

Electronic Supporting Information

for

Highly Active Sustainable Ferrocenated Iron Oxide  
Nanocatalysts for the Decolorization of Methylene Blue

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## Experimental section

All chemicals ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) (Merck), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) (Fluka), ferrocene (Acros), sulfuric acid (RCI Lab Scan), sodium chloride (Fisher chemical), and methylene blue (Merck) were analytical grade and used as received.

The ferrocene-trapped iron oxide nanoparticles were characterized by X-ray powder diffraction (XRD). The XRD pattern was obtained on a Bruker D8 ADVANCE diffractometer with  $\text{Cu-K}\alpha$  radiation between  $10^\circ$  to  $80^\circ$ . The morphology images of nanoparticles were obtained by transmission electron microscopy (TEM) model JEOL JEM-2100 on copper grid covered by formvar. Fourier transform infrared spectroscopy (FTIR) was performed on Perkin Series to identify the functional groups in iron oxide. The UV-visible spectrophotometer was carried out on JASCO V-530 in range of 350-700 nm and scan speed of 1000 nm/min. Thermal analysis (DSC/TGA) was performed on TA instruments SDT2960 Simultaneous using the heating rate at  $20^\circ\text{C}/\text{min}$  from room temperature to  $800^\circ\text{C}$  under nitrogen gas. Electrospray ionization (ESI) was carried out on microTOF, and positive ion mode. Electron paramagnetic resonance spectroscopy (EPR) was carried out on JEOL JES-RE2X operated at X-band microwave (8.8-9.6 GHz), magnetic field range of 3.1 T, cylindrical cavity resonator ( $\text{TE}_{011}$  mode), and program ES-PRIT. Vibrating sample magnetometer (VSM) was performed on electromagnet in model HV-4H, Hall probe-based gaussmeter on model Lakeshore 455, and field range up to  $\pm 9$  kOe. X-ray photoelectron spectroscopy (XPS) was performed on Kratos Axis Ultra. Brunauer-Emmett-Teller (BET) was measured surface area, pore size and volume using a Quantachrome Autosorb Automated Gas Sorption System in nitrogen adsorption. The zeta potential technique was carried out with Zetasizer Nano-ZS

model ZEN 3600. Elemental analyses were performed on a Perkin-Elmer series II CHNS/O Analyzer 2400.

**General Synthesis of ferrocenated iron oxide nanoparticles** The synthesis was carried out using the coprecipitation of iron sources and ferrocenium ion at different ratio including different bases. The following procedure is for **A1** or **A3**. Other ratios can be adjusted accordingly. Concentrated sulfuric acid ( $0.3 \text{ cm}^3$ ) was added to ferrocene (6.84 g, 36.75 mmol) and stirred for 2 minutes giving a blue viscous solution. Water ( $5 \text{ cm}^3$ ) was then added and stirred for 30 min. A solution of ferrous chloride tetrahydrate (1.55 g, 12.25 mmol) and ferric chloride hexahydrate (4.15 g, 25.6 mmol) in  $80 \text{ cm}^3$  de-ionized water was then added into the ferrocenium solution and stirred for 1 hour. A saturated NaOH or  $4.83 \text{ mol/dm}^3$   $\text{NH}_4\text{OH}$  solution was slowly added dropwise to adjust pH to 12 giving an orange precipitate. The mixture was then stirred for 2 hours. The orange precipitate was collected by centrifugation at 4500 rpm for 20 minutes. The product was purified by alternate washing with de-ionized water, collected by centrifugation for 6 times, and checked sulfate salt with dropwise de-ionized water after washing in  $\text{BaCl}_2$  solution. The orange solid was then incubated at  $80 \text{ }^\circ\text{C}$  for 24 hours giving 8.69 g product. The product may be further calcined at  $500 \text{ }^\circ\text{C}$  for 5 hours to give **A2** catalyst.

**Decolorization of methylene blue** The desired catalyst (0.100 g) was added into a solution of methylene blue ( $9.97 \times 10^{-6} \text{ mol/dm}^3$ ,  $100 \text{ cm}^3$ ). The reaction flask was wrapped with aluminium foil and kept in the dark box while stirring. At desired time,  $3 \text{ cm}^3$  of the solution mixture was collected for analysis. The catalyst was separated from the mixture by centrifugation at 4500 rpm for 3 minutes. The clear supernatant was analyzed by UV-visible spectrophotometer and ESI-MS.

**The reusability of catalyst** The resulting catalyst separated by centrifugation at 4500 rpm for 3 minutes was then added a solution of methylene blue ( $9.97 \times 10^{-6}$  mol/dm<sup>3</sup>, 100 cm<sup>3</sup>) for the second run. The process was repeated as needed. For the reactivation with 0.1 mol/dm<sup>3</sup> sodium chloride and de-ionized water, the reaction was carried out similarly except that before the addition of methylene blue for each subsequent run, the catalyst was added a solution of the reactivator (100 cm<sup>3</sup>), stirred for 10 minutes, and separated by centrifugation at 4500 rpm for 3 minutes.

**EPR spin trapping** Stock solution of spin trap in solvent as phosphate buffer was prepared by ferrocenated oxide nanocatalyst (3.04 mg) was dissolved in 5,5-dimethyl-1-pyrroline N-oxide (DMPO) ( $7.64 \times 10^{-6}$  mol/dm<sup>3</sup>), phosphate buffer pH 7.4 (50 mmol/dm<sup>3</sup>, 2 cm<sup>3</sup>), and incubate for 20 minutes. All EPR spectrums were average of 1000 scans and simulated the spectra with WinSim 2002 program.

**Table S1.** Zeta potential values of iron oxide nanocatalysts.

<b>Sample Code</b>	<b>Zeta Potential (mV)</b>
<b>A1</b>	- 8.83
<b>A2</b>	- 6.08
<b>A3</b>	- 9.49
<b>A4</b>	- 7.00
<b>B1</b>	- 8.73
<b>B2</b>	- 7.14
<b>B3</b>	- 10.06
<b>B4</b>	- 7.55
<b>C1</b>	- 8.96
<b>C2</b>	- 6.70
<b>C3</b>	- 9.65
<b>C4</b>	- 6.94

**Table S2.** The binding energy of (a) Fe 2*p*, (b) O 1*s*, and (c) C 1*s* of ferrocenated iron oxide nanoparticles.

<b>Sample Code</b>	<b>Binding Energy (eV)</b>	<b>Characteristic</b>
<b>A1 – Fe 2<i>p</i></b>	707.9	Ferrocene (Fe <sup>2+</sup> )
	710.3	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	711.7	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	713.4	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	723.5	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	725.1	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	726.9	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	728.7	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
<b>A2 – Fe 2<i>p</i></b>	709.7	Fe <sup>2+</sup> 2 <i>p</i> <sub>3/2</sub>
	711.1	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	713.1	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	723.0	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	724.6	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	726.5	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
<b>A3 – Fe 2<i>p</i></b>	708.0	Ferrocene (Fe <sup>2+</sup> )
	710.5	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	711.8	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	713.3	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	722.6	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	724.1	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	725.4	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	726.9	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>

Sample Code	Binding Energy (eV)	Characteristic
<b>B1</b> – Fe 2 <i>p</i>	708.0	Ferrocene (Fe <sup>2+</sup> )
	710.6	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	711.9	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	713.6	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	722.8	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	724.7	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	726.2	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	727.4	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
<b>B3</b> – Fe 2 <i>p</i>	707.9	Ferrocene (Fe <sup>2+</sup> )
	710.5	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	711.8	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	713.2	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	722.8	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	724.1	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	725.7	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	727.4	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
<b>C1</b> – Fe 2 <i>p</i>	709.2	Fe <sup>2+</sup> 2 <i>p</i> <sub>3/2</sub>
	711.0	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	713.0	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	722.5	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	724.5	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	726.6	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
<b>C3</b> – Fe 2 <i>p</i>	709.8	Fe <sup>2+</sup> 2 <i>p</i> <sub>3/2</sub>
	711.5	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	713.0	Fe <sup>3+</sup> 2 <i>p</i> <sub>3/2</sub>
	723.7	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	725.1	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>
	726.6	Fe <sup>3+</sup> 2 <i>p</i> <sub>1/2</sub>

<b>Sample Code</b>	<b>Binding Energy (eV)</b>	<b>Characteristic</b>
<b>A1</b> – O <i>1s</i>	530.0	Fe-O
	531.6	C-O
	532.8	O-H
<b>A2</b> – O <i>1s</i>	530.0	Fe-O
	531.6	C-O
	532.7	O-H
<b>A3</b> – O <i>1s</i>	530.1	Fe-O
	531.9	C-O
	532.9	O-H
<b>B1</b> – O <i>1s</i>	530.2	Fe-O
	531.5	C-O
	532.4	O-H
<b>B3</b> – O <i>1s</i>	530.2	Fe-O
	531.5	C-O
	532.3	O-H
<b>C1</b> – O <i>1s</i>	529.6	Fe-O
	531.7	C-O
	533.1	O-H
<b>C3</b> – O <i>1s</i>	530.1	Fe-O
	531.5	C-O
	532.4	O-H

<b>Sample Code</b>	<b>Binding Energy (eV)</b>	<b>Characteristic</b>
<b>A1 – C 1s</b>	285.0	C-C
	286.5	C-O
	288.4	O-C-C
<b>A2 – C 1s</b>	285.0	C-C
	286.6	C-O
	288.8	O-C-C
<b>A3 – C 1s</b>	284.9	C-C
	286.0	C-O
	288.6	O-C-C
<b>B1 – C 1s</b>	284.9	C-C
	286.4	C-O
	288.4	O-C-C
<b>B3 – C 1s</b>	284.9	C-C
	286.1	C-O
	288.6	O-C-C
<b>C1 – C 1s</b>	285.0	C-C
	286.6	C-O
	288.9	O-C-C
<b>C3 – C 1s</b>	285.0	C-C
	286.2	C-O
	288.8	O-C-C

**Table S3.**The percentage of weight loss at 400 °C and 700°C of prepared samples.

<b>Sample Code</b>	<b>Weight loss at 400 °C (%)</b>	<b>Weight loss at 700 °C (%)</b>
<b>A1</b>	65.95	69.73
<b>A2</b>	0.55	0.69
<b>A3</b>	63.67	67.33
<b>A4</b>	1.94	3.05
<b>B1</b>	74.12	76.47
<b>B2</b>	0.77	0.94
<b>B3</b>	73.87	74.40
<b>B4</b>	2.22	4.15
<b>C1</b>	13.39	13.44
<b>C2</b>	1.34	1.81
<b>C3</b>	10.92	10.88
<b>C4</b>	0.42	0.46

**Table S4.** BET analysis of prepared samples.

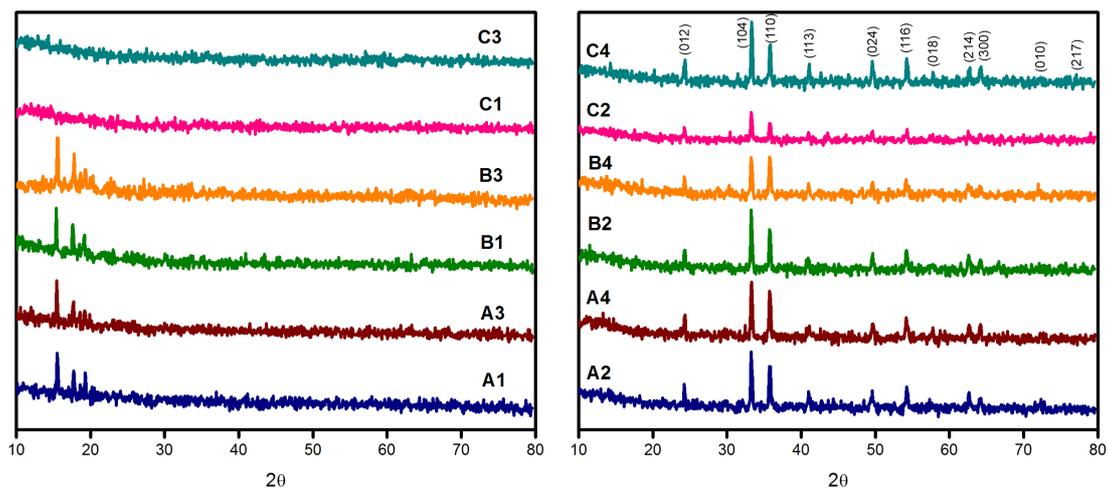
<b>Sample Code</b>	<b>Surface Area (m<sup>2</sup>/g)</b>	<b>Pore Volume (cc/g)</b>	<b>Pore Size (nm)</b>
<b>A1</b>	41.23	0.15	14.07
<b>A2</b>	35.71	0.07	8.34
<b>A3</b>	40.11	0.20	20.41
<b>A4</b>	28.26	0.09	13.44
<b>B1</b>	33.31	0.10	12.13
<b>B2</b>	33.38	0.11	13.35
<b>B3</b>	91.11	0.34	14.81
<b>B4</b>	23.76	0.14	23.39
<b>C1</b>	201.50	0.30	5.94
<b>C2</b>	27.73	0.18	25.70
<b>C3</b>	73.71	0.31	16.98
<b>C4</b>	31.82	0.08	10.95

**Table S5.** CHN analysis of prepared samples.

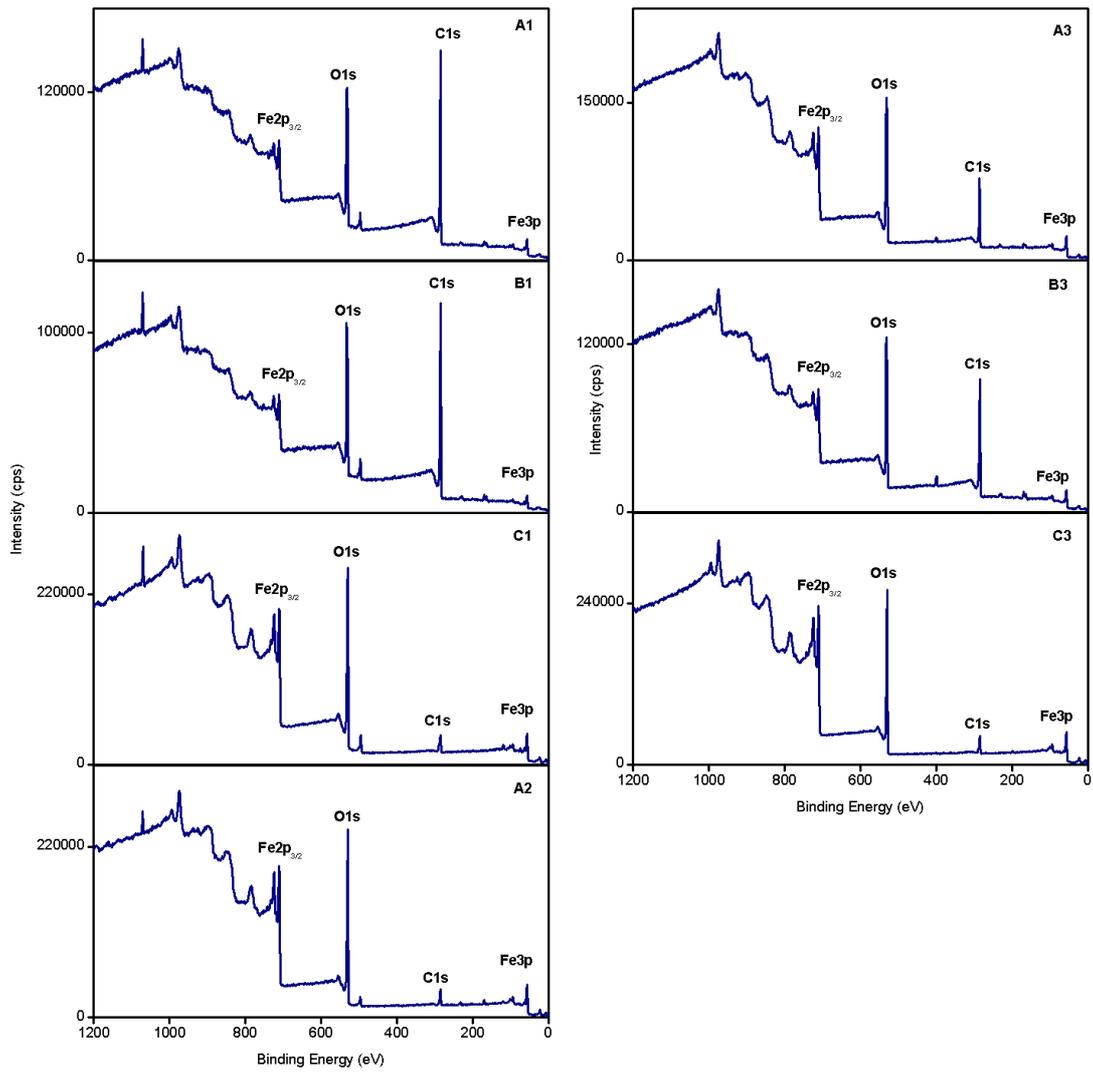
<b>Sample Code</b>	<b>%C</b>	<b>%H</b>
<b>A1</b>	41.36	3.86
<b>A2</b>	0.18	0.14
<b>A3</b>	40.45	3.77
<b>A4</b>	0.12	0.11
<b>B1</b>	46.79	3.99
<b>B2</b>	0.22	0
<b>B3</b>	47.20	4.12
<b>B4</b>	0.22	0.11
<b>C1</b>	0.64	0.92
<b>C2</b>	0.53	0.07
<b>C3</b>	0.34	0.91
<b>C4</b>	0.05	0.02

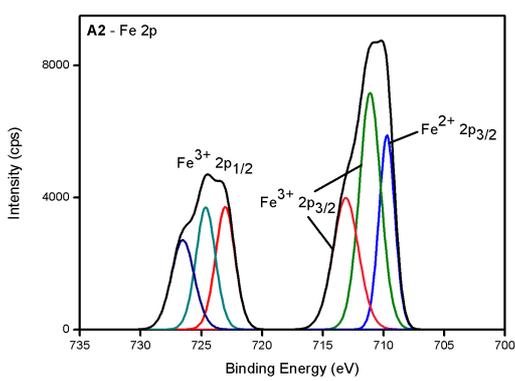
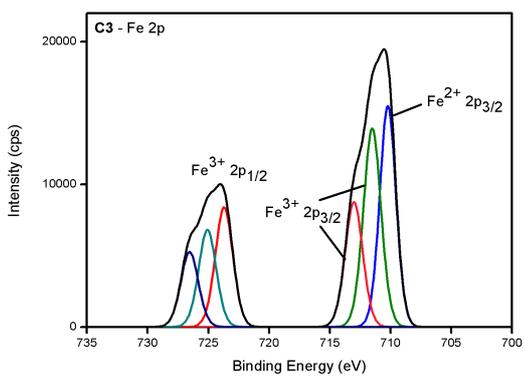
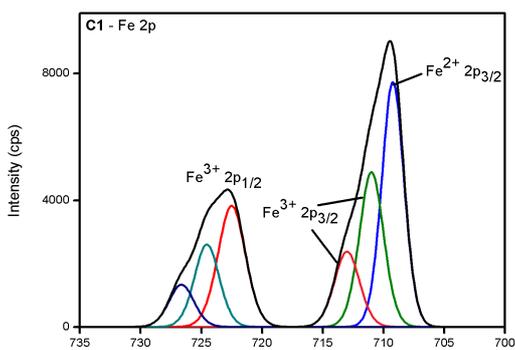
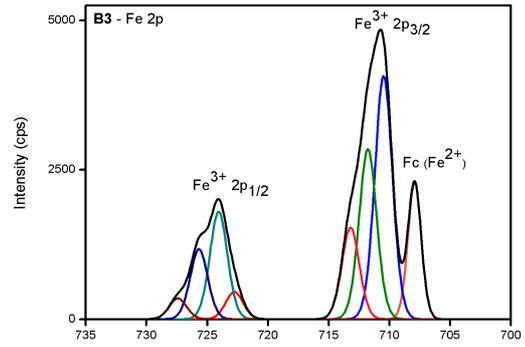
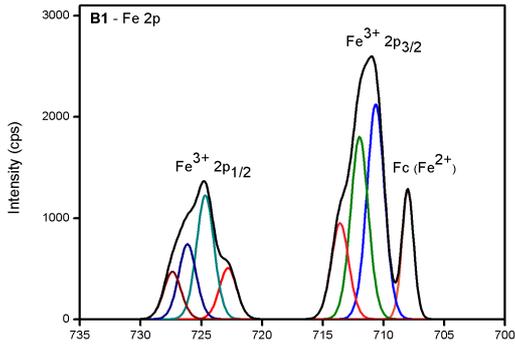
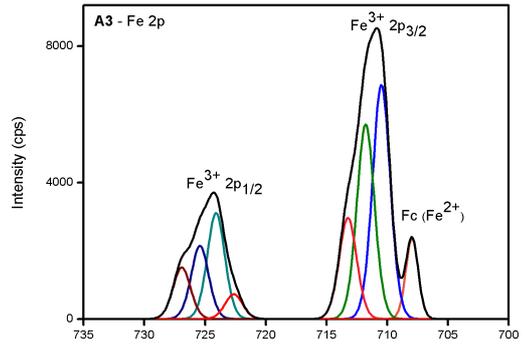
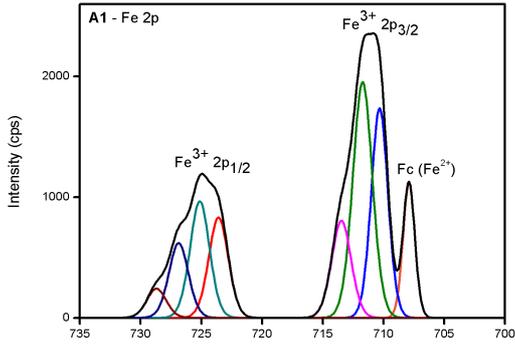
**Table S6.** The simulation of superoxide and hydroxyl adducts described with the hyperfine splitting constant of nitrogen and hydrogen on EPR.

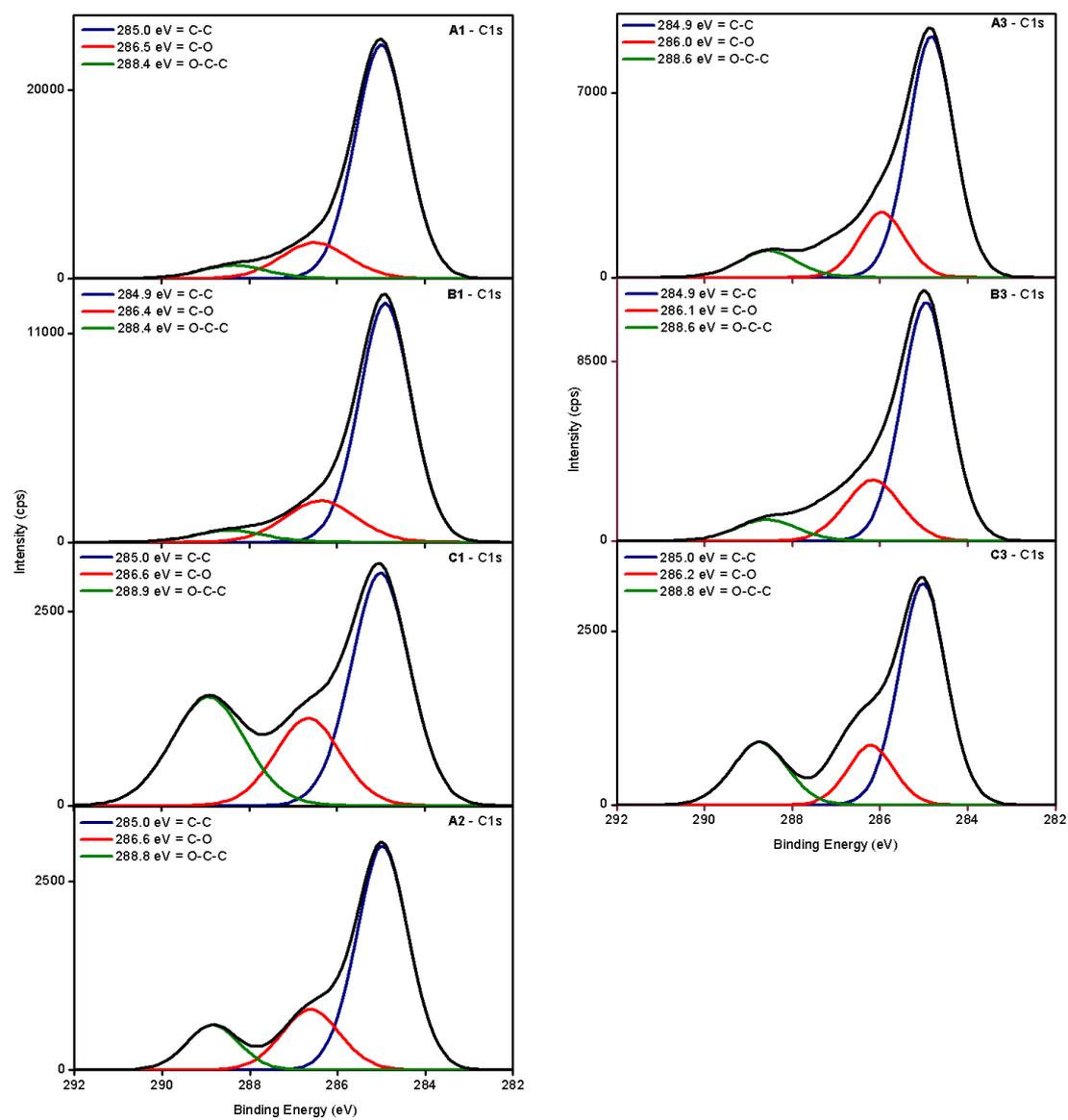
Sample	DMPO adduct	Hyperfine splitting constant of nitrogen (G)	Hyperfine splitting constant of hydrogen (G)
<b>A1</b> in DMPO / phosphate buffer (1 <sup>st</sup> time)	DMPO-OOH (~72%) DMPOX (~20%) DMPO-OH (~8%)	15.44 (a <sub>N</sub> ) 14.80 (a <sub>N</sub> ) 14.41 (a <sub>N</sub> )	22.85 (a <sub>H1</sub> ), 0.46 (a <sub>H2</sub> ) - 14.62 (a <sub>H</sub> )
<b>A1</b> reactivated with sodium chloride in DMPO / phosphate buffer (12 <sup>th</sup> times)	DMPO-OOH (~40%) DMPOX (~46%) DMPO-OH (~14%)	15.00 (a <sub>N</sub> ) 14.30 (a <sub>N</sub> ) 14.43 (a <sub>N</sub> )	22.35 (a <sub>H1</sub> ), 0.60 (a <sub>H2</sub> ) - 14.45 (a <sub>H</sub> )
<b>A1</b> reactivated with de-ionized water in DMPO / phosphate buffer (12 <sup>th</sup> times)	DMPO-OOH (~36%) DMPOX (~53%) DMPO-OH (~11%)	15.28 (a <sub>N</sub> ) 14.46 (a <sub>N</sub> ) 14.41 (a <sub>N</sub> )	22.30 (a <sub>H1</sub> ), 0.56 (a <sub>H2</sub> ) - 14.40 (a <sub>H</sub> )



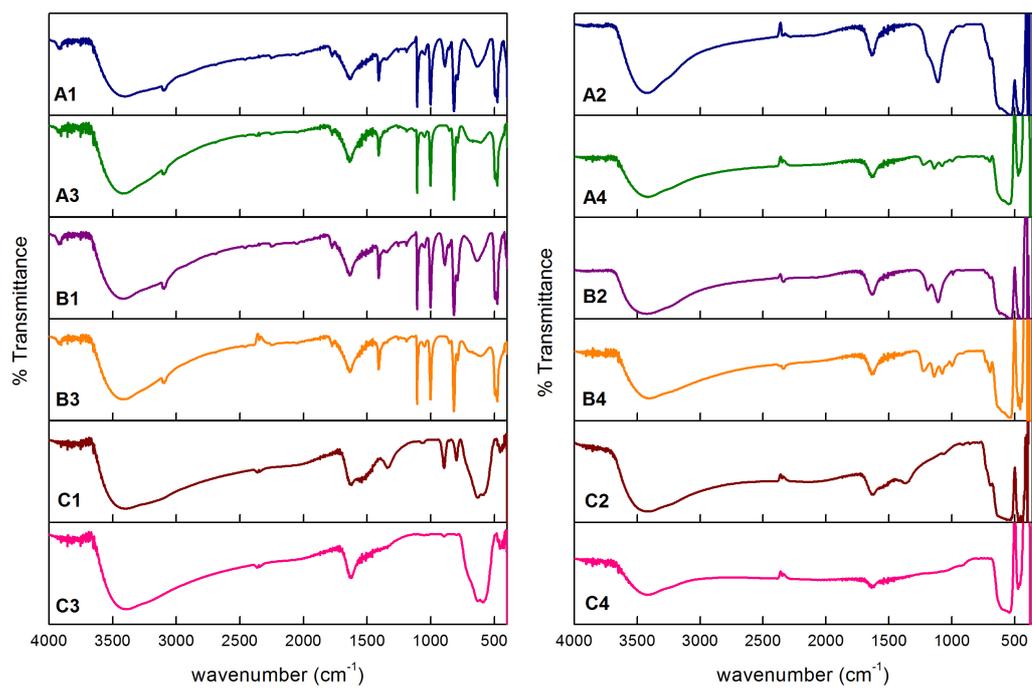
**Figure S1.** The XRD patterns of iron oxide before and after calcination.



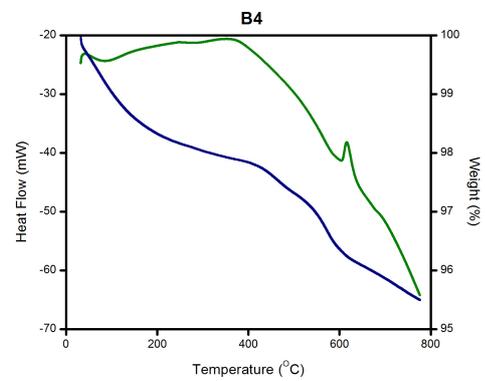
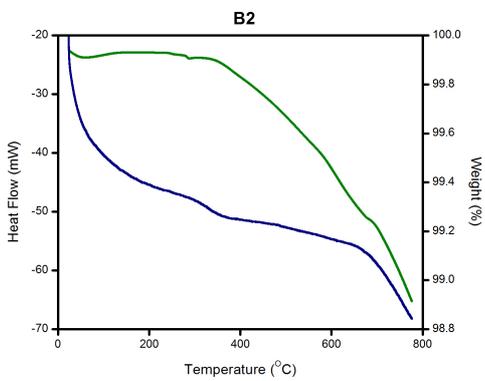
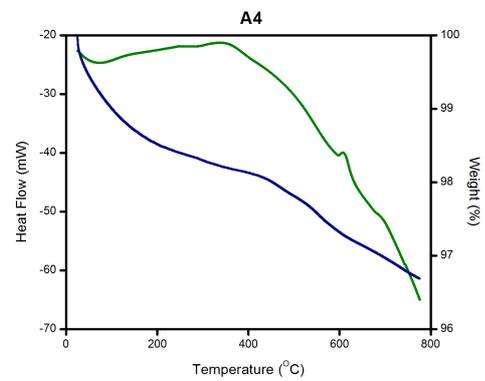
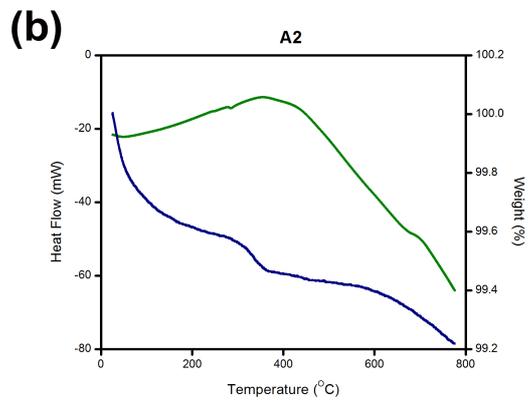
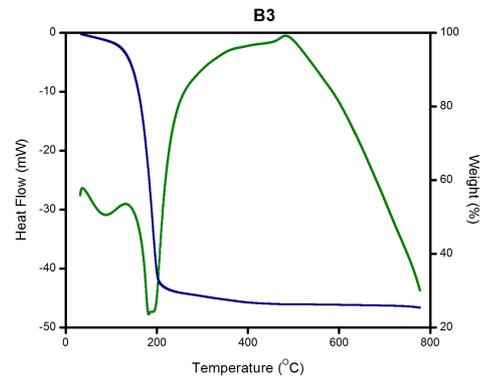
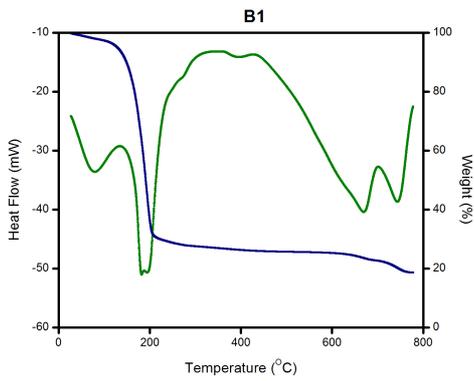
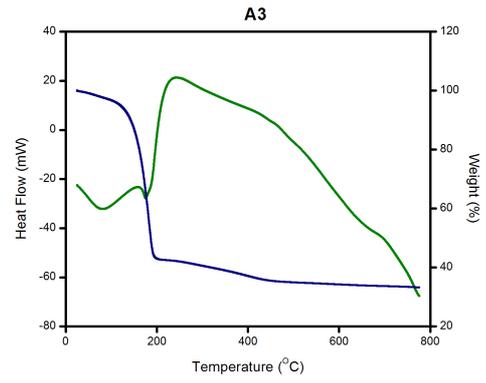
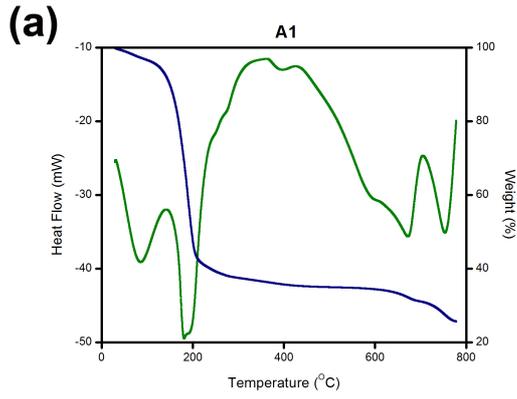


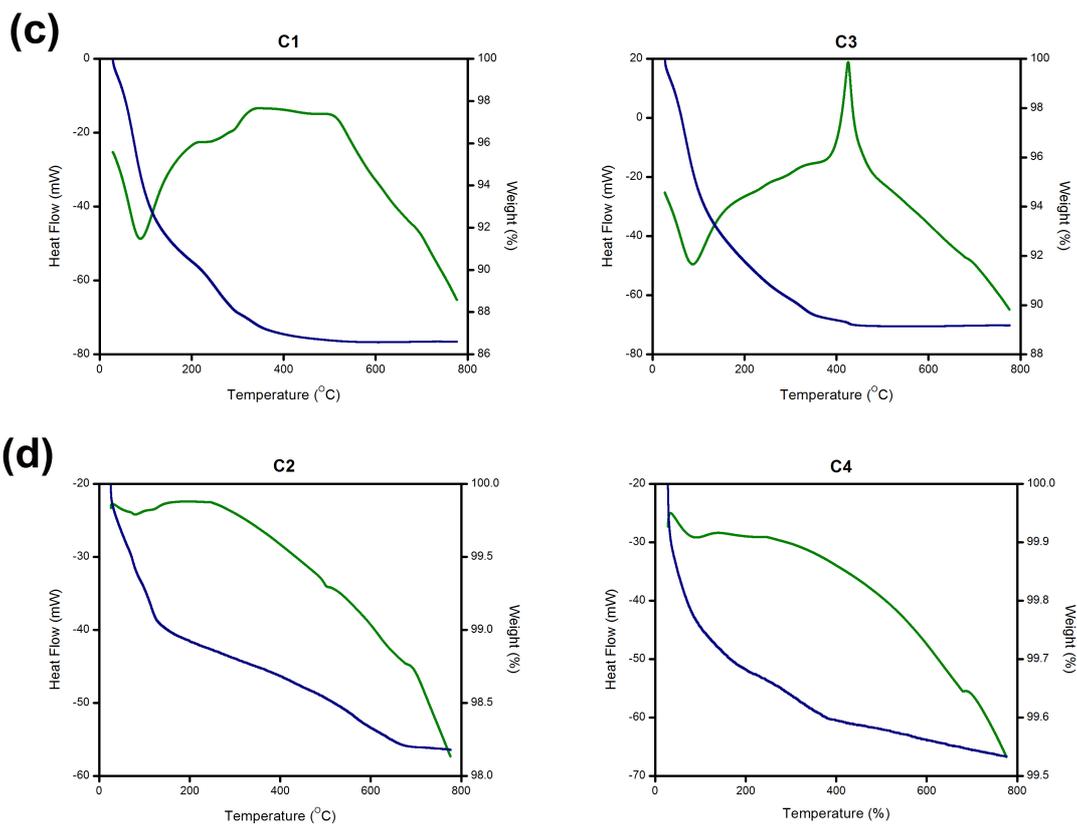


**Figure S2.** XPS spectra of prepared samples.

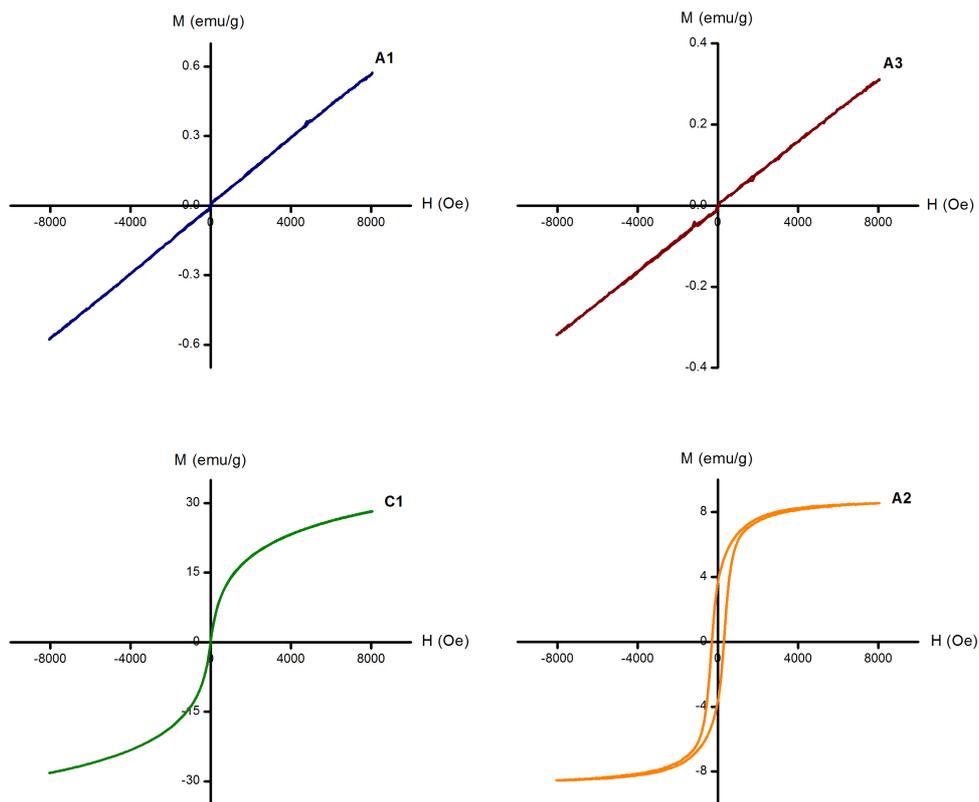


**Figure S3.** FTIR spectra of prepared samples (left) before calcination and (right) after calcination at 500 °C, 5 hours.

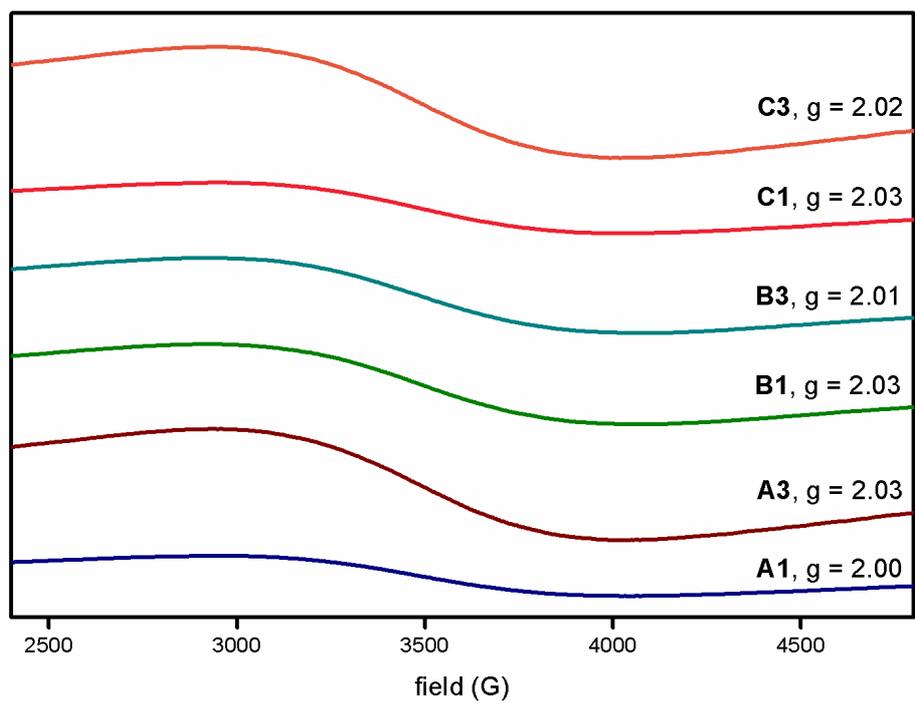




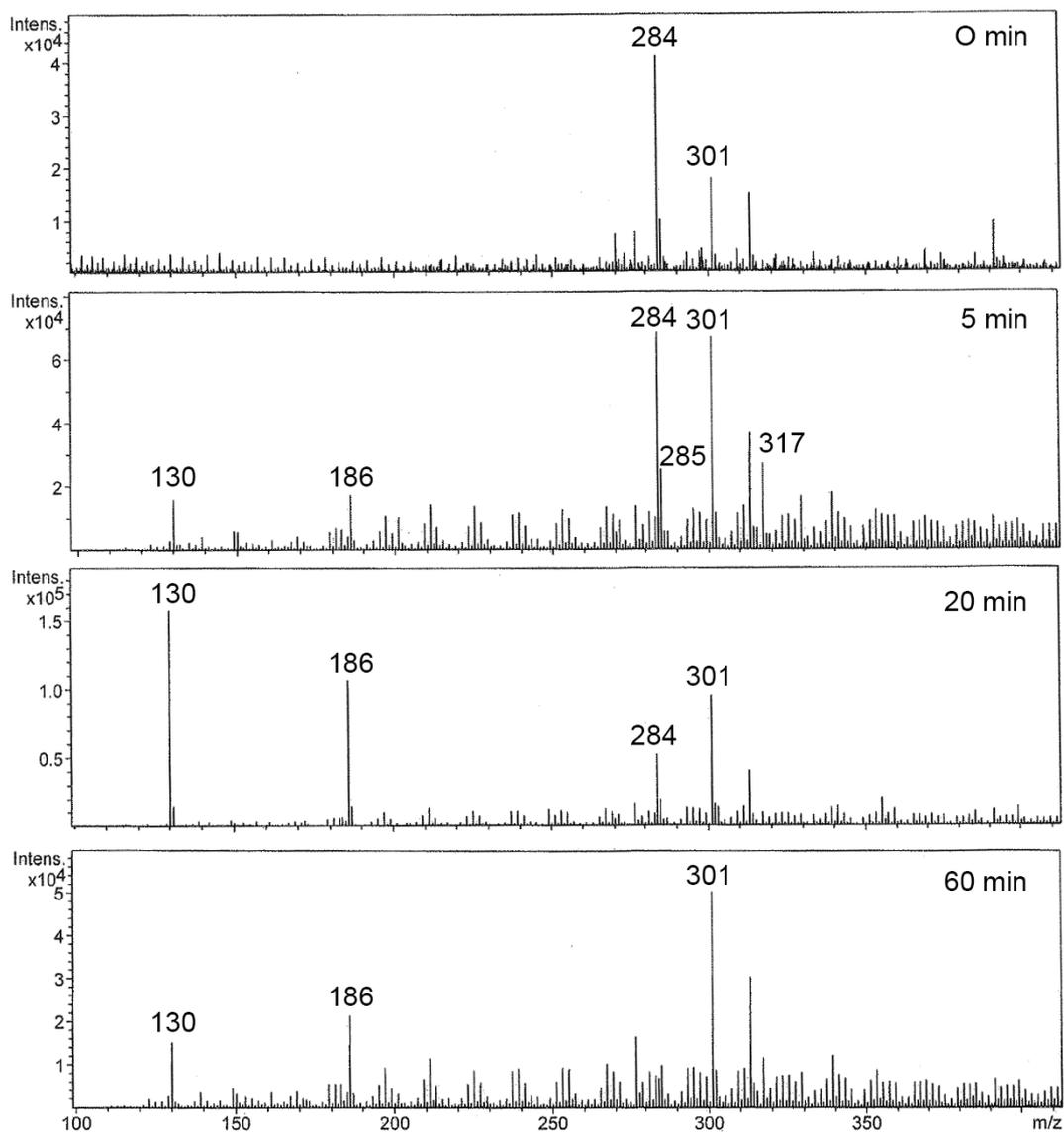
**Figure S4.** DSC/TGA of prepared samples.



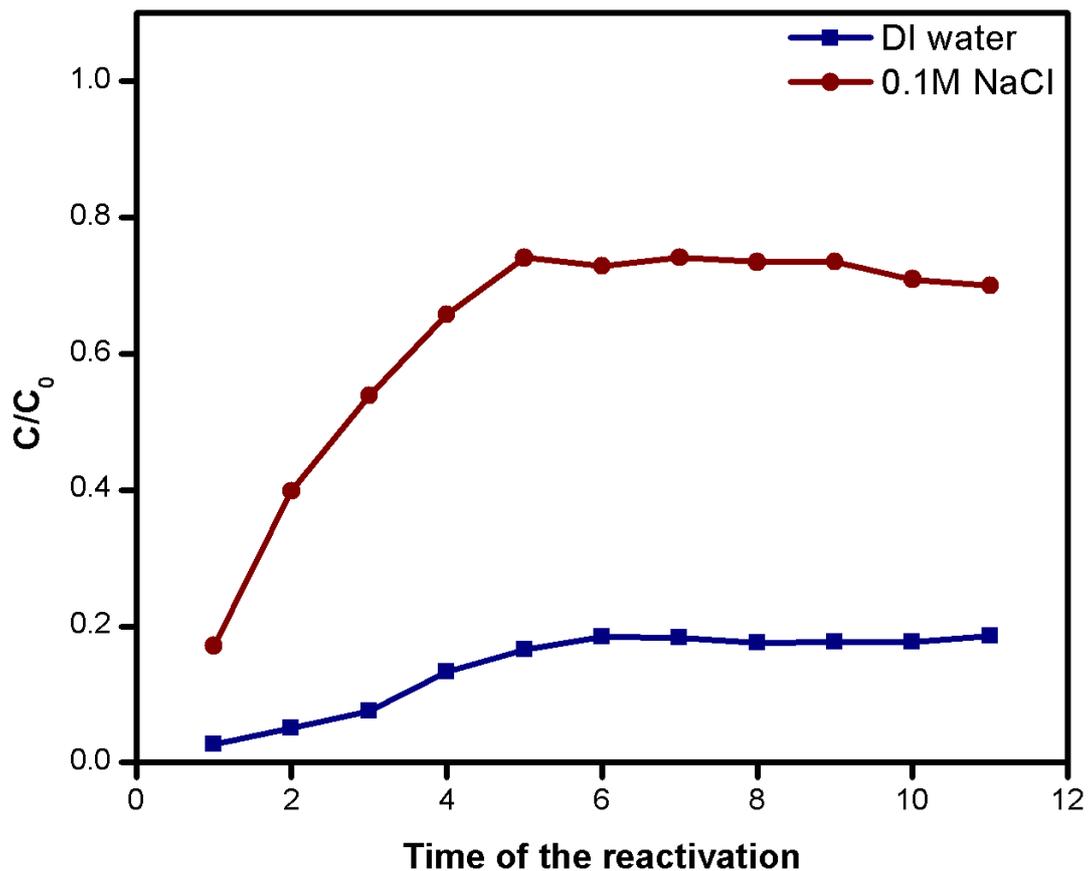
**Figure S5.** The magnetization curves of **A1**, **A2**, **A3**, and **C1** samples.



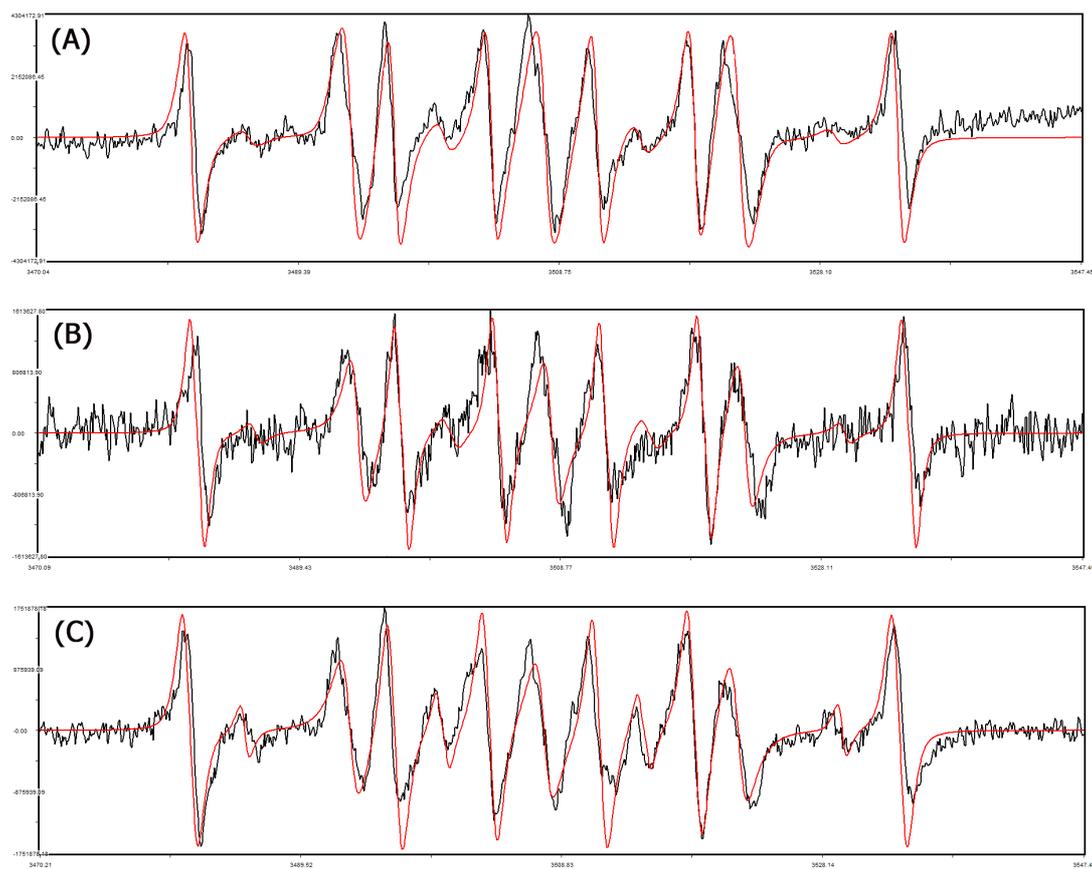
**Figure S6.** EPR spectra of prepared samples without calcination.



**Figure S7.** ESI-MS of decolorized methylene blue catalyzed by A1 catalyst.



**Figure S8.** Concentration of methylene blue vs. time of the reactivation of de-ionized water and 0.1 mol/dm<sup>3</sup> sodium chloride in methylene blue solution by A1 catalyst.



**Figure S9.** EPR spectra of **A1** in DMPO adduct and phosphate buffer after incubating for 20 minutes (A) **A1** in the 1<sup>st</sup> time (B) **A1** after reactivated with NaCl in the 12<sup>th</sup> times, and (C) **A1** after reactivated with DI water in the 12<sup>th</sup> times with experiment data in black line and red line for the simulation.

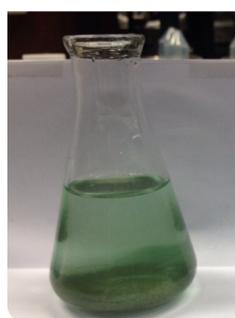
A1 in MB  
under air  
5 min



A1 in MB  
under Ar  
5 min



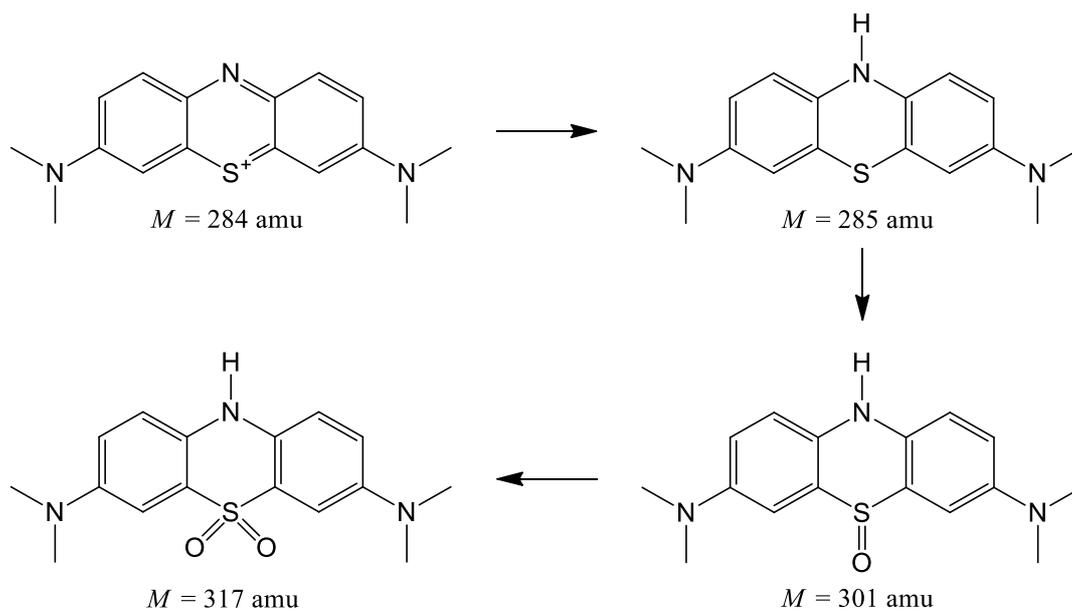
A1 in MB  
under air  
20 min



A1 in MB  
under Ar  
20 min



**Figure S10.** The comparison of the decolorization of methylene blue under air and Ar atmospheres.



**Scheme S1.** Possible decolorization products from methylene blue.