

Valorization of Petroleum coke into High-Quality Few-Layer Graphene through Liquid-Phase Exfoliation

Masfer Alkahtani

`mqhtani@kacst.gov.sa`

King Abdulaziz City for Science and Technology (KACST)

Yahya Alzahrani

KACST

Abdulmalik Alessa

KACST

Abdulaziz Alromaeh

KACST

Majed Aljomah

KACST

Faisal Alghannam

KACST

Fahad Albaqami

KACST

Anas Almuqhim

KACST

Abdulaziz Aljuwair

KACST

Ramu Banavath

Texas A&M University

Micah Green

Texas A&M University

Philip Hemmer

Texas A&M University

Article

Keywords: Petroleum coke, Graphene, Low-cost carbon feedstock, Liquid-phase exfoliation, Carbon waste valorization

Posted Date: August 14th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-9893745/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Scientific Reports on October 7th, 2026.
See the published version at <https://doi.org/10.1038/s41598-026-74440-4>.

Abstract

Low-value fuel-grade petroleum coke (pet coke), an abundant byproduct from petroleum refining operations, is traditionally used in low-value fuel and metallurgical applications owing to its high carbon content and ability to be used in the synthesis of advanced carbon materials. In this paper, we demonstrate a non-oxidation-based route for producing conductive few-layer graphene from pet coke through sequential isopropanol assisted pre-treatment, thermal desulfurization, and CO₂ assisted liquid phase exfoliation. Unlike conventional graphene synthesis processes using high temperature chemical vapor deposition, oxidation reduction-based Hummer's type methods, or exfoliation from expensive graphite sources, our approach enables the conversion of inexpensive pet coke into graphene nanosheets using a scalable solvent assisted route. The thermal activation promotes the degree of graphitization to 78% and purity of petcoke, while CO₂ assisted exfoliation allows for the formation of wrinkled few layer graphene sheets with thicknesses ranging from 3–5 layers. Structural and electrical characterization confirm the improvement in graphene exfoliation to 93.5%, decrease in disorder, and efficient production of graphene nanoflakes. The graphene dispersions display stability up to six months and can be transformed into conductive films with a maximum electrical conductivity of 872 S m⁻¹ after thermal annealing. This work establishes pet coke as a promising low-cost carbon resource for sustainable graphene production and offers a practical route for transforming refinery waste into value-added materials for energy storage, conductive coatings, composites, and carbon-based technologies.

Introduction

Low-value fuel-grade pet coke is an abundant, carbon-rich by-product of oil refining, produced during delayed and fluid coking of heavy residual oils. Despite its large supply and low cost, it is still primarily used as fuel or metallurgical carbon[1–3]. Traditional applications of this low-value fuel-grade pet coke result in a little economic profit and usually cause considerable environmental hazards related to sulfur and heteroatom content, as well as trace metal contamination and emissions upon burning[3, 4]. Conversion of pet coke into valuable graphene and other advanced carbon materials is a promising route for carbon waste recycling, eco-friendly materials production, and carbon manufacturing[2, 5].

Economic attractiveness of the proposed conversion becomes apparent when one compares pet coke pricing with that of graphene materials. According to Q1 2026 market reports, prices of pet coke vary between USD 185 and 586 per metric ton, with regional differences (approximately USD 185 t⁻¹ in India, USD 359 t⁻¹ in China, USD 385 t⁻¹ in the United States, USD 450 t⁻¹ in Brazil, and USD 586 t⁻¹ in South Korea) [6–9]. On the other hand, graphene materials are traditionally sold in kilograms. For instance, industrial graphene nanoplatelets and few-layer powders usually have prices from tens to hundreds of USD per kilogram, while specialty materials can cost much more depending on the layer number, size, defects, purity, surface properties, and intended uses[5, 10]. For instance, commercial graphene prices remain strongly dependent on grade, quality and purchase volume, with reported values ranging from ~ USD 20 to 2,000 kg⁻¹. Even if future large-volume production routes reduce graphene prices toward the low tens of USD kg⁻¹, this would still correspond to ~ USD 10,000–40,000 t⁻¹, far above the value of low-

value fuel-grade petroleum coke[11]. Grand View Research predicts a rise from USD 341.4 million in 2025 to USD 4.57 billion in 2033, for a 39% CAGR[12]. An even higher estimate comes from Mordor Intelligence, with a predicted growth from USD 2.09 billion in 2025 to USD 15.20 billion by 2031[13]. The rise would be caused by increasing demands for graphene as material for energy storage, conductive additive, coating, polymeric composite, thermal conductor, sensors, electronics, and fabrication technologies. Thus, the existence of cost-efficient raw materials and suitable transformation technologies would be crucial to move graphene from specialty materials to industry-wide use.

Despite all these advantages, graphene fabrication is confronted with several problems regarding cost, scalability, controllability, and environmental friendliness [14–18]. One of the efficient graphene production techniques involves mechanical exfoliation; however, by nature, this method cannot achieve a high-throughput process and is thus inadequate for large-scale fabrication[19]. Amongst others, there are oxidation procedures used for the formation of graphene oxide that can be performed through the Hummers, modified Hummer's methods[20, 21] and electrochemical exfoliation methods[22]. However, these oxidation methods require harsh conditions such as strong acids and oxidants, rigorous washing steps, and then reduction of the graphene. Most importantly, oxidation results in the damage of graphene's sp^2 carbon network and formation of functional groups that affect its conductivity[20, 21, 23].

LPE has been demonstrated to be an effective strategy in scalable synthesis of few-layer graphene via delamination of graphite material in milder conditions[24–26]. Unlike oxidation-reduction process, LPE maintains the graphene basal plane as a result of avoiding strong oxidative reaction chemistry. In general, conventional LPE approaches have relied on toxic, high-boiling, and difficult-to-eliminate solvents like N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF), creating issues related to solvent toxicity, solvent removal, and costs. As a result, recent trends in this area have shifted the focus toward the use of process-friendly low-boiling point solvents and solvent mixtures, as well as alcohol solvent mixtures, in order to facilitate easier solvent elimination and make a more practical route to the large-scale fabrication of graphene possible[27]. Also, LPE approaches are fully compatible with existing processing approaches, including bath sonication, probe sonication, high-shear mixing, and continuous flow LPE. [15, 24, 26–29].

Petroleum coke has been identified as an economically viable carbon precursor material for the production of graphene family materials such as graphene oxide, reduced graphene oxide, electrochemically-exfoliated graphene, and graphene-like carbons. Most of the reported approaches depend upon oxidative processing or electrochemical and chemical activation methods. The hummers type of oxidative approach on heat-treated petroleum coke has been used for the production of graphene oxide that is then thermally or hydrothermally reduced to produce reduced graphene oxide; although effective, this method involves the introduction of oxygen-related defects in the carbon structure and requires an extra step of reduction to restore conductivity[16]. Electrochemical exfoliation approach has also revealed that graphene could be produced using petroleum coke, but the process depends upon nitric acid treatment, electrochemical potential, extensive washing, and two-stage centrifugation process for separating graphene from other non-graphene materials[1]. In the reported study[1], The yield of

graphene obtained through isolation from coke was found to be around 1.6%, thereby pointing to the difficulty involved in directly producing graphene from coke owing to its heterogeneous nature, contamination with impurities, and lower degree of graphitic order as compared to graphite. There have been other techniques involving phosphoric acid activation and subsequent electrochemical exfoliation in sulfuric acid that have produced graphene-like products useful in electrochemical energy storage devices, but these processes still require use of strong acids and high temperature treatments[30].

According to recent studies, petroleum coke emerges as an interesting option as a carbon precursor; however, at the same time, the issues involved in scaling up the process of converting it into high-quality graphene have been highlighted [6]. These studies recognize the potential of petroleum coke as a prospective but largely unexploited source of graphitic materials on one hand, and identify the major barriers that prevent its application on the other hand: rigorous chemical treatment, oxidation-induced damage, low isolation efficiency, and complex purification. There is an immediate need for development of environmentally-friendly, non-oxidizing, and more efficient method to produce few-layer graphene from petroleum coke.

In this work, we demonstrate an oxidation-free strategy for valorizing pet coke into highly conductive few-layer graphene through sequential IPA pretreatment, thermal purification/desulfurization, and CO₂-assisted liquid-phase exfoliation. This integrated process produces few-layer graphene in high yield, with excellent structural quality, electrical conductivity, and dispersion stability, achieving performance comparable to or exceeding few-layer graphene produced from commercial graphite reported in the literature. It is significant to note that the process is not limited to pet coke only; rather, it can be used for other carbonaceous substances as well, including asphaltenes, spent coffee grounds, and biochar. By coupling refinery-waste upgrading with scalable graphene production, this approach provides a practical route for expanding the graphene economy while creating added value from low-cost and underutilized carbon resources.

Results and Discussion

Figure 1a presents the main stages of the process of graphene preparation from pet coke including prewashing with isopropyl alcohol (IPA), annealing at high temperature under argon atmosphere, assisted liquid-phase exfoliation with CO₂ via sonication in IPA/CO₂ saturated aqueous media, and separation of the few-layers graphene. The initial as-received pet coke was crushed below 90 μm particle size and prewashed with hot IPA to remove hydrocarbon impurities, tar residues, and surface contaminants (detailed in the materials and methods section, section 1 in the supporting Information, and **Figure S1**). After prewashing, the precursor showed a more homogeneous character. The appearance of clearer D- and G-bands in the Raman spectrum shown in **Figure S1(b and d)** proved more exposed carbon framework ready for graphitization and subsequent exfoliation with CO₂. In this process, IPA pretreatment improves the wetting of pet coke particles, removes oils and tar-like residues, and enhances compatibility with the subsequent exfoliation medium. This step is particularly important for scalability because IPA has low surface tension, good affinity toward sp²-rich carbon surfaces, easy

post-processing separation, relatively low cost, and lower health and safety risks compared with chlorinated solvents[27, 28].

The X-ray diffraction analysis (XRD) was used for studying the changes in the structure of the prewashed pet coke sample as a function of thermal activation temperature. **Figure 1b** demonstrates that the as-received pet coke belongs to low-grade, disordered carbon with a wide and relatively weak (002) peak at $2\theta = 25.36^\circ$ corresponding to interlayer distance $d_{002} = 0.351$ nm. As compared with the ideal graphite with $d_{002} = 0.3354$ nm, such interlayer spacing indicates turbostratic and partly amorphous which does not yield the good quality of crystalline graphene.

With increasing thermal annealing temperature up to 1000 °C, the sharpness and position of the (002) shift to higher 2θ values. Thermal treatment at 1200 °C results in further improvement in the stacking coherence of the crystallites as evidenced by even sharper and stronger (002) peak. The most prominent change in the structure occurs upon heating to 1400 °C resulting in shifting of the peak to $2\theta = 26.41^\circ$ corresponding to $d_{002} = 0.337$ nm. Thermal treatment in the presence of an inert atmosphere not only reduces sulfur (discussed later) and other heteroatom content but also induces the ordering of pet coke structure, thus facilitating exfoliation and subsequent processing[31]. Based on the Mering–Maire relationship using non-graphitized $d_{002} = 0.344$ nm and ideal graphite with $d_{002} = 0.3354$ nm, the sample of pet coke annealed at 1400 °C shows an approximate value of the graphitization degree close to 78% [32]. This calculation was generalized for all annealed pet coke sample as summarized in Table 1 and detailed in section 2 in the supporting Information.

The Raman data for the graphene products produced using liquid-phase exfoliation of the pet coke samples are shown in **Figure 1c**, whereas the calculated XRD and Raman parameters are listed in Table 1. As mentioned above, unmodified pet coke shows very low exfoliation efficiency, resulting in the low I_{2D}/I_G ratio of 0.28. It indicates that simple ultrasonication of pet coke as a starting material is not sufficient for the production of graphene with few layers. In turn, increasing the temperature for pet coke annealing leads to a higher I_{2D}/I_G ratio up to 0.67 for graphene obtained from pet coke annealed at 1400 °C (Raman spectrum of pet coke annealed to 1400 °C is shown in **Figure S1(c)**). At the same time, the I_D/I_G ratio drops from 1.12 down to 0.60, which reflects lower disorder in graphene and implies better ordering of its structure. Thus, it becomes evident based on the Raman data that thermal treatment significantly improves not only exfoliation efficiency but also the quality of obtained few-layer graphene.

Different solvents were used in order to improve the graphene exfoliation process, including acetone, chloroform, isopropanol (IPA), and an IPA/CO₂-saturated water solution. According to the Raman analysis of the prepared suspensions, the IPA/CO₂-H₂O solvent mixture resulted in the best response. Specifically, graphene flakes obtained from the use of this solvent mixture had the lowest I_D/I_G ratio (0.40) and highest I_{2D}/I_G ratio (0.73) compared to the other solvents utilized (Supporting Information **Section S3, Figure S2**). This outcome was caused by the combination of stabilizing properties of IPA towards graphitic surface and enhanced cavitation-induced delamination of graphene due to CO₂

presence in the solvent. CO₂-assisted exfoliation with the help of sonication provides a way to exfoliate pet coke into few-layer graphene while providing colloidal stability due to shear forces caused by cavitation. The liquid phase enriched by CO₂ can be regarded as gas-enriched solvent and its effect on sonication has been studied before in the context of cavitation dynamics. Prior litterateurs have shown that dissolved gases have a strong effect on the acoustic cavitation by affecting such cavitation properties as bubble nucleation, rectified diffusion, bubble growth and collapse behavior, coalescence, cavitation intensity[33-35]. Therefore, CO₂ saturation in the liquid phase can contribute to the cavitation-assisted interfacial disruption during sonication-induced delamination assisted by IPA and nanosheet stabilization. On the contrary, chloroform resulted in the worse graphene exfoliation, characterized by the highest I_D/I_G ratio (0.97) and lowest I_{2D}/I_G ratio (0.35). Overall, it can be concluded that high-temperature thermal treatment and the use of IPA/CO₂-H₂O mixture are both required for obtaining few-layer graphene from petroleum coke.

Table 1: Evolution of structure for pet coke (starting pet coke samples) and exfoliated few-layers graphene from each pet coke sample based on their annealing temperatures. The structural properties for the x-ray's diffraction data represent the amount of graphitization within the pet coke precursors, whereas the Raman ratios are based on I_{2D}/I_G ratios after being sonicated using CO₂ gas.

Sample	Annealing Temperature (°C)	XRD (002) Position (2θ)	d ₀₀₂ (nm)	Estimated graphitization degree (%)	I _{2D} /I _G (Raman*)	Yield
As-received PC		25.36°	0.351	0	0.28	N/A
PC-1000	1000	~25.8°	~0.345	~ 0	0.30	Limited FLG
PC-1200	1200	~26.1°	~0.340	~ 33%	0.46	Effective FLG
PC-1400	1400	26.41°	0.337	~ 78%	0.67	3-5 layers FLG

The morphological changes from dense coke particles to graphene nanosheets, post-thermal activation and liquid-phase exfoliation, are shown in **Figure 2**. The dense, irregular, and strongly agglomerated pet coke has a surface of granules. The SEM images under low and high magnification, as presented in **Figure 2(a-b)**, clearly show the presence of compact block-shaped particles without any lamella-sheet appearance. This implies that the graphitic phases in the precursor are poorly developed and embedded in dense carbonaceous matrix. On the other hand, the graphene material formed after IPA treatment, 1400 °C annealing, and CO₂-assisted ultrasonic treatment possesses unique flake-like appearance. **Figure 2(c-d)** shows the presence of platelet structures having wrinkles, step terraces, and loosely packed restacking. All these features point towards the formation of exfoliated graphene nanoplatelets

via liquid phase processing route. From the morphological point of view, it is evident that the process not only involved cleaning/grinding of pet coke but also delamination of the material.

Further proof of few-layer graphene formation is provided by the high-resolution TEM image in **Figure 2(e)**. The low-magnification TEM images show electron-transparent, crumpled, and overlapping sheets having lateral sizes reaching hundreds of nanometers. The sheet folding edges suggest thin graphene sheets and not densely packed carbon clusters. High resolution TEM (HRTEM) studies have shown that graphitic lattice planes and their edges contain up to 3-5 layers, as seen in **Figure 2(f)**. The FFT image of the same HRTEM picture shows that the material is of crystalline graphite structure, thus ruling out the possibility of an amorphous carbon material.

Spectra shown in **Figure S3** further depict Raman data along with the respective TEM pictures of the products obtained from as-received pet coke and from pet coke annealed at 1000, 1200, and 1400 °C. It was found that increased activation temperature contributes significantly to the development of more distinct Raman signals of exfoliated graphene, as well as to forming thinner, electron-transparent layers. In particular, it can be observed that samples annealed at 1400 °C possess the most pronounced D, G, and 2D peaks as well as the most distinct few-layered structure.

The analysis of elemental purity during the conversion of pet coke into few-layer graphene was carried out by SEM–EDS analysis. The pristine pet coke showed tightly packed, irregular particles with heterogeneous morphological features as shown in **Figure S4(a)**. According to the results of the elemental map and EDS analysis, the raw material had a high content of carbon along with the significant amount of sulfur, oxygen, and minor traces of iron as illustrated in **Figure S4(b and c)**. The EDS spectrum of the raw material showed the presence of 81.4 wt% of carbon, 7.0 wt% of oxygen, 8.78 wt% of sulfur, and 2.82 wt% of iron, confirming the high sulfur content of the initial pet coke sample and indicating the need for thermal desulfurization before exfoliation.

After the treatment of the pet coke sample with IPA, high-temperature thermal activation, and CO₂-assisted exfoliation, there were observed changes in the sample morphology and chemical composition. The SEM images of the resulting product showed a flat layered structure corresponding to exfoliated graphene flakes as demonstrated in **Figure 2(c and d)** and **Figure S5(a and b)**. EDS mapping demonstrated a high concentration of carbon with low levels of sulfur and oxygen as shown in **Figure S5(c)**. In addition, the treated sample had approximately 96.6 wt% of carbon, 2.1 wt% of sulfur, and 1.4 wt% of oxygen, without any traces of iron in the selected region as shown in **Figure S5(d)**. Thus, sulfur elimination from 8.78 to 2.1 wt% indicates that the treatment procedure reduces sulfur concentration by about 76%.

We next fine-tuned the graphene exfoliation process using the normalized Raman I_D/I_G and I_{2D}/I_G intensity ratios as indicators of graphene quality and exfoliation efficiency. **Figure 3** summarizes the effects of sonication time, dispersion concentration, IPA:CO₂-saturated water ratio, and sonication power on the Raman intensity ratios. In general, higher I_{2D}/I_G values indicate more efficient exfoliation into

thinner graphene nanosheets, while lower I_D/I_G values correspond to reduced defect formation during exfoliation. Therefore, the optimal condition is identified by maximizing I_{2D}/I_G while minimizing I_D/I_G .

The influence of sonication time was first investigated because liquid-phase exfoliation requires a balance between sufficient delamination and preservation of the structural integrity of the graphene nanosheets. This effect is clearly shown in **Figure 3(a)**, where short sonication times are accompanied by very small values of I_{2D}/I_G . Indeed, this effect is illustrated schematically in **Figure S6** alongside with the TEM images, where short sonication leads to the formation of very thick and stacked graphitic flakes in contrast to well-exfoliated nanosheets obtained after long sonication. The dependence of the Raman peaks evolution during sonication from 1 to 23 h, see **Figure S7**, confirms their dependence on the time of sonication process.

With increasing sonication time, delamination becomes more effective, and the optimum range is found at 10–12 h, where the highest I_{2D}/I_G values are obtained. At the same time, the I_D/I_G values remain relatively low, indicating that efficient exfoliation is achieved without introducing excessive structural defects. This is consistent with the TEM images in **Figure S6**, which show thin, laterally extended, and transparent graphene nanosheets after optimal sonication. In contrast, excessive sonication does not further improve graphene quality. Instead, prolonged acoustic exposure leads to fragmentation of the nanosheets into smaller, irregular graphitic flakes, as also shown schematically and by TEM in **Figure S6**. The reason behind the intermediate I_{2D}/I_G values during long sonication times is due to the possible damage caused by the sonication process on the edges and surfaces of graphene.

The impact of concentration on exfoliation efficiency is illustrated in **Figure 3(b)**, an outcome that has been confirmed by the Raman analysis data presented in **Figure S8**. Suspensions of 1, 3, 5, 7, 10, 13, 15, and 20 mg mL⁻¹ demonstrate the characteristic D, G, and 2D bands of graphitic carbon. At lower concentrations, the number of graphitic particles available for exfoliation remains small. With increasing concentration, the value of I_{2D}/I_G increases and reaches its maximum point at 10 mg mL⁻¹ while the value of I_D/I_G becomes minimal. Consequently, the optimum concentration turns out to be 10 mg mL⁻¹ which provides both appropriate concentration and efficient exfoliation due to acoustic cavitation. The decrease in the ratio I_{2D}/I_G seen at larger concentrations is a result of denser suspensions and less acoustic energy being transferred.

The relative amount of IPA to the CO₂-saturated water is especially influential in the process, which is also illustrated graphically in **Figure 4(c)** and further confirmed by the normalized Raman spectra in **Figure S9**. The Raman spectrum recorded for solvent mixtures at ratios of 4:1, 3:2, 1:1, 2:3, and 1:4 shows the distinctive D, G, and 2D bands. Out of those mixtures, the 3:3 mixture corresponds to an equal amount of IPA to CO₂-saturated water and provides the minimum I_D/I_G of 0.52 and maximum I_{2D}/I_G of 0.68.

Influence of solvent ratio can be seen in **Figure S10**. When there is excess IPA concentration combined with low concentration of CO₂ saturated water, IPA helps in wetting and stabilizing the graphite surface

while the low concentration of CO₂ saturated water limits the formation and collapse of gas-rich cavitation microbubbles and decreases the ability of the liquid medium to penetrate between graphitic layers. Complete exfoliation can be achieved when both solvent concentrations are equal, with IPA stabilizing the exfoliated graphene surface while CO₂ saturated water causes cavitation hence allowing penetration of liquids between layers of graphite. In this case, the dispersion is dark, homogeneous, and stable without any signs of precipitation. However, increasing concentration of CO₂ saturated water above optimal level results in poor compatibility between solvent and graphene leading to re-stacking and precipitation as shown in **Figure S10**.

Figure 3(d) illustrates the effect of sonication power, and the normalized Raman spectra obtained using sonication powers of 240, 300, 400, and 500 W are presented in **Figure S11**. All the Raman spectra show characteristic peaks of D, G, and 2D bands that indicate the formation of graphitic carbon structures. Higher sonication power favors cavitation and therefore exfoliation, as seen in higher I_{2D}/I_G ratios. The highest I_{2D}/I_G ratio was observed at 500 W along with lower I_D/I_G ratio as compared with those values obtained using lower powers.

It is shown from **Figures 3 and S6-S11** that the optimized conditions for exfoliation process include sonication duration of 10-12 h, dispersion concentration of 10 mg mL⁻¹, IPA/CO₂ saturated water solvent in ratio of 1:1 and sonication power of 500 W. With such conditions, CO₂-assisted liquid phase exfoliation can be successfully applied to obtain few-layered graphene by thermal activation of petcoke.

The graphene-rich fraction was achieved through liquid phase exfoliation of the thermally desulfurized pet coke sample, and subsequently mild centrifugation of the exfoliated suspension at 500 rpm for 3 minutes to eliminate large flakes and less exfoliated material. This suspension was drop cast on silicon wafer for AFM imaging. As shown in **Figure 4(a)**, the AFM micrograph shows dense dispersion of nano-flakes with very little clustering, showing that the step of mild centrifugation was effective in enriching the suspension with small size graphene flakes. AFM micrograph of an individual nano-flake or a clustered flake as seen in **Figure 4(b)** confirms the platelet-like morphology of the exfoliated product.

The lateral size distribution obtained from AFM image analysis is summarized in **Figure 4(c)**. A total of 245 detectable features were counted, among which 229 features exhibited lateral dimensions below 0.6 μm. This corresponds to a number-based nanoflake population fraction of approximately 93.5%. The detailed spot-detection procedure used to extract the lateral size distribution is provided in **Figure S12**. In this supporting figure, graphene flakes and spots in the AFM image are highlighted by green outlines generated using an image-segmentation method calibrated with the 5 μm scale bar. The text portion of the scale bar was excluded from the quantitative analysis to avoid false detection. The segmented flakes were then used to determine the lateral size distribution and calculate the number fraction of features below 0.6 μm.

The result indicates that the analyzed fraction is strongly enriched in small graphene nanoflakes. Together with the TEM/HRTEM observations, which suggest that the exfoliated flakes mainly consist of

approximately 3–5 graphene layers, the AFM results support the conclusion that the optimized exfoliation and fractionation procedure produces a graphene-rich product.

A typical atomic force microscopy (AFM) height profile of such a flake/restacked cluster as shown in **Figure 4(b)** can be seen in **Figure 4(d)**. A flat baseline was observed on the silicon substrate with a subsequent fast rise in the height near the flake boundary. In this way, a step-like feature with a height of a few nanometers can be identified, which corresponds to a height increase within the range of 5–7 nm. Such a small height change confirms that it could be either a graphene flake with just a few layers or a local restacking of some clusters of the graphene flakes.

The long-term stability of graphene dispersions is critical for their practical use in inks, coatings, fillers, and electrode slurries. **Figure 5** evaluates the stability of the optimized pet coke-based graphene dispersion in water-ethanol solvent combination with 1:1 volume ratio [38]. As shown in **Figure 5(a)**, the dispersion retains its stability over time without any signs of settling down.

As seen from the Raman spectra measured for a period of six months, given in **Figure 5(b)**, there is no change observed in the D, G, and 2D peaks, which implies the absence of any change to the sp^2 hybridization structure of the carbon sheets even after the period of storage. The absence of any considerable broadening or formation of additional peaks related to defects in the material shows that the graphene is not chemically degraded by the dispersion medium.

This statement is validated with data obtained using zeta potential and DLS shown in **Figure 5(d)**. Zeta potential does not change significantly for six months maintaining a relatively constant value of ~ -25 mV, whereas the hydrodynamic diameter does not exceed 0.5–0.6 μm . However, although a zeta potential below -30 mV is often associated with highly stable electrostatic dispersion, in the current case, the stabilization of dispersed carbon nanoparticles can be due to electrostatic repulsion combined with solvent–graphene interaction and decreased aggregating tendency in aqueous/ethanol environment. Thus, one may conclude that petcoke-based graphene is suitable for being used as a stable liquid dispersion.

The electrical performance of the pet coke-derived graphene was evaluated and benchmarked against reported graphene films prepared from coke- and graphite-based precursors, as summarized in **Table 2**. In this work, few-layer graphene, mainly consisting of 3–5 layers, was produced through IPA pretreatment, thermal activation of pet coke at 1400°C under Ar, and CO_2 -assisted liquid-phase exfoliation. The drop-cast petcoke-derived FLG film exhibited an electrical conductivity of 165 S m^{-1} without pressure treatment, post-deposition annealing, or chemical doping, demonstrating that the exfoliated nanosheets already form a conductive percolated network under simple film-processing conditions. Processing the same material into a vacuum-filtered buckypaper increased the conductivity to 365 S m^{-1} , which can be attributed to improved nanosheet packing density, reduced void space, and enhanced interflake contact.

The obtained conductivity is also competitive with graphene films prepared from graphite-based starting materials by liquid-phase exfoliation. For example, graphene films produced from surface-enhanced flake graphite (SEFG) and primary artificial graphite (PA) using liquid-phase exfoliation were reported to exhibit conductivities of approximately 86 and 200 S m⁻¹, respectively[29]. The present drop-cast petcoke-derived FLG film, with a conductivity of 165 S m⁻¹, approaches this graphite-derived benchmark despite being prepared from a low-value refinery by-product rather than commercial graphite. Moreover, the vacuum-filtered petcoke-derived buckypaper reached 365 S m⁻¹ without post-film annealing, exceeding the reported SEFG/PA-derived graphene film conductivity.

A direct comparison with the coke-derived graphene benchmark reported by Saha et al.[1] further highlights the competitiveness of the present approach. In that study, graphene nanosheets were produced from petroleum/needle coke by electrochemical exfoliation, followed by vacuum filtration and high-temperature annealing at 1100 °C for 12 h[1], yielding a buckypaper conductivity of 474 ± 11.9 S m⁻¹. In the present work, the petcoke-derived FLG buckypaper reached 365 S m⁻¹ without post-film annealing and increased to 475 S m⁻¹ after annealing at only 500 °C, matching the conductivity reported by Saha et al. after 1100 °C annealing. Further annealing at 800 and 1400 °C increased the conductivity to 520 and 872 S m⁻¹, respectively, exceeding both the graphite-derived SEFG/PA benchmark and the previously reported coke-derived graphene benchmark. These results demonstrate that the combined thermal purification/desulfurization and CO₂-assisted exfoliation strategy can convert low-value pet coke into electrically conductive few-layer graphene films with performance comparable to, and after optimized annealing superior to, graphene films derived from both graphite and coke precursors.

Table 2: Electrical conductivity of petroleum coke-derived few-layer graphene films prepared under different processing conditions.

Sample / Condition	Sheet resistance, Rs (Ω sq ⁻¹)	Film thickness (μm)	Electrical conductivity, σ (S m ⁻¹)
Petcoke-derived FLG film	6061	1.0	165
Densified petcoke-derived FLG film	2740	1.0	365
Petcoke-derived FLG film annealed at 500 °C	2105	1.0	475
Petcoke-derived FLG film annealed at 800 °C	1923	1.0	520
Petcoke-derived FLG film annealed at 1400 °C	1147	1.0	872

Finally, A central advantage of this strategy is its ability to valorize different carbon resources using the same oxidation-free processing. In order to show that this technique is generally applicable, the protocol was tested on four different carbon-containing materials, namely graphite, asphaltene, spent coffee grounds, and biochar, as shown in **Figure 6(a)**, having diverse sources, structures, and contaminant

compositions. In all cases, a pre-wash with IPA followed by annealing with argon and sonication in IPA/CO₂-H₂O resulted in graphene-like few-layer sheets.

The results from Raman spectroscopy show that the products made from all feedstocks contain the characteristic D, G, and 2D peaks for graphitic carbons, thereby demonstrating that similar processing produces graphene-like materials from a broad spectrum of feedstocks, as shown in **Figure 6(b)**. The existence of distinct 2D peak in all products suggests that successful exfoliation of the graphene materials into few layer materials has been achieved while different intensity levels of the D band indicate different quality level and level of defects in the material due to its different feedstock source. The graphene material prepared from graphite shows lower degree of disorder and higher intensity of graphitic structure, which is expected from a well-ordered feedstock. In contrast, the materials prepared from asphaltene, coffee and biochar show higher intensities of D peaks, due to the defect and heteroatom containing nature of carbon structures.

The representative transmission electron microscopy (TEM) images shown in **Figure 6(c-f)** offer even more evidence of the generality of the method by showing the presence of thin, clear, and wrinkled nanosheets from all feedstocks studied. A more detailed analysis of the graphene produced from each precursor that covers graphene sheet thickness distribution, lateral dimensions, elemental and chemical composition, defects and their nature, and electrical properties would provide important information on feedstock-specific differences. However, such studies are beyond the scope of this work and need to be addressed in subsequent focused investigations. Overall, the obtained Raman and TEM results confirm that the described methodology is a universal tool for graphene production from inexpensive and wasteful carbon sources.

Conclusion

This paper demonstrates a scalable and oxidation-free strategy for valorizing pet coke into few-layer conductive graphene. The process involves pretreatment using IPA, thermal desulfurization, and CO₂ assisted exfoliation without any need for strong oxidants. It was shown that IPA pretreatment improved the wettability of pet coke and assisted in removing surface residues, while thermal activation at 1400 °C under Ar promoted graphitic ordering and purification. This was confirmed by the shift of the XRD (002) peak from around 25.36° to 26.41°, corresponding to a decrease in interlayer spacing from 0.351 to 0.337 nm. Thermal treatment also increased the carbon concentration from 81.4 to 96.6 wt.% and reduced the sulfur concentration from 8.78 to 2.0 wt.%, corresponding to approximately 77% sulfur removal. These structural and compositional improvements enabled more effective exfoliation during the subsequent CO₂-assisted liquid-phase process. Raman spectroscopy of the exfoliated graphene showed an increase in the I_{2D}/I_G ratio from 0.28 to 0.67, together with a decrease in the I_D/I_G ratio from 1.12 to 0.60, confirming improved exfoliation and reduced structural disorder. SEM, TEM, HRTEM, and AFM analyses further verified the formation of wrinkled few-layer graphene nanosheets, mainly 3–5 layers thick. AFM-based statistical analysis showed that 93.5% of the

detected nanoflake population had lateral dimensions below 0.6 μm , indicating strong enrichment of small few-layer graphene nanoflakes.

The prepared graphene dispersions showed stability for six months based on the value of zeta potential of about -25 mV and the size of about 0.5-0.6 μm . Conductive films exhibited high electrical conductivities of up to 872 S m^{-1} after vacuum filtration and argon annealing. This oxidation-free strategy was further extended to graphite, asphaltene, spent coffee grounds and biochar, demonstrating its versatility across diverse carbon feedstocks. Finally, the reported results prove that pet coke is a suitable low-cost source for sustainable few-layer graphene synthesis for many promising applications, especially in the energy storage.

Materials and Methods

1. Materials

Raw pet coke sample was sourced locally from Saudi Aramco Total Refining & Petrochemical Company (SATORP, Jubail, Saudi Arabia), while isopropanol (IPA, 99.999%, Sigma-Aldrich) was used as both pretreatment agent, dispersant, and wash solution. Water enriched with CO_2 or freshly bubbled sparkling water was the medium for the cavitation-assisted exfoliation process. Inert argon gas (99.999%) was used during heat treatment procedures.

All chemicals were used without further purification when no other specifications were provided. The raw pet coke represented the only substance to be processed via pretreatment involving washing with hot IPA followed by further rinsing in IPA to remove surface oils, tar-like contaminants, and any other loosely adsorbed impurities before thermal treatments and exfoliation. Glass slides and membrane filters were used as substrates/supports for preparing graphene films and buckypapers, respectively. Deionized water was used for cleaning when required.

2. Solvent Pretreatment of Petroleum Coke

Prior to thermal treatment, the as-received pet coke was subjected to an IPA-based solvent pretreatment, as detailed in Supplementary Materials **Section 1** and schematically shown in **Figure S1**. First, the raw pet coke was ground and sieved to obtain particles smaller than 90 μm . The sieved powder was then dispersed in high-purity isopropanol under mild heating and continuous stirring for 6 h to remove weakly bound hydrocarbons, residual oils, tar-like surface species, fine particles, and other loosely attached impurities. After pretreatment, the pet coke was washed several times with fresh IPA and dried overnight at $80\text{ }^\circ\text{C}$ before thermal processing.

3. Thermal Activation of Pet coke samples.

After IPA pretreatment and drying, the pet coke powder was thermally activated in a tube furnace under continuous argon flow. The dried sample was placed in a high-temperature-resistant crucible and heated under an inert argon atmosphere. The thermal treatment was carried out in two sequential steps: first,

the sample was heated to 500 °C and held for 5 h to promote carbonization and removal of residual volatile species. The temperature was then increased to the target high-temperature annealing condition of 1400 °C and maintained for 8 h to enhance graphitic ordering and thermal purification of the petroleum coke. After annealing, the furnace was allowed to cool naturally to room temperature under argon before the thermally activated pet coke was collected.

The same two-step thermal protocol was applied to all pet coke samples annealed between 1000 and 1400 °C, with the final high-temperature holding step adjusted according to the target annealing temperature.

4. CO₂-Assisted Liquid-Phase Exfoliation

The thermally activated pet coke was exfoliated using a mixed IPA/CO₂-saturated aqueous medium. The exfoliation medium was prepared by combining IPA with CO₂-saturated water, or freshly prepared sparkling water, at different volume ratios to evaluate the effect of solvent composition on exfoliation efficiency. The optimized solvent system consisted of equal volumes of IPA and CO₂-saturated water and was therefore used for subsequent exfoliation experiments. IPA was used to improve wetting and dispersion stability of the graphitic carbon layers, whereas the CO₂-saturated aqueous phase was introduced to enhance acoustic cavitation and facilitate solvent penetration between graphitic layers during sonication.

For exfoliation, the thermally activated pet coke was dispersed in the optimized IPA:CO₂-saturated water mixture at a concentration of approximately 10 mg mL⁻¹. The dispersion was then subjected to ultrasonic treatment at 500 W for 10–12 h. During sonication, acoustic cavitation promoted delamination of the graphitic domains into few-layer graphene nanosheets.

5. Structural and Chemical Characterization

5.1 X-Ray Diffraction

X-ray diffraction was used to study the structure development in pet coke when exposed to thermal treatment and exfoliation. X-ray diffraction data of the annealed pet coke and graphene samples were recorded for the starting material petroleum coke, pet coke subjected to thermal treatment, and the final exfoliated graphene. Graphitic carbon (002) reflection was considered to determine the interlayer spacing and stacking. Interlayer spacing was calculated based on Bragg's equation as detailed in section S2 in the supporting information.

5.2 Raman Spectroscopy

Raman spectra of graphene samples were performed using a home-built Raman system equipped with a 532 nm laser excitation source (10 mW) and a custom-built spectrometer. The measurements were carried out to evaluate the degree of graphitization, structural disorder, and exfoliation efficiency of the petroleum-coke-derived carbon products. The Raman spectra were obtained from several areas on each

sample in order to obtain representative data, taking into consideration the possibility of variations due to spatial differences within the samples.

The analysis of the specific carbon bands for Raman spectroscopy was carried out in order to assess defect concentration, ordering graphitization, and synthesis of few layers of graphene. The intensity ratios I_D/I_G and I_{2D}/I_G were extracted from the spectra and used as key indicators of structural disorder and exfoliation quality, respectively.

6. Morphological Characterization

6.1 Scanning Electron Microscopy

High-resolution field-emission scanning electron microscopy (FE-SEM; JEOL JSM-7500F and FEI QUANTA 600) was used to examine the morphology and Energy-Dispersive X-Ray Spectroscopy of the exfoliated graphene flakes. Samples were deposited on Si substrates and sputter-coated with a thin Pt/Pd layer (~5 nm) using a Cressington 208HR sputter coater prior to imaging. The lateral flake size was estimated from representative SEM images using ImageJ analysis.

6.2 Transmission Electron Microscopy

Transmission electron microscopy and high-resolution TEM (TEM/HRTEM) were performed using a Titan Themis 300 S/TEM to examine the morphology, layer structure, and crystallinity of the exfoliated graphene sheets. Samples were prepared by dispersing the graphene powder in IPA by sonication, followed by drop-casting onto lacey formvar/carbon-coated 300-mesh copper grids and drying before analysis. Elemental mapping was also collected using the same instrument.

6.3 Atomic Force Microscopy

Atomic force microscopy (AFM) was used to evaluate the thickness and lateral size of the exfoliated graphene nanosheets. Diluted graphene suspensions were drop-cast onto flat Si/SiO₂ or mica substrates and dried prior to analysis. The height profile of some typical flakes was used for estimating the thickness of nanosheets, while lateral sizes were estimated from the images collected by the atomic force microscope.

7. Zeta potential measurements

The zeta potential for the graphene sheets in an aqueous environment was measured using the Zetasizer Nano ZS90 with a DTS1070 capillary cell. This test was done by diluting the dispersion of graphene to about 0.05 mg/mL, ensuring that a homogeneous suspension is attained. The samples were tested five times, and the results presented herein represent their averages.

8. Electrical Conductivity Measurements

The electrical conductivity of the graphene films was measured using a four-point probe setup consisting of a Signatone S-302 resistivity stand coupled with a Keithley 2000 multimeter. Graphene inks were prepared by dispersing petcoke-derived graphene in a DI water/ethanol mixture (1:1 v/v). The dispersion was then deposited onto vacuum-filtered graphene buckypaper to improve interflake connectivity and form a continuous conductive film. Prior to ink preparation, selected graphene samples were annealed under an argon atmosphere at 500 °C, 800 °C, or 1400 °C to remove residual volatile species and improve film conductivity. The resulting films were dried before four-probe sheet resistance measurements. For sheet resistance measurements using four-point probes, the electrical conductivity was determined using the equation $\sigma = 1/(R_s t)$, where R_s is the sheet resistance and t is the film thickness. Film thickness was measured using AFM.

Declarations

Data and materials availability

All data supporting the findings of this study are available within the paper and its Supplementary Information.

Acknowledgements

This work was supported by King Abdulaziz City for Science and Technology (KACST), the Oil Sustainability Program (OSP), and CEER company. PH acknowledge support of the Air Force Office of Scientific Research under award number FA9550-23-1-0436.

Author contributions

M.H.A. conceived and supervised the project, designed the methodology, performed the main experiments, analyzed the data, and wrote the manuscript. Y.A.A., A.M.A., A. Alromaeh, M.M.A., F.A., F.H.A., A. Almuqhim, and A. Aljuwair contributed to materials processing, characterization, electrical measurements, and data analysis. R.B. contributed to advanced characterization and data interpretation. M.J.G. and P.R.H. contributed to conceptual guidance, supervision, interpretation of results, and manuscript revision. All authors discussed the results, reviewed the manuscript, and approved the final version.

Funding

The authors acknowledge the financial support from King Abdulaziz City for Science and Technology (KACST), the Oil Sustainability Program (OSP), and CEER company.

Competing interest

The authors declare no competing interests.

References

1. Saha, S. et al. *Sustainable production of graphene from petroleum coke using electrochemical exfoliation*. npj 2D Materials and Applications, **5**(1): p. 75. (2021).
2. Sawarkar, A. N. et al. Petroleum Residue Upgrading Via Delayed Coking: A Review. *Can. J. Chem. Eng.* **85** (1), 1–24 (2007).
3. Oberschelp, C., Pfister, S. & Hellweg, S. Global site-specific health impacts of fossil energy, steel mills, oil refineries and cement plants. *Sci. Rep.* **13** (1), 13708 (2023).
4. Caruso, J. A. et al. Petroleum Coke in the Urban Environment: A Review of Potential Health Effects. *Int. J. Environ. Res. Public Health.* **12** (6), 6218–6231 (2015).
5. Luong, D. X. et al. Gram-scale bottom-up flash graphene synthesis. *Nature* **577** (7792), 647–651 (2020).
6. Cabral, R. L. B. et al. A minireview on the utilization of petroleum coke as a precursor for carbon-based nanomaterials (CNMs): perspectives and potential applications. *RSC Adv.* **14** (28), 19953–19968 (2024).
7. Media, A. *Petroleum Coke Price Assessments and Market Commentary, Q1 2026* (Argus Media, 2026).
8. Fastmarkets *Graphite Price Assessments: Natural Flake Graphite and Spherical Graphite, Q1 2026*. Fastmarkets, (2026).
9. Group, I. *Petroleum Coke Prices, Index, Chart, Trend and Demand – Q1 2026* (IMARC Group, 2026).
10. La, D. D. et al. Scalable Fabrication of Modified Graphene Nanoplatelets as an Effective Additive for Engine Lubricant Oil. *Nanomaterials* **10** (5), 877 (2020).
11. Wu, D. N. et al. Mass production of graphene using high-power rapid joule heating method. *Chem. Eng. J.* **505**, 159725 (2025).
12. Research, G. V. *Graphene Market Size, Share & Trends Analysis Report, 2033* (Grand View Research, 2025).
13. Intelligence, M. *Graphene Market Size, Share, Trends & Research Report*. Mordor Intelligence, (2026).
14. Alkhatani, M. et al. Petroleum coke-derived graphene as a low-cost electrode material for efficient perovskite solar cells. *Nanoscale Adv.* **7** (15), 4710–4720 (2025).
15. Choi, S. H. et al. Large-scale synthesis of graphene and other 2D materials towards industrialization. *Nat. Commun.* **13** (1), 1484 (2022).
16. Kumar, C. et al. Petroleum coke derived reduced graphene oxide as an electrocatalyst for water splitting. *Diam. Relat. Mater.* **140**, 110433 (2023).
17. Sang, M. et al. Electronic and Thermal Properties of Graphene and Recent Advances in Graphene Based Electronics Applications. *Nanomaterials* **9** (3), 374 (2019).
18. Li, X. et al. *Environmental impacts of graphene at industrial production scale and its application in electric heating technology* Vol. 199, p. 107250 (Resources, Conservation and Recycling, 2023).

19. Yi, M. & Shen, Z. A review on mechanical exfoliation for the scalable production of graphene. *J. Mater. Chem. A*. **3** (22), 11700–11715 (2015).
20. Anegbe, B. et al. Graphene oxide synthesis and applications in emerging contaminant removal: a comprehensive review. *Environ. Sci. Europe*. **36** (1), 15 (2024).
21. Méndez-Lozano, N., Pérez-Reynoso, F. & González-Gutiérrez, C. Eco-Friendly Approach for Graphene Oxide Synthesis by Modified Hummers Method. *Materials* **15** (20), 7228 (2022).
22. Lim, S., Chang, M. & Lee, W. A comprehensive review of electrochemical exfoliation of graphite for tunable graphene architecture: Mechanistic insights, design principles, functional derivatives, and emerging applications. *Carbon* **246**, 120888 (2026).
23. Bing, C. et al. Effects of reduction method on reduced graphene oxide and its electrochemical energy storage performance. *Diam. Relat. Mater.* **114**, 108305 (2021).
24. Paton, K. R. et al. Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nat. Mater.* **13** (6), 624–630 (2014).
25. Stafford, J. et al. Towards scale-up of graphene production via nonoxidizing liquid exfoliation methods. *AIChE J.* **64** (9), 3246–3276 (2018).
26. Xu, Y. et al. Liquid-Phase Exfoliation of Graphene: An Overview on Exfoliation Media, Techniques, and Challenges. *Nanomaterials* **8** (11), 942 (2018).
27. O'Neill, A. et al. Graphene Dispersion and Exfoliation in Low Boiling Point Solvents. *J. Phys. Chem. C*. **115** (13), 5422–5428 (2011).
28. Hernandez, Y. et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat. Nanotechnol.* **3** (9), 563–568 (2008).
29. Çelik, Y., Flahaut, E. & Suvacı, E. A comparative study on few-layer graphene production by exfoliation of different starting materials in a low boiling point solvent. *FlatChem* **1**, 74–88 (2017).
30. Singaramohan, D. P. R., Veerasamy, S. & Thomas, M. Santhoshini Priya Natesan, Balasubramanian *Synthesis of graphene by electrochemical exfoliation from petroleum coke for electrochemical energy storage application: Original scientific paper.* *J. Electrochem. Sci. Eng.* **13** (6), 881–893 (2023).
31. Al-Haj-Ibrahim, H. & Morsi, B. I. Desulfurization of petroleum coke: a review. *Ind. Eng. Chem. Res.* **31** (8), 1835–1840 (1992).
32. Hou, D. et al. Influence of order degree of coaly graphite on its structure change during preparation of graphene oxide. *J. Materiomics*. **6** (3), 628–641 (2020).
33. Rooze, J. et al. Dissolved gas and ultrasonic cavitation – A review. *Ultrason. Sonochem.* **20** (1), 1–11 (2013).
34. Kang, B. K., Kim, M. S. & Park, J. G. Effect of dissolved gases in water on acoustic cavitation and bubble growth rate in 0.83MHz megasonic of interest to wafer cleaning. *Ultrason. Sonochem.* **21** (4), 1496–1503 (2014).
35. Gireesan, S. & Pandit, A. B. Modeling the effect of carbon-dioxide gas on cavitation. *Ultrason. Sonochem.* **34**, 721–728 (2017).

Figures

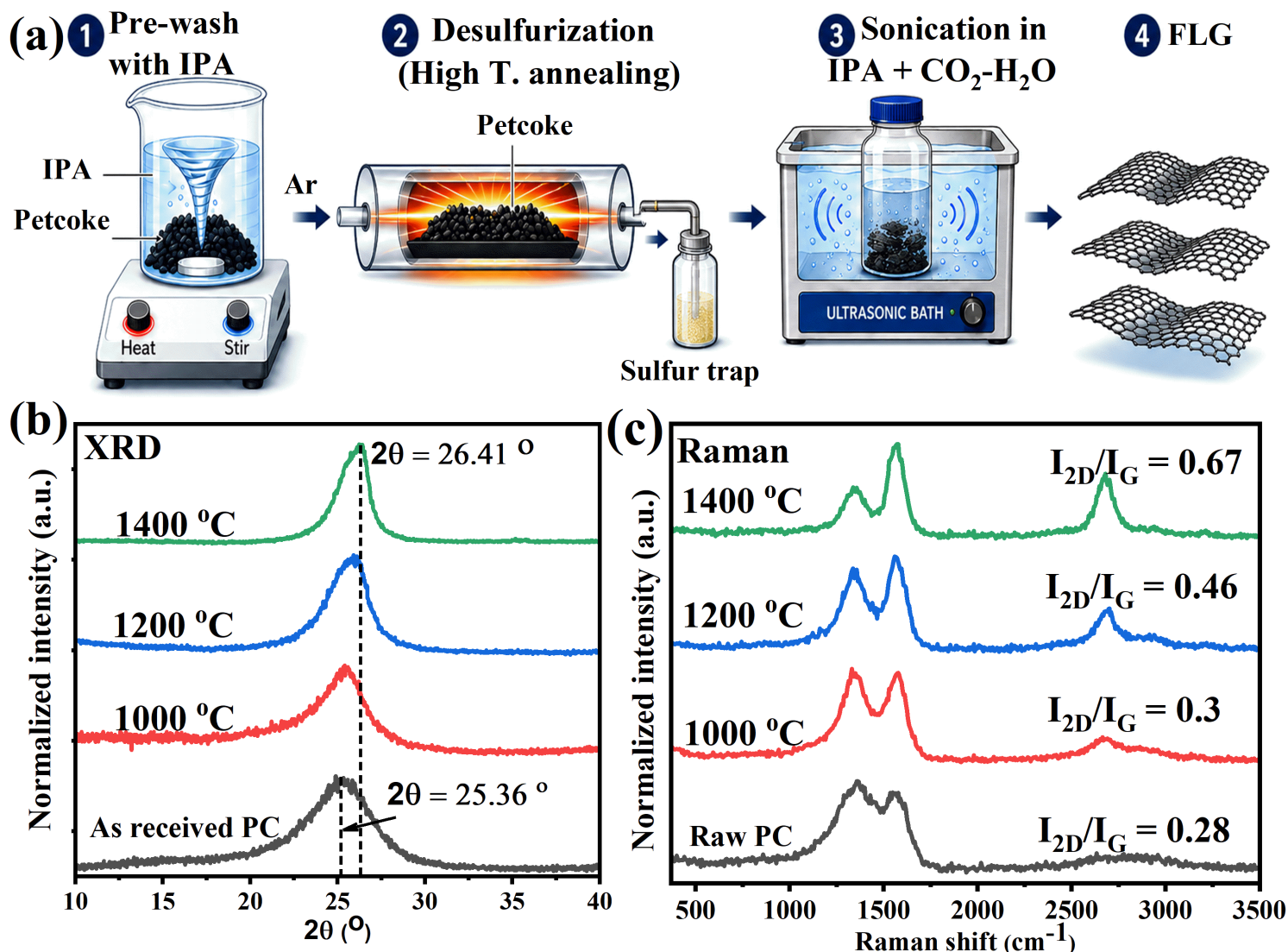


Figure 1

Valorization of pet coke into few-layer graphene by thermal activation and CO₂-mediated exfoliation. (a) Scheme showing the valorization process for pet coke into few-layer graphene by means of IPA pre-washing, thermal activation under high-temperature Ar, exfoliation via IPA/CO₂-saturated solution sonication, and isolation of graphene nanosheets. In the thermal desulfurization process, the sulfur compounds released from pet coke are carried by the argon gas stream to a collector, where sulfur-rich precipitates form, most likely consisting of elemental sulfur and associated condensable sulfur compounds. (b) XRD patterns showing the structure activation of pet coke by annealing, indicated by the sharpness of the carbon (002) diffraction peak and its position change from $2\theta = 25.36^\circ$ to 26.41° , which corresponds to a reduction in d_{002} from 0.351 to 0.337 nm. (c) Raman spectra illustrating the development of I_{2D}/I_G ratio from 0.28 of unprocessed pet coke to 0.67 at 1400 °C annealing temperature, demonstrating increased graphitization of pet coke and improvement in the formation of few-layer graphene.

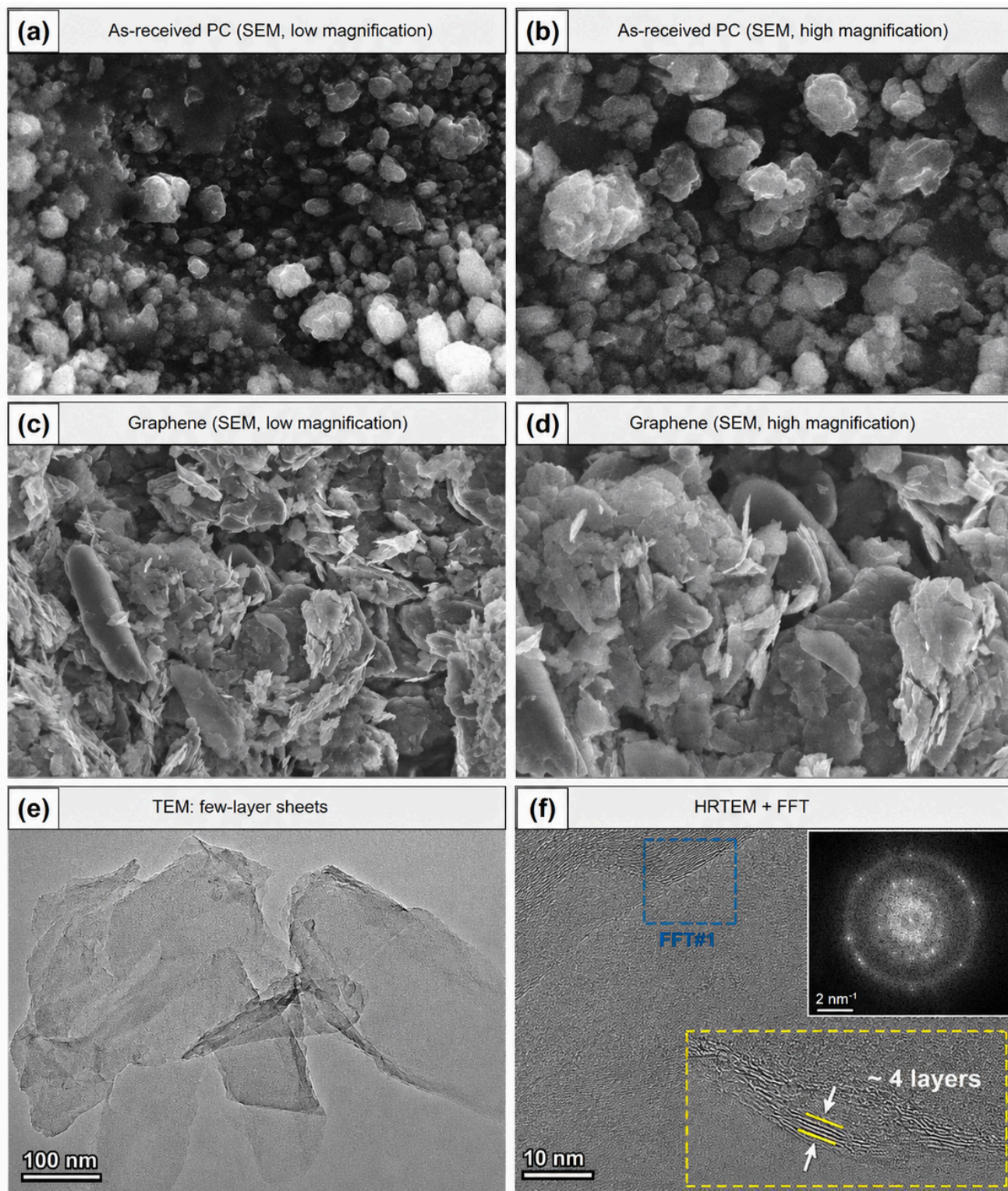


Figure 2

Morphology evolution from pet coke to few-layer graphene. (a,b) SEM micrograph of as-received petcoke, showing densely packed, irregularly shaped, granular structures with little lamellar morphology. (c,d) SEM micrographs of few-layer graphene after optimization, which exhibit flaky, layered, wrinkled, and loosely stacked nanoflakes. (e) TEM micrograph of exfoliated few-layer graphene, showing

transparent flakes. (f) HRTEM micrograph along with FFT pattern, proving ordered graphitic structure with thickness about 3 to 5 layers.

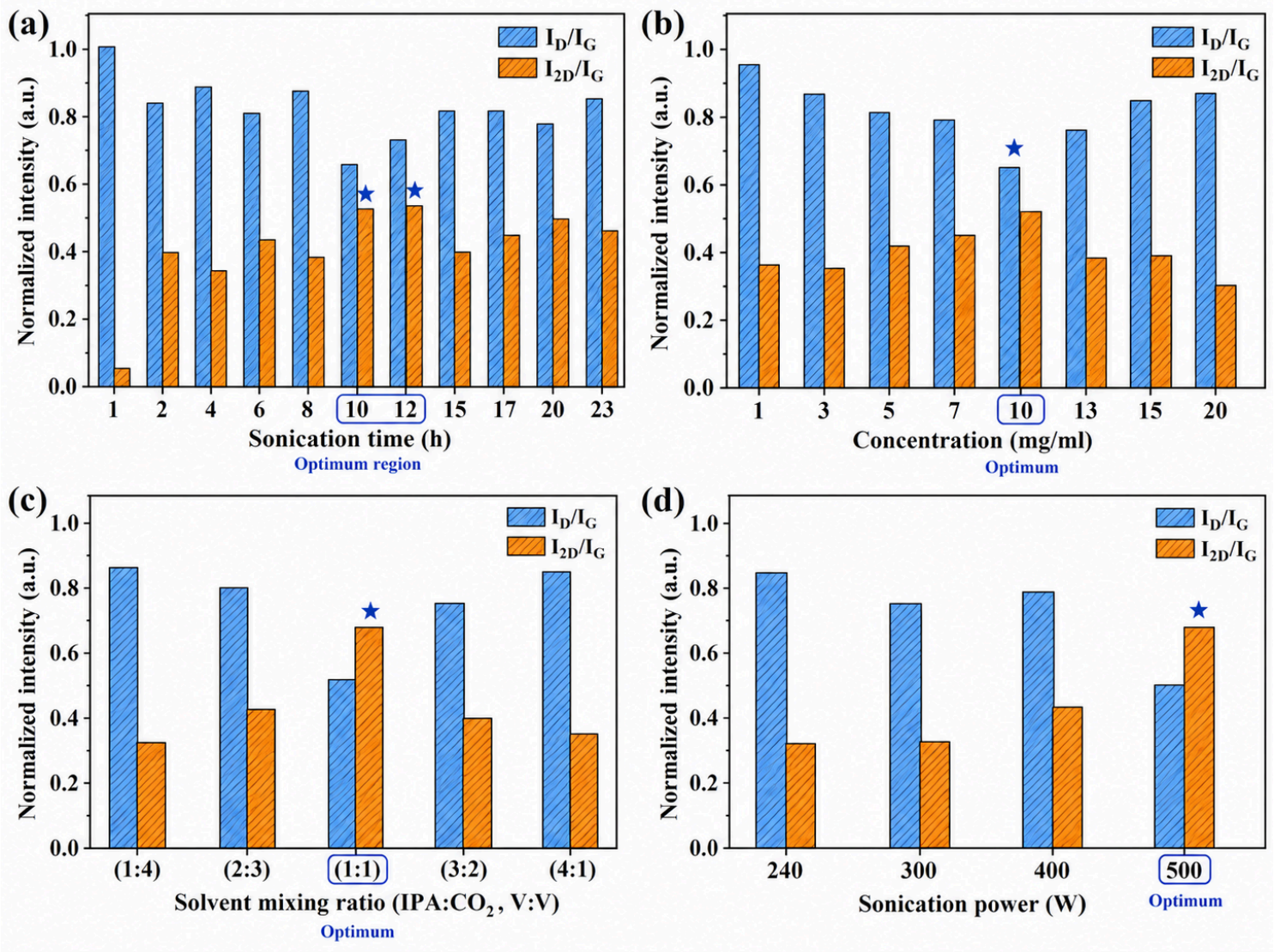


Figure 3

Optimization of CO₂-aided liquid phase exfoliation of annealed petcoke. The I_D/I_G and I_{2D}/I_G ratios measured using the Raman technique are utilized in determining defects generated and few layer graphene synthesized in terms of (a) sonication time, (b) concentration of dispersion, (c) IPA:CO₂ ratio, and (d) sonication power. Optimal process parameters will ensure an optimal balance between delamination and preservation of the sp² carbon framework through maximum I_{2D}/I_G and minimum I_D/I_G .

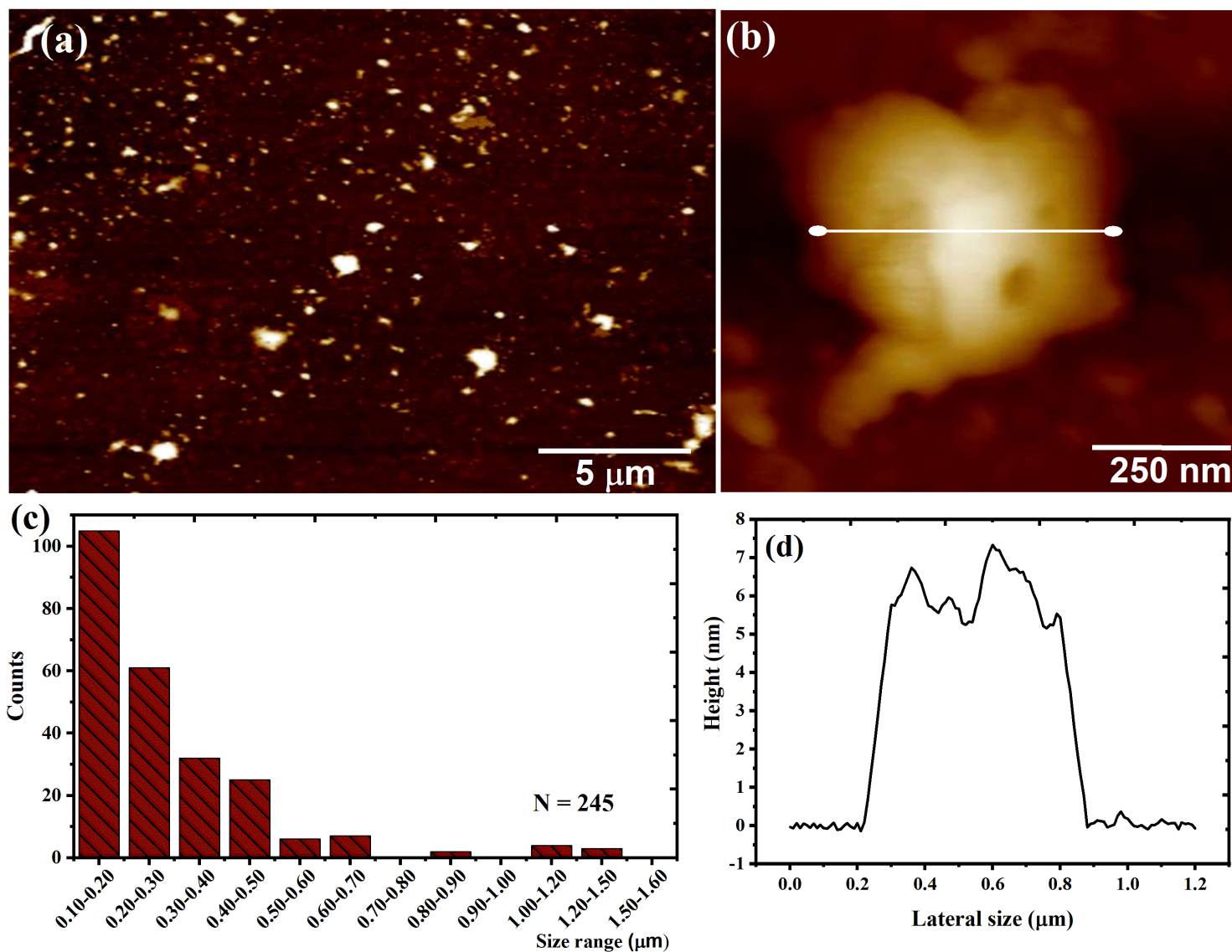


Figure 4

AFM study of graphene nanoflake distribution obtained from pet coke. (a) Typical AFM image of the graphene- sample after mild centrifugation and drop-coating on silicon, showing nanoflake dispersion with little aggregation. (b) High-magnification AFM image of a single flake or restacked cluster of flakes. (c) Size distribution map from scale-bar-based image analysis, where 229 out of 245 features have a size $< 0.6 \mu\text{m}$, corresponding to 93.5% nanoflakes based on number distribution. (d) AFM height profile extracted across the selected feature in panel (b).

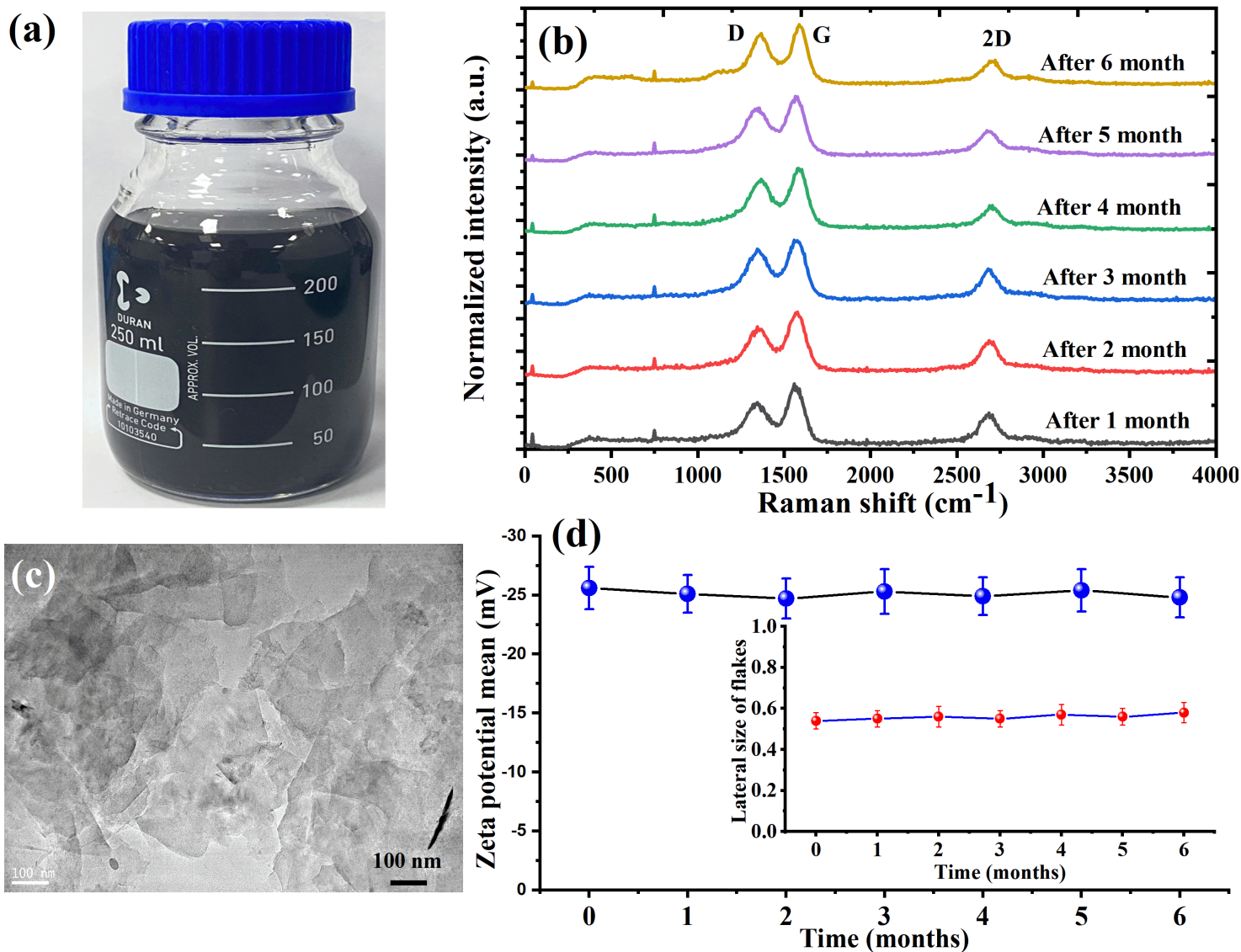


Figure 5

Graphene dispersion stability based on pet coke with time. (a) Image of graphene dispensed in the combination of 1:1 proportion of deionized water and ethanol acting as cosolvents. (b) Raman spectra obtained within a period of six months, in which all D, G, and 2D peaks can be observed, which shows that the sp^2 carbon structure is stable. (c) TEM images taken after a period of time, showing thin layers of graphene sheets. (d) Zeta potential measurements of the dispersion in six months still stable at -25 mV; Inset: hydrodynamic size less than 0.5 to 0.6 μm .

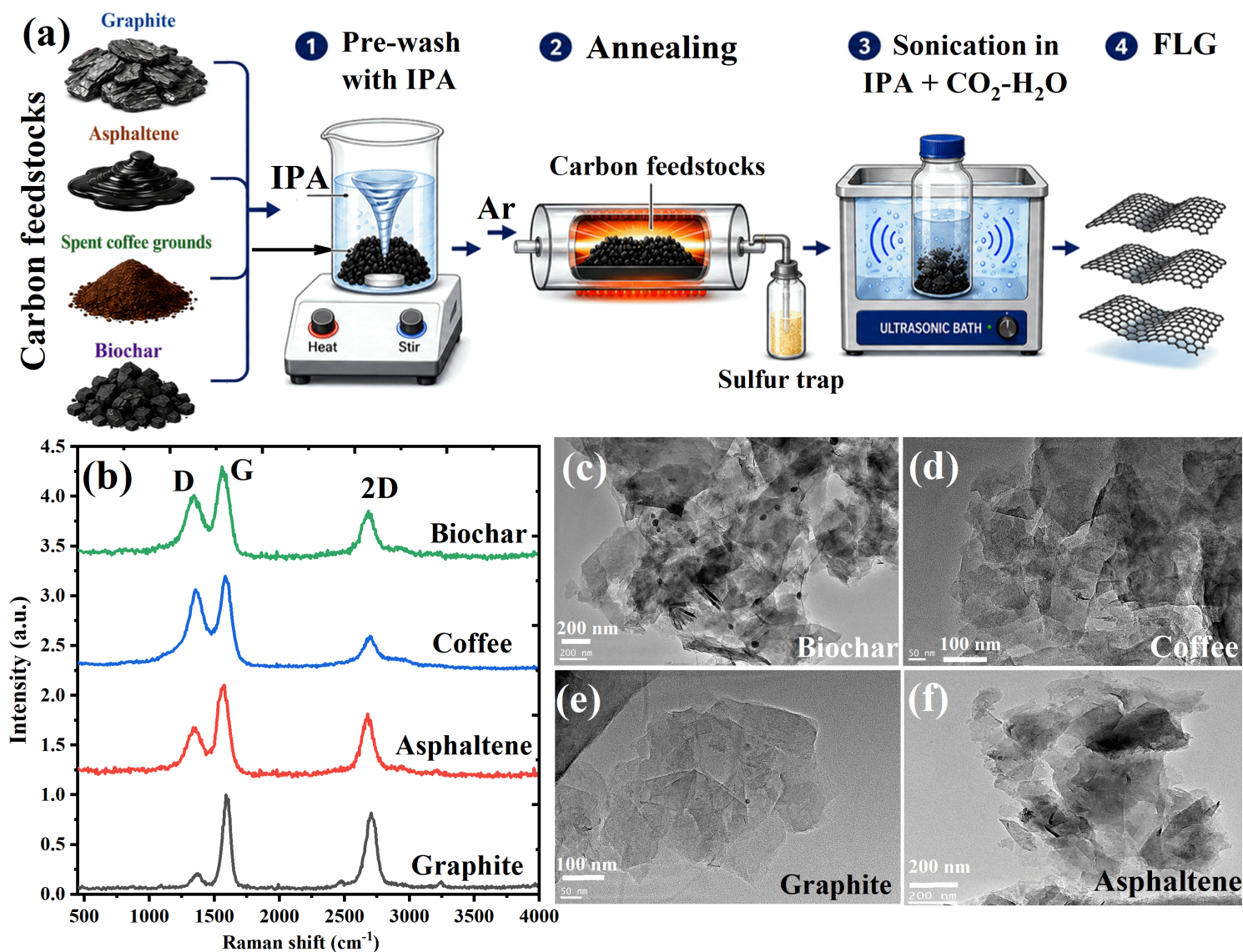


Figure 6

Universal synthesis of few-layer graphene without oxidation from different carbon sources. (a) Schematic representation of the methodology used for the preparation of few-layer graphene starting from graphite, asphaltene, used coffee grounds, and biochar by using the three steps of washing with isopropanol (IPA), Ar treatment, and CO₂ sonication in IPA/CO₂-H₂O. (b) Raman spectra obtained from all of the materials, showing the presence of the characteristic peaks from the D, G, and 2D regions for graphitic carbon materials. The strong 2D peak from all samples demonstrates effective exfoliation in a few-layer material, whereas the D peak variation is due to the disorder of the precursors. (c-f) TEM images from graphene made from biochar, used coffee grounds, graphite, and asphaltene.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supportinginformationforsubmission.docx](#)