Electronic Supplementary Material (ESI) for RSC Advances.

Sustainable Preparation of Sun-light Active α-Fe_2O_3 Nanoparticles using Iron containing Ionic Liquids for Photocatalytic Applications

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Supporting Information

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Annexure S1: Synthesis of ILs, [C$_n$mim][Cl]

Synthesis of ILs, [C$_n$mim][Cl] (n = 4, 8 and 16) was done using method reported in literature with slight modifications.[1] The synthesized ILs have been characterised using ^{1}H-NMR spectroscopy. The characterization data for ILs is provided as Annexure S1 and Figure S1-S3 (Supporting Information). ^{1}H-NMR spectra were recorded on Brüker Ascend 400 spectrometer (AVANCE III HD console) using $CDCl_3$ as solvent.

Synthesis of iron containing ionic liquids (MILs)

Iron (metal) containing MILs were synthesized using the method reported in literature with slight modification.[2-3] Equimolar amount of [C$_n$mim][Cl] (n = 4, 8 and 16) with $FeCl_3{\cdot}6H_2O$ were stirred in round bottom flask for 4-5 hours using dichloromethane as solvent at room temperature. The product is dried using sodium sulphate while the solvent was evaporated through rotary evaporator resulting in a formation of [C$_n$mim][$FeCl_4$] (n = 4, 8 and 16). The obtained MILs were washed twice with diethyl ether and distilled water followed by vacuum dying at 80°C for 24 h for removal of moisture. The synthesized MILs shows characteristic peaks of $[FeCl_4]^-$ in Raman and UV-visible spectra, (Figure S4 and S5, Supporting Information, respectively), confirming the formation of [C$_n$mim][$FeCl_4$].

Characterization of [C$_n$mim][Cl] ILs

^{1}H NMR and mass spectroscopy data for synthesized ILs:

[C$_4$mim][Cl]: ^{1}H NMR (400 MHz, $CDCl_3$, δ-ppm) 0.876 (t, 3H, C*H$_3$*), 1.245 (m, 2H, (-C*H$_2$*-CH$_3$)), 1.903 (q, 2H, (N$^+$-CH$_2$- C*H$_2$*-)), 4.132 (s, 3H, N-C*H$_3$*), 4.316 (t, 3H, N$^+$-C*H$_2$*-CH$_2$-), 7.290 (d, 1H, N-C*H*-CH-N$^+$), 7.416 (d, 1H, N-CH-C*H*-N$^+$), 10.67 (s, 1H, N-C*H*-N$^+$).

[C$_8$mim][Cl]: ^{1}H NMR (400 MHz, $CDCl_3$, δ-ppm) 0.872 (t, 3H, C*H$_3$*), 1.288 (br m, 2H, (-C*H$_2$*-CH$_3$)), 1.904 (q, 2H, (N$^+$-CH$_2$- C*H$_2$*-)), 4.129 (s, 3H, N-C*H$_3$*), 4.318 (t, 3H, N$^+$-C*H$_2$*-CH$_2$-), 7.332 (d, 1H, N-C*H*-CH-N$^+$), 7.477 (d, 1H, N-CH-C*H*-N$^+$), 10.55 (s, 1H, N-C*H*-N$^+$).

[C$_{16}$mim][Cl]: ^{1}H NMR (400 MHz, CDCl$_3$, δ-ppm) 0.879 (t, 3H, CH_3), 1.245 (br m, 2H, (-CH_2-CH$_3$)), 1.903 (q, 2H, (N$^+$-CH$_2$- CH_2-)), 4.132 (s, 3H, N-CH_3), 4.316 (t, 3H, N$^+$-CH_2-CH$_2$-), 7.290 (d, 1H, N-CH-CH-N$^+$), 7.416 (d, 1H, N-CH-CH-N$^+$), 10.67 (s, 1H, N-CH-N$^+$).

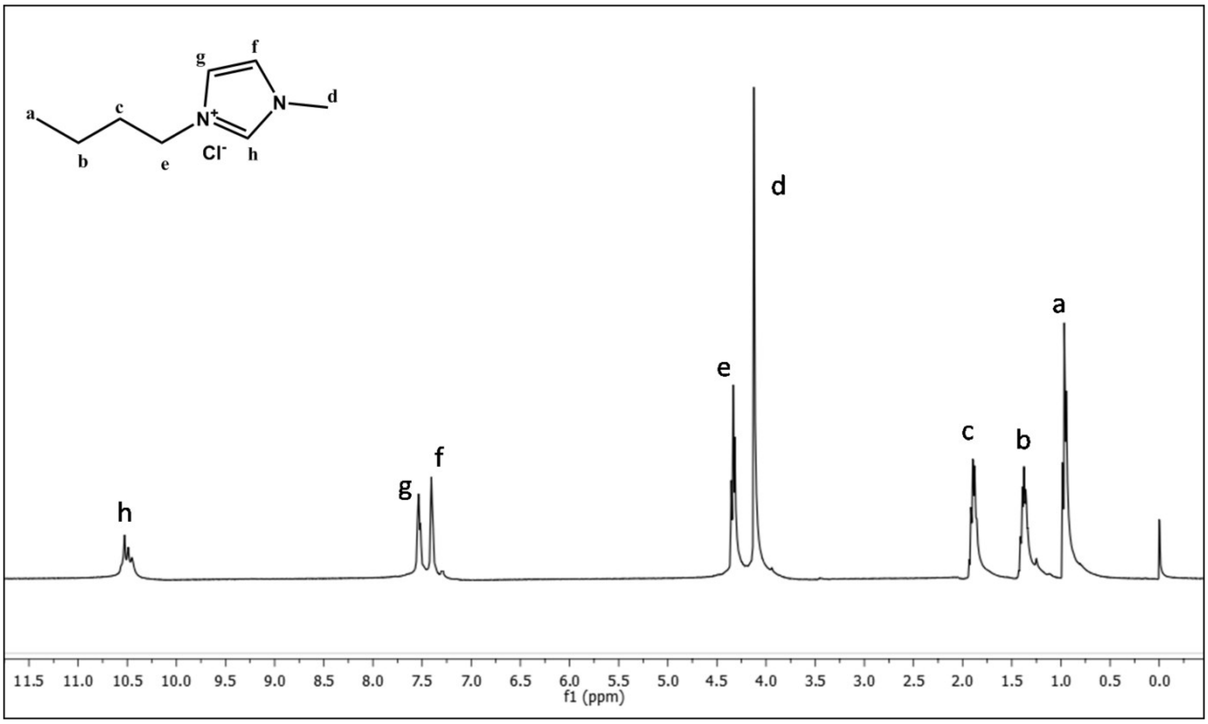

Figure S1: ^{1}H NMR spectra of [C$_4$mim][Cl].

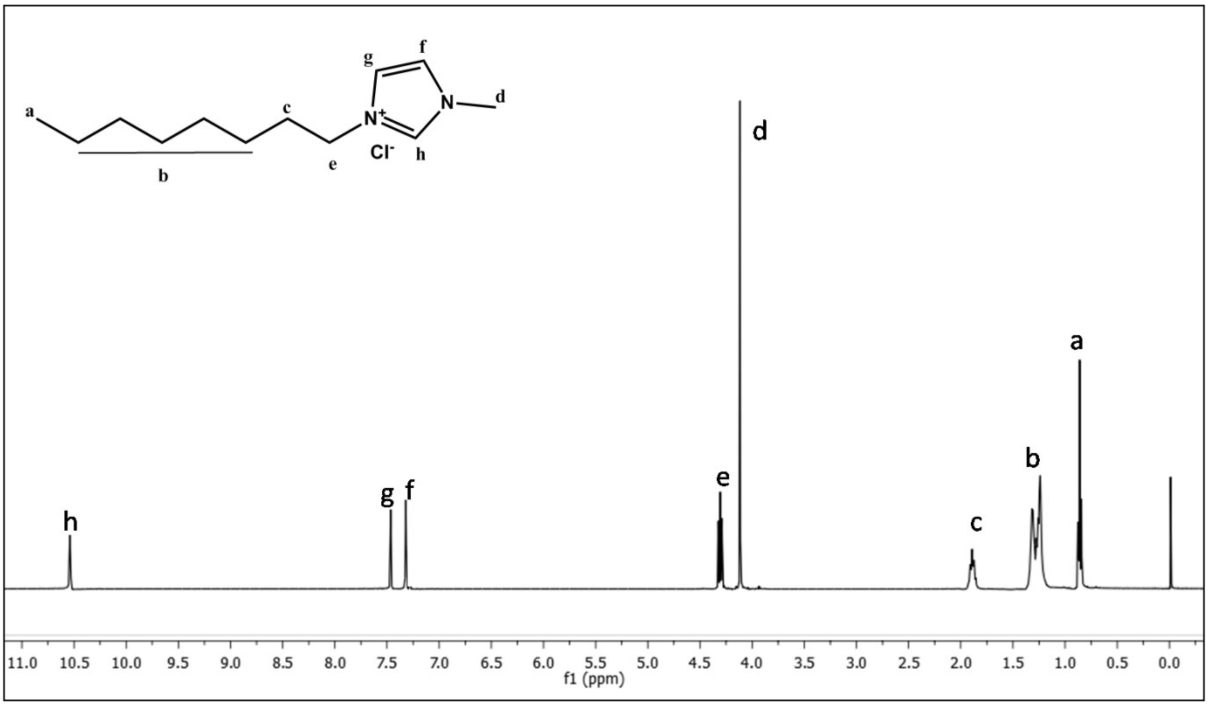

Figure S2: ^{1}H NMR spectra of [C$_8$mim][Cl].

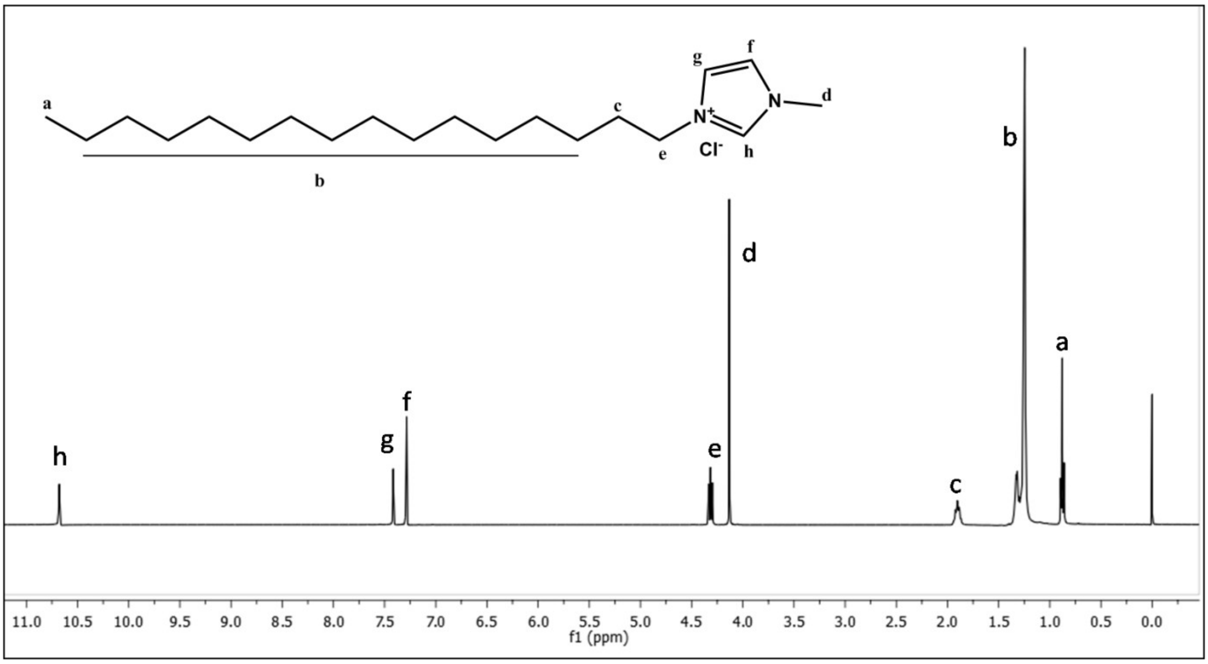

Figure S3: ^{1}H NMR spectra of [C_{16}mim][Cl].

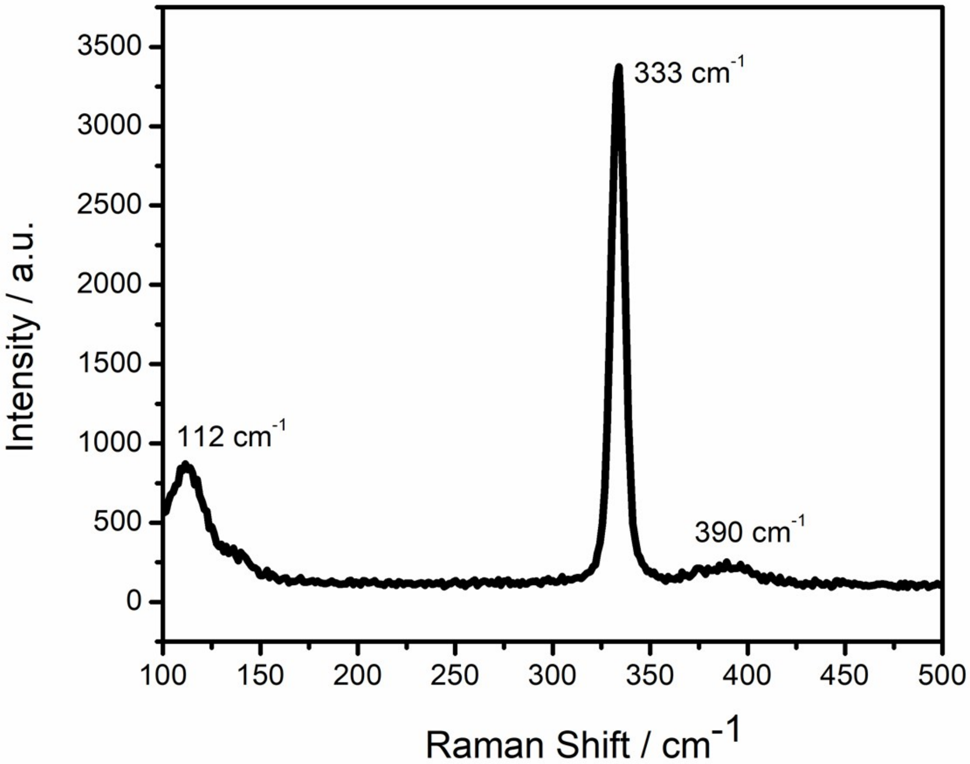

Figure S4: Raman spectra of [C_{16}mim][$FeCl_4$] as representative, showing the three characteristic peaks at 112, 333 and 390 cm^{-1}, which is in accordance with the literature reports.[4]

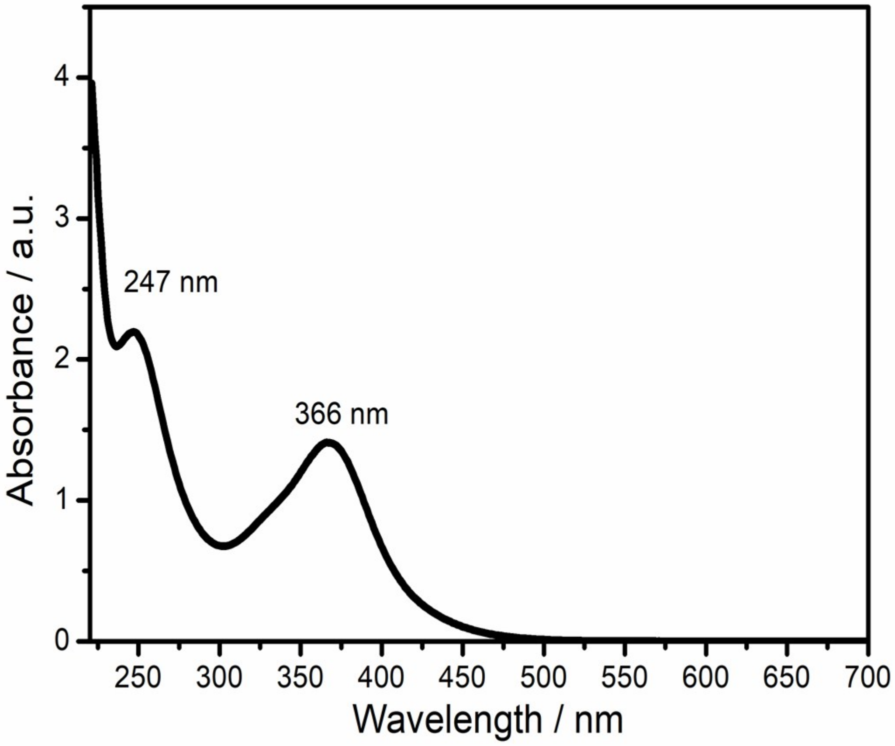

Figure S5: Absorbance spectra [C_{16}mim][$FeCl_4$] as representative, showing the characteristic peaks 247 and 366 nm, which is in accordance with the literature reports.[5]

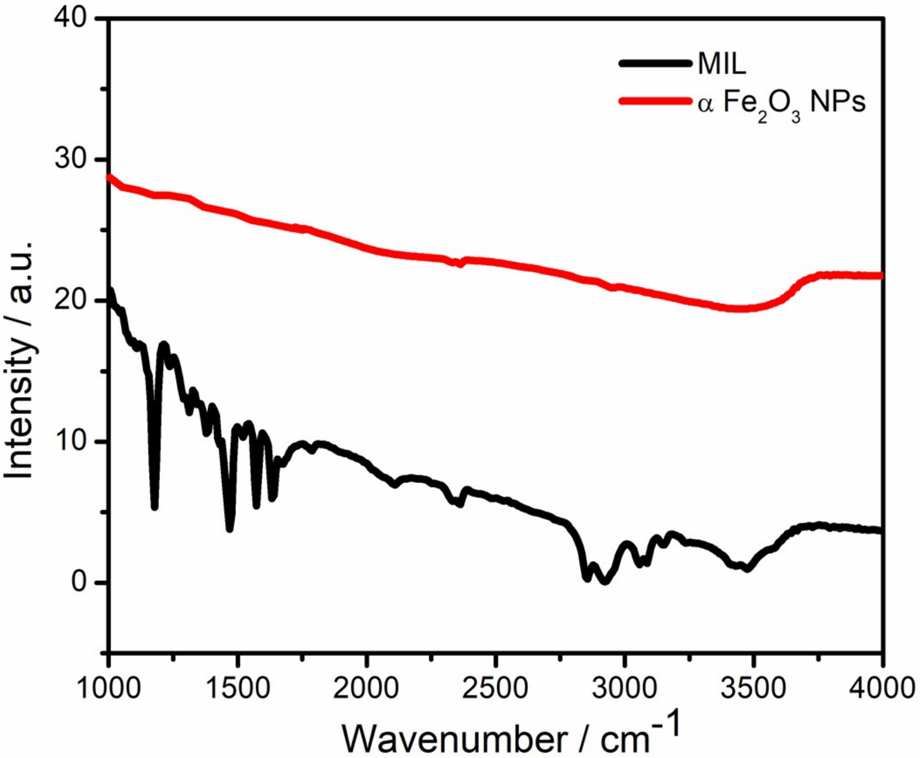

Figure S6: FT-IR spectra of MIL and synthesized α-Fe_2O_3, after removal of MIL, have no absorption peak corresponding to MIL, indicating complete removal of MIL after washing.

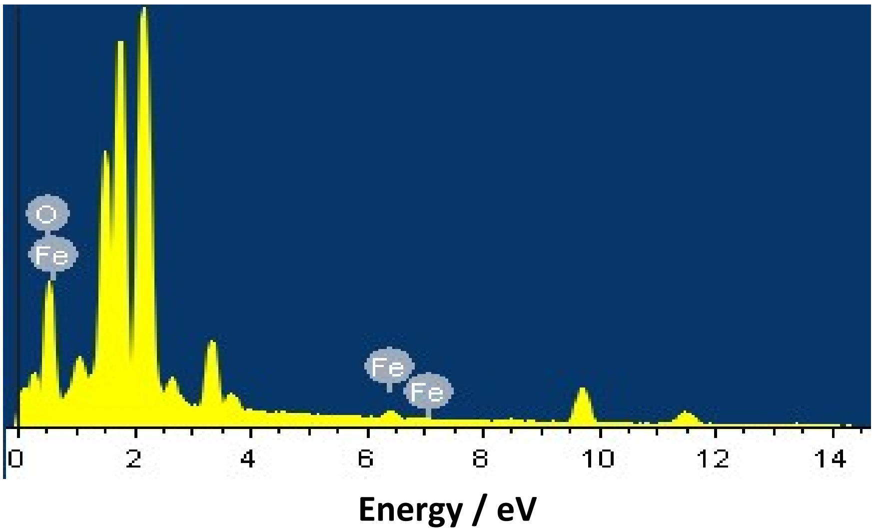

Figure S7: Energy dispersive X-ray spectroscopy (EDAX) spectra of prepared α-Fe_2O_3 NPs.

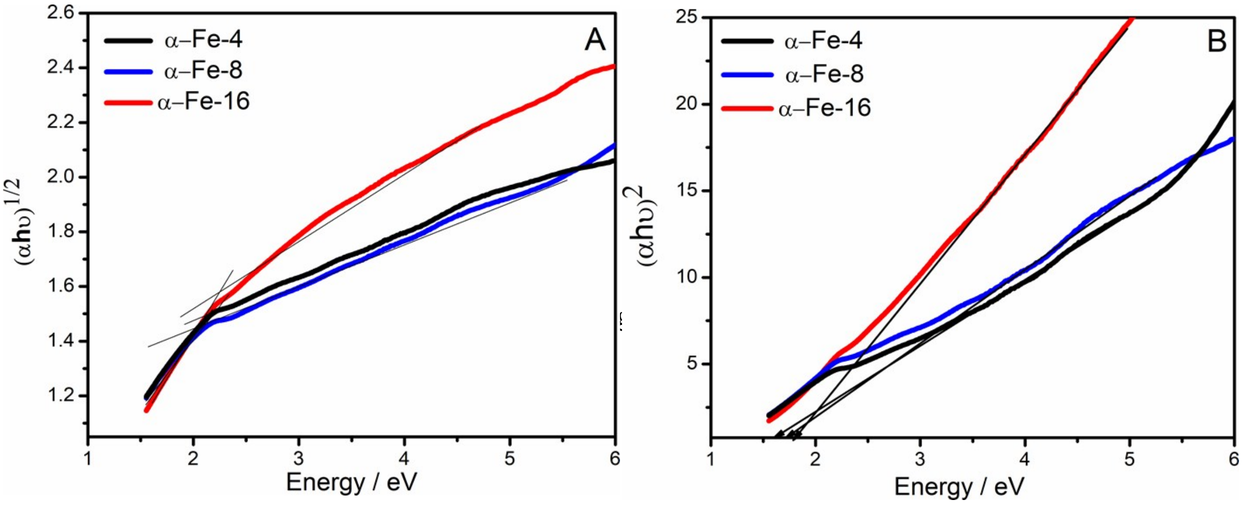

Figure S8: Tauc plot to measure (A) direct band gap and (B) indirect band gap of synthesised α-Fe_2O_3 NPs.

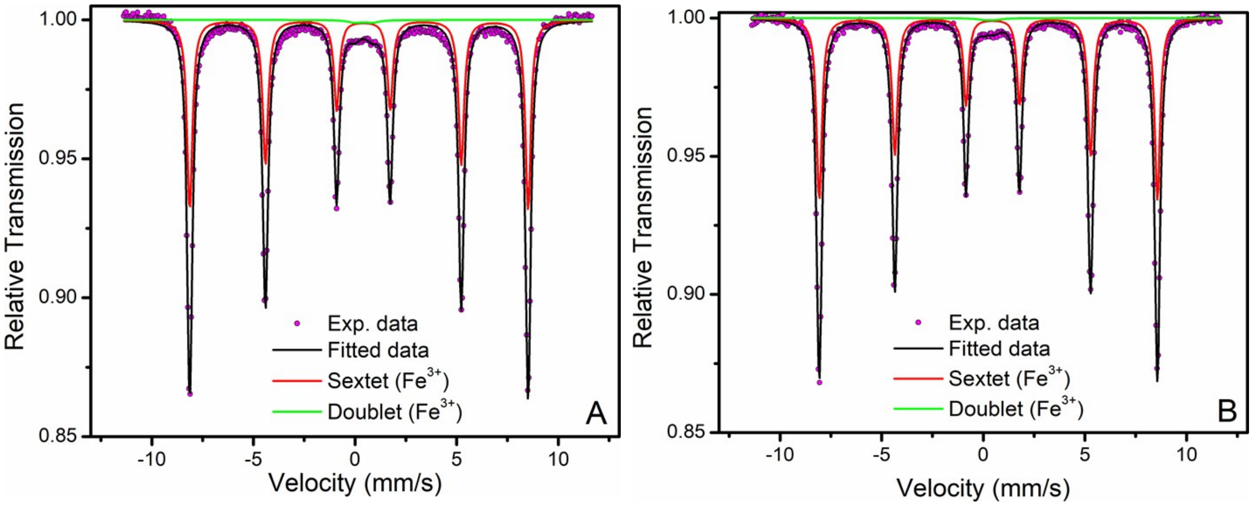

Figure S9: Mössbauer spectra of (A) α-Fe-4; and (B) α-Fe-8.

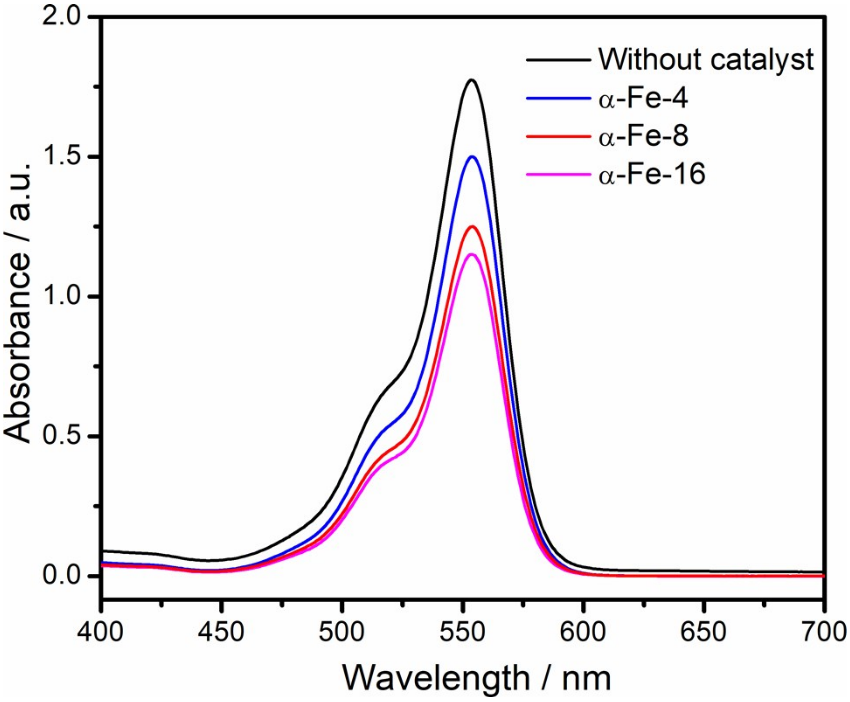

Figure S10: Variation in absorbance band of RhB dye using different catalyst after stirring for 30 min in dark.

Table S1: Characteristic parameters of synthesized α-Fe_2O_3 NPs calculated from XRD, UV-Visible and TEM measurements.

Sample	2θ	d_{104} / (Å)	β	D^a / (nm)	Band gap^c / eV	Band gap^d / eV	D^b / (nm)
α-Fe-4	33.40	2.679	3.8×10^{-3}	40.0	2.12	1.42	95.5
α-Fe-8	33.30	2.687	4.4×10^{-3}	34.4	2.10	1.61	44.5
α-Fe-16	33.28	2.689	4.6×10^{-3}	32.1	2.25	1.86	35.5

d_{104} is interplaner distance for (104) plane, β is half-line width, D^a and D^b are the crystallite sizes obtained from XRD and TEM measurements respectively, c and d refers to direct and indirect band gap, respectively.

Table S2: Mössbauer parameters of α-Fe_2O_3 NPs obtained from Mössbauer spectra recorded at room temperature

Sample Code	Iron Sites	H_{hf} / Tesla	Δ / mm/s	δ / mm/s	Relative area R_A (%)
α-Fe-4	Sextet	51.63	-0.219	0.30	98.04
	Doublet	–	0.859	0.42	1.96
α-Fe-8	Sextet	51.59	-0.217	0.36	98.7
	Doublet	–	0.539	0.31	1.3
α-Fe-16	Sextet	51.47	-0.219	0.35	99.6
	Doublet	–	0.275	0.20	0.4

Standard error in H_{hf}, Δ and δ is ±0.002, ±0.006 and ±0.003, respectively

References

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2. F. G. Sherif, L. J. Shyu, C. C. Greco, U.S. Patent, 5,824, 832 (1998). 25.
3. Q. F. Yue, H. G. Yang, M. L. Zhang, X. F. Bai, *Adv. Mater. Sci. Eng.*, 2014, 454756
4. M. S. Sitze, E. R. Schreiter, E. V. Patterson, R. G. Freeman, *Inorg. Chem.* 2001, **40**, 2298-2304.
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