Demonstration of Enhanced Thermal Stability, Dielectric Constant and Low Tangent Loss by Particle-Reinforced Silver/poly (Vinylidene Difluoride) Polymer Nanocomposites

Manoranjan Behera 1,*, Susanta Kumar Biswal 2, Mohammed A Ahemad 2, Bhabani Shanker Panda 2

1 Silicon Institute of Technology, Bhubaneswar, India
2 Department of Chemistry, Centurion University of Technology and Management, Odisha, India
* Correspondence: manoranjan@silicon.ac.in;

Abstract: Silver (Ag)/poly (vinylidene fluoride) (PVDF) polymer nanocomposite films consisting of Ag nanoparticles (NPs) in the concentration range 10-50 mM were developed by a solution casting route. FTIR spectra reveal the interaction between the fluorine atom of PVDF and Ag NPs. FTIR spectra hint at a weak interaction held between NPs and the polymer. XRD pattern suggests that Ag NPs are crystalline. The characteristic diffraction peaks were observed at 38.4°, 46.3°, 64.7°, and 78.12° in the 2θ range 10–80°. These peaks were indexed as the (111), (200), (220), and (311) planes of face-centered cubic (fcc) Ag-crystal, respectively. TGA study confirms enhancement in the decomposition temperature of PVDF polymer upon addition of NPs with a percolation threshold at 20 mM Ag NPs. SEM images show that NPs are well embedded in PVDF matrix and needle-shaped diameter in the ranges 100-200 nm. A study of dielectric properties using LCR meter suggests that the dielectric constant of the as-synthesized PVDF film has increased up to 50 upon addition of Ag nano-fillers (50 mM) to the PVDF polymer matrix. Our results suggest that nanocomposite film containing 20 mM Ag NPs can be efficiently used for high-temperature charge storage applications.

Keywords: polymer nanocomposites; poly(vinylidene difluoride); nanoparticles; thermal stability; charge storage; dielectric constant; tangent loss.

1. Introduction

Modifications in the properties of polymers can be done by adding filling agents in various proportions to it. When fillers like metals, metal oxides, carbons, etc., are added to polymers (thermoplastic/thermosetting/elastomers), it results in composites. We call it polymer nanocomposites (PNCs) when filling agents are in the nano-scale range (1-100 nm). The introduction of nanomaterials into a polymer causes the exhibition of entirely novel properties by the PNCs. PNCs show enhanced properties such as electrical conductivity, insulating behavior, elasticity, greater strength, barrier, and greater reactivity-characteristics that cannot be demonstrated either at the micro- or macroscale or by polymer itself. It also makes the PNCs easily extruded or molded. The properties of a PNC depend on many parameters like size, concentrations, shape, distributions of the filler, and interfacial interaction between matrix and reinforcing agent. PNCs exhibits remarkable enhancement in properties like a mechanical, gas barrier, charge storage, thermal, electrical, magnetic, etc., if we compare to conventional...
composites. PNCs with elevated dielectric constant, high thermal stability and little dielectric loss are of paramount importance to be used as capacitors, sensors, and actuators [1-6]. PNCs are synthesized either by in-situ or ex-situ route. Some of the important synthetic routes are the sol-gel process, intercalative polymerization, direct mixing, etc. [3-6].

In this study, we have chosen poly (vinylidene difluoride) PVDF polymer as matrix material and silver (Ag) nanoparticles (NPs) as filling material in developing PNCs. Amongst many polar polymers, PVDF stands unique due to its excellent piezoelectric properties, semi-crystalline nature, high permittivity, low dissipation factor, the exhibition of enhanced sensing properties upon doping with nanofillers, and low acoustic impedance, which match with water or many living tissues [1-4]. The properties like highly non-reactivity, water insolubility, stimuli responsivity, ease of processability, good thermal and mechanical property make this polymer unique. This polymer is used in various applications such as actuators, sensors, and transducers [5, 6-10]. Though it exists in many crystalline forms, the polar β-phase, in particular, is the most pertinent for sensible applications [4-10]. When metal NPs like Ag, Au, Cu, etc., are added to the polymer matrix, it increases the matrix's electrical conductivity. However, Ag NPs are widely used as nanofillers due to their implementation in various novel applications in print media, image technology, sensing, catalysis, bioengineering, photovoltaics, and nano-electronics [11-13].

Kumaran et al. [11] have studied the Ag NPs induced Electromagnetic Interference (EMI) shielding in Ag-PVDF PNC films. They reported that upon addition of Ag NPs, the conductivity values of PNCs are increased up to 2.5 times compared to neat PVDF having a value of 2.70 S/cm at 1MHz. An enhancement in the dielectric constant value and decrease in the dielectric loss for the PNC film was reported by them. The EMI shielding effectiveness of the composites is 29.1 dB at 12.4 GHz for the two samples, a sample having 5 wt. % Ag and another of 10 wt % graphite in PVDF. Liu et al. [15] developed and fabricated Ag (0.5–2%)-PVDF) PNCs and studied their tensile properties, wetting, antifouling characteristics. They have reported that both elastic modulus and tensile strength have improved remarkably upon the addition of NPs into it. They studied antibacterial activities of the PNCs against gram-negative and Gram-positive bacteria. Liu et al. [16] studied the dielectric property of BaTiO₃ nanofiber-Ag-PVDF hybrid PNCs. Due to nanomaterials' doping, the dielectric constant and energy storage density of PNCs has increased drastically. Audoit et al. [20] studied electrical bulk. The surface conductivity of the Ag-PVDF PMCs containing filler concentration varies between 4–20 vol %. They observed electrical percolation and were found at 5.9 vol.% for bulk conductivity and 6.9 vol.% for surface conductivity.

In this article, we discussed the synthesis of Ag NPs using raw fruits of the Bokul tree (Mimusops elengi, L.). We are the first to report on this. Then we discussed the development of PVDF/Ag PNCs via a solution casting route. The developed PNCs films were then characterized using various instrumental techniques like UV-Visible & FTIR spectrophotometer, XRD, TGA- thermal analyzer, SEM, and LCR meter.
2. Materials and Methods

2.1. Methods of development of PVDF/Ag PNCs.

2.1.1. Preparation of PVDF solution.

At first, 3.0 g of PVDF polymer of average molecular weight 5,30,000 was dissolved in 100 mL of N,N-Dimethyl Formamide (DMF) solvent. Then the mixture was placed in a hot magnetic stirrer maintained at 60 °C. Then the mixture was stirred for 2 h to get a homogeneous polymer solution. The two chemicals procured were from the Sigma-Aldrich industry and used as received in developing PNCs.

2.1.2. Preparation of plant extract.

We had collected raw fruits of a matured Bakul tree (Mimusops elengi, L.) found on the campus of Silicon Institute of Technology, Bhubaneswar, Odisha, India. Then, 8.1 g fruits were weighed and immersed in a beaker containing 100 mL of deionized water (i.e., 81 mg/L) and then placed in a hot magnetic stirrer plate maintained at 100 °C for 1.5 h. During the heating process, the beaker was covered with a watch glass to avoid loss of water. The aqueous extract was filtered using Whatman 42 paper (2.5 µm) and stored in a refrigerator maintained at ~10 °C. The extract is colorless/slightly milky to naked eyes.

2.1.3. Synthesis of Ag NPs.

10 mL of Mimusops elengi, L. aqueous extract solution, was taken in a 50 mL beaker and placed in a hot magnetic stirrer maintained at 70 °C. Then 1 mL of 32 mM aqueous silver nitrate solution was added to it drop-wise using a micro-pipette. The formation of Ag NPs was indicated by the formation of a chocolate color solution. So far as our knowledge and intensive literature study is a concern, to date, no one has used Mimusops elengi, L. raw fruits extract in synthesizing Ag NPs in an aqueous medium. We have prepared Ag nanocolloids of various concentrations (i.e., 10 mM, 20 mM, 30 mM, 40 mM, and 50 mM Ag NPs) in an aqueous fruit extract.

2.1.4. Development of PNC film.

10 mL of PVDF solution in DMF was taken in a 50 mL beaker and placed in a magnetic stirrer maintained at 30 °C. Then 1 mL of Ag nanocolloids was added drop-wise using a micro-pipette to the PVDF solution under stirring conditions. The stirring was done for 20 min, and then the mixture was poured into a Petri-dish and then placed in a hot plate maintained at 60 °C for 1 h to develop PNC film. In this manner, we have developed five PNC films of different Ag contents.

2.2. Experimental measurements of PNCs.

After developing PNC films, we characterized our samples using various instruments like UV-Visible spectrometer, FTIR Spectrometer, X-ray diffractometer, scanning electron microscopic, thermal analyzer, and LCR meter. For collecting absorbance Vs. wavelength data for all the prepared samples, we used a UV-Visible spectrometer (Model-Perkin-Elmer Lambda 750 spectrophotometer). Perkin-Elmer FTIR Spectrometer (Spectrum 65) was used in collecting the FTIR data in the wavenumber region (400 to 4000 cm⁻¹). An X-ray diffractometer
(PHILIPS model PW-1710) was used to know about crystalline nature. To prepare the sample for XRD, we have taken a quartz substrate and then fixed the PNC film onto it. CuKα target was used in this instrument. We studied scanning electron microscopic (SEM) images of selective samples of PNC films. Oxford model Leo1550 VP SEM was used to take the images. While taking the images, the accelerated voltage was fixed between 2-10 kV ranges. Perkin-Elmer model DT-40, Shimadzu Co. Japan thermal analyzer was used to study its thermal stability. We have varied the frequency ‘f’ between 100 Hz - 5 MHz. The dielectric constant (ε) data were collected at room temperature. We have used a HIOKI 3532 50LCR HiTESTER LCR meter for the same.

3. Results and Discussion

3.1. Study of UV-Visible and FTIR spectra.

UV-Vis optical absorption spectra in 200–900 nm wavelength regions were studied by us to corroborate the formation of Ag NPs in the PVDF-Ag PNCs film at RT. The absorption spectra of five PNCs consisting of (a) 0.0, (b) 10, (c) 20, (d) 30, and (e) 50 mM Ag NPs were shown in Fig. 1. We observed two absorption bands in the spectrum. One intense band is observed near 200 nm, and it is from the PVDF polymer [1,5]. Another broadband near 450 nm is ascribed to the surface Plasmon resonance (SPR) band [16,17]. It is well known that SPR band is observed only for NPs [17-24]. It is also observed from the plot that with increasing the Ag-content, the intensity of SPR band is increasing due to many NPs. The SPR band (as shown in Fig. 2A.) is shifting to a higher wavelength side with increasing Ag-content. A red-shift of band occurs when the size of the nano-cluster increases [17]. Red-shifting of SPR band also indicates non-spherical (plate-like or needle shape morphology) NPs [18]. In a PNC, if there will be an increase in the Ag content, then definitely there will be a decrease in the relative number of PVDF molecules.

![Figure 1](image1.png)

**Figure 1.** (A) The UV-Vis spectra of PNCs consisting of (a) 0.0, (b) 10, (c) 20, (d) 30, and (e) 50 mM Ag NPs.

![Figure 2](image2.png)

**Figure 2.** (A) Shows the SPR band in PNCs and (B) Variation of absorbance of SPR band with Ag-content.
When the concentration of encapsulating agent (PVDF) will decrease, it will cause the particle to increase their size. The intensity of the band near 198 nm is also increasing with increasing NP content. It suggests NPs help the PVDF polymer absorb UV light strongly in this low wavelength region [1]. This characteristic is important for an industrial application like UV-light protection. We also studied the variation of absorbance value of SPR peak at 400 nm against Ag content (Fig. 2B). A nonlinear variation between two parameters was observed with a percolation threshold at 20 mM Ag. A nonlinear variation between absorbance and NPs content is a signature of donor-acceptor type interaction between the polymer and NP [25-27].

We studied FTIR spectra (shown in Fig. 3) of five films consisting of (a) 0, (b) 10, (c) 20, (d) 30, and (e) 50 mM Ag NPs. We compare the FTIR bands of pure PVDF with bands obtained after incorporating Ag NPs into PVDF matrix. This study helps the researcher in identifying the role of the polymer as a capping agent. The various FTIR bands of neat PVDF polymer shows bands at 3350 cm\(^{-1}\), 3020 cm\(^{-1}\), 2925 cm\(^{-1}\), 1400 cm\(^{-1}\), 1430 cm\(^{-1}\), 1450 cm\(^{-1}\), 1330 cm\(^{-1}\), 1175 cm\(^{-1}\) and 675 cm\(^{-1}\). The band at 3350 cm\(^{-1}\) is from O-H stretching vibration [27-29]. The bands at 3020 cm\(^{-1}\) and 2925 cm\(^{-1}\) are from C-H stretching vibrations. The bands at 1400 cm\(^{-1}\) and 1175 cm\(^{-1}\) comes from C-F stretching. CH\(_2\) bending vibration occurs at 1430 cm\(^{-1}\). The bands at 1450 cm\(^{-1}\), 1175 cm\(^{-1}\) and 675 cm\(^{-1}\) bands are from polymer chain defect [1,7,20,28-30]. In the presence of Ag NPs, it is observed that the intensity of some of the selective vibrational bands (i.e., C-H\(_2\) bending) has increased drastically. Even some band (i.e., C-H\(_2\) bending) shifts from their original position. An increase in band intensity and shifting of the band suggests some interaction occurs between NPs and F-atoms of PVDF polymer [20,22-25]. Introduction of NPs into the PVDF polymer results in the formation of \(\beta\)-phase as it induces electrostatic interaction between NPs and the polymer (the >CF\(_2\) dipole). It causes the PVDF chain to be straightened and helps in acquiring a zigzag conformation of \(\beta\)-polymorph. Otherwise, it may adopt coiled TGTG conformation that leads to the formation of PVDF \(\alpha\)-phase [31].

![Figure 3. The FTIR spectra of PNC films consisting of (a) 0, (b) 10, (c) 20, (d) 30, and (e) 50 mM Ag NPs.](https://biointerfaceresearch.com/)

### 3.2. Study of XRD patterns, thermo-grams, and SEM images.

The XRD pattern (shown in Fig. 4) was studied to confirm the electroactive PVDF phase in the film. It also helps in knowing about the crystalline nature & presence of Ag NPs in the PNC. The XRD pattern of undoped PVDF shows that PVDF is crystalline in nature with \(\alpha\)-phase in DMF solvent. The peak at 18.5\(^0\) from (202) plane suggests the formation of only [5,31]. In a sample consisting of 10 mM and 20 mM Ag NPs, the XRD patterns contain peaks from the \(\beta\) phase of PVDF and Ag NPs. The peak at 20.8\(^0\) is from (200) plane of \(\beta\) phase as per JCPDS File No: 38–1638 [1,11]. The diffraction peaks were observed at 38.12\(^0\), 44.3\(^0\), 64.4\(^0\),...
and 77.4° match with a cubic phase of Ag (JCPDS File No: 89-3722). These peaks corresponded to (111), (200), (220), and (311) peaks of crystallite fcc Ag NPs present in the PVDF matrix, respectively [11,19,32,33]. Presence diffraction peaks of both electroactive PVDF phase in Ag NPs suggest that NPs are helping the polymer convert α to β-phase. The electroactive PVDF phase in PNC enhances the dielectric properties of the PNC film.

**Figure 4.** XRD patterns of (a) PVDF; (b) PVDF-Ag film with 10 mM Ag NPs; and (c) PVDF-Ag film with 20 mM Ag NPs.

We study the thermograms to get information about the thermal stability of our developed PNC films. Fig. 5A shows the variation of weight loss (%) against neat PVDF and PNC films’ temperature. The thermograms show that samples were thermally stable in the temperature ranges 50-400 °C. PVDF starts degrading (T onset) at 430 °C and it continue upto 600 °C. The pure PVDF showed 80 % weight loss and measured temperatures, whereas PNCs showed relatively less (~70 %). For PNC films, the onset of degradation temperature has increased from 430 °C (neat PVDF) to 480 °C for a PNC film containing 50 mM Ag NPs and reached a maximum at 20 mM Ag doping to PVDF polymer. This suggests that NPs are helping the polymer to withstand high temperatures. This is due to strong interfacial interaction between needles shaped Ag NPs of high surface area and PVDF polymer (see SEM images). This kind of particle reinforced nano-composites exhibits high strength because of the enhanced thermal stability. This conclusion is further strengthened by the FTIR and XRD study that the formation of highly polar β-PVDF phase in the PNC film helps enhance the packing density of NPs in PVDF matrix and hence increasing the thermal stability [31]. We also studied the variation of decomposition temperature against the Ag content (Fig. 5B). The decomposition temperature varies non-linearly with Ag content with a percolation threshold at 20 mM Ag. This result implies that PNC with 20 mM Ag content has a relatively uniform distribution of Ag needles in the PVDF matrix and an intertwined structure.

**Figure 5.** (A)Thermo-gravimetric analysis of neat PVDF and PVDF with Ag NPs: (a) PVDF, (b) PVDF with 10 mM Ag NPs, (c) PVDF with 20 mM Ag NPs and (d) PVDF with 50 mM Ag NPs; (B) Variation of decomposition temperature Vs. Ag content.
There is a nearly 80% weight loss for neat PVDF in the temperature range 436 to 510°C, as reported by Al Hazmi et al. [31]. In the presence of 5 wt% Cu₂O, the weight loss rate has decreased to 60% in their sample. “They reported that the improvement of the thermal stability in PNC films is due to the incorporation of the Cu₂O NPs in the PVDF and efficient packing of the polar crystalline β-phase in the nanocomposites”. “Campos et al. [34] have also reported that due to incorporation of CaCO₃ particles into PVDF matrix, the thermal stability of PNC film has increased drastically”. In our case, we found that nearly 80% weight loss occurs for the neat PVDF in the temperature range 440 to 550°C. The weight loss rate has decreased to 70% for PNC film containing 50 mM Ag NPs with 3 wt% PVDF. Fakhri et al. [35] have studied the thermal stability of PVDF-Cu PNCs. They reported onset degradation temperature, T onset, as 490°C for neat PVDF, while the introduction of the NPs has slightly increased the onset degradation temperature. “In case of 0.5 GO/Cu-PVDF, 1.0 GO/Cu-PVDF and 5.0 GO/Cu-PVDF, the degradation temperature onset shifted to 491, 496 and 492°C respectively, while the degradation temperatures for PNC containing GO/Cu were reported to be 494°C, 499°C and 501°C for PNCs filled with 0.5, 1.0% wt and 5.0%wt., respectively” [35]. Better packing of the polar crystallites in β-PVDF composites in the presence of NPs as compared to the non-polar α-phase of neat PVDF is the main reason for exhibiting superior thermal stability of these PNCs films.

Yang et al. [36] have reported an energy density of 9.3 J/Cm³ in Niobium-Barium Titanate (NBT) doped PVDF with a loading of 2.5% NBT. It is reported that carbon nanotube-barium titanate doped PVDF exhibits excellent dielectric and thermal behavior [37]. Sahoo et al. [38] have suggested that the exhibition of improved dielectric and ferroelectric behavior by Fe-doped ZnO/PVDF-TrFe polymer nanocomposite is due to the reduced crystallite size of NPs. Chen et al. [39] have reported that enhancement in the thermal conductivity and dielectric breakdown strength of PVDF upon incorporating boron nitride nano-sheets is due to good interface compatibility between the two phases. Incorporation of Ag-coated clay results in the enhancement of the dielectric strength and the breakdown strength as a result of more interfacial polarization [40]. It is reported that doping of Au-decorated Barium Titanate NPs in PVDF polymer results in enhancing the dielectric constant of the polymer [41].

SEM images give information about the morphology, size details, and size distribution of the NPs. Fig. 6 depicts SEM images of PNC films contacting AgNPs (A) 10, (B) 20 mM Ag, and (C) 50 mM Ag NPs with 3.0 g/L PVDF. From Fig. 6A, it is found that the Ag-NPs were crosslinked by PVDF polymer. Images show that particles are needle shape, and their average diameter lies between 100-150 nm.

**Figure 6.** SEM image of PVDF-Ag films containing (A) 10, (B) 20, and (C) 50 mM Ag NPs.
The size distribution for a PNC having 20 mM Ag content is seen to be almost uniform. Kumaran et al. [11] have reported that in Ag/Graphite/PVDF PNC film, Ag-NPs of size 10-20 nm were embedded uniformly. Audoit et al. [20] have reported Ag microplates (1.15 µm) of various morphologies that were uniformly embedded in a PVDF matrix. As the Ag-content has increased from 10 mM to 50 mM, the diameter of NPs has increased, and agglomeration is seen (Fig. 6C).

3.3. Study of dielectric properties.

Fig. 7A shows the plot of dielectric constant against frequency for the un-doped and the Ag NPs doped PVDF PNCs consisting of (a) 0, (b) 10, (c) 20, (d) 30, and (e) 50 mM Ag NPs at room temperature. For PVDF polymer, the variation of dielectric constant against frequency was found to be almost constant. For all the PNCs films, the dielectric constant decreases with frequency due to decreased dipolar contribution at higher frequencies or due to slow relaxation of interfacial polarization [14,19,42,43]. Chandraprabha et al. [38] had reported a similar cause for a decrease in dielectric constant with frequency in polythiophene-cobalt polymer nanocomposites. It is seen from the plot that an enhancement in the dielectric constant of Ag/PVDF PNCs was seen as compared to the virgin PVDF. The neat PVDF showed a dielectric constant value of 8 at frequency 100 Hz, while that of a PNC film consisting of 50 mM Ag NPs has exhibited a dielectric constant around 50 at the same frequency. It is reported that the inclusion of conducting fillers in a polymer matrix causes an enhancement in dielectric constant value [4]. This enhancement in the dielectric constant value is nearly 6 times. This prominent enhancement is due to the formation of a network of micro-capacitors in PVDF matrix due to many Ag NPs [44-47]. This resulted in Maxwelle-Wagnere-Sillars (MWS) polarization effect [19,31,35,45-47]. This MWS effect causes trapping of free charges along the interface between the PVDF and Ag NPs, and thereby, a significant enhancement of the dielectric constant was achieved [31,35,47].

Chen et al. [47] have reported a dielectric constant value as large as 90 for Ag coated TiO$_2$-PVDF nanocomposite at 100 Hz. Liu et al. [48] have reported a dielectric constant 100 for (Barium Titanate nanofibre-Ag) doped PVDF PNC at 100 Hz. As we have already mentioned in the previous section, the inclusion of Ag NPs into the PVDF matrix causes phase transition of PVDF from non-polar $\alpha$-phase to polar $\beta$-phase. It is reported that the $\beta$-phase of PVDF plays a vital role in improving the dielectric constant in the PNCs compared to the neat PVDF [35-47].
Fig. 7B illustrates the variations of dielectric constant as a function of different concentrations of Ag NPs in PNCs at room temperature. The dielectric constant value varies non-linearly with NP-contents with a percolation threshold at 20 mM Ag NPs. It is found from the figure that the dielectric constant value increases with Ag content up to 20 mM and then decreases with an increase in NP content. There is a decrease in the dielectric constant value beyond 20 mM Ag due to interfacial defects caused by the agglomeration of NPs (see FESEM image, Fig. 6C) [49-51]. Moharana and Mahaling [49] have reported a similar behavior between these two parameters for bismuth ferrite doped polystyrene nanocomposites.

Fig. 8A shows the variation of dielectric loss against frequency for various Ag/PVDF PNCs consisting of (a) 0, (b) 10, (c) 20, (d) 30, and (e) 50 mM Ag NPs at RT. It is observed that dielectric loss in PNC films is less than neat PVDF at 500 Hz. For sample-b & c, the dielectric loss increases with frequency. However, for sample-d & e, it is fast increasing and then decreasing with frequency. For samples, b & c, an increase in dielectric loss with increasing frequency is due to the polymer's glass transition relaxation [52].

![Figure 8. (A) Variation of tangent loss against frequency of PNC consisting of (a) 0, (b) 10, (c) 20, (d) 30, and (e) 50 mM Ag NPs at RT. (B) Variation of tangent loss against NP-contents at 1000 Hz.](image)

We also studied the variation of dielectric loss against Ag NPs content for PNCs at RT. From Fig. 8B it is observed that dielectric loss is lowest for the PNC containing 20 mM Ag NPs. This may be ascribed to the agglomeration of Ag NPs in the polymer matrix (see SEM image, Fig. 6C), which results in a decrease in the conductivity of Ag NPs [42]. It is reported in the literature that a decrease in the conductivity of Ag NPs causes hindrance of leakage current in the PNC and hence low loss [42].

4. Conclusions

For the first time, we have developed Ag NPs using an aqueous raw fruit extract of *Mimusops elengi, L.* and added them in a requisite amount to PVDF polymer solution to prepare PNCs films by a solution casting route. The developed PNCs were characterized to found that a film containing 20 mM Ag NPs with 3.0 g/L PVDF has exhibited enhanced thermal stability & dielectric strength with low dielectric loss due to the percolation effect relative to others. In particular, this PNC film has a scope to be used in high-temperature charge storage applications.

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Conflicts of Interest

On behalf of all authors, the corresponding authors (MB and SKB) states that there is no conflict of interest among the contributors.

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