Preparation and Qualitative and Quantitative Analysis of Graphene Oxide (Postprint)

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Abstract

Using flake graphite as the raw material, graphene oxide (GO) was prepared via a chemical intercalation oxidation-crushing method employing sulfuric acid and potassium permanganate. The as-prepared graphene oxide was analyzed and characterized by scanning electron microscopy (SEM), laser particle size analysis, Fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy (UV-vis), and atomic force microscopy (AFM). The results revealed that UV-Vis spectra in the vicinity of 230 nm can distinguish graphene oxide from graphite oxide. The findings demonstrate that UV spectroscopy can be utilized for both qualitative and quantitative analysis of graphene oxide solutions. This method enables the acquisition of optimal conditions for graphene oxide preparation. Mechanism analysis results indicate that the structural characteristic of graphene oxide, primarily its discontinuous π-π^* conjugated system, is responsible for the generation of multiple absorption peaks with varying intensities near 230 nm in its UV spectrum.

Full Text

Preamble

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Preparation and Qualitative/Quantitative Analysis of Graphene Oxide

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Abstract

Graphene oxide (GO) was prepared by chemical intercalation-oxidation and sonicated crushing methods using flake graphite, sulfuric acid, and potassium permanganate as raw materials. The prepared GO was characterized by scanning electron microscopy (SEM), laser particle size analysis, Fourier-transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-vis), and atomic force microscopy (AFM). The results demonstrate that UV-vis spectroscopy around 230 nm can differentiate graphene oxide from graphite oxide. The UV-vis spectra enable both qualitative and quantitative analysis of GO solutions, thereby allowing optimization of GO preparation conditions. Mechanistic analysis reveals that the appearance of multiple absorption peaks near 230 nm in the UV spectra of GO originates from the distinctive structure of discontinuous π-π^* conjugated systems in graphene oxide.

Keywords: inorganic non-metallic materials, graphene oxide, quantitative analysis, UV-vis spectroscopy, mechanism

Introduction

Graphene is a novel two-dimensional material composed of carbon atoms arranged in a hexagonal honeycomb lattice through sp^2 hybridized orbitals, forming a planar film only one atom thick [1]. To distinguish graphene from graphite, materials with fewer than 10 layers of sp^2-hybridized carbon sheets are generally termed graphene, while those with more than 10 layers are called graphite. Graphene oxide refers to films where the graphite layers have been oxidized on both surfaces and within the interlayers [2], yet still maintain fewer than 10 layers of sp^2-hybridized hexagonal honeycomb structure.

Atomic force microscopy (AFM) or transmission electron microscopy (TEM) can be used for qualitative analysis of graphene oxide, requiring transfer of GO from solution to a substrate surface. Quantitative testing can only be performed sheet-by-sheet, with GO quantity determined indirectly through statistical methods. During quantitative measurement, only extremely small solution volumes (typically microliter scale) can be used [3-6], and multiple GO sheets may stack together, leading to highly inaccurate representation of solution concentration. Moreover, these methods are costly.

Graphene oxide has extensive application potential. Investigating its preparation mechanisms, characterization methods, and physicochemical properties is crucial for improving preparation techniques and deepening mechanistic understanding [7-10]. This paper focuses on the preparation of graphene oxide and its qualitative and quantitative analysis.

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1. Experimental Methods

1.1 Chemical Preparation of Graphene Oxide (GO)

Graphene oxide was prepared using a modified Hummers method [11]. In an ice-water bath, flake graphite was slowly added to sulfuric acid and mixed uniformly. Potassium permanganate was then added slowly under stirring, with the oxidant amount calculated as multiples of graphite mass. Samples were prepared with $KMnO_4$ at 12%, 50%, 100%, 200%, 250%, 300%, 350%, 400%, 450%, and 500% of graphite mass. After complete addition, the mixture was continuously stirred in the ice bath for 5 hours, followed by reduction with 5% hydrogen peroxide for 1 hour. The product was washed repeatedly with water until pH 7, then filtered and dried to obtain graphite oxide.

The graphite oxide was dispersed as a suspension and subjected to ultrasonic crushing. After sonication, centrifugation was performed to remove thicker graphite oxide from the bottom. The supernatant in the centrifuge tube was the graphene oxide (GO) solution, designated as SK12, SK50, SK100, SK150, SK200, SK300, and SK350 according to the $KMnO_4$ dosage.

1.2 Characterization of GO

UV-vis absorption characteristics were analyzed using a spectrophotometer (Shanghai Jinghua, Model 754). AFM (Asylum Research Corporation, MFP-3D-SA) was used to measure sheet thickness. Particle size was analyzed using a laser particle size analyzer (Malvern, Zetasizer Nano-zs90). Microstructure was observed via SEM (Hitachi, S4800). FT-IR analysis was performed using a Thermo Electron Corporation NICOLET 380 spectrometer.

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2. Results and Discussion

2.1 Qualitative UV-Vis Analysis of Graphene Oxide

UV-vis spectroscopy was used to analyze the absorption characteristics of GO prepared with different $KMnO_4$ dosages, as shown in [Figure 1: see original paper]. When the oxidant dosage exceeded 350% of graphite mass, the UV-vis spectrum showed a strong absorption peak at 230 nm. At 300% and 200% dosage, a prominent shoulder peak appeared at 230 nm. At 150% dosage, multiple lower shoulder peaks were observed, while at 100% dosage, no obvious

absorption peak was detected at 230 nm. These results indicate that oxidant dosage significantly affects the UV-vis spectra of GO solutions, with peak intensity gradually decreasing as oxidant dosage decreases. The absorption peak at 230 nm in the UV-vis region is characteristic of graphene oxide and serves as an important indicator for GO detection and characterization.

AFM observations of GO under different oxidant dosages are shown in [Figure 2: see original paper]. The results demonstrate varying GO thicknesses under different preparation conditions. As oxidant dosage decreased, GO thickness increased progressively from approximately 0.8 nm (single layer) and 1.5 nm (double layer) to 4.5 nm (multilayer) and even thicker structures of several tens of nanometers. This aligns with previous reports showing that chemically exfoliated single-layer graphene thickness ranges from 0.7-1.6 nm [12]. Statistical analysis of GO with different layer thicknesses reveals that oxidant dosages above 350% primarily yield single-layer GO; 300% dosage produces mainly 1-3 layer GO; and 200% dosage results predominantly in GO with more than 4 layers [13]. When $KMnO_4$ dosage was only 12% of graphite mass, the post-sonication supernatant was clear, and AFM observation revealed no GO-like products, indicating that oxidant dosage plays a critical role in GO preparation [14].

Particle size analysis of GO sheets using laser granulometry is presented in [Figure 3: see original paper]. As oxidant dosage varies, GO particle size changes gradually. At 24% $KMnO_4$ dosage, the result showed a broad single peak. At 50% dosage, a small peak appeared on the left side of the broad peak. At 200% dosage, this left-side peak became sharp and exceeded the intensity of the broad peak, while the broad peak shifted leftward, indicating decreasing size. At 300% dosage, the broad peak narrowed and continued shifting leftward by approximately 200-300 nm, with more concentrated size distribution. These results are consistent with AFM observations, demonstrating that higher oxidant dosage leads to smaller GO dimensions. However, the absolute sizes measured by laser granulometry differ somewhat from AFM results, likely because laser granulometry measures bulk properties while AFM characterizes individual sheets.

Morphological and structural analysis of graphite oxide is important since GO is obtained through ultrasonic crushing of graphite oxide. [Figure 4: see original paper] shows SEM images of graphite oxide prepared with different $KMnO_4$ dosages. At 12% dosage, sheet thickness reached 5-6 m, while at 350% dosage, thickness was only about 0.5-0.8 m. As $KMnO_4$ dosage increased, graphite oxide sheets became progressively thinner. These dimensional changes before and after sonication correlate with laser particle size analysis results, confirming that oxidant dosage is a key factor for preparing single-layer graphene.

FT-IR spectra of GO under different oxidant dosages are shown in [Figure 5: see original paper]. In the high-frequency region, the band near 3450 cm^{-1} corresponds to O-H stretching vibrations, while the broad peak at 3000-3700 cm^{-1} originates from water molecules adsorbed on GO. Peaks near 2925 and 2850 cm^{-1} correspond to -CH_2- bending vibrations. In the mid-frequency re-

gion, the peak near 1718 cm^{-1} belongs to carboxylic acid and carbonyl groups at GO edges. The band at approximately 1635 cm^{-1} corresponds to graphite C=C bonds, while the peak near 1400 cm^{-1} is attributed to C-O stretching of edge carboxylic acids. The absorption around 1100 cm^{-1} results from C-OH stretching of alcohol groups [15]. The presence of these oxygen-containing groups confirms graphite oxidation, and these polar groups, particularly surface hydroxyls, facilitate hydrogen bonding with water molecules, explaining GO' s good hydrophilicity [16]. FT-IR results indicate that oxidation introduces various oxygen-containing bonds (C=O, C-O, etc.) onto the carbon atoms of the large π-bond system, converting some sp^2 hybrid orbitals to sp^3. Higher oxidant dosage produces more pronounced oxygen group peaks, which only become consistent when oxidant dosage exceeds 200% of graphite mass. During ultrasonic crushing, the weak interlayer van der Waals forces, further reduced by intercalated species, allow shear forces to exfoliate single layers along the c-axis. The size of these single layers is closely related to $KMnO_4$ dosage, sonication time, power, and solvent.

2.2 Quantitative UV-Vis Analysis

2.2.1 Preparation of GO Standard Solutions and Calibration Curve

For quantitative analysis, SK350 graphite oxide was dispersed as a suspension and ultrasonically crushed. After centrifugation, the thicker bottom deposit was dried to obtain solid residue. The GO concentration was determined indirectly by subtracting the dried residue mass from the initial graphite oxide mass (weight difference method). This solution was diluted to 1/4 of its original concentration as Standard 1. Portions of Standard 1 were further diluted to 1/2, 1/4, and 1/8 of its concentration, designated as Standards 2, 3, and 4. The absorbance of these standards was measured at 230 nm. Additionally, 200 mL aliquots of each concentration were placed in pre-weighed 250 mL beakers and dried at 80°C to obtain the mass of GO, from which mass concentrations (C) were calculated as true values. A calibration curve was established by plotting mass concentration versus absorbance at 230 nm, as shown in [Figure 6: see original paper].

To validate the method, three freshly prepared GO samples (C1, C2, C3) were prepared, sonicated, and diluted to measurable concentrations for UV analysis at 230 nm. Measured concentrations (X) were obtained from the calibration curve, while true concentrations (T) were determined by evaporation and weighing. Relative error was calculated as $E = |X - T|/T \times 100\%$. Results are listed in . Three experimental trials demonstrated that UV spectroscopy can qualitatively and quantitatively determine GO concentration at 230 nm with errors below 6%, which is acceptable for GO applications. This method is low-cost and convenient.

2.3 Application of UV-Vis Quantitative Analysis

Ultrasonic conditions are critical in GO preparation. [Figure 7a: see original paper] shows the effect of sonication time on GO UV-vis spectra. As crushing time increases, the absorption peak at 230 nm intensifies and becomes narrower and more prominent, indicating that longer sonication facilitates GO production and enhances UV absorption at 230 nm. No absorption peak appears when sonication time is less than 10 minutes, suggesting insufficient GO formation. After 20 minutes, the preparation effect stabilizes, with a measured concentration of 0.66 $mg \cdot mL^{-1}$ based on the calibration curve.

The effect of ultrasonic power is shown in [Figure 7b: see original paper]. As power increases, the 230 nm absorption peak intensity gradually rises, becoming particularly prominent at 400 W, indicating that higher power yields higher concentration and thinner GO sheets. The sample at 400 W showed a concentration of 0.042 $mg \cdot mL^{-1}$. Therefore, using UV spectroscopy analysis based on absorption near 230 nm, optimal GO preparation conditions were determined to be: oxidant dosage at 350% of graphite mass, sonication time of 20 minutes, and ultrasonic power of 400 W.

2.4 Mechanism of Peak Splitting

The peak splitting phenomenon observed near 230 nm in [Figure 1: see original paper] and [Figure 7: see original paper] can be explained by GO structure. During ultrasonic exfoliation, weak interlayer van der Waals forces, further diminished by intercalated species, allow shear forces to detach single layers along the c-axis, forming single- or multi-layer GO structures. GO exhibits a structure dominated by discontinuous π-π^* conjugated systems, which produce UV absorption peaks near 230 nm [17,18]. The UV-vis spectra of GO primarily relate to two conjugation effects: (1) Oxidation converts some sp^2 to sp^3 hybrid orbitals, dispersing the conjugation of remaining sp^2 orbitals into multiple continuous or discontinuous large π bonds, as shown by red circles in [Figure 8: see original paper]. This indicates that insufficiently oxidized GO exhibits distinct localized state distributions with high disorder, resulting in multiple absorption peaks at 100%-350% oxidant dosage in [Figure 1: see original paper]. (2) These discontinuous large π bonds connect to C=O and C-O groups on carbon atoms. Different numbers of these groups cause varying degrees of bathochromic shift and absorption intensity when attached to sp^2-hybridized carbon atoms, leading to multiple absorption peaks with different positions and intensities. (3) The bonding at junctions of discontinuous large π bonds is weaker than original sp^2 bonds. As sonication time and power increase, these discontinuous π bonds gradually break, forming smaller GO sheets. The reduction of disordered structures makes the UV absorption peaks smoother, with peak splitting diminishing.

3. Conclusion

Graphene oxide can be prepared by chemical intercalation-oxidation and ultrasonic crushing using sulfuric acid and potassium permanganate. Based on the UV absorption characteristics of GO, the peak at 230 nm in the UV-vis region serves as a characteristic feature for qualitative and quantitative detection, with analytical errors below 6% in three experimental trials. Graphite oxidation forms discontinuous large π bonds, giving GO distinct localized state distributions and high disorder, which produces multiple absorption peaks of varying intensities in the UV region.

References

1. Novoselov K S, Electric field effect in atomically thin carbon films, *Science*, 306, 666(2004)
2. Dubin S, Gilje S, Wang K, Hall A S, Farrar J, Varshneya R, Yang Y, Kaner R B, A one-step, solvothermal reduction method for producing reduced graphene oxide dispersions in organic solvents, *ACS Nano*, 4(7), 3845(2010)
3. Osvath Z, Darabont A, Nemes-Incze P, Horváth Z E, László P Biró, Graphene layers from thermal oxidation of exfoliated graphite plates, *Carbon*, 45(15), 3022(2007)
4. Graf D, Molitor F, Ensslin K, Stampfer C, Jungen A, Hierold C, Wirtz L, Spatially resolved raman spectroscopy of single- and few-layer graphene, *Nano Lett.*, 7(2), 238(2007)
5. Meyer J C, Geim A K, Katsnelson M I, Novoselov K S, Booth T J, Roth S, The structure of suspended graphene sheets, *Nature*, 446(7131), 60(2007)
6. Wu Z S, Ren W, Gao L, Liu B, Jiang C, Cheng H M, Synthesis of high-quality graphene with a pre-determined number of layers, *Carbon*, 47(2), 493(2009)
7. G. Eda, Y. Y. Lin, C. Mattevi, H. Yamaguchi, H. A. Chen, I. S. Chen, C. W. Chen, M. Chhowalla, Blue photoluminescence from chemically derived graphene oxide, *Adv. Mater.*, 22(4), 505(2010)
8. Eda G, Chhowalla M, Chemically derived graphene oxide: towards large-area thin-film electronics and optoelectronics, *Adv. Mater.*, 22(22), 2392(2010)
9. D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R. D. Piner, S. Stankovich, I. Jung, D. A. Field, C. A. Ventrice Jr and R. S. Ruoff, Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy *Carbon*, 47(1), 145(2009)

10. Mermoux M, Chabre Y, Rousseau A, FT-IR and 13C NMR study of graphite oxide, *Carbon*, 29(3), 469(1991)

11. W. S. Hummers, R. E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.*, 80(6), 1339(1958)

12. Li D, Muller M B, Gilje S, Kaner R B, Wallace G G, Processable aqueous dispersions of graphene nanosheets, *Nat. Nanotechnol.*, 3, 101(2008)

13. Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen S T, Ruoff R S, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, 45(7), 1558(2007)

14. Lawrence Verbit, The benzene ring as an optically active chromophore, *J. Am. Chem. Soc.*, 87(7), 1617(1965)

15. Haruo Hosoya, Jiro Tanaka, Saburo Nagakura, Ultraviolet absorption spectra of monomer and dimer of benzoic acid, *J. Mol. Spectrosc.*, 8(1-6), 257(1962)

16. Mermoux M, Chabre Y, Rousseau A, FT-IR and 13C NMR study of graphite oxide, *Carbon*, 29(3), 469(1991)

17. G. Eda, Y. Y. Lin, C. Mattevi, H. Yamaguchi, H. A. Chen, I. S. Chen, C. W. Chen, M. Chhowalla, Blue photoluminescence from chemically derived graphene oxide, *Adv. Mater.*, 22(4), 505(2010)

18. Eda G, Chhowalla M, Chemically derived graphene oxide: towards large-area thin-film electronics and optoelectronics, *Adv. Mater.*, 22(22), 2392(2010)

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