Green Tea Extract Synthesized Gold Nanoparticles and Percolative Behaviour of KH₂PO₄/PVA Composite Film: A High Dielectric Material

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ABSTRACT

Gold nanoparticles (AuNPs) of about 5 nm diameter were biosynthesized at room temperature using $HAuCl_4$ as the precursor and green tea leaves extract as the reducing agent. The PVA/ KH_2PO_4 (KDP) composite film showed percolative behaviour around 2.5wt% KDP. Interestingly, addition of 0.05 wt% of AuNPs to the PVA/2.5wt%KDP percolative composite film (with percolation threshold of 2.5 wt% KDP) destroys percolative behaviour of this composite film. Furthermore, the PVA/2.5wt% KDP/0.05wt% AuNPs nanocomposite film exhibited high room temperature dielectric permittivity (ε'). High value of ε' of the films promises direct application in capacitors

Keywords- *Biosynthesis, AuNPs, Polymer nanocomposite, high dielectric*

1. INTRODUCTION

Metallic nanoparticles incorporated with polymers have attracted much attention due to their distinguishing optical, electrical and catalytic properties. Such materials have got potential applications in different fields such as bioengineering, photonics, and electronics [1]. Among various metal nanoparticles, gold nanoparticles (AuNP) are being widely used in optics, electrochemistry, catalysis, biomedicine (drug delivery etc.) and in electronic sensing devices because of its stability, less toxic and biocompatible character [2-5]. A lot of chemical and electrochemical techniques have been developed for the synthesis of AuNPs. However, in such processes creation of environmentally harmful and toxic chemicals during synthesis of AuNPs is almost inevitable. Recently, there has been renewed interest for the preparation of Au, Ag or other noble metal [6-8] nanoparticles applying the green chemistry principles [6-8]. Green chemistry becoming popular recently, which encourages the design of products and processes that minimize the use and generation of hazardous substances [9].
To address the current synthetic approaches one may include the use of environmentally benign solvents, biodegradable polymers, and nontoxic chemicals. In the synthesis of metal nanoparticles by reduction of the corresponding metal ion salt solutions, there are three opportunities to attribute green chemistry principles viz. choices of (i) solvent, (ii) reducing agent, and (iii) the capping agent (or dispersing agent) to be used. In this context, there has been increasing interest in identifying environmental friendly materials that are multifunctional. Due to high water solubility, low toxicity and biodegradability, tea (black or green) is the most widely used behaviourally active drug in the world [10]. In addition, the presence of polyphenols, catechins, flavonoids and phytochemicals in tea are responsible for the reduction of auric chloride $HAuCl_4$ to the AuNPs [11]. Recently Begum et. al.[12] have reported the synthesis of AuNPs using black tea leaves extracts but the process is more complicated and too costly as some additional chemicals such as CH_2Cl_2 extract and ethyl acetate extract were used. Moreover, very little [20] attempt has so far been made to test the possible applications of such biosynthesized naoparticles for the technological or medical implication.

For any practical application of AuNPs, it is necessary to stabilize the nanoparticles (NPs) which can be done by making a composite [13, 20]. It is well known that the high dielectric permittivity composite materials have been considered to be one of the potential candidates for integration into electronic devices. Owing to the continuous development towards the miniaturization of electronics, newer dielectric materials are sought which would enable to achieve high energy density for capacitor applications [14]. Ceramics possessing very high dielectric permittivity are being used as voltage capacitors due to their high breakdown voltages. However, they are brittle, suffer from poor mechanical strength and hence cannot be exposed to high fields. Polymer films such as polyester, polycarbonate, polypropylene and polyvinyl alcohol (PVA) are being used in the fabrication of low leakage capacitors. Though polymers possess relatively low dielectric permittivity, they can withstand high fields, are flexible and easy to process. By combining the advantages of both matrix and filler, one can fabricate

new hybrid materials with high dielectric permittivity, and high breakdown voltages to achieve high volume efficiency and energy storage density for applications in capacitors as electric energy storage devices [15,16]. Hence in order to enhance the dielectric permittivity of polymers, by the addition of inorganic nano fillers, metal nanoparticles are more attractive due to their intriguing properties arising from their size associated with large surface area. The insertion of nanoscale fillers may improve the electrical and dielectric properties of the host polymers and the properties can be tailored to a particular performance requirement [17,20]. But the final properties of a nanocomposite depend on the method of preparation, particle size and the effective dispersion of ceramic particles in the polymer matrix [18,19].

Very recently we have reported PVA/ferroelectric KDP composite films with different concentration of KDP where percolative behaviour was observed for a particular concentration (threshold value) i.e 2.5 wt% of KDP showing around 80 times increase of dielectric constant [20]. Use of such threshold value also minimizes the filler concentration which is an important criteria for the use of the threshold value in making a composite. In order to examine the effect of metal nanoparticles (Ag and AU) on the percolative character and dielectric constant of the PVA/KDP composite, our plan in this paper is to introduce AuNPs in this studied composite.

2. EXPERIMENTAL DETAILS

Auric chloride(Sigma Aldrich, USA) was used for the synthesis of AuNPs. High grade raw green tea leaves used were collected from Darjeeling (Inidia). PVA((99%) with average molecular weight of 94,000g/mol)/KDP percolative composite film with typical concentration of KDP was prepared using conventional solution castings technique used earlier [20]. For the preparation of PVA/KDP/AuNPs nanocomposite films with various concentrations of AuNPs, three step processes have been followed. In the first step for the synthesis of AuNPs, 2 g of tea leaves was boiled in 100 ml of water and filtered through a 25 ml Teflon filter. The tea extract of 80 ml obtained was then allowed to settle at room temperature (300 K). 10^{-3} M of $HAuCl_4$ salt was dissolved in 50 ml de-ionised (DI) water in a separate beaker. Requisite amount of $HAuCl_4$ solution was then added drop by drop with 10 ml of tea extract. The mixture was then shaken to ensure homogeneous mixing. It was noticed that the colour of the resulting mixture changed from light brown to black within 1 min, indicating the formation of AuNPs, which were not stable. In the second step, 10 g of PVA powder was dissolved in 200 ml DI water in a separate beaker at $80^{\circ}C$ for 3 hours by constant stirring to form homogeneous mother solution. 2.5 wt% KDP (of 1 g PVA) was then added into 20 ml PVA solution (taken from mother solution) and the resulting mixture was stirred for 1h at $80^{\circ}C$. So that PVA/2.5 wt% KDP composite solution is obtained. In the third step, AuNPs were stabilized by adding AuNPs solution into 20 ml PVA/2.5 wt% KDP solution and the final resulting mixture was stirred for

further 1h at $80^{\circ}C$ to ensure uniform and homogeneous composition. In the similar manner the nanocomposite solution with different concentration of AuNPs 0 to 0.05 wt% (keeping amount of tea extract constant in each case, only concentration of $HAuCl_4$ solution changes) were made. Finally, the nanocomposite solutions were then poured into plastic petridishes for few days for air drying at room temperature (300 K). The films each of uniform thickness (~ 200 μm) thus obtained were named as PVA/KDP/AuNPs nanocomposite films.

The x-ray diffraction (XRD) pattern of PVA/2.5 wt% KDP composite film and PVA/2.5 wt% KDP/AuNPs nanocomposite film were performed with SEIFERT XRD 3000P Diffractometer using CuK$_\alpha$ radiation. The grain morphology of the polished surfaces of composite and nano-composite samples was examined by Field Emission Scanning Electron Microscopy. For the determination of the size of AuNPs HRTEM (Model JEM-2010, JEOL) measurements were carried out. FTIR spectroscopy study of nanocomposite film was carried out using SHIMADZU-8000 spectrometer in the range 400–4000 cm^{-1}. The percentage weight loss and melting temperature (T_m) of different samples were obtained from TGA and DSC measurements using a MAS-5800, model DSC 200 differential scanning calorimeter. Dielectric permittivity measurements were performed using HP4192A Impedance Analyzer and with a homemade liquid nitrogen cryostat in the temperature range 200–340 K.

3. RESULTS AND DISCUSSIONS

Figure 1(a) shows the presence of number of peaks for a typical concentration (2.5 wt %) of KDP which indicates that at this typical concentration, the grains of KDP are sensitive and highly oriented within the PVA matrix. Figure 1(b) shows many peaks corresponding to diffraction by (111), (200), (220) and (311) planes confirms the presence of crystalline AuNPs that tack on the broad peak due to the polymer structure indicate that the particles are face-centred cubic (fcc) crystallites [21]. Also when 0.05 wt% AuNPs were embedded in PVA/2.5 wt% KDP film, the intensity of the peaks increased greatly, implying that the crystalline behaviour of PVA was increased.
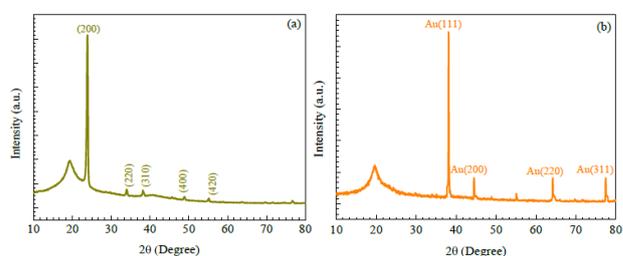

Fig.1 XRD patterns of (a) PVA/2.5 wt% KDP composite film and (b) PVA/2.5 wt% KDP/0.05 wt% AuNPs nanocomposite film.

Figure 2(a) shows the FESEM micrograph of PVA/2.5 wt% KDP composite film which shows a network formed by KDP grains that get self connected within the PVA

matrix for a typical concentration i.e. 2.5wt% of KDP. Figure 2(b) displays the energy dispersive X-ray (EDX) spectra of PVA/KDP percolative composite film of the same sample for which FESEM [fig.2(a)] has been done indicates the presence of peak of expected elements C, O, P and K etc. On the other hand, figure 2(c) represents the FESEM micrograph of PVA/2.5wt% KDP/0.05wt% AuNPs nanocomposite film which shows the presence of many clusters of AuNPs. It is noticed that the network formed by the KDP grains get almost destroyed due to the influence of 0.05wt% AuNPs. The morphological changes along with the other features strongly suggest that the growth of inorganic crystals is largely influenced by the organic macromolecules that are present during their formation. This can be attributed to the chemistry at the inorganic organic interface during the nucleation and growth of the particles.
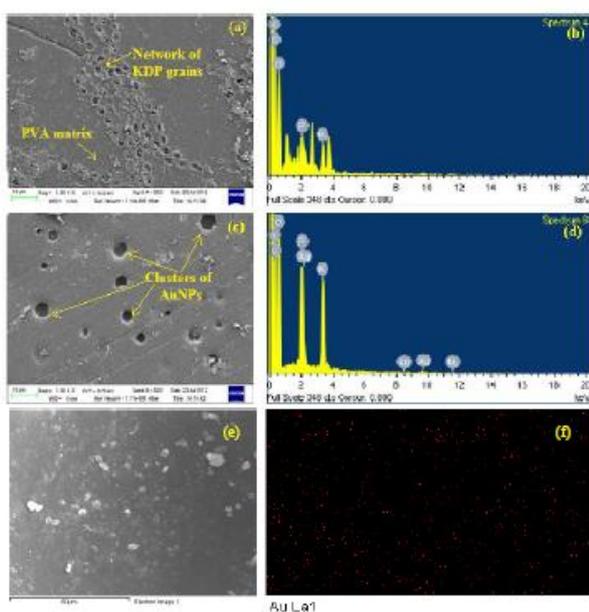

Fig.2 (a & b) FESEM micrograph and EDX spectra of PVA/2.5 wt% KDP composite film respectively. (c & d) FESEM micrograph and EDX spectra of PVA/2.5 wt% KDP/0.05 wt% AuNPs nanocomposite films and (e & f) FESEM micrograph of same area of the sample for which EDX has been done in (d) and CAI analysis of AuNPs of the sample taken for (d).

Figure 2(d) shows the EDX spectra of KDP/PVA/AuNPs nanocomposite film which indicates the presence of peak of all expected elements C, O, P, K and Au. The area on which the EDX study has been done is shown in the corresponding FESEM image in figure 2(e). In order to obtain quantitative information of the gold content, computer assisted image (CAI) has been displayed in figure 2(f). From the typical distributions of AuNPs within the composite film it is evident that AuNPs are distributed almost uniformly within the matrix.
The average size of biosynthesized AuNPs of about 5 nm in diameter is confirmed by HRTEM image of nanocomposite solution with 0.05 wt% AuNPs as shown in figure 3(a). Hybrid shapes of AuNPs i.e. from small nano aggregates to highly branched flower-like nanostructures was clearly seen which completely destroy the network of KDP grains. The biomolecules [11] present within tea extract interact with metal ions and serves as a reducing agent. Gold ions have a good affinity to proteins present within the tea extract. Hence, tea extract allows the tiny gold nuclei to bigger particles by fusing with another one. Figure 3(b) represents the selected area electron diffraction (SAED) pattern clearly shows the presence of sharp diffraction spots, which indicates the formation of highly crystalline AuNPs.
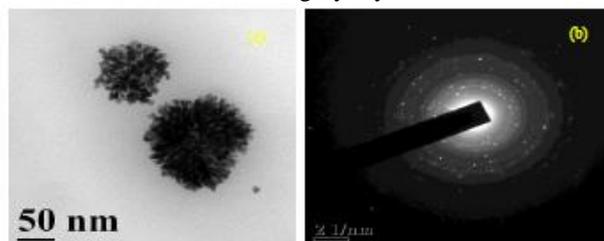

Fig.3 (a) HRTEM image and (b) SAED pattern of 2.5 wt% KDP/0.05 wt% AuNPs nanocomposite solution.

The FTIR spectroscopy for PVA, PVA/2.5wt% KDP composite and PVA/2.5wt% KDP/0.05wt% AuNPs nanocomposite films in the wavenumber region of 400–4000 cm^{-1} have been performed to understand the interaction between the inorganic fillers and the organic polymer media is shown in figure 4.

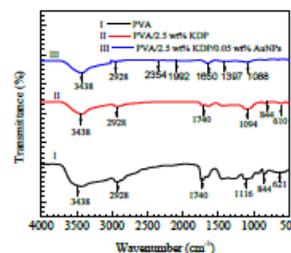
Fig.4 FTIR spectra of pure PVA, PVA/2.5 wt% KDP composite and PVA/2.5 wt% KDP/0.05 wt% AuNPs nanocomposite films.

The broad high absorption peak at 3438 cm^{-1} is assumed to arise from the O-H stretching frequencies of PVA and water hydroxyl groups. In PVA/2.5 wt% KDP composite film, peaks at 2928, 1116 and 844 cm^{-1} are attributed to the C-H stretching, C-H-O bending and C-O stretching, respectively, due to the characteristics of the KDP filler. The band at 1740 cm^{-1} is attributed to the carbonyl functional groups in the films and the intensity of this band in the composite films decreases. It is also noticed that the addition of the phosphate causes the shift of O-H bending vibration from 621 to 610 cm^{-1}. The peak at 1116 cm^{-1} assigned to C-O stretching of the secondary alcohol of PVA, is shifted to 1094 cm^{-1} in the composite film [20]. On the other hand in gold nanocomposite film, the bands at, 2354, 1952, 1650 and 1088 cm^{-1} are associated with the stretching vibrations for–C=C– [(in-ring) aromatic], –C–C– [(in-ring) aromatic], –C=C–and C–O (polyols), respectively.[12]. In particular, the 1088 cm^{-1} band arises most probably from the C–O group of polyols such as hydroxyflavones and catechins. Probably, the negatively

charged phosphate groups are not linked properly through hydrogen bonds with the positively charged domains of the polymer causes the band at 610cm^{-1} get disappeared in case of nanocomposite sample. In addition, the interactions between the potassium ions and the negatively charged functional groups of the polymeric chains like the hydroxyl groups in PVA did not appear as there is poor slight stretching in these groups as well. Thus we see that the bands appeared in pure PVA film [11] gets weakened in nanocomposite film. Another change is that the ratio of intensity decreased in the band at 1650 cm^{-1}. This suggested that very strong interaction between AuNPs and the polymer matrix took place over the –OH groups. The –C=C–C–O, C–O implying that the –OH group in PVA might be oxidized into C=O group during the reaction of Au^{III} with PVA. They themselves get oxidized to α, β-unsaturated carbonyl groups leading to a broad peak at 1650 cm^{-1} (for reduction of Au^{III}). The tentative mechanism of oxidation [22] is illustrated in Figure 5.
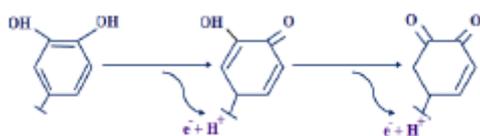

Fig.5 Scheme illustrating tentative mechanism of polyol oxidation by metal ions to α, β-unsaturated carbonyl groups.

The UV–vis spectrum of the prepared nanocomposite solution with 0.05 wt% AuNPs has been displayed in figure 6 which shows a maximum (max) at 540 nm. This peak is assigned to the surface plasmon resonance (SPR) band of AuNPs formed by the reduction of Au^{III} ions which is the signature for the AuNPs formation, apart from the color change. Our results thus demonstrate that both the tea extract and PVA are responsible for producing stable NPs by the biogenic reduction of Au^{III} ions. Moreover, the inset of figure 6 shows the formation of AuNPs via color change. Inset 6(a–c) represent the tea extract, auric chloride solution and their resulting mixture respectively. It is noticed that on adding tea extract with auric chloride solution, the color of the resulting mixture changes to black within 1 min, which proves the formation of AuNPs. In solution the polymer molecules get dispersed and orient themselves favorably according to the charges distributed on them. This allows them to interact with the inorganic ions like that of potassium and gold. PVA is basically a single chain poly-ol which is rich in hydroxyl (OH) groups. These OH groups however undergo both inter- and intra-molecular hydrogen bonding making PVA solution viscous. The lone pairs of electrons of the OH groups that do not participate in such hydrogen bonding can easily co-ordinate with the metal ions which often have high charge density and vacant d-orbitals (for transition metals like gold). When such co-ordination takes place between one metal ion and several adjacent OH groups the metal ion gets covered with PVA chains. Thus, we consider that the organic–inorganic interaction

to be of vital significance in the synthesis of NPs for important applications.
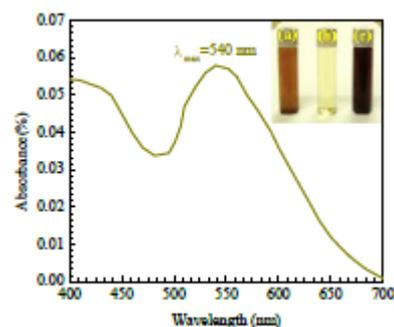

Fig.6 UV–vis spectrum of the nanocomposite solution with 0.05 wt% AuNPs. The inset shows the photographs indicating (a) Green tea extract (b) HAuCl$_4$ solution and (c) Formation of AuNPs due to color change after adding (a) and (b).

The incorporation of fillers into a polymer matrix can bring about changes in the thermal characteristics of the resulting nanocomposite. One benchmark that is used to compare the thermal behaviour of nanocomposite is the glass transition temperature (T$_g$). Changes in the value of T$_g$ have been reported for polymer composites containing a wide variety of fillers and polymers, but most recently for composites containing nanoscale fillers [23]. The thermal properties of PVA/2.5 wt% KDP composite film and PVA/2.5 wt% KDP nanocomposite film embedded with AuNPs have been studied. Figure 7(a) shows a typical TGA thermogram of weight loss as a function of temperature for pure PVA film and PVA/2.5 wt% KDP nanocomposite film embedded with 0.05 wt% AuNPs, as measured under nitrogen atmosphere. Major weight losses are observed in the range of 200–460 ^{o}C for PVA and PVA/KDP/0.05wt% AuNPs nanocomposite film, which may be correspondent to the structural decomposition of the polymer [24]. Obviously, the thermal decomposition of nanocomposite film shifted towards higher temperature range than that of bare PVA film, which confirms the enhanced thermal stability of nanocomposite film. DSC traces of bare PVA film and PVA/2.5 wt % KDP/0.05 wt% AuNPs nanocomposite film has been shown in figure 7(b). These films exhibit endothermic melting (Tm) peaks corresponding to pure PVA and AuNPs doped composite at about 227 and 222 ^{o}C corresponding to the melting temperature (T$_m$), respectively [24]. It is noticed that the T$_m$ peak of the nanocomposite film shifted significantly towards lower temperature (by 5°C) regime, implying that the nanocomposite film possesses improved crystalinity, extending the range of applicability. Hergeth et al. [25] also put forwarded almost similar conclusion from their study on polymer composites containing quartz powder filler particles produced by emulsion polymerization technique.

Figure 8 shows the dependence of effective dielectric permittivity (ε') on the AuNPs concentrations of the

present nanocomposite film measured at 1 kHz and at room temperature (RT).
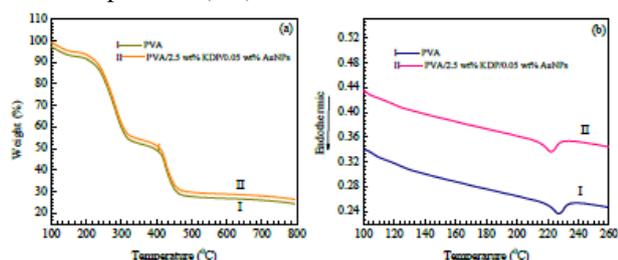

Fig.7 (a) TGA thermogram of weight loss and (b) DSC traces as a function of temperature for pure PVA film and PVA/2.5 wt% KDP film embedded with 0.05 wt% AuNPs.

It is seen that the addition of AuNPs results in much higher ε' value and that the increase in ε' becomes more apparent at the relatively high loading level. It is of particular interest that ε' value of the nanocomposite increases notably when the AuNPs loading level is 0.05 wt%, shows the maximum value of 590, which is almost 180 times of pure PVA film at 1 kHz and RT. The increase in ε' in the nanocomposite film could be understood according to the "boundary layer capacitor effect" [26]. At this high AuNPs loading levels, the nanocomposite can be simulated by means of a large number of equivalent elementary capacitors where the single AuNPs or clusters are isolated by thin dielectric insulating layers and can act as electrodes when an external electric field is applied on the nanocomposite, which give rise to high dielectric permittivity [25]. Another interesting finding is that there is no percolation in the AuNPs weight fraction range of 0 to 0.05 wt%.
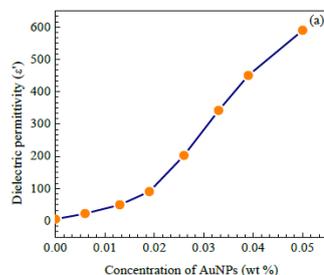

Fig.8 Dependence of effective permittivity as a function of concentration of AuNPs in the PVA/2.5 wt% KDP/AuNPs nanocomposite films at 1 kHz and room temperature.

4. CONCLUSIONS

In this work, we have shown the influence of green tea extract derived gold nanoparticles (AuNPs) on the PVA/KDP percolative composite film prepared by solvent casting technique followed by bio-reduction method. The addition of AuNPs changes its structural, thermal, dielectric properties remarkably. The network formed by 2.5wt% KDP grains within the PVA matrix seems to be destroyed after the addition of a typical concentration (0.05 wt %) of AuNPs is confirmed by FESEM image. XRD, EDX, FTIR, UV-Vis spectra confirm the presence of AuNPs in the nanocomposite sample. The size of

AuNPs is confirmed by HRTEM image. TGA curve indicated that the thermal stability of PVA is improved when loaded with AuNPs. Additionally, the structure of the polymer in the vicinity of the AuNPs altered from the amorphous to a higher ordered state was confirmed by XRD, DSC plots. Broadband dielectric spectroscopy measurements exhibited the maximum value of effective permittivity (~590) for PVA/2.5 wt% KDP/0.05 wt% AuNPs nanocomposite film which is almost 110 times higher than that of the pure PVA film at 1 kHz and room temperature (300 K). Such nanocomposite film is considered as a promising candidate material for embedded capacitor applications. Moreover, the results also suggest that the green synthesized AuNPs with a size less than 10 nm are a promising new class of percolation destroying agent which might have some applications as disease (like to stop spreading cancer cells) therapeutic agents.

REFERENCES

[1] A. Kiesow , J E Morris, C. Radehaus and A. Heilmann *J. Appl. Phys.* 94, 6988-90, 2003.

[2] M. Daniel and D .Astruc *Chem. Rev*. 104, 293,2004

[3] K. Kneipp, H. Kneipp and J. Kneipp *Acc. Chem. Res*. 39, 443, 2006.

[4] M. T. Castaneda, A. Merkoci, M. Pumera and S. Alegret *Bios. Bioelect.* 22, 1961, 2007.

[5] T. Ishida and M. Haruta *Angew. Chem. Int. Ed*. 46 7154, 2007.

[6] M. N. Nadagouda and R. S. Varma, *Green Chem*. 9, 632, 2007.

[7] J. A. Dahl, L. S. Maddux and J. E. Hutchison, *Chem. Rev.* 107, 2228, 2007.

[8] A. Kumar *Nat. Mater.* 7, 236, 2008.

[9] P. T. Anastas and J. C. Warner "*Green Chemistry, Theory and Practice*" (Oxford University Press, New York), 1998.

[10] M. C. Moulton, L. K. B. Stolle, M. N. Nadagouda, S. Kunzelman, S. M. Hussaina and R. S. Varma, *Nanoscale* 2, 763, 2010.

[11] M. J. Uddin, B. Chaudhuri, K. Pramanik, T. R. Middya and B. K. Chaudhuri *Mater. Sci. Eng. B* 177, 1741, 2012.

[12] N. A. Begum, S. Mondal, S. Basub, R. A. Laskara, D. Mandal, *Colloids Surfaces B Biointerfaces* 71, 113, 2009.

[13] H. K. Chitte1, N. S. Bhat, D. C. Karmakar. *World J. Nano Sc. Engg*. 2, 19, 2012.

[14] P. Thomas, S. Satapathy, K. Dwarakanath and K. B. R. Varma. *eXPRESS Polym. Lett.* 4**,** 632, 2010.

[15] C. J. Dias and D. K. Das-Gupta *IEEE Trans. Dielec. Elect. Insu.* 3, 706, 1996.

[16] D. H. Kuo, C. C. Chang, T. Y. Su, W. K. Wang and B. Y. Lin *J. Euro. Ceramic Society* 21, 1171, 2001.

[17] H. S. Nalwa, "Handbook of low and high dielectric permittivity materials and their applications" (Academic Press, San Diego), 1999.

[18] C. K. Chiang and R. Popielarz, *Ferroelectrics* 275, 1, 2002.

[19] G. A. Kontos, A. L. Soulintzis, P.K. Karahaliou, G. C. Psarras, S. N. Georga, C. A. Krontiras, and M. N. Pisanias *Exp. Polym. Lett.* 1, 781, 2007.

[20] M. J. Uddin, J. Sannigrahi, M. G. Masud, D. Bhadra, and B. K. Chaudhuri, *J. Appl. Polym. Sc.* 125, 2363, 2012.

[21] L. Balan, V. Melinte, T. Buruiana, R. Schneider and L. Vidal, *Nanotechnology* 23, 415705, 2012.

[22] F. Janerio, O. Corduneann and M. O. Brett *Electroanalysis* 17, 1059, 2005.

[23] B. J. Ash, L. S. Schadler and R. W. Siegel Mater. Lett. 55, 83, 2002.

[24] Yu Y H, Lin C Y, Yeh J M and Lin W.H *Polymer (Guildf)* 44, 3553, 2003.

[25] W. D. Hergeth, U. J. Steinau, H. J. Bittrich, G. Simon G and K. Schmutzler, *Polymer* 30, 254,1989.

[26] M. Panda, V. Srinivas, and A. K. Thakur *Appl. Phys. Lett.* 92, 132905, 2008.