ASX ANNOUNCEMENT

first graphene
The world's leading graphene company

2nd AUG 2021

ARC Hub develops test protocol to confirm quality of PureGRAPH® Graphene

HIGHLIGHTS

- **Researchers have developed a robust test method to detect the presence of "fake" graphene**

- **The test is based on thermogravimetric analysis (TGA)**

- **Confirms that PureGRAPH® products are high-quality, pristine, low defect few layer graphene platelets**

First Graphene Limited (ASX:FGR; "First Graphene" or "the Company") is pleased to announce the publication of a scientific paper written by researchers at Australian Research Council's Graphene Research Hub ("ARC Hub"), the University of Adelaide Node, which describes a robust analytical process that can be used to detect "counterfeit" graphene materials. First Graphene's PureGRAPH® was used as the pristine graphene that was used as a control during the test development.

The paper, titled "*Accounting Carbonaceous Counterfeits in Graphene Materials Using the Thermogravimetric (TGA) Approach*" was written by researchers led by Professor Dusan Losic, leader of the Nano Research Group at The University of Adelaide and Director of the ARC Hub. It was published on 28th July 2021 in Analytical Chemistry, a peer-reviewed research journal devoted to the dissemination of new and original knowledge in all branches of analytical chemistry.

The researchers have successfully demonstrated that TGA is a viable method that can be used to detect impurities in "bulk" graphene samples. This is currently not possible with other commonly used characterisation techniques, such as Raman spectroscopy or powder X Ray Diffraction. TGA is a robust, simple and commonly used test method, that measures the loss in weight of a sample as it is heated under controlled conditions. It provides a unique "signature" that can be used to confirm the presence of graphene or other related carbon products (graphene oxide, reduced graphene oxide, activated carbon, carbon black) and to show whether impurities are present.

The work presented in the paper is highly relevant to the graphene industry because it can be used to give end users the confidence that they are being supplied with high-quality graphene platelets.

First Graphene's Research and Development Team, based at the Graphene Engineering Innovation Centre, also have extensive experience of using this method. Professor Losic's work therefore compliments First Graphene's extensive work in understanding, characterising and controlling the properties of its range of graphene products. This is key to providing confidence to end users that PureGRAPH® is consistently high quality graphene platelets. Previous work by Professor Losic's group has shown these can be "tailored" for end users by functionalising the platelets with specific chemicals. This demonstrates the versatility and unique nature of PureGRAPH® products.

Michael Bell, Chief Executive Officer of First Graphene said: *"This is another excellent piece of work from the ARC Graphene Research Hub. It demonstrates our commitment to*

providing a robust supply of high-quality graphene platelets, which has been independently validated by Professor Losic's team of scientific experts. It is a great example of how the scientific community can help to support the industry at this key stage of commercialisation of graphene products."

Professor Dusan Losic, leader of the Nano Research Group at the University of Adelaide, said: "Our team continues to develop simple and robust methods to support the characterisation and quality control of bulk graphene powders. We are aware of the need to prevent poor quality "fake" graphene from entering the supply chain and we expect that the TGA method presented in this paper will play an important role in this process."

Investors

Michael Bell
Managing Director & CEO
First Graphene Limited
michael.bell@firstgraphene.net
+ 61 1300 660 448

Media

Simon Shepherdson
General Manager Media
Spoke Corporate
simon@spokecorporate.com
+ 61 413 809 404

About First Graphene Ltd (ASX: FGR)

First Graphene Ltd. is the leading supplier of high-performing, graphene products. The company has a robust manufacturing platform based upon captive supply of high-purity raw materials and an established 100 tonne/year graphene production capacity. Commercial applications are now being progressed in composites, elastomers, fire retardancy, construction and energy storage.

First Graphene Ltd. is publicly listed in Australia (ASX:FGR) and has a primary manufacturing base in Henderson, near Perth, WA. The company is incorporated in the UK as First Graphene (UK) Ltd. and is a Tier 1 partner at the Graphene Engineering and Innovation Centre (GEIC), Manchester, UK.

PureGRAPH® Range of Products

PureGRAPH® *graphene powders and* **PureGRAPH**® **AQUA** *pastes with lateral platelet sizes of 50µm, 20µm, 10µm and 5µm, as well as* **PureGRAPH® MB-LDPE 20-30** *masterbatch for thermoplastics, are available in tonnage volumes. The products are high performing additives, characterised by their high quality and ease of use.*

First Graphene Limited	**Directors:**	**Trading Symbols**	
ABN 50 007 870 760	Warwick Grigor	**Australia:**	FGR
			FGROC
1 Sepia Close	Michael Quinert		
Henderson WA 6166			
T: +61 1300 660 448	Dr Andy Goodwin	**Frankfurt:**	FSE:M11
E: info@firstgraphene.net			
W: firstgraphene.net	Michael Bell	**USA OTCQB:**	FGPHF

With authority of the board, this announcement has been authorised for release by Aditya Asthana, Chief Financial Officer and Company Secretary.

Accounting Carbonaceous Counterfeits in Graphene Materials Using the Thermogravimetric Analysis (TGA) Approach

Dusan Losic,* Farzaneh Farivar, Pei Lay Yap, and Afshin Karami

Cite This: https://doi.org/10.1021/acs.analchem.1c02662

Read Online

ACCESS | 📊 Metrics & More | 📰 Article Recommendations | 🆂🅸 Supporting Information

ABSTRACT: Counterfeits in the supply chain of high-value advanced materials such as graphene and their derivatives have become a concerning problem with a potential negative impact on this growing and emerging industry. Recent studies have revealed alarming facts that a large percentage of manufactured graphene materials on market are not graphene, raising considerable concerns for the end users. The common and recommended methods for the characterization of graphene materials, such as transmission electron microscopy (TEM), atomic force microscopy (AFM), and Raman spectroscopy based on spot analysis and probing properties of individual graphene particles, are limited to provide the determination of the properties of "bulk" graphene powders at a large scale and the identification of non-graphene components or purposely included additives. These limitations are creating counterfeit opportunities by adding low-cost black carbonaceous materials into manufactured graphene powders. To address this problem, it is critical to have reliable characterization methods, which can probe the specific properties of graphene powders at bulk scale, confirm their typical graphene signature, and detect the presence of unwanted additional compounds, where the thermogravimetric analysis (TGA) method is one of the most promising methods to perform this challenging task. This paper presents the evaluation of the TGA method and its ability to detect low-cost carbon additives such as graphite, carbon black, biochar, and activated carbon as potential counterfeiting materials to graphene materials and their derivatives such as graphene oxide (GO) and reduced GO. The superior performance of the TGA method is demonstrated here, showing its excellent capability to successfully detect these additives when mixed with graphene materials, which is not possible by two other comparative methods (Raman spectroscopy and powder X-ray diffraction (XRD)), which are used as the common characterization methods for graphene materials.
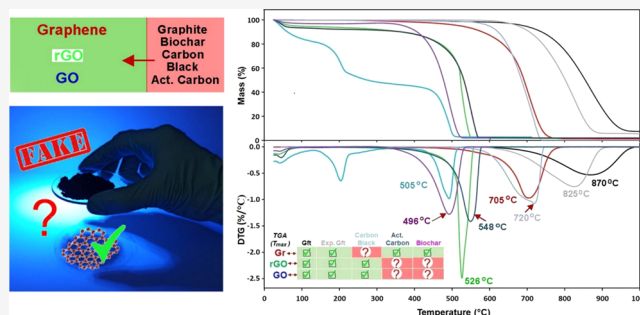
1. INTRODUCTION

Graphene, a two-dimensional (2D) carbon material with a single atomic structure of sp^2 carbon, since its discovery in 2004, has been described as the material of 21st century and a new disruptive technology, as a result of the combination of its unique properties.[1] Its wide range of applications have been demonstrated in recent years ranging from lightweight composites, protective coatings, electronic devices, sensors, energy production, storage, and so on.[2−4] Translation of these applications from academia to industry is rapidly progressing in recent years underpinning the fast growth of new emerging graphene industry across many sectors.[2,5,6] Industrial manufacturing and supply of high-quality graphene materials for industrial applications have been recognized as one of the key requirements for the growth of emerging graphene industry. Many graphene manufacturing processes have been developed, and a thousand companies worldwide have claimed industrial production of graphene materials and their derivatives.[6−9] Recent comprehensive studies on the quality evaluation of these industrially produced graphene materials revealed concerning findings that a large percentage of graphene available on market

are not graphene but a mixture of graphene, graphitic, and other carbonaceous materials.[10−12] These reports triggered considerable concerns for downstream graphene end users with a potential serious impact on the future of the entire graphene industry. Graphene is a black powder with physical appearance not much different from many other low-cost commercially available carbon materials such as graphite, carbon black, biochar coal, and activated carbon. Some of these carbon materials are used or generated during graphene production, and their presence deemed as impurities may decrease the performance of graphene materials for many applications. Owing to their similarity, their presence in graphene powders cannot be detected visually, which creates opportunities to

counterfeit graphene materials and make financial gains. The problem became more significant when the key characterization methods recommended by International standards based on spot analysis and probing single graphene particles may fail to disriminate these additives and detect "fake" graphene, making the graphene supply chain vulnerable.[10−12]

The graphene materials, their forms and properties are defined by the International Organization for Standardization (ISO).[13−15] Based on this standard, graphene materials can appear in different forms, such as powders, films, and dispersions, and have single, double, or few layers (<10), with different sizes, functionalities, and other properties[16−18] To prove these properties and confirm that the characterized material is graphene, new ISO standards have been recently published to specify the analytical techniques for characterizing their structural properties and chemical composition such as number of layer/thickness, lateral flake size, level of disorder sp^2 structure, specific surface area, etc.[15] Most of these methods that are accepted as the most trusted, such as Raman spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), are spot characterization methods that can probe individual or few graphene particles dispersed on the substrate. Unfortunately, these methods have the limitations of probing a very large number of graphene particles (+500) from one sample and not able to provide representative properties of bulk materials in powder form at large scales (kg or tonnes). As a result, these methods, with reduced number of spot testing, could easily miss to detect the presence of non-graphene impurities or fake additives using low-cost carbonaceous materials. Moreover, these techniques need skilled technical operators and are also very expensive, time-consuming, and not affordable for the majority of industries and the end users of graphene materials, which are usually small and medium-sized enterprise (SME) companies. Hence, there is a significant demand to implement a more representative, simple, and low-cost analytical method that can provide information on bulk properties for industrially produced graphene materials. Several analytical methods such as thermogravimetric analysis (TGA), powder X-ray diffraction (XRD), gas physisorption (Brunauer−Emmett−Teller, BET), particle size distribution (PSD) analysis, ultraviolet−visible (UV−vis) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and pH titration techniques can meet these requirements and provide complementary information about the bulk properties of graphene powder such as the crystal and graphitic structure, surface area, chemical composition, impurities, and functional groups.[13−18] Among them, TGA has been routinely used in the industry for the characterization of the thermal properties, chemical composition, and impurities of minerals, polymers, and carbon materials, but surprisingly, it has not been explored beyond its conventional use for advanced characterizations and the quality control of graphene materials.[19−21]

In our recent study, we demonstrated how the TGA method-based analytical approach can be used as a valuable quality control and analytical tool for the qualitative and quantitative analysis of graphene powders, not considered before.[22,23] TGA is shown as a simple and reliable method that can detect "fake graphene" and the presence of nongraphene carbon impurities as a result of the manufacturing process.[22,23] The main conclusion from this study revealed that the key components of nongraphene impurities from graphitic nonexfoliated particles and Graphene oxide (GO) have distinctive thermal decomposition properties that can be elegantly distinguished from graphene by TGA measurements using the first-derivative thermogravimetric (DTG) analysis based on a distinctive number of decomposition peaks, their shapes, and temperature of maximum mass loss rate (T_{max}). Typical TGA signature of the representative few-layer graphene (FLG) material was confirmed and related to other properties (number of layers, defects, sp^2 carbon, etc.) provided by complementary methods (TEM, Raman spectroscopy, XPS, and AFM) showing the capability of the TGA method to successfully detect other carbon impurities from manufacturing process.

The aim of this study is to evaluate the use of the TGA method to detect the presence of selected carbonaceous materials such as graphite, carbon black, biochar, and activated carbon as potential counterfeiting additives for commercial graphene powder materials including FLG pristine graphene, GO, and reduced graphene oxide (rGO). These carbon materials were selected because of their large commercial availability on market, physical similarity, and low cost compared with more expensive graphene materials. The baseline comparative characterization of these carbon and graphene materials was performed by a series of methods including TEM, SEM, Raman spectroscopy, XRD, FTIR, and TGA to determine their structural and chemical characteristics such as morphology, number of layers, defects, chemical compositions, and crystallinity. Artificial counterfeiting model mixtures of selected four carbon additives with three commercial graphene powder materials (Gr-FLG, GO, and rGO) with additive concentrations of 10% (w/w) were prepared. They are comparatively characterized by Raman spectroscopy, XRD, and TGA methods to evaluate their ability to detect these counterfeiting carbon additives in graphene powder mixtures. The TGA/DTG graphs of these selected graphene materials and their counterfeiting mixtures were generated to determine the DTG peak shape, surface area, and T_{max} as the key identification parameters. Results from this study provide important information about the ability of the TGA method to be used as a fast and reliable method for detecting fake graphene generated by carbonaceous counterfeiting additives.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation. Pristine graphene powders with few graphene layers (Gr) were obtained from First Graphene Ltd manufactured by industrial electrochemical process. This sample represents pristine graphene (FLG) with an average particle size of ca. 5 μm with a size distribution of 2−10 μm. Commercial GO and rGO materials were supplied by The Sixth Element (China). Graphite in the form of graphite flakes obtained from a local graphite company (Uley, Eyre Peninsula, SA, Australia) was sieved to ≤25 μm. Carbon black material was obtained from ChemSupply (Australia), activated carbon (Haycarb, Sri Lanka), and biochar (Permachar, Australia) was crushed and sieved below 25 μm prior to analysis. Digital photographs of these materials are presented in Figure S1 (Supporting Information). The models of artificial mixtures were prepared by adding these carbon additives with 10% (w/w) concentration into commercial FLG, GO, and rGO powders, followed by physical mixing to obtain a series of uniform mixtures.

2.2. Thermogravimetric Analysis (TGA). TGA measurements were conducted on a Mettler Toledo TGA/DSC 2 and TA Insyruments Q500 Series under the same conditions with a heating rate of 10 °C/min under air atmosphere with a flow rate

of 60 mL/min and 20 ml/min nitrogen used as a balance protective gas. The TGA graphs were collected from all prepared samples, in powder forms, showing typical mass loss with regard to temperature, and the related DTG graphs were generated showing mass loss rate versus temperature. The DTG graphs and T_{max} values were used to demonstrate the ability of the TGA method to detect counterfeiting carbon additives in graphene materials.

2.3. Other Characterizations. The morphologies of commercial FLG graphene, GO, and rGO used in this study were confirmed by field emission scanning electron microscopy (FE-SEM, Quanta 450 FEG, FEI) at an operating voltage of 10 kV and transmission electron microscopy (TEM, Philips CM200, Japan) at 200 kV. FTIR spectroscopy (Nicolet 6700, Thermo Fisher) was used to confirm the functional groups in the samples in the range of 500−4000 cm^{-1}. The Raman spectroscopy characterization of graphene, GO and other carbon materials was performed using LabRAM HR Evolution (Horiba Jvon Yvon Technology, Japan) with a 532 nm laser (mpc3000) as the excitation source in the range of 500−3500 cm^{-1}. The crystal structure of samples was analysed by powder X-ray diffraction on aD4 ENDEAVOR (Bruker, Co Ka. lambda=0.178897 mm). The instrument was operated at 35kV and 30 mA with diffraction data collected by scanning from 5-80 0 with a step size of 0.2 0 . Particle size distribution (PSD) of the samples was determined using a a Mastersizer 2000 (Malvern Instruments, U.K.).

3. RESULTS AND DISCUSSION

3.1. Baseline Characterization of Graphene Materials and Carbonaceous Counterfeits. Visual examination of three selected commercial graphene and four carbon powder materials used in this study showed high similarity, i.e., similar physical appearance including dark brown (GO) and black (all carbon materials investigated in this study except for GO), powder texture, lightweight, and no smell (Figure S1). Interestingly, visual examination of counterfeiting model mixtures made of 10% graphite, carbon black, activated carbon, and biochar in three graphene materials such as graphene, rGO, and GO showed no visual difference compared with pure graphene materials before the additions. Based on the preliminary observation, visual examination can be hardly used to detect these counterfeits; hence, instrumental characterization is required to identify their presence in graphene materials.

The SEM technique was used as the first method for the baseline characterization to confirm the morphology and particle size of graphene and carbon materials used in this study, with their typical structures presented in Figure 1. From these electron micrographs, graphene materials exhibit similar micron-sized 2D sheet morphology, which is remarkably different from thick particles of graphite, activated carbon, and biochar, and nano-sized spherical particles of carbon black. From these results, a conclusion that can be drawn at the SEM morphological examination could be successfully used to identify these carbonaceous counterfeits if they are added in large quantities (>10%). It is worth noting that SEM characterization also requires testing of a large number of samples because the observation of these micron-sized or nano-sized particles can be easily overlooked by the examination of few samples or spots.

To further obtain the baseline properties of graphene materials in this work, their structural and chemical character-
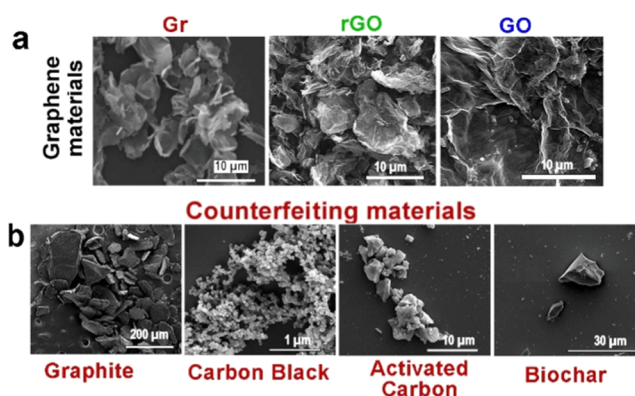

Figure 1. Comparative SEM images of (a) graphene materials (pristine graphene (FLG)), rGO, and GO) and (b) potential carbon counterfeiting materials (graphite, carbon black, activated carbon, and biochar) showing their typical morphologies.

izations were performed using a broad range of characterization methods including TEM, XPS, Raman spectroscopy, AFM, XRD, and PSD, which results are summarized in Figure S2 and Table S1 (Supporting Information). These results confirmed the typical properties of high-quality graphene (FLG), rGO, and GO as expected for these materials compared to the literature and our previous work.[9−11,22,23] More details and description of their properties are provided in the Supporting Information.

3.2. Evaluation of Carbon Counterfeits in Graphene Materials by Raman and XRD Analyses. As recommended by ISO on the structural characterization of graphene from powders and dispersions, two key graphene characterization methods, Raman spectroscopy and XRD, were used here to evaluate their ability to detect selected carbonaceous counterfeits in graphene materials in this study.[15] For that purpose, we collected comparative Raman spectroscopy and XRD data from graphene materials (Gr, GO, rGO) and selected carbon counterfeits, including graphite, carbon black, activated carbon, and biochar, which are presented in Figure 2 and Table S2.

Raman spectra of graphene (FLG), rGO, and GO showing typical signature of these materials represented by characteristic D, G, and 2D peaks; I_D/I_G and I_{2D}/I_G ratios; and 2D peak shape and position are presented in Figure S2. These specific peaks, their shape, position, and peak ratios, which are presented in Table S2, indicate their structural characteristics such as the defect level, number of layers, etc. We evaluated these individual Raman spectra of graphene, GO, and rGO and compared them with the Raman spectra of carbon materials, to assess the ability of this method to detect these potential carbon counterfeits when mixed with graphene materials, which are presented in Figure 2a. An analytical similarity assessment on Raman peaks between graphene and selected carbon materials (>10%) is presented in Figure 2b. These results indicate a high similarity in terms of Raman peak shape and peak position between graphene and graphite and expanded graphite for D and G bands with only minor differences captured on their 2D peaks.[24] All other carbon materials such as carbon black, activated carbon, and biochar have significantly different Raman plots in comparison to graphene and therefore can be detected by Raman spectroscopy. With respect to rGO and GO, distinct D and G peak shapes without 2D peak can be observed, which are significantly different from the Raman spectra of graphite and expanded graphite, indicating the ability to detect their additions in graphene using Raman analysis. However, other carbon
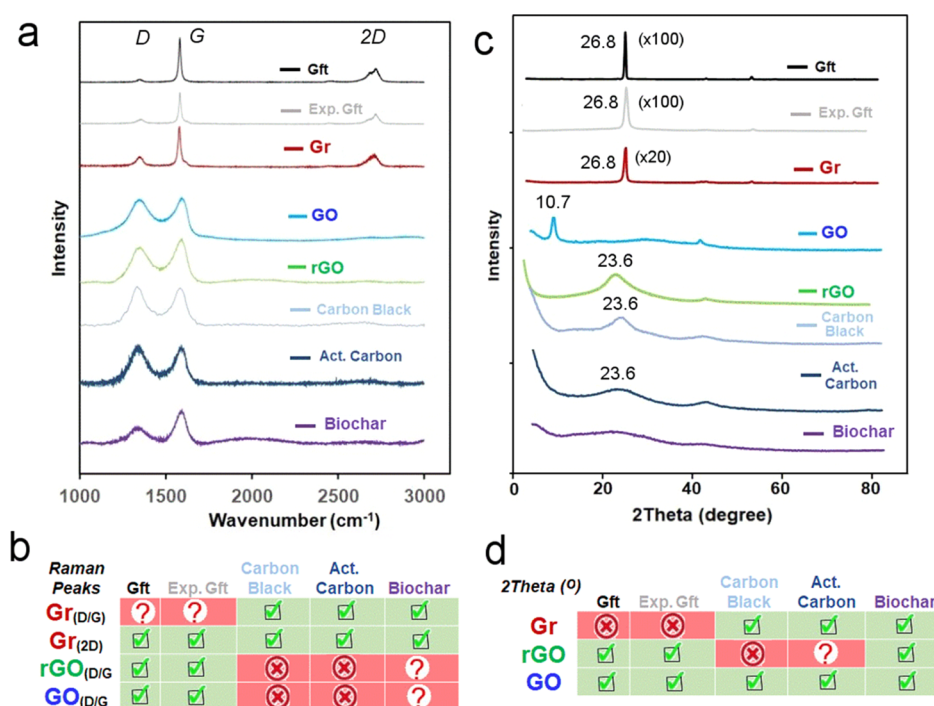
Figure 2. Comparative Raman and XRD spectra of individual graphene materials (pristine graphene, rGO, and GO) and potential carbon counterfeiting materials (graphite, expanded graphite, carbon black, biochar, and activated carbon). (a) Comparative Raman graphs with (b) analytical similarity assessment on key parameters of Raman graphs (D/G, 2D peaks) and the ability to detect the carbon additives in graphene powders. (c) Comparative XRD graphs with (d) analytical similarity assessment on the XRD graphs and their ability to detect these carbon additives in graphene powders. ("X" represents high similarity with lack of the detection, "?" represents high similarity with possible detection, and "tick sign" represents no similarity and high reliability for the detection of additives).

materials such as carbon black, activated carbon, and biochar showed similar hardly distinguishable Raman spectra compared to rGO and GO with the additions of these carbon additives unable to be detected by Raman spectroscopy. In this study, we did not perform and evaluate the Raman characterization of carbon counterfeit mixtures with graphene materials, which requires their dispersion in solution, deposition on substrate, and extensive examination and statistical analysis. Since Raman spectroscopy is a spot analysis, to obtain a reliable outcome and high confidence detection of these carbon counterfeits, large numbers of individual particles (>500) are required to be probed, which is laborious and not practical that indicates the limitation of the Raman spectroscopy method.

XRD is the second comparative method explored to perform direct analysis of materials in powder form with XRD graphs of graphene, rGO, and GO, as presented in Figure S2j and Table S2. These graphs showed typical signatures of these graphene materials as evidenced by their characteristic peaks at $2\theta = 26.5°$ for graphene, 23.3° for rGO, and 9.6° for GO, which are in agreement with the literature.[4−6,25] Individual XRD graphs of graphene materials were compared with the XRD profiles of the series of carbon materials to evaluate the ability of this method to detect these potential carbon counterfeits if they were mixed with graphene materials, as depicted in Figure 2c with the analytical similarity assessment presented in Figure 2d. These results indicate the high similarity between graphene and graphite and expanded graphite that is indistinguishable in terms of their peak positions. The XRD peak of rGO is discernible from graphite, but very similar to the XRD peak of carbon black, biochar and activated carbon, suggesting the limited level of their detection in the rGO sample using the XRD method. It was showed further that GO has remarkable distinctive XRD peaks

from all other carbon materials, indicating that they can be detected if these carbon additives were mixed with GO.

To further assess the capability of the XRD method for the detection of selected carbon counterfeits, a mixture of carbon additives (10%) with graphene, rGO, and GO was characterized using the XRD analysis with the results presented in Figure 3. Surprisingly, results showed that the XRD method can be only successfully applied in two cases (rGO + 10% graphite and GO + 10% graphite) to detect these carbon counterfeiting additives. In all other cases, significant overlapping of characteristic peaks of graphene materials with other carbon additives was observed. This confirmed the lack of the ability of the XRD method to detect their presence at 10% concentration.

The comprehensive Raman and XRD characterization in this study clearly concluded that both methods have significant limitations in detection ofcarbon counterfeits if they are added into graphene powder materials. In particular, the Raman technique, which is recognized as the "gold" standard for graphene characterization, failed to discriminate differences between D and G peaks, which are common for majority of the carbon materials. Hence, due to these limitations, alternative methods to detect these carbon additives as potential counterfeits or impurities are needed.

3.3. Evaluation of Carbon Counterfeits in Graphene Materials Using the TGA Method. In our previous work, we established the baseline of TGA/DTG characteristics of graphene materials such as few-layer graphene, GO, rGO, and graphite as their key impurities, as presented in Figure S4. These graphs show distinctive differences in the thermal decomposition behavior with identified characteristic parameters such as thermal stability (defined as the temperature at which the material starts to decompose), DTG peak range (position),
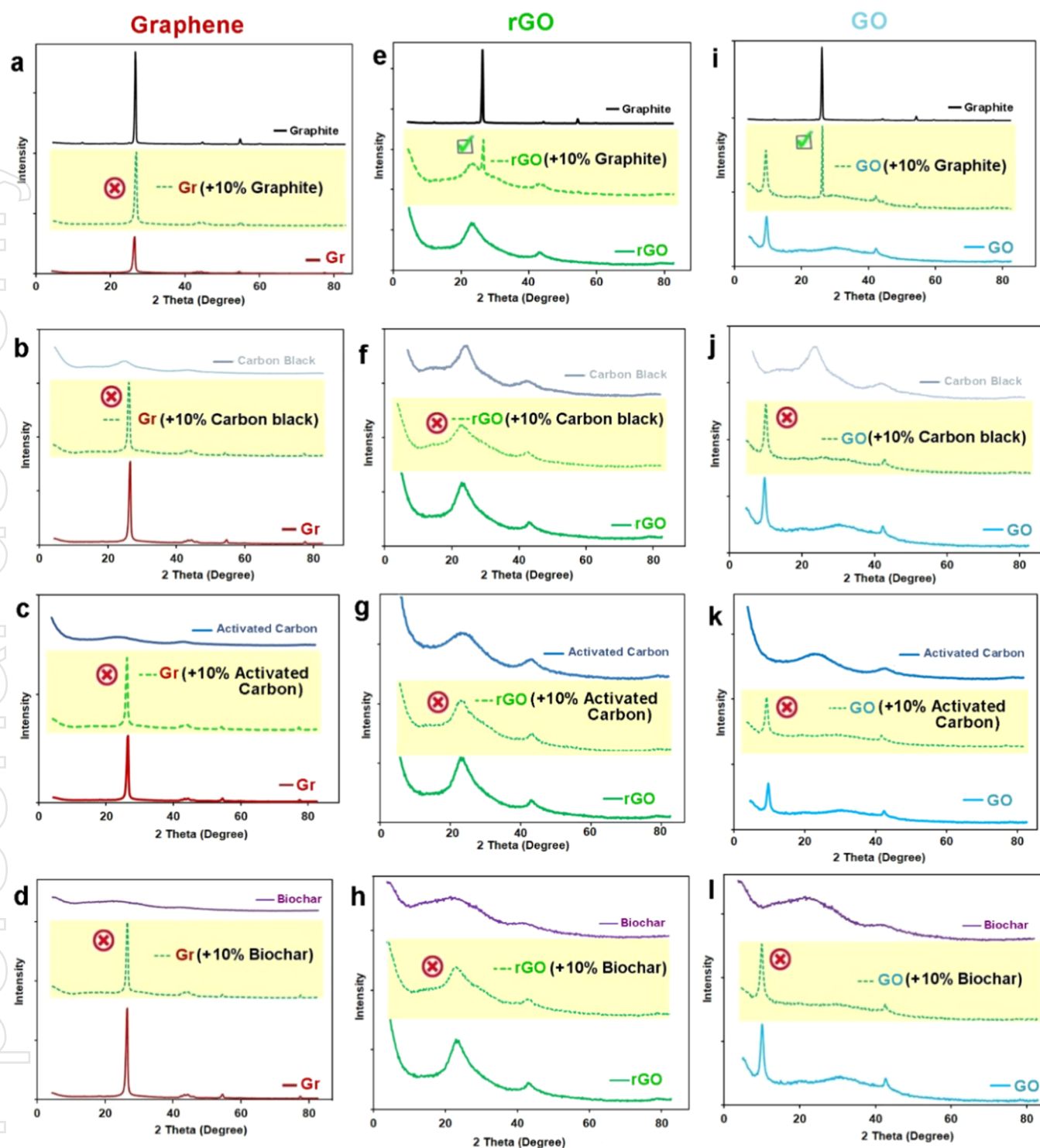
Figure 3. Comparative XRD graphs of graphene materials ((a–d) pristine graphene (FLG), (e–h) rGO, and (i–l) GO) and potential carbon counterfeiting materials (graphite, expanded graphite, carbon black, biochar, and activated carbon) including their mixtures with 10% concentrations.

DTG peak shape, and T_{max}, which are related to their intrinsic chemical and physical properties that can be used as benchmarked parameters against other carbon materials. To demonstrate the application of TGA as a potential method and simple analytical screening tool for the detection of carbonaceous counterfeits in graphene materials, we first established their individual TGA/DTG characteristics as summarized in Figure 4 and Table S3. The obtained TGA and DTG graphs show distinctive differences in their thermal oxidative

decomposition with the identified characteristic parameters such as thermal stability, DTG peak range (position), DTG peak shape, and T_{max}, which represents the intrinsic chemical and physical properties of carbonaceous materials, demonstrating the differences and similarities with graphene, rGO, and GO. Essentially, an initial assessment was performed using the DTG peak and T_{max} value as key parameters in assessing their similarity to evaluate the capability of this method to detect carbon counterfeits (table inset in Figure 4). This analysis in the
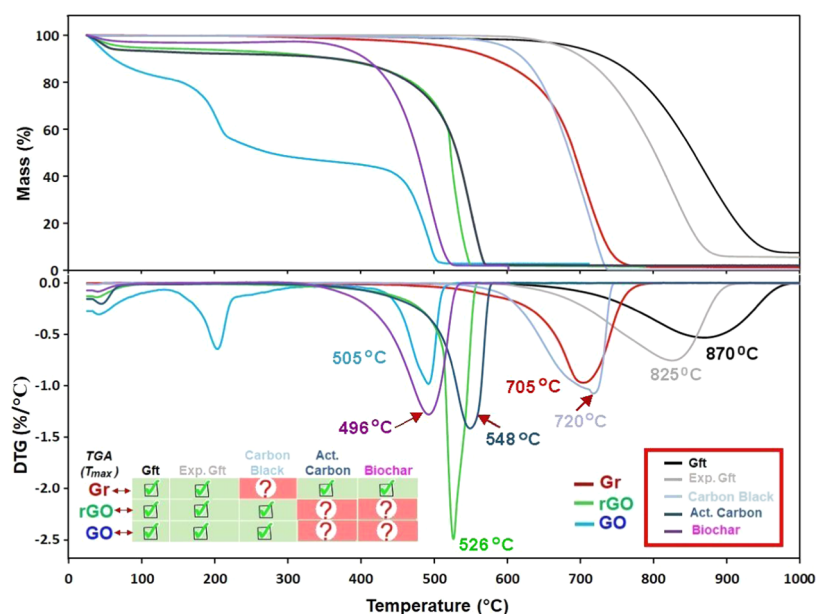
Figure 4. Comparative TGA/DTG graphs of graphene (pristine graphene (FLG), rGO, and GO) and potential carbon counterfeiting materials (graphite, expanded graphite, carbon black, biochar, and activated carbon) with the inset table showing an assessment of the ability of the TGA method to detect these carbon additives in graphene powders based on differences in DTG peaks and T_{max} values.

case of graphene showed that TGA/DTG peaks and T_{max} are distinctive from all carbon materials except for carbon black showing an overlapped DTG peak at a similar position. For GO and rGO, similarities on the DTG peaks and T_{max} positions with a slight overlap of peaks were observed for biochar and activated carbon, indicating a potential challenge for their detection using the TGA technique. Graphite is one of the most likely counterfeits for graphene material, which can be inherited as a result of a poor exfoliation during the production process or artificially added by the purpose. The TGA results showed that because graphite has a very high T_{max} value (>800 0C) compared to all graphene materials, it can be easily detected using the TGA method with high confidence and accuracy.

To evaluate the ability of the TGA method to detect selected carbon counterfeits in this work, TGA/DTG graphs showing comparative graphs of their mixture (10%) with graphene, rGO, and GO are presented in Figure 5. Remarkably, these outcomes confirmed previous results showing that the TGA method can be successfully adopted to detect these carbon additives when added with >10% concentration into graphene materials, in almost all cases. The method not only can perform qualitative detection but also achieve their quantitative determination of the amount of these additives as tabulated in Table S4. The quantitative determination of these carbon additives was not our primary focus in this study, and we observed some differences in quantitative values compared to 10%, which are likely results of impurities of these additives not considered in calculation. In our previous study, we confirmed the detection limit of 1% of graphite additives in graphene that we believe can be applied to most other carbon additives.[22] The cases where carbon additives have overlapped DTG peaks with the host graphene materials are observed for graphene, carbon black, GO, and rGO with biochar and activated carbon. We found that the DTG peaks of their 10% mixture could detect these carbon additives, but with limited peak separation in some cases having high similarity (e.g., carbon black and graphene). To improve the detection of these additives with overlapped DTG peaks, we explored several strategies including the second derivative of TGA curve

(D2TG) approach and reduced heating rate with the results summarized in Figure 6. The results showed that additional D2TG analysis in the case of graphene vs carbon black (Figure 6a) can be successfully used to improve their peak separation and detect these impurities with high confidence. The second strategy based on the reduction of heating rate from 10 to 2.5 °C/min also showed further improvement in the separation of these peaks (Figure 6b). Lowering the heating rate is recommended for TGA when additive components have overlapped DTG peaks, demonstrating the successful detection of carbon additives with very similar thermal properties to graphene materials. To evaluate the reliability and repeatability of this method, we performed a double-blind study and TGA analysis using two operators and two different TGA instruments showing no significant differences (Figure S5 and Table S5, Supporting information). In another study, we found the influence of sampling method using average graphene samples and random sample from 5 kg of powder batch showing slight difference and importance to prepare average sample (Figure S6). The presented results clearly confirmed that the TGA method is superior that can be successfully used to achieve low-cost carbon counterfeiting in graphene materials and perform their qualitative and quantitative analysis that is not possible using other conventional characterization methods recommended for their quality control. Additionally, we would like to highlight that the analysis of counterfeiting materials in graphene should not rely on single characterization method and that complementary methods are often recommended to accomplish highly reliable results.

4. CONCLUSIONS

In conclusion, it was demonstrated that the TGA-DTG method can be successfully used for the qualitative and quantitative determination of potential low-cost carbon counterfeiting materials such as graphite, carbon black, activated carbon, and biochar in industrially produced graphene materials such as graphene (FLG), rGO, and GO. The method is based on the characteristic DTG peak shape and T_{max}, from DTG curves that
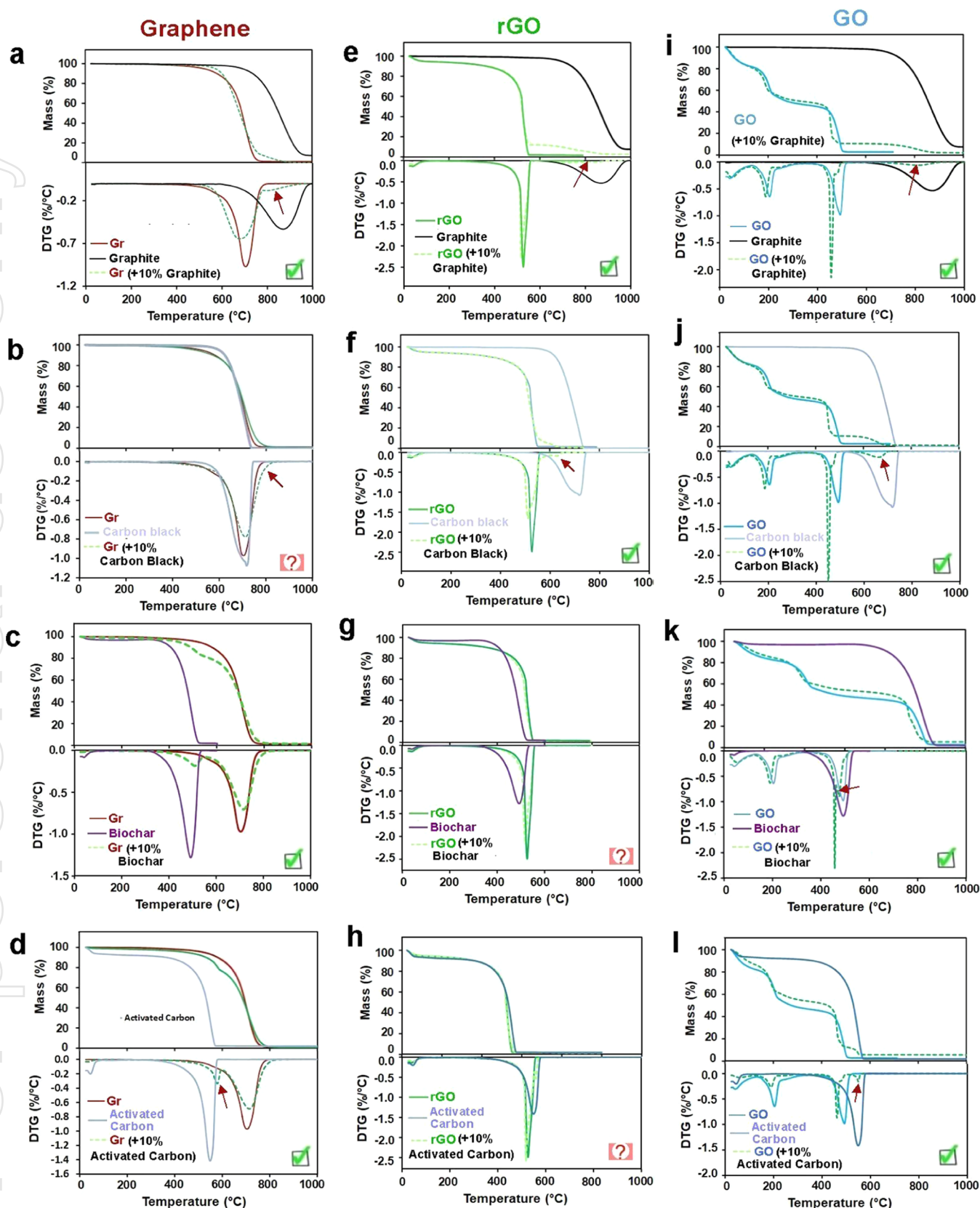
Figure 5. Comparative TGA/DTG graphs of graphene materials ((a−d) pristine graphene (FLG), (e−h) rGO, and (i−l) GO) and potential carbon counterfeiting materials (graphite, expanded graphite, carbon black, biochar, and activated carbon) including their mixtures with 10% concentrations.

can clearly distinguish these carbon additives from graphene materials, not to mention that detecting them at >10% in graphene materials is challenging by other conventional graphene characterization methods. Comparative evaluation of Raman and XRD methods showed analytical limitation to perform this task, which creates an opportunity for counter-
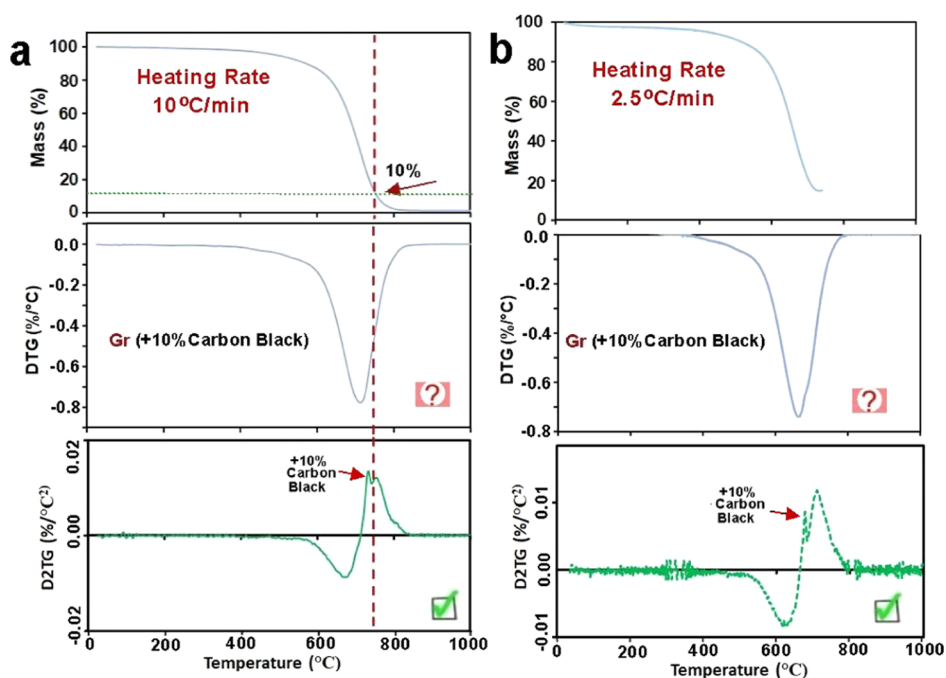
Figure 6. TGA/DTG analysis of graphene mixed with carbon black (10%) as the most difficult case having overlapped DTG peaks. (a) Use of D2TG peaks applied to show successful separation between graphene and carbon black peaks and successful calculation of carbon black %. (b) Use TGA conditions with slower heating rate showing successful detection of most difficult counterfeiting material (carbon black) with similar thermal properties to graphene.

feiting materials to be undetected and pass the quality control using these methods. Prospectively, TGA shows superior performance and is a cheap, rapid, simple, and highly reliable method to prevent this potential counterfeit and will provide more confidence on the quality of industrially produced bulk graphene powders that is critical for the emerging graphene industry and the end users across broad sectors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.1c02662.

> Photos of materials used in this study; SEM, TEM, XPS, Raman, FTIR, AFM, and PSD analyses of graphene, rGO, and GO used in this study; characterization of graphene, rGO, and GO; and derived parameters from TGA-DTG curves of all tested materials (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Dusan Losic − *School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia; ARC Hub for Graphene Enabled Industry Transformation, The University of Adelaide, Adelaide, SA 5005, Australia;* ⓞ orcid.org/0000-0002-1930-072X; Email: dusan.losic@adelaide.edu.au

Authors

Farzaneh Farivar − *School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia; ARC Hub for Graphene Enabled Industry Transformation, The University of Adelaide, Adelaide, SA 5005, Australia*

Pei Lay Yap − *School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia; ARC Hub for Graphene Enabled Industry Transformation, The University of Adelaide, Adelaide, SA 5005, Australia*

Afshin Karami − *School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia;* ⓞ orcid.org/0000-0002-8881-4468

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.analchem.1c02662

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Novoselov, K. S.; Fal, V.; Colombo, L.; Gellert, P.; Schwab, M.; Kim, K. *Nature* **2012**, *490*, 192−200.

(2) Ferrari, A. C.; et al. *Nanoscale* **2015**, *7*, 4598−4810.

(3) El-Kady, M. F.; Shao, Y.; Kaner, R. B. *Nat. Rev. Mater.* **2016**, *1*, No. 16033.

(4) Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I.; Holland, B.; Byrne, M.; Gun'Ko, Y. K.; et al. *Nat. Nanotechnol.* **2008**, *3*, 563.

(5) Wang, G.; Yang, J.; Park, J.; Gou, X.; Wang, B.; Liu, H.; Yao, J. *J. Phys. Chem. C* **2008**, *112*, 8192−8195.

(6) Reiss, T.; Hjelt, K.; Ferrari, A. C. *Nat. Nanotechnol.* **2019**, *14*, 907−910.

(7) Backes, C.; et al. *2D Mater.* **2020**, *7*, No. 022001.

(8) Zhu, Y.; Ji, H.; Cheng, H.-M.; Ruoff, R. S. *Natl. Sci. Rev.* **2018**, *5*, 90−101.

(9) Parviz, D.; Irin, F.; Shah, S. A.; Das, S.; Sweeney, C. B.; Green, M. J. *Adv. Mater.* **2016**, *28*, 8796−8818.

(10) Kauling, A. P.; Seefeldt, A. T.; Pisoni, D. P.; Pradeep, R. C.; Bentini, R.; Oliveira, R. V.; Novoselov, K. S.; Castro Neto, A. H. *Adv. Mater.* **2018**, *30*, No. 1803784.

(11) Kovtun, A.; Treossi, E.; Mirotta, N.; Scidà, A.; Liscio, A.; Christian, M.; Valorosi, F.; Boschi, A.; Young, R. J.; Galiotis, C.; et al. *2D Mater.* **2019**, *6*, No. 025006.

(12) Bøggild, P. *Nature* **2018**, *562*, 502−503.

(13) ISO. Nanotechnologies—Vocabulary—Part 13: Graphene andrelated two-dimensional (2D) materials, 2017.

(14) ISO. Nanotechnologies, Matrix of Properties and Meas-urement Techniques for Graphene and Related Two-dimensional (2D) Materials. *Nanotechnologies—Matrix of Properties and Meas-urement Techniques for Graphene and Related Two-dimensional (2D) Materials*; ISO: Geneva, 2019.

(15) ISO. *Nanotechnologies—Structural Characterization of Graphene, Part 1: Graphene from Powders and Dispersions (ISO/TS 21356-1:2021)*; ISO: Geneva, 2021.

(16) Bianco, A.; Cheng, H.-M.; Enoki, T.; Gogotsi, Y.; Hurt, R. H.; Koratkar, N.; Kyotani, T.; Monthioux, M.; Park, C. R.; Tascon, J. M. D.; Zhang, J. *Carbon* **2013**, *65*, 1−6.

(17) The British Standards Institution (BSI). Properties of graphene flakes. Guide (PAS 1201:2018), 2018.

(18) Pollard, A.; Paton, K.; Clifford, C.; Legge, E. *Characterisation of the Structure of Graphene*, Good Practice Guide No 145, National Physical Laboratory (NPL); NPL: London, U.K., 2017.

(19) Shtein, M.; Pri Bar, I.; Varenik, M.; Regev, O. *Anal. Chem.* **2015**, *87*, 4076−4080.

(20) Bannov, A. G.; Popov, M. V.; Kurmashov, P. B. *J. Therm. Anal. Calorim.* **2020**, *142*, 349−370.

(21) Qiu, Y.; Collin, F.; Hurt, R. H.; Külaots, I. *Carbon* **2016**, *96*, 20−28.

(22) Farivar, F.; Lay Yap, P.; Hassan, K.; Tung, T. T.; Tran, D. N. H.; Pollard, A. J.; Losic, D. *Carbon* **2021**, *179*, 505−513.

(23) Farivar, F.; Lay Yap, P.; Karunagaran, R. U.; Losic, D. *C - J. Carbon Res.* **2021**, *7*, No. 41.

(24) Ferrari, A. C.; Basko, D. M. *Nat. Nanotechnol.* **2013**, *8*, 235.

(25) Yap, P. L.; Kabiri, S.; Tran, D. N. H.; Losic, D. *ACS Appl. Mater. Interfaces* **2019**, *11*, 6350−6362.