CHAPTER I

INTRODUCTION

In recent years, conductive polymers synthesized in the form of nanoparticles have become of particular interest since their unique morphology, and their high specific surface area, usually result in certain advantages such as enhanced responsiveness for sensor applications (Virji, Huang, Kaner, Weiller, 2004; Huang, Virji, Weiller, Kaner, 2004), improved dispersion (Li, Zhao, Zhuang, Wang, Gu, 2007), and a low percolation threshold for electrical conductivity in composite materials (Banerjee, Mandal, 1995; Wang, Jing, 2007).

In past, many types of conductive polymers such as polyacetylene, polypyrrole, polythiophene, poly(*p*-phenylene) *etc.* have been explored. However, much research have been conducted on the nanostructures of polyaniline (PANI) because of its facile synthesis, good environmental stability, ease of conductivity control by changing the oxidation states and protonation states, and cheap in monomer (Cho, Park, Hwang, Choi, 2004; Zhang, Wang, 2006; Li Gou, Wei, MacDiarmid, Lelkes, 2006; Cheng, Ng, Chan, 2005). PANI nanostructures have been extensively studied for the wide ranges of application such as sensors (Ma, Wang, Li, Chen, Bai, 2006: Xing, Zhao, Jing, Wang, 2006), analytical separation (Gubta Hellgardt, Wakeman 2006), proposed as diagnostic (Zhu, Chang, He, Fang 2006; Tahir, Alocilja, Grooms 2005), applied in the electrorheological studies (Choi, Kim, Cho, Kim, Jhon 1997; Lim, Park, Park 2002), and catalyst (Kantam, Roy, Roy, Subhas, Sreedhar, Choudary 2007; Amaya, Saio, Hirao 2007). In such applications, control of the size and morphology of PANI nanostructures is generally crucial due to their strong influence on the associated properties.

Various PANI nanostructure morphologies — including tubules (Stejskal, Sapurina, Trchova, Konyushenko, Holler, 2006; Wei, Kvarnstrom, Lindfors, Ivaska, 2006), fibers (Wang, Jing, Kong, 2007; Chiou, Epstein, 2005), and spheres (Cheng, Ng, Chan, 2005; Wu, Bein, 1994) — have been synthesized by either the chemical or electrochemical polymerization of aniline with the aid of a hard template, such as a zeolite channel (Cao *et al.*, 1992; Wu, Bein, 1994), track-etched polycarbonate (Liu, Kaner, 2004; Martin, 1996), or anodized alumina (Wang, Chen, Li, 2002; Xiong,

Wang, Xia, 2004), or a soft template, such as a surfactant (Xiong, Wang, Xia, 2004; Yang *et al.*, 2005), or polyelectrolyte (Lu *et al.*, 2005). Moreover, physical methods such as electrospinning (Li, Gou, *et al.*, 2006), and mechanical stretching (Gu *et al.* 2005; He, Li, Tao, 2001), interfacial polymerization (He, 2005; Huang, Kaner, 2004), rapid mixing polymerization (Wang, Jing, 2008), sonochemical synthesis (Jing *et al.*, 2006; 2007), radiolytic synthesis (Wang, Jing, 2005), photolithographic synthesis (Werake *et al.*, 2005), and seeded polymerization (Zhang, Goux, Manohar, 2004) have been utilized in the synthesis of PANI nanostructures as well. Among the mentioned methods, the template synthesis, however, might be the most effective method to synthesized PANI nanostructures with controllable particle morphology and size (Mazur *et al.*, 2003). However, the complicate processes for pre-fabrication of the template as well as the post-treatment for removing the template are required (Zhang, Wan, 2002), hence hampers the use of this template technique. Therefore, the finding of other facile methods which can diminish the drawbacks of the template synthesis, while retaining the ability to produce the uniform morphology with narrow size distribution of the synthesized PANI nanostructures, remains a challenge.

In the present work, we describe the other interesting approaches to synthesize various morphologies of PANI nanoparticles by using the specific substances which can serve as templates in the condition for PANI synthesis. Moreover, these template substances can be easily removed after the formation of PANI nanoparticles was completed.

Chlorophyllin is a water-soluble derivative of chlorophyll whose structure consists of a conjugated porphyrin moiety chelated around a central Cu^{II} ion. Under acidic conditions for PANI synthesis, it was established in this study that chlorophyllin forms a nanorod-like structure and consequently serves as the *in-situ* seed for the adsorption of anilinium ion (protonated aniline) and, subsequently, polymerization of aniline on its surface. In the present work, it is proposed that the anilinium ion may be adsorbed on the surface of the nanorod-like chlorophyllin seed due to electrostatic interaction and/or hydrogen bonding interactions, thus forming surface nucleation sites. Alternatively, after addition of ammoniumperoxodisulfate (APS), used as an oxidant, polymerization of the anilinium ion is initiated and adsorption of PANI oligomers on the seed particle surfaces may preferentially occur

through hydrophobic interactions (Stejskal, Sapurina, 2004; Zhang, Manohar, 2004). After removal of the chlorophyllin template by simply washing with acetone or 0.5-M NaOH solution, the resulting products exhibited a homogeneous nanofibrillar morphology with a chemical structure identical to that of PANI synthesized by conventional methods (without the addition of chlorophyllin).

Apart from the use of chlorophyllin as a template to synthesize PANI nanofibrils, carboxymethyl chitin (CM-chitin) is another interesting template material which was used in this work. CM-chitin is a water soluble derivative of chitin obtained via the carboxymethylation of chitin powder with monochloroacetic acid under basic conditions. CM-chitin can self-assemble and exhibits an weak emulsifying property under acidic conditions, which is the condition for PANI synthesis, due to their amphiphilic structure (Ueno, Yokota, Kitaoka, Wariishi, 2007), consisting of the equatorial hydrophilic groups (including -OH, -NH$_3^+$, -NH-COCH$_3$, and -OCH$_2$COOH), which act as the hydrophilic shell, and the axial hydrophobic planes, which act as the hydrophobic core. The hydrophobic core serves as the reaction template, whose size in the nanometer range, for monomer accumulation and subsequent polymerization when the oxidant is added. After the polymerization of aniline in the presence of CM-chitin template was completed, the globular PANI nanoparticles whose surfaces are covered with radially aligned PANI dendrites were obtained. In addition, it was further found that size of the synthesized PANI nanoparticles decreased when the CM-chitin concentration was increased. This was explained in that a higher number of nucleating sites leads to a lower amount of monomer uptake in each hydrophobic core; the result is a decrease in size of the dendritic PANI nanoparticles. Owing to the solubility of CM-chitin in water, the CM-chitin template, moreover, is easily removed by washing with water to obtain pristine dendritic PANI nanoparticles. A possible formation mechanism is proposed based on self-assembly between the CM-chitin chains and the aniline monomer. Moreover, it was explored in this dissertation that CM-chitin not only serves as the template for synthesizing the polyaniline nanoparticles but it can also apply to synthesize the uniform morphology and narrow size distribution of other conductive polymer nanoparticles, such as polypyrrole (PPY).

In addition, it was further found that the hydrogel network, such as a cross-linked CM-chitin, can be served as a template for synthesizing the PANI nanoparticles with uniform morphology and with narrow size distribution as well. Generally, hydrogels are three-dimensional network structures, obtained by physically or chemically cross-linking hydrophilic polymers. Due to the ability to absorb a large amount of water into the individual pores in their networks, each pore of the hydrogel can function as a single nanoreactor or a template to sequester the monomers for subsequent polymerization. By cross-linking with glutaraldehyde, CM-chitin exhibits the hydrogel properties and the different cross-linked density of CM-chitin can be obtained by varying the amount of glutaraldehyde added. By using the cross-linked CM-chitin as a template for the polymerization of aniline, it was also found that the glutaraldehyde concentration used to prepare the cross-linked CM-chitin template determines the size of the resulting PANI nanoparticles. Specifically, as the glutaraldehyde concentration increased, the size of PANI nanoparticles produced in the cross-linked CM-chitin decreased. Thus, a higher degree of cross-linking of CM-chitin (*i.e.* a higher glutaraldehyde concentration) results in formation of smaller-sized PANI nanoparticles, presumable because of a reduction in size of the pore spaces within the network structure (Mohan et al. 2007). Therefore, we can obtain the PANI nanoparticles with controlled size by controlling the cross-linked density of the CM-chitin template.

Although, this present work describes many facile methods to synthesize various morphologies of conductive polymer nanoparticles, however, a low ability to process the obtained conductive polymer nanoparticles into final products with high mechanical strength hinders their applications. Therefore, many attentions have been given to solve this drawback by fabricating the polymer nanocomposite. Polymer nanocomposite between conductive polymer nanoparticles and other polymer matrixes might be an easy and effective method for improving the processability and mechanical properties of the conductive polymer nanoparticles while preserving its inherent electrical properties. However, in the fabrication of nanocomposite materials, the rheological and dispersion behaviours of conductive polymer nanoparticles in the polymer matrixes are quite important because they can be used to predict the processability and final properties of the nanocomposite products. SEM

measurement was used to investigate the dispersion behaviour of the synthesized polypyrrole (PPY) nanoparticles in CM-chitin matrix compared with their macroscopic counterparts (bigger size) synthesized by conventional route. From the result, it was suggested that the PPY nanoparticles can disperse thoroughly in the CM-chitin matrix, while, at the same blend composition, the distinct aggregation or partially phase separation easily occurs when the size of the PPY particles increase up to the range of micrometer.

Rheological measurements of the synthesized polypyrrole nanoparticles dispersed in alginate solution were investigated, in comparison to that of its macroparticles. It was found that the addition of PPY nanoparticles can reduce the viscosity of alginate, on the other hand, the addition of larger size PPY macroparticles results in the significant increase in viscosity of alginate. Additionally, it was also found that many parameters including particle size and electronic state of PPY can influence the rheological behaviours of the PPY/alginate suspension.

In summary, the dissertation demonstrates simple approaches to synthesize the various morphologies of conductive polymer nanoparticles by using the specific substances, including chlorophyllin, CM-chitin, and cross-linked CM-chitin, which are easily prepared and removed, as templates. The obtained conductive polymer nanoparticles suspended in polymer solutions were subjected to investigate the rheological properties and dispersion behaviour in order to find the superior behaviours of the synthesized conductive polymer nanoparticles compared to those of conventionally synthesized particles (bigger size).