Supporting Information

For

Scavenger-supported photocatalytic evidence of an extended type I electronic structure of TiO_2@Fe_2O_3 interface

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KEYWORDS

TiO_2, Fe_2O_3, heterostructures, band diagram, interface, electron transfer, photocatalysis

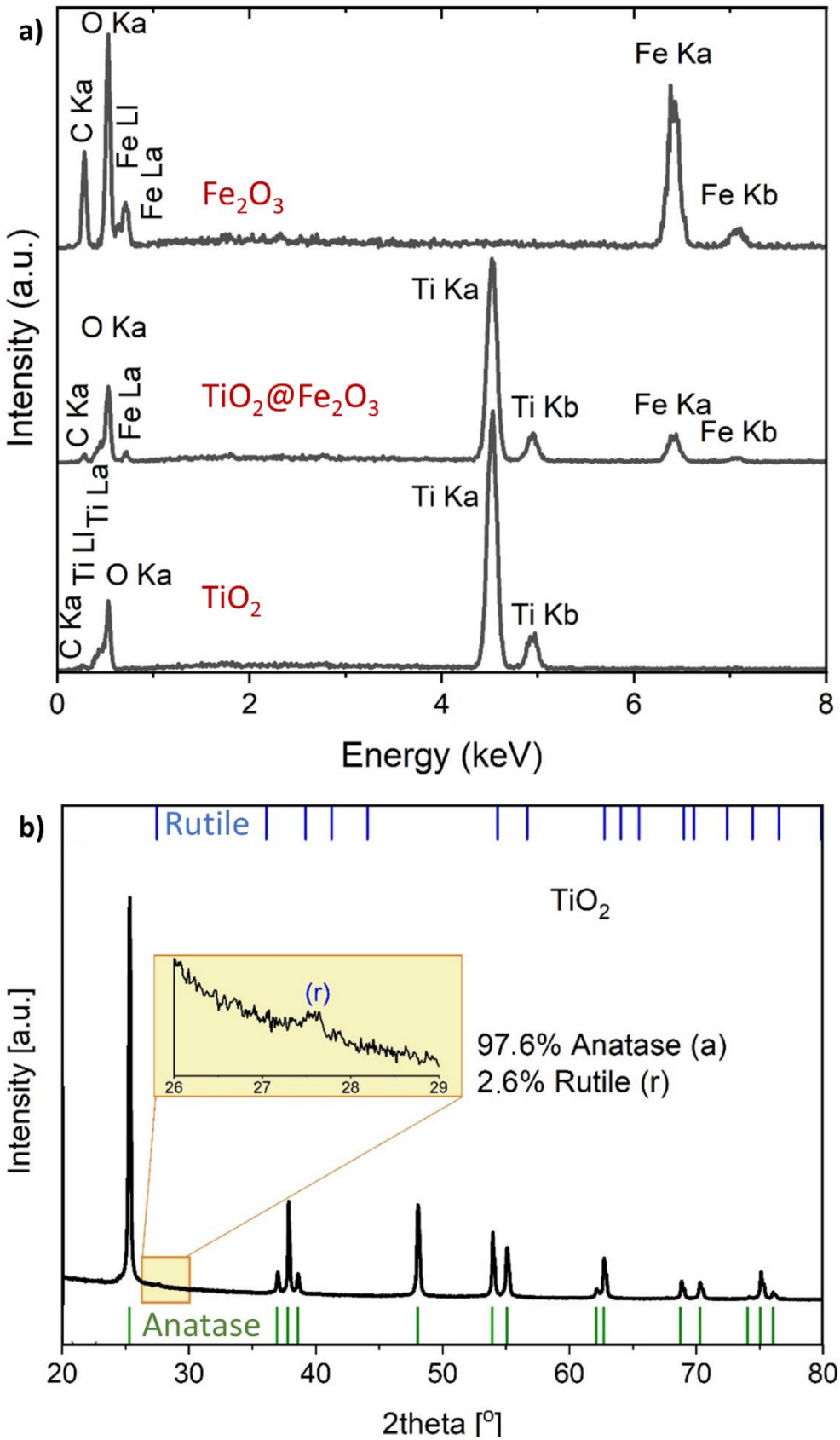

Figure S1. a) EDX spectrum of selected nanomaterials, b) X-ray diffraction pattern of TiO_2 nanocrystals with traces of rutile.

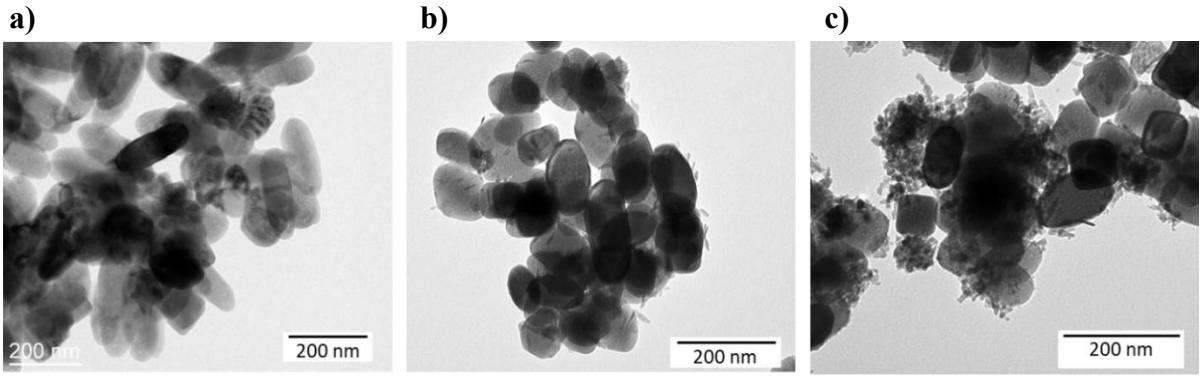

Figure S2. TEM images of a) TiO_2@2%Fe_2O_3, b) TiO_2@10%Fe_2O_3, c) TiO_2@20%Fe_2O_3.

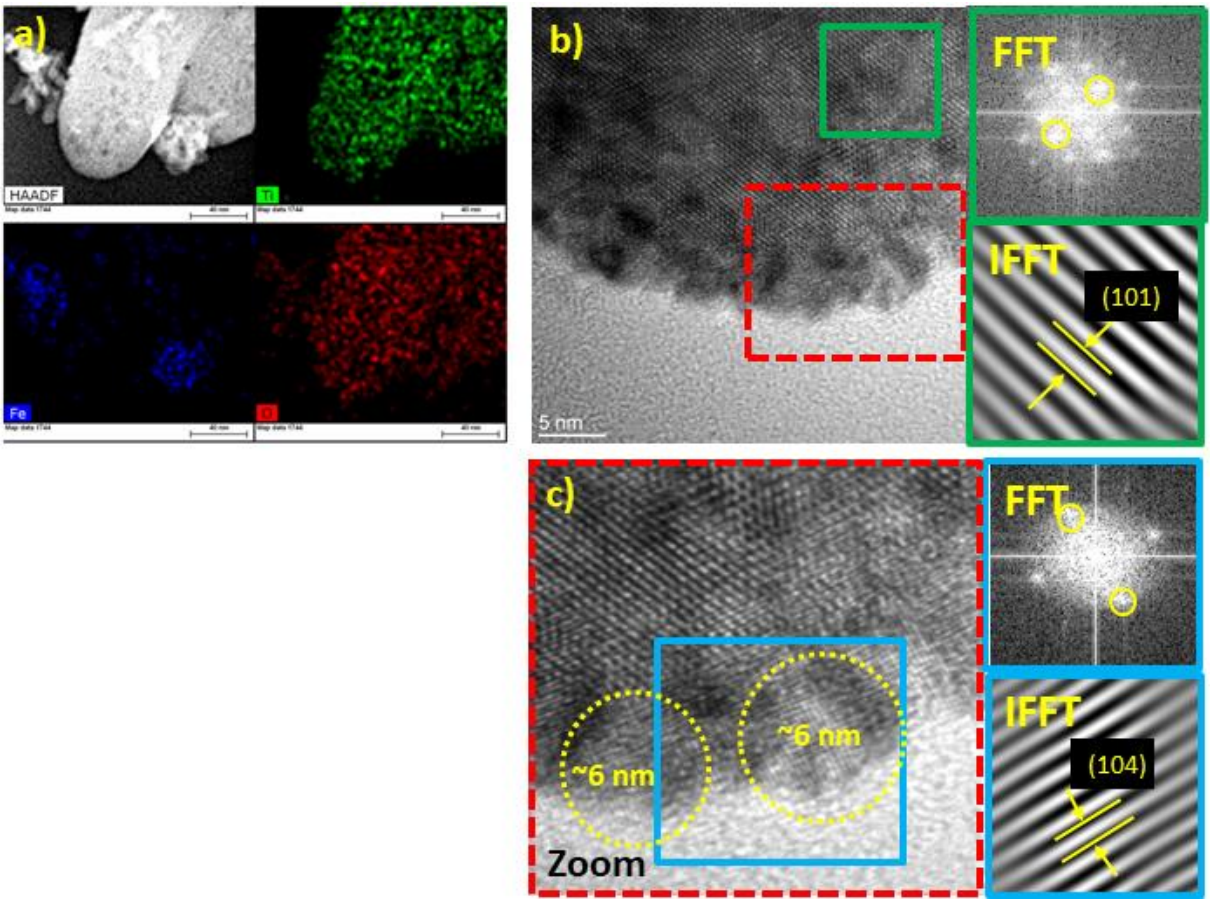

Figure S3. TiO_2@20%Fe_2O_3 sample a) EDX mapping images; b) HRTEM images with Fast Fourier Transform and IFFT analysis indicate the existence of (101) plane of anatase TiO_2; c) FFT of the blue rectangle from the zoomed area shows hematite nanoparticles of 6 nm size with the (104) plane of α-Fe_2O_3.

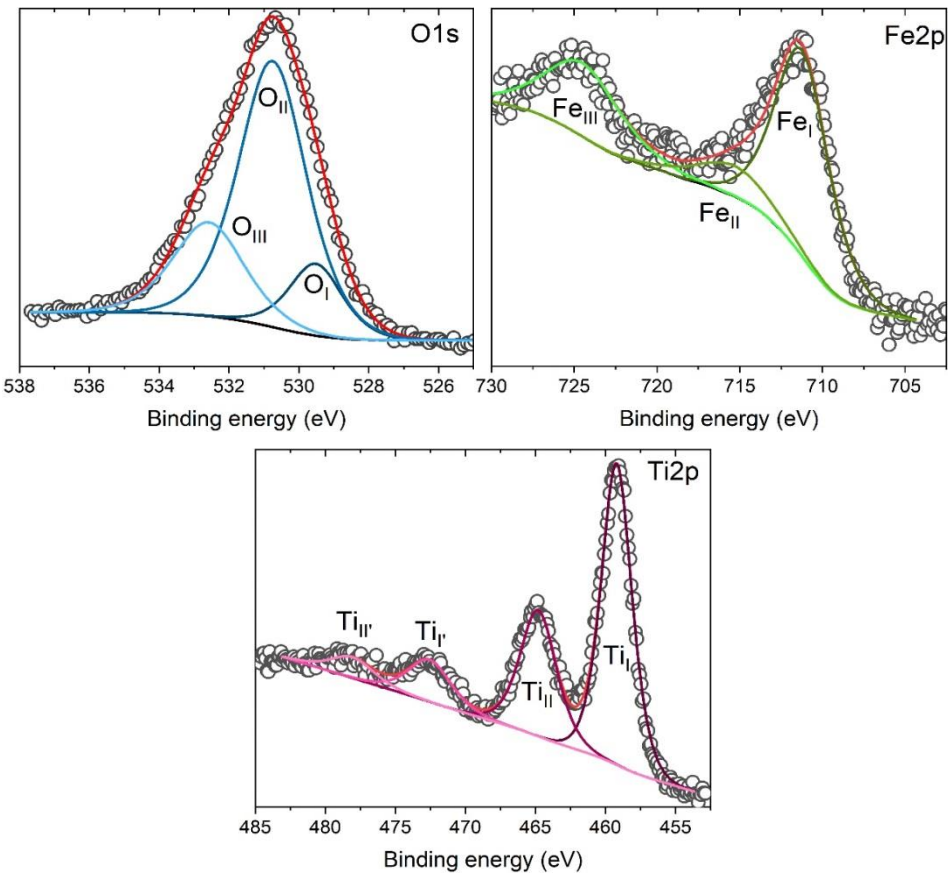

Figure S4. Deconvolution of the XPS spectra of O1s, Ti2p and Fe2p of TiO_2 nanocrystals heavily modified with Fe_2O_3 (TiO_2@20%Fe_2O_3).

Table S1. Characteristic binding energies of Ti2p, O1s, and Fe2p determined from XPS analysis for TiO_2 heavily modified with Fe_2O_3 (TiO_2@20%Fe_2O_3).

Symbol	Binding energy (eV)	Type of bonding	Ref.
		Ti2p	
Ti_I	459.2(3)	Ti2p$_{3/2}$, O-Ti-O	[1]
Ti_{II}	464.9(3)	Ti2p$_{1/2}$, O-Ti-O	[1]
$Ti_{I'}$	472.7(3)	satellite of Ti2p$_{3/2}$, O-Ti-O	[1]
$Ti_{II'}$	478.3(3)	satellite of Ti2p$_{1/2}$, O-Ti-O	[1]
		O1s	
O_I	529.5(4)	Ti-O-Ti	[2]
O_{II}	530.8(4)	oxygen vacancies or defects	[2]
O_{III}	532.8(4)	chemisorbed species e.g. OH^-, H_2O, O^{2-}	[2]
		Fe2p	
Fe_I	711.5(5)	Fe2p$_{3/2}$, Fe^{3+} in Fe_2O_3	[3–5]
Fe_{II}	715.6(5)	satellite of Fe2p$_{3/2}$, Fe^{3+} in Fe_2O_3	[3–5]
Fe_{III}	724.8(5)	Fe2p$_{1/2}$, Fe^{3+} in Fe_2O_3	[3–5]

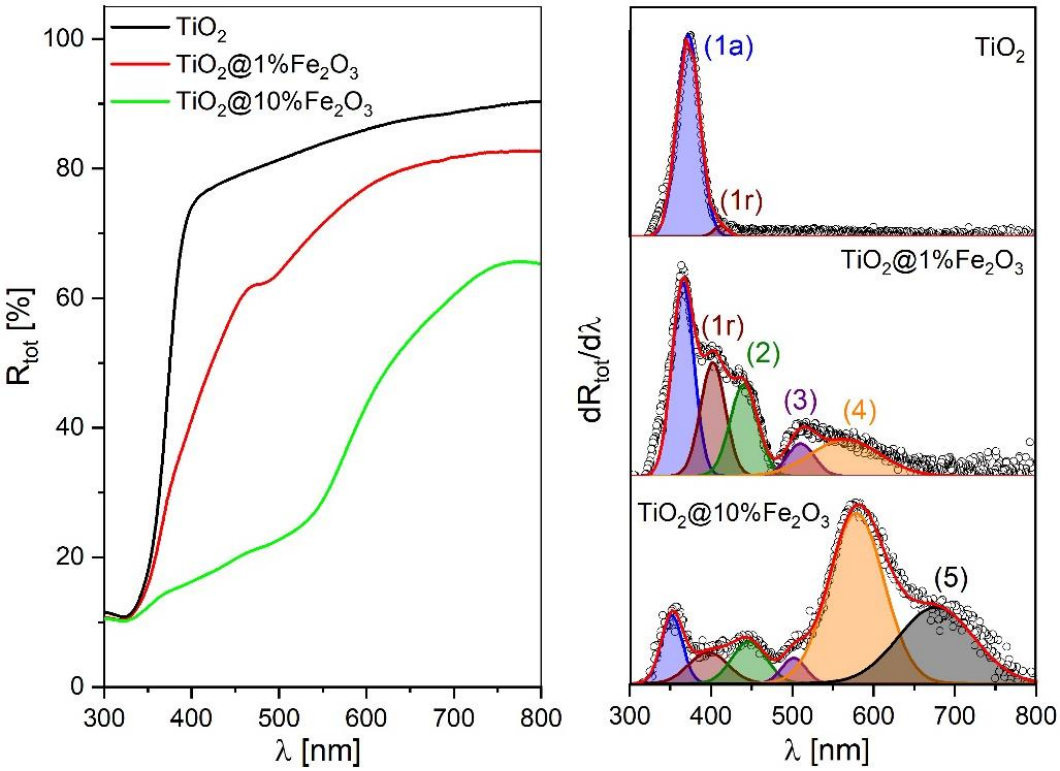

Figure S5. Spectral dependence of total reflectance (left-hand side) and first derivative spectra $dR_{tot}/d\lambda$ (right-hand side) for TiO_2 NCs before and after modification with Fe_2O_3.

Table S2. Energies of the optical transitions for TiO_2 and $TiO_2@Fe_2O_3$ nanomaterials obtained from the first derivative plot. Transition energies were determined with an uncertainty of 0.02 eV.

Sample	**(1a) (eV)**	**1r (eV)**	**(2) (eV)**	**(3) (eV)**	**(4) (eV)**	**(5) (eV)**
(TiO_2)*	3.32	-	-	-	-	-
TiO_2	3.34	3.04				
($TiO_2@0.2\%Fe_2O_3$)*	3.36	-	3.02	-	-	-
$TiO_2@1\%Fe_2O_3$	3.40	3.08	2.82	2.43	2.19	--
($TiO_2@2\%Fe_2O_3$)*	3.43	-	2.92	2.48	2.17	1.84
$TiO_2@10\%Fe_2O_3$	3.54	3.14	2.79	2.48	2.15	1.84
($TiO_2@20\%Fe_2O_3$)*	3.52	-	2.81	2.48	2.13	1.81
Fe_2O_3	-	-	-	-	2.11	1.78

* In this case, TiO_2 nanocrystals appears only as anatase phase.

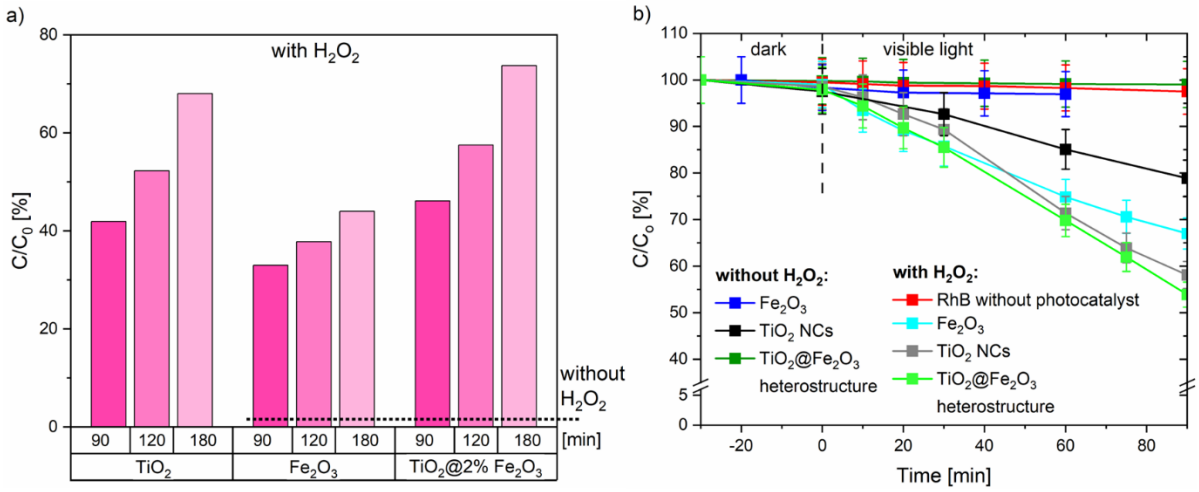

Figure S6. (a) Photocatalytic decomposition of RhB dye under visible radiation for pure oxides vs. TiO_2@2%Fe_2O_3 heterojunction, (b) comparison of photocatalytic activity with and without addition of H_2O_2 to the photocatalytic system.

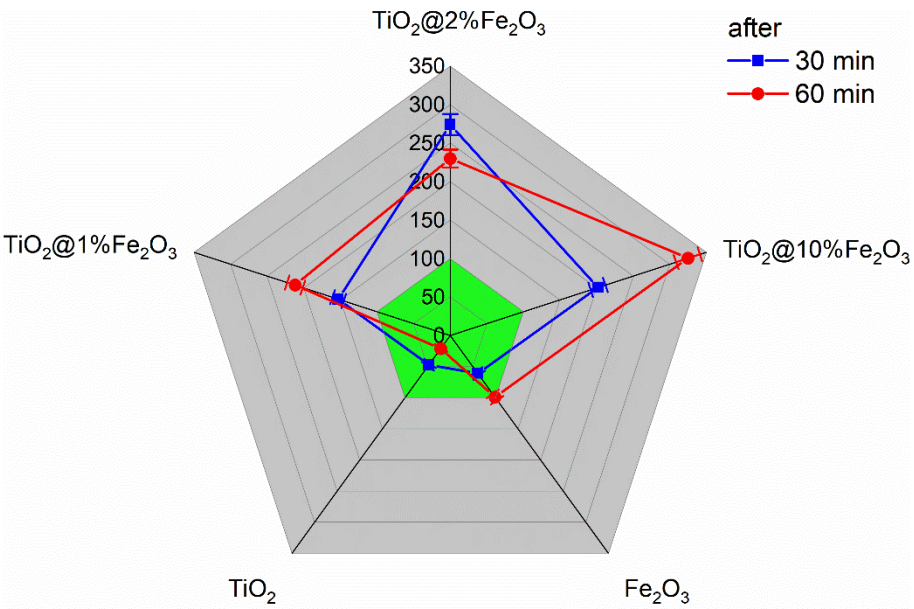

Figure S7. Normalized dye degradation after 30 and 60 min, in the presence of scavenger of holes.

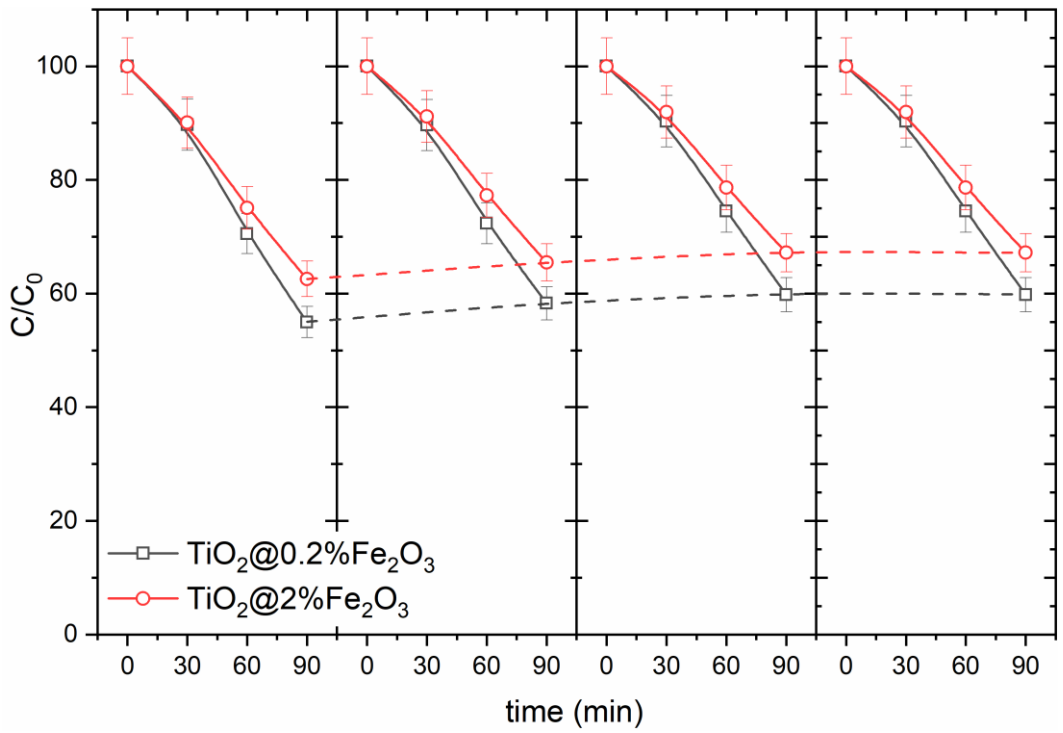

Figure S8. Recycled photocatalytic process of Rhodamine B in the presents of $TiO_2@Fe_2O_3$ and H_2O_2.

References

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