CHAPTER I

INTRODUCTION

Green chemistry involves a reduction or elimination of the use or generation of hazardous substances. It plays an important role in nanotechnology research.[1] The green synthesis of metal nanoparticles could take advantage of green chemistry principles by employing green reagents (e.g., solvent, reducing agent, and stabilizing agent) under mild reaction conditions.[1, 2] The nanoparticles (NPs) of noble metals such as silver (Ag), palladium (Pd), gold (Au), and platinum (Pt) synthesis using green reagents such as a reducing/stabilizing agent have been reported. Particularly, platinum nanostructures are very attractive for nanotechnology research because it has been widely used in many applications (e.g., catalyst).[3, 4] Moreover, it is well known that the properties of platinum metal depend on particle size, shape, compositions, and structures,[3] i.e., especially, size- and shape-dependent catalytic and optical activities.[5, 6] Therefore, it would display the significant advantage if the green synthesis method for fabrication of platinum nanostructures with morphologies controllable is developed.

As mentioned above, the feature properties of platinum nanoparticles (Pt NPs) have been used for a variety of catalyst applications (e.g., hydrogenation reaction and oxidation reaction).[6] Especially, it served as an oxidative catalyst for the alcohol oxidation, e.g., glycerol, due to the similarly of the reactive with molecular oxygen of both hydroxyl groups causes the poor selectivity to desire product. Therefore the specific catalyst has been used for catalysis of the reaction. Glycerol is a greatly important reagent in industry because it can be obtained in large amount from the production of biodiesel, nontoxic, edible, biosustainable and biodegradable materials.[7–10] Therefore, it provides a very great advantage if the glycerol could be transformed into value-added chemicals. For instance, glyceric acid is one of the important intermediates for organic synthesis which can be obtained as a product of

the glycerol oxidation reaction.[11] In the past decade, it was well known that the catalysis of oxidation reaction of primary alcohol with novel metal strongly dependent on the basicity of the reaction medium leading to external homogeneous base solution required. Consequently, the catalysis reaction in basic solution shows the drawback of product formed in acid salt (e.g., glycerate) resulting in the solution needs additional neutralization and acidification in order to get the free product.[12] Nowadays, the glycerol oxidation reaction in base-free reaction have been demonstrated such as the reaction was carried out by using the drastically oxygen flow (150 mL/min),[12] or using basic support material (hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 nH_2O$ (Mg-Al-CO_3)).[13] From the viewpoint of green synthesis, the molecular oxygen is the greener oxidant as well as water. Hence, the complete green method has been successfully developed if the support-metal catalyst synthesized by green reagent and their catalytic activity for oxidation of glycerol can be performed under mild condition.

The attractive nanostructures of platinum are not only in zero-dimensional (e.g., spherical shape) but also one-dimensional, 1-D (e.g., rod and wires), two-dimensional, 2-D (e.g., plates), and three-dimension, 3-D (e.g., octahedron faceted).[14, 15] Especially, one-dimensional platinum nanostructure displays its unique combination of dimensions at multiple length scale and nanometer-sized wall thickness leading to provide high surface area. Therefore, it can use as catalyst without the need of high-surface-area support.[16] Several techniques including impregnation method,[17] chemical reduction with a capping agent,[18] template directed electrodeposition,[19] and galvanic displacement have been used for synthesis of platinum nanostructures (1-D).[20] However, the galvanic displacement is a simple and green as well as efficient method to fabricated platinum nanostructures. Hence, it will become more effective method if the platinum hollow nanostructure (platinum nanotube or platinum hollow fiber) with a very high aspect ratio was constructed.

In this research, the chemical reduction method referring to green chemistry principles was developed for the synthesis of Pt NPs. The developed method was applied for the preparation of supported Pt NPs catalyst and they were used for catalysis of oxidation reaction of glycerol. In addition, the simple galvanic method

between commercial aluminum foil and silver ions was used for construction of high aspect ratio silver fiber. An obtained silver fiber was served as a template for fabrication of platinum hollow structure.