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Thermoelectric Properties of Polyaniline Films with Different Doping Concentrations of (±)-10-Camphorsulfonic Acid

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The temperature dependence of the thermoelectric properties was investigated for polyaniline (PANI) films doped with different concentrations of (±)-10-camphorsulfonic acid (CSA) with molar ratio x of CSA to two phenyl-nitrogen units of $x = 1$ to 0.2. All PANI-CSA films exhibit p-type conduction. The temperature dependence of the electrical conductivity of the films with low CSA concentrations is consistent with a transport mechanism of variable-range hopping. On the other hand, the Seebeck coefficient above room temperature shows a linear increase with temperature, attributed to the metallic nature of PANI-CSA. As the CSA concentration decreases, the absolute value of the Seebeck coefficient increases while the electrical conductivity extremely decreases, probably due to the changes not only in the carrier concentration but also in the degree of structural disorder. The power factor increases monotonically with increasing CSA concentration toward $x = 1$ (the maximum limit). The thermal conductivity value of CSA-PANI film with $x = 1$ is as low as about $0.20\ \mathrm{W\ m^{-1}\ K^{-1}}$ in the through-plane direction and about $0.67\ \mathrm{W\ m^{-1}\ K^{-1}}$ in the in-plane direction. The thermoelectric figure of merit ZT in the in-plane direction is estimated to be approximately 1×10^{-3} for $x = 1$.

Key words: Conducting polymer, polyaniline, doping concentration, variable-range hopping, thermoelectric properties, anisotropy

INTRODUCTION

Conducting polymers, such as polyaniline (PANI), polypyrrole, and polythiophene, have several attractive features for use as thermoelectric materials because of their thermal conductivity much lower than that of inorganic thermoelectric materials as well as their potential low cost due to available resources, easy synthesis, and easy processing into a versatile form.[1–3] The electrical properties of PANI can be controlled both by charge transfer doping and by protonation. PANI is converted from the semiconducting (insulating) emeraldine base form to the conducting emeraldine salt form by doping with camphorsulfonic acid (CSA).[4–6] Moreover, PANI-CSA exhibits excellent environmental and thermal stability. These properties make polyaniline attractive as a thermoelectric material for potential use in a variety of applications if the thermoelectric power factor $PF = S^2\sigma$, where S is the Seebeck coefficient and σ is the electrical conductivity, of conducting PANI-CSA can be considerably improved. In inorganic semiconductor thermoelectric materials, both the Seebeck coefficient and the electrical conductivity depend on the carrier concentration, and the optimization of the carrier concentration is an essential approach to improve the power factor. Recently, Bubnova et al.[7] reported that the charge carrier concentration of

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