Supplementary material

Effects of copper and vanadium deposition in multi-walled hydrogen trititanate and mixed-phase anatase/trititanate nanotubes

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Catalytic performance H-TNT-V-C623

a) UV-light irradiation

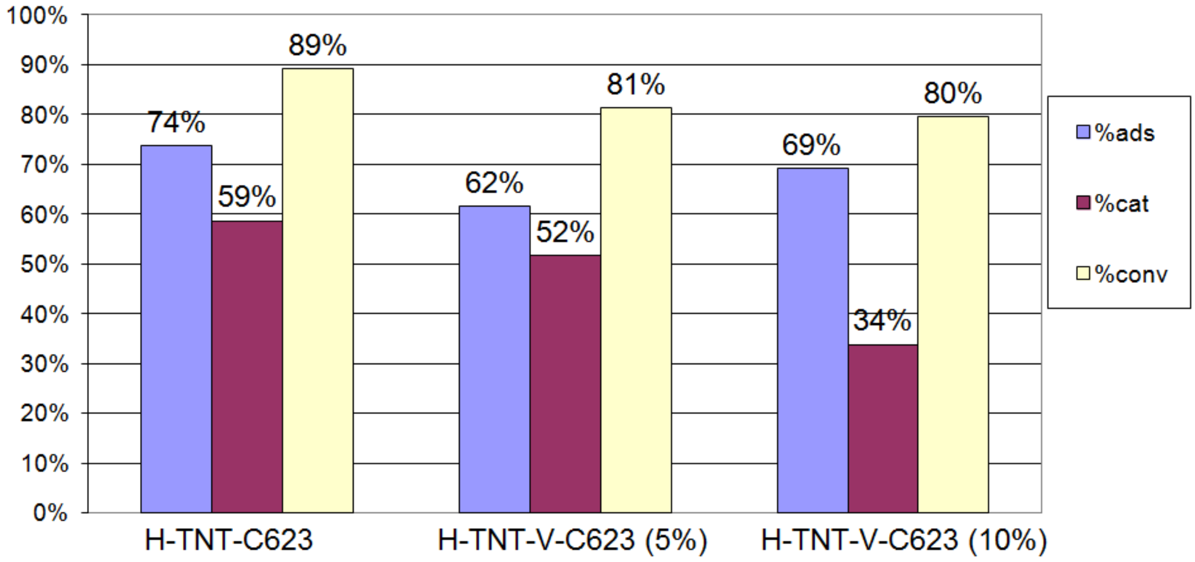

Figure S1. Comparison of the UV photocatalytic degradation of rhodamine 6G of the control mixed-phase anatase/trititanate samle (H-TNT-C623) and H-TNT-V-C623 samples with initial VO(acac)$_2$ loading of 5% and 10%. Blue represents the initial adsorption of rhodamine 6G after contacting rhodamine with the trititanate samples for 30 minutes in dark measured by evaluating the UV/visible absorption spectrum of the supernatant rhodamine 6G solution. Purple represents the subsequent photocatalytic reduction of the remaining R6G in solution. In light yellow the overall reduction of the R6G in solution (adsorption + photodegradation) is given. The vanadium-doped trititanate samples perform less well compared to the H-TNT-C623 sample.

b) **Visible light illumination**

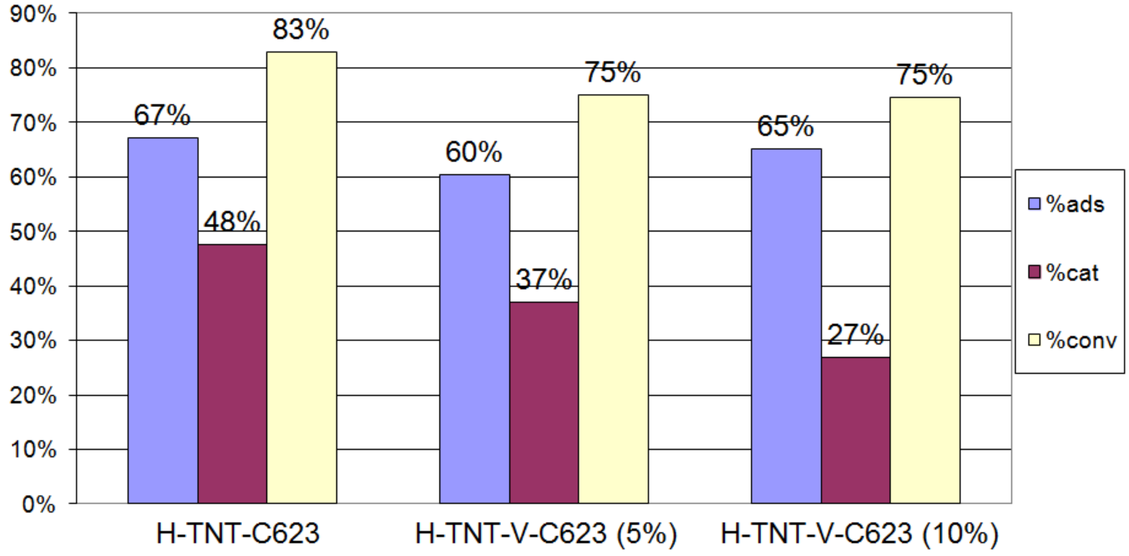

Figure S2. Comparison of the visible light photocatalytic degradation of rhodamine 6G of the control mixed-phase anatase/trititanate sample (H-TNT-C623) and H-TNT-V-C623 samples with initial $VO(acac)_2$ loading of 5% and 10%. Color code is as in Figure S1. Again, the vanadium-doped trititanate samples perform less well compared to the H-TNT-C623 sample.

EPR experiments monitoring visible light illumination of H-TNT-V and H-TNT-V-C623

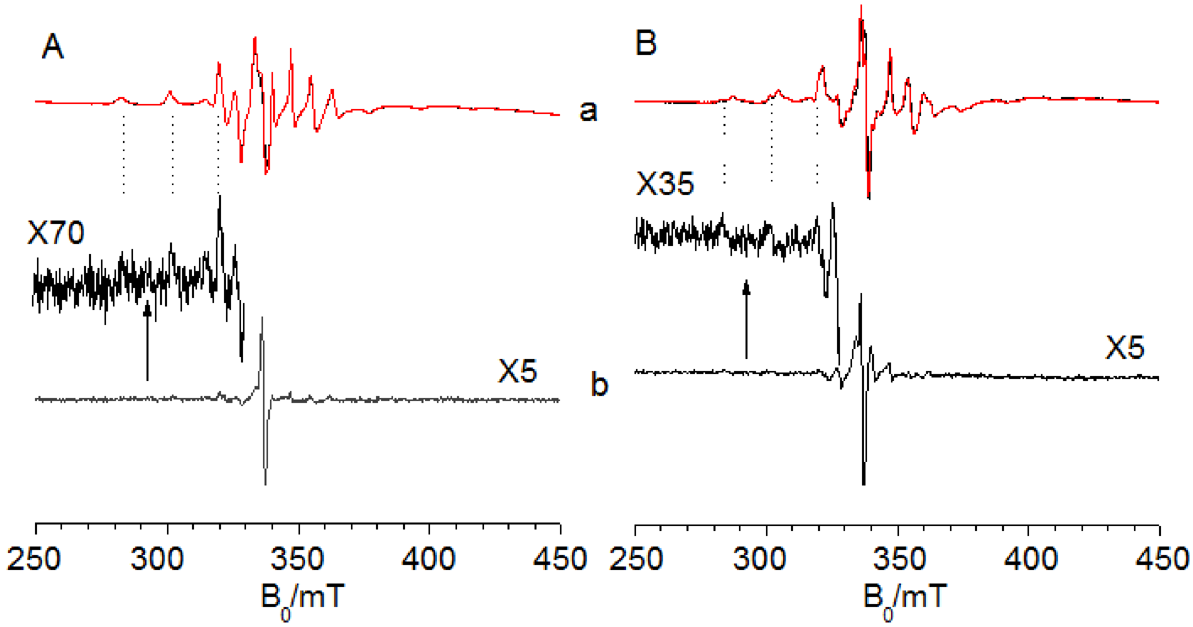

Figure S3. Light-induced EPR experiments on (A) H-TNT-V (10% VO(acac)$_2$ loading) and (B) H-TNT-V-C623 (with initial VO(acac)$_2$ loading of 10%). Illumination was done with the 406.7 nm laser line. (a) EPR spectrum before (black) and after 50 minutes light illumination (red), (b) difference spectrum. The light-induced signal is much weaker than in the case of UV illumination (see Figure 5). It consists of a weak contribution of species 2 and a signal due to a strong contribution of an F^+ center.

Catalytic performance H-TNT-Cu-C623

a) UV-light irradiation

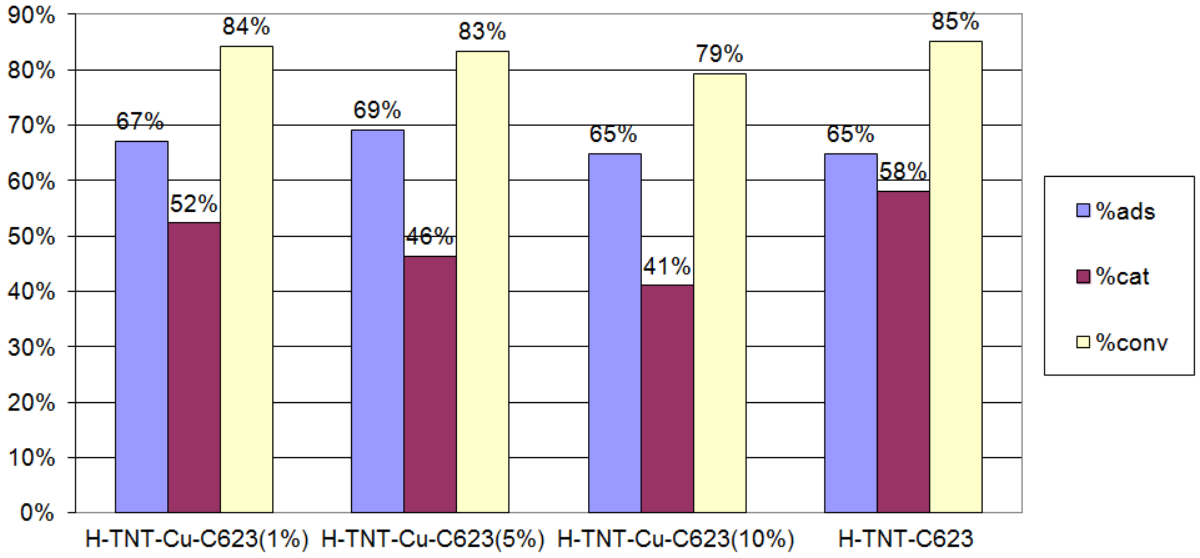

Figure S4. Comparison of the UV photocatalytic degradation of rhodamine 6G of the control mixed-phase anatase/trititanate samle (H-TNT-C623) and H-TNT-Cu-C623 samples with initial Cu(acac)$_2$ loading of 1%, 5% and 10%. The color code is as in Figures S1 and S2. The copper-doped trititanate samples perform comparable well to slight less in comparison to the controle H-TNT-C623 sample.

b) Visible light irradiation

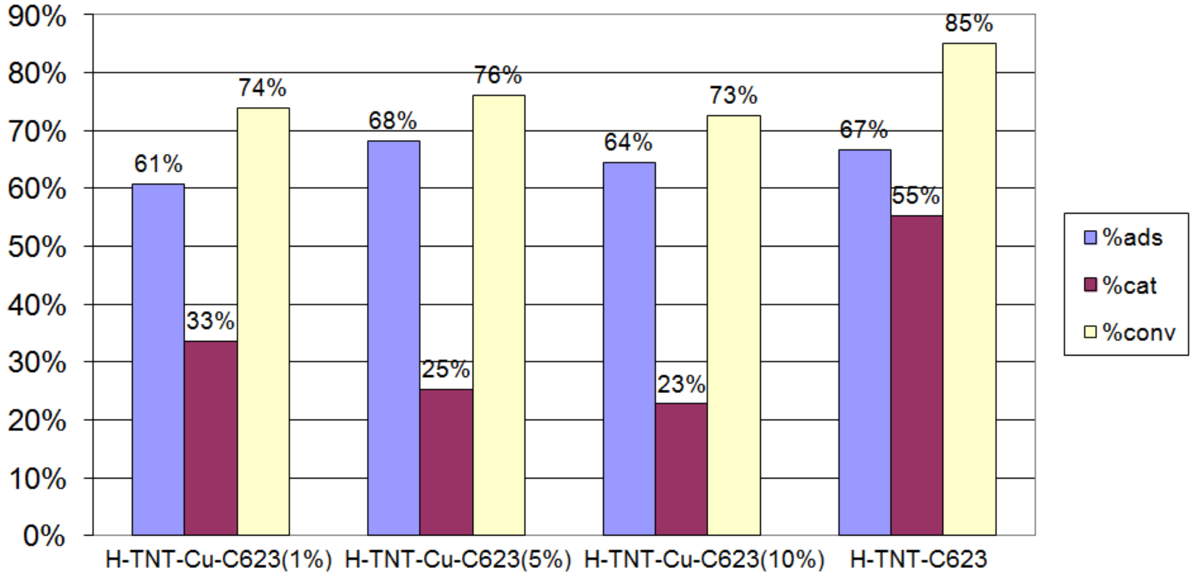

Figure S5. Comparison of the visible photocatalytic degradation of rhodamine 6G of the control mixed-phase anatase/trititanate sample (H-TNT-C623) and H-TNT-Cu-C623 samples with initial Cu(acac)$_2$ loading of 1%, 5% and 10%. Color code is as in Figure S1. Again, the copper-doped trititanate samples perform less well compared to the H-TNT-C623 sample.

Enlargement Figure 6a

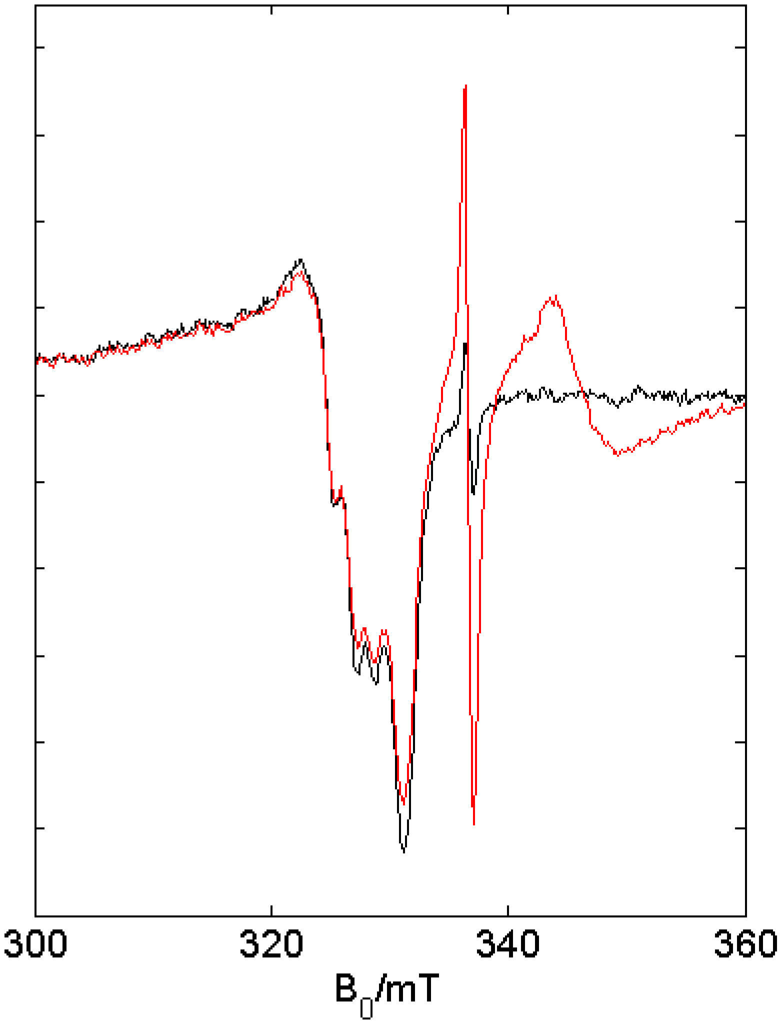

Figure S6. Enlargement of region of Figure 6a in order to highlight change in Cu(II) EPR signal.

FTIR – PAS measurements

FTIR-PAS (photoacoustic Fourier transform infrared) spectra were recorded on a Nicolet 20 SX spectrometer, equipped with a McClelland photoacoustic cell under dry conditions. About 1000 scans were taken with a resolution of 8 cm^{-1}. The PAS spectrometer was placed in an isolated bench, which was constantly purged with dry nitrogen to ensure complete dry conditions.

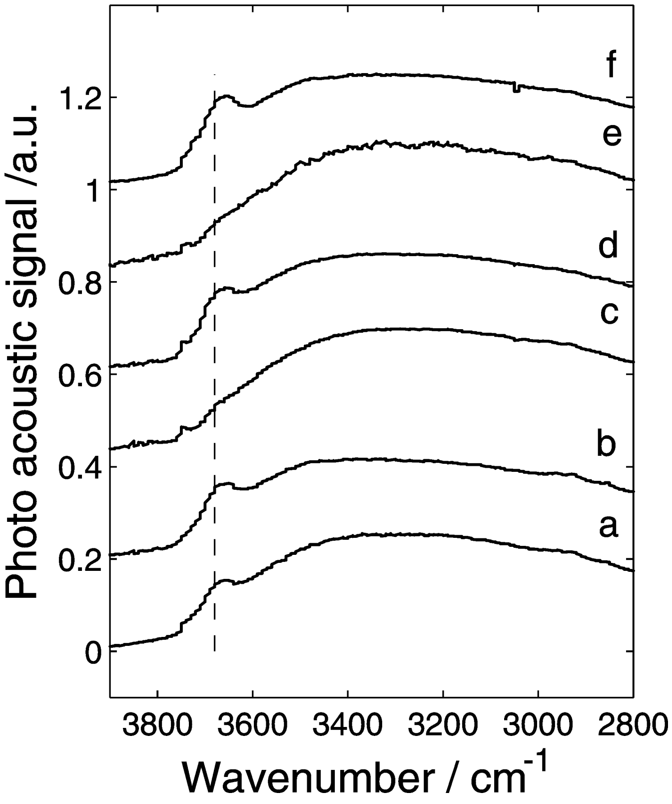

Figure S7. FT-IR PAS spectra of (a) H-TNT, (b) H-TNT-C623, (c) H-TNT-V with 5% VO(acac)$_2$ loading, (d) H-TNT-V-C623 with initial 5% VO(acac)$_2$ loading, (e) H-TNT-Cu with 5% Cu(acac)$_2$ loading, (d) H-TNT-Cu-C623 with initial 5% Cu(acac)$_2$ loading. The vibration at 3680 cm^{-1} is indicated with dashed line.

Figure S7 shows the FTIR-PAS spectra of the different materials under study in the range of the vibrations of the OH groups of the mesoporous materials. The vibration at ~3680 cm^{-1} stems from the acidic OH groups [M. Primet *et al*., *J. Phys. Chem*. 75, (1971), 1216]. This vibration is clearly visible in the trititanate tubes before and after calcination (Figure S7 a and b). However, when VO(acac)$_2$ or Cu(acac)$_2$ complexes are deposited on the tubes (Figure S7 c and e), these signals disappear. It was earlier shown [Y. Segura, *et al*., *J. Phys. Chem. B*, 110 (2006) 948] that VO(acac)$_2$ indeed preferentially attach to more acidic OH groups of TiO$_2$ materials. The disappearance of these signals, indicates a good coverage of the surface by the metal-acac complexes. Upon calcination, the signal of the acidic OH groups is restored (Figure S7 d and f), indicating that the removal of the acac ligands frees the acidic hydroxyl groups.