Distinction of electron pathways at titanium oxide / liquid interfaces in photocatalic processes and co-catalyst effect

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Electronic Supplementary Information (ESI):

Examples of the fitting curves for the heterodyne transient grating (HD-TG) responses obtained by the MEM analyses (Figure S1)

Time constant distributions were obtained by the MEM analyses in the time range of 10^{-7} to 10^{-5} s. In this MEM analysis, the response was assumed by a sum of exponential functions with discrete time constants. The entropy of the error between the function and data is maximized under the constraints; the dispersion of the error is set at the actually measurement error, and the normalization of the pre-exponential factors. The data point was reduced to 2000 points from the original data to reduce the calculation time for the MEM analyses. The fitting curves were obtained from the sum of the exponential functions with the time constants obtained by the MEM analysis. The oscillation responses corresponding due to the acoustic grating in 10^{-7} – 10^{-6} s was neglected for the fitting.

Phase dependence of the HD-TG responses and the transient absorption response for a TiO_2 thin film in ethanol (Figure S2)

The heterodyne transient grating (HD-TG) responses were obtained by the setup described in the experimental section. The transient absorption (TA) measurement was measured at the same probe wavelength, 532 nm just by removing a plate of the transmission grating used for the HD-TG measurement. Since the sample is excited with a grating pattern in the HD-TG technique, diffusive processes such as thermal diffusion, diffusion of carriers or chemical species, also cause the decay of the response by diffusing out the refractive index pattern. By checking the grating spacing dependence, it can be confirmed if the decay is induced by the diffusion processes or the intrinsic decay due to the lifetime for carriers or intermediate species. The grating dependence was shown in Figure 2S. Only the thermal part in the responses showed the grating dependence and the other parts did not depend on it.

In principle, the heterodyne signal intensity is expressed as follows:

$$I(t) = I_{ref} + ((\Delta n(t))^2 + (\Delta k(t))^2)I_{pr} + 2E_{ref}E_{pr}(\Delta n(t) \times \cos(\phi + \phi_0) + \Delta k(t) \times \sin(\phi + \phi_0))$$

where I_{ref} and I_{pr} represent the intensities of the reference and probe, respectively; E_{ref} and E_{pr} represent the electric field of the reference and probe, respectively; ϕ, the phase difference between

the signal and the refernence. ϕ_0 is the initial phase difference and ϕ is given by $\phi = (2\pi / \lambda_{pr})\Delta l$, where Δl is the optical path difference between the signal and reference fields. By changing the distance between a sample and the transmission grating, the phase ϕ can be continuously changed, and when it is changed by π, the HD-TG response is reversed in sign. By adjusting $\phi + \phi_0 = n\pi$, the refractive index change is selectively observed, and the corresponding HD-TG response is shown in figure S2 (80 μm (+)), and also the response after changing $\phi + \phi_0$ by π is shown in figure S2 (80 μm (-)). The phase shift was confirmed by the thermal response of a reference sample. (20 mM nitrobenzene /cyclohexane) Only the responses after 10^{-3} s did not have the phase dependence, and remained a positive signal. The responses after 10^{-3} s were compared with the response of the transient absorption at the same wavelength, which is shown on the same graph. The TA response almost overlapped with those of the HD-TG responses. It was confirmed that the response after 10^{-3} s was due to the absorption change in the TiO_2 thin film by the UV photoirradiation.

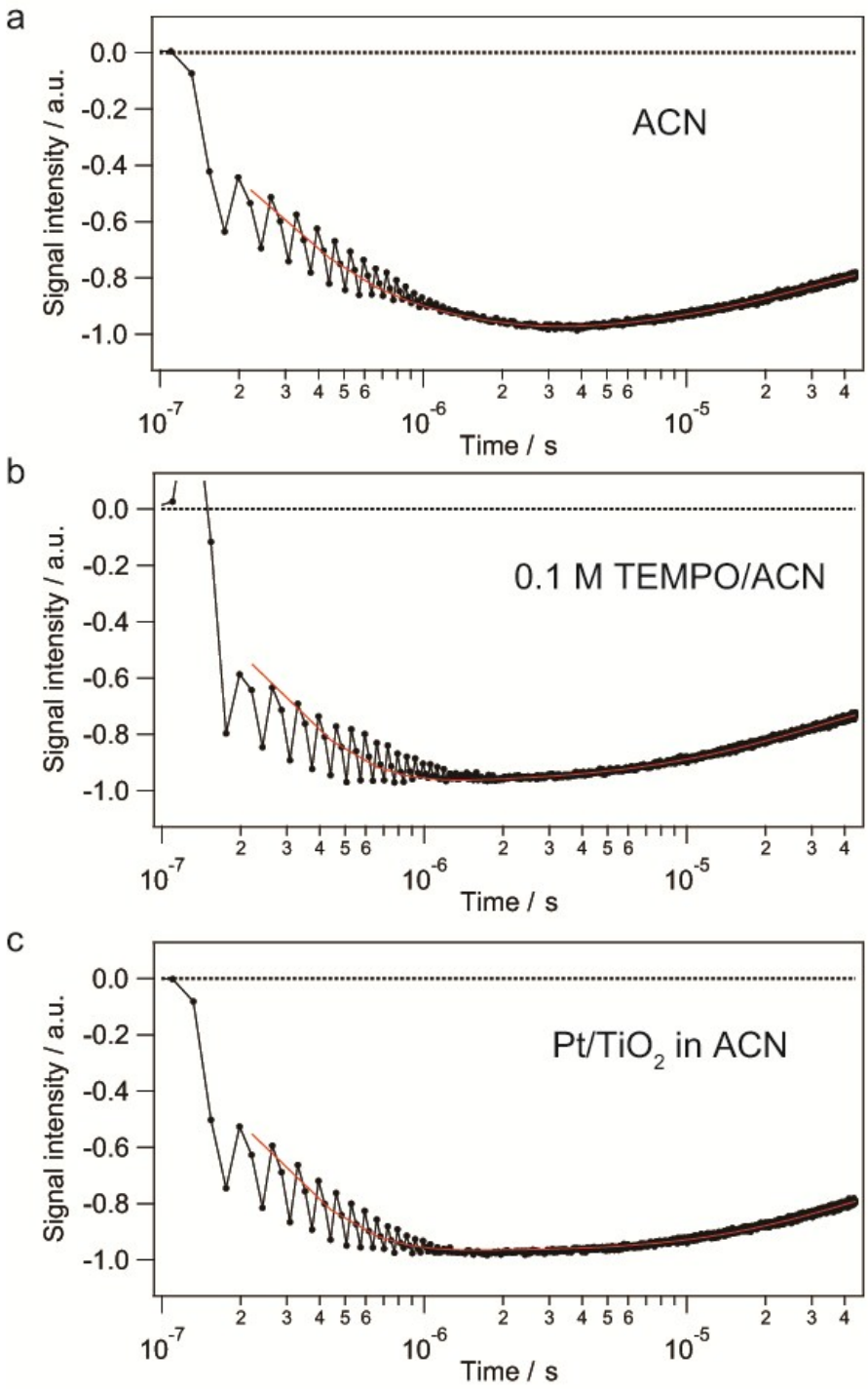

Figure S1. The HD-TG responses (black solid line with circles) and the corresponding fitted curves (red line) obtained by the MEM/NLS analyses for (a) a TiO_2 thin film in acetonitrile and (b) a TiO_2 thin film in 0.1 M TEMPO/acetonitrile, and (c) a Pt/TiO_2 thin film in acetonitrile. The oscillation responses corresponding due to the acoustic grating was neglected for the fitting.

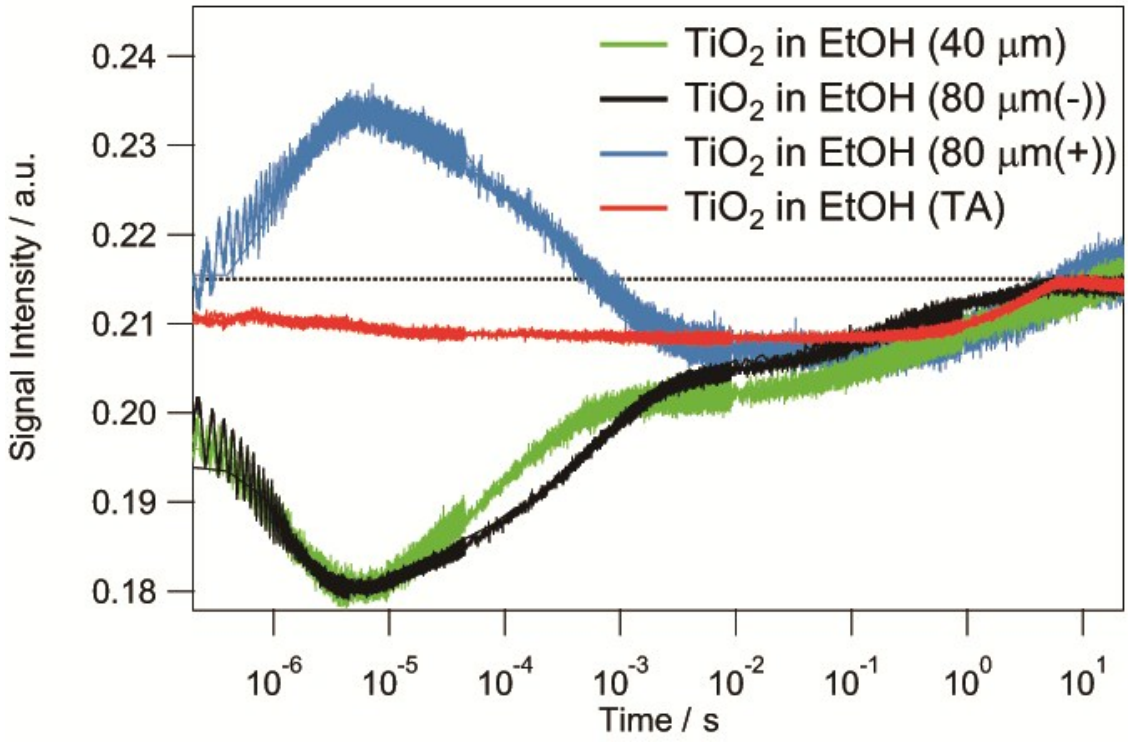

Figure S2. The HD-TG and TA responses for a TiO_2 thin film in ethanol. The HD-TG responses were obtained with the grating spacing (Λ) of 80 μm (black) and 40 μm (green). The response after changing the phase for the heterodyne detection by π for the grating spacing of 80 μm is also shown (blue). The horizontal black dashed line shows the background level for these measurements.