

## New Morphology of Conducting Polythiophene

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### Introduction

Electrically conducting polymers (CP) have rapidly become a subject of considerable interest among academic and industrial researchers due to their curious electronic, magnetic, and optical properties [1-4]. Polythiophene (PTh) is one of the most studied electrically conducting conjugated polymers due to its flexibility, ease of doping, and good thermal and electrical stability. PTh has been often considered as a role model for the study of charge transport in CP with a nondegenerate ground state; on the other hand, the high environmental stability of both its doped and undoped states together with its structural versatility have led to multiple developments aimed at applications in plastic photovoltaic, OLED, electrochromic or smart windows, antistatic coatings, sensors, nanoelectronic, and optical devices [5].

Sugimoto et al. has been reported a very simple method for the polymerization of polythiophene and its derivatives [6]. This method is now well-established as one of the most widely used and straightforward methods to prepare PTh and its derivatives. Wan et al. recently developed a simple method of *in-situ* doping polymerization in the presence of  $\beta$ -naphthalene sulfonic acid as the dopant [7]. *In-situ* doping polymerization is much easier without the micro-porous membrane, as the template or the anchoring materials bind the polymer to the wall of the micro-porous membrane, instead of the template synthesis method. More recently, gamma-irradiation has been used extensively to generate novel nano/micro particles of polymeric materials with unusual properties, since it can help prepare particles at room temperature and in ambient pressure, and it is easily controlled and adaptable, and also it can't induce impurities into the materials. Here, we present the novel synthesis and unique physical properties for a new constitutional view of spherical conducting polythiophene by the *in-situ* gamma radiation-induced oxidative polymerization method, and describe the characterizations in detail.

### Experimental

In a typical synthesis, anhydrous  $\text{FeCl}_3$  (0.0129 M) in 100 ml of  $\text{CHCl}_3$  solution was added to a 250 ml capacity high-density polyethylene bottle and sonicated for 10 minutes at room temperature. Thiophene monomer (0.0125 M) with 50 ml of  $\text{CHCl}_3$  solution was added gradually (drop wise) to the above solution with constant stirring. The resultant solution was deaerated by bubbling with argon to remove of the dissolved oxygen before irradiation. Then, it was sealed and radiated by a  $^{60}\text{Co}$   $\gamma$ -ray source at a rate of ca. 20 kGy for one hr under atmospheric pressure at ambient temperature. After irradiation, the sample was washed carefully with an excess of distilled water, methanol, hydrochloric acid (0.1 M), and acetone, respectively, to remove the unused initiator, and other impurities. The obtained black powder was dried under a vacuum dryer at room temperature for 24 hr.

### Results and Discussion

A typical morphology of spherical PTh was investigated by field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (TEM). As shown in Figure 1, the FE-SEM images show the uniform view of the individual (Fig. 1a) spherical conducting polythiophene with the particles size in micrometer scale (e.g. 0.5 -10  $\mu\text{m}$ ) as well as the larger giant particles. The similar morphological structure of the sphere-shaped virgin polythiophene was also imaged by TEM, as shown in Figure 1b. From FE-SEM and TEM images, it identified clearly that the conducting polythiophene formed new morphology as like buckyball structure and their insides were hollowed.

Proof of the polythiophene component for our sample was provided by the FT-IR and XRD data presented in Figure 2. In FT-IR spectrum (Figure 2a), there are several low intensity peaks present in

the range of 2800-3100  $\text{cm}^{-1}$ , which can be attributed to the aromatic C-H stretching vibrations [8]. The absorption in this region is obscured by the bipolaron absorption of the doped PTh. The range of 600-1500  $\text{cm}^{-1}$  is the fingerprint region of PTh. The peak at approximately 798  $\text{cm}^{-1}$  is usually ascribed to the aromatic C-H out-of-plane deformation mode as reported by other groups [9], while other peaks in this region are attributed to the ring stretching modes. The C-S bending mode was identified at approximately 702  $\text{cm}^{-1}$ , which indicates the presence of a thiophene monomer [10]. In Figure 2b, the XRD pattern exhibits a broad amorphous diffraction peak at approximately  $2\theta = 14\text{-}19^\circ$  ranges. This broad peak centered at around  $17^\circ$  corresponding to intermolecular  $\pi$ - $\pi$  stacking emerges for polythiophene [11].

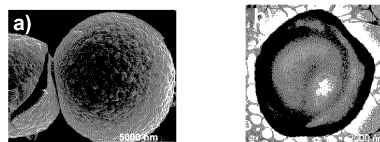
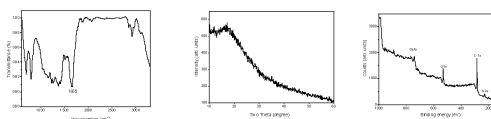


Fig. 1: (a) FE-SEM and (b) TEM images of spherical PTh.

Fig. 2: (a) FT-IR, (b) XRD and (c) XPS data of spherical PTh.



To further clarify the chemical situation of the elements, we measured the XPS of the samples. The S-2p core-level spectrum of the PTh (Fig. 2c) can be deconvoluted into at least two spin-orbit-split doublet (S-2p<sub>3/2</sub> and S-2p<sub>1/2</sub>) peaks at approximately 163.6 and 163.7 eV, which are attributed to the neutral sulphur atoms, respectively [12]. This indicates that the chemical environment of the S element, in pure PTh is almost identical.

### Conclusions

We have demonstrated a new morphology, micrometer particle sizes of buckyball-shaped giant spherical conducting polythiophene synthesized by the *in-situ* radiolysis oxidative polymerization method. This novel synthesis shows interesting findings as well as the new structural view of conducting polythiophene synthesized successfully. It is hypothesized that, because of the simplicity and robustness of this procedure, these giant morphology of virgin spherical polythiophene could be create a new research topic among the academic and industrial researchers.

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