Green Fabrication of Graphene Aerogel Using Pineapple Juice for Efficient Degradation of Synthetic Dyes

Supporting Information

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1. Experimental

1.1 Determination of total polyphenol content

The total polyphenol content in the juice was determined using the Folin-Ciocalteu method, a widely accepted standard for quantifying total polyphenols in food and plant-derived products [1, 2]. Specifically, a standard calibration curve was prepared using gallic acid as the reference compound, with concentrations ranging from 1.0296 to 14.4144 µg/mL.

To perform the assay, 1 mL of Folin-Ciocalteu reagent was pipetted into test tubes containing the respective gallic acid standard solutions and incubated in the dark for 5 minutes. Subsequently, 7% Na_2CO_3 was added to bring the final volume to 5.0 mL, followed by a further incubation in the dark for 30 minutes. The absorbance was then measured at 650 nm using an UV-vis spectrophotometer. For the juice sample, 0.1 mL of juice was pipetted into a test tube and processed using the same procedure as the standard. The experiment was performed in triplicate for accuracy. The total polyphenol content of the juice sample was calculated using Eq. (1)

$$P = \frac{x \times V}{V_m} \qquad (1)$$

In which P is the total polyphenol content (µg GAE/mL juice), x is the concentration derived from the gallic acid calibration curve (µg/mL), V is the total volume (mL), and V_m is the volume of the juice sample (mL).

1.2 Determination of vitamin C content

The vitamin C content in pineapple juice was determined using iodine titration, a widely used method for quantifying ascorbic acid based on its reducing properties. The required reagents were prepared as follows: 10% potassium iodide (KI) and 10% potassium iodate (KIO_3) solutions were prepared by dissolving 5.0 g of KI and 5.0 g of KIO_3 separately in distilled water, transferring each solution to a 100 mL volumetric flask, and diluting to the mark. A 0.05% (w/v) sodium thiosulfate ($Na_2S_2O_3$) standard solution was prepared by accurately weighing 0.08 g of $Na_2S_2O_3$, dissolving it in distilled water, transferring the solution into a 100 mL volumetric flask, and diluting to the mark with distilled water under continuous stirring to ensure complete dissolution. The 0.5% starch indicator was prepared by dissolving 0.25 g of starch in 50 mL of distilled water, transferring the solution to a 100 mL volumetric flask, and diluting to the mark with distilled. The 5% sulfuric acid (H_2SO_4) solution was prepared by carefully adding 5 mL of concentrated H_2SO_4 to 95 mL of distilled water with continuous stirring. The titration procedure was conducted as follows: 30 mL of pineapple juice was pipetted into a conical flask, followed by the addition of 1.0 mL of 10% KIO_3, 5.0 mL of 10% KI, and 5.0 mL of 5% H_2SO_4 to facilitate the generation of iodine through the reaction between

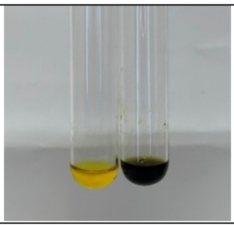
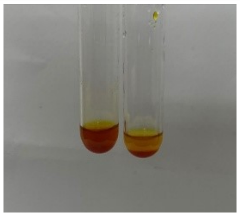
KIO_3 and KI. The mixture was incubated in the dark for 5 minutes to ensure complete reaction. Titration was then carried out using 0.05% $Na_2S_2O_3$, added dropwise until the solution turned yellow. Subsequently, 2.0 mL of starch indicator was introduced, causing the solution to turn blue-black. The titration continued with further addition of 0.05% $Na_2S_2O_3$ until the blue-black color disappeared, indicating the endpoint. The experiment was performed in triplicate for accuracy. The vitamin C content in the pineapple juice was calculated using Equation (2) [3, 4].

$$C = \frac{(N \times V)_{\mathrm{Na_2S_2O_3\ blank}} - (N \times V)_{\mathrm{Na_2S_2O_3\ sample}}}{V_m} \times \frac{M_{VTC}}{2} \times 100 \qquad (2)$$

In which C is the vitamin C content in pineapple juice (mg), N is the concentration of the standard $Na_2S_2O_3$ (%),$V_{Na_2S_2O_3}$ is the consumed titration volume of $Na_2S_2O_3$ (mL), V_m is the volume of the juice sample (mL), and M_{VTC} is the molecular weight of vitamin C (g/mol).

1.3 Qualitative identification of additional compounds

Table S1. Results for qualitative identification of compounds in pineapple juice

Compounds	**Indicators**	**Sample photographs (Left: DI water; Right: Pineapple juice)**		**Results**
		Before	**After**	
Tannin	$FeCl_3$ 3%			A dark blue color appeared. Tannin was present
Flavonoid	NaOH 1M			A deep yellow color appeared. Flavonoid was present
Alkaloid	Dragendorff			A reddish-brown precipitate appeared. Alkaloid was present

1.4 Fabrication of graphene oxide

Graphene oxide (GO) was synthesized using the modified Hummers method. First, 25 mL of concentrated H_2SO_4 was added to a round-bottom flask placed in an ice-water bath maintained at a temperature below 10°C, with continuous magnetic stirring. After 15 minutes, 0.5 g of graphite and 0.5 g of $NaNO_2$ were sequentially added to the mixture, which was stirred for 30 minutes. Subsequently, 3 g of $KMnO_4$ was slowly added in small portions to prevent the formation of $KMnO_4$ aggregates. The mixture was stirred continuously for 1 hour, during which it turned dark green. Next, the round-bottom flask was removed from the ice bath, and transferred to a heating mantle inside a fume hood. The temperature was set to 35°C, and the mixture was stirred continuously for 1 hour. Then, 40 mL of distilled water was added, and the temperature was increased to 90°C, with continued stirring for another hour, during which the solution turned brown. The heating was then turned off, and 100 mL of distilled water was added. Stirring continued for additional 1 hour, ensuring that the solution cooled down. After this, 5 mL of H_2O_2 was added dropwise, followed by continuous stirring for 15 minutes. At this stage, the solution color changed from brown to yellowish-brown. Upon completion of the reaction, the product was filtered and washed with acetone until a neutral pH (~7) was achieved. The solid product was then dried overnight at 50–60°C to obtain graphite oxide. Finally, the graphite oxide was dispersed in water and subjected to ultrasonication for 12 hours at 700 W to yield the final GO suspension.

1.4 Synthesis of Fe_3O_4 nanoparticles

To synthesize Fe_3O_4 nanoparticles (NPs) functionalized with citric acid, an appropriate quantity of $FeCl_2\cdot4H_2O$ and $FeCl_3\cdot6H_2O$ was first dissolved in 80 mL of deionized (DI) water under ultrasonication for 30 minutes to achieve a homogeneous mixture. The solution was then gradually heated to 70°C and maintained at this temperature for another 30 minutes. Subsequently, 20 mL of NH_4OH was slowly introduced dropwise to induce the precipitation of Fe_3O_4 nanoparticles. Once the NH_4OH addition was completed, 1.2 g of citric acid was added to the reaction medium, and the mixture was continuously stirred for an additional 30 minutes, leading to the formation of black precipitates. The reaction system was then left to cool naturally to room temperature. The resulting Fe_3O_4 NPs, functionalized with citric acid, were collected by centrifugation at 9000 rpm. The precipitated solid underwent multiple washing steps using DI water and ethanol to remove any unreacted components or byproducts. After purification, the solid was subjected to drying in an oven at 60°C for several hours to eliminate residual moisture. The final dried product was then finely ground to yield citric acid-functionalized Fe_3O_4 nanoparticles, designated as Fe_3O_4@COOH.

2. Results and discussion

2.1 Total polyphenol content in pineapple juice

The calibration curve was established to describe the relationship between UV-Vis absorbance and gallic acid concentration, yielding the equation $y = 0.0875x + 0.0028$ with a correlation coefficient $R^2 = 0.9983$. This high R^2 value indicates good linearity, enabling accurate determination of the polyphenol content in the samples.

Table S2. The data of the calibration curve

Concentration (μg/mL)	1.0296	2.0592	4.1184	6.1776	8.2368	10.2960	12.3552	14.4144
Absorbance (Abs)	0.089	0.159	0.378	0.547	0.745	0.91	1.096	1.238

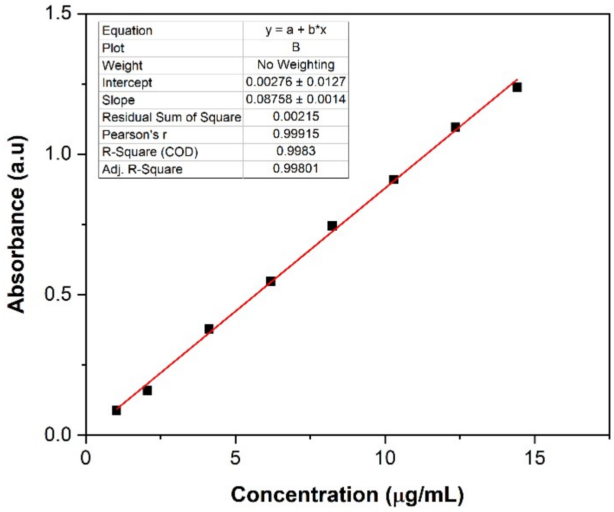


Figure S1. The gallic acid calibration curve

Table S3. The data of calculated total polyphenol content in pineapple juice

Sample	**V_m (mL)**	**V (mL)**	**Abs**	**x (μg/mL)**	**P calculated from eq.(1)**	**Average**	**RSD**
Pineapple juice	0.1	5.0	1.020	11.612	580.60	579.83	0.15%
			1.017	11.578	578.90		
			1.019	11.600	580.00		

The total polyphenol content of the pineapple juice was 579.83 ± 0.86 µg GAE/mL juice, with three replicates, as presented in Table S2. When compared with previous studies on the total polyphenol content in fruit juices, values such as 0.79 ± 0.07 mg GAE/g juice [1], 573.9 mg GAE/L in orange juice [5], 377.3 mg GAE/L in apple juice [6], and 410.9 ± 2.1 mg GAE/L in guava nectar and juice have been reported [7]. Additionally, fresh mango has been shown to contain 9.26 ± 0.77 mg GAE/g [8].

The findings of this study indicate that the total polyphenol content in pineapple juice samples is higher than that reported in previous studies on pineapple juice and fresh fruit juices. However, variations in polyphenol content among different fruits may be influenced by factors such as fruit maturity, with tropical fruits generally exhibiting relatively high polyphenol levels [9].

2.2 The vitamin C contents in pineapple juice

The vitamin C content in pineapple juice was determined to be 44.98 ± 0.85 mg/100 mL, with three replicates, as presented in Table S3. Previous studies have reported vitamin C concentrations in pineapple juice of 54.68 ± 21.67 mg/g [3] and 6.40 ± 0.18 mg/100 mL [4], suggesting that the results of this study are reasonably consistent when applying the iodine titration method. While the iodine titration method provides reliable results for most samples when used exclusively for vitamin C determination, its accuracy may be affected in samples with very dark colors, as color interference can impact the titration endpoint observation.

Table S4. The data on the vitamin C content in pineapple juice

Sample	**No. Of test**	**N (%)**	$V_{Na_2S_2O_3}$ **(mL)**	**V$_m$ (mL)**	**M$_{VTC}$ (g/mol)**	**C (mg) from Formula (2)**	**Average**	**SD**
Pineapple juice	1	0.05	1.6	30	176.124	45.47	44.98	0.85
	2		1.7			44.00		
	3		1.6			45.47		
Blank			4.7					

2.3 Morphology and chemical structures of the as-prepared materials

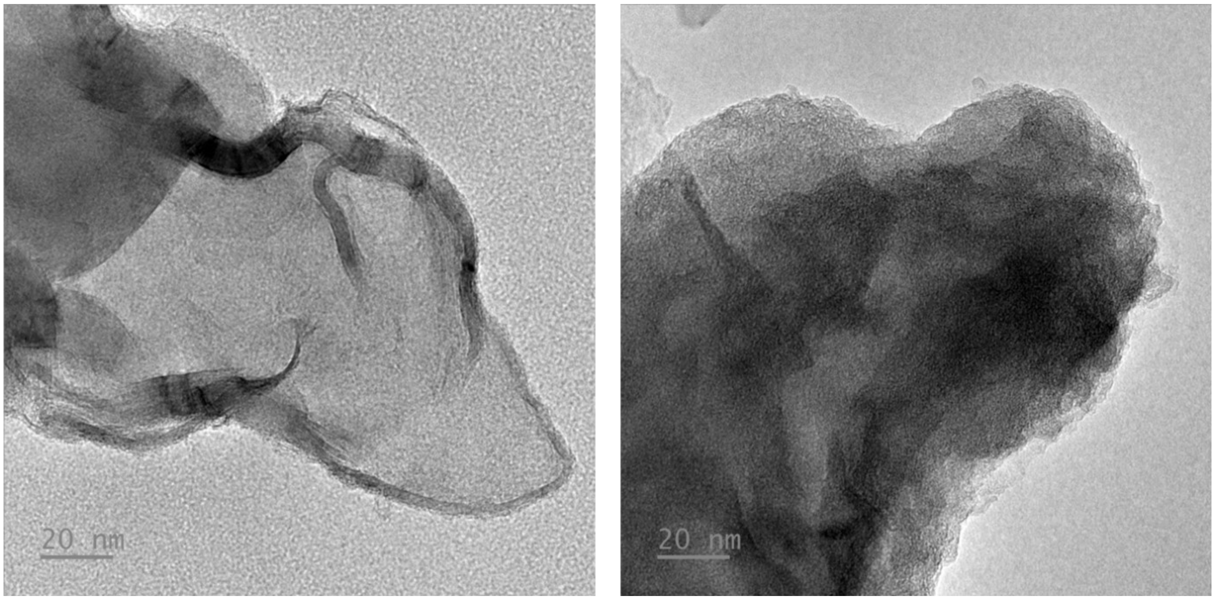


Figure S2. TEM images of (a) GO and (b) GO incorporated with Fe_3O_4@COOH

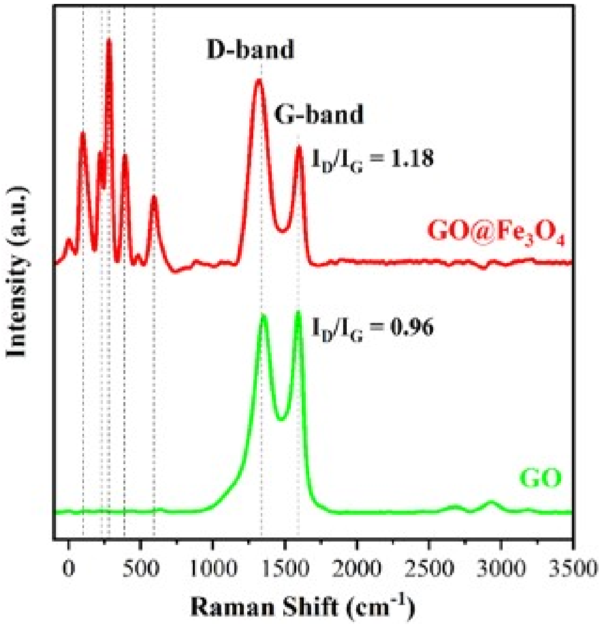


Figure S3. Raman spectra of GO and GO@Fe$_3$O$_4$

In this study, TEM measurements were not performed for GA@Fe$_3$O$_4$ because TEM analysis requires the sample to be dispersed in a solvent followed by evaporation. This process is considered inappropriate to the 3D structure of the aerogel. Instead, TEM measurements were conducted for GO and GO incorporated with Fe$_3$O$_4$@COOH (GO@Fe$_3$O$_4$) to confirm the presence of nanoparticles on the GO plane. Fig. S2 presents the TEM images of GO and GO@Fe$_3$O$_4$. As observed, the GO flakes consist of multiple layers with well-defined edges and a stacked morphology. Upon incorporation of Fe$_3$O$_4$ NPs, the TEM images reveal that the nanoparticles are uniformly distributed across the GO surface. Further characterization was performed using Raman spectroscopy to confirm the presence of Fe$_3$O$_4$ NPs.

As shown in Fig. S3, the Raman spectrum of GO displays two characteristic peaks typical of carbon-based materials: the D-band and G-band, located at 1347.52 cm^{-1} and 1591.91 cm^{-1}, respectively [10]. The D-band arises due to structural defects in GO caused by the presence of oxygen-containing functional groups (hydroxyl, epoxy, and carbonyl), which disrupt the sp^2 hybridized carbon network. Meanwhile, the G-band corresponds to the vibrational mode of C=C bonds in the crystalline lattice of graphene, indicating that graphitic domains (hexagonal carbon lattice) remain in the GO structure. In the Raman spectrum of GO@Fe$_3$O$_4$, in addition to the characteristic D-band and G-band peaks similar to those in GO, additional peaks corresponding to Fe$_3$O$_4$ NPs are observed, confirming their successful incorporation [11]. Specifically, peaks at 104.70 cm^{-1} and 226.89 cm^{-1} are attributed to the magnetization vibrations of Fe$_3$O$_4$. The peak at 287.47 cm^{-1} is assigned to Fe–O–Fe vibrations, while peaks at 395.04 cm^{-1} and 600.78 cm^{-1} correspond to the stretching vibrations of Fe–O. A crucial parameter for evaluating structural disorder in

GO is the intensity ratio (I_D/I_G) of the D-band to the G-band in the Raman spectrum [12, 13]. A higher I_D/I_G ratio indicates increased disorder and defect density, which may arise from incomplete carbon chains, substituted carbon atoms, and lattice distortions. As shown in Fig. S3, the I_D/I_G ratio for GO is 0.96, whereas for GO@Fe_3O_4, it is calculated as 1.18. This increase suggests that the incorporation of Fe_3O_4 NPs induces greater structural disorder in GO, as previously reported in literature. The even distribution of Fe_3O_4 nanoparticles across the GO plane further contributes to the disruption of the sp^2 carbon network, increasing the degree of disorder in the material.

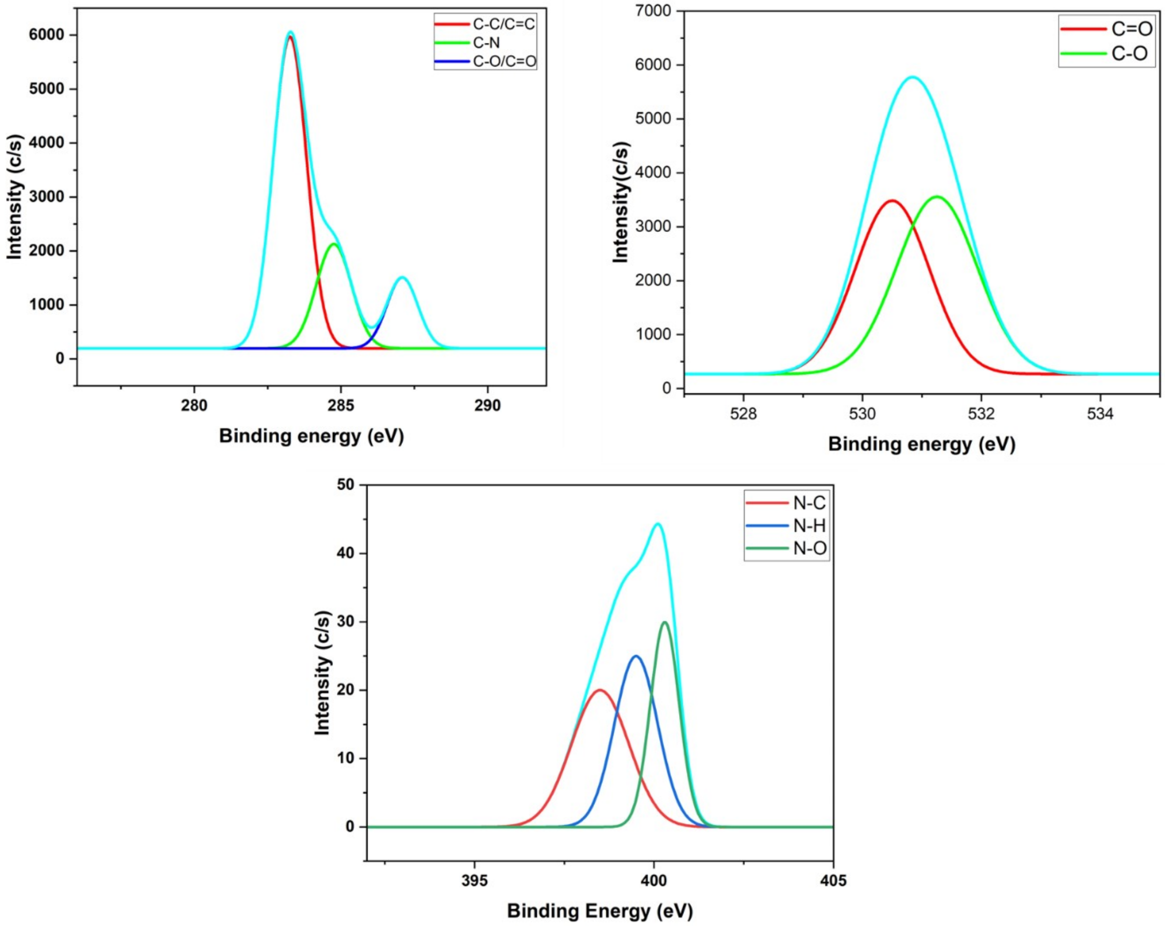


Figure S4. XPS spectra of GA (without Fe_3O_4), including the C 1s, O 1s, and N 1s orbitals.

In the XPS spectrum, no Fe 2p signals, which is characteristic of Fe_3O_4 nanoparticles, were detected, confirming the absence of Fe_3O_4. Additionally, a difference was observed in the O 1s region compared to that of GA@Fe_3O_4. Especifically, the peak at a binding energy of 532.3 eV, attributed to O–H bonding, was significantly diminished. This suggests the absence of citric acid-stabilized Fe_3O_4 nanoparticles, which typically exhibit a high density of O–H groups in their carboxyl functionalities. Furthermore, this observation provides strong evidence that the original GO was effectively reduced by the pineapple juice, as indicated by the substantial decrease in oxygen-containing functional groups.

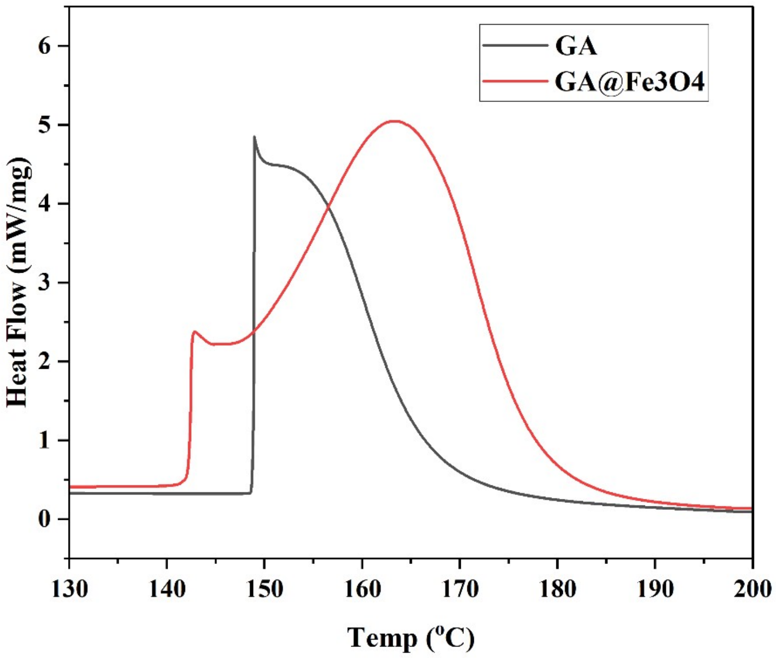
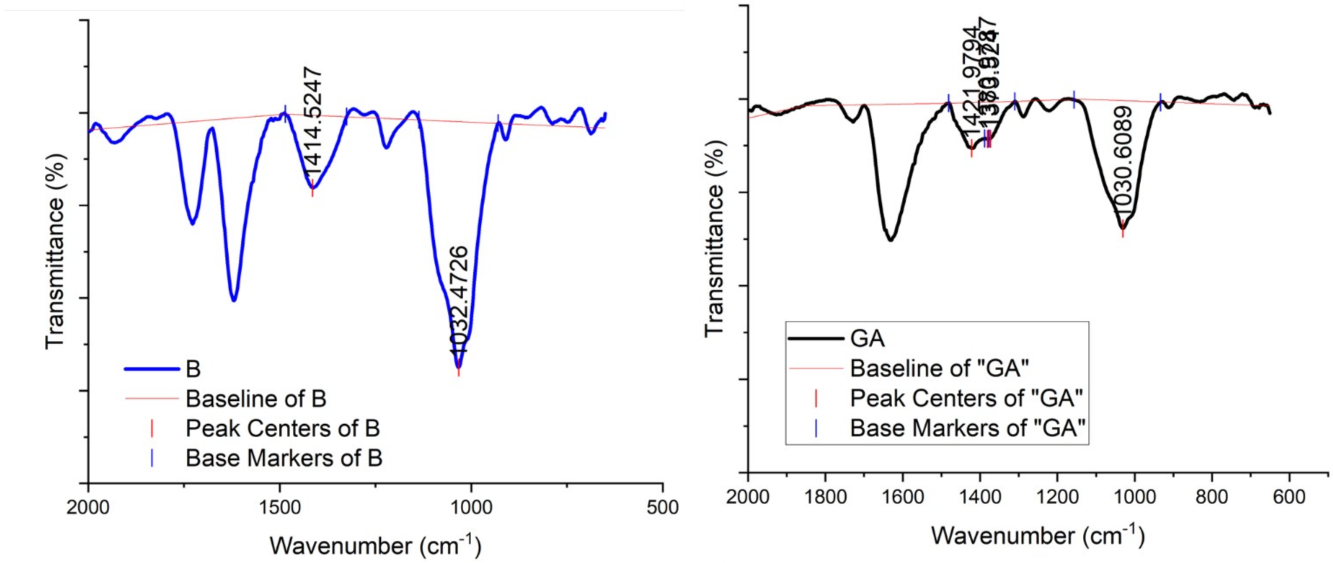


Figure S5. DSC analyis of GA and GA@Fe_3O_4

DSC analysis revealed a broad endothermic peak in the range of 150–175 °C for both GA and GA@Fe_3O_4, with GA@Fe_3O_4 exhibiting a higher onset and peak temperature (~168 °C) compared to GA (~160 °C). The increase in thermal energy requirement and the broadening of the peak suggest enhanced thermal stability and stronger interfacial interactions resulting from the incorporation of Fe_3O_4 nanoparticles. Furthermore, the initial endothermic peak observed in GA@Fe_3O_4 may be attributed to the decomposition of citric acid stabilized on the surface of the Fe_3O_4 NPs.



(a)

(b)

Figure S6. FTIR peak areas were calculated using OriginPro for (a) GO and (b) GA samples.

The areas under the band from 927 to 1486 cm-1 were calculated to reveal reduction efficiency from GO to GA.

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