

## The sacrificial role of graphene oxide in stabilising Fenton-like catalyst GO-Fe<sub>3</sub>O<sub>4</sub>

Nor Aida Zubir<sup>a,b</sup>, Christelle Yacou<sup>a</sup>, Julius Motuzas<sup>a</sup>, Xiwang Zhang<sup>c</sup>, X. S. Zhao<sup>a</sup>, João C. Diniz da Costa<sup>a</sup>

<sup>a</sup> The University of Queensland, FIM<sup>2</sup>Lab – Functional and Interfacial Materials and Membranes, School of Chemical Engineering, The University of Queensland, Brisbane, Qld 4072, Australia.

<sup>b</sup> Universiti Teknologi MARA (UiTM), Faculty of Chemical Engineering, 13500 Pulau Pinang, Malaysia.

<sup>c</sup> Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia.

### Electronic Supplementary Information

#### 1.0 Experimental

##### 1.1 Materials and preparation of GO-Fe<sub>3</sub>O<sub>4</sub> nanocomposites

All reagents and solvents used in this work were commercially purchased and used as received. Graphite flakes, FeCl<sub>3</sub>·6H<sub>2</sub>O (97%), FeCl<sub>2</sub>·4H<sub>2</sub>O (99%) and AO7 (Orange II; 85%) were obtained from Sigma-Aldrich.

Graphite oxide (GO) was synthesised via a modified Hummer's method. Exfoliation of GO was then carried out by ultrasonication. The GO-Fe<sub>3</sub>O<sub>4</sub> materials were prepared by co-precipitating pre-hydrolysed ferric and ferrous salts in the presence of GO. Briefly, an aqueous solution (100 mL) containing FeCl<sub>3</sub>·6H<sub>2</sub>O (4 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (2 mmol) was prepared with an initial pH of 1.48 and subsequently adjusted to pH 4 via addition of NaOH (1 M). Then, the GO solution (50 mL, 0.55 mg/mL) was gradually added into the iron oxide solution under constant stirring for 30 min. The pH was further lowered to 10 by adding NaOH (1 M) to the mixture which was then aged at constant stirring for a further 30 min at room temperature. The resulting black precipitate was magnetically separated and washed three times with deionized water and ethanol followed by drying for 48 h in an oven at 60 °C. Blank samples of Fe<sub>3</sub>O<sub>4</sub> were also prepared by the same synthesis method though without the addition of GO solution.

## 1.2 Characterisation

X-ray photoelectron spectroscopy (XPS) was performed on Kratos Axis ULTRA X-ray photoelectron spectrometer equipped with monochromatic Al K $\alpha$  ( $h\nu = 1486.6$  eV) radiation to quantitatively analyse the chemical composition of GO–Fe<sub>3</sub>O<sub>4</sub> nanocomposites. The curve fitting was performed using a Gaussian–Lorentzian peak shape and Shirley background function. The C 1s photoelectron binding energy was set at 284.6 eV and used as a reference for calibrating all peak positions. Microstructural investigation was carried out by high resolution transmission electron microscopy (HRTEM, JOEL 2010) with an accelerating voltage of 200 kV. Samples were prepared by placing a drop of diluted sample dispersion in ethanol onto a carbon-coated copper grid and dried at room temperature. Field emission scanning electron microscope (FESEM) images were obtained using JEOL JSM-7001F. Atomic force microscopy (AFM) images of GO and GO–Fe<sub>3</sub>O<sub>4</sub> nanocomposites on a freshly cleaved mica surface were taken with a Veeco MultiMode AFM in tapping mode using OLTESPA-R3 silicon probe (Bruker). The XRD patterns of the nanocomposites were obtained using X-ray diffraction by a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA using filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Leaching of iron into solution was analysed by Inductively Coupled Plasma-Optical Emission spectroscopy (ICP-OES) (PerkinElmer).

## 1.3 Catalytic experiment

The stability and catalytic activity of nanocomposites was tested in continuous operation up to seven cycles at optimised reaction conditions [24] (0.2 g L<sup>-1</sup> GO–Fe<sub>3</sub>O<sub>4</sub>, initial pH of 3, 22 mM H<sub>2</sub>O<sub>2</sub>, 0.1 mM AO7 at 25 °C) for the oxidative degradation of AO7. The oxidative degradation was carried out without reclaiming the nanocomposite throughout the stability test. A known amount of AO7 stock solution was added into the reaction mixture in each cycle of reaction to keep its initial concentration constant prior to the re-initiation of reaction by H<sub>2</sub>O<sub>2</sub>. Sampling was carried out periodically and the concentration of AO7 was determined by measuring the absorbance of the solution at 484 nm on an Evolution 220 UV –Vis spectrophotometer (Thermo Fisher Sci.).

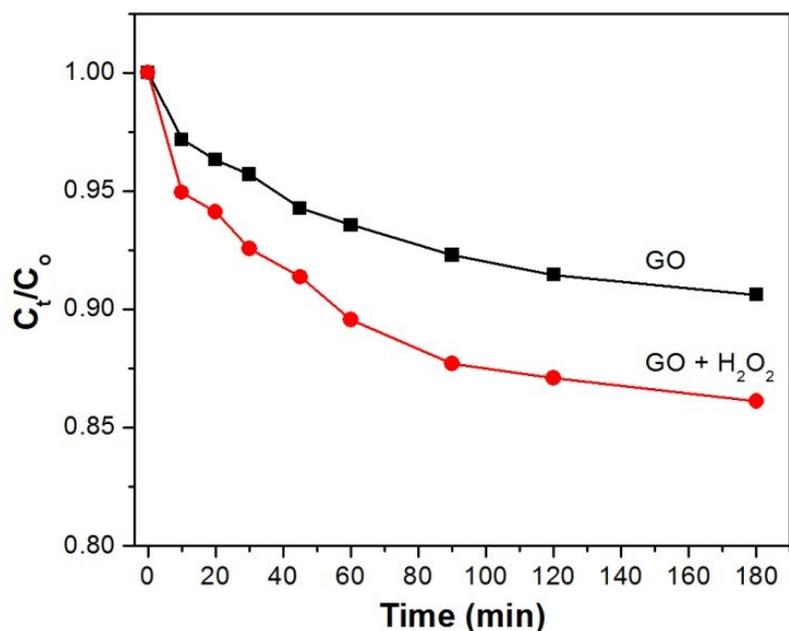
## 2.0 Results

**Table S1.** Atomic surface concentration of Fe<sup>3+</sup> and Fe<sup>2+</sup> on the samples before and after long-term stability test.

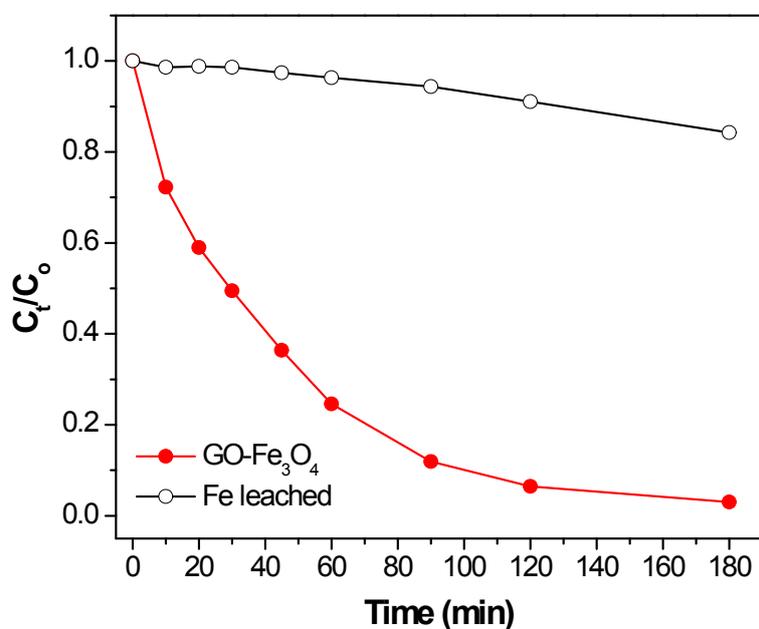
Sample	Cycles	Fe 2p <sub>3/2</sub>		Fe 2p <sub>1/2</sub>		Fe <sup>3+</sup> /Fe <sup>2+</sup>
		Fe <sup>2+</sup> (%)	Fe <sup>3+</sup> (%)	Fe <sup>2+</sup> (%)	Fe <sup>3+</sup> (%)	ratio
Fe <sub>3</sub> O <sub>4</sub>	0	26.24	43.15	7.026	23.58	2.01
	1	21.51	45.79	8.57	24.13	2.32
	3	20.47	50.02	7.56	21.95	2.57
	5	18.65	49.52	8.14	23.69	2.73
	7	16.07	51.56	7.13	25.24	3.31
GO-Fe <sub>3</sub> O <sub>4</sub>	0	24.96	44.97	8.31	21.76	2.01
	1	25.01	43.96	8.24	22.79	2.01
	3	24.9	44.53	8.34	22.23	2.01
	5	24.55	43.92	8.71	22.81	2.01
	7	24.85	43.77	8.46	22.91	2.00

**Table S2.** Deconvolution results of C 1s spectra for GO-Fe<sub>3</sub>O<sub>4</sub> nanocomposites before and after long-term stability test.

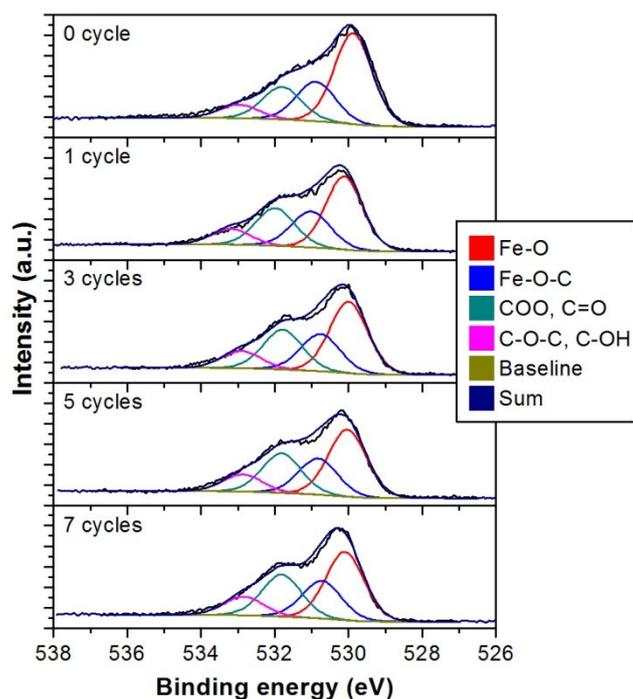
Cycles	Relative concentration of functional groups (At. %)			Reduction
	C=C sp <sup>2</sup>	C-C sp <sup>3</sup>	C=O	percentage of C=C sp <sup>2</sup> carbon domain (%)
0	61.40	15.29	4.67	0.00
1	60.95	15.07	4.90	0.73
3	53.31	16.01	7.83	13.18
5	51.62	16.48	8.27	15.93
7	49.91	16.93	8.80	18.71



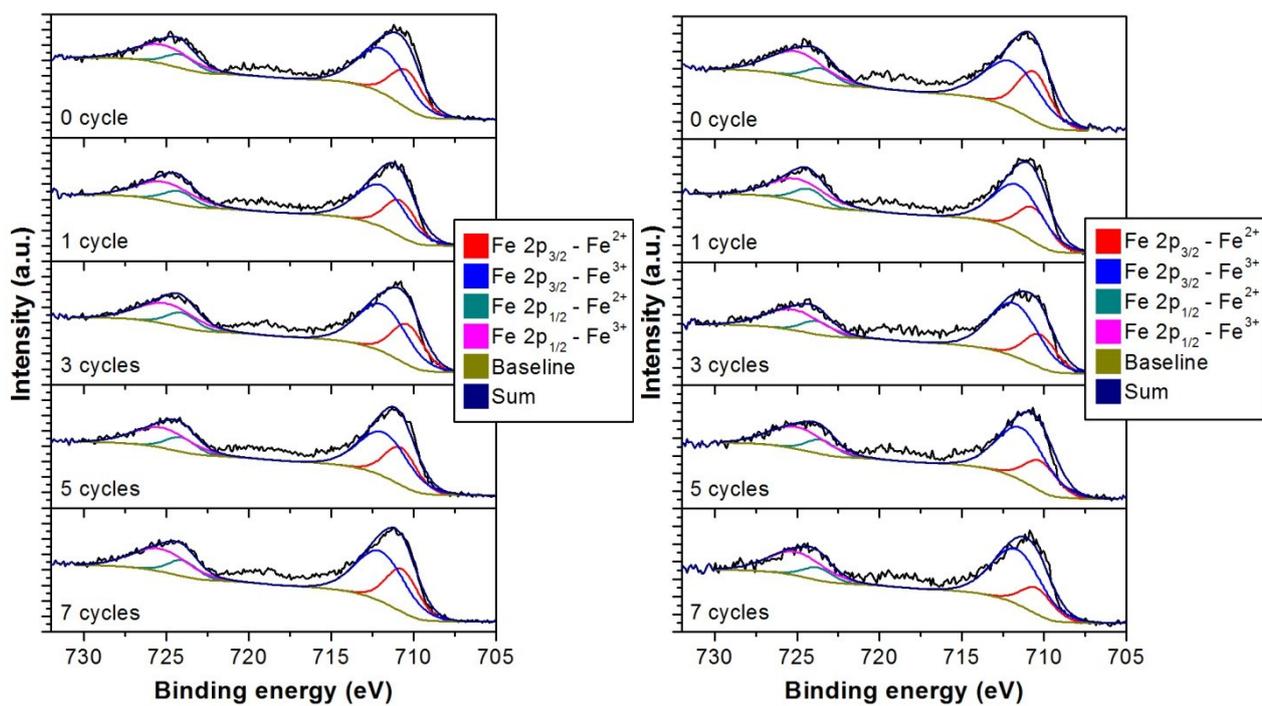
**Figure S1.** AO7 adsorption in GO (●), and AO7 degradation (○) in the presence of GO and H<sub>2</sub>O<sub>2</sub>. The AO7 degradation curve was copied from reference 6(N.A. Zubir, C. Yacou, J. Motuzas, X. Zhang and J.C. Diniz da Costa, Sci. Rep., 2014, 4, 4594).



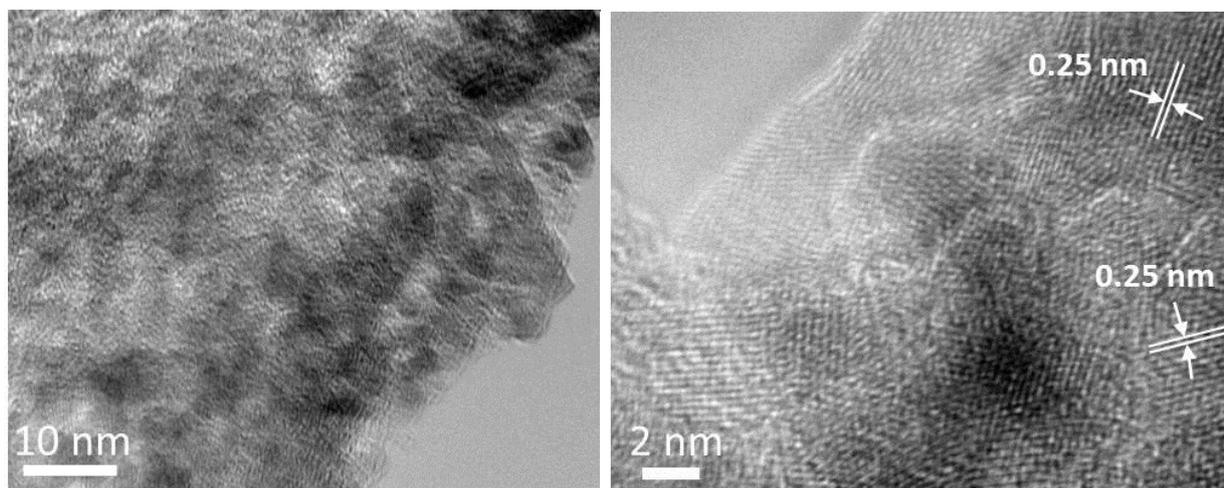
**Figure S2.** The effect of homogeneous and heterogeneous Fenton-like reaction on degradation of AO7. Experimental conditions: AO7 0.1 mM, H<sub>2</sub>O<sub>2</sub> 22 mM, pH 3 and T=25 °C.



**Figure S3.** O 1s core-level XPS spectra of GO-Fe<sub>3</sub>O<sub>4</sub> nanocomposites.



**Figure S4.** Fe 2p core-level XPS spectra of (a-left) GO-Fe<sub>3</sub>O<sub>4</sub> nanocomposites and (b-right) Fe<sub>3</sub>O<sub>4</sub> NPs.



**Figure S5.** HRTEM images at different magnifications of pristine of the used GO-Fe<sub>3</sub>O<sub>4</sub> after long-7 cycles of stability test.