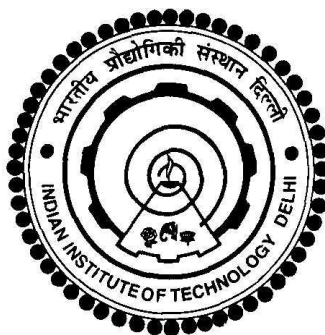


**SYNTHESIS OF BILAYER AND TRILAYER GRAPHENE
SUSPENSIONS BY ELECTROCHEMICAL EXFOLIATION OF
GRAPHITE**

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October, 2018

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by

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DEPARTMENT OF CHEMICAL ENGINEERING

submitted

in fulfillment of the requirements of degree of Doctor of Philosophy

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Certificate

This is to certify that the thesis entitled “**Synthesis of Bilayer and Trilayer Graphene Suspensions by Electrochemical Exfoliation of Graphite**”, being submitted by **Ms. Afkham Mir** to the Indian Institute of Technology Delhi, New Delhi, for the award of the degree of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide research work carried out by him. Ms. Afkham Mir has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

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Abstract

Graphene, a single atomic layer of graphite, has emerged as one of the most exciting materials since its discovery in 2004. It has remarkable properties of high electrical conductivity, high thermal conductivity, high tensile strength etc. A single layer of graphene, however, lacks a band gap in its electronic structure which limits its application in the electronic industry. Bilayer and trilayer graphene, on the other hand, display an induced band gap of 200 and 120 eV in the presence of an applied electric field. This makes bi- and tri-layer graphene a promising material in various applications like FETs, opto-electronic devices etc. Bi- and tri-layer graphene are traditionally synthesized using the mechanical exfoliation of graphite, which is a simple method but is not scalable, or from chemical vapor deposition of a carbon source on a suitable substrate, which is both a complex and an expensive method. To harness the amazing properties of bilayer and trilayer graphene, there is need for a scalable synthesis method which produces large flakes of bi- and tri-layer graphene and is cost efficient. A very promising route for the bulk production of bi- and tri-layer graphene is the electrochemical exfoliation of graphite. Electrochemical exfoliation proceeds via intercalation of the ions present in the electrolyte followed by the subsequent expansion and then exfoliation to yield the graphene flakes. However it produces graphene with a scatter in the layer numbers.

In this study, the electrochemical exfoliation of graphite was carried out in a modified way which involved prior intercalation of the HOPG electrode to form stage specific intercalated graphite electrode in the aqueous medium and its subsequent exfoliation at a higher rate to form stage-specific graphite-*bisulfate* (GB) particles. These GB particles were then mildly sonicated in a favorable medium to yield stage pure graphene flakes. This method allowed us to have a better control on the stage number of the intermediate graphite intercalation compound. Highly ordered pyrolytic graphite (HOPG) was

intercalated at a very low current density (0.66 mA/cm^2) to form pure stage III graphite-bisulfate (GB) intercalation product in low concentrations sulfuric acid. Low current density enabled a proper intercalation of the anions and a low electrolyte concentration lessened the degree of functionalization. It was immediately followed by the exfoliation of the pre-intercalated electrode at high current densities to form Stage III GB particles. The dried Stage III GB particles were then mildly sonicated in DMF, a good solvent for graphene dispersion and then centrifuged. In contrast to the previously reported methods of electrochemical exfoliation, this technique enabled the synthesis of large sized flakes, with an average flake area of $\sim 18 \text{ }\mu\text{m}^2$ and an average trilayer area of 88% in the graphene flakes. The values obtained are much higher than any previously reported value for graphene synthesized via the electrochemical route.

The operating parameters for the synthesis of trilayer graphene were also optimized, and it was found that the increasing exfoliation current increased the trilayer content but decreased the average flake size. Similarly, an initial increase in sonication intensity increased the trilayer content but at higher sonication intensities the flake size reduced. Finally the centrifugation speed was tuned to separate the largest flake sizes of trilayer graphene. Rosin Rammler distribution was used to describe the size distribution and it was found that an exfoliation current of 167 mA/cm^2 , a sonication intensity of 150 W/cm^2 and a centrifugation rpm of 2000 for 6 min resulted in the maximum average flake size of $\sim 18 \text{ }\mu\text{m}^2$ with an average trilayer area of 88% in graphene flakes.

A similar procedure was used to synthesize bilayer graphene flakes, with a prior intercalation to Stage II Graphite bisulfate followed by the exfoliation of the intercalated electrode. The longer intercalation time required for the formation of stage II GB electrode, had an effect on the degree of the functionalization of bilayer graphene flakes. The exfoliated GB particles were washed, dried, sonicated and then centrifuged to form

bilayer graphene suspension. About half of the flakes in the suspension had an average bilayer area content of 95% and 16% of the flakes have size more than $10\text{ }\mu\text{m}^2$.

The synthesis parameters for the bilayer graphene were also optimized. Exfoliation current, sonication intensity and the centrifugation speed have a pronounced effect on the size distribution of the final bilayer graphene flakes obtained. These parameters were optimized to get the highest average bilayer content of 90% in the graphene suspension and an average flake size of $\sim 6\text{ }\mu\text{m}^2$.

The synthesized bi- and tri-layer graphene suspensions were to form graphene films over FTO glass substrate and the capacitive properties of the films were determined. The maximum capacitance for trilayer graphene film electrode was 238 F/g and the maximum capacitance of bilayer film electrode was 373 F/g. The capacitance value for bilayer film was much higher than the values reported in the literature for graphene films. The contribution to the capacitance from the easily accessible graphene surface of the film and from the inner surface, that showed diffusion limitation, was quantitatively determined. In addition, the contribution of the pseudocapacitance arising out of slight degree of oxidation of the graphene flakes during synthesis, was also measured. The pseudocapacitive charge storage was $\sim 13.5\%$ of the total charge stored by the bilayer graphene film electrode and $\sim 10.8\%$ for the trilayer graphene film electrode.

सार

ग्रेफेन, ग्रेफाइट की एक परमाणु परत, 2004 में अपनी खोज के बाद से सबसे रोमांचक सामग्री में से एक के रूप में उभरा है। इसमें उच्च विद्युत चालकता, उच्च थर्मल चालकता, उच्च तन्यता शक्ति आदि के उल्लेखनीय गुण हैं। हालांकि, ग्रेफेन की एक परत, इसकी इलेक्ट्रॉनिक संरचना में बैंड अंतर की कमी है जो इलेक्ट्रॉनिक उद्योग में अपने आवेदन को सीमित करता है। दूसरी तरफ बिलायर और त्रिलियर ग्रेफेन, एक लागू विद्युत क्षेत्र की उपस्थिति में 200 और 120 ईवी के प्रेरित बैंड अंतर प्रदर्शित करते हैं। यह द्वि-और त्रि-परत ग्रेफेन विभिन्न अनुप्रयोगों जैसे एफईटी, ओटो-इलेक्ट्रॉनिक उपकरणों इत्यादि में एक आशाजनक सामग्री बनाता है। बाय- और त्रि-परत graphene पारंपरिक रूप से ग्रेफाइट के यांत्रिक अपपत्रण का उपयोग कर संश्लेषित कर रहे हैं, जो एक साधारण विधि है लेकिन स्केलेबल नहीं है, या एक उपयुक्त सबस्ट्रेट पर कार्बन स्रोत के रासायनिक वाष्प जमावट से, जो एक जटिल और महंगी विधि दोनों है। बिलायर और ट्रिलियर ग्रेफेन के अद्भुत गुणों का उपयोग करने के लिए, स्केलेबल संश्लेषण विधि की आवश्यकता होती है जो द्वि-और त्रि-परत ग्रेफेन के बड़े फ्लेक्स उत्पन्न करती है और लागत प्रभावी होती है। द्वि-और त्रि-परत ग्रेफेन के थोक उत्पादन के लिए एक बहुत ही आशाजनक मार्ग ग्रेफाइट के इलेक्ट्रोकेमिकल अपपत्रण है। इलेक्ट्रोकेमिकल एक्सोफ्लोएशन इलेक्ट्रोलाइट में मौजूद आयनों के अंतराल के माध्यम से आगे बढ़ता है और उसके बाद ग्रेफेन फ्लेक्स पैदा करने के लिए बहिष्कार होता है।

इस अध्ययन में, ग्रेफाइट के इलेक्ट्रोकेमिकल एक्सफोलाइएशन को एक संशोधित तरीके से किया गया था जिसमें एचओपीजी इलेक्ट्रोड के पूर्व अंतःक्रिया को जलीय माध्यम में चरण विशिष्ट अंतराल वाले ग्रेफाइट इलेक्ट्रोड बनाने के लिए शामिल किया गया था और इसके बाद के उच्च गति पर इसके बाद के बहिष्कार चरण-विशिष्ट ग्रेफाइट- बिसाल्फेट (जीबी) कण। इन जीबी कणों को हल्के ढंग से एक अनुकूल माध्यम में सोनिकेट किया गया था ताकि चरण शुद्ध ग्रेफेन गुच्छे पैदा करने के लिए। इस विधि ने हमें इंटरमीडिएट ग्रेफाइट इंटरकेशेशन यौगिक के चरण संख्या पर बेहतर

नियंत्रण करने की अनुमति दी। उच्च सांद्रता सल्फरिक एसिड में शुद्ध चरण III ग्रेफाइट-बिसाल्फेट (जीबी) इंटरकलेशन उत्पाद बनाने के लिए अत्यधिक कम वर्तमान घनत्व (0.66 एमए / सेमी²) पर अत्यधिक आदेशित पायरोलाइटिक ग्रेफाइट (एचओपीजी) को अंतःस्थापित किया गया था। कम वर्तमान घनत्व ने आयनों के उचित अंतराल को सक्षम किया और कम इलेक्ट्रोलाइट एकाग्रता ने कार्यान्वयन की डिग्री को कम किया। स्टेज III जीबी कणों के निर्माण के लिए उच्च वर्तमान घनत्व पर पूर्व-अंतराल वाले इलेक्ट्रोड के बहिष्करण के तुरंत बाद इसका पीछा किया गया। सूखे चरण III जीबी कणों को फिर डीएमएफ में हल्के ढंग से सोनिकेट किया गया था, ग्रेफेन फैलाव के लिए एक अच्छा विलायक और फिर अपकेंद्रित। इलेक्ट्रोकेमिकल एक्सप्लॉएशन की पूर्व रिपोर्ट की गई विधियों के विपरीत, इस तकनीक ने बड़े आकार के फ्लेक्स के संश्लेषण को सक्षम किया, जिसमें ~ 18 माइक्रोन 2 के औसत फ्लेक क्षेत्र और ग्रेफेन फ्लेक्स में 88% का औसत ट्रिलियर क्षेत्र था। प्राप्त मूल्य इलेक्ट्रोकेमिकल मार्ग के माध्यम से संश्लेषित ग्रेफेन के लिए पहले बताए गए मूल्य से कहीं अधिक हैं।

ट्रिलियर ग्रेफेन के संश्लेषण के लिए ऑपरेटिंग पैरामीटर भी अनुकूलित किए गए थे, और यह पाया गया कि बढ़ते एक्सप्लोएशन ने ट्रिलियर सामग्री में वृद्धि की है लेकिन औसत फ्लेक आकार में कमी आई है। इसी तरह, सोनिकेट तीव्रता में प्रारंभिक वृद्धि त्रि परत सामग्री में वृद्धि हुई लेकिन उच्च सोनिकेट तीव्रता पर फ्लेक आकार कम हो गया। आखिर में सेंट्रीफ्यूगेशन की गति ट्राइलेयर ग्रेफेन के सबसे बड़े फ्लेक आकार को अलग करने के लिए ट्यून किया गया था। रोज़िन रैमरर वितरण का आकार वितरण का वर्णन करने के लिए उपयोग किया गया था और यह पाया गया कि 167 एमए / सेमी² का एक्सफोलाइजेशन वर्तमान, 150 डब्ल्यू / सेमी² की सोनिकेट तीव्रता और 6 मिनट के लिए 2000 के एक सेंट्रीफ्यूगेशन आरपीएम के परिणामस्वरूप अधिकतम औसत फ्लेक आकार ~ ग्रेफेन गुच्छे में 88% के औसत त्रि परत क्षेत्र के साथ 18 माइक्रोन 2।

एक समान प्रक्रिया का उपयोग बिलायर ग्रेफेन फ्लेक्स को संश्लेषित करने के लिए किया गया था, जिसमें स्टेज II ग्रेफाइट बिसाल्फेट के पूर्व अंतराल के साथ अंतराल वाले इलेक्ट्रोड के बहिष्कार के बाद किया गया था। चरण II जीबी इलेक्ट्रोड के गठन के लिए आवश्यक लंबे अंतराल का समय, बिलायर ग्रेफेन फ्लेक्स के कार्यान्वयन की डिग्री पर प्रभाव पड़ा। अपपत्रित होना जीबी कण धोया, सूखे, सोनिकेट थे और फिर दोहरी परत ग्रेफेन निलंबन बनाने के लिए अपकेंद्रित । निलंबन में लगभग आधे गुच्छों में औसत बिलायर क्षेत्र की सामग्री 95% थी और 16% गुच्छे के आकार 10 माइक्रोन 2 से अधिक थे।

बिलायर graphene के लिए संश्लेषण पैरामीटर भी अनुकूलित किया गया था। एक्सोफ्लोएशन वर्तमान, सोनिकेट तीव्रता और अपकेंद्रित गति प्राप्त अंतिम दोहरी परत ग्रेफेन गुच्छे के आकार वितरण पर एक स्पष्ट प्रभाव पड़ता है। इन पैरामीटर को ग्रेफेन निलंबन में 90% की उच्चतम औसत बिलायर सामग्री और ~ 6 माइक्रोन 2 के औसत फ्लेक आकार प्राप्त करने के लिए अनुकूलित किया गया था।

संश्लेषित द्वि- और त्रिकोणीय परत ग्रेफेन निलंबन एफटीओ ग्लास सबस्ट्रेट पर ग्रेफेन फिल्मों बनाने के लिए थे और फिल्मों के संधारित्र गुण निर्धारित किए गए थे। त्रयी के लिए अधिकतम क्षमता संश्लेषित द्वि- और त्रिकोणीय परत ग्रेफेन निलंबन एफटीओ ग्लास सबस्ट्रेट पर ग्रेफेन फिल्मों बनाने के लिए थे और फिल्मों के समाई गुण निर्धारित किए गए थे। ट्रिलियर ग्रेफेन फिल्म इलेक्ट्रोड के लिए अधिकतम क्षमता 238 एफ / जी थी और बिलायर फिल्म इलेक्ट्रोड का अधिकतम क्षमता 373 एफ / जी था। बिलायर फिल्म के लिए कैपेसिटेंस वैल्यू ग्रेफेन फिल्मों के लिए साहित्य में बताए गए मूल्यों की तुलना में काफी अधिक थी। फिल्म की आसानी से सुलभ ग्रेफेन सतह से और आंतरिक सतह से समाई में योगदान, जो प्रसार सीमा दिखाया गया था, मात्रात्मक रूप से निर्धारित किया गया था। इसके अलावा, संश्लेषण के दौरान ग्रेफेन गुच्छे के थोड़ी सी डिग्री ऑक्सीकरण से उत्पन्न छद्म संकोच का योगदान भी मापा गया था।

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