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Flexo-green Polypyrrole – Silver nanocomposite films for thermoelectric power generation

Meetu Bharti [a,b], Ajay Singh [a,*], Soumen Samanta [a], A.K. Debnath [a], D.K. Aswal [a,c], K.P. Muthe [a], S.C. Gadkari [a]

[a] Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[b] All India Jat Heroes' Memorial College, Rohtak 124001, Haryana, India
[c] National Physical Laboratory, New Delhi 110012, India

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ABSTRACT

Conducting polymers offer various advantages over inorganic thermoelectric materials such as eco-friendliness, a reduced manufacturing cost, flexibility, low thermal conductivity and amenability to tuning of electrical properties through doping; have recently drawn much attention for conversion of low temperature waste heat (≤150 °C) into electricity. In this study, we investigated the thermoelectric properties of hybrid films of polypyrrole and silver (PPy-Ag). These films were prepared on biaxially oriented polyethylene terephthalate (BOPET) flexible substrates by eco-friendly one pot photo-polymerization method using aqueous solution of silver nitrate ($AgNO_3$) as photo initiator. Detailed characterization of the samples revealed that morphology of composite films reorganized with the change in $AgNO_3$ concentration during synthesis. Increasing $AgNO_3$ concentrations resulted in PPy films containing Ag nanoparticles, nanoclusters as well as macroclusters. With alteration in concentration and size of Ag particles in PPy matrix, it has been observed that the electrical conductivity of the films increased (1.5–17.3 S cm^{-1}), thermal conductivity decreased (0.16–0.002 Wm^{-1} K^{-1}), while Seebeck coefficient moderately reduced from 10.9 μV/K to 5.8 μV/K. Nearly same doping ($N^+/N \sim 0.35$) content, improved conjugation length and incorporation of Ag between the PPy chains resulted in improved charge carrier mobility/electrical conductivity in the PPy–Ag films. It is proposed that the interface of Ag and PPy served as scattering sites for phonons, thus leading to reduction of thermal conductivity. This synergetic combination of high electrical conductivity, extremely low thermal conductivity along with moderate Seebeck coefficient in the PPy-Ag films resulted in the highest figure-of-merit of $\sim 7.4 \times 10^{-3}$ at 335 K among reported PPy based materials. A prototype thermoelectric power generator was fabricated by integrating six numbers of PPy-Ag films. The fabricated device exhibited maximum voltage and power respectively as 6 mV and ~30 pW. The present work opens new avenues for the thermoelectric applications of rarely explored flexible PPy-Ag films prepared by a simple nature-friendly photo-chemical process at room temperature.
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1. Introduction

Thermoelectricity, owing to its various advantages over other energy conversion technologies, is gaining attention in this modern era of industrialization and urbanization that currently is struggling hard with the issues like energy economy in terms of waste heat recovery and global warming [1]. Low temperature waste heat generated by human body, geo-thermal sources, electronic and electrical systems can be harnessed using thermoelectric power generators (TEGs) for its conversion into useful electrical energy [1–2]. The efficiency with which this conversion takes place is defined by a dimensionless figure-of-merit $ZT \sim \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the average temperature of operation [3–5]. For a given material, these parameters (α, σ and κ) are known to maintain a detrimental interdependence which limits further enhancements in ZT. Therefore, for development of thermoelectric materials having superior ZT, it is a pre-requisite that this intrinsic linkage of thermal and electrical transport properties is decoupled [3]. Inorganic semiconductors in particular, are being investigated extensively due to their relatively higher α and σ values [4–10]. Recently many efforts are being made to suppress their inherently high κ (without comprising the power factor) to achieve further improvement in their ZT. Bi_2Te_3 based alloys are conventional inorganic semiconductor thermoelectric materials that are widely used for power generation applications and thermoelectric

* Corresponding author.
E-mail address: asb_barc@yahoo.com (A. Singh).

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refrigeration in the lower temperature range (<150 °C). These materials however suffer from the problem of toxicity, inflexibility, high manufacturing/processing cost due to scarcity of Te [3–5]. Therefore, as an alternative to these materials conducting polymers (CPs) being low cost, non-toxic, light weight with their low κ and mechanical flexibility, have attracted a strong focus as promising thermoelectric materials [11,12]. Consequently, various CPs are being explored for their potential thermoelectric applications and efforts are being directed towards improvement of their thermoelectric performance [13]. These efforts include synthesis of nanostructured polymers as well as creating hybrid materials by combining useful features of both the organic and inorganic realms.

Polypyrrole (PPy) is one of the oldest conventional CP and widely sought-after due to its excellent stability under environmental conditions and biocompatibility. Various groups have reported power factors and *ZT* for pure PPy [14–18] and its composites [19,20]. Also combinations of PPy with different metals such as Pt, Au, Ag and Cu have been reported in literature [21–25]. Among these, PPy-Ag nano-composites are quite interesting owing to their extraordinary physico-chemical properties arising from their high surface area and the quantum size effects and also from the point of their potential applications as electro-catalysts, chemical sensors and electrode materials [26]. In spite of this, to the best of our knowledge, PPy-Ag films have not been investigated yet for thermoelectric applications.

In this study, we report the thermoelectric properties of polypyrrole-silver (PPy-Ag) composites films synthesized on hydroxylated flexible substrates (BOPET sheet). The PPy-Ag films were photo-polymerized using UV radiation (~365 nm) and silver nitrate ($AgNO_3$) as photo initiator. The hybrid PPy-Ag films prepared with 1.2 M of $AgNO_3$ have exhibited the highest *ZT* of $\sim 7.4 \times 10^{-3}$ at 335 K, which is the best value achieved so far, for the PPy based materials. Plausible mechanisms for the improvement in *ZT* of the PPy-Ag films with the optimized Ag concentration have been discussed. To demonstrate the practical application of PPy-Ag films for thermoelectric power generation, films with the highest *ZT* have been used to develop a prototype TEG with six thermoelements connected electrically in series as well as in parallel. The output power ~30 pW (for a temperature difference of 140 K) obtained from PPy-Ag films based TEG although has been found low, yet the novel strategies [27,28] that have been recently emphasized in the field of organic thermoelectrics can be applied for enhancing the performance of TEGs. This being the first ever attempt to exhibit the prospect of polypyrrole-based materials for developing TEG will surely pave towards the development of promising energy harvesting devices.

2. Experimental procedures

2.1. Materials and surface modification of flexible BOPET sheets

Pyrrole (Sigma-Aldrich, purity ≥98%) was refrigerated in the dark prior to synthesis. Before using pyrrole, it was distilled by vacuum distillation process to remove the polymerized products and impurities. Analytical grade silver nitrate (Sigma-Aldrich, purity ~99.9%) in the as-received form was used in the synthesis. The organic solvents used, were also of analytical grade while deionized (DI) water was used for washing and solution preparation. BOPET sheets of thickness ~100 μm were procured from DuPont and these sheets were cut into size of ~45 mm × 11 mm to deposit films. The BOPET sheets were ultrasonically cleaned for 30 min using chloroform and ethanol respectively and then purged with Argon for drying. After this, to graft the PPy molecules on BOPET, the surface of BOPET was hydroxylated by dipping it in the potassium hydroxide (KOH)-containing dimethyl sulphoxide (DMSO) solution (120 mg KOH dissolved in 30 ml DMSO and 10 ml DI water) [26]. The sheets were left to react with KOH for 10 min, then were thoroughly washed with DI water and again dried by purging with Argon.

2.2. Deposition of PPy-Ag nanocomposites films on hydroxylated BOPET substrates

It is important to note that the hydroxylation of BOPET is important to have uniform and adherent PPy-Ag films. The films grown on a non-hydroxylated substrate are patchy due to uneven wetting of the hydrophobic surface of the BOPET. The hydroxylated sheets were dipped in aqueous solution of pyrrole (Py) and $AgNO_3$ poured in reagent glass bottles to deposit nano-composite films on their surfaces. The solution containing varied concentrations of $AgNO_3$ as photo-initiator (i.e. from 0.3 M to 1.5 M) and fixed concentration of pyrrole (0.5 M) was exposed to UV radiation for 30 min. The wavelength of UV lamp (Spectrolinker, XL-1500UV cross linker) was set at 365 nm while the distance from the source to sample was kept 12.5 cm. After deposition, samples were thoroughly cleaned with deionized water and ethanol to remove any unreacted species. Finally, the deposited films were dried for 1 h at 65 °C in an oven. Schematic shown in Fig. 1 provides detailed mechanism of photo-polymerization route used in this study, to synthesize PPy-Ag nanocomposite films. The preliminary step of reaction includes the excitation of Ag^+ on UV irradiation, easing the transfer of electron (oxidation) from pyrrole monomer to Ag^+. This eventually results in the formation of pyrrole radicals and Ag in the metallic state. The pyrrole radicals then undergo the polymerization process following dimerization and chain growth. Notably, this reaction can also occur in absence of UV light but the rate of the reaction rate will be extremely slow.

In simple manner, the chemical reaction for photopolymerization (shown in Fig. 1) can be described by following equation.

$$3Py + 3AgNO_3 + h\nu \rightarrow [Py\text{-}Py\text{-}Py]^{+}NO_3^{-} + 3Ag + 2HNO_3 \quad (1)$$

2.3. Characterization

2.3.1. Structural/morphological characterization

The synthesized films were characterized by X-ray diffraction, under ambient conditions on a Proto AXRD Bench top Powder diffractometer using Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscope (Model: SEMART PS-250, PEMTRON, S. Korea) was used to image the morphology of the samples. Surface sensitive X-ray photoelectron spectroscopy (XPS) measurements were carried out using Mg-Kα (1253.6 eV) source and DESA-150 electron analyzer (Staib Instruments, Germany). The binding-energy scale was calibrated to Au-$4f_{7/2}$ line of ~84.0 eV and C-1s line of ~284.6 eV. X-rays were incident at an angle of ~54.7 degree relative to the analyzer for collecting XPS data of the films. The other parameters were; step size: 38 meV, dwell time: 100 ms, scanning time: 15–20 min depending upon the number of scans. To record high-resolution XPS spectra, an average of 15 scans was taken. While fitting the XPS data with 2 or more peaks, the boundary condition of full-width at half maximum (FWHM)) for each peak was applied. The XPS peaks were fitted using a combination of Gaussian and Lorentzian distributions. Base line corrections of the data were done using Shirley Background subtraction method. High-resolution transmission electron microscopy (HRTEM) images of the PPy-Ag films were captured using JEOL (Japan) make JEM 2100F microscope having resolution of 0.01 nm at an accelerating voltage of 200 kV. The prepared PPy-Ag films were also characterized by Fourier transform infra-red spectroscopy (Bruker 80V).

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