# Supporting information

# Enhanced photocatalytic degradation of methylene blue and adsorption of arsenic (III) by reduced graphene oxide (rGO)-metal oxide (TiO$_2$/Fe$_3$O$_4$) based nanocomposites

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# S1.Nanocomposite preparations

## Preparation of graphene oxide

Graphene oxide (GO) was prepared by modified Hummer's method [1]. In brief, 5 g graphite powder was added to a mixed solution of 140 ml $H_2SO_4$ and 2.5 g $NaNO_3$. The mixture was vigorously stirred in an ice bath for 30 min. Subsequently, 15 g of $KMnO_4$ was slowly added to this stirred solution, which apparently changed the mixture color into green. The mixture was further stirred for 30 min. After completion of mixing, the resultant mixture was shifted to the water bath, and stirred for 30 min at 35 °C. The appearance of mixture gradually became pasty and color was changed from green to brown. Again, temperature was raised to 98 °C and 230 ml of DI water was added drop wise to the mixture stirred for 30 min. Subsequently, the mixture was allowed to cool at room temperature. Further, the solution was filtered and washed several times with DI water to remove the remaining solvent and impurities. After reaching at neutral pH, the resultant GO was dried at 80 °C for 24 h in ambient condition.

## Preparation of binary rGO-Fe$_3$O$_4$ nanocomposite

The rGO-Fe$_3$O$_4$ nanocomposite was synthesized by simple solvothermal reaction according to ref [2]. In a typical process, the as-prepared GO (0.5 g) was mixed in 80 mL of ethylene glycol and ultrasonicated for 1 h for the preparation of a homogenous dispersion. Further, at room temperature, 1.6 g $FeCl_3.6H_2O$ and 3.2 g NaAc were dissolved in the dispersion and stirred for 30 min. Subsequently, the solution was transferred to a $N_2$ purged Teflon-lined stainless-steel autoclave (200 mL) at 200 °C for 6 h followed by natural cooling at room temperature. Further, the as obtained black precipitate was ultrasonicated for 15 min and washed with ethanol as well

as with DI water for several times. Subsequently, the resultant nanocomposite was dried at 60 °C in the vacuum oven for 12 h.

**Preparation of binary rGO-TiO$_2$ nanocomposite**

The rGO-TiO$_2$ was synthesized by using a simple solvothermal method [3]. The as synthesized GO (0.5 mg/ml) was dispersed in 100 ml of water followed by sonication for 1 h to form a homogenous solution. The resultant solution was kept into a deep freezer below 5 °C. Simultaneously, for the preparation of TiO$_2$, 3 ml of TTIB was added to the stirred solution of EG (15 ml) and HAc (3 ml) in an ice bath at 5 °C. Further, the chilled GO solution was added slowly into TiO$_2$ solution and stirred vigorously for 1 h. Consequently, the resultant solution was transferred into a N$_2$ purged Teflon lined stainless steel autoclave (200 mL) for 8 h at 180 °C. After the completion of reaction, a grayish precipitate was obtained, which was washed with ethanol and DI water several times followed by drying at 60 °C for 12 h.

**Preparation of ternary rGO-Fe$_3$O$_4$-TiO$_2$ nanocomposite**

The ternary composite rGO-Fe$_3$O$_4$-TiO$_2$ was synthesized by using a very simple wet chemical method. Here, GO (0.5 mg/ml) was dispersed in the DI water and sonicated for 1 h, which made a homogeneous solution. Further, 0.1 mg/ml portion of Fe$_3$O$_4$ was mixed with GO solution and stirred for 1 h at room temperature. The resultant solution was washed with DI water and then filtered by 0.2 micron membrane filter. Subsequently the filtrate was dispersed into a solution of alcohol and water (140:10 v/v) and heated upto 70 °C. For TiO$_2$ incorporation, 500 µl of TTIB and 300 µl of H$_2$SO$_4$ were mixed in the above solution and stirred vigorously for another 12 h at

70 °C. The prepared rGO-$Fe_3O_4$-$TiO_2$ nanocomposite was washed with ethanol as well as in DI water and dried in vacuum oven at 60 °C for 12 h.

**Photocatalytic analysis**

The photocatalytic activity of synthesized binary and ternary nanocomposite was evaluated with the degradation of organic dye MB in a homemade closed setup under UV and visible light irradiation, both. The photocatalytic reactor was fabricated from the aluminum sheets having dimensions 15cm x 15cm x 30cm, where self-rectified 125-watt high-pressure mercury vapor (HPMV) bulb and white phosphor coated bulb were used as the UV and visible radiation sources, respectively. The working distance between the illumination source and catalyst solution was kept 20 cm and prior to photocatalytic experiment, both radiation sources were illuminated for 15 min. For the evaluation of photocatalytic degradation, dye solution was prepared by adding a measured amount (0.5 mg/ml) of rGO-$Fe_3O_4$, rGO-$TiO_2$ and rGO-$Fe_3O_4$-$TiO_2$ in 100 ml DI water separately, where the concentration of MB was kept 1 mg/L. For the initiation of Fenton like reaction, 1 ml of $H_2O_2$ (30 %) was also mixed with above photocatalytic solutions. Subsequently, the solution was irradiated with UV and visible light and a measured amount of the irradiated solutions was collected at a known time interval. All the photocatalytic experiments were performed under continuous stirring.

**Adsorption analysis**

To evaluate the adsorption efficiency of as synthesized binary and ternary nanocomposite, batch adsorption experiments have been carried out with Arsenic (III) contaminant. Adsorption isotherms were obtained by adding 10 mg of each nanocomposite to 50 mL of Arsenic (III)

solutions (pH 7.0) with varying concentrations of 3, 5, 7 and 10 ppm for 2 h. Adsorption kinetics were studied by adding 10 mg of each composite with 50 mL of 10 ppm Arsenic (III) solutions (pH 7.0) for 30, 60, 90 and 120 min time intervals. Here, all the experiments were carried out at room temperature. For homogenous dispersion of each nanocomposite, all the adsorption solutions were placed on a mechanical shaker at a speed of 140 rpm. The resultant suspensions were filtered out by 0.22 micro membrane filter and the residual concentration of Arsenic (III) was quantified. The initial and final concentration of Arsenic in solution was determined by atomic adsorption spectroscopy.
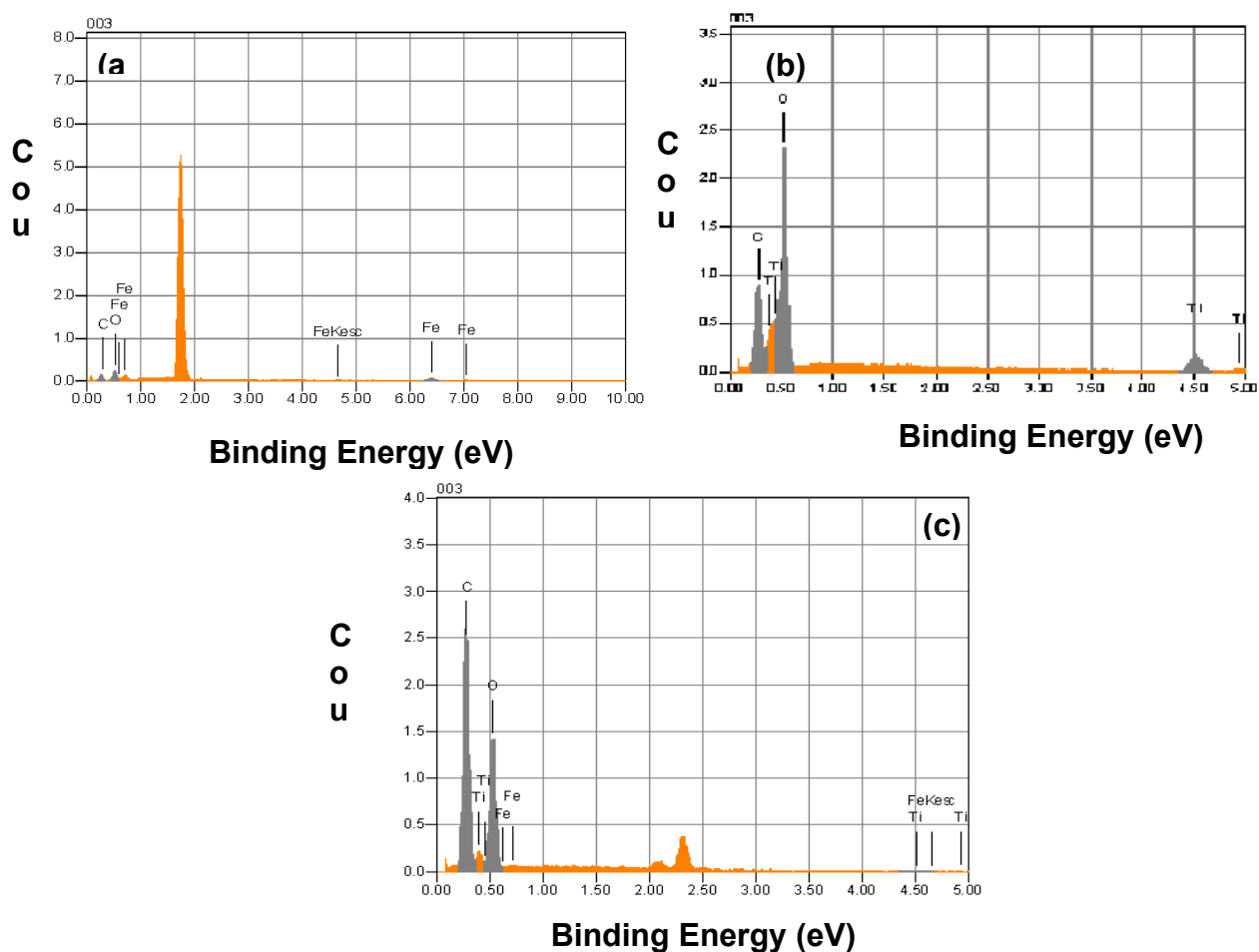
## S2.Results and discussions



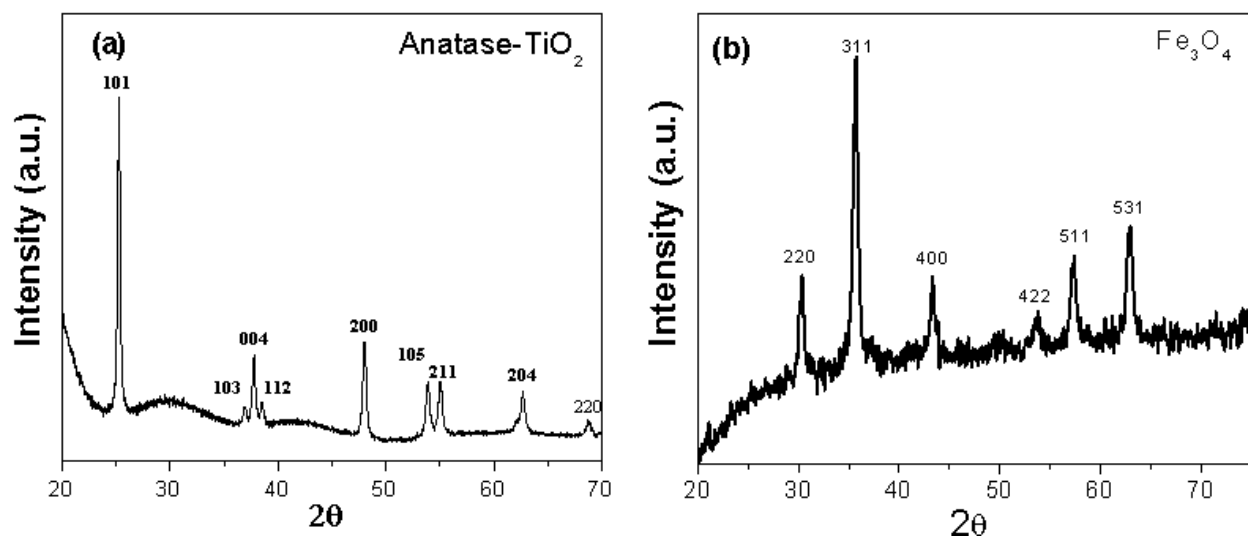**Fig.S1**: EDX spectrum of (a) rGO-TiO$_2$, (b) rGO-Fe$_3$O$_4$ and (c) rGO-Fe$_3$O$_4$-TiO$_2$.

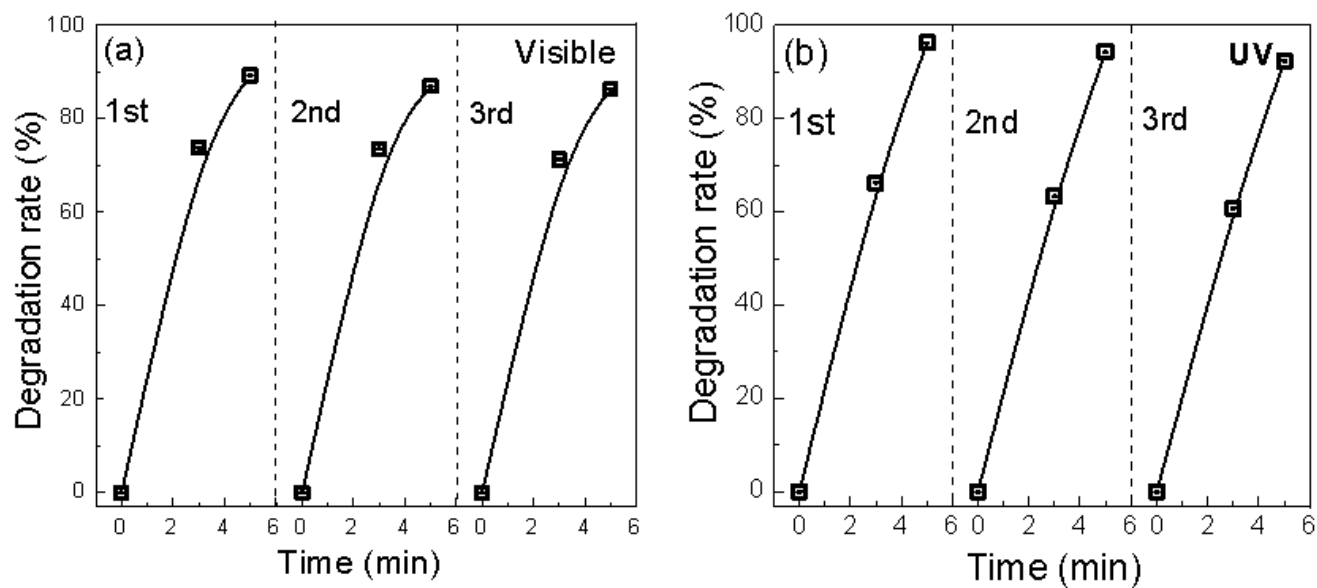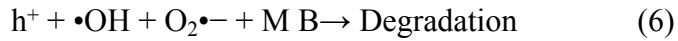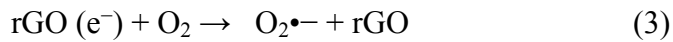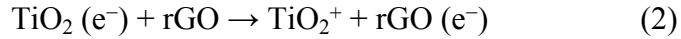**Fig.S2**: XRD of synthesized (a) antase $TiO_2$ and (b) $Fe_3O_4$.



**Fig.S3:** Recycled runs for the photocatalytic degradation of MB using rGO-$Fe_3O_4$-$TiO_2$

nanocomposite in presence of $H_2O_2$ (a) visible and (b) UV light irradiation.

**S3: Photocatalytic mechanism of MB degradation by TiO$_2$ and binary rGO-TiO$_2$**

The photocatalytic degradation of organic pollutant MB by TiO$_2$ and binary rGO-TiO$_2$ nanocomposite can be explained by following equations:
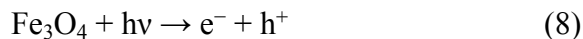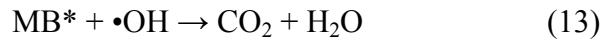
$$TiO_2 + h\upsilon \rightarrow \quad e^- + h^+ \qquad\qquad (1)$$

$$TiO_2 (e^-) + rGO \rightarrow TiO_2{}^+ + rGO (e^-) \qquad\qquad (2)$$

$$rGO (e^-) + O_2 \rightarrow \quad O_2{}^{\bullet-} + rGO \qquad\qquad (3)$$

$$O_2{}^{\bullet-} + H^+ \rightarrow HO\bullet \qquad\qquad (4)$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \qquad\qquad (5)$$

$$h^+ + \bullet OH + O_2{}^{\bullet-} + M\ B \rightarrow Degradation \qquad\qquad (6)$$

**S4**: In addition, in presence of UV irradiation, H$_2$O$_2$ plays vital role in degradation of MB as it generate two hydroxyl radical generate two hydroxyl radical, according to following equation [4].

$$H_2O_2 + h\upsilon \rightarrow 2\ HO\bullet \qquad\qquad (7)$$

**S5: Photocatalytic mechanism of MB degradation by Fe$_3$O$_4$ and binary rGO-Fe$_3$O$_4$**

The photo-degradation of MB by Fe$_3$O$_4$ and rGO-Fe$_3$O$_4$ nanocomposite under UV irradiation can be described by the following mechanism.

$$Fe_3O_4 + h\nu \rightarrow e^- + h^+ \qquad\qquad (8)$$

$$MB + h\nu \rightarrow MB^* \qquad\qquad (9)$$

$$Fe_3O_4 + rGO \rightarrow Fe_3O_4 + rGO\ (e^-) \qquad\qquad (10)$$

$$rGO\ (e^-) + O_2 \rightarrow rGO + O_2^{\bullet-} \qquad\qquad (11)$$

$$Fe_3O_4\ (h^+) + OH^- \rightarrow Fe_3O_4 + {\bullet}OH \qquad\qquad (12)$$

$$MB^* + {\bullet}OH \rightarrow CO_2 + H_2O \qquad\qquad (13)$$
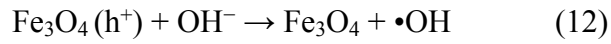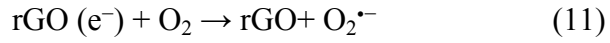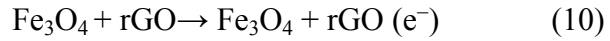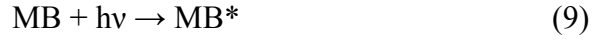
**S6**: Moreover, in the presence of $H_2O_2$, $Fe_3O_4$ nanoparticles initiate heterogeneous Fenton-like reaction, which further enhance adsorption rate due to catalytic degradation of MB molecules, .These reaction can be explained by the  following mechanism [5].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \qquad\qquad (14)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\bullet} + H^+ \qquad\qquad (15)$$

**Table S1.** EDX data for binary and ternary nanocomposites

| Samples→<br>Element↓ | wt.% | | |
|---|---|---|---|
| | rGO-TiO$_2$ | rGO-Fe$_3$O$_4$ | rGO-Fe$_3$O$_4$-TiO$_2$ |
| C | 24.45 | 28.14 | 20.38 |
| O | 55.32 | 54.98 | 71.67 |
| Ti | 20.23 | ---- | 6.64 |
| Fe | ---- | 16.88 | 1.32 |

**Table S2**. BET and BJH analysis of GO and as synthesized nanocomposites

| Sample | BET<br>Surface area<br>(m$^2$/g) | BJH<br>Pore surface<br>area (m$^2$/g) | BJH<br>Pore Volume<br>(cc/gm) | BJH<br>Pore radius<br>(Å) |
|---|---|---|---|---|
| GO | 47.100 | 159.058 | 0.279 | 18.120 |
| rGO-Fe$_3$O$_4$ | 84.503 | 90.220 | 0.366 | 18.156 |
| rGO-TiO$_2$ | 246.278 | 142.357 | 0.232 | 18.13 |
| rGO-Fe$_3$O$_4$-TiO$_2$ | 173.107 | 74.883 | 0.114 | 18.062 |

**Table S3** : Rate constant of synthesized nanocomposites

| Substrate | Samples | Rate constant (visible) k (min$^{-1}$) | Rate constant (UV) k (min$^{-1}$) |
|---|---|---|---|
| | TiO$_2$ | 0.03 | 0.10 |
| Methylene blue (MB) | rGO-TiO2 | 0.11 | 0.13 |
| | Fe$_3$O4 | 0.005 | 0.01 |
| | rGO-Fe$_3$O$_4$ | 0.02 | 0.04 |
| | rGO-Fe$_3$O$_4$-TiO$_2$ | 0.44 | 0.58 |

**Table S4**. Langmuir and Freundlich adsorption isotherm parameters of the As(III) adsorption on nanocomposites at room temperature (pH~7.0)

| Isotherm | Parameters | | |
|---|---|---|---|
| **Langmuir** | $Q_m$ **(mg/g )** | $K_L$ **(Lmg$^{-1}$ )** | **R$^2$** |
| rGO-TiO$_2$ | 10.06 | 0.140 | 0.9703 |
| rGO-Fe$_3$O$_4$ | 33.22 | 0.071 | 0.9903 |
| rGO-Fe$_3$O$_4$-TiO$_2$ | 147.05 | 0.016 | 0.9815 |
| **Freundlich** | **K$_f$** **(L mg$^{-1}$)** | **n** | **R$^2$** |
| rGO-TiO$_2$ | 1.77086 | 1.89 | 0.9864 |
| rGO-Fe$_3$O$_4$ | 1.01478 | 1.42 | 0.9967 |
| rGO-Fe$_3$O$_4$-TiO$_2$ | 0.90714 | 1.09 | 0.9995 |

**Table S5**. Kinetic parameters for the adsorption of As(III) obtained by pseudo second order model and intraparticle diffusion model at room temperature (pH~7.0)

| Nanocomposites | $Q_e$ (mg/g) | $K_1$ (g /mg min) | $h_0$ (mg /g min) | $K_i$ ( mg/g min$^{0.5}$) | $R^2$ |
|---|---|---|---|---|---|
| rGO-TiO$_2$ | 9.00 | 1.56 x 10$^{-3}$ | 0.126 | 0.5242 | 0.9559 |
| rGO-Fe$_3$O$_4$ | 20.16 | 1.12 x 10$^{-3}$ | 0.455 | 1.3747 | 0.9913 |
| rGO-Fe$_3$O$_4$-TiO$_2$ | 27.32 | 0.87 x 10$^{-3}$ | 0.650 | 1.8817 | 0.9766 |

where, $h_0$ is the initial adsorption rate and obtained by [6],

$$h_0 = K_1 \times Q_e^2$$

**References:**

[1]     W. S. Hummers Jr and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.

[2]     C. Santhosh, P. Kollu, S. Doshi, M. Sharma, D. Bahadur, M. T. Vanchinathan, P. Saravanan, B.-S. Kim and A. N. Grace, *RSC Adv.*, 2014, **4**, 28300-28308.

[3]     L.-L. Tan, W.-J. Ong, S.-P. Chai and A. R. Mohamed, *Nanoscale Res Lett*, 2013, **8**, 1-9.

[4]     J. Baxendale and J. Wilson, *Trans. Faraday Soc.*, 1957, **53**, 344-356.

[5]     Y. Qin, M. Long, B. Tan and B. Zhou, *Nano-Micro Letters*, 2014, **6**, 125-135.

[6]     Y. S. Ho and G. McKay, *Chem. Eng. J.*, 1998, **70**, 115-124.