

# The influence of hydrochloric acid doping on the microstructure and thermoelectric properties of poly(*p*-phenylenediamine) nanoparticles



Yuanxun Chen<sup>a</sup>, Qin Kou<sup>a</sup>, Kefeng Cai<sup>a,\*</sup>, Junlin Yin<sup>a</sup>, Shirley Shen<sup>b</sup>

<sup>a</sup> Key Laboratory of Advanced Civil Engineering Materials (Tongji University), Ministry of Education, School of Materials Science & Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, China

<sup>b</sup> CSIRO Manufacturing, Gate 5, Bayview Road, Clayton, VIC 3168, Australia

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## ABSTRACT

Conductive poly(*p*-phenylenediamine) (PpPD) nanopowders doped with different-concentration hydrochloric acid (HCl) were synthesized by a typical chemical oxidative polymerization method. The PpPD powders were characterized by the Fourier transform infrared spectroscopy, UV–vis spectroscopy, <sup>1</sup>H nuclear magnetic resonance spectroscopy and transmission electron microscope. The results showed that the morphology of the products changed from mainly spherical nanoparticles of the pure PpPD to rod-like nanoparticles of HCl doped PpPD. The pure PpPD showed n-type conduction whereas the HCl doped PpPD exhibited p-type conduction. The PpPD doped by 1 M HCl showed a maximum power factor of about 0.56 μW m<sup>-1</sup> K<sup>-2</sup> at room temperature. The mechanism of the change of the conduction type has also been discussed.

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## 1. Introduction

Thermoelectric (TE) materials, which can convert waste heat to electrical energy and vice versa, have attracted more and more attention in recent years due to increasing demand of energy [1]. The performance of TE materials is evaluated by the dimensionless figure of merit  $ZT = S^2\sigma T/\kappa$ , where  $T$  is the absolute temperature, and  $S$ ,  $\sigma$ ,  $T$ , and  $\kappa$  are the Seebeck coefficient, electrical conductivity, and thermal conductivity of the material, respectively. Higher  $S$ , higher  $\sigma$  and lower  $\kappa$  are required to achieve a higher  $ZT$ . However, optimizing  $ZT$  is very challenging, because  $S$ ,  $\sigma$ , and  $\kappa$  are a function of the carrier concentration. Especially, Seebeck coefficient has an inverse relation with electrical conductivity which requires a low carrier concentration will decrease the electrical conductivity; furthermore, a large electrical conductivity is always accompanied with a high thermal conductivity in most cases.

The most conventional TE materials are inorganic materials, such as Bi<sub>2</sub>Te<sub>3</sub> [2], PbTe [3], and their alloys [4–7], and filled skutterudites [8–10]. However, these materials have disadvantages, such as toxicity, expensive and complicated manufacturing process, which limit their extensively applications. Compared with

inorganic TE materials, conducting polymers, including polythiophene (PTh) [11], polyaniline (PANI) [12], polypyrrole (PPy) [13] and their derivatives, have attracted more and more attention, since they have advantages of abundance, easy simple synthesis processability, intrinsic low thermal conductivity, non-toxicity, low cost, and good flexibility [14–17]. Among these materials, PANI has been intensively investigated recently as a promising TE material. Untreated PANI does not have excellent electrical conductivity [18]. But the conductivity of PANI could vary in a wide range by protonation and charge-transfer doping. It is easy to modulate its electrical conductivity by switching the chemical salt form to chemical base form. The emeraldine salt (ES) state will come into being from the emeraldine base (EB) oxidation state of PANI by doping with a protonic acid, which changes the electronic structure of the polymer chain into a polaronic lattice and results in a high conductivity [19]. Therefore, the chemical structure, the micro-morphology and electrical properties of PANI and PANI-based composites have been widely investigated.

Many researchers have found that PANI doped with an organic acid, such as camphorsulfonic acid (CSA) [19], β-naphthalene sulfonic acid (β-NSA) [20], could exhibit significantly improved TE performance. Toshima et al. [21] found that CSA-doped PANI film in an emeraldine form had 6 times higher  $ZT$  value than CSA-PANI bulk at 300 K. In addition, doping with an inorganic acid, such as HCl [22] or boric acid [23], could also improve the TE performance of the materials.

\* Corresponding author.

E-mail address: [kfcai@tongji.edu.cn](mailto:kfcai@tongji.edu.cn) (K. Cai).

Recently, derivatives of PANI have attracted increasing attention because they also show novel properties. One of the derivatives is poly(*p*-phenyldiamine) (PpPD), which can be generally synthesized in the presence of an oxidant in an acidic condition. It has been studied for applications in electronic devices, such as supercapacitors [24] and batteries [25]. However, its TE properties have hardly been studied. In 2014, Liu et al. [26] synthesized the PpPD/graphene (GN) composites via in-situ polymerization in acidic solution and investigated the TE performance of the composites. By adding GN, the electrical conductivity was improved and the highest ZT value reached  $3.63 \times 10^{-4}$  at 328 K for a composite containing 50 wt% GN. Our group prepared PbSe nanoparticle modified PpPD nanowires via a template-free method. The pure PpPD nanowires had a very large Seebeck coefficient (2692  $\mu\text{V/K}$ ) but low electrical conductivity ( $1.2 \times 10^{-4} \text{ S/m}$ ) [27]. As the PbSe content increased, the Seebeck coefficient of the composite decreased and the electrical conductivity quickly improved, and the power factor of the composite was much higher than that of the pristine PpPD. To the best of our knowledge, the effect of the proton acid doping on the TE performance of PpPD has not been reported.

In this work, PpPD doped with different-concentration HCl have been prepared by a simple oxidative polymerization method. The influence of the HCl concentration on the morphology and TE performance of the PpPD has been studied.

## 2. Experimental

### 2.1. Preparation of PpPD

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd and were directly used without further purification. PpPD was synthesized by a chemical oxidative polymerization method using ammonium persulfate (APS) as an oxidant. In order to investigate the effect of HCl concentration on the TE performance of the product, HCl with different concentrations (0, 0.5, 1 or 1.5 M) was used. A typical preparation process for 1 M HCl doped PpPD is described as follows: 10 mmol *p*-phenylenediamine was dissolved in 40 mL deionized water with magnetic stirring at room temperature for 30 min. Then 10 mL of the HCl aqueous solution was added slowly to the above solution under vigorous stirring for 30 min. After that, 10 mmol APS aqueous solution dissolving in 50 mL deionized water was dropped into the above mixture at a rate of one drop every 2 s with constantly stirring. The reaction was kept at room temperature for 24 h. Finally, the product was

separated by centrifugation at 4000 rpm for 5 min. The black precipitation was washed with deionized water and ethanol to remove the residual oxidant and other by-product several times until the supernatant was colorless, and then the product was dried in vacuum at 60 °C for 24 h. The sample doped with other concentrations of HCl was prepared by the same process. The samples were marked as PpPD-0, PpPD-0.5, PpPD-1, and PpPD-1.5, for the products prepared when 0, 0.5, 1 and 1.5 M HCl was used, respectively.

### 2.2. Measurement and characterization

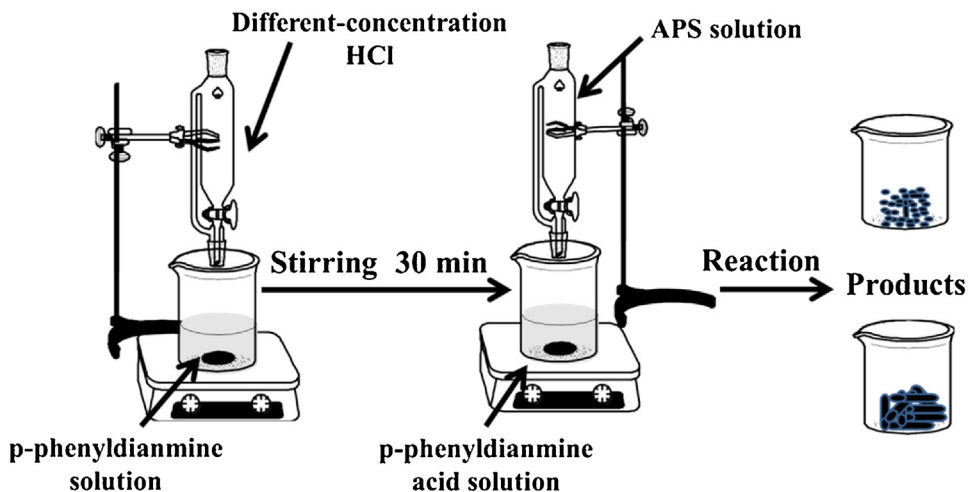
The structure of as-prepared PpPD was characterized by the UV-vis spectra (U-3310/NST) at 25 °C in NMP solvent, Fourier transform infrared spectroscopy (FTIR) (EQUINOX 55) and  $^1\text{H}$  nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) (AVANCE III). The morphology was observed by transmission electron microscopy (TEM, Hitachi H-800). In order to evaluate the effect of HCl doping on the TE properties of the PpPD, the electrical conductivity and Seebeck coefficient of the powders were measured after cold pressing into pellets. Electrical conductivity was measured using a steady-state four-probe technique with a square wave current ( $\sim 10 \text{ mA}$  in amplitude) using an Ecopia HMS-3000. The Seebeck coefficient was determined by the slope of the linear relationship between the thermal electromotive force and temperature difference ( $\sim 5\text{--}15 \text{ K}$ ) between two ends on one side of each pellet.

## 3. Results and discussion

PpPD doped with various concentrations (0, 0.5, 1 or 1.5 M) of HCl was synthesized by a typical chemical oxidative polymerization method using APS as an oxidant. The reaction process is shown as in Scheme 1.

### 3.1. Chemical oxidation polymerization mechanism

The formation mechanism of PpPD is not fully clear due to its complexity. It is believed that the process is very similar to that of PANI. All the PpPD samples in this work were oxidized by APS. According to the Cataldoi' s opinion [28], the initial step is the formation of a linear polymer with quinonediimine pendant groups or with pendant diamino groups, and the final step is the formation of a ladder polymer also called pernigraniline structure consisting of alternating groups of benzenoid and quinoid rings. The radical polymerization process of many polymers includes



Scheme 1. The scheme of the polymerization reaction process.

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