Enhanced performance of surface-modified TiO_2 photocatalysts prepared *via* a visible-light photosynthetic route

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Supporting Information

Experimental details

Materials

TiO_2 powder (Hombikat UV 100, anatase, Sachtleben, Germany, specific surface area (BET) ~ 300 m^2/g, crystallite size < 10 nm), benzene (J.T. Baker), 4-chlorophenol (Fluka), and barium sulfate (Sigma-Aldrich) were used as received.

Preparation of TiO_2-B-VIS

1 g of TiO_2 (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 $\lambda > 455$ 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, $\lambda > 320$ nm) and a corresponding cut-off filter: GG455 (Schott) cut-off filter for VIS-only irradiation ($\lambda > 455$ nm); short-wave-pass filter 400FL07 (Schott) for UV-only irradiation ($\lambda < 400$ 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 (Sarstedt, 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 $BaSO_4$ 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 $BaSO_4$ and spread onto the sampling plate prior to the measurement. The background reflectance of $BaSO_4$ (reference) was measured before. The Kubelka-Munk function $F(R_\infty)$ was calculated as $F(R_\infty) = (1- R_\infty)^2/2R_\infty$, where R_∞ 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 a 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 5×10^{-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, ${}^{*}E_{\mathrm{Fn}}$, ($|E_{\mathrm{C}} - {}^{*}E_{\mathrm{Fn}}| < 0.1$ V). The values of ${}^{*}E_{\mathrm{Fn}}$ 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; $E_{\mathrm{MV}^{2+/+\bullet}} = -0.45$ V vs. NHE). The inflection point (pH_0) of the potential-pH curve (Fig. S4) determines the pH value at which ${}^{*}E_{\mathrm{Fn}}$ coincides with $E_{\mathrm{MV}^{2+/+\bullet}}$. Assuming Nernstian shift of band edges the values of ${}^{*}E_{\mathrm{Fn}}$ at pH = 7 can be then obtained from equation: ${}^{*}E_{\mathrm{Fn}} = E_{\mathrm{MV}^{2+/+\bullet}} + 0.059\,(pH_0 - 7)$.

References:

S1. Moulder, J. F.; Chastain, J. Handbook of X-ray photoelectron spectroscopy; Perkin-Elmer Corporation: Eden Prairie, Minn, 1992.

S2. A. M. Roy, G. C. De, N. Sasmal and S. S. Bhattacharyya, *Int. J. Hydrogen Energy*, 1995, **20**, 627-630.

S3. R. Beranek, *Adv. Phys. Chem.*, 2011, DOI:10.1155/2011/786759.

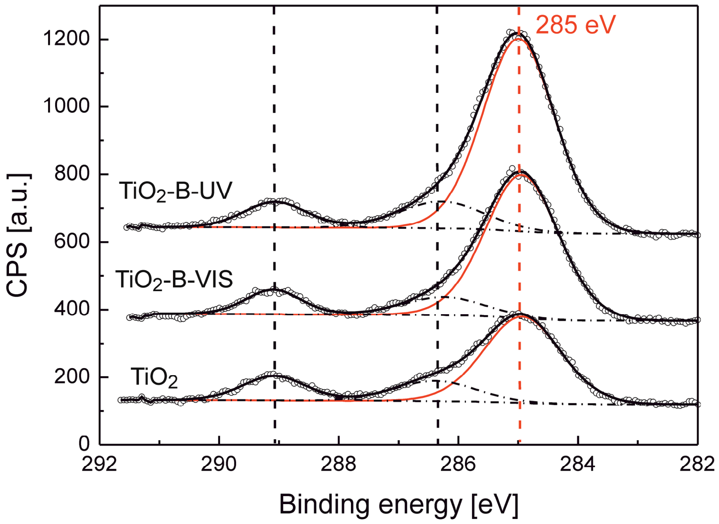

Figure S1. High-resolution C1s XP spectra of pristine TiO_2 and TiO_2-B-VIS. For comparison, an XP spectrum of TiO_2 modified in benzene under UV light ($\lambda > 320$ nm) irradiation (2 hours) is shown (TiO_2-B-UV).

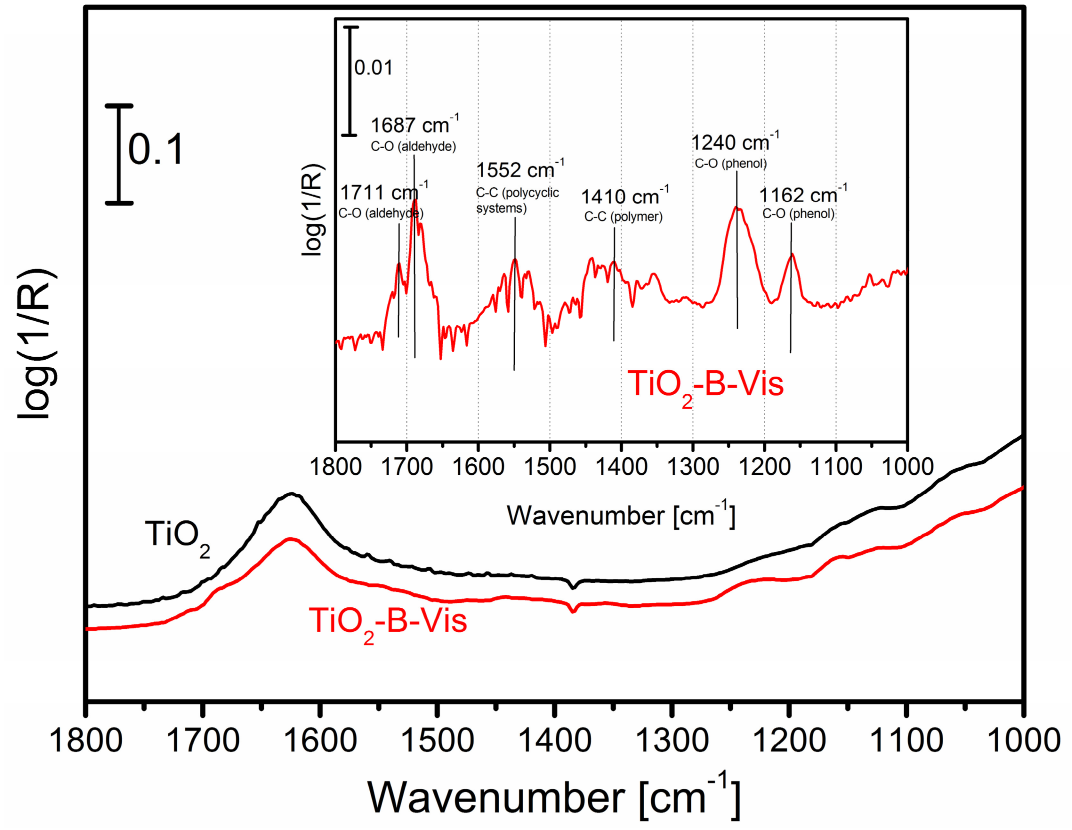

Figure S2. Diffuse reflectance infrared spectra of the TiO_2 and TiO_2-B-VIS. Spectra were obtained from an average of 500 scans and converted into log(1/R). The inset shows a difference spectrum in which the spectrum of the TiO_2 support has been subtracted from the TiO_2-B-VIS sample spectrum to show more clearly the vibration bands originating from the carbonaceous deposits.

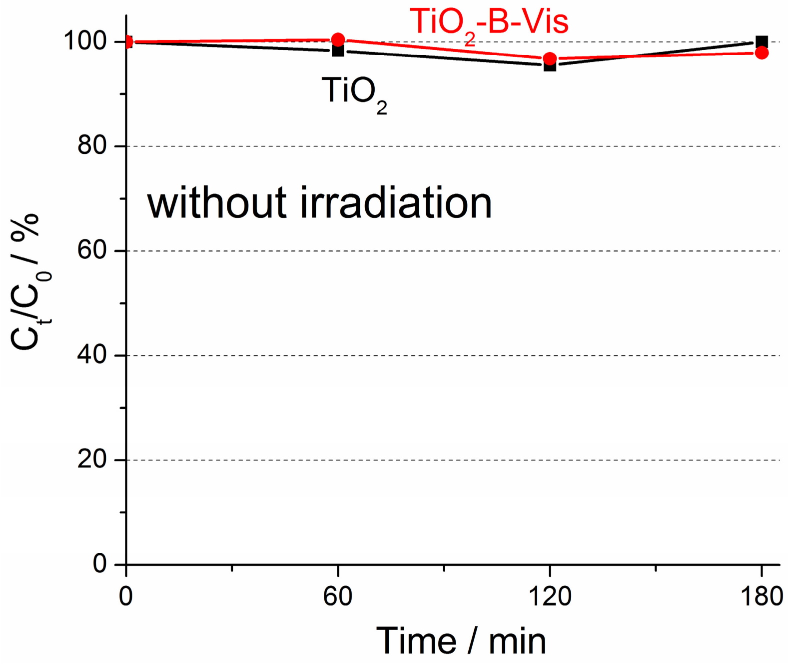

Figure S3. 4-CP concentration changes in suspensions of TiO_2 and TiO_2-B-VIS stirred in the dark.

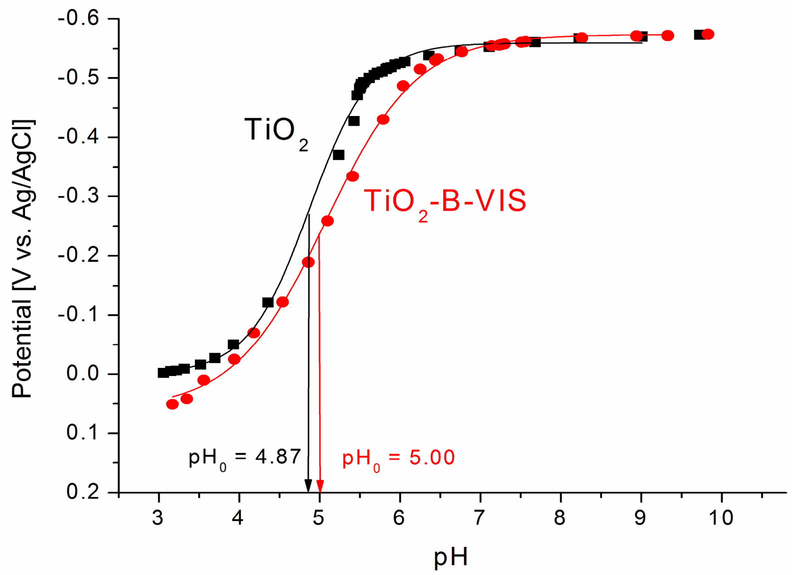

Figure S4. pH dependence of the potential of a Pt electrode immersed in an irradiated suspension of pristine TiO_2 and TiO_2-B-VIS in the presence of $(MV)Cl_2$. $^{*}E_{Fn} = E_{MV^{2+/+\cdot}} + 0.059\ (pH_0 - 7)$: –0.58 V vs. NHE ($TiO_2$); –0.57 V vs. NHE ($TiO_2$-B-VIS)

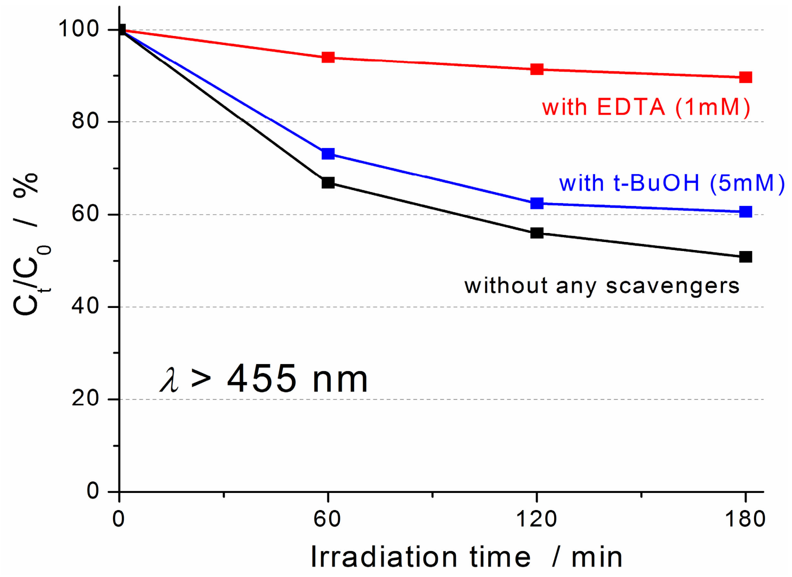

Figure S5. Photocatalytic degradation of 4-CP at TiO_2-B-VIS under visible light irradiation (λ > 455 nm) without and with addition of different scavengers.

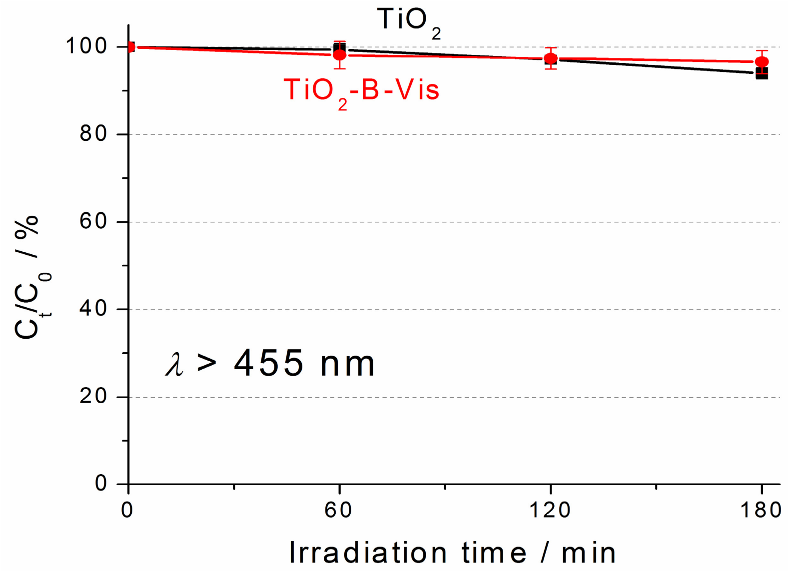

Figure S6. Photocatalytic degradation of diethyl phthalate at pristine TiO_2 and TiO_2-B-VIS under visible light irradiation (λ > 455 nm).