

Electronic Supplementary Information (ESI)

Photo-induced direct interfacial charge transfer at TiO₂ modified with hexacyanoferrate(III)

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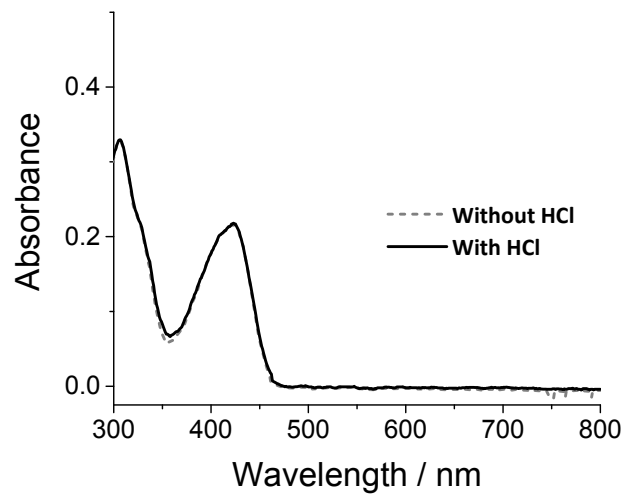


Figure S1. UV-visible absorption spectra for $K_3[Fe(CN)_6]$ in the acidic solutions which we used for the synthesis with (solid line) and without (dashed line) HCl.

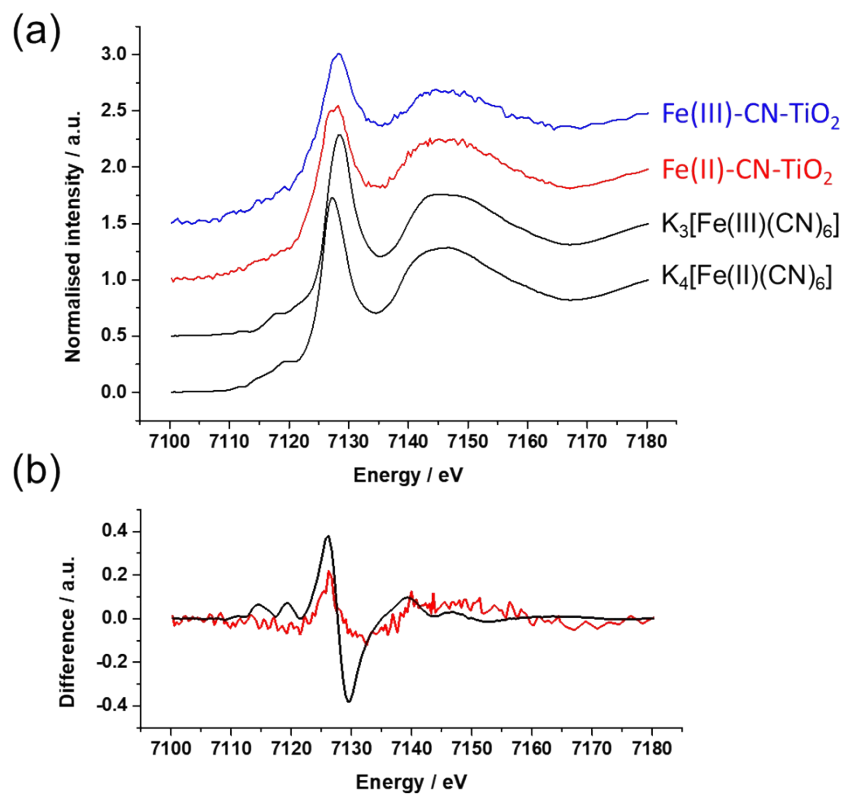


Figure S2. (a) Fe-K edge XANES spectra for K₄[Fe(CN)₆], K₃[Fe(CN)₆], Fe(II)-CN-TiO₂ and Fe(III)-CN-TiO₂. (b) Differences between K₄[Fe(CN)₆] and K₃[Fe(CN)₆] (black), and between Fe(II)-CN-TiO₂ and Fe(III)-CN-TiO₂ (red). For the XAFS measurements, 0.032 wt% Fe modified Fe(II)-CN-TiO₂ and Fe(III)-CN-TiO₂ were used.

K₄[Fe(CN)₆] and K₃[Fe(CN)₆] exhibited the 1s to 4p transition peak at 7127.2 and 7128.4 eV, respectively, which are essentially consistent with the previous studies.^{S1} The transition peaks of Fe(II)- and Fe(III)-CN-TiO₂ were located at 7127.5 eV and 7128.3, respectively. These results reveal

that the oxidation state of the Fe species in Fe-CN-TiO₂ basically corresponded to that of these precursors. However, the XANES signals for our samples were too noisy to quantitatively identify the ratio of Fe(III)/Fe(II) because of the low content of Fe. The further characterization of oxidation state is under progress in our laboratory by using more sensitive methods, such as Mössbauer and soft X-ray absorption spectrometry.

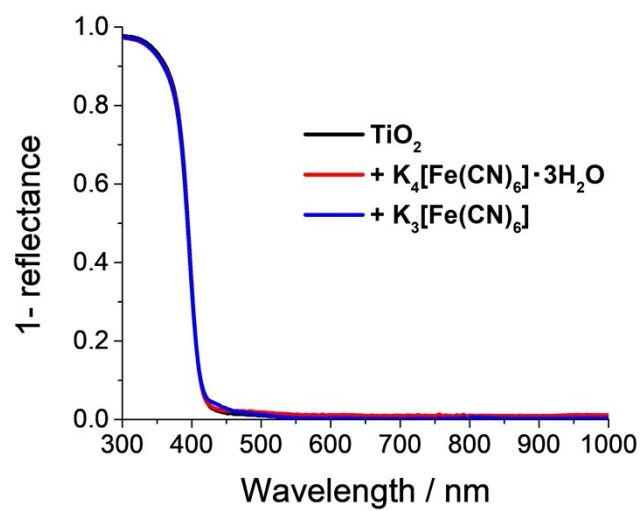


Figure S3. UV-visible reflectance spectra for TiO₂ (black), and the physical mixture of K₃[Fe(CN)₆]/TiO₂ (blue) and K₄[Fe(CN)₆] · 3H₂O/TiO₂ (red). Fe ratio:0.010 wt%.

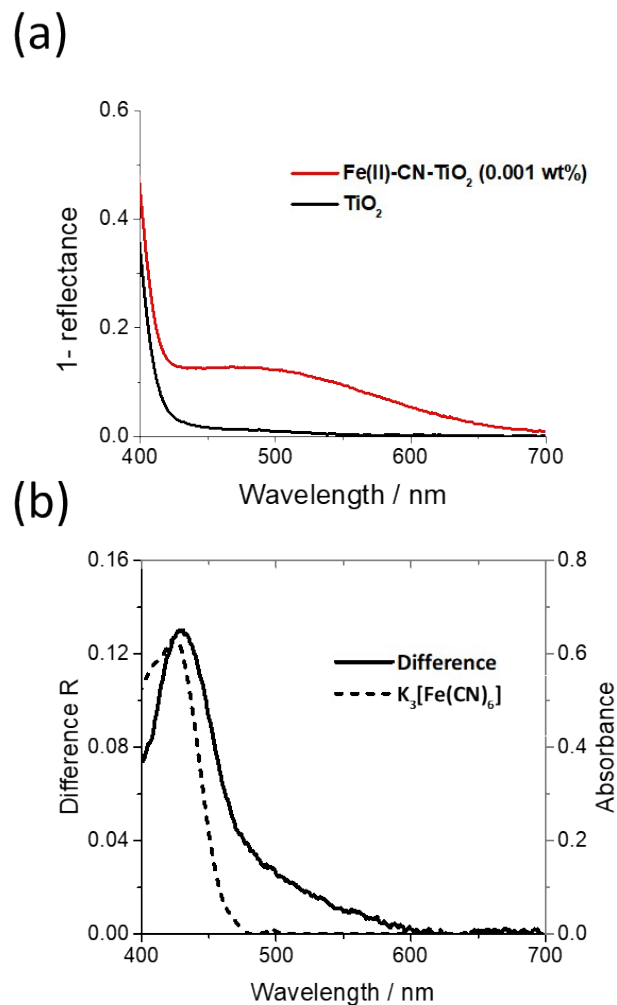


Figure S4. (a) UV-visible reflectance spectra for TiO_2 (black) and 0.001 wt% Fe modified Fe(II)-CN- TiO_2 (red) (b) The difference spectra between 0.010 wt% Fe modified Fe(III)-CN- TiO_2 and 0.001 wt% Fe modified Fe(II)-CN- TiO_2 and absorption spectrum of $\text{K}_3[\text{Fe}(\text{CN})_6]$. For the difference spectra, we normalized each spectra by the reflectance at 630 nm.

We cannot exclude the existence of Fe(II) in Fe(III)-CN- TiO_2 . However, the absorption of Fe(III)-CN- TiO_2 in the range of 480 nm to 650 nm was a little smaller than that of Fe(II)-CN- TiO_2 with low Fe content. Therefore, the concentration of Fe(II) in Fe(III)-CN- TiO_2 was below 0.001 wt % (just 10 % of all Fe atoms).

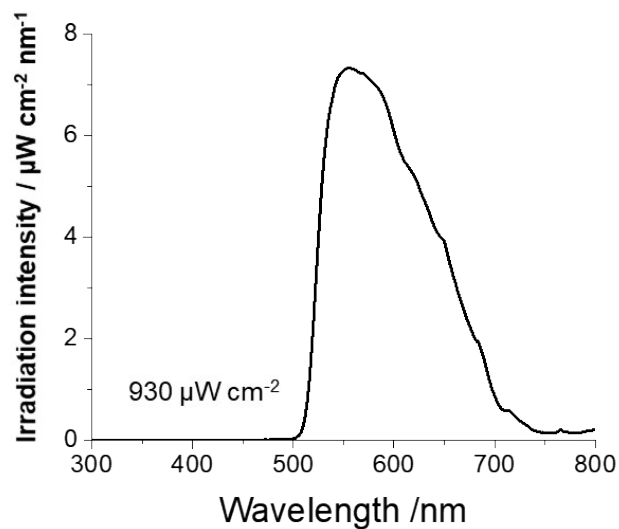


Figure S5. Light source used for investigation of the changes in the diffuse reflectance spectra of Fe(III)-CN-TiO₂.

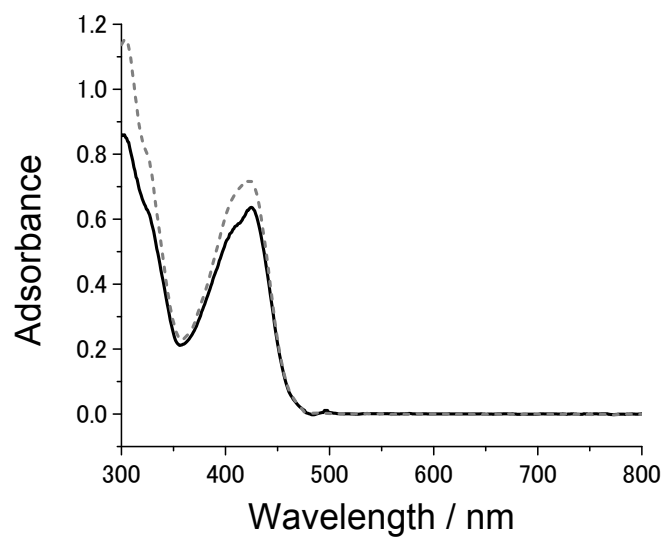


Figure S6. UV-visible absorption spectra for 0.6 mM K₃[Fe(CN)₆] aqueous solution before (solid line) and after (dashed line) visible light irradiation (21 h).

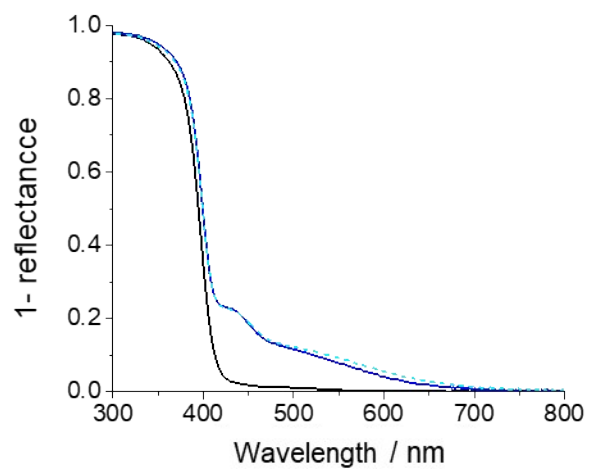


Figure S7. UV-visible reflectance spectra for bare TiO₂ (black line), and for Fe(III)-CN-TiO₂ before (solid blue line) and after (dotted light blue line) dark storage at 60 °C (1.5 h).

[S1] F. Grandjean, L. Samain and G. J. Long, *Dalton Transactions*, 2016, **45**, 18018.