Indian Journal of Chemical Technology
Vol. 29, November 2022, pp. 760-765
DOI: 10.56042/ijct.v29i6.67351

Nanocomposite cotton fabrics with *in situ* formed copper nanoparticles using citrus lemon leaf extract as reducing agent

Manjula K[1], Ashok B[2], Krishnamurthy Goud K[2], Hariram N[3], Narsimlu N[2], Varada Rajulu A[4] & Srinivas CH*[,2]

[1,2]Department of Physics, University College of Science, Osmania University, Hyderabad Telangana 500 007, India

[3]Department of Biotechnology, Kalasalingam University, Krishnan Kovil 626 126, Tamil Nadu, India.

[4]International Research Centre, Kalasalingam University, Krishnan Kovil 626 126, Tamil Nadu, India.

E-mail: drchsphy.ou@gmail.com

Received: *19 August 2022; accepted*: *21 October 2022*

Nanocomposite cotton fabrics (NCCFs) with *in situ* formed copper nanoparticles (CuNPs) using aqueous extraction of citrus lemon leaves as reducing agent have been made. The NCCFs have been analyzed by SEM, FTIR, XRD and TGA techniques and antibacterial test. The CuNPS have been roughly spherical in shape with a mean size in the range of 82-114 nm. The OH and C-OH groups of leaf extract has played an important role in the generation of the CuNPs in the NCCFs as established by the FTIR spectral analysis. The XRD analysis has indicated that the formation of CuNPs in NCCFs lowered the crystallinity of NCCFs. The thermal stability of NCCFs has been lowered by the CuNPs. However, the NCCFs with *in situ* generated CuNPs exhibited higher antibacterial activity against both gram-negative and gram-positive bacteria and hence can be effectively used as antibacterial wound dressing and hospital bed materials.

Keywords: Antibacterial activity, Citrus lemon leaf, Copper nanoparticles, Cotton fabrics, *In situ* formation

In order to minimize environmental impact and applications of metal nanoparticles (MNPs) in health sector, essentially depends on non usage of toxic or harmful chemicals during their synthesis. Many areas of research including medicine, catalysis, photo electricity, sensors and industrial manufacture etc., have been revolutionized by nanotechnology[1-3]. The demand for the development of materials with antimicrobial properties has driven different studies encompassing metal nanoparticles (MNPs) and cotton fabrics[4,5]. The present paper has been focusing on functionalization of cotton fabrics with copper nanoparticles (CuNPs) through green synthesis methods where reducing and stabilizing agents are obtained from lemon leaf extract.

Experimental Section

Leaf extract preparation

Citrus lemon belongs to *Rutaceae* which is widely grown commercially worldwide. The fresh green citrus lemon leaves were collected from campus of Science and Humanities Block of University College of Engineering, Osmania University, Hyderabad, Telangana state, India. After thoroughly washed using distilled water and dried in shade quantity of 100 g of the dry leaves was soaked in 900 mL of preheated deionised water (80°C) by water bath method for 20 min duration. After cooling to ambient temperature, extract was filtered which may be readily usable or can be stored at 5°C for 3 to 4 days for further usage. The lemon leaf extract as plant extract contains phytochemicals consisting of active alkaloids, phenols, terpenoids, quinines, amides, flavonoids, proteins and alcohols[6].

Matrix preparation

The pristine cotton fabrics had been procured from local market. The thoroughly washed pristine cotton fabrics of dimensions of 150 mm × 100 mm were immersed along the inside walls of glass beakers which contain prepared lemon leaf extract. These systems were then placed on magnetic stirrer at room temperature and maintain stirring rate 300 rpm for 24 h. A thin phytochemical layer of citrus lemon leaf extract could be adhered strongly by molecular forces on cotton surface[7]. The cotton fabrics colour turned into light greenish during this process indicating the infusion of the phytochemicals of lemon leaf extract. The cotton fabrics infused by lemon leaf extract were employed as cotton matrix.

In situ formation of CuNPs in the cotton fabrics

Copper (II) suplhate pentahydrate had been procured from SDFCL and used as received without

further purification. The systems of $CuSO_4.5H_2O$ solutions with different concentrations i.e., 1mM, 5mM, 25mM, 125mM and 250mM were prepared in separate beakers. In each, beaker a cotton matrix piece was introduced. These systems were then placed on magnetic stirrer at room temperature and maintain stirring rate 300 rpm for 24 h. During this process, the cotton matrix colour turned from light greenish to brown, primarily which may be due to Cu particles deposition on the cotton fabric which is designated as nanocomposite cotton fabric (NCCF). In the NCCF, lemon leaf extract reduced CuNPs were absorbed and diffused on the cotton fabric surface by electrostatic interaction between the Cu ion particles & negatively charged –OH groups in the cellulosic chain of cotton[8]. The NCCFs having *in situ* formed CuNPs were thoroughly washed in deionised water and dried. The NCCFs colour was retained even after repeated washings.

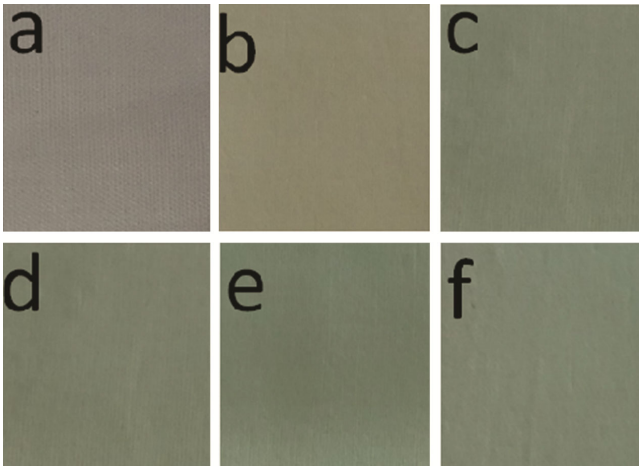

Fig. 1 — Digital images of NCCFs matrix made using (a) 1 mM; (b) 5 mM; (c) 25 mM; (d) 125 mM; (e) 250 mM and (f) source solutions.

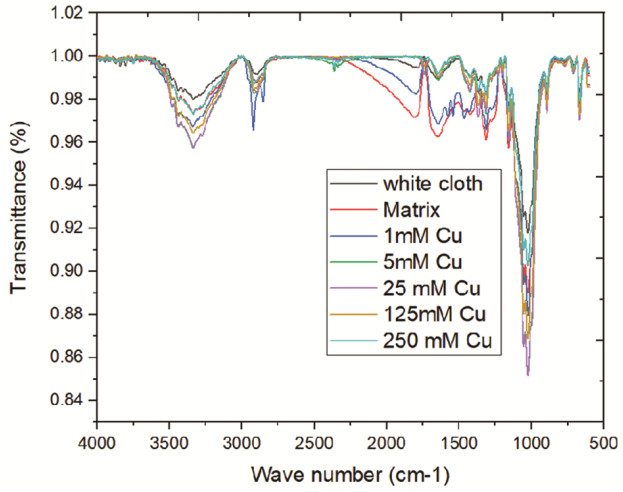

Fig. 2 — FTIR spectra of white cloth, matrix and all NCCFs with *in situ* generated CuNPs using 1, 5, 25, 125 and 250 mM source solutions.

Results and Discussion

Digital images of NCCF

In order to visualize the changes between the pristine white cotton fabric, cotton matrix and the nanocomposite cotton fabrics (NCCFs) with *in situ* generated CuNPs, using 1, 5, 25, 125 and 250 mM source solution concentrations, their digital images were recorded by Sony digital Camera and are presented in Fig. 1 (a-f). The colour of the matrix changed to light brown due to insitu generated CuNPs by bioreduction of infused lemon leaf extract of cotton matrix.

FTIR analysis

The FTIR spectral study of pristine white cotton fabric, cotton matrix and nanocomposite cotton fabrics (NCCFs) with different concentrations of source solutions have been plotted as shown in Fig. 2 and tabulated the peak positions assigned to cotton matrix and NCCFs in Table 1.

It is clearly evident from the Fig. 2 that the intensity of the main bands in the NCCFs is lower than the matrix indicating the involvement of the OH and C-OH groups of the leaf extract in reducing and stabilizing the generated CuNPs in the NCCFs. Further, the band at 1747 cm^{-1} of the matrix (due to the C=O group of the flavonoids of the leaf extract in the matrix) is found to be absent in the NCCFs establishing its involvement in the generation of CuNPs. Hence, the groups of OH, COH and C=O groups of matrix are responsible for the generation of CuNPs in the NCCFs.

SEM analysis

From Fig. 3 (a) and (b), it can be observed that the NCCFs had roughly spherical CuNPs distributed fairly uniformly. Similar observation was made in NCCFs made using other concentrated source solutions. From

Table 1 — Peak positions and assignments of matrix and NCCFs.

Peak position (cm^{-1})	Assignment
3330	-OH
2899	$-CH_2$
1747	-C=O
1655	Crystallization of water
1032	-COH
1311	-CH
895	-CH
667	-CH

Fig. 3(c), it can be observed that the generated CuNPs in the NCCF using 1 mM source solution are with sizes ranging from 50 to 120 nm with most of them in the 91-100 nm size range with a mean value of 89 nm. Similarly, from Fig. 3(d), it is evident that the NCCF using 250 mM source solution has the CuNPs in the same size range of 50 to 120 nm but most of them were in the size range of 51 to 60 nm with a mean value of 82 nm. The remaining NCCFs made using the source solutions with concentrations of 5, 25 and 125mM are consisting of mean values of 114, 114, 103nm respectively. Fig. 3 (e) and (f) indicates EDX spectra of the NCCFs which confirm the presence of the Cu element in them.

XRD analysis

In order to study the effect of the generated CuNPs on the crystalline nature of the NCCFs, X-ray analysis was carried out. The X-ray diffractograms of the matrix and the NCCFs with generated CuNPs are shown in Fig. 4.

It can also be observed that the intensity of the main peaks of the NCCFs is lower than that of the matrix indicating that the generted CuNPs in the NCCFs lowered the crystalanity of the NCCFs. Similar observation was made by[9].

From Fig. 4 (a), it can be seen that the diffractograms of the matrix and the NCCFs with in situ generated CuNPs are almost at the same 2θ

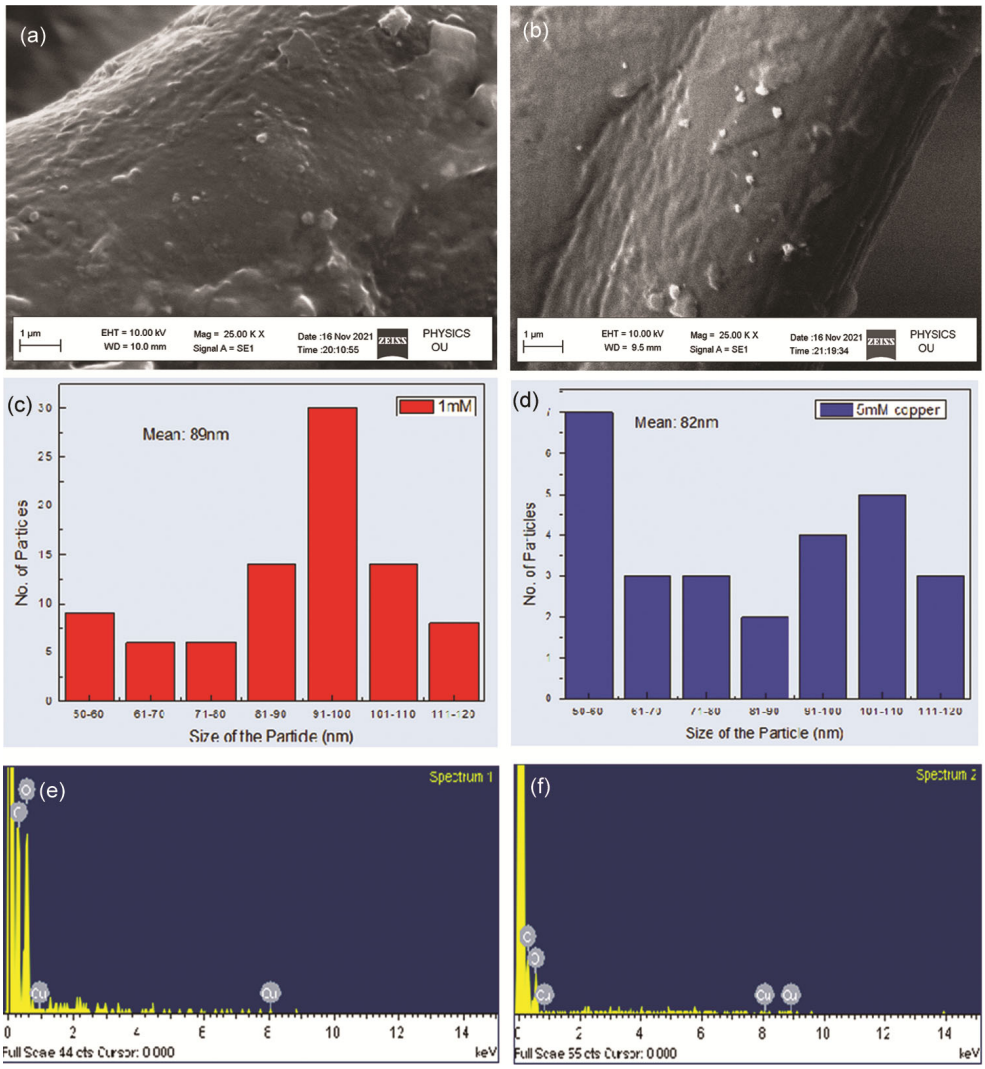

Fig. 3 — (a) SEM image of NCCFs with *in situ* generated CuNPs made using 1mM source solutions; (b) SEM image of NCCFs with *in situ* generated CuNPs made using 250 mM source solutions; (c) Size distribution of the *in situ* generated CuNPs using 1mM source solution; (d) Size distribution of the *in situ* generated CuNPs using 250 mM source solution; (e) EDX spectra of NCCFs with *in situ* generated CuNPs using 1 mM source solution and (f) EDX spectra of NCCFs with *in situ* generated CuNPs made using 250 mM source solution.

positions. The main common peaks in the matrix and the NCCFs at 2θ= 14.6°, 16.5° and 22.6° arose due to the reflections from (110), (110) and (200) planes of cellulose-I structure[10,11]. The other weak peak at 2θ=34° arose due to the reflections from (004) plane of cellulose. In addition to these main peaks, there exist very faint peaks which are obscured by the intense main peaks. In order to observe these masked peaks, as an example, the diffractogram of the NCCFs with *in situ* generated CuNPs using 250 mM source solution was expanded in the 2θ= 35° to 80° and presented in Fig. 4 (b). From Fig. 4(b), the peaks observed at 2θ=42°, 49.8° and 74° correspond to the reflections from (111), (200) and (220) of CuNPs[12,13]. Besides these, the bands observed at 2θ=37° and 61.3° belong to the reflection from (111) and (220) planes of Cu_2O nanoparticles[14]. Thus the NCCFs had both CuNPs and Cu_2O NPs. This is understandable as some of the CuNPs have been oxidized to Cu_2O NPs and Cu is a good oxidizing agent. Similar observation was made by[15].

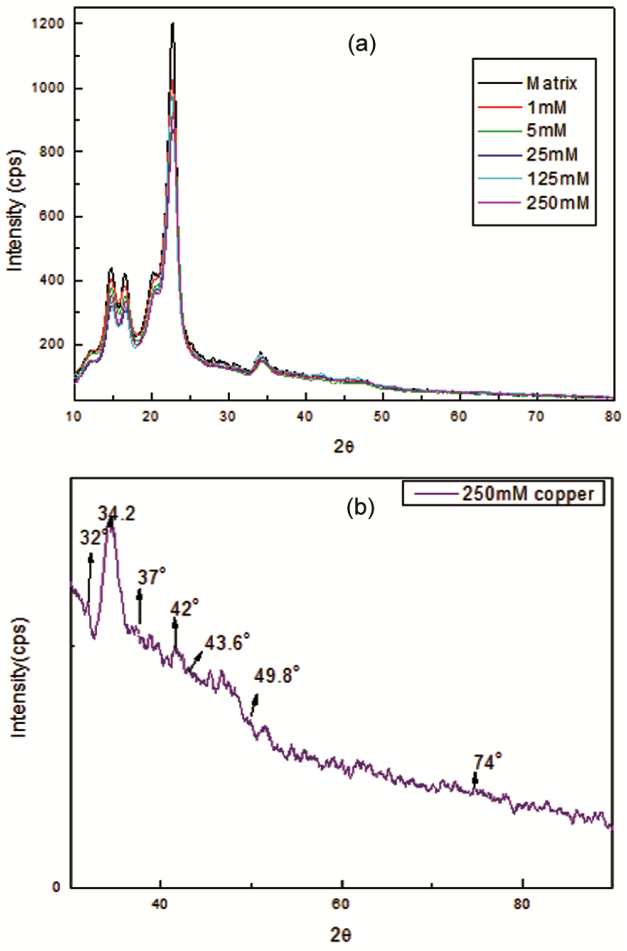

Fig. 4 — X-ray diffractograms of the matrix and the NCCFs with *in situ* generated CuNPs using (a) 1, 5, 25, 125, 250 mM source solutions and (b) expanded diffractogram of the NCCF with *in situ* generated CuNPs using 250 mM source solution in 2θ= 35° to 80°.

Thermogravimetric analysis

In order to study the effect of the generated CuNPs on the thermal stability of the NCCFs, the thermogravimetric analysis has been carried out. The derivative thermograms of the matrix and the NCCFs using 1, 5, 25, 125 and 250 mM source solutions are presented in Fig. 5.

From Fig. 5, it can be seen that the inflection temperatures (temperatures where the degradation rate is maximum) of the matrix and the NCCFs with *in situ* generated CuNPs using 1, 5, 25, 125 and 250 mM source solutions were found to be at 368, 361, 355, 349, 336 and 316°C respectively. This clearly indicates that the thermal stability of the NCCFs was lowered by the generated CuNPs. This may be due to the lowering of the crystallinity of the NCCFs by the generated CuNPs as revealed by the X-ray analysis. Similar observation was made in the studies by Sadanand *et al.* [9].

Antibacterial activity

To examine the antibacterial activity of the NCCF with *in situ* generated CuNPs the test against the gram negative (*E. coli* and *P. aeruginosa*) and gram positive (*S. aureus* and *B. subitilis*) was conducted employing the different concentrated source solutions 1, 5, 25, 125, 250 mM.

Using Fig. 6 (a-d), the diameters of zones of clearance were measured and the values are presented in Table 2.

From Fig. 6 and Table 2, it is evident that both the white cloth and matrix did not form any clear zones

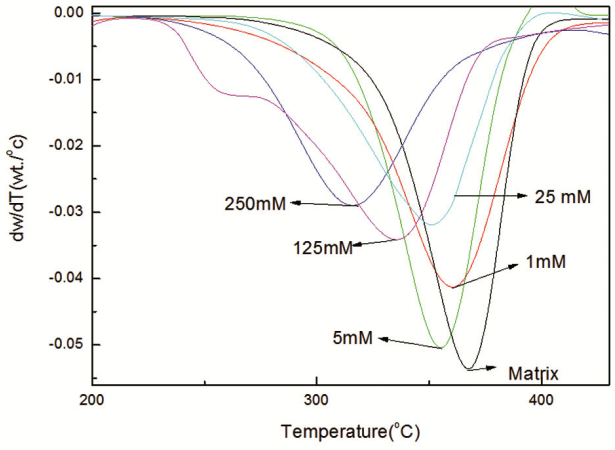

Fig. 5 — Derivative thermograms of matrix and the NCCFs prepared using 1, 5, 25, 125 and 250 mM source solutions.

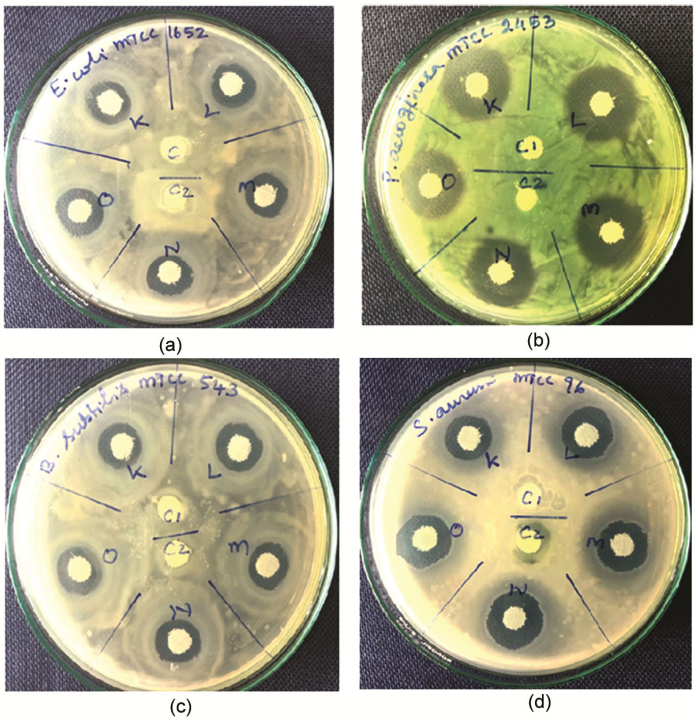

Fig. 6 — (a) *E. coli* MTCC 1652; (b) *Pseudomonas aeroginosa* MTCC2453; (c) *Bacillus subtilis* MTCC 543 and (d) *Staphylococcus aureus* MTCC96.

Table 2 — Diameters of zone of inhibition for white cloth, matrix and the NCFs made using 1, 5, 25, 125 and 250 mM source solutions against different bacteria.

Sample	Diameter of the Zone of Inhibition (nm)			
	E. coli (mm)	*P. aeruginosa* (mm)	*B. subtilis* (mm)	*S. aureus* (mm)
White cloth (C1)	0	0	0	0
Matrix (C2)	0	0	0	0
1mM (K)	19	27	17	20
5mM (L)	18	30	18	21
25 mM (M)	18	29	15	24
125 mM (N)	19	27	17	21
250 mM (O)	21	27	18	22

indicating their inability to inhibit the growth of the bacteria. However, the NCCFs with in situ generated CuNPs formed clear inhibition zones with diameters ranging from 15 to 30 mm indicating their effective antibacterial activity. Hence these NCFs with in situ generated CuNPs employing lemon leaf extract as a bioreductant can find applications as antibacterial apparels and hospital bed materials.

Conclusion

The studies of XRD, SEM with EDX confirms nanocomposite cotton fabrics with *in situ* formed Cu nanoparticles by lemon leaf extract as bioreductant. The FTIR spectra of matrix and the NCCFs are similar except intensity changes between the spectra of the matrix and NCCFs. The CuNPs formed in NCCFs are with size between 51 to 60 nm. The NCCFs have shown good antibacterial activity against gram positive and gram negative and these NCCFs with *in situ* generated CuNPs employing lemon leaf extract as a bioreductant can find applications as antibacterial apparels and hospital bed materials. These NCCFs can be considered as potential antibacterial medical fabrics and aprons.

Acknowledgement

The authors are profusely thankful to the Department of Physics, UCE(A), Osmania University for providing research lab.

References

1 Murugan E & Yogaraj V, *Adv Mat Proc*, 2 (2018) 247.
2 Santhoshkumar S & Murugan E, *Dalton Trans*, 50 (2021) 17988.
3 Murugan E, Santhosh Kumar S, Reshna K M & Govindaraju S, *J Mater Sci*, 54 (2019) 5294.
4 Murugan E, Gopinath P, Shanmugayya V & Mathivanan N, J *Appl Poly Sci*, 117 (2010) 3673.
5 Daisy P, Jasmine R, Ignacimuthu S & Murugan E, *Phytomedicine*, 16 (2009) 252.
6 Geetha T S & Geetha N, *IJPRIF*, 6 (2014) 521.

7 Singhal G, Bhavesh R, Kasariya K, Sharma A R & Singh R P, *J Nanopart Res*, 13 (2011) 2981.
8 Mohamed Rehan, Hamada M Mashaly, Salwa Mowafi A, Abou El-Kheir & Hossam E Emam, *Dyes Pig,* 118 (2015) 9.
9 Sadanand V, Rajini N, Rajulu A V & Satyanarayana B, *Carbohydr Polym*, 150 (2016) 32.
10 Yogaraj V, Gowtham G, Akshata C R, Manikandan R, Murugan E & Arumugam M, *J Drug Deliv Sci Technol*, 58 (2020) 101785.
11 Khan S, Ul-Islam M, Khattak W A, Ullah M W & Park J K, *Carbohydr Polym*, 127 (2015) 86.
12 Murugan E, Akshata C R, Yogaraj V, Sudhandiran G & Babu D, *Ceram Int*, 48 (2022) 16000.
13 Ashok B, Hariram N, Siengchin S & Rajulu A V, *J Bioresour Bioprod*, *5* (2020) 189.
14 Sachin S, Sawant, Ashok B, Bhagwat, Chandrashekar M & Mahajan, *J Nano Electron Phys*, 8 (2016) 01036.
15 Phuthotham M, Siengchin S, Ashok B & Rajulu A V, *Mater Res Exp*, 7 (2019) 015010.