

# Growth Study of Ag/AgTCNQ Thin Film at Solid-Liquid Interface

A Thesis

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# Certificate

This is to certify that this dissertation entitled “**Growth Study of Ag/AgTCNQ Thin Film at Solid-Liquid Interface**” towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by **Aswani S L** at **Indian Institute of Science Education and Research, Pune** under the supervision of **Dr. Nirmalya Ballav, Department of Chemistry**, during the academic year 2019-2020.



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# Declaration

I hereby declare that the matter embodied in the report entitled “**Growth Study of Ag/AgTCNQ Thin Film at Solid-Liquid Interface**” is 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 Dr. Nirmalya Ballav and the same has not been submitted by me to any other University or Institution.




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**This thesis is dedicated to**

**Amma, Achan and**

**Nitheesh**

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## Abstract

Metal- tetracyanoquinodimethane (M-TCNQ) where M stands for Cu or Ag are an interesting class of semiconducting material due to their potential application in the field of opto-electronics, catalysis, sensing and many more. Thin films of M-TCNQ (M = Cu/Ag) shows bistable switching under the application of light, heat or electric field, however, to make CuTCNQ and AgTCNQ thin films through solution processable methods, Cu or Ag substrates, respectively, were required. For the first time, from our lab, demonstrated the fabrication of AgTCNQ thin film on functionalized Au substrate through sacrificing CuTCNQ thin film. Till now, in order to get AgTCNQ thin film with nanoparticles, authors have modified the thin film by adding nanoparticles externally after fabricating AgTCNQ thin film. It was challenging to fabricate Ag/AgTCNQ thin film directly onto Au substrate without any sacrificial template through simple solution processable method. Herein, for the first time we have demonstrated the successful fabrication of high-quality Ag/AgTCNQ thin film directly on Au substrate by employing Layer-by-Layer (LbL) technique. The as-synthesized thin film showed thermally driven resistive switching as well as the ability to catalyze single electron transfer reaction.

## Introduction

Thin films are defined as 5nm to 1 $\mu$ m thick layer of materials that are deposited densely on a substrate in a well ordered manner.<sup>1</sup> Due to their reduced size and high surface area to volume ratio, properties of thin films differ distinctly from that of their respective bulk counterparts.<sup>2, 3</sup> Thin films can be used as decorative, protective, optical coatings and their applications further extends in the field of catalysis, fuel cells, data storage devices, sensors, solar cells, batteries, transistor, nanotechnology and in microelectronics.<sup>4, 5</sup> Apart from these, one of the major advantages of thin films is their several tunable defects by modulating the growth process, in turn leading to the tunable physicochemical response.<sup>6-9</sup>

Coordination Polymers configured into thin films, constitute a rapidly enlarging area in material chemistry due to their potential applications in the area of photochemistry, electrochemistry, catalysis, super hydrophobic surfaces and many more.<sup>10</sup> 7,7',8,8'-

tetracyanoquinodimethane (TCNQ) is a well-known redox-active organic linker exhibiting multiple oxidation states ( $\text{TCNQ}^0$ ,  $\text{TCNQ}^-$ ,  $\text{TCNQ}^{2-}$ ) and it can ligate with numerous transition metal ions, generating an interesting class of M-TCNQs.<sup>11-14</sup> Also, M-TCNQ such as Cu-TCNQ can exist in two structurally distinct phases namely, phase-I and phase-II exhibiting distinct electrical and magnetic response.<sup>15</sup> Further, M-TCNQs (M = Cu/Ag) are 2D semiconductors possessing resistive switching and field emission properties.<sup>16-19</sup> Electrical switching property of AgTCNQ as a function of electric field was first discovered by Potember et al, followed by various reports stating the reason of this electrical response to be the transition from one structural phase to another until recently where the switching has been explained as an interfacial phenomenon.<sup>20, 21</sup> Earlier, only light or electric field induced switching abilities of AgTCNQ thin films were observed and recently temperature induced resistive switching was also demonstrated in our lab.<sup>22</sup> So far in literature, AgTCNQ thin films are prepared through techniques such as vacuum deposition, thermal co-deposition of Ag and TCNQ on suitable substrates, electrocrystallization, photocrystallization, or directly onto Ag substrate or onto functionalized Au substrate via templating CuTCNQ as a sacrificial layer.<sup>22-24</sup> Various physical parameters such as morphology and thickness of AgTCNQ thin film depends on the experimental conditions and could be modulated to achieve different morphologies ranging from nano-micro wires, needle shaped crystals to dendrites.<sup>25</sup> M-TCNQ (M = Cu/Ag) thin films being 2D semiconductors became an interesting class of materials due to their application in several electronic appliances.<sup>26</sup> Their abilities are not only explored in electronics but also in biomedical field where AgTCNQ nanowires were found to be active in antimicrobial actions against gram positive and gram negative bacteria.<sup>27</sup> Further, AgTCNQ thin films and bulk samples were investigated over the past few years for various applications such as photo-oxidation of water to oxygen, for reduction of carcinogenic  $\text{Cr}^{\text{VI}}$  etc.<sup>25, 28</sup>

AgTCNQ thin film, embedded with Ag nanoparticles, grown directly onto a non-silver substrate has not observed till now to the best of our knowledge. Also, AgTCNQ thin films grown through solution processable methods by dipping silver substrates into TCNQ solution are mostly not ordered due to the interpenetration of TCNQ network over layers.<sup>29</sup>

Herein, we describe the first time fabrication of Ag/AgTCNQ thin films directly grown on a non silver substrate using Layer-by-Layer approach.

## **Materials and Methods**

### ***Chemicals Required***

Copper(II) acetate [Cu(OAc)<sub>2</sub>·H<sub>2</sub>O], Silver(I) Nitrate (AgNO<sub>3</sub>), Silver(I) acetate [AgCH<sub>3</sub>COO], Silver(I) tetrafluoroborate (AgBF<sub>4</sub>), 7,7',8,8'-tetracyanoquinodimethane (TCNQ), Au (100nm) coated silicon wafer, 11-Mercaptoundecanoic acid (MUDA), Hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>), Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) were purchased from Sigma-Aldrich. Ethanol was used as solvent. All chemicals were used as such without any further purification.

### ***Substrate Cleaning***

Au wafer was sonicated for 1 min each in a series of solvents distilled water, acetone, methanol, isopropanol and then dipped in piranha solution [H<sub>2</sub>SO<sub>4</sub> (98%)/H<sub>2</sub>O<sub>2</sub> (30%)-v/v 3:1] for 30 min followed by washing with distilled water and then dried with N<sub>2</sub> gas.

### ***Preparation of Self-Assembled Monolayer (SAM)***

Au coated silicon wafer was functionalized by dipping it into 1mM MUDA solution (ethanol: acetic acid ~ 9:1) for ~48 h. Carboxy functionalized (-COOH) Au substrate was then washed with ethanol and dried with N<sub>2</sub> gas.

### ***Fabrication of Ag/AgTCNQ Thin Film***

All Thin films were fabricated using Layer-by-Layer (LbL) method. Direct growth of Ag/AgTCNQ thin film on non silver substrate through solution processable method is achieved by two methods.

#### **a) Using bimetallic source for LbL growth:**

Carboxy terminated Au substrate was first dipped into a mixture of Cu(OAc)<sub>2</sub> and AgNO<sub>3</sub>

ethanolic solution as metal source for 10 min indicating 0.5 cycle of LbL growth followed by washing with methanol and drying with N<sub>2</sub> gas and then transferred to 1mM TCNQ ethanolic solution as ligand for 10 min to complete 1 cycle. This procedure was continued till 50 cycles at room temperature. To establish the stoichiometric concentration needed to grow film, we performed experiments with 1:1, 1:2, 2:1, 0:1, 1:0 equimolar concentrations of Cu(OAc)<sub>2</sub>:AgNO<sub>3</sub>.

#### **b) Using Ag(I)OAc as metal source for LbL growth**

Carboxy terminated Au substrate was dipped into 1mM Ag(I)OAc ethanolic solution for 10 min, washed with ethanol then dried with N<sub>2</sub> gas and then transferred to 1mM ethanolic TCNQ solution to complete 1 cycle of Layer-by-Layer growth. This was continued till 50 cycles at room temperature.

#### **Synthesis of bulk Ag/AgTCNQ**

Simple solution precipitation method was used for bulk sample preparation. Ag/AgTCNQ bulk was prepared by just mixing 1mM 10 ml AgNO<sub>3</sub> ethanolic solution with 1mM 10 ml TCNQ ethanolic solution. Precipitate formed was filtered after 24h, washed with methanol and dried to obtain Ag/AgTCNQ bulk. It was also synthesized through an alternative way by mixing Cu(OAc)<sub>2</sub> and AgNO<sub>3</sub> ethanolic solution (final volume 10 ml) with 1 mM 10 ml TCNQ ethanolic solution. Precipitates obtained were collected after 24h, washed with methanol and dried. Metal salts were varied in 1:1, 1:2 and 2:1 equimolar concentration and in all three cases Ag/AgTCNQ was obtained as final product.

#### ***Ag/AgTCNQ Thin film as a catalyst***

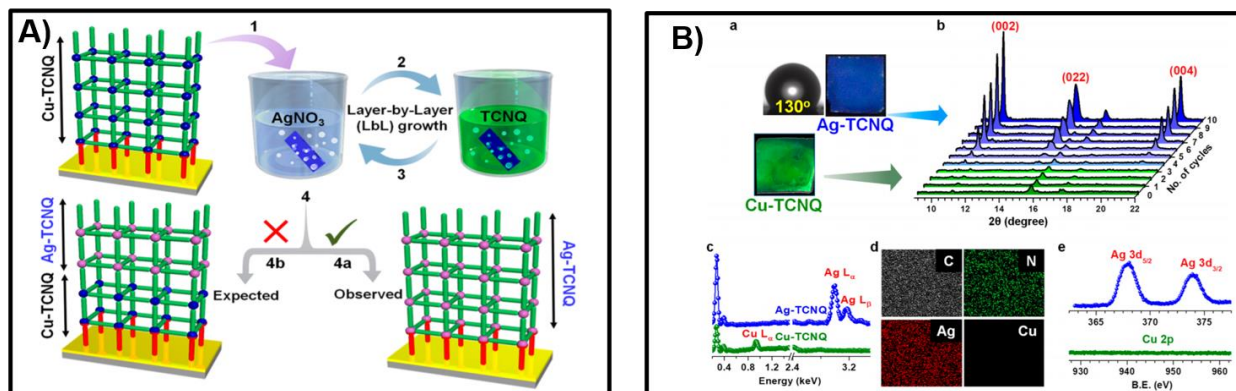
As fabricated Ag/AgTCNQ thin film is immersed in 10ml aqueous solution of 1mM ferricyanide containing 0.1M thiosulphate as reducing agent. Time dependent absorption spectroscopic studies were carried out for 1h in 3ml similar concentrated solutions. The catalytic activity of the Ag/AgTCNQ thin film is probed through the decrease in the intensity in absorption spectra of ferricyanide and it's activity is compared with that of CuTCNQ thin film grown through the same procedure.

## Characterization

Structure and crystallinity of thin films and bulk samples were probed using Out-of- plane X-Ray Diffraction technique from a Bruker D8 advance diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The uniformity and elemental compositions of Ag/AgTCNQ thin films were analyzed with Zeiss Ultra Plus Field Emission Scanning Electron Microscopy (FESEM) with Energy Dispersive X-Ray Spectroscopy (EDXS) attachment. Further high-resolution imaging was done using High Resolution Transmission Electron Microscopy (HRTEM) connected with Selected Area Electron Diffraction (SAED) technique in UHR FEG-TEM, JEOL JEM 2100F Field emission transmission electron microscope. Contact angle measurements were taken in Holmarc's Contact Angle meter. Raman spectra ( $\lambda_{\text{exc}} = 632 \text{ nm}$ ) were recorded under Raman microscope (LabRAM HR, HorbiaJobinYvon) with a 50X objective lens. Solid state/liquid state UV-vis absorption spectra were recorded on Shimadzu UV- 3600 UV VIS-NIR spectrophotometer. Electrical measurements ( $I$ - $V$ ) on various thin film samples were carried out by Keithley 4200 SCS Parameter Analyzer system attached to Everbeing probe station (equipped with thermal chuck) with EGaIn as a top electrode. pH measurements were carried out by H1 9 1 24 H1 9 1 25 Portable Waterproof pH meters from HANNA instruments.

## Results and Discussion

Earlier, AgTCNQ thin film was grown using Ag as the template through solution processable methods.<sup>23, 24</sup> Recently our group reported, for the first time, fabrication of AgTCNQ thin film on a non silver substrate by using CuTCNQ thin film as a sacrificial template, on SAM/Au template at  $60 \text{ }^\circ\text{C}$ . The aim of the authors was to use CuTCNQ as a template so as to generate an electronic heterostructure of CuTCNQ/AgTCNQ thin film, rather they observed sacrificial growth of AgTCNQ thin film (Fig 1).<sup>23</sup> This work inspired us to think whether CuTCNQ thin film, as a whole, is required for AgTCNQ thin film formation or any form of Cu can serve this purpose. So, our aim was to directly grow Ag/AgTCNQ thin film on non silver substrate.

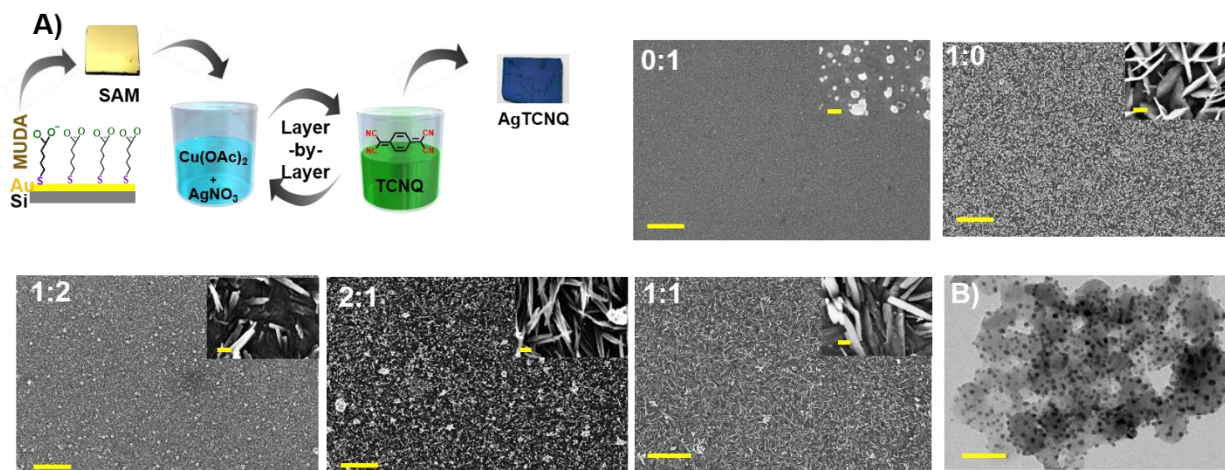


**Fig 1.** Sacrificial growth of AgTCNQ thin film. A) Schematic diagram of sacrificial LbL growth, dipping CuTCNQ thin film into  $\text{AgNO}_3$  (1), into TCNQ (2), again into  $\text{AgNO}_3$  (3), observed AgTCNQ thin film (4a), expected hybrid thin film (4b). B) Optical images of CuTCNQ thin film (green), optical image of AgTCNQ thin film (blue) and its water contact angle image (a), Out-of-plane XRD showing CuTCNQ to AgTCNQ transformation (b), EDXS spectra recorded on thin films obtained in step I (CuTCNQ) and step II (AgTCNQ) (c), Elemental mapping on the AgTCNQ thin film obtained in step II (d), Ag 3d and Cu 2p XPS data recorded on AgTCNQ film obtained in step II (e). (Adapted with permission from *J. Phys. Chem. Lett.* **2017**, 8, 20, 5008 © 2017 American Chemical Society)

We have chosen simple and cost-effective solution processable layer-by-layer (LbL) technique to grow Ag/AgTCNQ thin film through chemical reactions at solid-liquid interface. Highly ordered and controlled growth of thin films can be achieved through LbL approach where functionalized Au was used as substrate to grow Ag/AgTCNQ thin films. SAM formation on gold was checked through water contact angle (CA) measurements. Pristine gold has CA  $\sim 65^\circ$  and after SAM formation on Au CA reduces to  $\sim 27^\circ$ . For LbL growth, we have dipped SAM/Au in a mixture of  $\text{Cu}(\text{OAc})_2$  and  $\text{AgNO}_3$  ethanolic bimetallic solution for 10 min and it is washed with ethanol, dried with  $\text{N}_2$  gas and then transferred to 1mM TCNQ ethanolic solution for 10 min to complete one cycle (Fig 2. A). This process is repeated for 50 cycles at ambient conditions.

To establish the stoichiometric concentration needed to grow film, we performed experiments with 1:1, 1:2, 2:1 equimolar concentrations of  $\text{Cu}(\text{OAc})_2:\text{AgNO}_3$  at similar conditions. In all the three cases, blue coloured thin film which is the characteristic feature

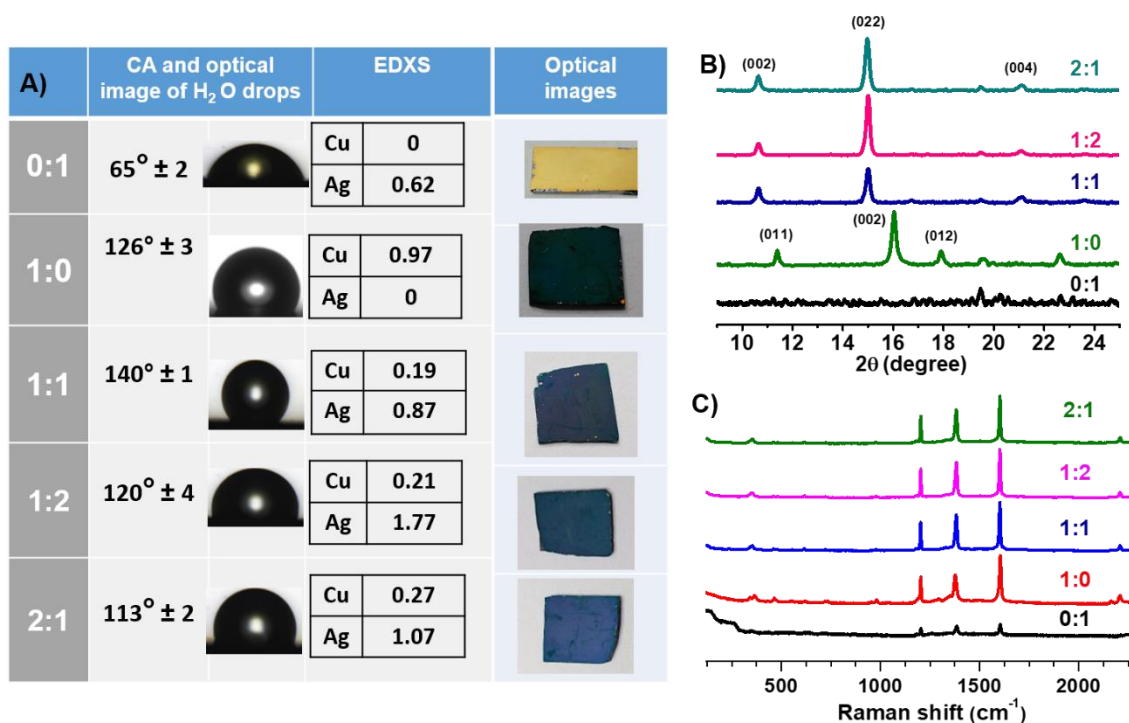
of Ag/AgTCNQ was observed (Fig 3A). As a control, LbL growth with 1:0 and 0:1 (Cu:Ag) was also carried out. Green coloured thin film which is the characteristics of CuTCNQ is



**Fig 2.** A) Schematic diagram of LbL approach using bimetallic solution for the growth of Ag/AgTCNQ thin film directly on SAM/Au. 0:1, 1:0, 1:2, 2:1 and 1:1 are FESEM images of the respective Cu:Ag thin films, scale bar is 10  $\mu\text{m}$  (inset: zoomed in FESEM images of respective thin films, scale bar is 200 nm). B) HRTEM image of 1:1 Cu:Ag thin film showing the presence of Ag nanoparticles. [scale bar is 100 nm].

observed for 1:0 (Cu:Ag) and no thin film formation observed for 0:1 (Cu:Ag) (Fig 3A, optical images of thin films obtained), in line with the previous reports of no Ag/AgTCNQ thin film formation on SAM/Au with  $\text{AgNO}_3$  as the metal salt. Ag/AgTCNQ film formation and its crystalline nature in 1:1, 1:2, 2:1 Cu:Ag cases was confirmed with out-of-plane XRD measurement. Prominent diffraction peaks at  $2\theta$  values of  $\sim 10.4^\circ$ ,  $\sim 14.5^\circ$  and  $\sim 21.5^\circ$  observed are characteristic of AgTCNQ corresponding to (002), (022), (004) planes of phase-I structure respectively (Fig 3B).<sup>22, 30</sup> Again in 1:0 (Cu:Ag) case, CuTCNQ film formation was confirmed from out-of-plane XRD data. CuTCNQ has prominent diffraction peaks at  $\sim 11^\circ$ ,  $\sim 15.6^\circ$  and  $\sim 17.6^\circ$  corresponding to (011), (002) and (012) (hkl) planes of phase I structure respectively and it is well matched with the reported values (Fig 3B).<sup>31</sup> CA of water measurements on the thin films revealed highly hydrophobic nature of 1:0, 1:1, 2:1, 1:2 Cu:Ag thin films (Fig 3A). FESEM images showed dense and uniform thin film formation for all Cu:Ag cases except for 0:1 (Fig 2. 0:1, 1:0. 1:2, 1:1, 2:1) and exclusive growth of Ag/AgTCNQ in 1:1, 1:2 and 2:1 Cu:Ag was also confirmed from EDXS

analysis (Fig 3A). Interestingly, only a minimum concentration of 1:10 Cu:Ag is required for Ag/AgTCNQ thin film formation, indicating the role of Cu(II) acetate as a catalyst. Thus, through our as described fabrication method we not only reduced the effort needed in making CuTCNQ thin film as a sacrificial template but also achieved the direct growth of Ag/AgTCNQ thin films on SAM/Au substrate at room temperature, for the first time. Further, HRTEM images unveiled that our AgTCNQ thin films grown in all three cases [1:1, 1:2, 2:1 (Cu:Ag)] is embedded with Ag nanoparticles (Fig 2B). Protic solvent, ethanol is used for the thin film fabrication since there was no film formation observed with acetonitrile, an aprotic solvent.



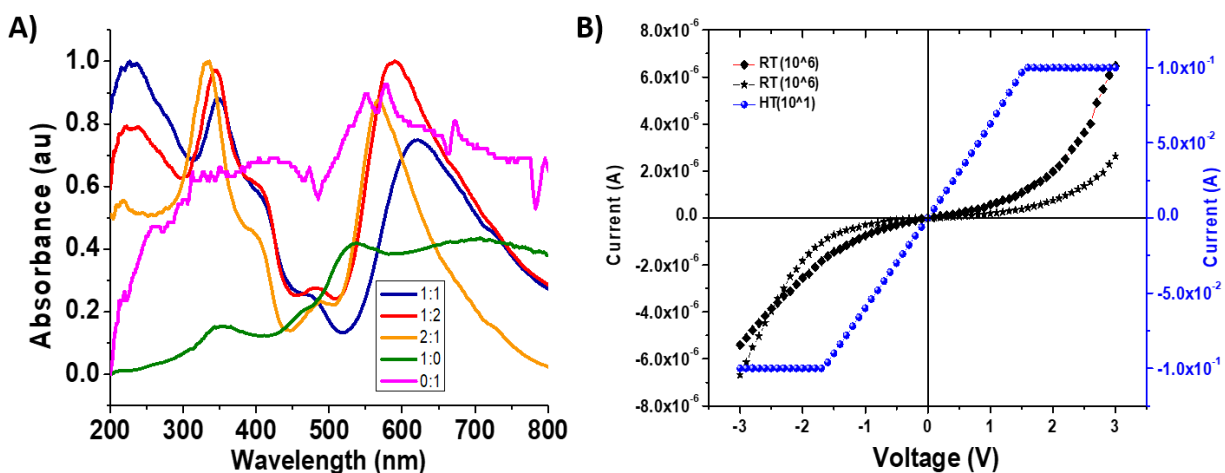
**Fig 3.** A) Contact angle, optical images of water drops, EDXS analysis and optical images of Cu:Ag thin films (if formed/Au substrate). B) Out-of-plane XRD of Cu:Ag thin films showing AgTCNQ formation in 1:1, 1:2, 2:1 Cu:Ag, CuTCNQ formation in 1:0 Cu:Ag and no film formation in 0:1 Cu:Ag. C) Raman spectra of Cu:Ag thin films.

To the best of our knowledge, this is the first time demonstration of direct fabrication of Ag/AgTCNQ thin film onto a non silver substrate through solution processable method at ambient conditions, also, the LbL growth technique employed here yielded Ag/AgTCNQ thin film embedded inherently with Ag nanoparticles – a rare system of metal



nanoparticles inherently embedded into a semiconducting matrix. we were the first to directly grow Ag/AgTCNQ thin film on non silver substrate through solution processable method at ambient conditions and the LbL growth technique employed here could fabricate AgTCNQ thin film system exhibiting metal nanoparticles inherently embedded into a semiconducting matrix.

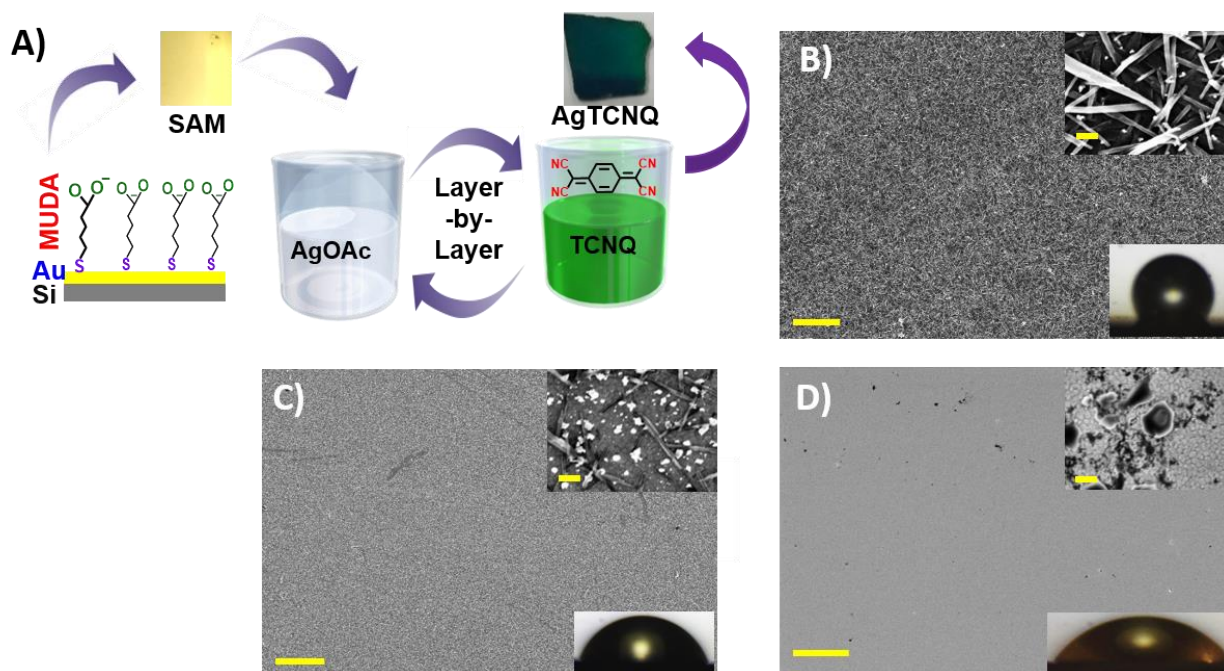
Bonding Scenario in all thin films was studied using Raman Spectroscopy. Vibrational peaks at  $\sim 2206$ ,  $\sim 1374$ ,  $\sim 1603$  and  $\sim 1204$   $\text{cm}^{-1}$  confirmed the formation of thin films with TCNQ in the radical anion state and those corresponds to CN stretching, C-CN stretching, C=C ring stretching and C=C-H bending modes respectively (Fig 3C).<sup>32</sup> To study the absorption feature of thin films, Solid state UV spectroscopic measurements were carried out. UV-Vis absorption bands of thin films 1:1, 1:2, 2:1 Cu:Ag also matched with that of pure Ag/Ag-TCNQ. Ag/Ag-TCNQ have peaks at  $\sim 374$  and  $\sim 630$  nm in UV-Vis spectrum. Peak at  $\sim 630$  nm is due to TCNQ radical anions of Ag-TCNQ, confirming the absence of neutral and unreacted TCNQ (Fig 4A).<sup>33</sup> I-V measurements on 1:1 (Cu:Ag) AgTCNQ thin film showed resistive switching properties with an increase in electrical conductance value by the order of  $10^5$  as a function of temperature (Fig 4B).



**Fig 4.** A) Solid State UV-Vis spectra of Cu:Ag thin films. B) I-V graph of 1:1 Cu:Ag thin film.

The incapability of Ag/AgTCNQ film formation with only  $\text{AgNO}_3$  metal salt was well studied in our group, even with varied end groups of functionalized Au from  $-\text{COOH}$  to  $-\text{OH}/-\text{SH}$  or  $-\text{NH}_2$ .<sup>22</sup> So here, we have studied the possibility of forming Ag/AgTCNQ thin film

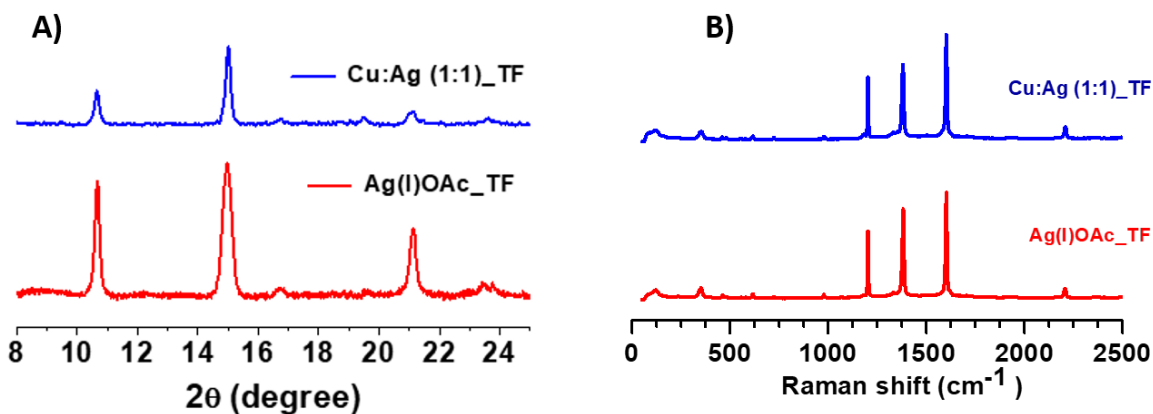
directly on MUDA SAM/Au substrate by varying different silver(I) salts. We have tried fabricating Ag/AgTCNQ thin films with Ag(I)OAc, Ag(I)BF<sub>4</sub> and Ag(I)Cl salts in the same environmental conditions (Fig 5B, C, D respectively). Surprisingly, direct growth of dense and uniform Ag/AgTCNQ thin film on carboxy terminated Au substrate was observed only when Ag(I)OAc is used as metal salt through LbL approach (Fig 5A and B).



**Fig 5.** A) Schematic diagram of LbL approach using monometallic solution. B), C) and D) FESEM images of thin film grown using Ag(I)OAc (dense and uniform film), Ag(I)BF<sub>4</sub> (no film/low quality film), Ag(I)Cl (no film), respectively [scale bar is 10 μm] (inset: zoomed in FESEM images for respective metal salts (top right) [scale bar is 200 nm], optical image of water drops on respective film/substrates (bottom right)). Water contact angle for the Ag/AgTCNQ thin film grown with Ag(I)OAc salt is  $\sim 126^\circ$ .

FESEM revealed the formation of dense and uniform thin film embedded with Ag nanoparticles with Ag(I)OAc (Fig 5B). The presence of nanoparticles was further confirmed from HRTEM imaging. Well diffracted out of plane XRD peaks at  $2\theta$  values of  $\sim 10.4^\circ$ ,  $\sim 14.5^\circ$  and  $\sim 21.5^\circ$  again confirmed the growth of Ag/AgTCNQ thin film with Ag(I)OAc metal salt (Fig 6A). Directly grown Ag/AgTCNQ thin film with Ag(I)OAc salt shows similar Raman vibrational bands as that of 1:1 (Cu:Ag) Ag/AgTCNQ, grown with bimetallic precursor metal solution and both matched well with previous reports (Fig 6B).<sup>32</sup>

Also, the absorption spectra features and the resistive switching properties remains same for the directly grown thin film with acetate salt.



**Fig 6.** A) Comparison of out-of-plane XRD patterns of Ag/AgTCNQ thin films grown through bimetallic Cu:Ag 1:1 approach and through using monometallic Ag(I)OAc salt. B) Comparison of Raman Spectra of Ag/AgTCNQ thin films grown through bimetallic Cu:Ag 1:1 approach and through using monometallic Ag(I)OAc salt.

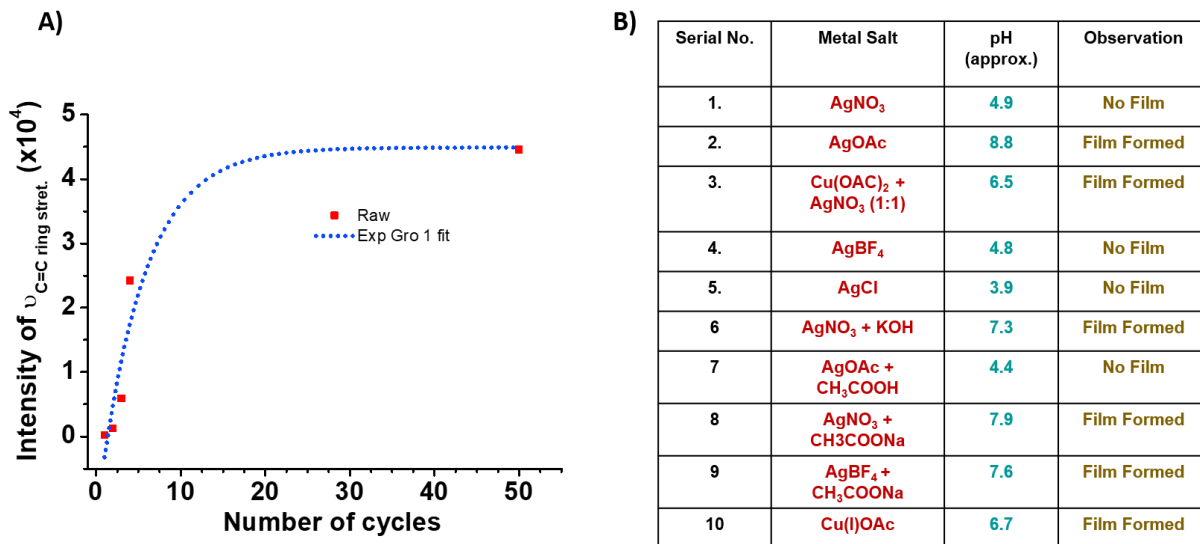
### ***Growth Mechanism for Ag/AgTCNQ thin film***

Growth of Ag/AgTCNQ thin film grown using Ag(I)OAc salt is studied using Raman spectroscopic technique. Spectroscopic measurements were done after each cycle of Layer-by-Layer growth, starting from 0.5 cycle. Increment in the intensity of vibrational peak at  $\sim 1603 \text{ cm}^{-1}$  (corresponding to C=C stretching of Ag/AgTCNQ) is plotted as a function of number of cycles. A rapid increase in the intensity of vibrational bands of Ag/AgTCNQ thin film was observed for initial cycles, followed by a slow increase and then saturation to a maximum value (Fig 7A). Intensity versus number of cycles plot shown below is fitted with exponential growth function, indicating first order growth kinetics

### ***Role of pH in the growth of thin films on MUDA SAM/Au***

Ag/AgTCNQ thin film was not forming directly on MUDA functionalized Au substrate when various counter ions of silver such as Ag(I)NO<sub>3</sub>, Ag(I)BF<sub>4</sub> and Ag(I)Cl are used as metal

source for LbL growth at ambient conditions up to 50 cycles. But remarkable thin film formation was observed when Ag(I)OAc is used as the only metal source. One of the possible reasons could be the counter ion, acetate, acting as a modulator for the growth of thin films. In order to further investigate that, some control experiments using LbL approach at similar conditions were performed; 1) growth of CuTCNQ using Cu(I)acetate as metal source and TCNQ as ligand, since it was reported that CuTCNQ thin film does not form with Cu(I) metal salt, 2) growth of M-TCNQ thin films using cobalt, nickel and manganese (M(II)) acetates as metal salt 3) incorporating acetate by adding sodium acetate/acetic acid to Ag(I)NO<sub>3</sub> and Ag(I)BF<sub>4</sub> metal salts to grow Ag/AgTCNQ thin film. Surprisingly, we observed dense and uniform CuTCNQ thin film with Cu(I)acetate metal salt and it was characterized with FESEM, XRD techniques. Thin film formation was also observed when sodium acetate is added in the Ag(I)NO<sub>3</sub> and Ag(I)BF<sub>4</sub> metal solutions, however interestingly, no thin film formation was observed for Co(II), Ni(II) and Mn(II) acetates and also for Ag(I)NO<sub>3</sub> and Ag(I)BF<sub>4</sub> even after adding concentrated acetic acid in both. Thus, the possibility of acetate as a modulator was ruled out. These observations directed us to check the pH of all the metal ion solutions that we used for LbL approach and the result is summarized in the table (Fig 7B). Also, there are reports on the effect of pH on the dimensionality or growth of coordination polymers.<sup>34, 35</sup> We found that only the metal solutions having pH  $\geq$  6.3 supports the formation of Ag/AgTCNQ thin films and in order to prove this hypothesis, the following experiments were done using LbL growth technique at similar conditions; (i) added acetic acid to Ag(I)OAc (Ag(I)OAc alone produces Ag/AgTCNQ thin film) and, (ii) added potassium hydroxide to Ag(I)NO<sub>3</sub> (Ag(I)NO<sub>3</sub> alone does not produce Ag/AgTCNQ thin film) to decrease and increase the pH respectively, and tried fabrication of thin films with these metal sources. In the first case, no thin film fabrication was observed (mixture of Ag(I)OAc and acetic acid), however successful thin film fabrication was observed in the second case (mixture of Ag(I)NO<sub>3</sub> and potassium hydroxide), emphasizing the crucial role of pH in Ag/AgTCNQ thin film formation where a pH  $\geq$  6.3 is essential (refer table in figure 7).



**Fig 7.** A) Plot of intensity (from Raman spectra) versus number of cycles of LbL growth. B) Table of pH measurements and observation for various metal solutions (in ethanol).

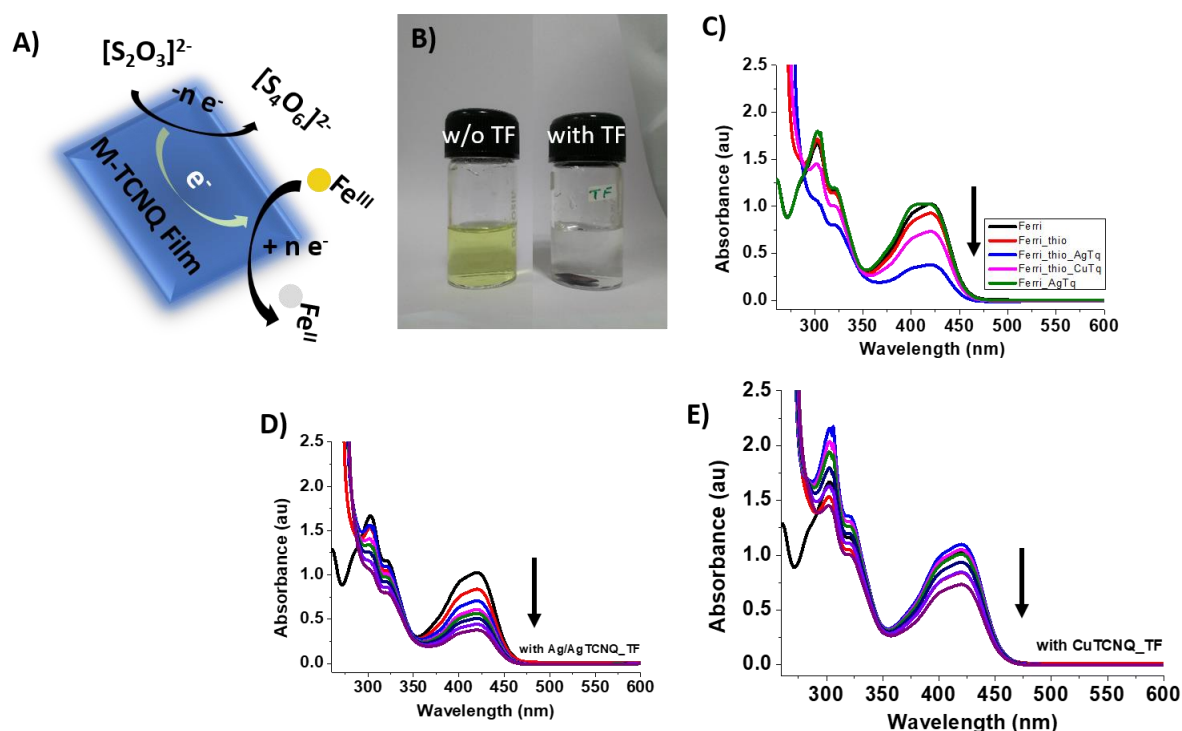
### *Ag/AgTCNQ thin film as a catalyst*

There has been several reports of M-TCNQ (M = Cu/Ag) acting as a catalyst and M-TCNQ modified with externally added nanoparticles for catalysis and nano particles or quantum dots as photocatalysts.<sup>36-39</sup> Since our Ag/AgTCNQ thin films have metal nanoparticles embedded in a semiconducting matrix, we investigated its catalytic property in the electron transfer reaction between thiosulphate ions and ferricyanide in aqueous solution and it was compared with that of CuTCNQ thin film grown under similar conditions. The reaction of interest can be written as



where ferricyanide reduction could be examined by monitoring the decrease in its characteristic peak at  $\sim 420$  nm using UV-Vis spectroscopy. Here, the rate of reduction of 1mM potassium ferricyanide by 0.1M thiosulphate ion is studied. There was no ferricyanide to ferrocyanide conversion when ferricyanide and thiosulphate was taken in equimolar concentration, so, an excess of thiosulphate ion was taken.

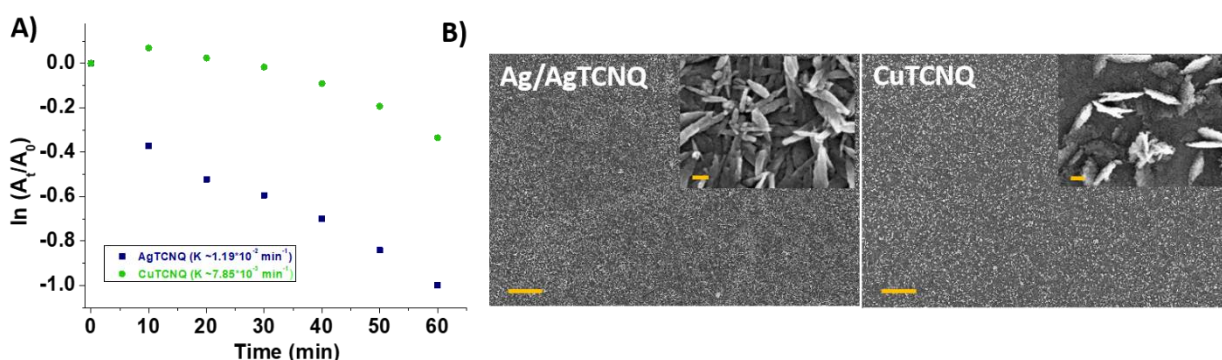
Ag/AgTCNQ thin film was dipped into aqueous solution of 1 mM ferricyanide containing 0.1 M thiosulphate. After ~10 min of exposing the film into the solution, the colour of the solution changed from light yellow to colourless, an indication of successful catalysis (Fig 8B). The reaction was carried out for 1h and UV-Vis spectra was recorded at regular intervals of 10 min. The same experiment was repeated with CuTCNQ thin film. We noticed subtle decrease in the ferricyanide absorption peak at ~420 nm, accompanied by increase in absorption of ferrocyanide at ~240 nm through an isosbestic point at ~285 nm which concludes the formation of ferrocyanide (Fig 8 C, D and E).



**Fig 8.** A) Schematic diagram of M-TCNQ thin films catalyzing electron transfer reactions at Solid-Liquid Interface. B) Optical image of mixture of ferricyanide and thiosulphate solution without (yellow colour) and with Ag/AgTCNQ thin film (colourless) respectively [images are taken after ~10 min of reaction]. C) UV-Vis spectra of ferricyanide solution upon reaction with only thiosulphate (red), with only Ag/AgTCNQ thin film (green), with both thiosulphate and Ag/AgTCNQ thin film (blue), with both thiosulphate and CuTCNQ thin film (pink). [All spectra were recorded after 1h of reaction, at room temperature]. D) Time dependent UV-Vis spectroscopy of reduction of ferricyanide solution with

Ag/AgTCNQ thin film. E) Time dependent UV-Vis spectroscopy of reduction of ferricyanide solution with CuTCNQ thin film

The kinetics of the reaction is calculated from the slope of the plot  $\ln(A_t/A_0)$  vs time, where  $A_t$  is the absorbance peak intensity at time  $t$  and  $A_0$  is its intensity at time zero (Fig 9A). Notably, Ag/AgTCNQ thin film catalyzed the electron transfer reaction more efficiently at the rate of  $\sim 1.12 \times 10^{-2} \text{ min}^{-1}$  as compared to CuTCNQ thin film at the rate of  $\sim 7.85 \times 10^{-3} \text{ min}^{-1}$ . The reason for such enhanced rate could be attributed to the solid-liquid interfacial phenomena, where at the interface, electrons from thiosulphate ions are injected to the surface of thin films and it is transferred to ferricyanide ions and thereby increasing the reaction kinetics (Fig 8A). Now the question might arise 'Can't Ag/AgTCNQ thin film itself reduce ferricyanide?'. To verify this, we have immersed our Ag/AgTCNQ thin film in the ferricyanide solution without thiosulphate ions, no changes were observed for the absorption features of ferricyanide solution even after 1h of exposure, thus ruling out the possibility of ferricyanide reduction by thin film (Fig 8C, green spectrum). Altogether, our thin film acts as a catalyst in the electron transfer reaction and the thin films were stable even after exposing them in the solution for 1h. FESEM images of both thin films taken after catalysis showed that the morphology was intact and they can be reused efficiently (Fig 9B).



**Fig 9.** A) Plot of  $[\ln(A_t/A_0)]$  versus time from which the rate constants for the reaction could be determined. B) FESEM images of thin films taken after 1h of catalysis [scale bar is 10  $\mu\text{m}$ ] (inset: zoomed in FESEM images of thin films [scale bar is 200 nm]).

## Conclusion

In conclusion, we were successful in fabricating Ag/AgTCNQ thin film directly onto non silver substrate, functionalized Au, at ambient conditions through two ways using LbL approach; 1) by taking bimetallic system as the precursor, 2) with monometallic silver acetate salt. Both the thin films were embedded with silver nanoparticles, thus through LbL approach we fabricated Ag/AgTCNQ thin film in which metal nanoparticles are intrinsically embedded into the semiconducting matrix. There has been reports of fabricating M-TCNQ films in which metal nanoparticles are extrinsically added to tune optical and chemical properties to improve catalysis. In that approach, our Ag/AgTCNQ thin films are promising candidates for various applications such as enhanced catalysis, optical components and electronic devices. Ag/AgTCNQ thin film fabricated here, follows first order growth kinetics and pH plays a crucial role in it's growth. Also, the catalytic property of Ag/AgTCNQ thin film is explored towards one electron transfer reaction with ferricyanide to ferrocyanide reduction and the performance was observed to be better than CuTCNQ thin film.



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## Thermally Driven Resistive Switching in Solution-Processable Thin Films of Coordination Polymers

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