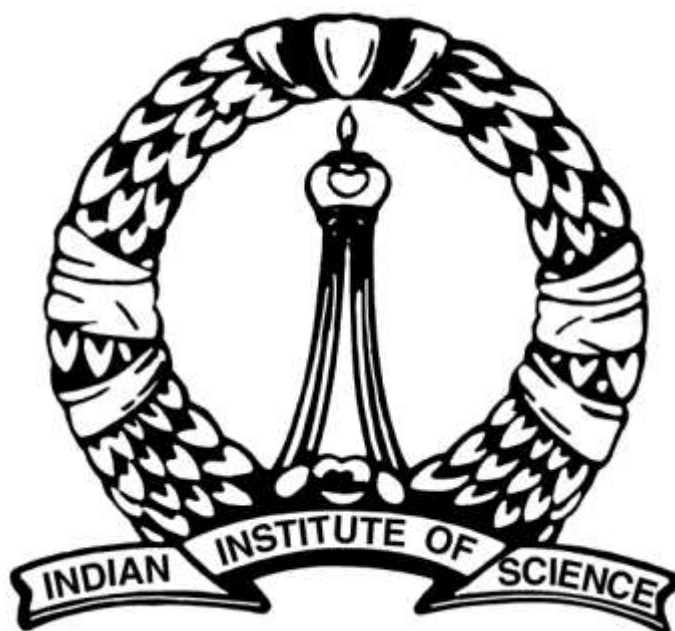


OUTREACH PROGRAM 2016
Dept. of Chemical Engineering
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A PROJECT REPORT ON
**SYNTHESIS OF SILVER NANOPARTICLES ON
APPROPRIATE SUPPORT FOR USE AS CATALYST**



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I. Introduction:

Over the years, the use of nanoparticles of silver, gold, palladium and platinum have been widely explored¹. Scientists have studied the catalytic properties of nanoparticles of different morphologies as there is significant influence of particle size and availability of active sites on catalysis²⁻⁶. The use of Ag nanoparticles (AgNPs) is of significant interest mainly due to the reduced cost of Ag compared to other noble metals such as Pt or Pd. Moreover, LSPR phenomenon in Ag makes it absorb intensely in the visible region⁷. This makes AgNPs an attractive option for catalysis especially under photo-illumination.

The dependence of the optical properties of silver on the size of the nanoparticles has been extensively studied. Hence AgNPs are also being looked at as substrates for biosensing and chemical sensing. AgNPs have also been used in fields other than catalysis. They have been found to be potentially good substrates for SERS⁹. SERS is used to detect trace levels of chemical and biological species thereby finding use in homeland security, biological sciences and in environmental remediation¹¹.

Despite the merits of using metals NPs as catalysts, their extension to industrial scales has been limited due to difficulties in regeneration⁸. To overcome this AgNPs have been immobilized on suitable supports such as oxides of metals and polymers^{9, 10}. Such innovations ensure ease of regeneration and are more economic.

In this report, we have investigated the use of cotton fabrics as support for silver nanoparticles for heterogeneous catalysis. Cotton fabrics are used on a daily basis and possess the advantage of being robust, flexible and economically viable¹². In addition these fabrics are also hydrophilic and are already in large scale production making them available readily.

Another aspect of this report is the investigation of photographic development of silver for deposition on the supporting fabric. One of the most unique properties of silver salts, especially halides is their heightened photosensitivity¹⁴. This property had been the basis of the silver photography industry. Despite the fact that the silver photography technique is outdated, the photochemistry of silver retains its scientific significance.

Catalytic properties of the Ag nanoparticles were measured using the reduction of potassium ferricyanide by sodium thiosulphate. To characterize the kinetics, we have studied the UV-Vis absorption spectra of ferricyanide.

II. Literature Survey:

Silver catalysis is of major significance industrially and commercially. According to <http://www.silverinstitute.org/site/silver-in-industry/catalysts/>, more than 150 million ounces of silver are used annually in catalyzing processes that produce ethylene oxide and formaldehyde. About 90% of the silver employed as an industrial catalyst is used for the production of ethylene oxide from ethylene. Ethylene oxide finds use in manufacturing many polymers, most of which we use of a daily basis. It is an ingredient in the manufacture of in molded items like insulating handles for stoves, key tops for computers, electrical control knobs, domestic appliance components, and electrical connector housings. It is also used in the manufacture of polyester which is used to make clothes. Interestingly, about 25% of the ethylene oxide production is used to produce antifreeze coolant for automobiles²⁴.

Thus it is natural that there is significant interest in the study of silver nanoparticles as catalysts. Silver nanoparticles, nanowires, dendrites etc. are all attracting keen interest due to their unique morphologies and physiochemical properties. In this section, we shall briefly survey some of the work done in the field.

Shaopeng Zhu et al have investigated nanoparticles with hierarchical nanostructures namely nanorods, nanosheets and nanobelts¹⁸. This group have used an indirect replacement reaction to synthesize 3D microstructures called hierarchical silver microparticles (HSMP) of silver composed of 2D nanostructures. The deposition of silver is done electrochemically on a Pt-Si substrate. An interesting feature of this study is the role of PVP in the nucleation and growth of Ag nanoparticles. It is seen that PVP causes the nucleation of the nanoparticles in a specific crystallographic direction and thus gives highly specific morphologies of HSMP. These were then used to catalyze the reduction of Rhodamine B (RhB) by NaBH₄.

There is increasing interest in the study of nanoparticle assemblies in the form of dendrites. Dendrites are crystalline masses with branching tree like structures. The extended surface area and attractive shapes of dendrites help enhance catalytic activity¹⁵. It has also been observed that bimetallic dendrites show better catalytic properties than those of a single metal which has led to interest in the research of bimetallic dendrites to study their catalytic activity¹⁷. Jianfeng Huang et al. have investigated the catalytic reduction of 4-nitrophenol to 4-aminophenol using Ag/Au bimetallic dendrites¹⁶. They have developed a method of synthesis wherein the existing Ag dendritic nanoparticles are replaced in a galvanic replacement reaction (GRR) with Au by using chlorauric acid (HAuCl₄) solution. They observed that with variation of exposure time to the acid, the morphology of the Ag/Au dendrites varied considerably with the gold concentration increasing with increased exposure to the solution.

This directional specificity of PVP has also been utilised in the formation of 1D structures like nanowires. Yugang Sun et al.¹⁹ have proposed a mechanism for how the nucleation process is influenced by PVP. The described synthesis involved reduction of silver nitrate by ethylene glycol in the presence of polyvinyl pyrrolidone (PVP). To explain the role of PVP, the authors have suggested a mechanism. In the first step, the silver ions are reduced to silver nanoparticles which show a bimodal size distribution, arising from heterogeneous and homogeneous nucleation. It is then observed that through Ostwald ripening, the larger particles form nanorods which are seen to

grow into nanowires as long as 50 micron with uniform diameter. To explain this specificity in growth, it has been suggested that the PVP has strong interactions between the {100} facets of the nanorods, leaving only the ends ({111} facets) free for further growth of AgNP. The author also provided SEM and TEM images which seem to support the proposed mechanism. The main advantage of using nanowires is the fact that they are capable of providing a conducting surface which enables these nanomaterials to be used in a wide range of sensors.

This research endeavor has focused on the photosensitivity of silver salts, namely halides and nitrates. This provides the scope for photographic development of silver nanoparticles onto a suitable substrate. An extensive and elaborate study of photographic development of Ag is given in Tadaaki Tani's book, "Silver Nanoparticles from silver halide photography to plasmonics"²⁰. The photolysis and reduction of AgX salts forms Ag clusters and very small Ag nanoparticles on the grain surface. Ag is stable as a dimer and hence, it is this Ag₂ dimer which is the nucleus of the Ag nanoparticle. These Ag nuclei when treated with a developing solution accept electrons from the reducing agent in the solution and in turn oxidize the silver cation of the neighboring AgX¹⁴. Thus, this process grows like a chain reaction resulting in a growth of silver nanoparticles. In this development procedure, deposition of Ag occurs on the interface of AgX and Ag resulting in the formation of filamentary nanoparticles. These filaments cover the surface entirely making the surface conducting.

A key feature of the research described in this report is the study of the catalytic activity of silver. There have been numerous publications investigating the catalytic property of Ag nanoparticles of varying morphologies. The main problem in using metal nanoparticles as catalysts is the difficulties involved in regeneration of the catalyst⁸. To overcome this, attempts have been made to affix silver on a suitable support which makes recycling and regeneration of the catalyst less tedious.

Bharat Baruah⁹ has described the immobilization of Ag nanoparticles on baby-wipes, thereby enabling easy recycle and regeneration of catalyst. He has followed a method wherein nanostructures are formed in the tissues by reduction of Ag⁺ of AgNO₃ to Ag by NaBH₄. The catalytic activity of such substrates has been tested using the reduction of 4-nitrophenol in NaBH₄. Similarly, Samuel R. Anderson¹ et al. managed to successfully immobilize silver and copper nanoparticles on cotton fabrics. This group also investigated the LSPR effects for photocatalysis. In this study, the nanostructures were assembled by first sensitizing the surface with Sn²⁺ and then using the tin to nucleate Pd on the fabric. When dissolved in Cu or Ag baths, the respective metal nanoparticles were deposited on the fabric, replacing the Pd nuclei. Catalytic performance in both light and dark conditions were studied using ferricyanide reduction by sodium thiosulphate. This was done to highlight the effect of LSPR phenomenon.

III. Experimental Section:

a. Materials:

All glassware used were washed with dionised water, labolene and were given an acid wash with aqua regia before rinsing with dionised water again. Deionized water from a MilliQ[®] system was used with specific resistance 18.2M ohm cm.

Triton X, silver nitrate, potassium bromide, metol, quinol, acetone, sodium sulphite, acetone, potassium ferricyanide and sodium thiosulphate were obtained from SD Fine Chemicals Ltd. Sodium borohydrate and APTMS solution were obtained from Sigma Aldrich and borax powder was obtained from Fischer Synthesis. All chemicals were analytical grade and were used as received without further purification.

The photographic developer solution was made by dissolving 0.4g Metol, 0.4g borax powder, 2g quinol and 20g sodium sulphite in 200ml deionized water.

b. Pre-treatment of fabrics:

All the cotton fabrics used in the experiments were pre-treated to remove any impurities that might have been present on the fabric. The treatment method was adopted by Barauni et al²¹. Square pieces of dimension 2cm by 2 cm of cotton fabric were cut and cleaned with Triton X 100 (1 g/L) for 30 min at 60 °C. Subsequently, the samples were rinsed with tap water and immersed in an acetone solution for 15 min before being dried at room temperature.

c. AgNP-1 synthesis by reduction of silver nitrate:

In the first method of synthesis, the pre-treated fabric was taken on a petri dish. 75µl of 1M AgNO₃ solution was pipetted onto the fabric such that the fabric was evenly wetted. The sample was then left to dry in a fume hood, protected from direct light using an aluminium foil. Once dried the substrate was exposed to a halogen lamp for 10 minutes. Then it was developed by dipping in a photographic developer solution. Once dried the fabric was washed with deionised water and dried at room temperature. The AgNP-fabric synthesized will be referred to as AgNP-1 henceforth.

d. AgNP-2 synthesis by reduction of AgBr:

In the second method, the pre-treated fabric was taken on a petri dish. 100µl of 2M KBr was pipetted onto the fabric and it was left to dry in a fume hood. After drying, 75µl of 1M AgNO₃ solution was pipetted onto the fabric such that the fabric was evenly wetted. Again the sample was left to dry in a fume hood, protected from light using an aluminium foil. Once dried the substrate was exposed to a halogen lamp for 10 minutes. Then it was developed by dipping in a photographic developer solution. Once dried the fabric was washed with deionised water and dried at room temperature. The AgNP-fabric synthesized will be referred to as AgNP-2 henceforth.

e. Silanization of fabric:

For silanization, a method described by Polwart et al.²² has been adopted. A 2% v/v APTMS solution with a 5% v/v water-ethanol mixture as solvent was prepared approximately 5 mins before use. The pre-treated fabrics were then agitated in this solution using sonification for 10

mins. After rinsing these treated substrates in ethanol to remove excess silane, these fabrics were cured at 110°C for 15 mins. Post curing, these fabrics were again rinsed in ethanol and deionised water.

f. Characterization of catalytic properties in reducing Ferricyanide using UV-Vis Spectrophotometry:

The catalytic activity of the AgNP-cotton samples prepared by various methods mentioned in the previous section were studied using the reduction of sodium ferricyanide to ferrocyanide by sodium thiosulphate. The reaction mixture was of 30ml volume with 1 mM sodium ferricyanide and 100 mM sodium thiosulphate. The reaction mixture was stirred at a rate of 1200 rpm.

To characterize the kinetics of pseudo first order reduction of potassium ferricyanide, we have used UV-Vis Spectrophotometry. The instrument used is an Agilent Technologies Cary Series UV-Vis Spectrophotometer.

g. Scanning Electron Microscope (SEM):

The SEM images were taken using a Carl Zeiss Ultra55 Scanning Electron Microscope.

IV. Results and Discussion:

1. Mechanism of formation and structure of AgNP:

a. AgNP-formed by reduction of AgNO₃:

The mechanism of formation of AgNP by reducing AgNO₃ is not clearly established. It has been suggested that when wetted with AgNO₃ solution, the Ag⁺ ions displace the hydrogen ions in the O-H linkages protruding from the cotton fibres⁹. On exposure to light from a halogen lamp for 10-15 mins, some of the ions reduce to metallic Ag. These centres of silver act as electrodes and help transfer electrons from the developer solution to the unreduced Ag ions which in turn get reduced. Thus the Ag(I) ions are reduced to Ag(0) state forming nanoclusters on the fabric. Further testing using EDX is advisable to confirm the presence of elemental silver.

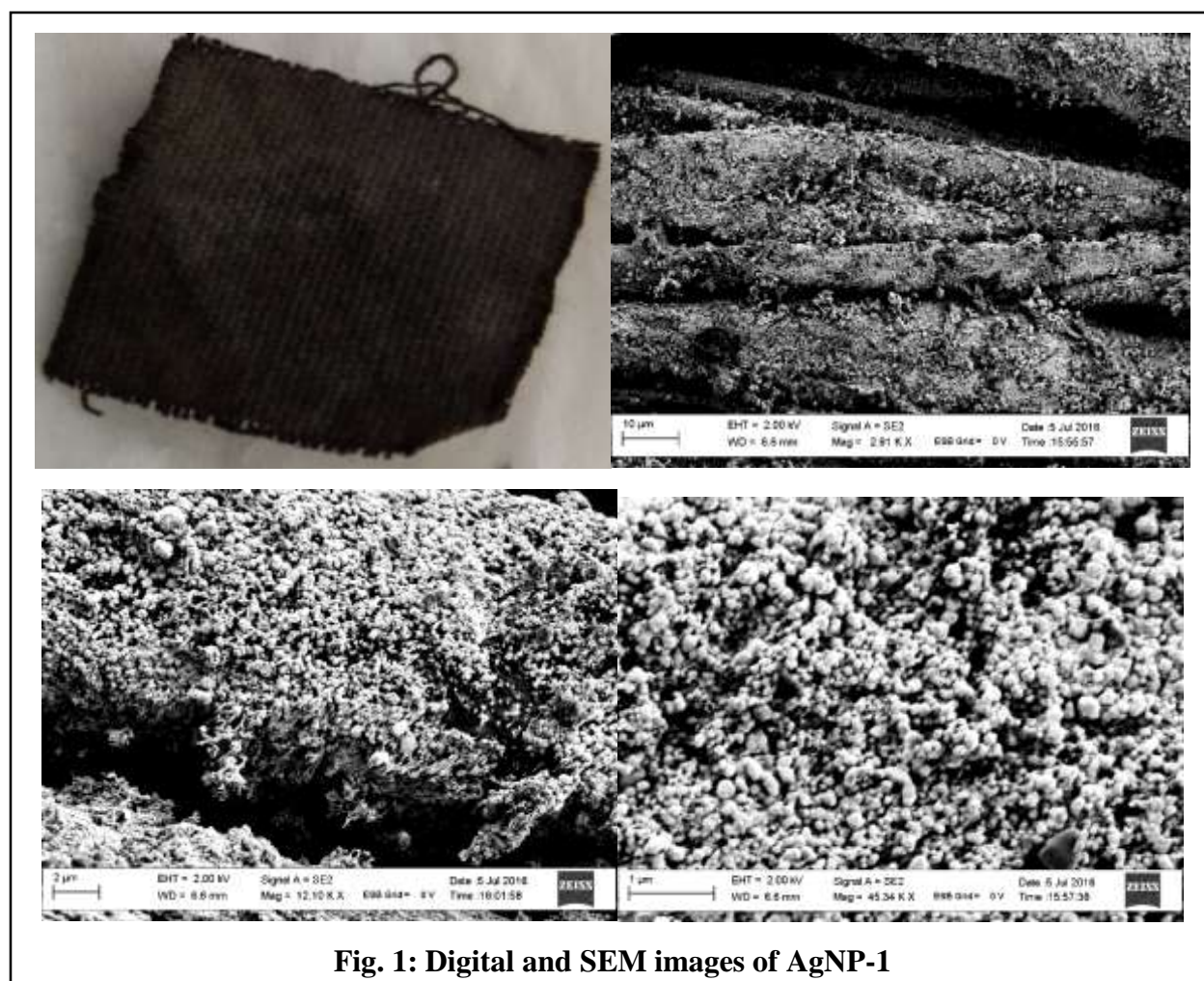


Fig. 1: Digital and SEM images of AgNP-1

The SEM images of the AgNP samples show that there is a uniform deposition of silver on the fabric. Furthermore the SEM images also show that as expected, nanoparticles are deposited by nitrate reduction.

b. AgNP-2 formed by photo reduction of AgBr:

It was observed that in the samples where AgNPs were produced by reduction of AgBr film on the surface of the fabric, the silver was washed off during use in the reaction mixture. The mechanism of development on silver by photographic reduction of AgX has been well studied.

The main advantage of using halides of silver lies in their insolubility in water. Thus a coating of silver bromide once deposited on the fabric does not wash away in an aqueous solution. On exposure to light, the photosensitive silver halide reduces to metallic silver forming silver nuclei. As explained previously in section II, on development there is reduction of silver ions to the metallic state is promoted by the transfer of electron through these nuclei from the developer. The deposition of AgNP occurs on the AgX-Ag_{nuclei} interface. Successive deposition of silver atoms causes the formation of filaments, thus resulting in the development of nanowires on the surface of the substrate. This is also shown by the SEM images shown below.

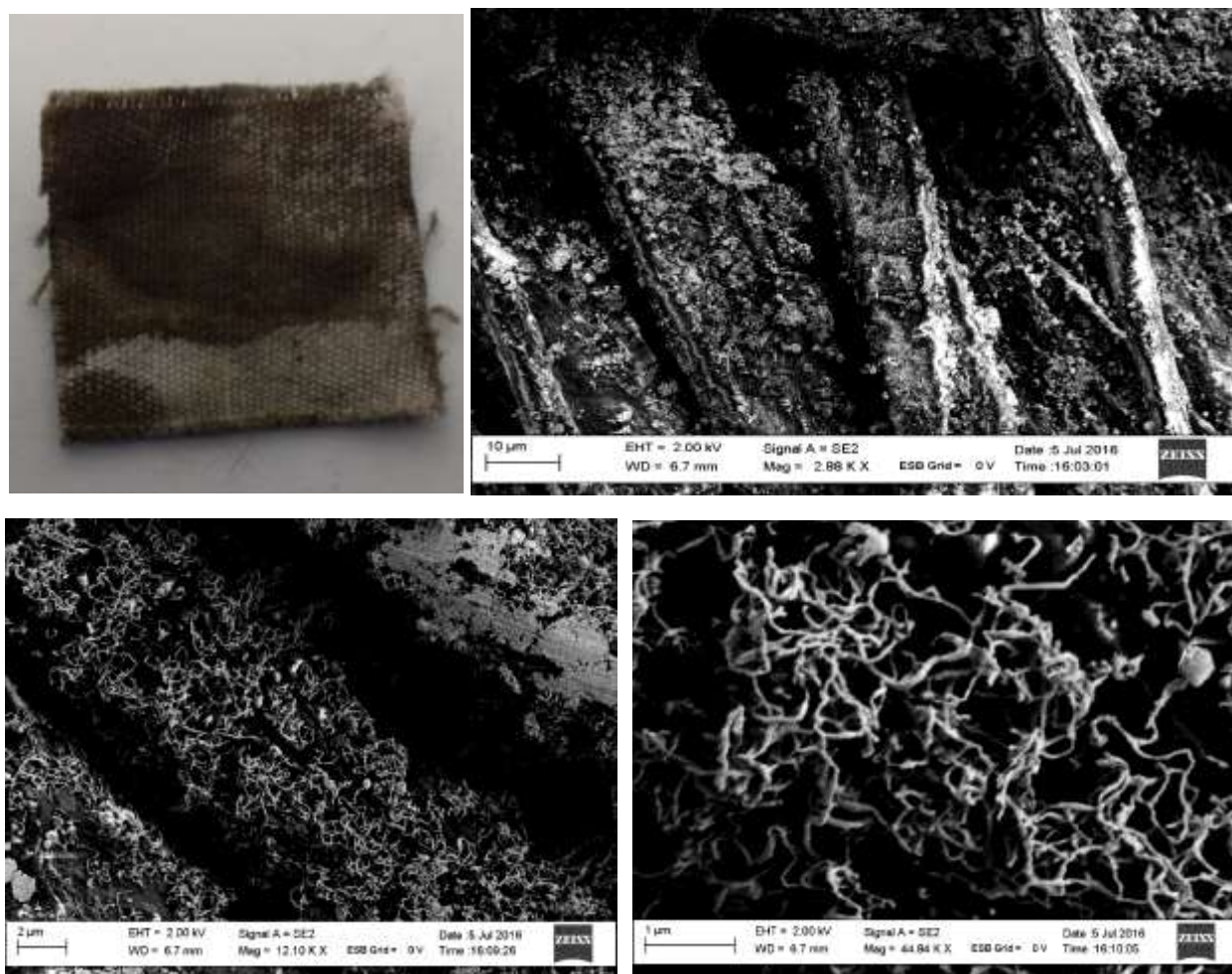


Fig. 2: SEM images of AgNP-2 showing formation of filamentous nanostructures which provide a conducting surface.

However, as evident from the digital image of the AgNP-2 given in fig. 2, the silver was not uniformly deposited on the surface. This is also evident from the SEM images in figure 2b. The SEM images are of the same AgNP-2 sample from fig. 2, but focusing on a different area which clearly has a much rarer concentration of silver. It emphasizes the inconsistent coverage of silver on the fabric surface. The reason, we believe, for the uneven distribution of AgBr on the surface of the fabric.

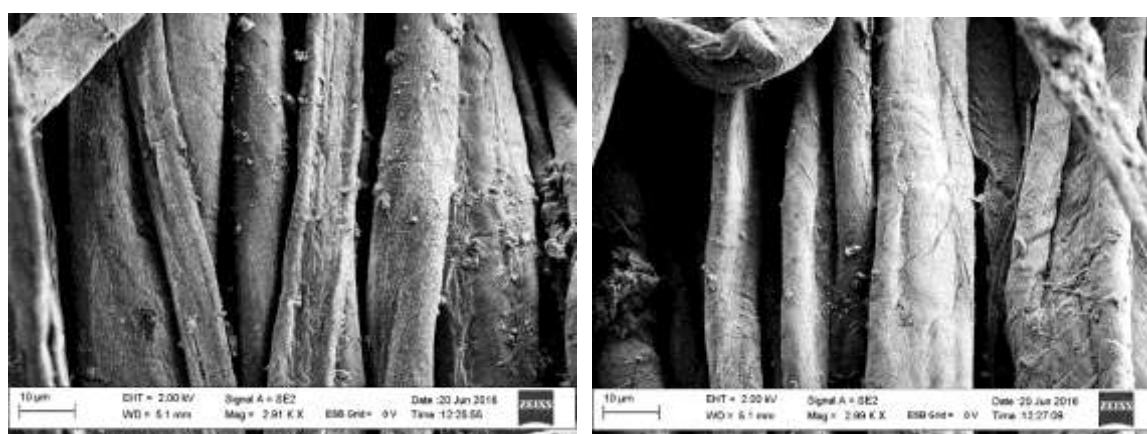


Fig. 2b SEM images from a part of AgNP-2 with rarer Ag coverage.

2. Catalytic Activity in ferricyanide reduction:

Since the concentration of thiosulphate is 100 times than that of ferricyanide, we can assume pseudo-first order kinetics with respect to ferricyanide. To characterize the kinetics, UV-Visible spectroscopy can be used wherein the decrease in absorption maxima of ferricyanide at around 420 nm indicates the progressive conversion of ferricyanide to ferrocyanide. Thus at any instant the (A/A_0) parameter is equivalent to the (C/C_0) parameter, where A_0 is the absorbance of the reaction mixture at time zero. Thus the negative slope of the graph of time vs $\ln(A/A_0)$ gives the rate constant for the pseudo first order reaction.

The time taken for 100 % conversion of ferricyanide to ferrocyanide for the different AgNP fabrics is tabulated below for one such experimental run.

Table 1: The kinetic data for one experimental run

Sample	1	2
Time for complete reduction	35min	1hr 20min
Rate constant	0.1067 min^{-1}	0.0188 min^{-1}

It was observed that the AgNP-1 samples which had been synthesized by reduction of AgNO_3 showed better catalytic performance than the AgNP-2 counterpart. This may be due to the fact that silver was washed off during use as catalyst from AgNP-2. The digital pictures of the samples (in fig 5) before and after use clearly demonstrate that appreciable quantity of silver was lost during use as catalyst.

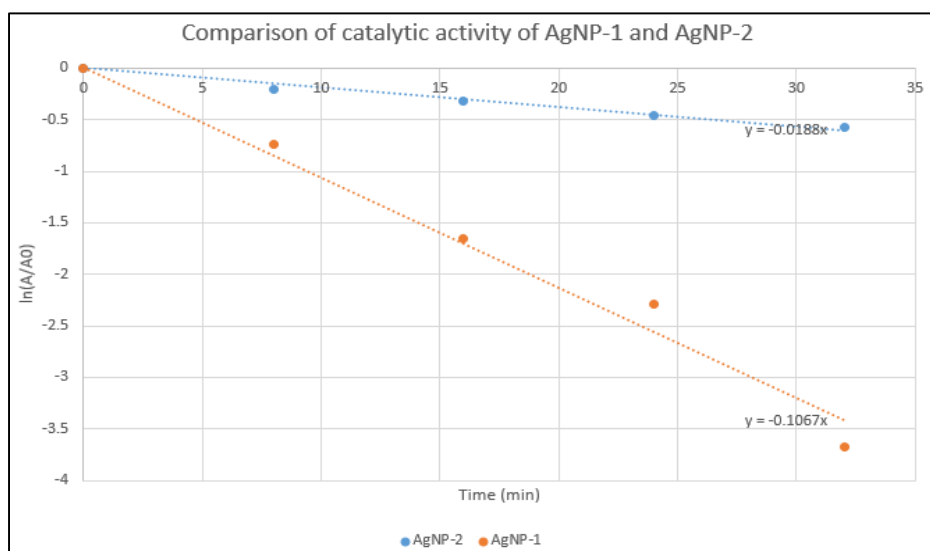


Fig 3. Comparison of the pseudo first order kinetics observed while using AgNP-1 and AgNP-2

3. Reusability of the catalyst:

a. AgNP-1:

AgNP-1 samples were used to reduce ferricyanide for 5 successive runs. The conversion after 30 mins in each of those runs is compared below.

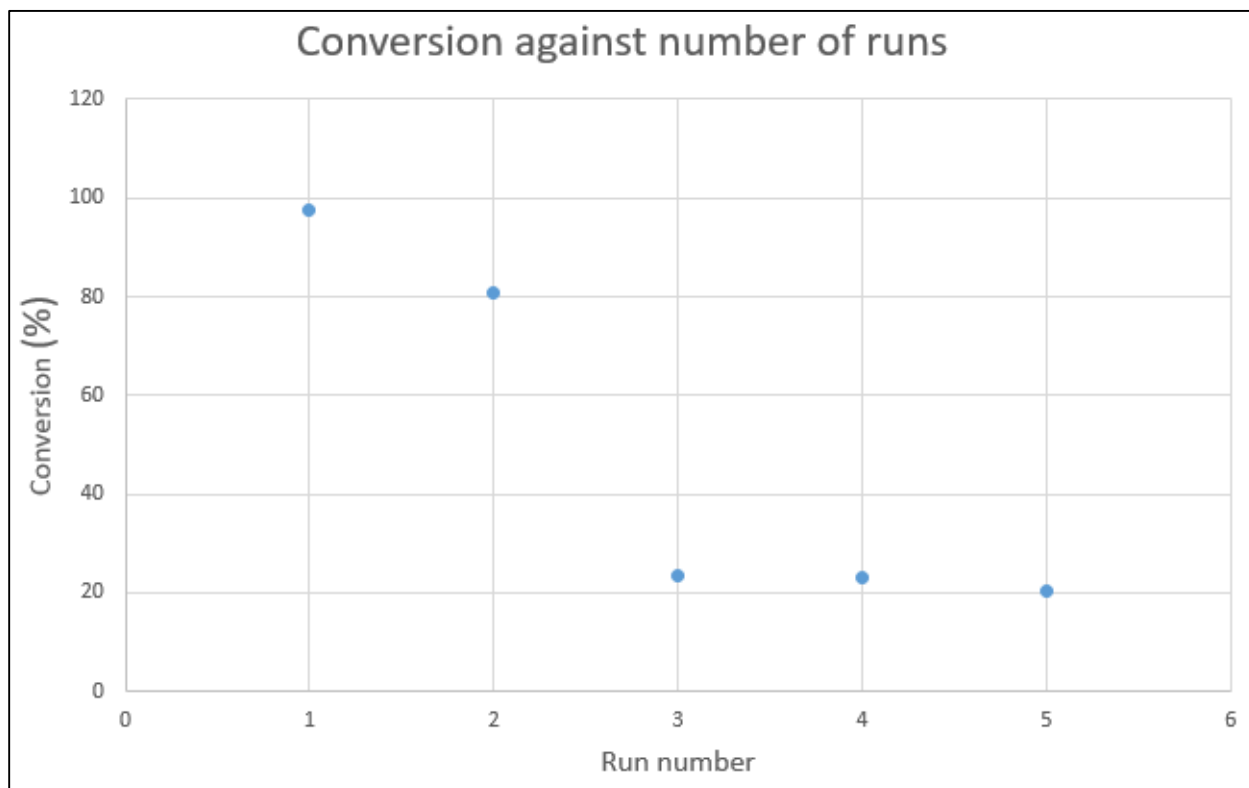


Fig. 4: The progressive conversion of ferricyanide by using the same substrate repeatedly

It is seen that the conversion during the second run is relatively high. However there is a drastic fall in the conversion from the third run. Conversion remains constant in runs 3,4 and relatively. This is probably due to the poisoning of silver by the products of the reaction and also by the washing off of Ag from the fabric. Thus, there is a progressive loss of silver in successive runs and this can be seen by comparing the digital images of the substrates after and before 5 consecutive uses.

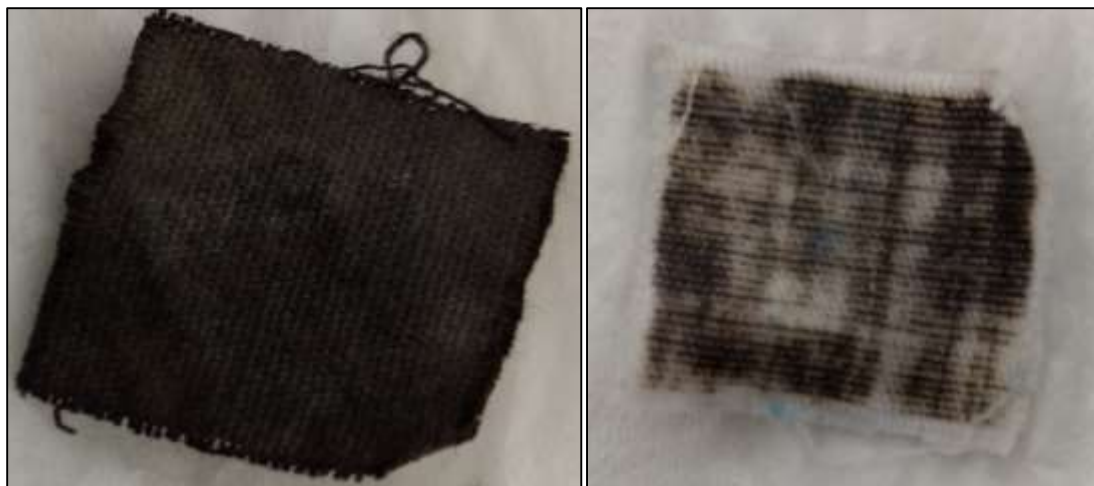


Fig. 5: AgNP-1 before and after 5 successive uses to reduce ferricyanide

b. AgNP-2:

In case of AgNP-2, it was seen that the silver was washed off the fabric after just one experiment. This is illustrated in the digital images attached here.



Fig. 6: On the right: AgNP-2 after one time use in reaction.

On the left: same sample before use as catalyst.

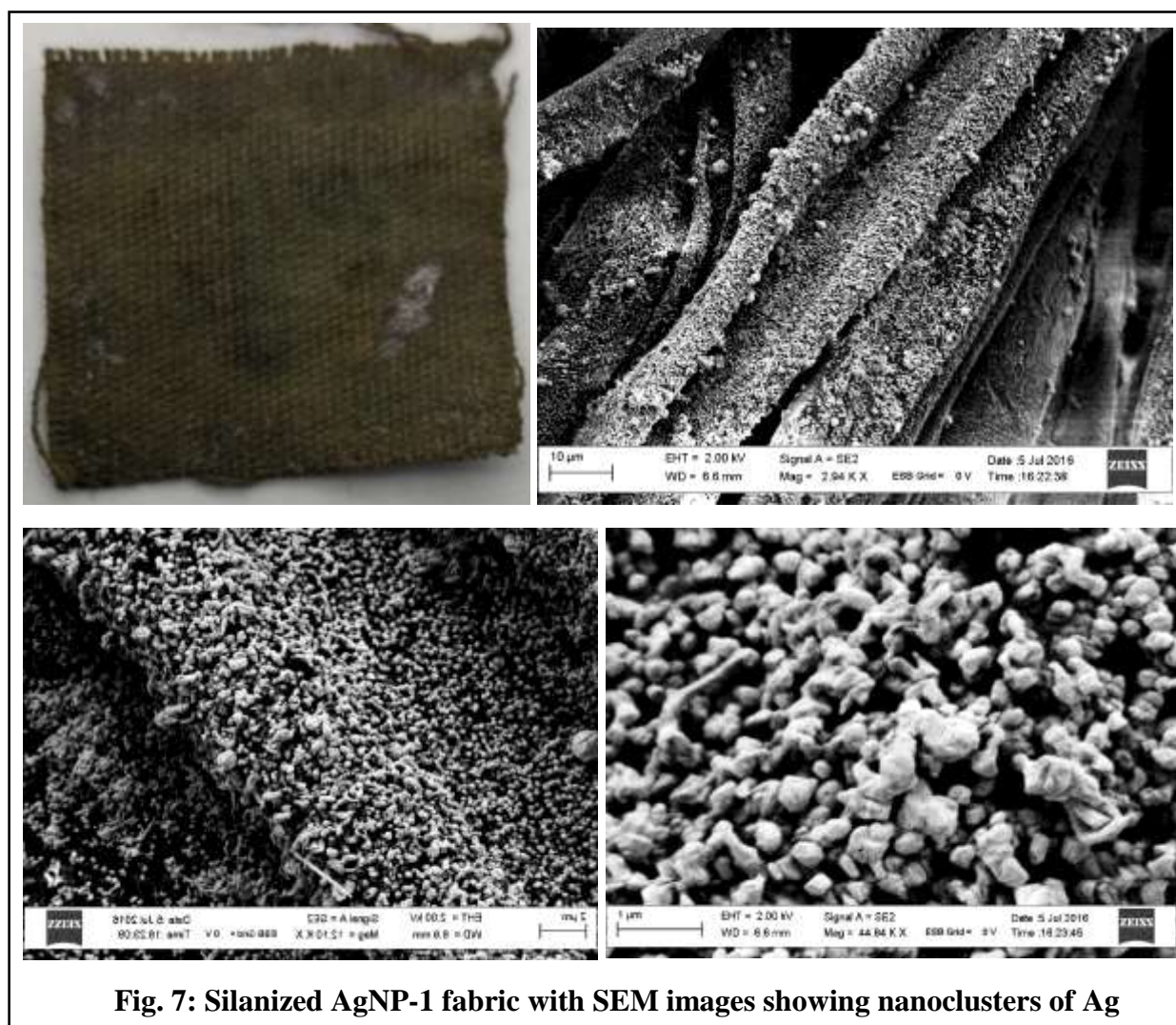
The same was observed in the case of silanized AgNP-2. Thus silver deposited on the fabric by photographic development of AgBr is not fit for use as catalyst as it is not reusable.

4. Effect of Silanization:

a. On morphology:

Silanization of a surface introduces Si-OH sites on the surface. It has been shown to improve the immobilization of metal nanoparticles on a surface²³. However, it was observed that the silanization of the cotton fabric before immobilizing silver did not improve the adhesion significantly.

One possible explanation of this observation may be given by studying the proposed mechanism for silver deposition of cotton fibres in the previous section. As mentioned it is postulated that Ag^+ ions replace the hydrogen in the O-H linkages. On reduction of this Ag^+ , we get Ag deposited as nanoparticles. Since there is an existing abundance of O-H linkages in the cellulose fibres which are the essential constituents of cotton, there are enough sites that silver can occupy. Hence, generation of silane sites might not have the expected positive impact on adhesion



The SEM images show similarity in the nature of nanoparticles and their coverage with that of the non-silanized AgNP. Thus, it follows that the catalytic activity of the two fabrics are similar. However, the distribution of Ag did not improve much.

Similarly, on comparing the SEM images of silanized AgNP-2 with those of non-silanized substrates, we again see similarities in the morphology, arrangement and distribution of AgNP.

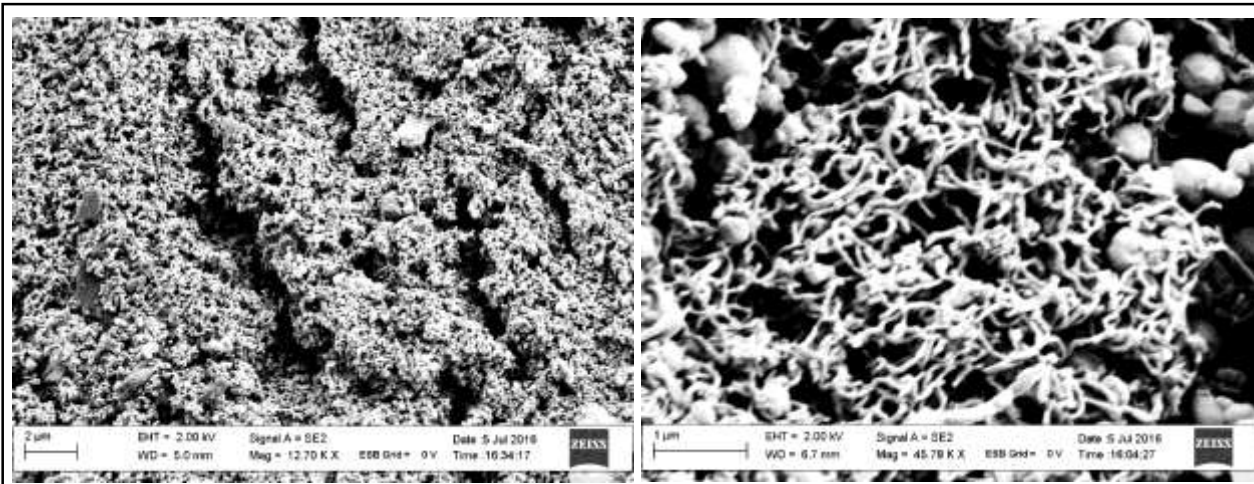


Fig. 8: SEM images of silanized AgNP-2

b. On catalytic activity:

On AgNP-1:

The kinetics observed while using both silanized and non-silanized AgNP-1 substrates were similar as shown by the graph given in figure 9.

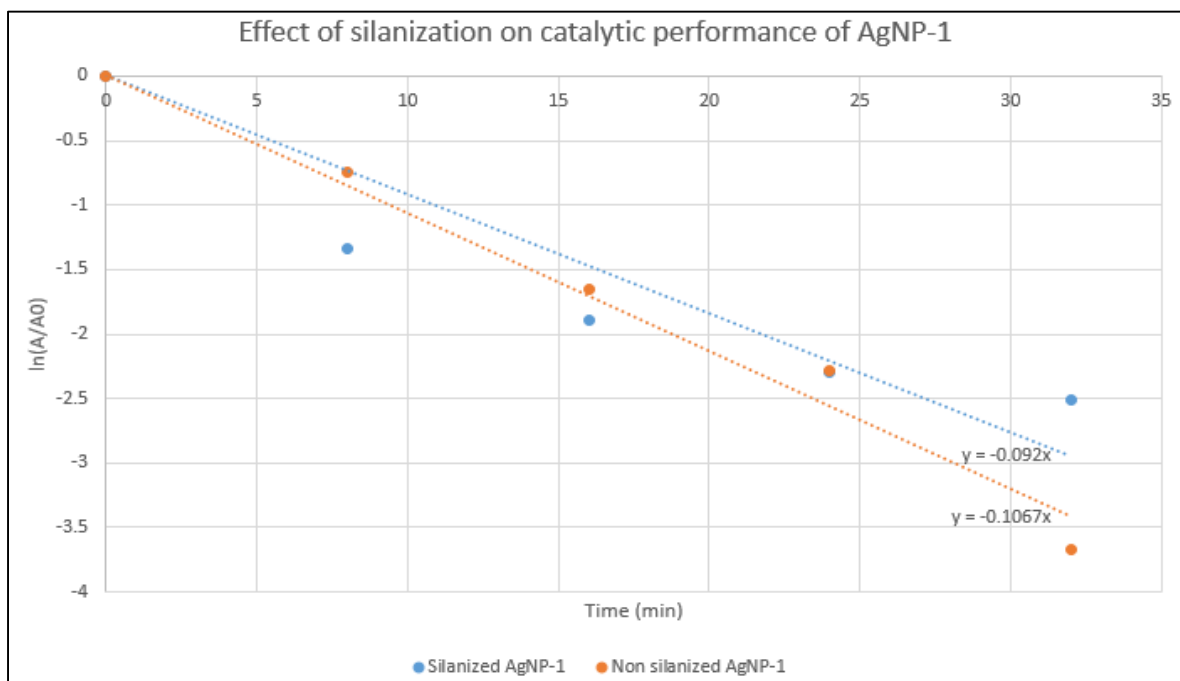


Fig 9. Effect of silanization on catalytic performance of AgNP-1

On AgNP-2:

The catalytic activity of both silanized and non silanized AgNP-1 was found to be similar. For AgNP-2, it was found that silanization helped improve the catalytic performance as the value of k is increased. However, adhesion of the AgNP also remained poor as they were washed off when immersed in the reaction mixture.

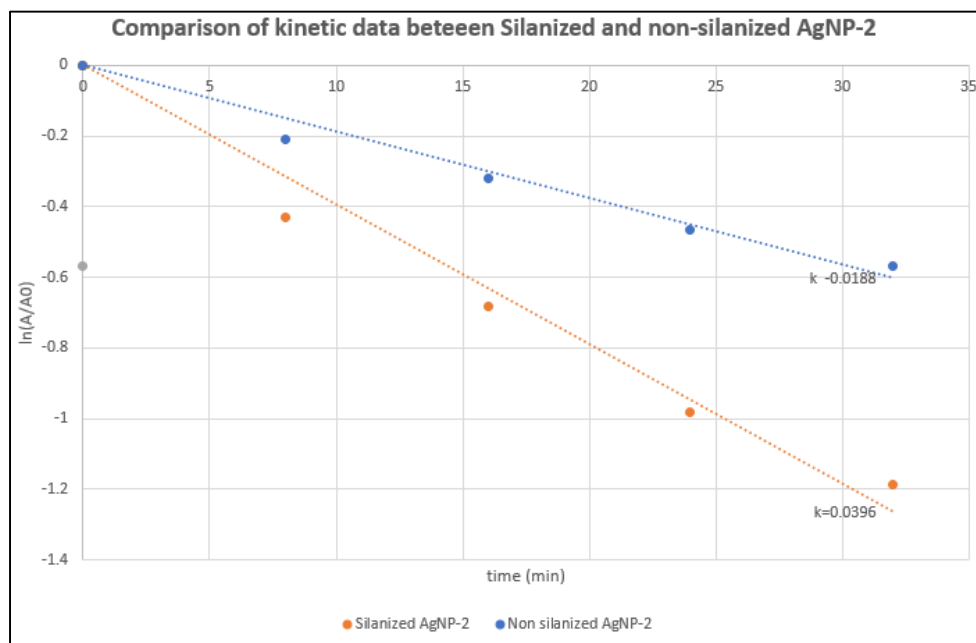


Fig. 10: Comparison of kinetics in silanized and non-silanized AgNP-2

Thus, it may be concluded that silanization of fabric before photographic development of AgBr improves adhesion of Ag onto the fabric.

5. Other modifications in AgNP fabrication procedure:

i. Dipping of fabric in AgNO₃ solution instead of drop-casting (AgNP-1b):

Instead of pipetting AgNO₃ onto the fabric, an alternative method of synthesizing AgNP was explored wherein the fabric was soaked in a silver nitrate solution of 50mM concentration for 30 mins. The fabric was then dried and developed photographically. The developed fabric had a brownish red colour due to the coverage by AgNP. The colour differs from AgNP-1 owing to the lesser concentration of Ag, indicating lesser loading of silver. The SEM images of the sample confirm the same.

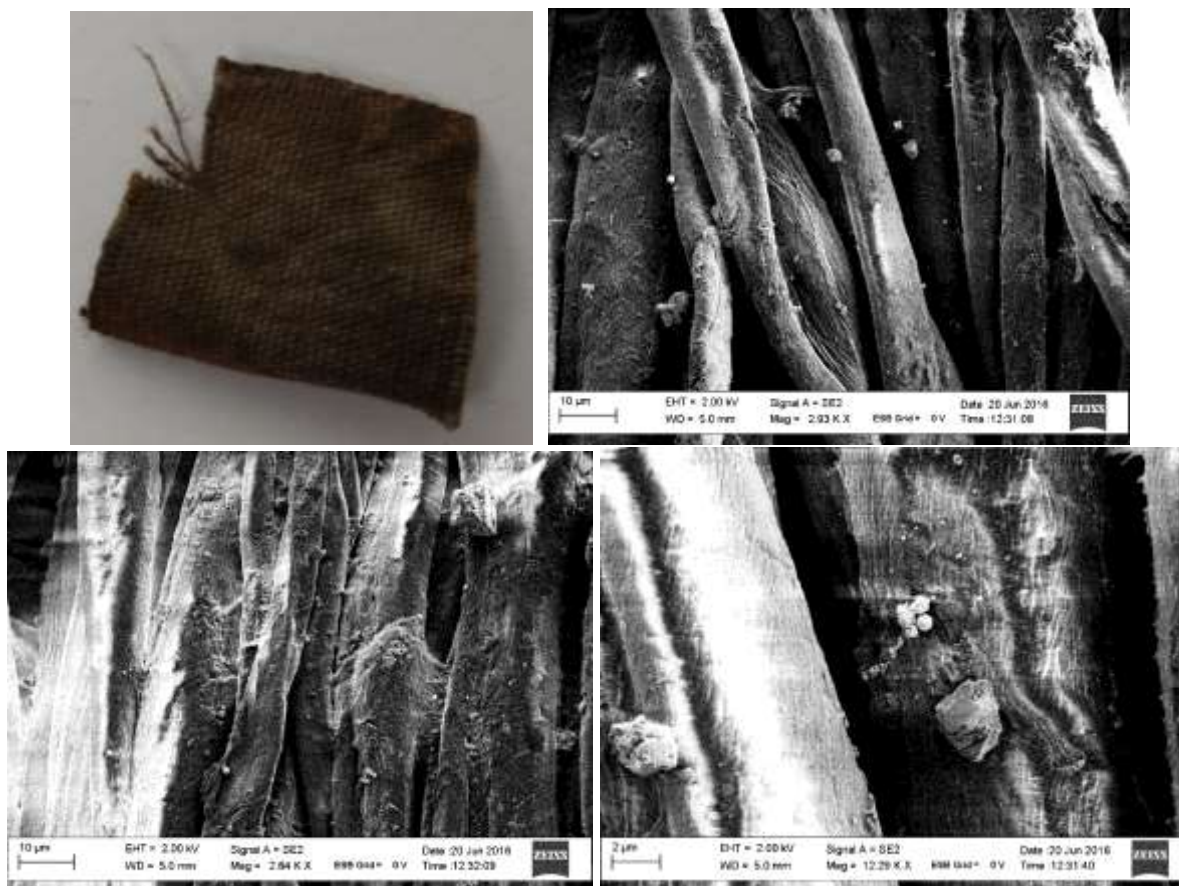


Fig. 11: SEM images of samples soaked in AgNO₃

On using the AgNP as catalyst, the silver was washed off in the CSTR within 10 minutes, thus making substrates developed by this method unsuitable for use as catalyst.



Fig. 12: AgNP-1b after use in reaction mixture once

ii. Synthesizing AgNP-2b from AgBr: dipping in 50mM AgNO₃:

In an attempt to ensure uniform coverage of silver after photographic development of AgBr, the pre-treated fabrics were dipped in the 2M solution of KBr/KI and then dried. Thereafter, the KBr coated fabric was soaked in 50mM AgNO₃ for 30 mins prior to being dried and developed photographically. A similar substrate was then fabricated using silanized fabric. It is notable here that these substrates showed a uniform coverage of Ag as shown in the SEM images below.

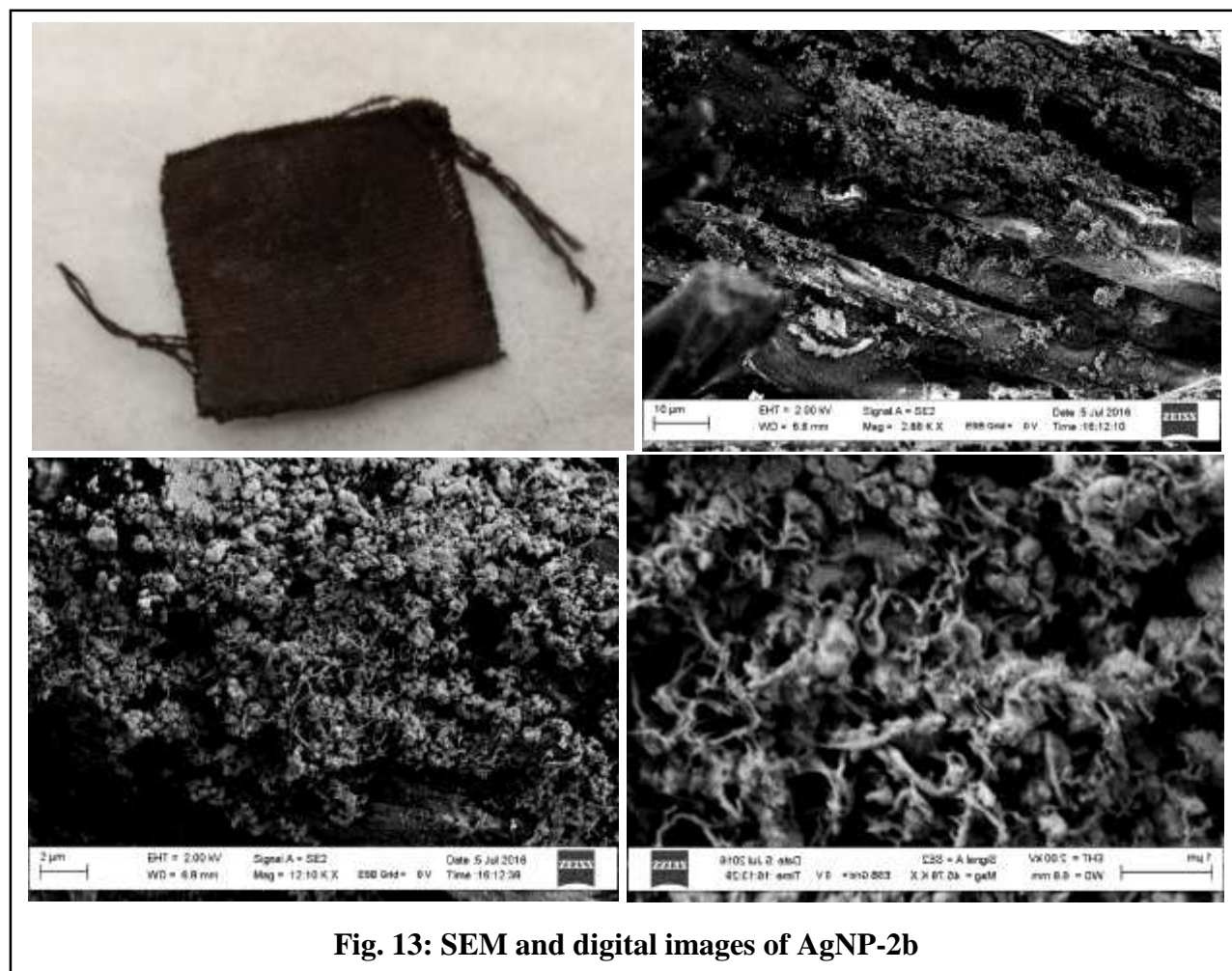


Fig. 13: SEM and digital images of AgNP-2b

The catalytic activity of the substrates was studied. However, the silver was washed off these substrates after 2 cycles. Hence, the fact remains that the AgNP formed on cotton by photographic development of AgBr cannot be reused for catalysis. This is evident from the pictures below.



Fig. 14: The AgNP-2b samples before use in reaction mixture, after one time use respectively (from Left to Right)

The catalytic performance in terms of kinetic data is given below. It is comparable to the performance silanized AgNP-2 (section IV.4.b).

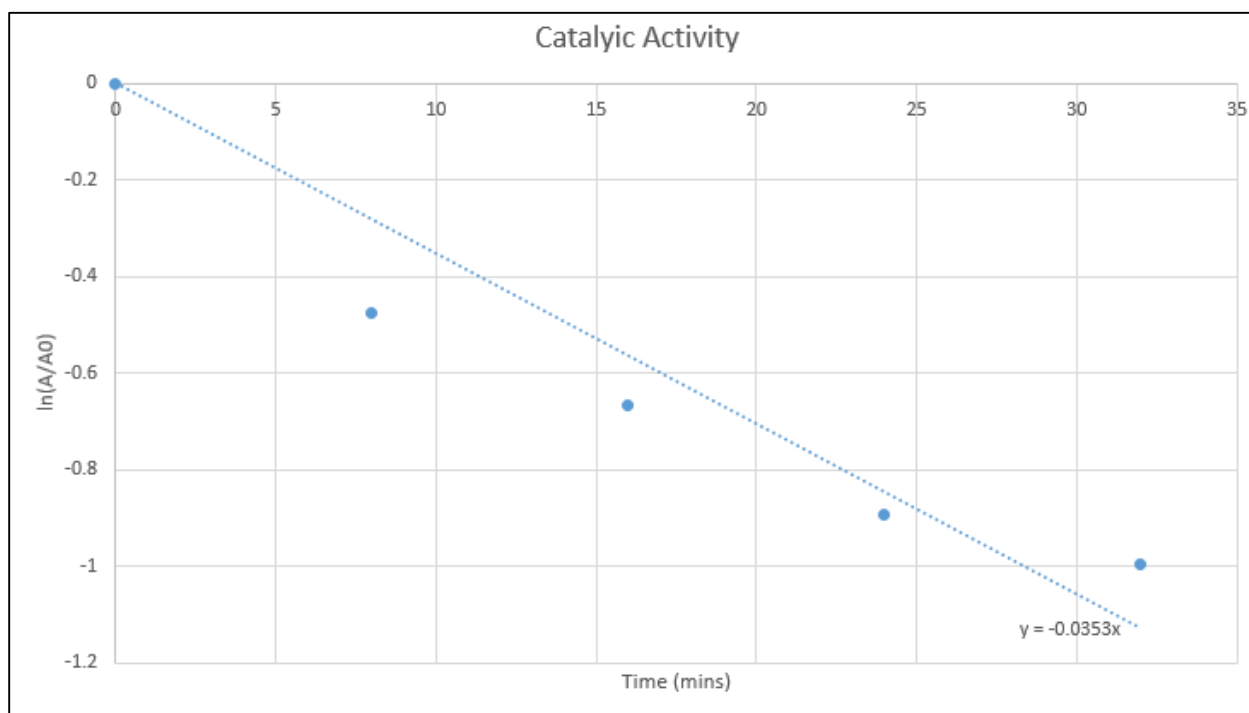


Fig. 15: Catalytic activity of AgNP-2b

iii. Using NaBH_4 to develop AgNP-1:

Instead of using the developing solution, the AgNP-1 substrates were developed using NaBH_4 . The AgNP-1 substrate formed however was found to show weaker poorer adhesion of silver than its counterpart developed using the quinolic developer. This was evident from the washing away of Ag during use as catalyst. The time taken for complete reduction was also much greater (1hr 5 mins).

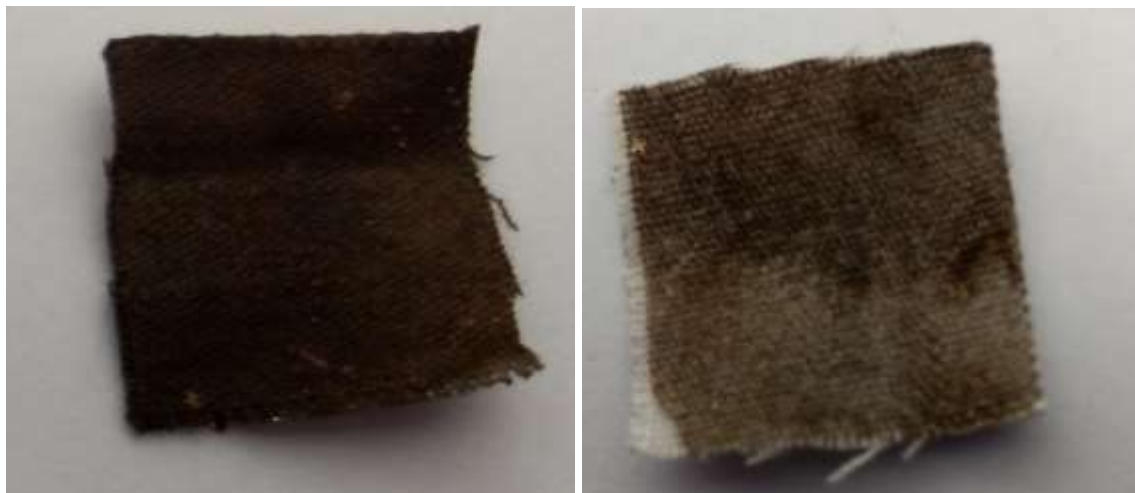


Fig. 16: AgNP-1 developed using NaBH_4 instead of photographic developer before and after use

The morphologies of the nanoparticles on the surface showed similarity to those of AgNP-1 as shown in the SEM images below.

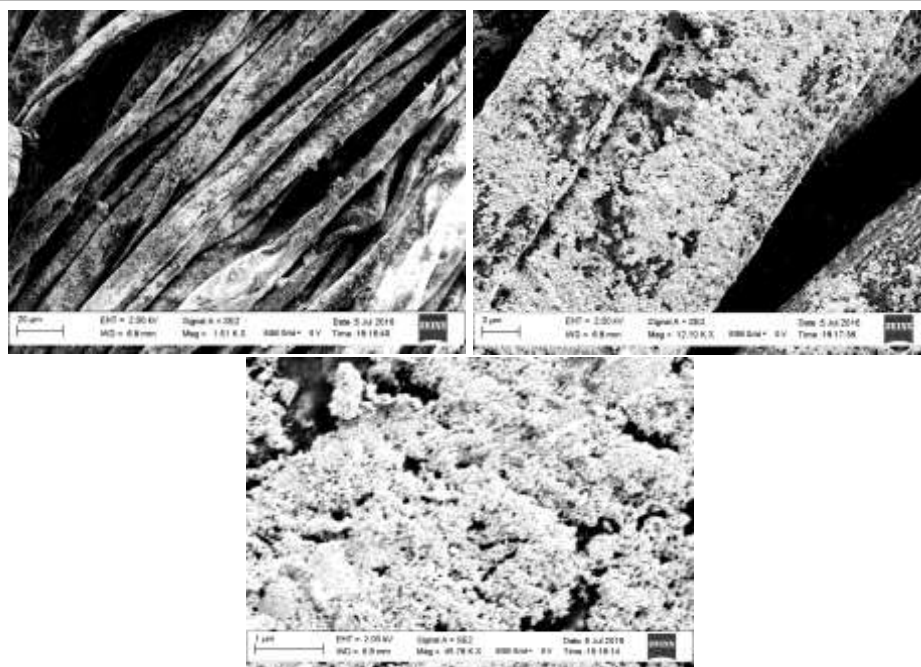


Fig. 17: SEM images of AgNP-1 developed using NABH_4

V. Summary:

First and foremost, the results reported in the above investigation suggest that silver nanoparticles on a supporting fabric are capable of catalysis. The time demonstrated by the substrate for 100% conversion of ferricyanide is consistent with that reported by Anderson et al¹ for a similar catalyst embedded cotton fabric. Thus, the results reported are promising and suggest that with further optimization and modifications, there is promise of large scale implementation of these composites.

The issue of regeneration and reactivation of the catalyst is pressing and research in that direction is a possible scope for future work. Another concerning issue is the loss of silver nanoparticles while use in catalysis. It is also clear that silanization of cotton prior to immobilization of AgNP-1 does not help significantly improve adhesion of Ag to fabric. Another notable observation is the fact that AgNP-1 formed by direct reduction of silver nitrate shows much better adhesion to fabric and catalytic performance than AgNP-2 formed by silver bromide photolysis and development. To achieve the same, it is possible that surface modification by pre-treatment or modification of the synthesis technique might help.

Thus it can be said that the catalytic performance of AgNP immobilized on the cotton fabric support is promising. However, to make this supported catalyst extendable to an industrial scale, there is need to fully understand the mechanism of the assembly of AgNP, the nature of their interactions with the cotton fabric and subsequent improvement of adhesion of NP to fabric.

VI. Scope for future work:

There is need of further research in order to ensure that the synthesized nanocomposites are suitable for use as catalysts with good reusability. To improve the adhesion of Ag onto the substrate, it might be advisable to look into pre-treatment methods like Ozone plasma treatment, RF treatment etc.

The reusability of a catalyst is decisive in its application on an industrial level. Further research is needed to examine possible regeneration techniques to ensure ease of recycle and reuse.

To better understand the underlying chemistry, it would be advisable to examine the nature of attraction between Ag and the fabric in both cases. Studying the mechanism of nucleation and growth of nanoparticles in both cases would hopefully shed light on this inconsistency. The suggestion that in case of AgNP-1, Ag⁺ ions replace the H atoms in the O-H linkages of cellulose⁹, might explain why these nanoparticles show better adhesion to the fabric. The nature of adhesion can be characterized by calculating the enthalpy of adsorption to find the nature of forces holding the nanoparticles in place.

Optimizing the loading of the metal on the fabric to get the best economic fit is also a possible area of future work.

VII. Acknowledgement:

Firstly I would like to thank the department of chemical engineering, Indian Institute of Science, Bangalore, for providing me with the opportunity to work on a high level research problem through the “Outreach Program”. There are not many institutions of such high calibre and reputation when it comes to research in India. I feel honoured to have had the opportunity to work at the esteemed institution and it was indeed a cherishable experience. I would like to thank my guide Dr Venugopal S for his guidance and unwavering support through the course of this project. I am also grateful to Mr Pushkaraj Joshi, PhD scholar at Dept of Chemical Engineering, IISc Bangalore, who was also very supportive and also chipped in with his valuable insights. I also extend my gratitude to all the faculty, students, research assistants, scholars and staff of the department for their support and help. Lastly but never the least, I thank my parents and my relatives for their unwavering support and for the encouragement they have given me.

References

1. Anderson, S.R., Mohammadtaheri, M., Kumar, D., O'mullane, A.P., Field, M.R., Ramanathan, R., Bansal, V., 2016. *Adv. Mater. Interfaces* 3.
2. R. Narayanan , M. A. El-Sayed , *J. Phys. Chem. B.* 2005 , 109 , 12663 .
3. Yang, M.-Q., Pan, X., Zhang, N., Xu, Y.-J., 2013. *CrystEngComm* 15, 6819.
4. Dutta, S., Sarkar, S., Ray, C., Roy, A., Sahoo, R., & Pal, T. (2014). *ACS Appl. Mater. Interfaces*, 6(12), 9134-9143.
5. Zhang, X., & Su, Z. (2012). *Adv. Mater. Advanced Materials*, 24(33), 4574-4577.
6. Huang, J., Vongehr, S., Tang, S., Lu, H., & Meng, X. (2010). *J. Phys. Chem. C*, 114(35), 15005-15010.
7. Y. Yu, J. Addai-Mensah, D. Losic, *Langmuir* 2010, 26, 14068.
8. G. Zheng , K. Kaefer , S. Mourdikoudis , L. Polavarapu , B. Vaz ,S. E. Cartmell , A. Bouleghlimat , N. J. Buurma , L. Yate , Á. R. de Lera , L. M. Liz-Marzán , I. Pastoriza-Santos , J. Pérez-Juste , *J. Phys. Chem. Lett.* 2014, 6, 230.
9. Baruah, B., 2016. *RSC Adv.* 6, 5016–5023.
10. Yu, Y., Addai-Mensah, J., Losic, D., 2010. *Langmuir* 26, 14068–14072.
11. M. E. Stewart, C. R. Anderton, L. B. Thompson, J. Maria, S. K. Gray, J. A. Rogers and R. G. Nuzzo, *Chem. Rev.*, 2008, 108, 494–521.
12. R. Ramanathan , S. Walia , A. E. Kandjani , S. Balendran , M. Mohammadtaheri , S. K. Bhargava , K. Kalantar-zadeh , V. Bansal , *Langmuir* 2015 , 31 , 1581 .
13. Mcfarland, A.D., Duyn, R.P.V., 2003. *Nano Lett.* 3, 1057–1062.
14. J.F. Hamilton, 1988, *Advances in Physics*, 37:4, 359-441.
15. Song, Y. J.; Yang, Y.; Medforth, C. J.; Pereira, E.; Singh, A. K.; Xu, H. F.;Jiang, Y.; Brinker, C. J.; van Swol, F.; Shelnutt, J. A. *J. Am. Chem. Soc.* 2004, 126,635–645.
16. Huang, J., Vongehr, S., Tang, S., Lu, H., Shen, J., Meng, X., 2009. *Langmuir* 25, 11890–11896.
17. Liu, J. H.; Wang, A. Q.; Chi, Y. S.; Lin, H. P.; Mou, C. Y. *J. Phys. Chem. B*, 2005, 109, 40–43.
18. Zhu, S., Huang, J., Tang, S., Meng, X., 2009. *Materials Chemistry and Physics* 118, 442–446.
19. Sun, Y., Mayers, B., Herricks, T., Xia, Y., 2003. *Nano Lett.* 3, 955–960.
20. Tani, T., n.d. Silver nanoparticles: from silver halide photography to plasmonics.
21. Barani, H., 2014. *New J. Chem.* 38, 4365.

22. Polwart, E., Keir, R.L., Davidson, C.M., Smith, W.E., Sadler, D.A., 2000. *Applied Spectroscopy* 54, 522–527.
23. Agnihotri, S., Mukherji, S., Mukherji, S., 2013. *Nanoscale* 5, 7328.
24. <http://www.silverinstitute.org/site/silver-in-industry/catalysts/>