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A Study on the Expansion of Graphite Layers Via In-Situ Polymerization of Melamine

Tuğrul YUMAK

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Research Article

Corresponding Author
Tuğrul YUMAK
tyumak@sinop.edu.tr

ORCID of the Author
T.Y.: 0000-0002-3688-3525

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Abstract

Graphene, renowned for its honeycomb lattice structure formed by densely packed sp^2 hybridized carbon atoms, possesses exceptional electronic, thermal, chemical, and mechanical properties. The van der Waals-coupled graphene layers give rise to the well-known AB stacking, forming graphite. Despite the existence of several methods for graphite production, the production of graphene on a large scale remains challenging due to the lack of efficient techniques and the introduction of structural defects during the production process. Exfoliated graphite (EG), a potential solution, is typically derived from the thermal treatment of graphite intercalation compounds (GICs). Melamine, notably displaying significant expansion properties at low temperatures, has been used as an intercalation compound in limited studies. This study investigates the potential of melamine to induce the expansion of graphene layers when incorporated into graphite and subjected to thermal treatment. Raman and X-ray diffraction analyses were employed to assess structural changes.

Keywords: Graphite, expansion of graphite, g-C_3N_4, thermal treatment

Melaminin Yerinde Polimerizasyonu ile Grafit Katmanlarının Genişletilmesi Üzerine Bir Çalışma

Sinop University, Faculty of Science and Arts, Department of Chemistry, Sinop, Türkiye

Öz

Yoğun bir şekilde paketlenmiş olup sp^2 hibritlenmiş karbon atomlarından oluşan bal peteği kafes yapısıyla bilinen grafen, olağanüstü elektronik, termal, kimyasal ve mekanik özelliklere sahiptir. Van der Waals ile birleştirilmiş grafen katmanları, iyi bilinen AB istiflenmesine yol açarak grafit oluşturur. Grafit üretimi için çeşitli yöntemlerin varlığına rağmen, büyük ölçekte grafen üretimi, etkili tekniklerin bulunmaması ve üretim süreci sırasında yapısal kusurların ortaya çıkması nedeniyle zorlu olmaya devam ediyor. Potansiyel bir çözüm olan pul pul dökülmüş grafit (EG), tipik olarak grafit interkalasyon bileşiklerinin (GIC'ler) ısıl işleminden üretilmektedir. Özellikle düşük sıcaklıklarda önemli genleşme özellikleri sergileyen melamin, sınırlı çalışmalarda bir ara bileşik olarak kullanılmıştır. Bu çalışmada melaminin grafit içerisine dahil edildip ısıl işleme tabi tutulduğunda grafen katmanlarının genişlemesini tetikleme potansiyeline odaklanılmıştır. Yapısal değişiklikleri değerlendirmek için Raman ve X-ışını kırınım analizleri kullanılmıştır.

Anahtar Kelimeler: Grafit, grafitin genişlemesi, g-C_3N_4, ısıl işlemler

Introduction

The honeycomb lattice structure formed by tightly packing sp^2 hybridized carbon atoms makes graphene an incredibly attractive material, with extraordinary electronic, thermal, chemical, and mechanical properties [1]. Van der Waals-coupled graphene layers shift in the horizontal plane, leading to the well-known AB stacking, which forms graphite [2]. Graphite can be produced through various methods, including micro-mechanical exfoliation of highly ordered pyrolytic graphite, epitaxial growth, chemical vapor deposition, and reduction of graphene oxide (GO). [3-5]. Graphene and its derivatives are promising candidates as components for applications in the field of energy storage and energy conversion materials, thermally and electrically conductive reinforced nanocomposites, nanoelectronics, and sensors, among many others [6]. Despite its outstanding physical properties, graphene's large-scale production is hindered by a lack of effective methods. Additionally, the production methods often introduce structural defects that significantly weaken its mechanical properties and other physical characteristics [7, 8]. Significantly larger amounts of graphene can be produced by physical and chemical exfoliation of bulk graphite [9-11], which has been extensively studied in the past, is cheap and scalable [12]. Exfoliated graphite (EG) is usually produced through the thermal treatment of graphite intercalation compounds (GICs) [13, 14]. Many approaches have been developed for the mass production of GICs, as well as the exfoliation of high-quality graphene using GICs [15]. Despite being a promising intercalation compound with its high expansion property, melamine has only been used in two studies. Reinheimer et al. patented the use of thermally expandable graphite intercalation compounds for producing fire-protection seals and their production method [16]. Duan et al., [17] discussed the synthesis of core-shell expandable graphite/melamine-formaldehyde particles and their flame-retardant applications. The transformation mechanism and the expansion of melamine to graphitic-C_3N_4 with the increasing temperature can be seen in somewhere else [18]. Since the thermal expansion of melamine occurs at relatively lower temperatures than graphite, it is thought that the penetrated melamine molecules in the graphite layers may force the expansion of graphene layers with the formation of the g-C_3N_4 structure by thermal treatment. To test the hypothesis, we exposed both pristine graphite and a melamine-graphite admixture to thermal treatment. The expansion of graphite layers was investigated by using X-ray diffraction and Raman techniques.

Experimental

The graphite-melamine mixtures were prepared by a simple mixing in solution technique. Graphite powder (Supelco) and melamine (Merck) were mixed in 50 mL water for 6 hours at room temperature. The solution was filtered under vacuum and dried at 105°C for 18h. The collected powders were placed in an alumina boat. The sample-loaded boat put in a stainless-steel reactor and exposed to thermal treatment. The sample definitions and experimental conditions are given in Table 1. Raman spectra were measured on a WITech alpha 300R with 532 nm DPSS laser excitation. A PANalytical Empyrean X-ray diffractometer with CuKα radiation source was used to determine crystallographic structure of the samples.

Table 1. *Sample definitions and experimental conditions*

Sample	**Material**	**Experimental Conditions**
TTG	Pristine Graphite	650°C - 2h - 5°C/min
TTG2M1	Graphite + Melamine (2:1 w/w)	650°C - 2h - 5°C/min

Results and Discussion

Raman Analysis

Figure 1 shows the Raman spectra of all samples. All Raman spectra were analyzed to determine the peak positions, peak widths, and peak areas, using Lorentzian-peak-fit profiles. Table 2 represents the Raman features of pristine graphite and synthesized samples. As seen in the Figure 1 and Table 2, the typical peaks of the graphite lattice, G band at 1575 cm^{-1} which arises from the in-plane C-C bond stretching in sp^2 hybridized carbon systems in the first order region, and 2D band at 2680 cm^{-1} in the second order region were detected. In addition, a weak disorder band caused by the graphite edges (D band) at approximately 1355 cm^{-1}was observed for pristine graphite. Compared to pristine graphite the thermal treatment led to a decrease in the peak intensity, and redshift in the peak positions of D, G, and 2D bands for the sample TTG. For the melamine-added sample (TTG2M1), an increase in the peak intensity for the D band, and an decrease in the peak intensity for the G and S1 bands were observed. In addition, redshift in the peak positions to the higher wavenumber can be clearly seen for all bands from Figure 1. D band was strongly influenced by melamine adding; a well-defined symmetric D peak in graphite became broader and asymmetric for the sample TTG2M1. A new relatively strong band at ≈1620 cm^{-1} appeared by the development of the D band. The intensity increase in both bands suggests that the melamine addition introduces a significant number of structural defects into the graphite lattice. Since the shift in the peak positions in Raman spectroscopy related to the length of chemical bonds and symmetry of molecules [19], it is obvious that the possible polymerization of melamine into g-C_3N_4 caused a significant change in the molecular chemistry of graphite layers. The observed redshift in the G and S1 bands with both the thermal treatment and melamine addition can be explained by the expansion of resulting material or improved crystallinity. Due to the hypothesis of this work, the d-spacing of graphite and composite materials was calculated by the XRD analysis.

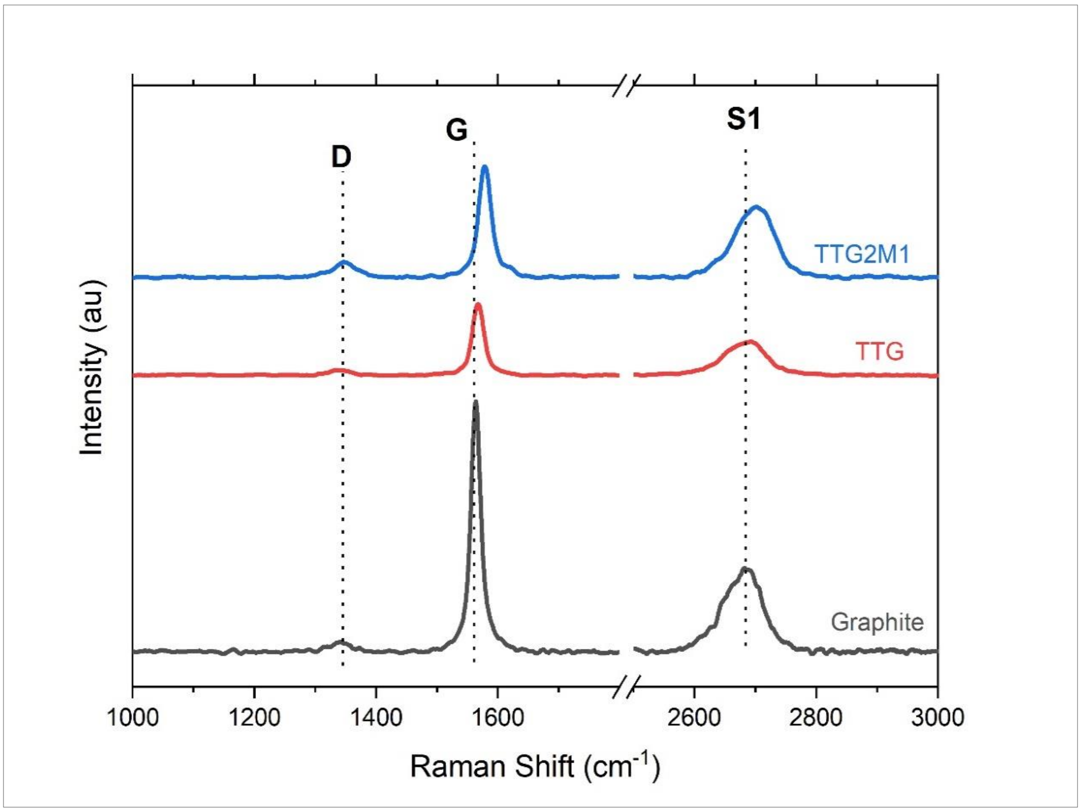

Figure 1. *Raman spectra (1000-3000 cm^{-1}) of the synthesized materials and pristine graphite*

As seen in Table 2, clear redshift in the D, G, and 2G bands was calculated for all samples. The FWHM of the G band was calculated as 18.04 to 20.64 and 23.03 for pristine graphite, TTG, and TTG2M1, respectively.

Table 2. *Raman features of pristine graphite and synthesized powders*

	D Band			G Band			S1 Band		
Sample	**Position**	**FWHM**	**Area**	**Position**	**FWHM**	**Area**	**Position**	**FWHM**	**Area**
Graphite	1340.06	40.93	4665	1563.93	18.04	51770	2680.65	64.25	62658
TTG	1339.37	35.55	2297	1567.72	20.64	17206	2683.91	69.58	27690
TTG2M1	1347.92	44.15	7770	1578.89	23.03	29859	2698.95	65.31	55385

Compared to pristine graphite, only thermal treatment resulted in a 3.79 cm^{-1} redshift, while the addition of melamine and thermal treatment resulted in a 14.96 cm^{-1} redshift in the G band. Similarly, the expanding of the resulting material or improved crystallinity may be responsible for the redshift. Moreover, the melamine loading led to a broadening in the G band (increase in the FWHM)., is evidence for the weakened of van der Walls forces between graphite layers [20]. The increasing degree of amorphization with melamine loading and thermal treatment is responsible of the broadening and redshift in G band [21]. As a result, it can be said that the redshift in the graphite peak (G band) and defect peak (D band) usually refers to p-type doping, expanding, and the compressed lattice of material.

The shift in the peak positions is evidence of the change of the chemical bond length of molecules by the thermal treatment and further melamine adding.

XRD Analysis

The pristine, thermally treated pristine, and melamine-loaded graphite samples were analyzed by XRD in the 20°-35° region with a slow scan rate. As shown in Figure 2 and Table 3 below, the sample TTG had a broader peak at 2θ of 26.33°, in comparison to that of pristine graphite (26.37°) which corresponded to a d-spacing of 3.385 Å (TTG) and 3.380 Å (Pristine Graphite). Due to the increasing d-space, it can be said that the spacing between the graphene layers was increased with the thermal treatment. In the case of melamine addition (TTG2M1), the peak positions shifted to higher 2θ degrees due to the decreasing d-spacing. This may be related to the formation of C_3N_4 between the graphene layers. In addition, an increase in the full width of half maximum (FWHM) values which is directly proportional to the crystal size according to Scherrer's formula was observed for the TTW sample.

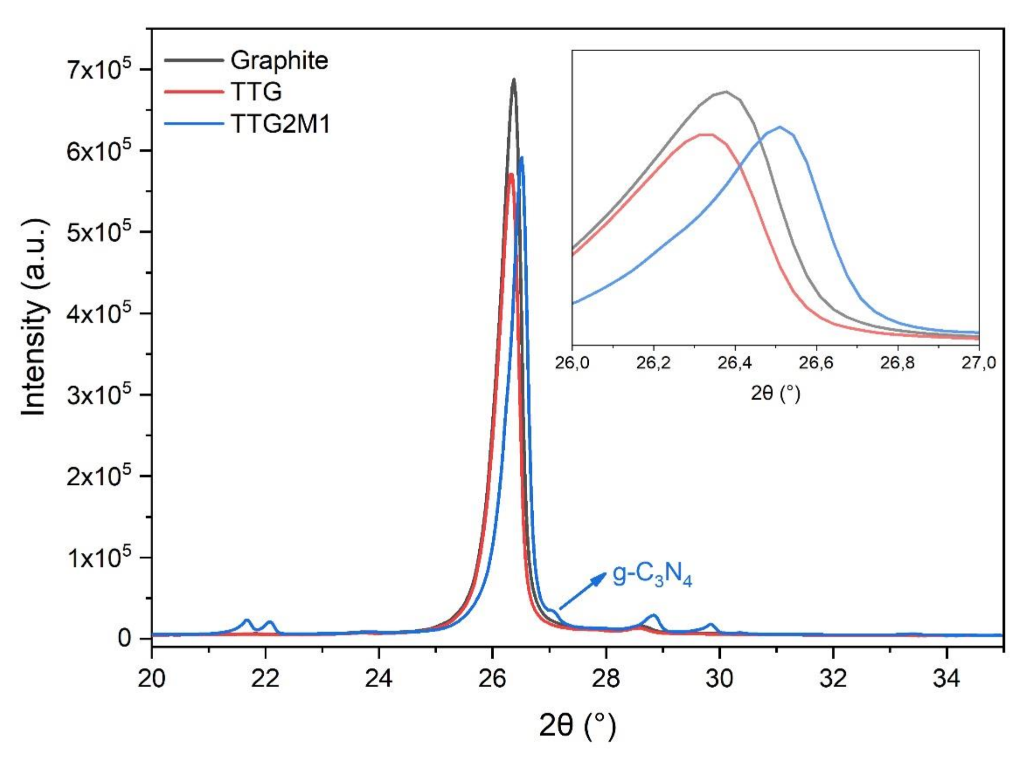

Figure 2. *XRD patterns of pristine and modified graphite samples*

Figure 3 shows the illustrated possible molecular structure of g-C_3N_4/Graphite. Since the pristine graphite and C_3N_4 have the major peak at same 2θ degrees (≈26), and low crystallinity, it is very hard to prove the formation of the C3N4 structure by XRD. However, the TTG2M1 samples had some different peaks, which are pointed as C3N4 by the library search&match, esp. the peak around 27.1°.

Table 3. *Main peak properties of pristine and modified graphite samples*

Sample	Pos. [°2θ]	FWHM Left [°2θ]	d-spacing [Å]
Graphite	26.3701	0.3572	3.37987
TTG	26.3276	0.3897	3.38523
TTG2M1	26.5047	0.1948	3.36300

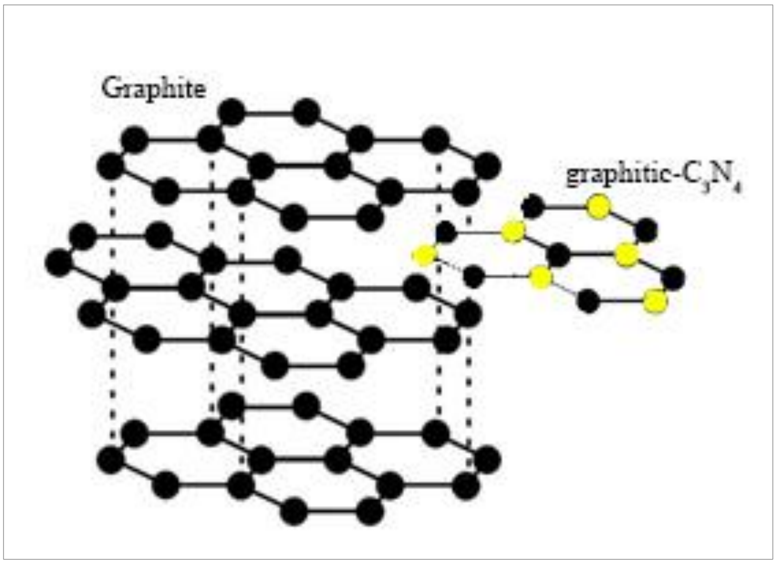

Figure 3. *Illustration of the possible molecular structure of g-C_3N_4/Graphite composite*

Because of its extensive range of applications, including composites and coatings, electronics, energy, membranes, sensors, and more, significant efforts are underway to acquire graphene with specific desired properties. Furthermore, an economically feasible, and scalable amount of graphene can be produced from exfoliated graphite (EG) which is usually produced by the thermal treatment of graphite intercalation compounds (GICs). Skowroński and Krawczyk focused on the electrochemical activity towards hydrogen sorption/desorption capacity of EG synthesized by using $NiCl_2$ as the intercalation compound [22]. It is reported that the sample exfoliated with $NiCl_2$, and heat treated at 800°C in air for 25 min showed the highest hydrogen storage capacity [22]. They concluded that this is resulted from the process of secondary exfoliation leading to the formation of porous graphite and simultaneous eruption of the $NiCl_2$ intercalate the transformation into nickel oxide [22]. Ka and Oh reported the synthesis of expanded graphite with a d-spacing of 0.404 nm from meso carbon micro beads (MCMB) via heat treatment of an oxidized form of MCMB [23]. As reported in this study, the BET surface area of the expanded graphite (21.8 m^2/g) is about 10-fold larger than the pristine material, however, it is quite small for an electrode material in capacitor applications [23]. Despite the small surface area, the expanded graphite electrode material has shown a promising capacitor behavior with a charge–discharge coulombic efficiency of >99% up to a working voltage of 3.7 V [23]. Morales et al. [24] reported the synthesis of few-layer graphene by an electrochemical treatment followed by microwave-assisted thermal expansion. Due to the Raman spectra presented in this work, it is reported that the sp^2 carbon structure did not change with the selection of the appropriate conditions [24]. An et al. [25] reported the synthesis of spheroidized graphite-derived multi-layered graphene from a battery-grade spheroidized natural graphite powder by using sulfuric acid and hydrogen peroxide as the intercalant and oxidant under microwave irradiation at 800W. It is found that the degree of graphitization calculated from the XRD results is 100% for the spheroidized natural graphite while it is 98.8% and 87.2%-95.3 for flake natural graphite and meso carbon microbead (MCMB), respectively [25]. It is concluded that the selected microwave conditions are inefficient and the selected GIC agents are not effective for the MCMB as a starting material [25]. The importance of the starting material, temperature, and the selection of intercalation species is also reported by Murugan et al. [26]. According to the results given in the brief literature summary presented above, it can be said that the selected experimental parameters in this work are appropriate for the synthesis for the expansion of graphite.

Conclusion

This study reveals the potential of melamine-induced expansion and structural modification in graphite layers, driven by thermal treatment. The observed changes in Raman and XRD analyses underscore the significant impact of melamine on the chemistry and structure of graphene, opening new avenues for advanced material development and applications. Moreover, an expanded form of graphite can be used for hydrogen storage, thermal energy storage, fuel cells, batteries, supercapacitors, sensors, etc.

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Conflict of Interests The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors Contribution The author read and approved the final manuscript

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