text{pH}_0 - 7)$: –0.58 V vs. NHE (TiO$_2$); –0.57 V vs. NHE (TiO$_2$-B-VIS)
**Figure S5.** Photocatalytic degradation of 4-CP at TiO$_2$-B-VIS under visible light irradiation ($\lambda > 455$ nm) without and with addition of different scavengers.

**Figure S6.** Photocatalytic degradation of diethyl phthalate at pristine TiO$_2$ and TiO$_2$-B-VIS under visible light irradiation ($\lambda > 455$ nm).