



# The comparative analyses of reduced graphene oxide (RGO) prepared via green, mild and chemical approaches

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## Abstract

In this work, the reducing power of three reductants: hydrazine (chemical), ascorbic acid (mild) and the extract of *Amaranthus hybridus* (green) were investigated. Graphene oxide (GO) was synthesized by modified Hummer's method and was reduced by hydrazine (RGO-HZ), ascorbic acid (RGO-AA) and the extract of *Amaranthus hybridus* (RGO-AH). GO, RGO-HZ, RGO-AA and RGO-AH were characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy and ultraviolet visible spectrometry. The FTIR spectra showed the presence of oxygen functionality groups in GO which were reduced in all RGOs. The morphological properties showed that RGOs sheets were exfoliated forming clusters with roughened surfaces while the optical energy band gaps of 2.19, 3.90, 3.60, and 3.20 eV were estimated for GO, RGO-HZ, RGO-AA and RGO-AH respectively. It can be concluded that the three reductants demonstrated good reducing capacities. The ascorbic acid and the extract of *Amaranthus hybridus*, apart from being environmentally friendly, can also be good substitutes for the dangerous chemical hydrazine.

**Keywords** Graphene oxide · Reduced graphene oxide · Hydrazine · Ascorbic acid · *Amaranthus hybridus*

## 1 Introduction

Reduced graphene oxide (RGO) is the reduction or removal of oxygen-containing functional groups from graphene oxide [1]. This can be achieved by using the environmentally friendly approach, hydrothermal, solvothermal, flash reduction, photocatalytic and chemical approach [2–6]. RGO prepared using hydrothermal method has good properties like structural stability and porosity which make it good for energy storage application [7], also the rapid heating process reduces the functionalized graphene sheets by decomposing oxygen containing groups at elevated temperatures and yields a clear solution these make it a good strategy for bulk quantity graphene production [8, 9]. Hydrothermal method of reduction has advantages over chemical process such as simplicity, scalability low defects contents [10], and production of RGO in a more

controllable route [11]. It is also one of the most attractive green method which uses water as the only chemical and involves a single step thereby making it possible to tailor the functional groups by adjusting the temperature and the time of reaction [12] but some of the defects are explosion of the structure if not slowly heated and large energy consumption [8].

The exfoliation of GO is one of the well-established methods for the mass production of RGO in the presence of some chemical reducing agents such as hydrazine and sodium borohydride [13, 14]. The use of strong chemical reducing agents such as hydrazine is found to be corrosive, highly explosive and toxic [15]. In addition, hydrazine seems to be a hepatotoxic and carcinogenic which can result in liver and DNA damage [16].

In order to overcome the toxicity problem of strong chemical reducing agents, many studies have proposed

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the use of the green chemistry approach for the reduction of GO using various biological molecules as reducing agents. These include vitamin C [17], melatonin [18], sugar [19], polyphenols of green tea [20, 21], bovine serum albumin [22], biomass of bacteria [23, 24]. Others include environmentally friendly approach like the use of extracts of some plants which are rich in antioxidants [24]. *Amaranthus hybridus*, called spinach, is a common vegetable that can easily be found in markets and in bulk, at a very cheap price. It can easily be cultivated in the garden beside or at the back of the house and as well on a large scale. It is nontoxic and an edible plant which has high nutritional value with a lot of health benefits and is extremely rich in antioxidants. Its extracts from the leaf can be obtained conveniently.

The extracts of *Amaranthus hybridus* is nontoxic and also extremely rich in antioxidants, which can be used for the reduction of GO. Therefore, the leaf extracts of *Amaranthus hybridus* could be a potential alternative reducing agent for GO. Ascorbic acid (Vitamin C) is a newly reported reducing reagent for GO, which is considered to be an ideal substitute for hydrazine relatively in terms of C/O ratio and conductivity [17]. In this work, we attempted to use ascorbic acid and *Amaranthus hybridus* as reducing agents to overcome the health and environmental hazards of hydrazine monohydrate and also to investigate the possibility of achieving the positive effects of hydrazine with ascorbic acid and *Amaranthus hybridus*.

## 2 Experimental details

### 2.1 Synthesis of graphene oxide (GO)

5 g of graphite (44  $\mu\text{m}$ , 99.8% carbon, Ash colour from Asbury Carbon, New Jersey, USA) and 2.5 g of  $\text{NaNO}_3$  were mixed with 108 mL of  $\text{H}_2\text{SO}_4$  and 12 mL of  $\text{H}_3\text{PO}_4$ , and stirred in an ice bath for 10 min. 15 g of  $\text{KMnO}_4$  was slowly added ensuring that the temperature of the mixture remained below 5 °C. The suspension was then left for 2 h in an ice bath and stirred for 60 min, after which it was stirred again in a 40 °C water bath for another 60 min. The temperature of the mixture was maintained at 98 °C for 60 min while water was added continuously. Deionized water was further added until the volume of the suspension was 400 mL. 15 mL of  $\text{H}_2\text{O}_2$  was added after 5 min to terminate the reaction. The reaction product was centrifuged and washed with deionized water and 5% HCl solution repeatedly. Finally, the product was oven dried at 60 °C.

### 2.2 Reduction of graphene oxide

In this work the prepared GO was reduced using three different routes; chemical reduction (using hydrazine monohydrate), mild reduction (using ascorbic acid) and green reduction (using the extract of *Amaranthus hybridus*).

### 2.3 Reduction of graphene oxide using hydrazine monohydrate

300.0 g of GO was dispersed in 100 mL of distilled water (3 mg/mL) and 0.1 mL of hydrazine monohydrate was added to the suspension in a beaker. The mixture was placed in an oil bath, stirred and maintained at 80 °C on a hot plate magnetic stirrer for 1 h. After this duration, the color of the solution changed from dark brown to black, which indicated that GO has been reduced by hydrazine. The obtained RGO was washed thrice with distilled water and filtered in order to remove residual  $\text{N}_2\text{H}_4$  from the solution. The black filtrate was then oven-dried at 60 °C and labelled RGO-HZ.

### 2.4 Reduction of graphene oxide using ascorbic acid (AA)

4.4 g of GO and 4.4 g of AA were mixed with 120 mL of distilled water and sonicated for 30 min at 60 °C. The reduction products were centrifuged at 10,000 r/s to remove the supernatant. Then, excess 30%  $\text{H}_2\text{O}_2$  was added to the black suspension to oxidize the remaining AA by sonicating for 30 min at 60 °C. After the sonication, the resulting mixture was centrifuged at 1000 r/s, washed with ethanol and distilled water thrice respectively and dried at 120 °C. This was labelled RGO-AA.

### 2.5 Reduction of graphene oxide using extract of *Amaranthus hybridus* (AH)

20 g of *Amaranthus hybridus* leaves was washed thoroughly with distilled water and then sliced into fine pieces. The finely cut *Amaranthus hybridus* leaves were soaked in 100 mL of sterile distilled water and then boiled for 2 min. After boiling, it was filtered through Whatman filter paper no. 1 to obtain *Amaranthus hybridus* extract. 10 mL of *Amaranthus hybridus* leaf extract was added to 40 mL of 0.5 mg/mL aqueous GO solution and then the mixture was kept in a tightly sealed glass bottle and stirred at 30 °C for 24 h. Then, using a magnetic stirrer heater, the suspension was stirred at 400 rpm at a temperature of 30 °C for 30 min. A homogeneous RGO suspension was obtained without aggregation. Then, the RGO was filtered

and washed with distilled water. Finally, a black RGO dispersion was obtained and oven-dried at 60 °C and was labelled RGO-AH.

## 2.6 Characterization of graphite, GO and RGOs

In order to confirm the functional groups, the degree of GO formation and reduction in the pristine and prepared samples, Fourier transform infrared (FTIR) spectroscopy was carried out using SHIMADZU FTIR-8400S. Scanning electron microscopy (Zeiss Ultra plus 55 field emission scanning electron microscope, FESEM) was conducted on each of the samples to study the morphology of the materials. The sample was placed in vacuum chamber with a working distance (Z height) of 3 mm using Z height control, operating at an accelerating voltage of 5 kV, and a current of 12  $\mu$ A. An electron beam was swept across the area of inspection and the topography of the sample was observed as image on the screen. Ultraviolet (UV) visible spectroscopy analysis was conducted on each sample using PYE UNICAM UV Visible spectrophotometer. For UV visible spectroscopy, 0.01 g of each sample was dissolved in 5 mL of ethylene glycol and placed in the sample holder and illuminated with a monochromatic beam of light.

## 3 Results and discussion

### 3.1 Functional group analysis of graphite and its derivatives

Figure 1 shows the FTIR of the powdered graphite, GO and RGOs. The existing C–OH and CO<sub>2</sub> peaks of 3391.71  $\text{cm}^{-1}$  and 2366.85  $\text{cm}^{-1}$  respectively were found in the graphite spectrum, which may be due to the porosity and hygroscopic nature of graphite. The characteristics peaks, at 3060.22, 1643.39, 1433.05, 1091.47, and 599.28  $\text{cm}^{-1}$  in the GO spectrum were due to C–H stretching, C=C stretching, C–H bending, C–O stretching, and OH out-of-plane bend respectively [19, 20]. These peaks did not appear in the spectrum of graphite indicating that the oxidation steps have introduced strong oxygen containing functional groups in GO [21, 22]. They were significantly reduced in all RGOs, which indicated that the GO has been successfully exfoliated to RGO [21].

The spectrum of RGO-HZ and RGO-AA are similar to that of the graphite, indicating the restoration of electronic conjugation within the graphene sheets [26]. The peaks 3060.22, 1643.39, 1433.05, 1091.47, and 599.28  $\text{cm}^{-1}$  of all the RGOs decreased significantly relatively to that of GO which is also a strong evidence of reduction [23–25]. When the intensity of these peaks in GO decreases in RGO, it indicates the removal of

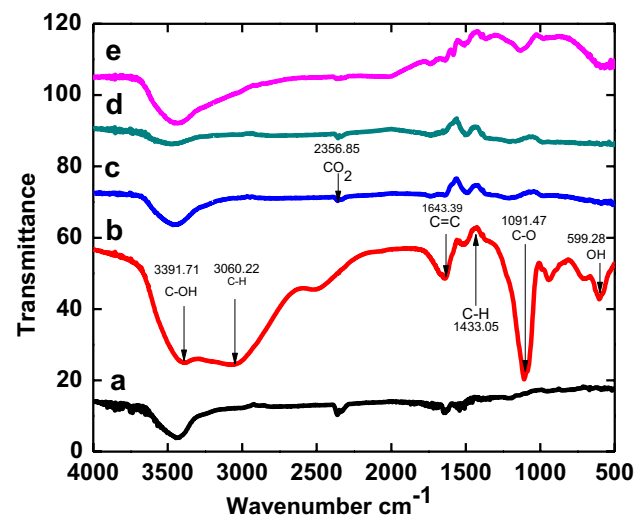


Fig. 1 FTIR Spectra for: **a** graphite, **b** GO, **c** RGO-HZ, **d** RGO-AA, **e** RGO-AH

oxygen—containing functional groups to a certain degree [18], and this can be noticed in all RGOs. The peak at 3391.71  $\text{cm}^{-1}$  was more pronounced in GO as a sign of oxidation of graphite to GO but significantly reduced in all RGOs as a sign of reduction of GO to RGO. The reduced peak (in RGOs) at 3391.71  $\text{cm}^{-1}$  was more pronounced in RGO-HZ than in RGO-AA indicating a better reduction of RGO-AA over RGO-HZ while peak 1433.05  $\text{cm}^{-1}$  was more pronounced in RGO-HZ than RGO-AH indicating a better reduction of RGO-AH over RGO-HZ. The result here showed that ascorbic acid and *Amaranthus hybridus* sharply and keenly competed with hydrazine as far as reduction from GO to RGO is concerned. Ascorbic acid and *Amaranthus hybridus* edged out hydrazine in the reduction process as shown in some of the peaks.

### 3.2 Scanning electron microscope (SEM) analysis of graphite and its derivatives

The surface morphology of graphite, GO, RGO-HZ, RGO-AA and RGO-AH are shown in Fig. 2a–e. GO sheet was exfoliated forming clusters with roughened surface. Upon reduction from GO to RGO, the surfaces of the samples become corrugated due to the escape of oxygen-containing groups during reduction process [27]. The corrugation is pronounced in all RGOs but the individual sheets are highly ordered in RGO-AH followed by RGO-AA indicating a better reducing power of *Amaranthus hybridus* and ascorbic acid over hydrazine [29]. This observation shows that *Amaranthus hybridus* and ascorbic acid, as reducing agents, can be good substitutes for hydrazine.

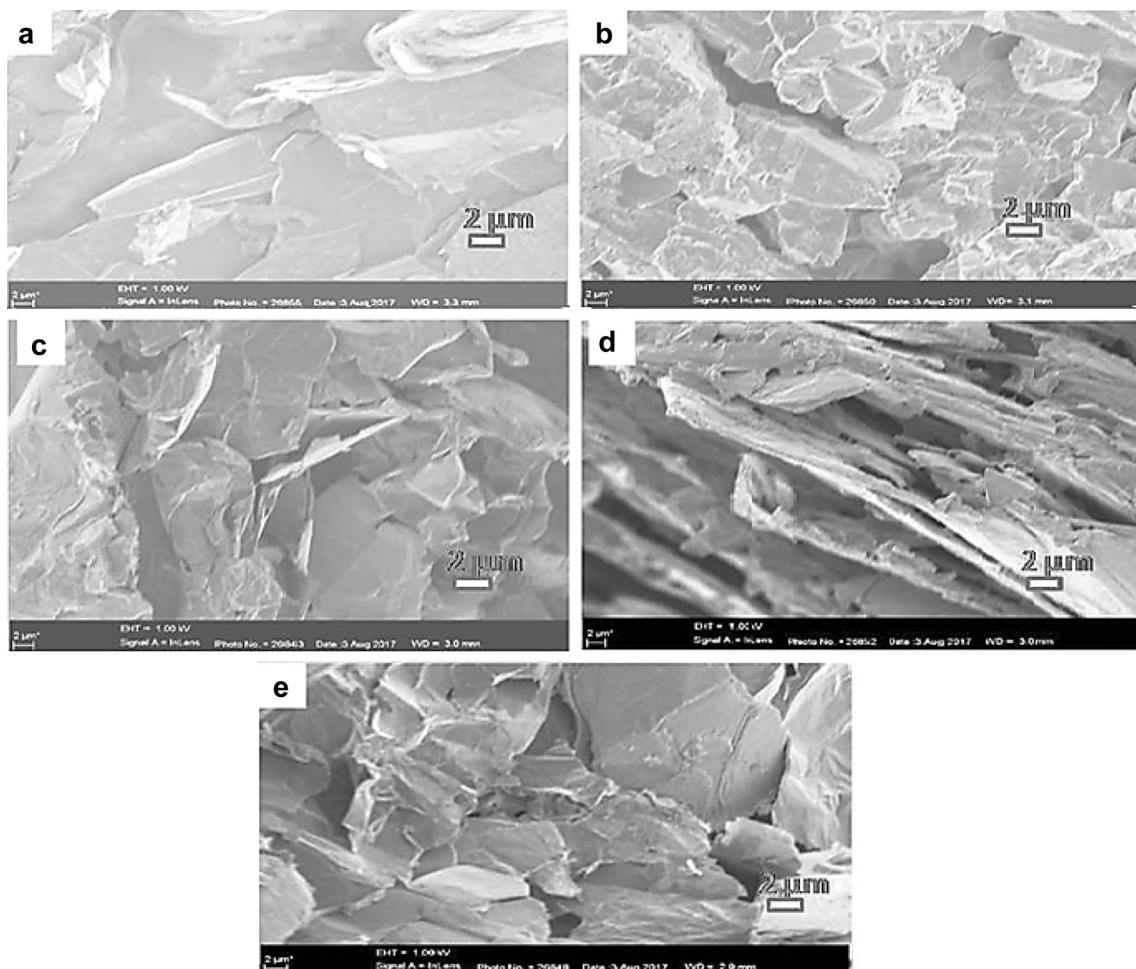


Fig. 2 Scanning electron micrograph of **a** graphite, **b** GO, **c** RGO-HZ, **d** RGO-AA

### 3.3 Ultraviolet (UV) visible spectrophotometer analysis of graphite and its derivatives

Figure 3a shows UV–visible absorbance spectra for graphite and its derivatives (GO, RGO-HZ, RGO-AA and RGO-AH). In the GO spectrum, a maximum absorption peak arises at a wavelength of 291 nm indicating  $n-\pi^*$  electron transitions in carbonyl and carboxyl functional groups [21–23]. The shift in the absorptions from 291 nm to 293, 314 and 304 nm, in the case of RGO-AH, RGO-AA and RGO-HZ respectively, is an indication that the electronic conjugation within graphene sheets is restored after the reduction. The shift of the peaks position of RGOs can also be due to a decrease in oxygen functional groups and an increase in aromatic rings causing electrons to be easily excited at a lower energy [24].

From the absorbance, the transmittance can be estimated using:

$$T = 10^{-A} \tag{1}$$

where  $A$  absorbance.

The transmittance (Fig. 3b) of all the RGOs are higher than that of the GO. The result also shows that more light was able to pass through RGO-HZ when compared to RGO-AA and RGO-AH, indicating that the optical absorption of hydrazine is higher than that of ascorbic acid and the leaf extract of *Amaranthus hybridus*.

The absorption coefficient,  $\alpha$ , can be calculated by the equation:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \tag{2}$$

where  $d$  is the thickness and  $T$  is the transmittance. From Eq. (2),  $\alpha^2$  can be calculated.

Figure 4a–d showed the plot of  $\alpha^2$  against the energy of the photon for graphite, GO, RGO-HZ, RGO-AA and RGO-AH respectively. The extrapolation of the linear part to the energy axis gave the band gap as 2.19, 3.90, 3.60, and 3.20 eV for GO, RGO-HZ, RGO-AA and RGO-AH respectively. The band gap of RGO-HZ is higher than that of RGO-AA and RGO-AH. The decrease in band gap for GO



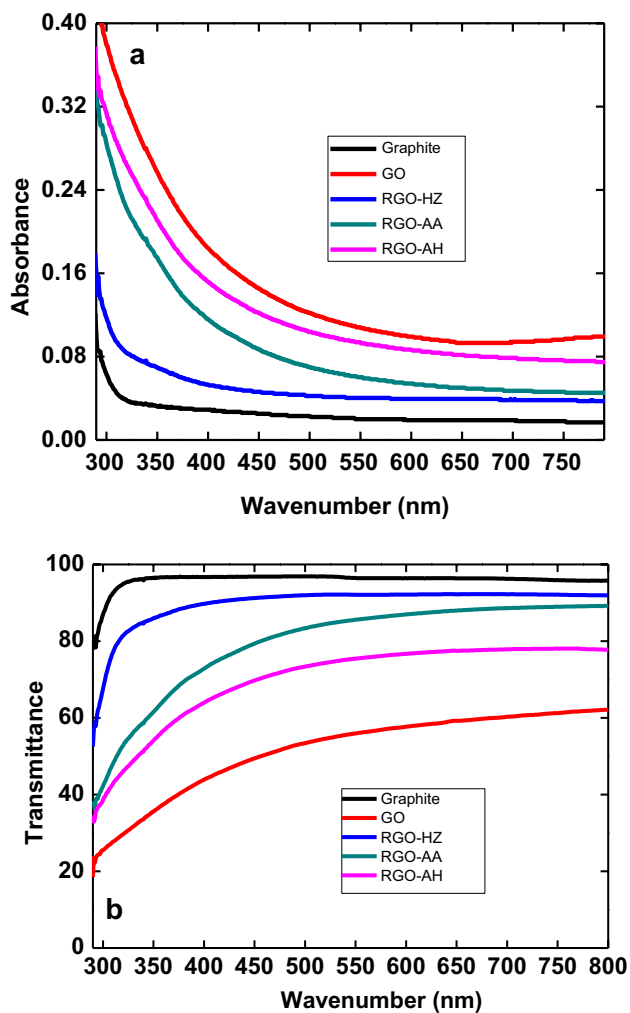
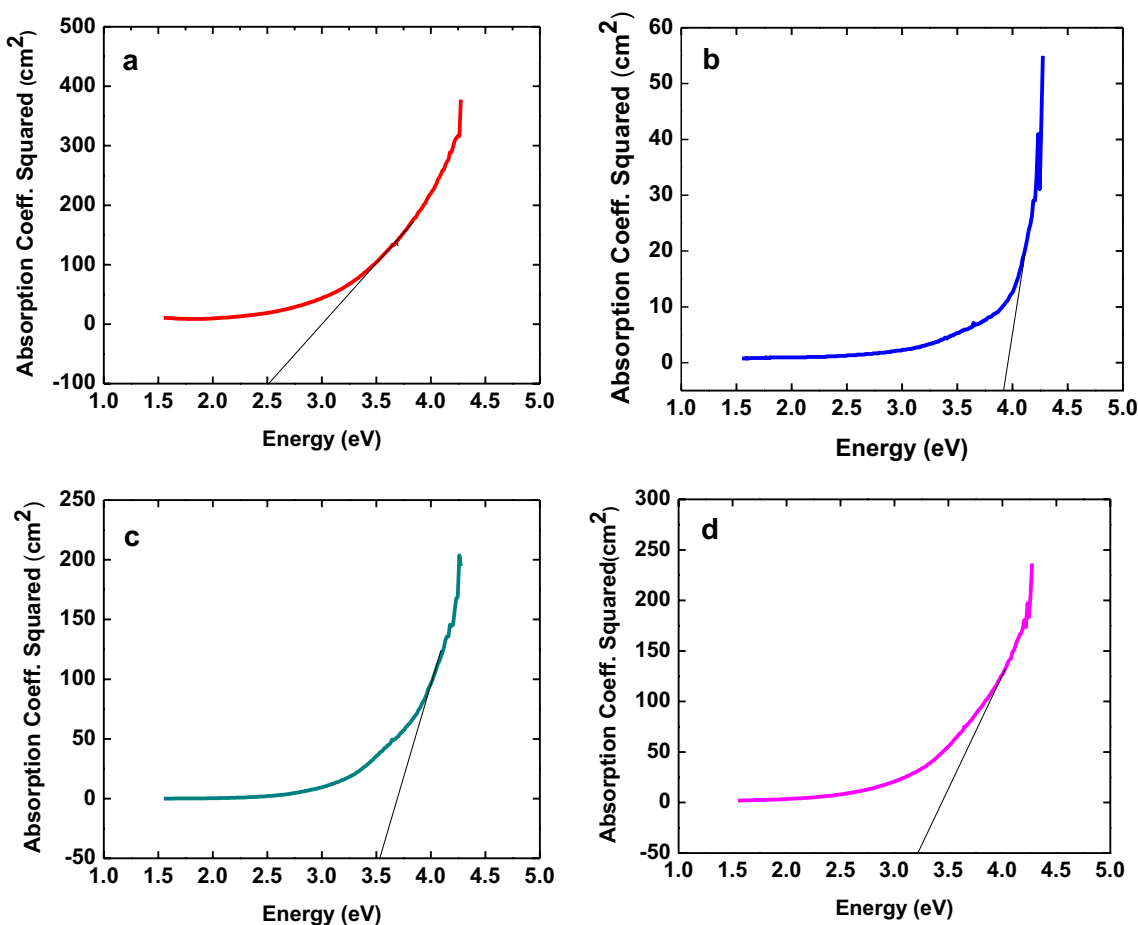


Fig. 3 UV-Visible spectra of **a** graphite and its derivative (Absorbance), **b** graphite and its derivative (Transmittance)

was probably due to exfoliation of graphite layer allowing easy transfer of electrons. Though it has been earlier reported [28] that ascorbic acid has a poor sensitivity as solid electrodes.

## 4 Conclusion

FTIR analysis showed the formation of GO by the appearance of some peaks not found in graphite but present in GO. Reduction of GO was also confirmed with some peaks in RGOs significantly decreased while some completely disappeared when compared to that of GO. The similarity between the spectra of graphite and all the RGOs is an indication that graphene has significantly restored its conjugated system. The FTIR confirmed that ascorbic acid and the leaf extract of *Amaranthus hybridus* as reducing agents sharply and keenly competed with hydrazine as far as reduction from GO to RGO is concerned. SEM analysis showed that GO sheet is exfoliated forming clusters with roughened surface. Upon reduction from GO to RGO, the surfaces of the samples become corrugated due to the escape of oxygen-containing groups during reduction process. The corrugation was pronounced in all RGOs but the individual sheets were highly ordered in RGO-AH followed by RGO-AA, indicating a better reduction of RGO-AH and RGO-AA over RGO-HZ. This observation showed that *Amaranthus hybridus* and ascorbic acid, as reducing agents, can be good substitutes for hydrazine. UV-visible analysis showed that the absorptions of reduced graphene red shifted from 291 nm to 293, 314 and 304 nm in the synthesized RGO-AH, RGO-AA and RGO-HZ respectively, suggesting that the electronic conjugation within graphene sheets was restored after the reaction, with the band gap of GO, RGO-HZ, RGO-AA and RGO-AH being 2.19, 3.90, 3.60 and 3.20 eV respectively. Summarily, with the FTIR, SEM and UV-visible spectroscopy results, it has been validated and confirmed in this study that, hydrazine, ascorbic acid and the leaf extract of *Amaranthus hybridus* are good reductants. The ascorbic acid and the extract of *Amaranthus hybridus*, apart from being environmentally friendly, can be good substitutes for the dangerous chemical hydrazine.



**Fig. 4** Absorption coefficient squared against energy of **a** GO, **b** RGO-HZ, **c** RGO-AA, **d** RGO-AH, **e** RGO-AH

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### Compliance with ethical standards

**Conflict of interest** The authors hereby declare that there is no conflict of interest.

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