An eco-friendly top down approach to nutrient incorporated electrospun seed coating for superior germination potential.

Vidya Krishnamoorthy, Sheeja Rajiv*

Department of Chemistry, Anna University, Chennai 600025, Tamil Nadu, India

*Correspondence to: Dr. Sheeja Rajiv, Department of Chemistry, Anna University, Chennai-600025, Tamil Nadu, India. Email: sheeja@annauniv.edu

ABSTRACT

In this work we have integrated the top down approach of electrospinning with reduction method of synthesising nanoparticles to form synthesised cobalt nanoparticles/urea incorporated Polyvinylpyrrolidone nanofibers. The advantages of the electrospun ultrathin fibrous polyvinylpyrrolidone (PVP) was applied to agriculture to improve crop yield. The fibers formed were characterised by microscopic, spectroscopic and thermal analysis. These fibers namely polymer PVP incorporated with urea, Co NPs separately and in combination were coated on cowpea seeds (Vigna unguiculata) to evaluate their effect on germination characteristics. The results obtained confirm that this seed coat would help in better protection of seed and lead to greater crop yield. On performing one way ANOVA, the difference in treatment had a significant effect on the germination parameters. The seed coatings containing both urea and Co NPs showed good germination rate among the samples. From the germination parameters the seed coating can be graded as follows: Uncoated < PVP < Co NPs incorporated PVP ≤ Urea incorporated PVP < Urea/ Co NPs incorporated PVP. The conductivity measurements of the steep water obtained by soaking the coated seeds in water at room temperature for a period of 24 hours also confirmed the effectiveness of the seed coatings. On addition of Co NPs, the utility of urea can be minimised for a good crop establishment. The dispersion of the cobalt nanoparticles (Co NPs) and urea into the polymer coating and the subsequent controlled release of the nutrients to the seed during germination has been achieved using the electrospinning process. We conclude that the use of biocompatible polymer seed coat, along with the integrated nutrients, forms an environment
friendly, germination enhancing and protective coating for the seed leading to a sustainable agricultural development.

**Keywords:** Electrospinning; Polyvinylpyrrolidone; Urea; Cobalt Nanoparticles; Cowpea Seeds; Seed germination.

1. **INTRODUCTION**

   In today’s world, global food scarcity is one of the major problems that needs to be addressed. It is therefore imperative to use technology in the field of agriculture to enhance crop yield and improve crop nutrition [1]. The application of nanotechnology in agriculture has been limited. Eco-friendly and biocompatible polymer nanofibers were fabricated using the top down approach namely electrospinning and metal nanoparticles were synthesised by eco-friendly reduction of metal salt. These nanoparticles were incorporated into the fibers. The present study was aimed at employing this process to create seed coating and evaluate their effect on germination rate, shoot and root length upon germination [2]. Electrospinning is a versatile method of creating nanofibers by subjecting polymer droplet to an electric field. It is considered beneficial and environment friendly [3]. The nanoscale fibers, formed by this process had superior characteristics compared to the bulk material [4]. They have high surface area, high mechanical strength, greater flexibility and no residual solvent at the end of the process [5]. These nanofibers have been used in filtration, tissue engineering, controlled drug release, energy devices, fibrous reinforcement composites etc.

   This novel method has now been used in various agricultural applications like controlled release fertilizers, seed coating etc but is still in its infancy [6]. Rhizobia incorporated PVA, electrospun on wheat seeds [7], urea loaded PVP fibers [8] and fungicide incorporated electrospun ethyl cellulose as seed coats [9] have been used to give good crop yield. In the study of effect of seed size on the rate of germination, it was found that larger seeds showed higher germination rate and produce more vigorous seedlings. This was attributed to the high amount of food reserve and greater enzyme activity owing to the size of the seed [10]. So it is relevant to store a fertilizer as a nutrition source in the polymer seed coating. The fertilizer amount being just enough to help the
growing seed without being toxic, which can be achieved by controlled release.

Germination being a crucial stage in the plant life, controls the plant numbers and therefore the crop yield. Achieving greater crop yield heavily depends on the seed quality. Food security can be sought by seed treatment because almost 90% of the food plants are propagated through their seed. In the present work, Cowpea (*Vigna unguiculata*) - an ecologically and economically important leguminous plant, rich in protein was chosen [11]. It is found that the nutritional content of cowpea is similar to that of common bean with the advantage of high folic acid content and low flatulence producing factor. This variety of bean also takes less cooking time comparatively leading to low fuel consumption.

The polymer used for the study – polyvinylpyrrolidone is water soluble, nontoxic and biocompatible. It is electrospun around the seed which forms a protective coating during storage and dissolves in water while sowing. The additives to the polymer solution are commonly known fertilizer urea and micronutrient cobalt. Urea is a well-known fertilizer with 46% nitrogen content. On dissolution it gives out ammonia and carbon dioxide hence is nontoxic [12]. Cobalt, being an important component of vitamin B₁₂, leghaemoglobin and enzymes present in nitrogen fixing bacteria [13], is an essential element for all living beings. As a part of a bacterial enzyme complex, cobalt is essential and it is necessary for rhizobial growth [14]. The amount of nanoparticles added are very low hence are not toxic. About 12mg/kg of cobalt added had favourable effect on plant growth, which is well below the prescribed LD₅₀ limit given for cobalt [15].

In the current work, seed coats were made by electrospinning PVP with Urea and Co NPs. The release of nutrients and the characterisations of such polymer matrices have been reported [8]. The objective was to evaluate the change in germination rate due to coating with nanofibers and understand the advantages of using a fiber coating. The secondary objective of the work was to check if addition of Co NPs had favourable effects on the germination pattern.

2. EXPERIMENTAL

2.1 Materials and Methods

Polyvinylpyrrolidone (PVP) (average molecular weight ~ 3, 60,000) was purchased from Sigma Aldrich. Co NPs were synthesised using cobalt acetate, sucrose and vegetable oil with ethanol as solvent [8] thereby employing environment friendly methods. Urea was
purchased from Qualigens fine chemical India Pvt. Ltd. Ethanol and chloroform were purchased from Sisco Research laboratories Pvt. Ltd Mumbai. All the chemicals and solvents were used without further purification and were kept at room temperature. Mature cowpea seeds were procured from local nursery and the viabilities of seeds were tested by floatation method.

2.2 Preparation of polymer solution and Electrospinning.

The solutions of PVP with urea and Co NPs were prepared as given, for electrospinning. All the preparations were carried out at room temperature (30 ± 2°C). PVP solution (A) was prepared by dissolving 0.5g of PVP into 10ml of chloroform/ethanol (4:1, v/v) mixed solution [2]. PVP-Co NPs solution (B) was prepared by dissolving 0.05g Co NPs (1% by weight of PVP) into solution (A). The Urea - PVP solution (C) was made by dissolving 1.3g of PVP and 0.26g of urea (20%by weight of PVP) in10ml of chloroform/ethanol (1:4, v/v) [16]. The Urea - PVP – Co NPs solution (D) was prepared by dissolving 0.05g of Co NPs initially into chloroform and prepared as in solution C. This was done due to greater solubility of urea in ethanol and Co NPs in chloroform solvents. The concentrations were allowed to stir for 4 h at room temperature to obtain a homogenous solution.

The cowpea seeds were coated with ultrafine fibers by electrospinning each of the prepared solutions namely PVP, urea incorporated PVP, Co NPs incorporated PVP and urea and Co NPs incorporated PVP solution around the seed. Electrospinning of the prepared solutions was done by loading each of the solutions into a 5 mL syringe attached to a stainless steel needle with an inner diameter of 0.3mm. With the help of a syringe pump the flow rate was adjusted at 5mL/h. The collector was a grounded aluminium foil placed at a distance of 15 cm from the needle and a power supply of 20kV was applied [8]. The seeds were placed on the aluminium foil (Figure 1. (a)) and the fibers from the needle were allowed to fall on the seeds. On turning the collector plate manually in intervals, the polymer fibers could be evenly coated on the seeds (Figure 1 (a)). The weights of the seeds, before and after coating were taken to ensure approximately equal amounts of coating material per seed. The fiber diameters were measured using “Digimimizer” Version 4.5.2, 2005- 2015 medcalc software
2.3 Characterisation and Conductivity Studies

The surface morphology of fibers was studied using a Tescan Vega 3 Scanning Electron Microscope (SEM). This was observed with a secondary electron detector at an accelerating voltage of 5-15 kV and at working distance of 11-15 mm. To make the fibers conductive, the fibers were coated with gold by sputtering before performing the SEM analysis.

The change in conductivity of the solutions formed on addition of approximately 1g (approximately 6 to7 seeds) of the uncoated and coated seeds were studied by monitoring the conductivity of the solution using Deep Vision Digital conductivity meter 611. The equipment was calibrated using a 0.01M solution of KCl (conductivity = 1.409 mS/cm at 25°C). The conductivity of the water sample which contained the seed depends on both the leakage of electrolyte from the seeds, the coating on the seed and the quantity of seeds present. The conductivity was measured in μS/cm for a known weight of seed and then reported as μS/cm/g by dividing the conductivity value by the seed weight taken. Air tight containers were used to store the sample used for testing in order to avoid evaporation and entry of dust particles. The sample was stirred before taking the readings.

2.4 Germination of seed

The germination studies were performed by placing the seeds on moist filter paper in a container, which was then placed at room temperature [17]. A glass trough was partitioned into 5 slots and lined with wet tissue paper (Fig. 1b). The seeds were divided into 5 sub samples of 25 seeds each. One of the sub samples, was not coated and was taken as the control. The other four sub samples were coated with PVP fibers, urea incorporated PVP fibers, Co NPs incorporated PVP fibers and urea and Co NPs incorporated PVP fibers. Germination studies were conducted by ‘in between paper method’ and therefore covered with another layer of wet tissue paper. The tissue paper was kept wet but not dripping using a spray bottle. They were allowed to remain in the dark.
and were examined every 24 h. The seeds which showed moulds or looked rotten were counted as dead and discarded.

The seeds were analysed till the root and shoot grew to a considerable length and the time taken for germination was studied. The study was done based on completely randomized experimental design with six replicates of 25 seeds each to ensure consistency of data. The number of seeds germinated was counted every 24 h and the shoot length of ten normal seedlings from each replication of each of the treatment were randomly selected and measured using a thread and a ruler. A seed was considered to have germinated when the radicle protruded from the seed coat.

From the measure of number of seeds germinated and their shoot lengths, the percentage germination, mean germination time, mean germination rate, germination index and seed vigour index were calculated using the formula as given in Table 2 [24, 25].

2.5 Statistical Analysis

The data obtained for germination percentage, mean germination time, germination rate, germination index, seed vigour index were studied by one way ANOVA, to test the effect of treatment of seed coat on germination. This test was carried out using Statistical Package for Social Sciences - SPSS 19.0 software (IBM). All the data was tested for homogeneity using levene’s test before conducting the one way ANOVA. Treatment effects were declared significant at $P < 0.05$ for all analyses. Tukey’s HSD test was used to test post hoc for difference among means.

3. RESULTS AND DISCUSSION

The polymer fiber matrix formed through the process of electrospinning with a dimension of 350 mm x 550 mm weighed about 36.7mg. Consequently a very fine
coating of nutrient incorporated polymer could be spun over the seed leading to efficient utilisation of nutrients compared to broadcasting etc. This fine coating along with its incorporated micro and macronutrients does not change the size, weight or shape of the seed as seen in Fig 1 (a) but this improves seed handling and addition of colour can also help in seed distinction. The consolidated values of the weights of seeds and their coating are given in Table 1.

Table 1 Weights and Electrospinning parameters

<table>
<thead>
<tr>
<th>S.No</th>
<th>Fiber Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fiber Diameter</td>
<td>878 ±192nm</td>
</tr>
<tr>
<td>2</td>
<td>Weight of Nanofiber Mat/ cm²</td>
<td>3.466 x 10⁻⁴g</td>
</tr>
</tbody>
</table>

WEIGHT OF SEEDS AND COATING

<table>
<thead>
<tr>
<th>Uncoated Seed(g)</th>
<th>Coated Seed(g)</th>
<th>Coating(g)</th>
<th>PVP (g)</th>
<th>Urea(g)</th>
<th>Co NPs per gram of seed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.048± 0.094</td>
<td>1.098± 0.095</td>
<td>0.051± 0.0049</td>
<td>~0.0412</td>
<td>~0.0082</td>
<td>~0.0016</td>
</tr>
</tbody>
</table>

SPINNING PARAMETERS

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Tip To Collector Distance</th>
<th>Flow Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>20kV</td>
<td>15cm</td>
<td>5mL/h</td>
</tr>
</tbody>
</table>

The fibers were characterised by XRD, SEM, FTIR, TGA and DTA and have been reported [8]. The XRD of the Co NPs showed crystalline nature with peaks observed at 44.3° and 51.5° which are characteristic of Face Centered Cubic Cobalt phase. The crystallites size ranged from 19 to 31.75 nm from Scherer equation. The FTIR confirmed that the fiber formation did not change the polymer nature during the process and also confirmed the incorporation of urea and Co NPs in the polymer matrix [8]. From fig. 2a it is also clear from the broadening of NH₂ band and shift of C=O, that hydrogen bonding was formed between NH₂ group of urea and the carbonyl of PVP. The TGA and DTA analysis showed good thermal stability with decomposition.
temperature of 449.40°C and weight loss of 72.56% as shown in fig. 2b.

The release of nutrient from fiber showed an initial release of 12% which is much less that the large burst release noted in films [8]. The water contact angle of the urea and CoNPs incorporated PVP fibers was found to be 19.8° confirming hydrophilic nature. The increase in water contact angle compared to pure PVP nanofibers is approximately 2°.

**3.1 Analysis of morphology by SEM.**

The SEM images of the fibers in fig. 3(a) show the formation of ultra-fine continuous, smooth, uniform and beadless fibers. The presence of Co NPs increased the conductivity of solution and hence the average diameters of Co NPs incorporated fibers were found to decrease compared to spinning of PVP alone under the similar conditions.

**Fig. 2 (a)** FTIR spectra of (i) Pure urea, (ii) Urea and CoNPs incorporated PVP fibers (iii) PVP fibers. **(b)** TGA and DTGA (c) Static water contact angle of Urea and CoNPs incorporated PVP fibers.
Figure 3. SEM images of (a) Urea and Co NPs incorporated PVP fibers and (b) Co NPs (c) Bar graph showing distribution of fiber diameter.

Fibers also showed presence of Co NPs on the surface. This leads to the efficient release pattern in the fibers. Fig. 3(c) shows the histogram for the distribution of fiber diameters for the urea and Co NPs incorporated nanofibers. It was observed that the maximum number of fibers were in the range of 700 to 1000nm. However fibers with diameters less than 600nm and more than 1200nm were also seen. The average fiber diameter was found to be ~878 nm. Even though a decrease in fiber diameter was expected due to addition of conductive Co NPs, an increase in fiber diameter was observed. This may be due to the addition of non-conducting urea to the solution [4].

The SEM images confirmed spherical characteristics and also aggregation of particles is evident. The average particle size was found to be ~85.3 nm which is less than the crystallite size calculated from Scherer equation.

3.2 Release of fertilizer from the coated and uncoated seeds.

EC test is a measure of integrity of seed membrane and is used to evaluate the seed vigour and seed deterioration process. Seeds, when immersed in water, exude ions, sugars and other metabolites As a damaged membrane permits larger leaching, the measure of conductivity gives an idea about the healthy seeds. It is seen that lower the conductivity of the seed solution, the more healthy the seed [20].
The conductivity of the uncoated seeds was found to be less than 1.5 μS cm⁻¹ g⁻¹. It was observed that there was an increase in the conductivity of the steep water with time for the both the coated and uncoated seeds as shown in Fig. 4. The conductivity of the uncoated seeds was higher than the coated ones. Among the coated seeds the order was PVP fiber < Urea incorporated PVP fiber < Urea/Co NPs incorporated PVP fiber coated seeds. This increase in conductivity may be attributed to the dissolution of the fibers and the urea hydrolysis with time.

Generally it is required that the pattern and rate of release of nutrient should be comparable with the rate of nutrient uptake by the plant, which follows sigmoidal pattern [21]. The nutrient release from the seed coating was based on the polymer erosion and degradation, which in turn leads to decrease in surface area as the coating erodes away. Soil properties such as pH, salinity, texture, ionic strength of the soil significantly affect the release of nutrients from fertilisers which are coated with hydrophilic polymer. The results therefore can give us an idea about the trend that maybe followed during nutrient release.

Figure 4. Conductivity changes in Steep water in (i) Uncoated Seed, Seeds coated with (ii) PVP fiber, (iii) urea incorporated PVP, (iv) urea and Co NPs incorporated PVP

3.3 Investigation of Germination parameters.

Cowpea, being a seed with vigorous growth pattern, showed good germination characteristics for all the five sub samples. It is reported that in the cowpea seeds the rate of imbibition during the first three to twelve hours depended primarily on the hilum size in the seed while the protein percentage in the cotyledons controlled the rate in the next 12 h [21]. The germination studies were conducted for a period of 5 days in which time the shoot length for the germinating cowpea increased to about 6cm and had to be placed in the soil for further growth [21]. Till the cotyledons start their
photosynthetic activity in the embryonic period called hypogeal germination, the seeds utilise the reserves stored within them for the growth of seedling. Therefore the presence of fertilizers like urea in the vicinity of the seed promotes the germination process. The five sub samples and their six replicates were subjected to germination and the results were studied and were subjected to one way ANOVA after testing for homogeneity. The mean ± standard deviations for all the germination parameters are tabulated Table 2.

### TABLE 2 VARIATION IN GERMINATION PARAMETERS

<table>
<thead>
<tr>
<th>COATING FORMULA</th>
<th>%G</th>
<th>MGT (day)</th>
<th>MR (day⁻¹)</th>
<th>GI (seed day)</th>
<th>SVI [(%G x L(cm))/100]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNCOATED</td>
<td>NONE</td>
<td>84. ± 2.73c</td>
<td>2.91±0.13</td>
<td>0.340±0.015</td>
<td>83.43±1.03c</td>
</tr>
<tr>
<td>FIBER COATING</td>
<td>PVP</td>
<td>86.72±1.366bc</td>
<td>2.95±0.09</td>
<td>0.337±0.014</td>
<td>87.06±1.63bc</td>
</tr>
<tr>
<td></td>
<td>PVP+ UREA</td>
<td>89.77± 2.89b</td>
<td>2.99±0.10</td>
<td>0.331±0.024</td>
<td>95.19±3.67b</td>
</tr>
<tr>
<td></td>
<td>PVP+Co NPs</td>
<td>86.80±1.081bc</td>
<td>2.92±0.22</td>
<td>0.339±0.028</td>
<td>89.96±1.95bc</td>
</tr>
<tr>
<td></td>
<td>PVP+ UREA + CoNPs</td>
<td>94.5 ± 1.45a</td>
<td>3.04±0.07</td>
<td>0.326±0.081</td>
<td>103.69±1.81a</td>
</tr>
</tbody>
</table>

Means within columns followed by the same small letter for each characteristic are not significantly different by the Tukey test (P < 0.05). (%G- percentage germination, MGT - mean germination time, MR-mean germination rate, GI- germination index, SVI- seed vigour index of the uncoated seed, the films coated seeds and the fibers coated seeds). (Where, Go, G, ni, ti, L, Lo are the number of seeds in the sample, number of seeds germinated, number of seeds germinated in time ti, shoot length of seed, shoot length of control respectively.)
Figure 5. (A) Percentage Germination Vs Coating ; (B) Mean Germination Time Vs Coating ; (C) Germination Index Vs Coating; (D) Seed Vigour Index Vs Coating [1, 2, 3, 4, 5 represent PVP, Urea incorporated PVP, Co NPs incorporated PVP, Urea and Co NPs
incorporated PVP and uncoated seed respectively. (E) Germination index Vs time for all five cases for the fibers.

The data were statistically analysed using analysis of variance using a completely randomized design. On statistical analysis, the germination percentage was significantly influenced by addition of nutrients. Almost 95% germination was recorded when the coating contained both urea and Co NPs. The percentage germination for each of the treatments is represented graphically in Fig.5 (A). The PVP coating containing either urea or Co NPs were comparable and showed a germination percentage less than the coating containing both urea and Co NPs but greater than those containing neither urea nor Co NPs. This is in accordance to the reported literature [15] that presence of 0.1µg of Cobalt in soybean shows nitrogen fixation and growth even in the absence of mineral nitrogen.

From Fig.5 (A), it is clear that fibers containing nutrients showed better germination percentage. This may be due to the availability of the small quantity of urea as a nutrient in the vicinity of the seed. Addition of Co NPs alone also does not seem to show a significant difference to the germination, but it was observed to be greater than the uncoated one. However, the combination of Co NPs and urea seemed to increase the germination rate considerably as confirmed by reports that cobalt aids in germination. This also shows that a good germination percentage could be achieved with minimum amount of urea by the addition of Co NPs, which is in confirmation with reports [13, 15]. This minimisation of urea may lead to lesser usage, leaching and thereby reduce environmental pollution and lead to sustainability.

The same trend was observed in the case of germination index and seed vigour index studies also, as seen in Fig. 5 (C) and (D) and Table 1. The germination index and seed vigour index were calculated as a function of seedling length. Clearly in both the cases the growth of seedling was significant for the seed treatment as seen in Tukey HSD test as seen in Table 1.

It is clear from Table 1, that the addition of Co NPs along with urea to the polymer matrix used for coating had significantly boosted all germination study parameters compared to the other coatings as is also seen in the enhanced flowering process in tomato plants [22]. The addition of Cobalt up to 12mg/kg increased the
growth rate while above this concentration the cobalt showed adverse effects to plant growth [19]. The root nodules of many leguminous plants contain cobalamin coenzyme which validates the role of cobalt in nitrogen fixation [23]. The presence of cobalt had a significant positive effect on the activity and numbers of the bacteria which fixes atmospheric nitrogen namely azotobacter and nitrobacter in leguminous plants [25]. Cobalt at 7.5 ppm levels are seen to induce positive effect and metabolic activity in Auxins and Gibberlins in the roots of tomato plants.

It is clear that the germination index increased with time as shown in Fig. 5 (E). When the seeds were coated with urea and Co NPs incorporated PVP, the germination index seemed to be consistently high. These coated seeds were stored for a period of 6 months in air tight containers before the germination test and can be stored for longer periods without any damage compared to the uncoated ones. Germination pattern of cowpea seeds in the laboratory seemed to show good results in 5 to 8 days [21].

The concentration of Co NPs used was 10mg/kg, hence it had both favourable effect as well as no toxicity as it is well below the LD<sub>50</sub> value. From the graphs the efficiency of the seed coating can be graded as follows: Uncoated ≤ PVP < Co NPs incorporated PVP ≤ Urea incorporated PVP < Urea/ Co NPs incorporated PVP.

The electrospinning process, allows the formation of fibers on the seed surface with no residual solvent. The fibers also allow the regulation of gases and moisture between the internal structure and the external environment, whereas in the case of dip coating (film coating) there is a possibility of the polymer solution clogging the tiny pores in the seed coat. The seed coat contains pores which are unevenly distributed through the surface and also the micropyle which is important for the germination is a pore. The imbibition rate depends on seed coat thickness, number of seed coat pores and size of micropyle and hilum. The fibers after coating allow passage of gases thereby allowing the seed to breathe which may not be possible in a film. In the fiber spinning technique, a portable fiber spinning can be employed. Large scale production of fiber coated seeds is possible through bowl electrospinning method [26].

4. Conclusions

In this work, seed coating applied using electrospinning technique and incorporated nutrient was found to improve germination rates of cowpea seeds. The higher surface area of the
nanofibers leads to an effective seed coating and efficient nutrient release. Addition of even small amounts of cobalt nanoparticles and urea to the polyvinylpyrrolidone seed coat facilitated nitrogen fixation and increased the availability of fertilizer in the vicinity of the seed. The addition of cobalt nanoparticles tends to minimise usage of urea in leguminous plants. The germination index and the seed vigour index that depend on the seedling growth were found to differ significantly on addition of these nutrients. The fibers may be sought after due to the ease of spinning operation which can ensure even coat and no residual solvent. Owing to the feasibility of electrospinning process and the favourable results obtained for the urea and cobalt nanoparticles incorporated polyvinylpyrrolidone coating, these can be used as seed coats for better stand establishment and crop yield of leguminous plants.

Acknowledgements

K. Vidya greatly acknowledges Department of Science & Technology, Government of India for financial support vide reference no (SR/WOS-A/CS-1074/2015) under Women Scientist Scheme to carry out this work. The authors gratefully acknowledge them instrumentation facility provided under FIST-DST and DRS-UGC to the Department of Chemistry, Anna University, Chennai.

Conflict of Interest: There is no conflict of interest with respect to the materials discussed in this manuscript.

References


