Iodine-Induced Enhancement in Electrical Conductivity of Electro-Deposited Thin Film of Copper-Carboxylate MOF

A Thesis

Submitted to

Indian Institute of Science Education and Research Pune

in Partial Fulfillment of the Requirements for the MSc Chemistry

Programme by

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Indian Institute of Science Education and Research

Pune, India

March, 2024

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Certificate

This is to certify that this dissertation entitled "***Iodine-Induced Enhancement in Electrical Conductivity of Electro-Deposited Thin Film of Copper-Carboxylate MOF***" towards the partial fulfillment of the MSc chemistry programme at the **Indian Institute of Science Education and Research, Pune** represents original research work carried out by **Aniruddha Shailendra Mahattam** at **Indian Institute of Science Education and Research, Pune** under the supervision of **Prof. Nirmalya Ballav, Chair, Department of Chemistry, Indian Institute of Science Education and Research, Pune** during the academic year 2023-2024.

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Declaration

I hereby declare that the matter embodied in the report entitled ***"Iodine-Induced Enhancement in Electrical Conductivity of Electro-Deposited Thin Film of Copper-Carboxylate MOF"*** are the results of the work carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research, Pune, under the supervision of Prof. Nirmala Ballav and the same has not been submitted elsewhere for any other degree.

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Acknowledgment

I would like to take this opportunity to acknowledge my thesis supervisor Prof. Nirmalya Ballav for allowing me to work in his lab. He has nurtured me and my ideas during the project line. Words fall short for expressing my gratitude towards him. He has not only guided me in scientific pursuits but also towards a better human being. I will be always grateful to him for giving freedom to chart my path and for bearing with my shortcomings patiently.

This acknowledgment would be incomplete without my mentor, Mr. Umashis as he had been inspiring and teaching me the ABCs of research and guiding me through numerous hurdles. His tolerance, lucidity, and readiness to impart his expertise to me, have been priceless resources that have helped me overcome obstacles and advance as a researcher.

I am grateful that I had my trusty lab partners, Nahid bhaiya, Ajay bhaiya, Sauvik, Aradhana, Kalyani, and Rimpa who had been rocks of support during this journey. They all have been important in my accomplishments, whether by contributing technical knowledge, assisting with troubleshooting tests, or just emotional support when I needed it the most. I am indebted to all of them for always being there to help me when I needed it. Specifically at times of difficulty, their knowledge has been invaluable.

I am grateful to all the office staff and technical staff who have always helped me out when I was in trouble. In research projects scientific data plays a very crucial and pivotal role so here is my heartfelt thanks to Mrs. Bhagyashree, Mr. Anil Shetty, and Mrs. Megha for always assisting me with scientific measurements of samples and getting me appropriate results, without these results, I would have been unable to proceed in this thesis project.

Friends are an integral part of one’s college life. I would like to thank all the friends, seniors, and juniors I had here at IISER. I would like to thank Samiksha, who has made

my life easier and memorable. I want to thank Abhishek, Keerthivason, Parth, Prabhakar, Kashish, Syamantak, Ankan, Ajit, Pavithra, Vartika, Yashasvi, Archita, and Mansi for giving me memories that will last lifelong with me.

Last but not least, my beloved family- Mummy, Pappa, Uarwashi, and my younger brother Yatharth, I am all because of them. Their blessings and well wishes have always led me through all the obstacles in my path to success. I get all my inner strength because of them. I show my sincere courtesy to my parents for standing by my decisions and giving me all the love and support I needed.

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Abstract

Imparting electrical conductivity into metal-organic frameworks (MOF) having a significantly high porous nature, and large surface area but extremely poor electrical conductivity opens doors for numerous applications of MOFs in electronics, optoelectronics, and supercapacitors. Using molecular iodine as a guest in the MOFs is an effective strategy for enhancing electrical conductivity. Herein, we demonstrate for the first-time fabrication of Cu-NDC thin film using an electrochemical deposition approach and thereby intercalation of molecular iodine into MOF thin film. The iodine-doped thin film resulted in nearly ~10^2 orders of increased electrical Conductance than the pristine thin film. The increased electrical performance can be attributed to the formation of I_3^- species due to the partial oxidation of the framework. Consequences as mentioned earlier make the molecular iodine doping strategy, a promising candidate for modulating the electrical conductivity of MOFs.

Introduction

Metal-organic frameworks (MOFs) are a special category of materials that have metal ion centers coordinated by multitopic organic ligands, nanoporous and crystalline in nature[1]. MOFs have been enormously explored for a diverse collection of applications including catalysis, gas sensing, separation, adsorption, and many others.[2] The porosity inhered by MOFs can be engineered with dopant molecules resulting in numerous applications. It has been almost a decade since Talin et al. demonstrated the tunable electrical conductivity where a small-molecule organic semiconductor, 7,7,8,8-tetracyanoquinodimethane (TCNQ) has guided the way to innovatively strategize, design, and tune the conductivity of a Cu-MOF (HKUST-1) by several orders of magnitude[3]. The doped TCNQ host infiltrated in the pore makes a continuous path by bridging four copper octahedra, ultimately giving rise to enhanced electrical conductivity. Recently, a report on the enhanced thermoelectric properties of $Cu_3(HHTP)_2$ via loading of molecular iodine into

the pores of MOF have been published[4]. $Cu_3(HHTP)_2$ thin film was made using a dip-coating method. The synthesized film was dipped in iodine solution in dichloromethane for a variable time to infiltrate iodine. Host-guest interactions between doped iodine and the framework resulted in the formation of I_3^- species due to the partial oxidation of the framework, enhancing the thermoelectric performance of the material. Two-dimensional (2D) π-d conjugated Ni(II) tetraaza[14]annulene doped with iodine showed enhanced electrical conductivity and paramagnetism due to partial oxidation[5]. The pristine MOF was ascertained to be electrically insulating in nature having $\sigma<10^{-10}$ S/cm. However, the iodine-dopped MOF pallet showed an incredibly high electrical conductivity of 0.01 S/cm.

However, apart from applications specifically related to porosity, MOFs lag in the field of electronics as their application in devices is concerted, majorly due to their intrinsic insulating nature.[6] The ineffective orbital overlap between inorganic metal nodes and organic linkers precludes the generation of an effective charge transport pathway in MOFs. However, efforts are being made to modulate the electrical conductivity in MOFs using both intrinsic and extrinsic approaches by various design strategies[6-8], which constitute hybridizing MOFs with other conductive media, linking metal sites with redox-active linkers, doping of redox-active guest molecules, and composite formation. One of the most popular choices among the strategies for imparting conductivity in a non-conducting MOF is the introduction of redox-active guest molecules, as the intrinsic pores serve as a platform for modulating the electrical transfer properties.

Through post-synthetic modification for enhancing electrical conductivity, iodine is commonly doped into the pores of MOFs as a redox-active molecule. This process leads to the refined electrical performance of the system due to the oxidative doping of MOFs by the guest iodine molecules[9-11]. Mainly, the MOF system's oxidative doping occurs due to metal ions' oxidation within the framework [9]. In systems where the oxidation of metal ions is not thermodynamically feasible, the oxidative doping of MOF could result from the interaction between guest I_2 and ligand π electron density. However, this phenomenon is often not observed.[10]. A report on the enhanced electrical performance by ~10^8

magnitudes as a consequence of iodine loading into the MOF has been previously published[12].

Motivated by the host-guest interactions of iodine-doped MOF systems and their accompanying enhancement in the electrical conductivity, herein, we report the first-time electrodeposition of Cu-NDC thin film on FTO substrate to the best of our knowledge and thereby iodine doping into the pores of the MOF thin film which results in a two-fold increase in the electrical conductance in the iodine doped than the pristine thin film. The increased conductance in the doped thin film can be attributed to the oxidative doping of iodine in the pristine thin film[10]. To comment on the bonding motif and host-guest interactions in the system, both the pristine and iodine-doped thin films were thoroughly characterized using microscopic as well as various spectroscopic techniques.

Materials and Methods

Chemicals

N,N-dimethylformamide, copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$], and tetraethylammonium tetrafluoroborate (TEAFB) were purchased from Sigma-Aldrich Co. LLC. 2,6-naphthalenedicarboxylic acid was purchased from Thermo Fisher Scientific Inc. Fluorine-dopped tin oxide (FTO) glass substrates were purchased from Sigma-Aldrich Co. LLC. Dimensions of FTO glass used was 1x3 cm^2. The thickness of the FTO used was 2.3mm.

All reagents and starting materials were commercially obtained and used without any further purification.

Substrate Cleaning

Firstly, the FTO sheet (10cm*10cm) was cut down into small pieces of dimensions 1x3 cm^2 and to remove surface impurities it was kept in 1M HCl for an hour, then sonicated with water for 15 minutes followed by acetone, ethanol, water, and isopropyl alcohol respectively for 15 minutes each. FTOs were dried in the air and used as working electrodes for electrochemical deposition (ECD).

Fabrication of Thin Film

A solution containing 10mM $Cu(NO_3)_2 \cdot 3H_2O$ as the metal node, 15mM 2,6-napthalenedicarboxylic acid as the linker, 10mM Et_3NHCl as a probase source, and 20mM tetraethylammonium tetrafluoroborate (TEAFB) as the supporting electrolyte in DMF was used in the ECD process. A classic three-electrode system was utilized. An FTO (1*3 cm^2) as a working electrode, a pure platinum (Pt) rod as a counter electrode, and Ag/AgCl as a reference electrode were used. A constant potential of -1.4V vs Ag/AgCl (3M KCl) was applied for 300 seconds. A uniform thin film of Cu-NDC was formed on the FTO surface.

Iodine Doping of Thin Film

The as-synthesized electrodeposited Cu-NDC thin film was then submerged in iodine vapor chamber for 2 hours so that iodine could enter into the pores of MOF. After 2 hours the iodine-doped Cu-NDC thin film (I_2@Cu-NDC) was taken out, dried in air, and used for further characterizations.

Characterization

The surface morphological analysis and uniformity of pristine Cu-NDC as well as iodine-doped Cu-NDC thin films were characterized with FESEM. Out-of-plane XRD data were recorded on a Bruker D8 Advanced diffractometer using Cu Kα radiation (λ = 1.5406 Å) at room temperature. Raman spectra were recorded using a Raman microscope - LabRAM HR, HorbiaJobinYvon. Electrical conductivity (*I-V*) measurements were carried out by the Keithley 4200 SCS Parameter Analyzer system with EGaIn as a top electrode for all the thin film samples.

Results and Discussion

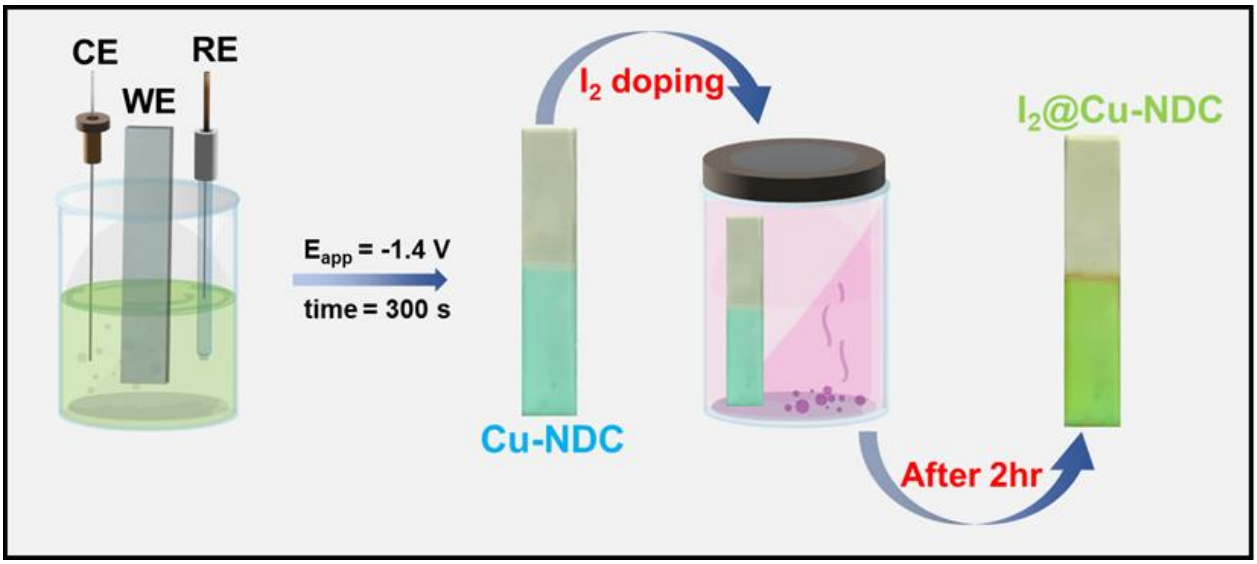

Figure 1. A graphical depiction of the electrochemical synthesis along with optical images of pristine Cu-NDC thin film on FTO substrate. Molecular iodine doping was performed by keeping Cu-NDC thin film in iodine chamber for 2 hours

In this work, electrodeposited Cu-NDC thin films were fabricated using an electrochemical cell. As depicted in the schematic (**Figure 1**) the pristine Cu-NDC and iodine-doped Cu-NDC thin films were fabricated using the reaction scheme (mentioned in **Figure 2**) and used for further characterizations.

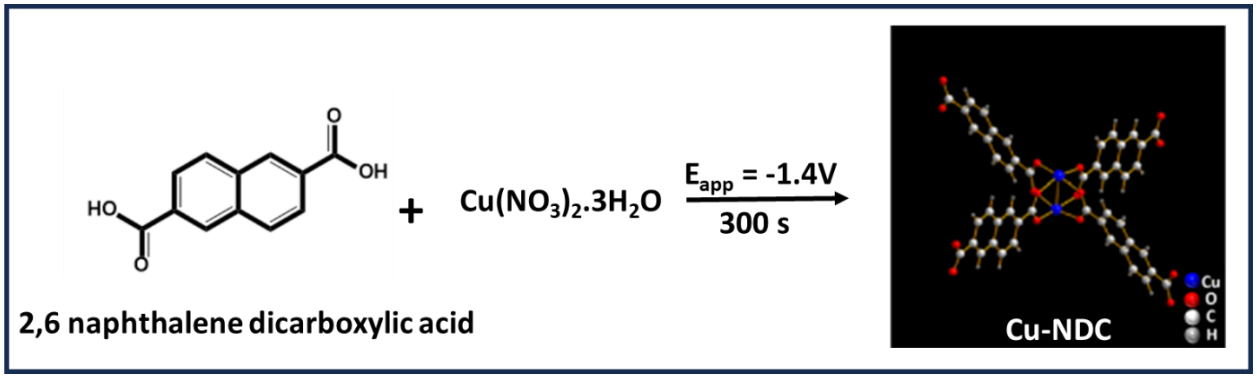

Figure 2. Reaction scheme for fabrication of Cu-NDC thin film. (image reproduced from Ref. 13, copyright 2021 Elsevier Ltd.)

The as-synthesized electrodeposited Cu-NDC and iodine-doped thin films were probed with Field Emission Scanning Electron Microscopy (FESEM) to evaluate their uniformity and coverage over the substrate. FESEM images (**Figure 3a, 3b**) display a continuous, uniform, and even distribution of Cu-NDC thin film spread over the FTO substrate surface. FESEM images of the iodine-doped thin film (**Figure 3c, 3d**) show a similar surface morphology as the pristine sample with small bulges at some spots. This probably can be due to the infiltration of iodine in the pores of MOF.

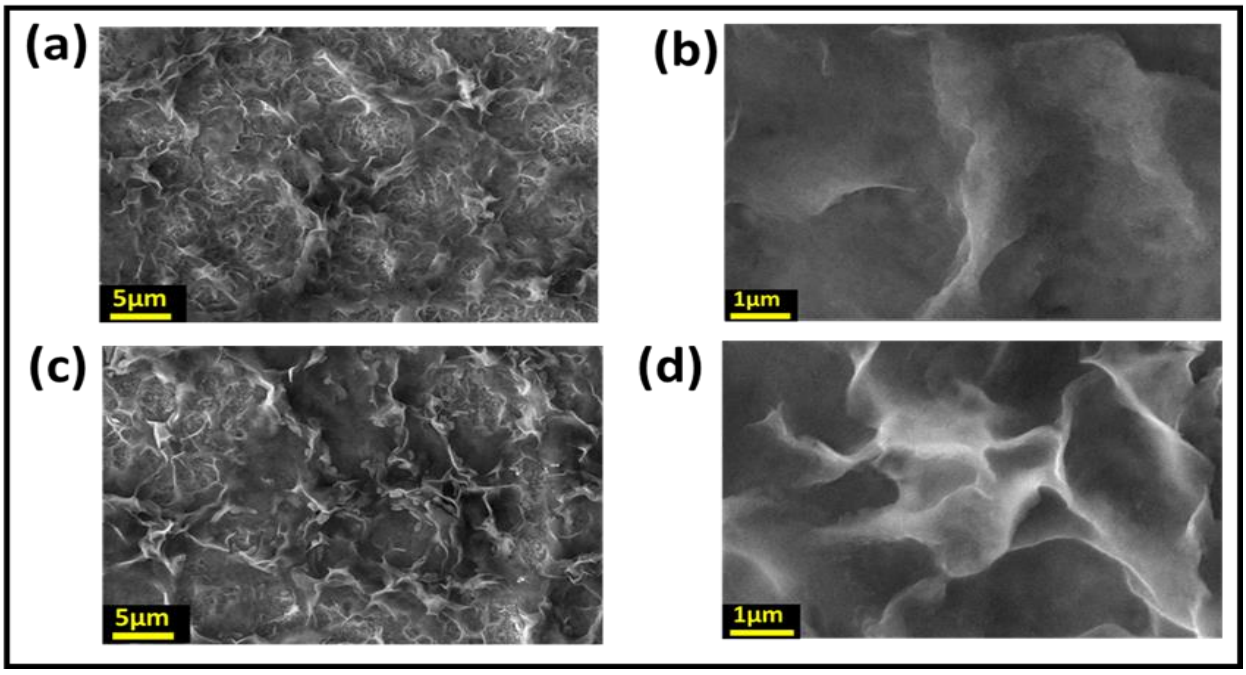

Figure 3. FE-SEM images of pristine Cu-NDC thin film (a and b) and iodine-doped Cu-NDC thin film (c and d) at different magnifications

The energy-dispersive X-ray spectroscopy (EDXS) of both the thin films were recorded. The EDXS spectra of Cu-NDC (**Figure 4c**) and I_2@Cu-NDC (**Figure 4d**) show the respective elemental composition. Elemental analysis of the iodine-doped thin film showed the uniform distribution of iodine over the surface of the thin film (**Figure 4b**).

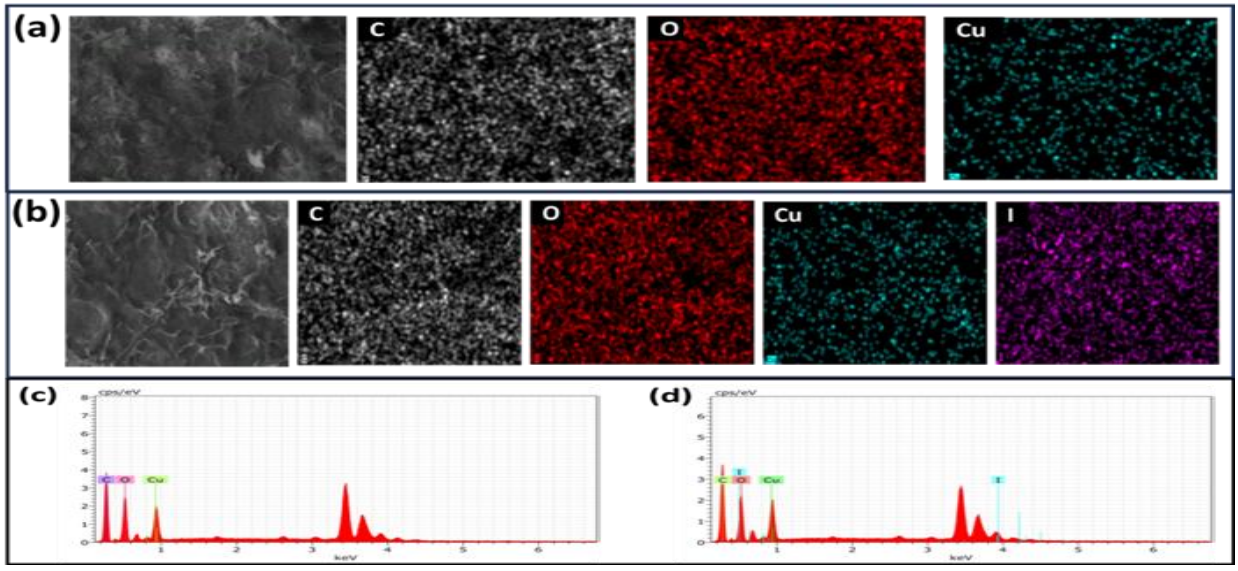

Figure 4. Surface elemental analysis of (a) Cu-NDC and (b) I_2@Cu-NDC thin film by EDXS analysis showing uniformly spread of iodine over the surface of I_2@Cu-NDC. EDXS spectra of Cu-NDC (c) and I_2@Cu-NDC (d) thin films

To confirm the successful fabrication of Cu-NDC thin film, out-of-plane powder X-ray diffraction (PXRD) patterns of pristine Cu-NDC, and I_2@Cu-NDC were recorded (**Figure 5a**) and compared with the previously reported [13]. The PXRD data confirms the successful fabrication of Cu-NDC using the electrodeposition technique. PXRD pattern remains unchanged even after the incorporation of iodine. This finding aligns with the similar surface morphological analysis of pristine as well as doped thin films suggested using FESEM images. Interestingly, in PXRD patterns of Cu-NDC thin film after I_2 loading, a new very intense peak at 2θ ~12.5° appears which possibly arises due to the I_2 incorporation within Cu-NDC MOF pores.

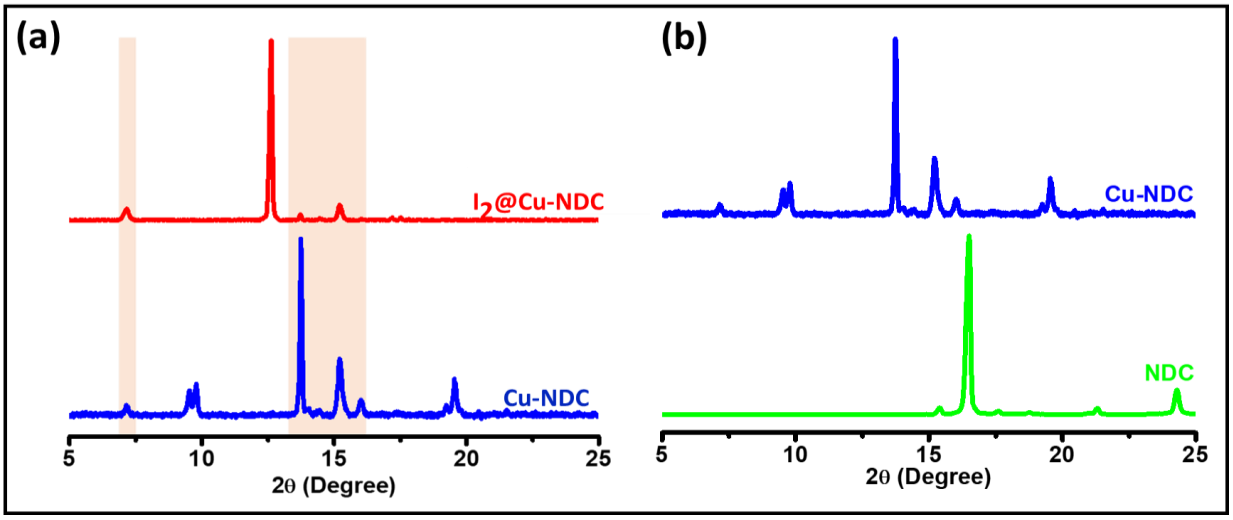

Figure 5. PXRD patterns of Cu-NDC (blue) and I_2@Cu-NDC (red) thin films (a), and Cu-NDC (blue) thin film and NDC ligand (green) (b)

Furthermore, the PXRD patterns of 2,6-naphthalene dicarboxylic acid (linker) and the Cu-NDC thin films were compared (**Figure 5b**). The data reveals that no unreacted NDC linker is present in the framework. This demonstrates the successful fabrication of Cu-NDC thin film without any unreacted precursors left in the system.

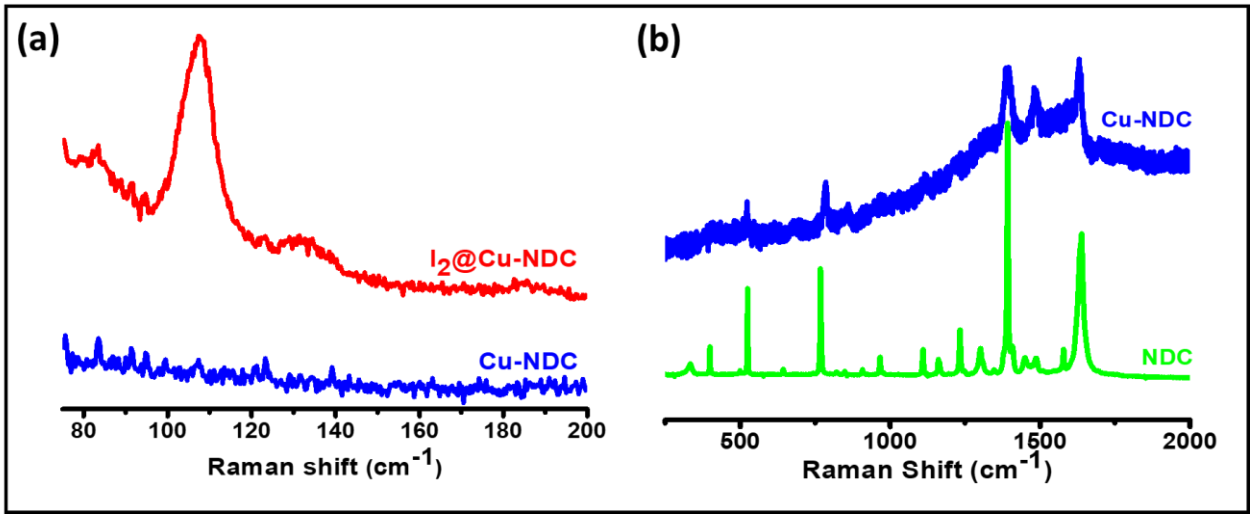

Figure 6. Raman analysis of Cu-NDC (blue) and I_2@Cu-NDC (red) thin films indicating incorporation of iodine (a), and Cu-NDC (blue) thin film and NDC ligand (green) (b)

To determine the nature of iodine species absorbed in the pores of Cu-NDC thin film after being immersed in iodine vapors for 2 hours, Raman spectroscopy was conducted. The pristine electrodeposited Cu-NDC thin film showed no Raman stretching band in the field of interest between 70-130 and 130-200 cm^{-1} caused by the absence of I_2 in the structure (**Figure 6a**). After iodine loading into the pristine thin film, a Raman stretching band peaking at ~108 cm^{-1} appears which is assigned to the asymmetric stretching mode of linear symmetric triiodide anion I_3^- within the pores[4,13]. Presumably, the charge transfer between the highly conjugated Cu-NDC framework and iodine results in the partial oxidation of iodine, forming the triiodide anion species[5]. In addition to this, neutral I_2 is not found in the iodine-dopped thin film as proposed by the absence of the band in the 130-200 cm^{-1} region in the Raman spectra (**Figure 6b**)[4].

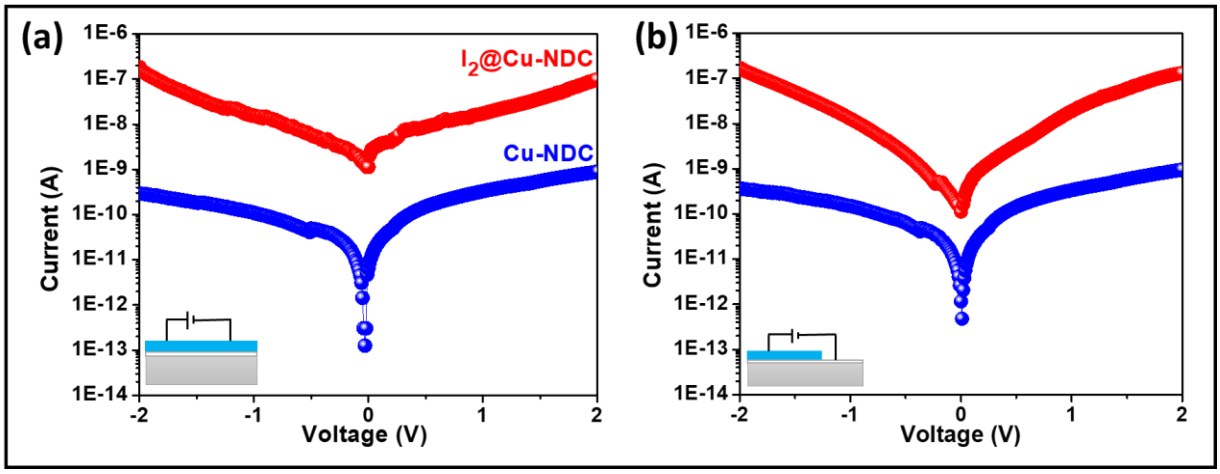

Figure 7. *I-V* characteristics (a) in-plane and (b) cross-plane of pristine (blue) and iodine-doped (red) thin films.

The in-plane *I-V* characteristics (**Figure 7a)** of iodine-doped and pristine thin films show that the iodine-doped thin film possesses a two-fold greater conductance value than the undoped Cu-NDC thin film, parallel to the plane of the film. The cause behind this enhanced electrical performance is the formation of the triiodide anion (I_3^-) within the framework The cross-plane *I-V* characteristics (**Figure 7b**) of both the thin films showed a similar trend as that of the in-plane *I-V* characteristics. This demonstrates both films

show similar trends in all directions. The direction parallel to the plane of the film and the direction perpendicular to the plane of the film show similar electrical behavior. Enhanced electrical conductance in cross-plane is an indication of the incorporation of iodine throughout the film uniformly.

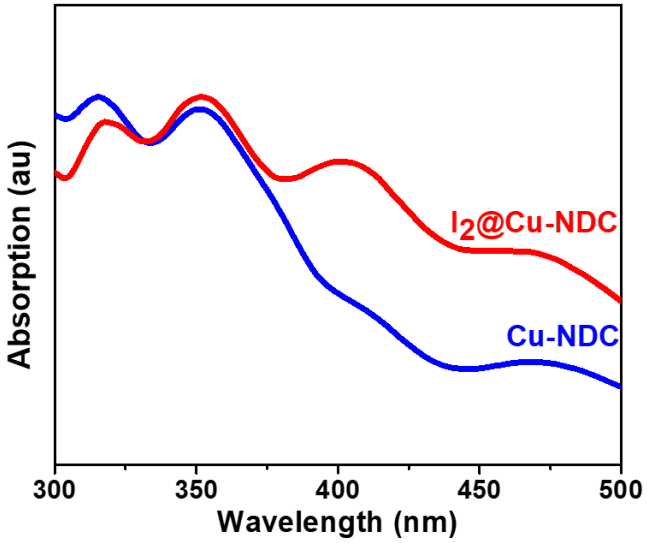

Figure 8. Solid-state UV-visible spectra of pristine (blue) and iodine-doped (red) thin films

The solid-state UV-visible absorption spectra (**Figure 8**) of Cu-NDC and I_2@Cu-NDC films were conducted to comment on the interconnection between the framework and absorbed I_2. In the solid-state UV-visible absorption spectra, the absorption peak at about ~480 nm appears that can be attributed to the ligand-to-metal charge-transfer transitions in the MOFs. An additional peak appearing at ~420 nm in the I_2@Cu-NDC thin film is a consequence of iodine absorption by the pristine thin film[4]. This explains the iodine capture without deforming the solid framework.

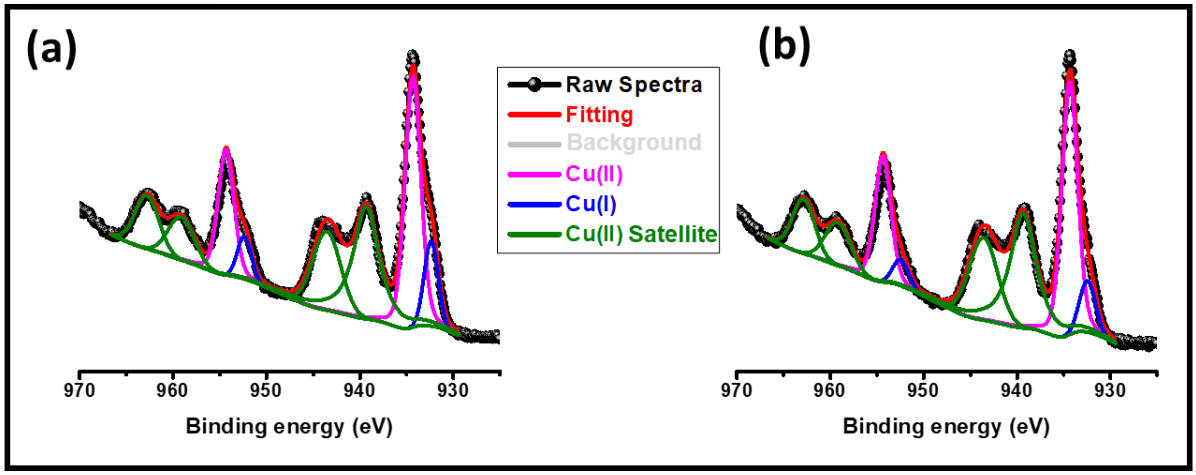

Figure 9. XPS analysis of Cu 2p (a) before and (b) after iodine doping in Cu-NDC thin film (I_2@Cu-NDC)

To investigate the bonding motif of and the host-guest interactions between the iodine and the framework by probing the valence state for each element, X-ray photoelectron spectroscopy (XPS) was conducted. As shown in **Figure 9**, the Cu 2s XPS spectrum of the Cu-NDC is divided into two doublets of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ and the corresponding peaks are at 954.04eV and 934.4 eV respectively, showing mixed valence states in both the films. Peaks at 954.04 eV and 934.8 eV are assigned to the Cu^{2+} state and peaks at 953.17 eV and 933.1 eV are assigned to the Cu^{+} state of the Cu in the framework. The Cu^{2+}**:** Cu^{+} ratio before iodine doping was ~3.6**:** 1 changed to ~5.4**:** 1 after doping, indicating partial oxidation of Cu^{+} to Cu^{2+}, which is a consequence of the redox reaction between molecular iodine and MOF[5].

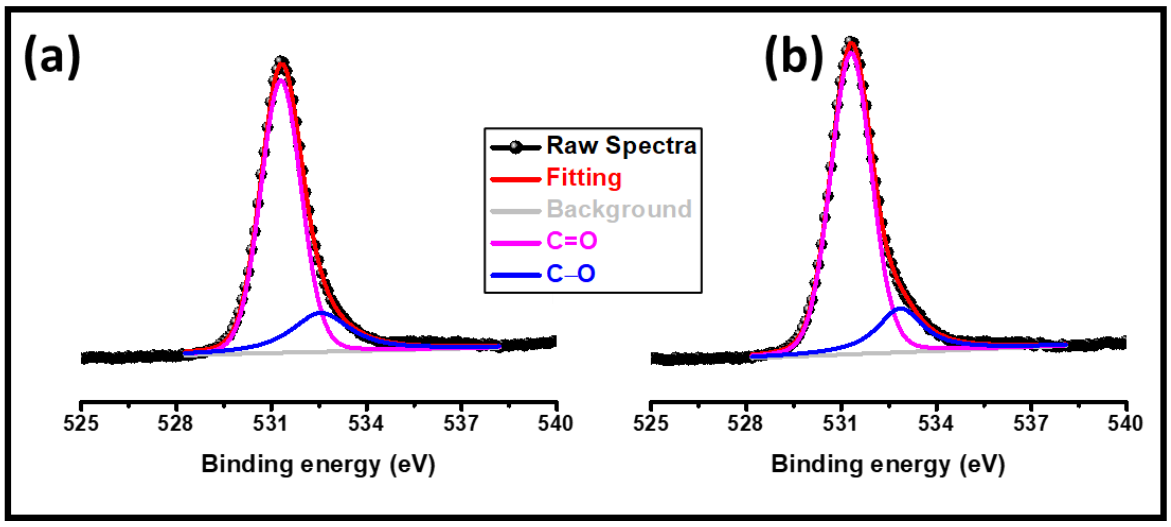

Figure 10. XPS spectra of O 1s (a) before and (b) after iodine doping in Cu-NDC thin film (I_2@Cu-NDC)

Similar observations were found in the XPS spectra of O 1s, wherein the C=O**:** C-O ratio before iodine doping was ~3.6**:** 1 changed to ~4.5**:** 1 after iodine doping. This implies oxygen is also involved in the host-guest interactions between iodine and the framework.

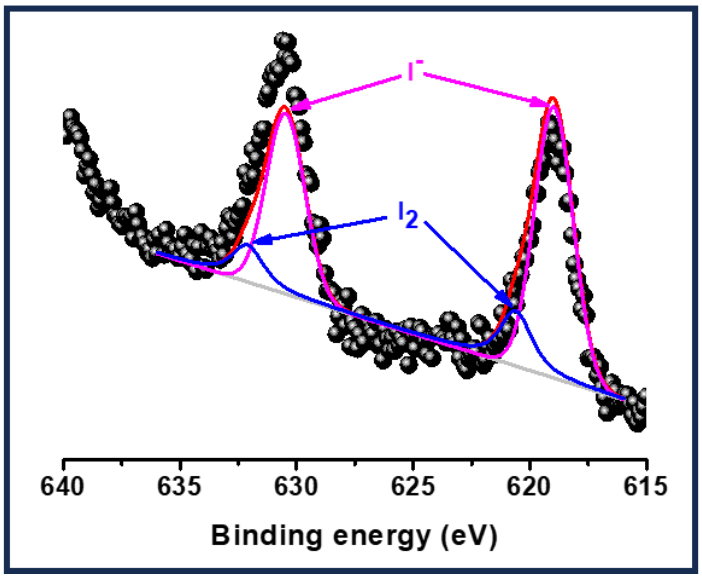

Figure 11. XPS spectra of I 3d after iodine doping in Cu-NDC thin film (I_2@Cu-NDC)

For I_2@Cu-NDC (**Figure 11**), the signal for I 3d demonstrates that the iodine molecules were successively infiltrated into the pores of Cu-NDC. The I 3d spectrum (it needs to be reproduced) is composed of I $3d_{3/2}$ and I $3d_{5/2}$. The peaks at 619.40 and 630.87 eV are indications of iodine anion (I^-), whereas peaks at 620.83 and 632.25 are attributed to the presence of molecular iodine (I_2). A combination of I^- and I_2 in the iodine doping MOFs gives rise to the I_3^- ions which effectively affirms redox reactions between I_2 molecules and Cu-NDC framework.

Conclusion

We demonstrated the successful fabrication of Cu-NDC thin film on an FTO-coated glass substrate for the first time by implementing the electrodeposition strategy. The as-synthesized thin film showed uniform coverage all over the substrate. Pristine thin film was then subjected to molecular doping using iodine as the guest molecule. For that, the electrodeposited Cu-NDC thin film was kept in iodine chamber (vapor phase of iodine) for 2 hours. Both the pristine and doped films were characterized by FESEM, EDXS elemental mapping, PXRD, X-ray photoelectron spectroscopy, UV-visible spectroscopy, and Raman spectroscopy. The electrical conductance quantification showed a two-fold times (~10^2 orders of magnitude) increase in the electrical conductance (in-plane and cross-plane) in the doped thin film than the pristine, as a consequence of partial-oxidation induced formation of I_3^- anion species in the pores of the framework. Thus, molecular iodine doping is a novel strategy for imparting electrical conductivity in MOF systems.

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