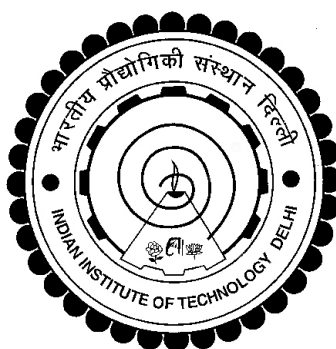


**CONTROLLED ELECTROCHEMICAL EXFOLIATION
OF HOPG FOR MONOLAYER, BILAYER, AND
TRILAYER GRAPHENE SYNTHESIS**

Isha Atrey



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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Controlled Electrochemical Exfoliation of HOPG for Monolayer, Bilayer, and Trilayer Graphene Synthesis

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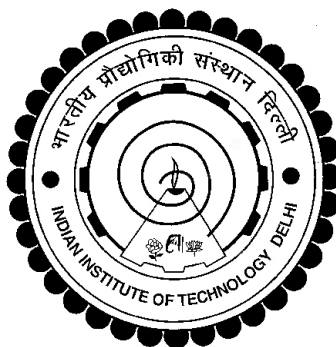
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Submitted

in fulfillment of the requirements of degree of Doctor of Philosophy

to the



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- *I would like to dedicate my thesis to my beloved parents for
teaching me the importance of education in life -*

Certificate

This is to certify that the thesis entitled “**Controlled Electrochemical Exfoliation of HOPG for Monolayer, Bilayer, and Trilayer Graphene Synthesis** ” submitted by **Miss Isha Atrey** to the Indian Institute of Technology 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. Miss Isha Atrey 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-atom-thick layer of sp^2 hybridized carbon atoms arranged in a hexagonal lattice, has transformed materials science with its remarkable properties, including a high surface area, exceptional electron mobility, outstanding thermal conductivity, and superior mechanical strength. Since its isolation in 2004, graphene has demonstrated unmatched potential in electronics, energy storage, and sensing applications. Monolayer graphene (MG) is the building block of all graphitic materials, features an extremely high surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), unparalleled thermal conductivity (up to $5000 \text{ W m}^{-1}\text{K}^{-1}$), exceptional electron mobility (up to $200,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), and nearly complete optical transparency ($\sim 97.7\%$). Bilayer graphene (BG), with two stacked layers, introduces interlayer coupling that slightly reduces these properties but still offers high thermal conductivity ($2500\text{--}3000 \text{ W m}^{-1}\text{K}^{-1}$), electron mobility ($15,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), and optical transparency ($\sim 95.4\%$), alongside a tunable electronic band gap ideal for transistors and photodetectors. Trilayer graphene (TG), composed of three layers, further transitions toward bulk behavior, with a surface area ($1017 \text{ m}^2 \text{ g}^{-1}$), thermal conductivity ($2000\text{--}3000 \text{ W m}^{-1}\text{K}^{-1}$) and optical transparency ($\sim 92.4\%$), lower than MG and BG, yet retaining sufficient electron mobility ($10,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) and mechanical strength for flexible electronics and quantum

computing. These forms of graphene demonstrate the critical importance of controlling layer thickness during synthesis, as the remarkable properties observed in thinner layers, are progressively diminished in thicker graphene, transitioning toward bulk-like behavior.

The bottom-up approaches, such as Chemical Vapor Deposition (CVD), for synthesizing MG, BG, and TG involve growing high-quality, precisely controlled graphene layers from fundamental carbon building blocks using specific catalysts and carefully regulated operating conditions. However, these methods face limitations such as substrate compatibility, defect introduction during graphene transfer, high production costs, and complex equipment, making them less viable for large-scale applications. In contrast, top-down approaches involve exfoliating graphite, where graphene layers are peeled apart by weakening the Van der Waals forces. These methods, including chemical, electrochemical, and mechanical techniques, offer scalable and cost-effective solutions for graphene production but often result in higher defect density, smaller flake sizes, and variability in the number of layers (layer polydispersity). Among these, electrochemical exfoliation of graphite stands out due to its ability to produce graphene with fewer defects and larger flake sizes. Electrochemical exfoliation of graphite involves intercalating guest species into graphite layers using an electric potential, followed by subsequent expansion and exfoliation to release graphene flakes. Furthermore, unlike bottom-up techniques, which are limited by substrate compatibility, electrochemical exfoliation offers a solution-processable approach that enables direct application of graphene to substrates.

In this work, electrochemical protocols were established to synthesize single-stage I–III graphite bisulfate (GB) compounds with minimal defect density, serv-

ing as precursors for controlled graphite exfoliation. Stage-I GB was exfoliated and sonicated to produce MG dispersions with $\sim 93.3\%$ yield, an average flake size of $\sim 136 \mu\text{m}^2$, and exhibiting optoelectrical properties comparable to those of CVD-grown MG. Similarly, single-stage II GB was processed to yield BG dispersions with $\sim 80.5\%$ yield and an average flake size of $93 \mu\text{m}^2$, while stage-III GB produced TG dispersions with a yield of $\sim 77.6\%$ and an average flake size of $\sim 96 \mu\text{m}^2$, both demonstrating properties akin to their CVD-grown counterparts. Furthermore, the synthesized MG, BG, and TG demonstrate low defect densities, reflected by an I_D/I_G ratio below 0.1. The atomic oxygen content is minimal, measured at 2.8%, 3.2%, and 3.6% for MG, BG, and TG, respectively, which is only slightly higher than the 2.1% found in pristine HOPG.

MG demonstrated excellent optoelectrical properties with an optical transmittance of $\sim 96.86\%$ and conductivity of $\sim 2.45 \times 10^6 \text{ S m}^{-1}$, while BG exhibited a slightly lower transmittance of $\sim 94.87\%$ and conductivity of $\sim 2.39 \times 10^6 \text{ S m}^{-1}$. TG showed an optical transmittance of $\sim 92.2\%$ and conductivity of $\sim 2.17 \times 10^6 \text{ S m}^{-1}$. In terms of electrochemical performance, MG achieved a specific capacitance of $\sim 666 \text{ F g}^{-1}$ in 1 M sodium sulfate at 1 A g^{-1} , retaining $\sim 60\%$ of its capacity at 8 A g^{-1} . In 5 M sulfuric acid, it delivered an impressive capacitance of $\sim 1363 \text{ F g}^{-1}$ with $\sim 74\%$ capacity retention at 8 A g^{-1} . BG exhibited specific capacitances of $\sim 363 \text{ F g}^{-1}$ in 1 M sodium sulfate and $\sim 521 \text{ F g}^{-1}$ in 5 M sulfuric acid, retaining $\sim 63\%$ and $\sim 92\%$ of its capacity, respectively, at 8 A g^{-1} . Similarly, TG recorded specific capacitances of $\sim 259 \text{ F g}^{-1}$ in 1 M sodium sulfate and $\sim 453 \text{ F g}^{-1}$ in 5 M sulfuric acid, with capacity retention of $\sim 67\%$ and $\sim 94\%$ at 8 F g^{-1} , respectively. To the best of my knowledge, the specific capacitance reported for MG, BG, and TG is the highest to date, surpassing

the values documented in the literature for electrochemically synthesized thicker graphene and reduced graphene oxide (RGO). Thus, these results underscore the exceptional potential of MG, BG, and TG for high-performance supercapacitive energy storage applications.

The findings presented in this work emphasize the effectiveness of electrochemical exfoliation as a scalable and cost-efficient method for yielding high-quality MG, BG, and TG with minimal defect densities and exceptional optoelectrical properties. By tailoring the synthesis protocols to achieve layer-monodispersity and optimal flake size, this research highlights the potential of graphene-based materials in advanced supercapacitive energy storage applications. These results pave the way for future exploration of graphene's unique properties across various industrial and technological domains, emphasizing its role as a critical material for next-generation energy solutions.

Keywords: Monolayer Graphene, Bilayer Graphene, Trilayer Graphene, Electrochemical Exfoliation, Graphite Bisulfate, Optoelectrical properties, Supercapacitive energy storage

सार

ग्राफीन, एक षट्कोणीय जाली में व्यवस्थित sp^2 संकरित कार्बन परमाणुओं की एक एकल-परमाणु-मोटी परत, ने अपने उल्लेखनीय गुणों के साथ पदार्थ विज्ञान को बदल दिया है, जिसमें एक उच्च सतह क्षेत्र, असाधारण इलेक्ट्रॉन गतिशीलता, उत्कृष्ट तापीय चालकता और बेहतर यांत्रिक शक्ति शामिल है। वर्ष 2004 में अपने अलगाव के बाद से, ग्राफीन ने इलेक्ट्रॉनिक्स, ऊर्जा भंडारण और संवेदन अनुप्रयोगों में बेजोड़ क्षमता का प्रदर्शन किया है। एकल परत ग्राफीन (MG) सभी ग्रेफाइटिक सामग्रियों का निर्माण खंड है, इसमें एक अत्यंत उच्च सतह क्षेत्र ($2630 \text{ m}^2 \text{ g}^{-1}$), अद्वितीय तापीय चालकता ($5000 \text{ W m}^{-1}\text{K}^{-1}$ तक), असाधारण इलेक्ट्रॉन गतिशीलता ($200,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ तक) और लगभग पूर्ण ऑप्टिकल पारदर्शिता ($\sim 97.7\%$) है। दो खड़ी परतों के साथ द्विपरत ग्राफीन (BG) इंटरलेयर युग्मन का परिचय देता है जो इन गुणों को थोड़ा कम करता है लेकिन फिर भी उच्च तापीय चालकता ($2500\text{--}3000 \text{ W m}^{-1}\text{K}^{-1}$), इलेक्ट्रॉन गतिशीलता ($15,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) और ऑप्टिकल पारदर्शिता $\text{m}^{-1}\text{K}^{-1}\text{ency}$ ($\sim 95.4\%$) प्रदान करता है, साथ ही ट्रांजिस्टर और फोटो डिटेक्टरों के लिए एक परिवर्तनशील इलेक्ट्रॉनिक बैंड गैप आदर्श है। तीन परतों से बना त्रिस्तरीय ग्राफीन (TG), सतह क्षेत्र ($1017 \text{ m}^2 \text{ g}^{-1}$), तापीय चालकता ($2000\text{--}3000 \text{ W m}^{-1}\text{K}^{-1}$) और ऑप्टिकल पारदर्शिता ($\sim 92.4\%$) के साथ, MG और BG से कम है, फिर भी लचीले इलेक्ट्रॉनिक्स और क्वांटम कंप्यूटिंग के लिए पर्याप्त इलेक्ट्रॉन गतिशीलता ($10,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) और यांत्रिक शक्ति बनाए रखता है। ग्राफीन के ये रूप संश्लेषण के दौरान परत की मोटाई को नियंत्रित करने के महत्वपूर्ण महत्व को प्रदर्शित करते हैं, क्योंकि पतली परतों में देखे जाने वाले उल्लेखनीय गुण, मोटे ग्राफीन में उत्तरोत्तर कम होते जाते हैं, जो थोक जैसे व्यवहार की ओर संक्रमण करते हैं।

MG, BG और TG के संश्लेषण के लिए रासायनिक वाष्प जमाव (CVD) जैसे नीचे से ऊपर के तरीकों में विशिष्ट उत्प्रेरकों और सावधानीपूर्वक विनियमित परिचालन स्थितियों का उपयोग करके मौलिक कार्बन बिल्डिंग ब्लॉकों से उच्च गुणवत्ता वाले, सटीक रूप से नियंत्रित ग्राफीन परतों को विकसित करना शामिल है। हालाँकि, इन विधियों में सबस्ट्रेट संगतता, ग्राफीन स्थानांतरण के दौरान दोष का परिचय, उच्च उत्पादन लागत और जटिल उपकरण जैसी सीमाएँ हैं, जो उन्हें बड़े पैमाने पर अनुप्रयोगों के लिए कम व्यवहार्य बनाती हैं। इसके विपरीत, ऊपर से नीचे के तरीकों में ग्रेफाइट को छिलना शामिल है, जहाँ वैन डेर वाल्स बलों को कमजोर करके ग्राफीन परतों को अलग-अलग किया जाता है। रासायनिक, विद्युत रासायनिक और यांत्रिक तकनीकों सहित ये विधियाँ ग्राफीन उत्पादन के लिए स्केलेबल और लागत प्रभावी समाधान प्रदान करती हैं, लेकिन अक्सर उच्च दोष घनत्व, छोटे फ्लेक आकार और परतों की संख्या में परिवर्तनशीलता का परिणाम देती हैं। इनमें से, ग्रेफाइट का विद्युत रासायनिक एक्सफोलिएशन कम दोषों और बड़े आकार के फ्लेक के साथ ग्राफीन का उत्पादन करने की अपनी क्षमता के कारण अलग है। ग्रेफाइट के इलेक्ट्रोकेमिकल एक्सफोलिएशन में इलेक्ट्रिक पोटेन्शियल का उपयोग करके अतिथि प्रजातियों को ग्रेफाइट परतों में इंटरकैलेट करना शामिल है, इसके बाद ग्राफीन के गुच्छे को छोड़ने के लिए विस्तार और एक्सफोलिएशन किया जाता है। इसके अलावा, बॉटम-अप तकनीकों के विपरीत, जो सबस्ट्रेट संगतता द्वारा

सीमित हैं, इलेक्ट्रोकेमिकल एक्सफोलिएशन एक समाधान-प्रक्रिया योग्य दृष्टिकोण प्रदान करता है जो सबस्ट्रेट पर ग्राफीन के सीधे अनुप्रयोग को सक्षम बनाता है।

इस कार्य में, न्यूनतम दोष घनत्व वाले सिंगलस्टेज I-III ग्रेफाइट बाइसल्फेट (GB) यौगिकों को संश्लेषित करने के लिए इलेक्ट्रोकेमिकल प्रोटोकॉल स्थापित किए गए थे, जो नियंत्रित ग्रेफाइट एक्सफोलिएशन के लिए अग्रदूत के रूप में काम करते हैं। स्टेज-I GB को एक्सफोलिएट किया गया और सोनिकेट किया गया ताकि MG फैलाव का उत्पादन किया जा सके जिसमें $\sim 93.3\%$ उपज, $\sim 136 \mu\text{m}^2$ का औसत फ्लेक आकार और CVD-ग्रोन MG के तुलनीय ऑटोइलेक्ट्रिकल गुण प्रदर्शित हों। इसी तरह, सिंगल-स्टेज II GB को संसाधित किया गया ताकि BG फैलाव का उत्पादन किया जा सके जिसमें $\sim 80.5\%$ उपज और $93 \mu\text{m}^2$ का औसत फ्लेक आकार हो, जबकि स्टेज-III GB ने $\sim 77.6\%$ की उपज और $\sim 96 \mu\text{m}^2$ के औसत फ्लेक आकार के साथ TG फैलाव का उत्पादन किया, दोनों ने अपने CVD उत्पादित समकक्षों के समान गुण प्रदर्शित किए। इसके अलावा, संश्लेषित MG, BG और TG कम दोष घनत्व प्रदर्शित करते हैं, जो 0.1 से नीचे आईडी/आईजी अनुपात द्वारा दर्शाया गया है। परमाणु ऑक्सीजन सामग्री न्यूनतम है, MG, BG और TG के लिए क्रमशः 2.8%, 3.2% और 3.6% मापी गई है, जो कि प्रिस्टिन एचओपीजी में पाए जाने वाले 2.1% से थोड़ा ही अधिक है।

MG ने लगभग 96.86% ऑप्टिकल संप्रेषण और लगभग $2.45 \times 10^6 \text{ S m}^{-1}$ की चालकता के साथ उत्कृष्ट ऑटोइलेक्ट्रिकल गुणों का प्रदर्शन किया, जबकि BG ने लगभग 94.87% का थोड़ा कम संप्रेषण और लगभग $2.39 \times 10^6 \text{ S m}^{-1}$ की चालकता प्रदर्शित की। TG ने लगभग 92.2% का ऑप्टिकल संप्रेषण और लगभग $2.17 \times 10^6 \text{ S m}^{-1}$ की चालकता दिखाई। विद्युत-रासायनिक प्रदर्शन के संदर्भ में, MG ने 1 A g^{-1} पर 1 M सोडियम सल्फेट में लगभग 666 F g^{-1} की विशिष्ट धारिता हासिल की, जिसने 8 A g^{-1} पर अपनी क्षमता का लगभग 60% बरकरार रखा। 5 M सल्फ्यूरिक एसिड में, इसने 8 A g^{-1} पर $\sim 74\%$ क्षमता प्रतिधारण के साथ $\sim 1363 \text{ F g}^{-1}$ की प्रभावशाली धारिता प्रदान की। BG ने 1 M सोडियम सल्फेट में $\sim 363 \text{ F g}^{-1}$ और 5 M सल्फ्यूरिक एसिड में $\sim 521 \text{ F g}^{-1}$ की विशिष्ट धारिता प्रदर्शित की, जिसने 8 A g^{-1} पर क्रमशः अपनी क्षमता का $\sim 63\%$ और $\sim 92\%$ बनाए रखा। इसी तरह, TG ने 1 M सोडियम सल्फेट में $\sim 259 \text{ F g}^{-1}$ और 5 M सल्फ्यूरिक एसिड में $\sim 453 \text{ F g}^{-1}$ की विशिष्ट धारिता दर्ज की, जिसमें 8 F g^{-1} पर क्रमशः $\sim 67\%$ और $\sim 94\%$ क्षमता प्रतिधारण था। मेरी जानकारी के अनुसार, MG, BG और TG के लिए रिपोर्ट की गई विशिष्ट धारिता आज तक की सबसे अधिक है, जो इलेक्ट्रोकेमिकली संश्लेषित मोटे ग्राफीन और कम ग्राफीन ऑक्साइड (RGO) के लिए साहित्य में दर्ज मूल्यों से अधिक है। इस प्रकार, ये परिणाम उच्च प्रदर्शन वाले सुपरकैपेसिटिव ऊर्जा भंडारण अनुप्रयोगों के लिए एमजी, बीजी और टीजी की असाधारण क्षमता को रेखांकित करते हैं।

इस कार्य में प्रस्तुत निष्कर्ष इलेक्ट्रोकेमिकल एक्सफोलिएशन की प्रभावशीलता पर जोर देते हैं, जो न्यूनतम दोष घनत्व और असाधारण ऑटोइलेक्ट्रिकल गुणों के साथ उच्च गुणवत्ता वाले एमजी, बीजी और टीजी प्राप्त करने के लिए एक स्केलेबल और लागत-कुशल विधि है। परत-मोनोडिस्पर्सिटी और इष्टतम फ्लेक आकार को प्राप्त करने के

लिए संश्लेषण प्रोटोकॉल को तैयार करके, यह शोध उन्नत सुपरकैपेसिटिव ऊर्जा भंडारण अनुप्रयोगों में ग्राफीन-आधारित सामग्रियों की क्षमता पर प्रकाश डालता है। ये परिणाम विभिन्न औद्योगिक और तकनीकी डोमेन में ग्राफीन के अद्वितीय गुणों की भविष्य की खोज का मार्ग प्रशस्त करते हैं, जो अगली पीढ़ी के ऊर्जा समाधानों के लिए एक महत्वपूर्ण सामग्री के रूप में इसकी भूमिका पर जोर देते हैं।

कीवर्ड: मोनोलेयर ग्राफीन, बिलेयर ग्राफीन, ट्रिलेयर ग्राफीन, इलेक्ट्रोकेमिकल एक्सफोलिएशन, ग्रेफाइट बिसल्फेट, ऑक्सीइलेक्ट्रिकल गुण, सुपरकैपेसिटिव ऊर्जा भंडारण

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List of symbols and abbreviations

Symbol	Definition
C_{sp}	Area of electrode (F g^{-1})
E_i	Initial potential of the discharge curve (V)
E_f	Final potential of the discharge curve (V)
m	mass of graphene coated on FTO current collector (g)
τ_0	Relaxation time of a supercapacitor (s)
Y_w	Bounded Warburg admittance ($\text{S s}^{0.5}$)
Y_{dl}	Double-layer capacitance admittance (F s^{n-1})
B_w	Bounded Warburg element ($\text{s}^{0.5}$)
n	Exponent in the constant phase element
f_0	frequency at -45 phase angle in Bode plot (Hz)
j	Current density (A g^{-1})
i	Current at a specific scan rate (A)
v	Scan rate during cyclic voltammetry (mV s^{-1})
a, b	Fit parameters for current-scan rate relationship
d	Interplanar spacing in crystal structures ($\text{\AA}$)
λ	Wavelength of X-ray radiation (nm)
I_c	Repeat distance of graphite bisulfate ($\text{\AA}$)
N	Stage index of graphite bisulfate
c_0	Interlayer distance in pristine graphite ($\text{\AA}$)
d_s	Interlayer distance of stage I graphite bisulfate ($\text{\AA}$)
$\Delta\phi_k$	Critical galvani potential (V)
$\Delta\phi_a$	Anion adsorption voltage (V)
$\Delta\phi_p$	Electrode polarization voltage (V)
C_a	Double-layer capacitance (F)

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Q_a	Area specific charge on electrode (C)
A^-	Bisulfate ions (intercalants)
MLT1.83	Monolithic stage I GB electrode synthesized at 1.83 V
EXF2.28_1	Stage I GB particles exfoliated at 2.28 V in 98% H_2SO_4
EXF2.28_2	Particles obtained from simultaneous intercalation and exfoliation at 2.28 V in 98% H_2SO_4
EXF2.35	Stage I GB particles exfoliated at 2.35 V in 98% H_2SO_4
MLT2.28	Residual electrode from simultaneous intercalation and exfoliation at 2.28 V in 98% H_2SO_4
D1	Dispersion of high-quality monolayer graphene with minimal defects and large flake size ($\sim 0.52 \text{ mg mL}^{-1}$ concentration)
D2	Dispersion of poorly dispersed, re-aggregated graphene flakes with lower concentration ($\sim 0.48 \text{ mg mL}^{-1}$) due to insufficient ultrasonication
D3	Dispersion of re-aggregated graphene flakes with moderate defect density and smaller flake size ($\sim 0.8 \text{ mg mL}^{-1}$ concentration) from increased ultrasonic power

Abbreviation Full form

HOPG	Highly oriented pyrolytic graphite
GB	Graphite bisulfate
MG	Monolayer graphene
BG	Bilayer graphene
TG	Trilayer Graphene
FLG	Few layer graphene
GIC	Graphite intercalation compound
GO	Graphene Oxide
RGO	Reduced graphene oxide
EDLC	Electric Double-Layer Capacitance
CVD	Chemical vapor deposition
XRD	X-Ray Diffraction
XPS	X-ray photoelectron spectroscopy
SAED	Selected area electron diffraction
AFM	Atomic force microscopy

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TEM	Transmission electron microscopy
HRTEM	High resolution transmission electron microscopy
CV	Cyclic voltammetry
LSV	Linear sweep voltammetry
GCD	Galvanostatic charge-discharge
FTO	Fluorine-doped tin oxide
NMP	N-Methyl-2-pyrrolidone
FET	Field-Effect Transistor
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
CPE	Constant phase element
BW	Bounded warburg
RF	Radio frequency
ITO	Indium tin oxide
FTO	Fluorine-doped tin oxide