

CHAPTER I

INTRODUCTION

Inorganic–organic hybrid material is a material that includes two moieties blended in the molecular scale (Kickelbick, 2007). Commonly one of these compounds is inorganic and the other one organic in nature therefore there were called “Inorganic–organic hybrid material”. Basically, inorganic–organic hybrid materials were composed of two moieties of inorganic building block and organic matrix. Nowadays, inorganic–organic hybrid materials received more attentions due to their potential synergistic properties derived from the combination of two or more precursors (Small, 2009). Due to the molecular scale blending, the inorganic–organic hybrid materials can favorably combine the often dissimilar properties of organic and inorganic components in one material. Another driving force for developing these materials is the possibility to create the multifunctional materials with unlimited properties. Due to the various kinds of inorganic building block with specific optical, electronic or magnetic properties and also various kinds organic polymer matrices which providing the strength, flexibility or process ability to the as-prepared material, these were generated the unlimited products without the limited properties. These were clearly revealed the power of hybrid materials to generate new material with unlimited properties from simpler matrices and building blocks (Kickelbick, 2007).

Various approaches have been done in order to prepare multifunctional hybrid materials which containing specific properties of metal and metal oxide nanoparticles. One of common methods is the mechanical mixing of a polymer with metal nanoparticles (Maneerung, Tokura, & Rujiravanit, 2008). However, the nanoscale of metal or metal oxide building block still had limitations due to the extremely high surface area. The dispersion of these nanoparticles in polymers or organic matrices was very difficult. There were always agglomerated to be a large particle with the lack of desired-properties. The *in situ* concept were applied In order to overcome these problems such as the *in situ* polymerization of a monomer in the presence of metal nanoparticles, or the *in situ* reduction or precipitation of metal salts in a polymer template (template-directed synthesis). Among the various preparation methods, the template-directed synthesis is interesting technique for preparing the

inorganic–organic hybrid materials. Because of the well-defined morphology and specific structure controlled such as dendrimers and two or three-dimensional ordered structures of nanoparticles could be achieved by using the template-directed synthesis method (Kickelbick, 2007). Moreover, the unique properties of inorganic–organic hybrid materials are directed related to their morphology, topology and pore structure. Therefore, the desired properties of the as-prepared inorganic–organic hybrid materials were controlled by the template characteristics. According to *in situ* synthesis concept, the precursor was firstly mixed or incorporated into an organic matrix then crystallization or precipitation of such particles were performed inside an organic matrix, the template should provide the structure for achieve the homogeneously dispersed of the precursors. Then, the dispersed-precursors should be trapped inside the template by electrostatic interaction between high polar functional groups of precursors and template. Finally, the template should support the crystallization or precipitation process of such particles. In order to achieve the inorganic–organic hybrid materials with desired properties, the template should provide the favor homogeneously crystallization or precipitation of such particles inside the matrix of template.

Among several of kinds of naturally organic template, bacterial cellulose (BC) was very attractive and interesting. BC is high purified nanofibrous cellulose produced from the metabolism process of *Acetobacter xylinum* (*A. xylinum*) bacteria by using glucose as a carbon source. BC is produced in the form of multilayer structure of three-dimensional nonwoven network of nanofibrous cellulose. Basically, BC has the same chemical structure as vascular plant cellulose, linear α -1,4-glucan chains (Czaja, Romanovicz, & Malcolm Brown, 2004) but the physical structure of the BC is totally different from the vascular plant cellulose. The three-dimensional structure was found only in the BC but not in the vascular plant cellulose (Rezaee, Solimani, & Forozandemogadam, 2005; Wan, Hong, Jia, Huang, Zhu, Wang, & Jiang, 2006; Grzegorzczyn & Ezak, 2007). This structure of BC resulted in high cellulose crystallinity (60–80%) and as high Young's modulus of 138 GPa and tensile strength of at least 2 GPa, which are almost equal to those of aramid fibers (Li, Chen, Hu, Shi, Shen, Zhang, & Wang, 2009). The nanometer scale diameter of BC fiber, about 100 times smaller than fibrils in plant cellulose, leads to a large surface area that can hold

large amount of water (up to 200 times of its dry mass) and display a great elasticity and a high wet strength. (Klemm, Schumann, Udhardt, & Marsch, 2001; Czaja, Young, Kawecki & Brown, 2007). One of the most important features of BC is its chemical purity. BC is free of lignin and hemicelluloses, whereas plant cellulose usually associates with these chemicals. Furthermore, the high chemical purity and high liquid absorption capacity resulted in a good biocompatibility of BC. These unique physical properties, mechanical properties, and chemical purity of BC leading to wide range of applications such as paper industrial, headphone membranes, food industrial (Li, Chen, Hu, Shi, Shen, Zhang, & Wang, 2009), biomaterials including temporary skin substitute, artificial blood vessels (Czaja, Young, Kawecki, & Brown, 2007; Kamel, 2007) and membrane for pervaporation of water-ethanol binary mixtures (Dubey, Saxena, Singh, Ramana & Chauhan, 2002). Moreover, BC also serves as an applicable matrix for impregnating of nanoparticles or nanowires such as cadmium sulfide nanoparticles (Li, Chen, Hu, Shi, Shen, Zhang, & Wang, 2009), silver chloride nanoparticles (Hu, Chen, Li, Shi, Shen, Zhang, & Wang, 2009), silver nanoparticles (Maneerung, Tokura, & Rujiravanit, 2008) and titania nanowires (Zhang & Qi, 2005).

Magnetic nanoparticles are nanoparticles of iron oxides. In nature, iron oxides exist in various forms including hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) (Cornell & Schwertmann, 2003). Hematite is blood-red iron oxide. It is the oldest known iron oxide and often is the end product of the transformation of other forms of iron oxides at ambient conditions (Teja & Koh, 2009). Maghemite is a metastable state of iron oxide. It is formed by weathering or low-temperature oxidation of magnetite (Majewski & Thierry, 2007). Magnetite is a black iron oxide. It exhibits the strongest magnetism of any transition metal oxides (Cornell & Schwertmann, 2003; Majewski & Thierry, 2007). It has been reported that, magnetite exhibits biocompatibility and low toxicity in human body (Majewski & Thierry, 2007; Tartaj *et al.*, 2003; Kim *et al.*, 2005; Tartaj *et al.*, 2005).

Silver is one of the most interesting metals due to its excellent electrical, thermal, optical and/or catalytic properties (Lu & Chou, 2008). Silver bulk exhibited the high electrical conductivity with 10^6 S/cm. Recently, nanometer-scaled silver have received a great deal of attention in various potential applications, such as conductors,

catalysts, chemical sensors, etc. (Haes, & Van Duyne, 2003; Magdassi et al., 2003; Nie, & Emory, 1997; Pradhan, Pal, & Pal, 2002; Ye, Lai, Liu, & Tholen, 1999). Due to their small sizes and large surface-to-volume ratios, nanometer-scaled silver have superior properties compared to their bulk counterparts, they are promising candidates for novel nanoscale electronic, optical and mechanical devices. In order to achieve the high efficiency of electrical conduction, the most importance requirement is the connection of as-prepared nanometer-scaled silver; the particles need to be well connected to form the conduction pathway (Zhang, Moon, Lin, Agar, & Wong, 2011).

Zinc Oxide (ZnO) is an important and attractive inorganic semiconductor since it exhibits wide band gap (3.37 eV) and large exciton-binding energy (60 meV) (Applerot, Perkash, Amirian, Girshevitz, & Gedanken, 2009). These unique characteristics of ZnO leading to a wide range of technological applications such as luminescence, photocatalyst, piezoelectric transducer, actuators, gas sensors and solar cells (Sulieman, Huang, Liu, & Tang, 2007; An, Cao, & Zhu, 2007; Li, Fang, Liu, Ren, Huang, & Zhao, 2008; Wu, Wu, & Lü, 2006; Liu, Huang, Li, Duan, & Ai, 2006; Cao, Lan, Zhao, Shen, & Yao, 2008; Jia, Yue, Zheng, & Xu, 2008). Recently, ZnO was received more and more attention on their nanoscale properties. Due to their small sizes and large surface-to-volume ratios which have superior properties compared to their bulk counterparts, they are promising candidates for novel nanoscale electronic, optical and mechanical devices (Hu, Chen, Zhou, & Wang, 2010). Moreover, the high specific surface area due to the reducing in particle size into micrometer or nanometer scale was also resulted in the antibacterial properties of ZnO particles (Jung, Oh, Lee, Yang, Park, Park, & Jeong, 2008).

In this present study, the inorganic–organic hybrid material of magnetic particles, silver particles, zinc oxide particles and BC were successfully prepared by using template-directed synthesis method. The cations precursor of magnetic, silver and zinc oxide particles were firstly homogeneously dispersed into the BC matrix. Then, these dispersed-cations were converted to be metal or metal oxide particles inside BC matrix. According to this preparation process, the nanofibrous structure of BC were expected to be an effective template for controlling the particle size, morphology, porous structure and distribution behavior of the as-synthesized metal or metal oxide particles. The well distribution with optimizing particle size of the as-

prepared metal or metal oxide particles were resulted in the synergistic properties between the as-synthesized metal or metal oxide particles and BC matrix. Therefore, the magnetic particle incorporated-BC, the silver particle incorporated-BC, the magnetic and silver particle incorporated-BC and the zinc oxide particle incorporated-BC were represented the new class of inorganic–organic hybrid material with combining the unique properties of the incorporated-metal or metal oxide particles and BC in one material.