Application of synthesized graphene in the treatment of wastewater

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**Abstract**

This research study presents an academic investigation on the development of a facile, low-cost, rapid and efficient method for the synthesis of highly expanded graphene using the thermal shock technique in an air atmosphere. The obtained samples were subjected to analysis using Fourier-transform infrared spectroscopy, X-ray diffraction spectroscopy and thermogravimetric analyses. A comparative analysis was conducted at three critical temperatures (750°C, 820°C and 870°C). The results demonstrated the effectiveness of the thermal shock technique in promoting rapid and significant expansion of the graphene structure by enhancing the internal forces within a remarkably short duration. Furthermore, the prepared samples exhibited outstanding thermal stability, along with a notable retention capability for green malachite (98%) and alizarine red (up to 100%).

**Keywords:** Expanded graphite; Synthesis; Thermal shock; Thermal stability; Filtration; Retention

1. Introduction

Since its discovery, graphene, a single layer material formed by the sp2 electron orbital hybridization tightly packed into a two-dimensional honeycomb lattice of carbon atoms with an atomic spacing of 1.42° [1–3], has attracted extensive focus from academic and industrial fields due to its specific surface area and storage modulus being two of the highest values reported at about 2,600 m²/g and 130 GPa, respectively [4], superior thermal, mechanical, electronic, optical characteristics [3,5,6]. Researchers incorporated this nanomaterial in various disciplines including electronics and batteries, energy storage, water treatment and many more [4]. However, the introduction of high-quality single layer graphene sheets free of defects into the industrial life still persists [5,6]. Hence, it is crucial to refine the manufacturing process in order to maximize the quality of graphene while insuring exceptional quality. Moreover, the key to future advancements lies on embracing easy-to-use, cost effective and environmentally sustainable approach [1].

Nowadays, most bulk-scale graphene is produced by a top-down approach [1], exfoliating graphite [7], oxidizing graphite via the Hummers’ method or Brodie’s method [8], followed by chemical or thermal reduction of graphite oxide (GO) which has always been one of the most advantageous and preferred method to obtain graphene in significant yields [2,9].

Effort has been performed to engineer the structure of GO materials for various specific applications, such as reduction (removing oxygen groups) and functionalization (adding other functionalities) [10,11]. The process of polymer functionalization of graphite oxide with dopants (acids or polymer molecules) has been proved to promote the self-exfoliating ability of graphene [8,12]. The addition of heat sensitive component is also effective for enhancing the inner pressure. Higher oxygen content can generate excessive gases which accelerate the exfoliation [5,8,13] confirmed that the functionalization of GO with PEG promoted its exfoliation into thin exfoliated nanosheets, also enlarge the basal spacing of the
GO. Only recently considerable attempts have been conducted to prove the effect of heat-treatments on thermal reduction and exfoliation of graphite compounds. Bannov et al. [14] tested the efficiency of programmable heating and thermal shock as methods of producing expanded graphite at temperatures of 800°C-1,200°C. Song et al. [11] subjected graphene oxide to thermal reduction treatment in temperature range of 1,100°C-2,000°C. Ahmed et al. [12] reported the effect of treatment at high temperature (2,000°C) on the exfoliation of a graphene. However, all of their studies are time-consuming, need either pre-treatments, water rinsing, purification steps and desiccation, also often require sophisticated materials such as vacuums and large amounts of solvents with high-energy mixing, shearing, sonication or electrochemical treatment [7]. Additionally to chemical and thermal exfoliation, microwave assisted exfoliation of graphite compounds has been also reported to be efficient and rapid [15,16].

Providing access to drinking and affordable water for a large human population is one of the major global challenges of the 21st century [17]. For that, huge research interest has been focused for removal of toxic contaminants released from battery manufacturing, chemical manufacturing, textile, pesticides and other industries such as dyes, heavy metals, pharmaceuticals, oils and solvents causing numerous serious problems for living organisms and the natural environment [10,18,19]. It is demonstrated that graphite-based materials, due to their important properties, can effectively remove dyes from wastewater [19,20].

Therefore, novel methods of graphene synthesis must be developed in order to improve the important characteristics for further applications. In this work, we propose a one-step approach that integrates oxidation, reduction and exfoliation processes for graphene synthesis enhanced by polyvinyl alcohol functionalization in order to optimize the exfoliation process. The key aspect of this method involves rapid heating at three carefully selected critical temperatures.

2. Experimental set-up

2.1. Materials

Graphite (purity of 99%, 80 µm of particle size) used in this study was in the form of graphite powder provided by a local company. Nitric acid HNO₃ (68%), sulfuric acid (98%) H₂SO₄ and potassium permanganate KMnO₄ were purchased from Sigma-Aldrich, Germany. Malachite green (MG) and alizarin red (AR) were provided from Biochem Chemopharma, France.

Rapid heating was carried out in a tubular furnace provided by Nabertherm GmbH, Germany.

2.2. Characterizations

The as-obtained samples were characterized by the following methods:

The surface chemical properties were determined by a FTIR spectrometer (IR Prestige-21, Shimadzu) via KBr tablets containing 0.5% of the analyte, with the spectra collected in the range of 4,000 and 400 cm⁻¹.

Thermogravimetry (TG) were carried out using a TA, SDT Q600 thermal analyzer (NETZSCH, Selb, Germany). The heating was conducted in an Al₂O₃ crucible. The stability of samples was analyzed at a heating rate of 10°C/min up to 1,000°C under argon gas flow of 50 mL/min.

The interlayer spacing of the obtained carbon materials was examined using X-ray diffractometer (600 Miniflex, Rigaku, Japan) equipped with a Cu X-ray tube (λ = 1.54 Å, 40 kV and 15 mA) was run at with 10°/min scan speed in the range of 20° = 5° to 80°. UV-Visible spectrophotometer SPECORD® 210 was used to determine the concentration of the treated dyes in each sample at a given wavelength (617 nm for GM, 480 nm for AR) using calibration curves.

2.3. Sample preparation

For the synthesis procedure, natural graphite powder (NG), intercalation agents (H₂SO₄) and oxidant (KMnO₄) were combined in a weight ratio of 1:2:1 and mixed for a short duration. Subsequently, after 24 h, the resulting mixture was subjected to thermal heat shock treatment in a pre-heated furnace at three distinct critical temperatures (750°C, 820°C, 870°C), enabling rapid accomplishment of oxidation, intercalation and exfoliation processes with a few seconds [15]. The heat treatment experiments were carried out under ambient atmosphere conditions using a furnace, employing a gradual heating rate of 10°C/min. Afterward, the samples were exposed to rapid heating at the specific temperatures of 750°C, 820°C and 870°C for only a few seconds.

Based on the different expansion temperatures, the EGs were labeled as EG-750, EG-820 and EG-870.

2.4. Filtration

This study aims to investigate the effectiveness of a specialized vertical filtration system for the separation of water from synthetic wastewater containing malachite green (MG) and AR dyes. The filtration system, based on a PVC-FPT union and PVC coupling [21], incorporates graphene synthesized at 750°C (Gr-750) as the filtering material. By utilizing a support layer of gravel and cotton to prevent material loss, a stable mass of 2 g of Gr-750 is placed within the assembly. Synthetic wastewater models comprising various concentrations (10⁻⁶ M, 10⁻⁴ M, and 10⁻³ M) of MG and AR dyes are used to assess the filtration system’s consistency and performance, providing insights into the potential application of graphene-based filters in efficient dye removal from wastewater.

The permeance recovered at time intervals were subjected to UV-visible analysis.

The retention rate of the permeates of the different samples is given by the following relationship:

\[ R(\%) = 1 - \frac{C_r}{C_i} \]

where \( R(\%) \): the retention, \( C_i \): the concentration of the initial solution, \( C_r \): the concentration of the permeate at a defined time.
3. Results and discussion

3.1. Synthesis

Rapid heating at the high temperatures leads to rapid decomposition and vaporization of the intercalated reagents that induces strong formation of a gases that instantaneously generates a strong driving force to strip the structure of graphite layers [14,20]. These procedures may help to produce channels and pore structures for adsorption [20].

3.2. Fourier-transform infrared spectroscopy analysis

Fig. 1 shows Fourier-transform infrared spectroscopy (FTIR) spectra of graphite and the as-obtained carbon materials Gr-870°C, Gr-820°C, Gr-750°C. The visualization of the spectra shows the presence of a broad band between 3,400 and 3,200 cm⁻¹ corresponding to the hydrogen elongation vibrations of the O–H hydroxyl groups due to water, carboxyl, phenol or alcohol. While the small bands between 1,650 and 1,500 cm⁻¹ is attributed to elongation vibrations of C=C groups, the spectra also show an intense band around 1,140 cm⁻¹ due to deformation vibrations of C–O bonds. The small band around 1,400 cm⁻¹ results from C–H deformation vibrations. The deformation vibration bands between 800 and 600 cm⁻¹ correspond to C–H deformation vibrations. The deformation vibration bands between 800 and 600 cm⁻¹ correspond to C–H bonds (adjacent =C–H). Nearly a flat line with no obvious peak was detected for graphite, suggesting no significant amount of oxygen functional groups was found in this carbon material [22]. Therefore, the oxygen-containing functional groups were successfully removed partially and the low amounts of residue of functional groups are still remain at the edge and basal plane of rGO [23]. It is also noticeable that peaks are less intense than those peaks at the same location in FTIR spectra of GO, which were also due to the removal oxygen.

3.3. X-ray diffraction analysis

Structural properties of the carbon materials were studied using X-ray diffractometer as presented in Fig. 2.

Fig. 2 shows X-ray diffraction (XRD) pattern of pristine graphite. It reveals that graphite sample are well arranged with a characteristic sharp (0 0 2) diffraction peak located at 20 = 26.515° corresponding to an interlayer spacing of \(d_{002} = 3.3589 \text{ Å}\). Fig. 2 shows the XRD patterns of the as-obtained graphene treated at 750°C, 820°C and 870°C. This is evidenced by the reappearance of the \((d_{002})\) diffraction line at 20 = 21.5°, 20 = 26.43° and 20 = 26.46° corresponding to a spacing of 4.14, 3.369 and 3.66 Å for Gr-750°C, Gr-820°C and Gr-850°C, respectively.

Both Gr-820°C and Gr-850°C have quite similar peak where interlayer distance values are close to 3.35 Å for pristine graphite indicating that carbon materials has been restored considerably with two dimensional ordered stacks after heat treatment [11]. While Gr-750°C d value (4.14 Å) is quite greater indicating that some oxygen is still intercalated into the interlayer spacings of graphite.

Also, a small (0 0 2) diffraction peaks can be observed on the XRD patterns of the graphene samples but with a weaker and lower intensity showing that the graphite lattice is still retained during the conversion from graphite to graphene. However, these peaks intensity is remarkably weaker compared with that of graphite, indicating the few-layer feature of the resultant graphene [9,24,25].
The peak C(002) in the sharp graphene shows that the formation of graphene has not been single layer [25].

3.4. Thermogravimetric analysis

The thermogravimetric analysis results illustrated in Fig. 3 offer useful insights to understand the thermal behavior of the carbonaceous decomposition of the as-obtained materials. The as prepared graphene materials and graphite samples were subjected to thermal decomposition up to 1,000°C in the nitrogen atmosphere to probe thermal characteristics. Graphite starts to decompose at 700°C~1,000°C and the thermogram of Gr-750°C is similar to that of graphene oxide and highlights 3 significant thermal events corresponding to the evaporation of water below 100°C, 100°C–200°C for partial decomposition of some unstable oxidated
The uptake of the dye particles could be due to the π–π interactions between the Gr-750°C and the benzene rings of MG and AR. Additionally, the adsorption of the dye particles on the provided adsorption sites could be due to the Van der Waals’ forces and hydrogen bonding [21].

4. Conclusion

In conclusion, this research proposes a cost-effective and efficient approach to thermally exfoliate graphite into few layers of graphene. Our method involves a unique high-temperature shock treatment in a tubular furnace, enabling simultaneous oxidation, intercalation, and exfoliation within a matter of seconds. We investigated the impact of expansion temperature on the physicochemical properties of the resulting carbonaceous materials. Moreover, the filtration assembly we developed effectively retained organic dyes, with retention rates ranging from 97% to 99%, and achieving complete retention (100%) for malachite green and alizarin red, respectively.

Future studies should aim to explore the exfoliation of graphite into defect-free single-layer graphene at elevated temperatures opening up opportunities for environmentally sustainable and economically viable approaches to address freshwater and wastewater remediation projects.

References


