Visible-light photocurrent response of TiO_2–polyheptazine hybrids: evidence for interfacial charge-transfer absorption

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Electronic Supplementary Information

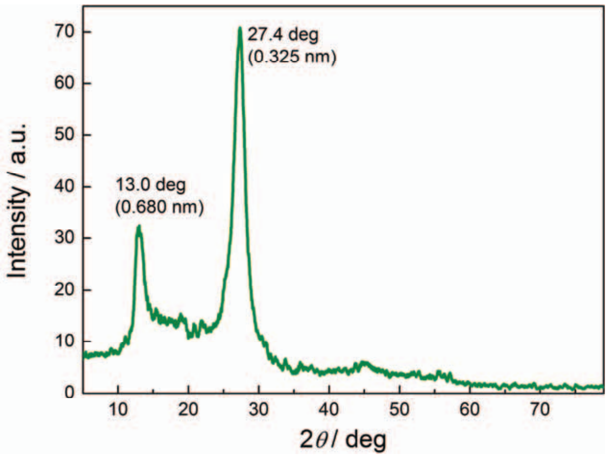

Figure S1: XRD spectrum of polyheptazine. The spectrum was smoothed by adjacent averaging over 20 points. The peak at 27.4 deg corresponds to the out-of-plane stacking distance (0.325 nm) between polyheptazine sheets. The peak at 13.0 deg is an in-plane feature and might correspond to the largest distance C–N in the "pore" of a polyheptazine sheet 6.71-6.81 Å)

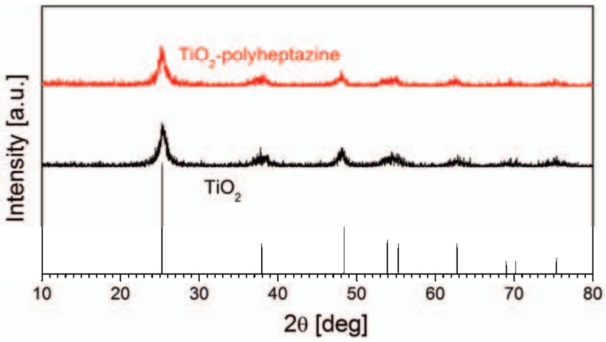

Figure S2: XRD spectra of TiO_2 (Hombikat UV 100) and TiO_2-polyheptazine hybrid. Spectra are off-set for clarity. Vertical lines show a literature pattern of anatase (ASTM file card No. 01-0562)

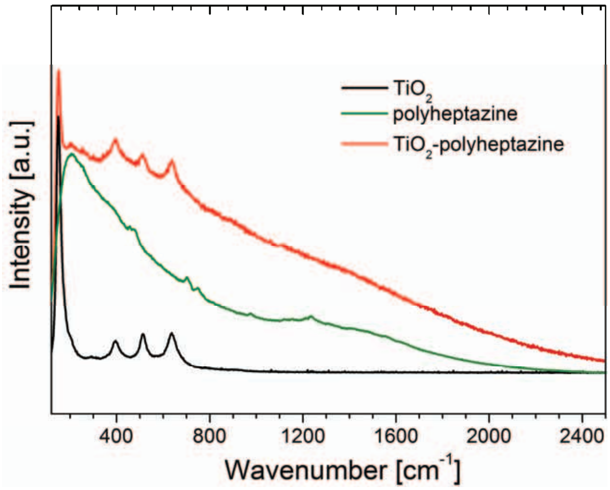

Figure S3: Raman spectra of TiO_2, polyheptazine, and TiO_2-polyheptazine hybrid. For excitation a low energy (785 nm) laser had to be used in order to avoid the photoluminescence of polyheptazine. The measurements were carried out in back scattering geometry by using the 785 nm line of laser-diode with a power density on the samples of about 0.1 W/cm^2. Spectra were collected in air and at room temperature with a triple spectrometer Jobin-Yvon Dilor integrated system with a spectral resolution of about 1 cm^{-1}. Spectra have been recorded in the Stokes region by a 1200 grooves/mm grating monochromator and a CCD detector system (Spectrum-one).

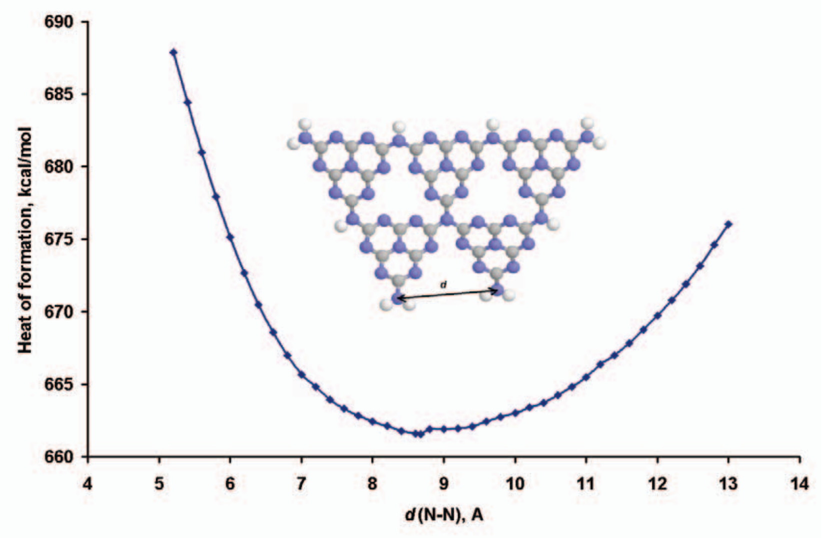

Figure S4: The influence of PH5 cluster deformation on the enthalpy of formation.

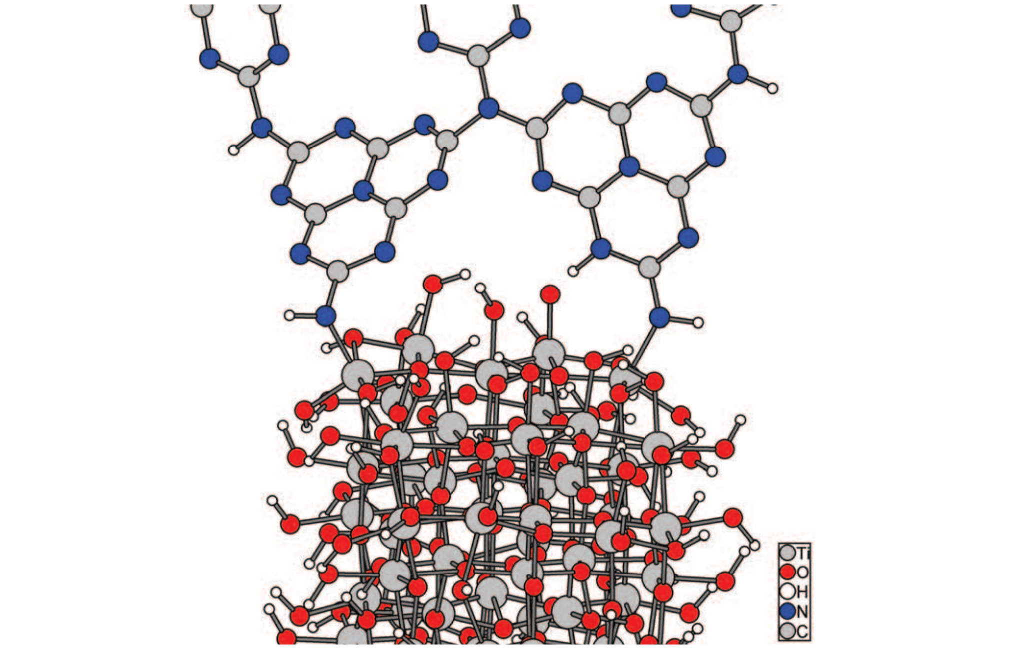

Figure S5: Ti54M1-H-amide system (derived from Ti54M1-amide, with surface hydroxyl proton spontaneously transferred to alpha-position of heptazine).

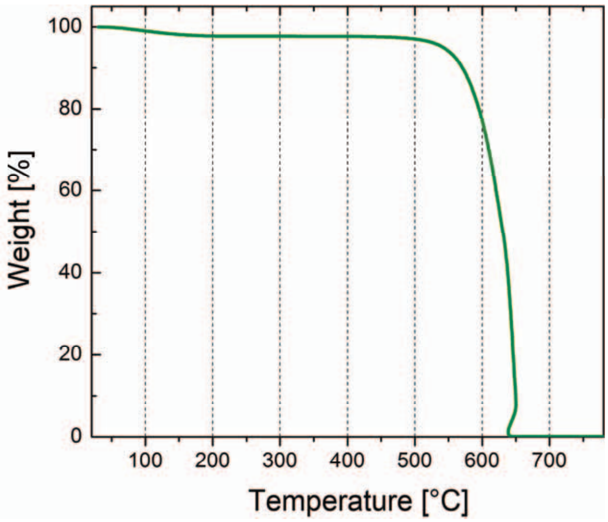

Figure S6: TGA thermogram of polyheptazine. Thermal analysis was performed using a TG-DTA Instrument (SDT 2960, TA Instruments) under air in the temperature range of 24–900 °C and a heating rate of 10 °C/min.

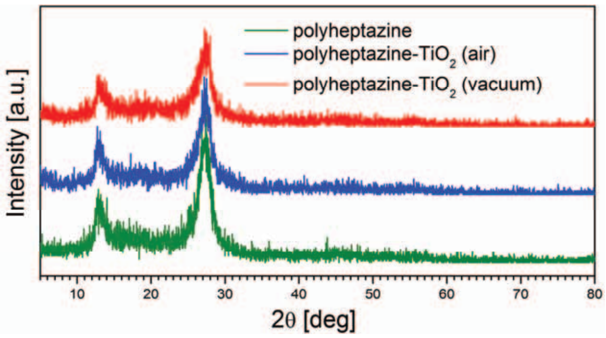

Figure S7: XRD spectra of polyheptazine, polyheptazine impregnated by TiO_2 after heating in air at 450 °C, and after additional heat treatment under vacuum (0.2 mbar) at 500 °C. Spectra are off-set for clarity.

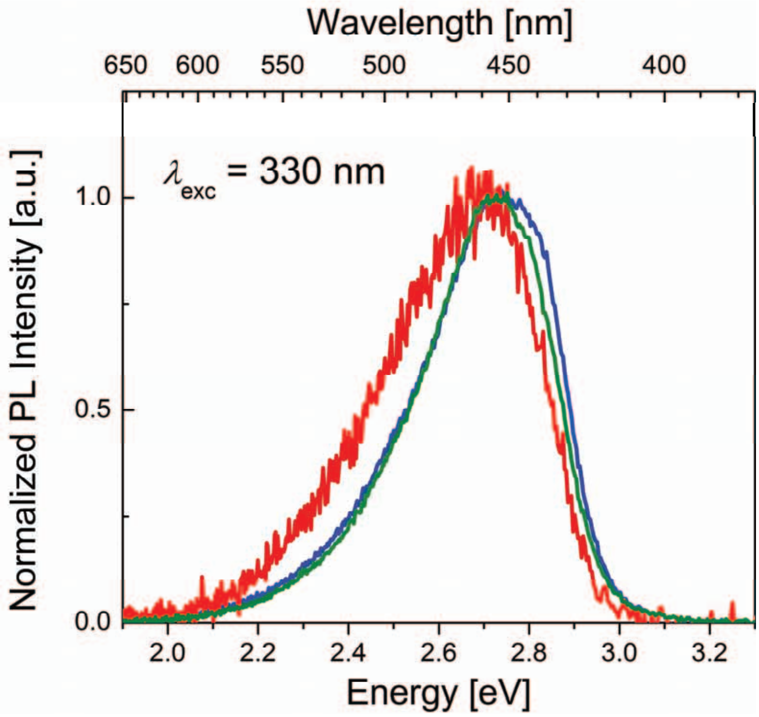

Figure S8: Normalized PL spectra of polyheptazine (*green*), polyheptazine impregnated by TiO_2 after heating in air at 450 °C (*blue*), and after additional heat treatment under vacuum (0.2 mbar) at 500 °C (*red*).

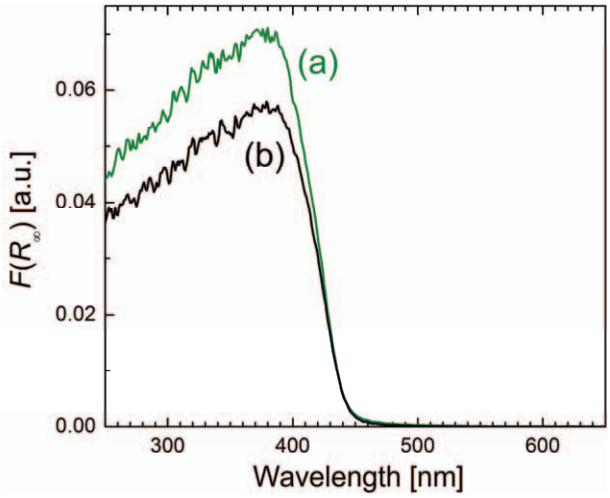

Figure S9: Absorption spectra (Kubelka-Munk function) of polyheptazine before (a) and after (b) heat treatment under vacuum at 500 °C for 1 hour.

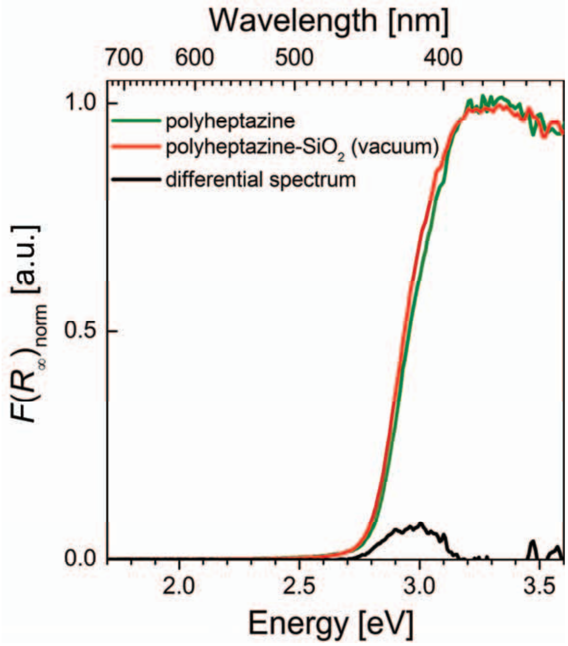

Figure S10: Normalized absorption spectra (Kubelka-Munk function) of polyheptazine (green) and polyheptazine impregnated with SiO_2 (heated under vacuum at 500 °C) for 1 hour.

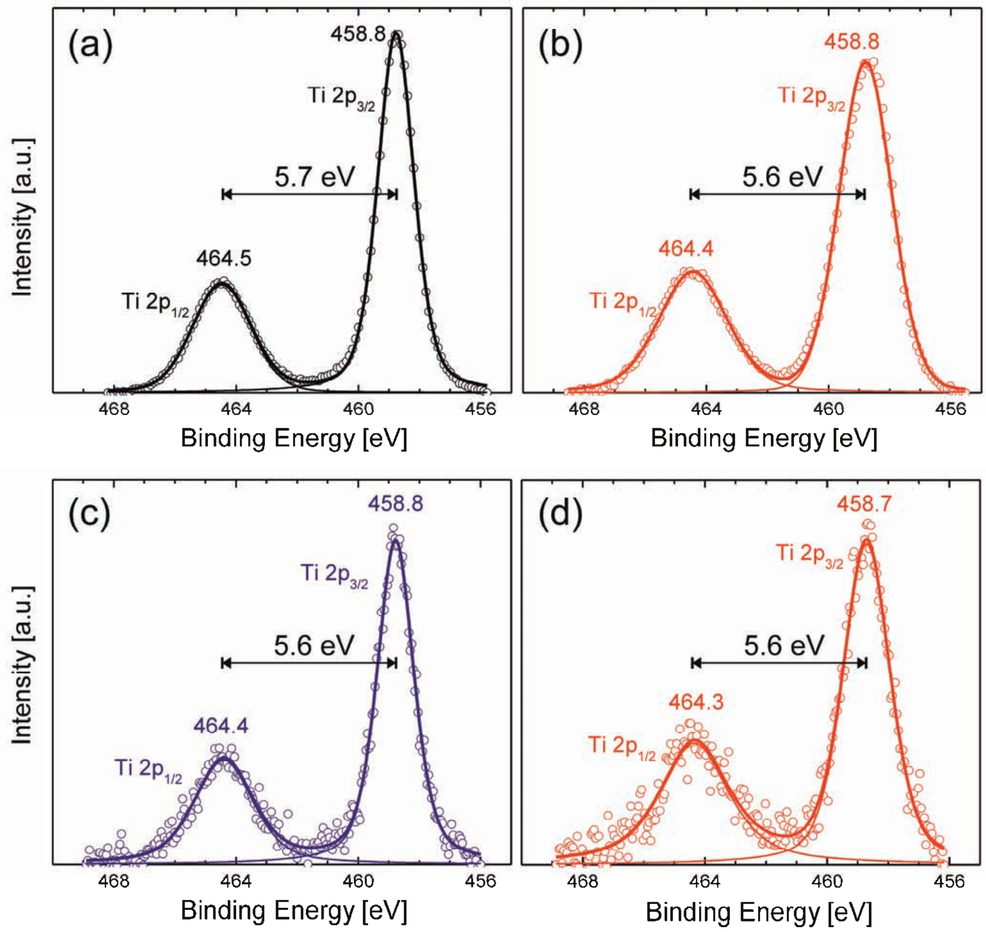

Figure S11: High-resolution Ti 2*p* XPS of pristine TiO_2 Hombikat UV 100 (a); TiO_2-polyheptazine hybrid (b); polyheptazine impregnated with TiO_2 after heating in air at 450 °C (c), and after additional heat treatment under vacuum (0.2 mbar) at 500 °C (d). The spectra are referenced to O 1s peak of TiO_2 at 530.0 eV. The spectra were taken with a PHI 5600 XPS (a, b) and a VG ESCALAB 220 IXL spectrometer with non-monochromatised AlKα radiation (hν=1486.6 eV). Fitting of the XPS data was accomplished using XPSPEAK41 software. A Shirley-type background subtraction was used.

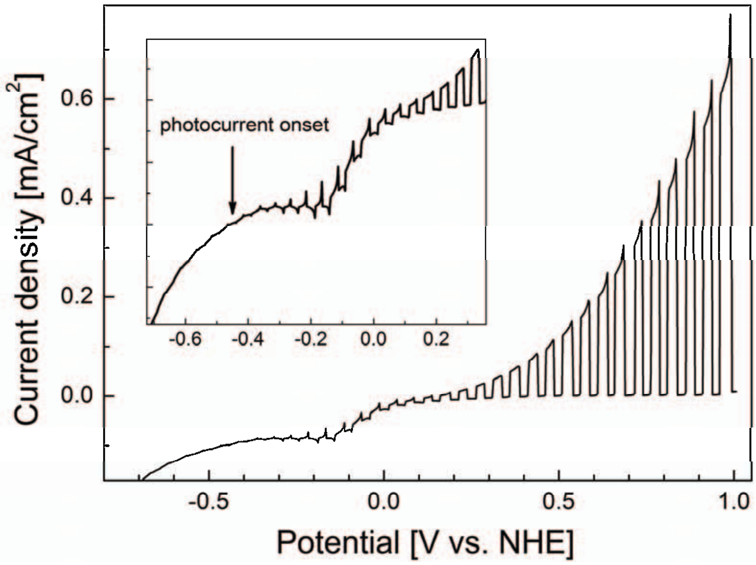

Figure S12: Photocurrent response of a TiO_2-polyheptazine hybrid electrode during a cathodic potential scan (scan rate 5 mV/s) measured under intermittent visible light (λ > 400 nm) irradiation from a 150 W Xenon lamp in a phosphate buffer (pH 7). The inset shows the zoomed low-potential range. The photocurrent onset potential is at ca. –0.45 V vs. NHE.