

IN-SITU FABRICATION AND THERMOELECTRIC PROPERTIES OF BISMUTH-POLYANILINE NANOCOMPOSITES

Yuanyuan Wang, Xi Yao and Kefeng Cai

Functional Materials Research Laboratory, Tongji University, 1239 Siping Road, Shanghai 200092, China.

Introduction

Thermoelectric (TE) materials have attracted much attention for their potential applications in harvesting electricity from waste heat, cooling, and thermal sensing. The performance of a TE material can be expressed by dimensionless figure of merit ZT ($ZT = \sigma S^2 T / \kappa$, where T is the absolute temperature, S the Seebeck coefficient, σ the electrical conductivity and κ the thermal conductivity). Traditionally, TE properties are only discussed for inorganic semiconductors, such as Bi_2Te_3 and its alloys, PbTe and its alloys, filled CoSb_3 skutterudites, and clathrates [1]. Recently, considerable attention has been paid to the TE properties of organic materials, especially conjugated polymers such as polyaniline (PANi), polypyrrole (PPy) and polythiophene (PTh) [2]. The thermal conductivity of conjugated polymers is usually much lower than that of inorganic materials, which leads to a relative high ratio of electric conductivity to thermal conductivity and is ideal to obtain better TE properties. Moreover, compared with inorganic TE materials, the conjugated polymer is relative low cost, easy synthesis and easy processing into versatile forms. Unfortunately, the ZT values of conjugated polymers are still much smaller than that of traditional TE materials.

Inorganic-organic nanocomposite structures provide a new method to improve the TE properties of materials. On the one hand, nanostructures have been shown theoretically, and to a certain extent experimentally, to exhibit enhanced TE properties [3, 4]. On the other hand, the association of a conjugated polymer with performed inorganic TE materials in nanoscale may exhibit synergic behavior leading to better TE properties to parent materials. In recent years, several inorganic-organic TE composites have been fabricated [5, 6]. In this work, Bi-PANi core-shell nanostructures were in-situ fabricated in synchronism at room temperature by interfacial polymerization. Bi nanostructures were also synthesized in similar condition as contrast experiments.

Experimental section

All agents were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd without further purification.

Synthesis of Bi nanostructures

A total of 1 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.02 mol KOH, 4 mmol sodium tartrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$), and 8 mmol KBH_4 were dissolved in sequence in 50 ml deionized water. A colorless and transparent solution was formed (Solution A). The solution was then diluted to 100 ml and placed at room temperature without stirring. 24 hours later, there were black precipitates on the bottom of the beaker. The black product obtained were washed by deionized water and absolute ethanol and filtered for several times and then dried in vacuum. The product is called sample I.

In-Situ fabrication of PANi-Bi nanocomposites by interfacial polymerization

The typical synthetic process of PANi-Bi composites was performed as following: First, 50 ml Solution A was prepared. Second, 1.14 g APS was dissolved in 50 ml deionized water and then added into Solution A. A homogeneous solution (Solution B) was obtained. Finally, Solution B was carefully transferred in 50 ml CCl_4 containing 0.9 ml of aniline monomer, generating an interfacial reaction between two phases. 24 hours later, the production obtained on the interface was collected and washed and called sample II.

Results and Discussion

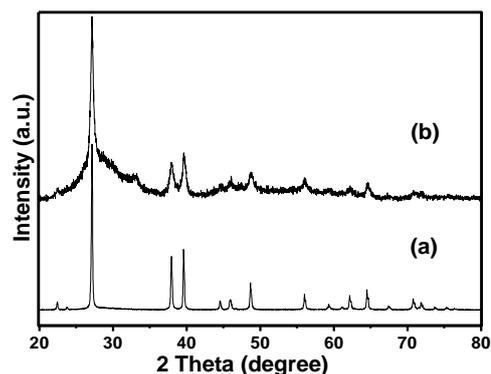


Fig.1 X-ray diffraction patterns of (a) sample I and (b) sample II

Figs. 1(a) and (b) show the XRD patterns of samples I and II, respectively. All the diffraction peaks for sample I can be indexed to the reported Bi (JCPDS card file, No. 44-1246). The pattern for sample II is quite similar to that of samples I and the much higher background could attribute to PANi.

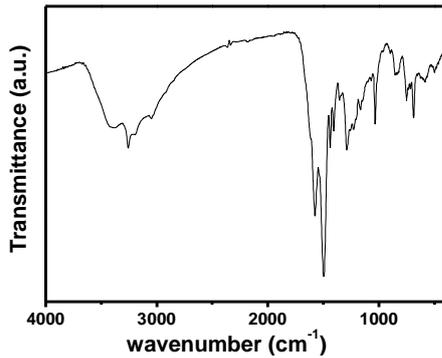


Fig.2 FT infrared transmission spectrum of sample II

The infrared spectrum for the sample II is shown in Fig.2, which corresponds to that for dedoped PANi [7]. There is no obvious peak for Bi in the spectrum, due to much weaker vibrational energy absorption of Bi than that of PANi within the infrared region. Combined the XRD, FTIR analysis results and experimental details, it can be deduced that sample I is Bi and sample II consists of Bi and PANi.

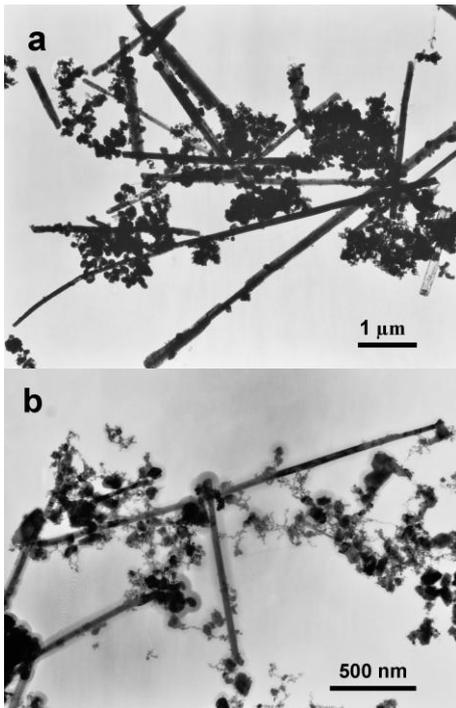


Fig.3 Typical TEM images for (a) sample I and (b) sample II

Table 1 Electrical conductivity and Seebeck coefficient of each sample measured at room temperature

samples	electrical conductivity (Sm^{-1})	Seebeck coefficient (μVK^{-1})
sample I	13.6	-167
sample II	7.4	-161

It can be seen in Fig. 3(a) that sample I is not

homogeneous and consists of nanoparticles and nanorods. Fig 3(b) shows that Bi nanoparticles and nanorods with darker contrast in sample II are well coated by PANi with lighter contrast. The size of the Bi nanostructures in sample II is much smaller than that in sample I, because a layer of PANi coated on them and there was no chance for them to further grow up.

The electrical conductivity and Seebeck coefficient of each sample after pressing at room temperature are shown in Table 1. Both the samples I and II have negative Seebeck coefficients, indicating they are n-type conductor. The electrical conductivity of sample I is 13.6 Sm^{-1} , which is lower than that of the bulk Bi reported in ref. [8]. This is because sample I consisting of nanostructures has a large quantity of interfaces, which will scatter the carriers transportation, and on the other hand it is porous due to cold pressing. For the same reason, its absolute value of Seebeck coefficient, $167 \mu\text{VK}^{-1}$, is higher than that reported in ref. [8]. Compared with sample I, sample II has lower electrical conductivity (7.4 Sm^{-1}) and absolute value of Seebeck coefficient ($161 \mu\text{VK}^{-1}$), due to the dedoped PANi coating on the Bi nanostructures. However, considering that the organic phase will help to greatly reduce the thermal conductivity of the composite, a better TE property of sample II could be expected.

Conclusion

In summary, Bi-PANi core-shell nanostructures were in-situ fabricated by the interfacial polymerization method at room temperature. The electrical conductivity and Seebeck coefficient of the composite nanoparticles after cold-pressing are about 7.4 Sm^{-1} and $-161 \mu\text{V}\cdot\text{K}^{-1}$, respectively.

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