

論文内容の要旨

論文題目 パラジウムナノ粒子集合体の構築、物性評価と
水素吸蔵材料への応用

(Construction and Characterization of Palladium Nanoparticle
Assemblies and Their Application to Hydrogen Storage Materials)

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Introduction

Metal nanoparticles show unique physical properties such as lower melting point and chemical properties such as high catalytic activity different from those of bulk metals owing to the change in lattice parameters and the higher ratio in the number of surface atoms compared to that of overall atoms. In the study of my Ph.D course, I focused on the hydrogen storage properties of metal nanoparticles which will be different from those of the bulk metals because both the natures of surface layer and internal metal core are crucial to the process to absorb hydrogen from dihydrogen gas. Hydrogen is expected to be employed for clean energy carrier and various metals and alloys have been investigated as dihydrogen storage materials. In this work, I studied hydrogen storage properties of palladium nanoparticles with network structure with tetrakis(terpyridine) ligands as bridging spacers and vanadium-palladium alloy nanoparticles.

1. Palladium nanoparticles with network structure using tetrakis(terpyridine) bridging ligand

Palladium metal is known for hydrogen storage metal and I have been studying palladium nanoparticles for their high stability and facile synthesis. In my master course, I studied metal-organic framework (MOF) type of palladium nanoparticle assemblies. It was aimed that hydrogen storage by metal nanoparticles and MOF were generated at the same time. For the synthesis of MOF type of nanoparticle assemblies, I connected palladium nanoparticles through ligand on their surface, and constructed network structure of nanoparticles. Previously, I used bis or tris(terpyridine) ligands as the bridging ligand to construct network structure. However, the porosity in the networks could not be controlled probably due to plane structure of ligands. Based on the results, I employed a new tetrahedral bridging ligand **1** in this study.

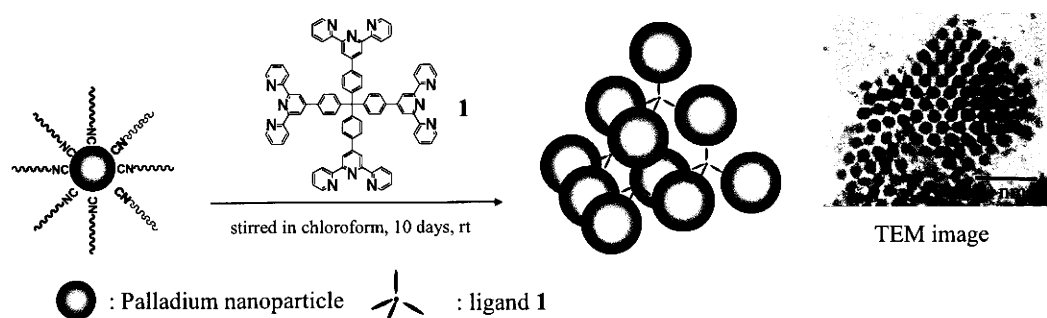
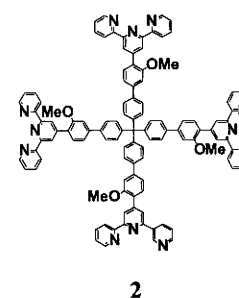


Figure 1. Synthesis of palladium nanoparticles with network structure

Initially, we designed and synthesized tetrakis(terpyridine) bridging ligand **1** by Suzuki coupling. The ligand has tetrahedral structure and terpyridine group on the each end. Tetrahedral structure helps construction of network structure effectively because of its three-dimensional structure. Then, to prepare the nanoparticle with network structure, ligand exchange reaction of the bridging ligand **1** with 1-pentyl isocyanide on palladium nanoparticles was carried out (Figure 1). Aggregation of the nanoparticles was confirmed by the TEM observations and the distance between nanoparticles was consistent with the value estimated from the size of the ligand. These results have confirmed the formation of the expected network structure of palladium nanoparticles. The hydrogen storage volume of nanoparticles with network structure showed 0.26 mass% at rt and 10 MPa.

Next, we designed tetrakis(terpyridine) ligand **2** to enlarge porous in network structure. This ligand has four methoxy groups on aromatic ring to improve solubility of ligand because the ligand **1** (without methoxy groups) hardly dissolved in solvent. The ligand **2** was synthesized by Suzuki coupling reaction and ligand exchange reaction with the bridging ligand **2** was carried out. The hydrogen storage volume of nanoparticles bridged by ligand **2** showed 0.33 mass% at rt and 10 MPa.



As another strategy to enlarge the pore size, bis(terpyridine)-metal complexation on palladium nanoparticle surface was employed (Figure 2). First, we examined the conditions to isolate palladium nanoparticles protected by ligand 1. Dispersed single palladium nanoparticles were obtained when more than 12 times of ligand 1 in mol ratio compared with palladium nanoparticles was employed. Addition of $\text{Fe}(\text{BF}_4)_2$ to the dispersion of ligand 1 protected palladium nanoparticles in CHCl_3 caused aggregation of nanoparticles, and the formation of porous nanoparticles network was confirmed by TEM. From the result of nitrogen adsorption measurement, the pore size of the network bridged by the bis(terpyridine)iron complexes was bigger than that of the previous ligand 2-bridged network. Hydrogen storage volume showed 0.25 mass% at rt and 10 MPa.

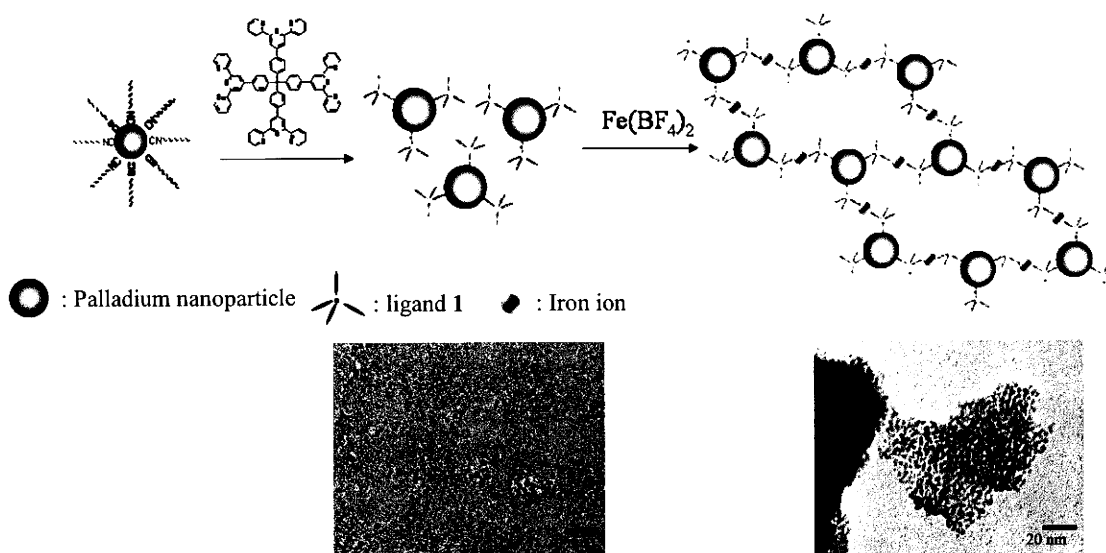


Figure 2. Synthesis of network structure using iron ion for bridging and their TEM images

2. Palladium nanoparticles with larger size and tetrahedral structure

Most of metals in nanoparticles are sited at their surface and sites for hydrogen storage in metal decreased. Synthesis of larger nanoparticles is effective for improvement of hydrogen storage volume. To synthesize pentyl isocyanide protected palladium nanoparticles with larger size, I examined synthesis by polyol method. I prepared palladium nanoparticles by reduction of $\text{PdCl}_2(\text{MeCN})_2$ with ethylene glycol in the presence of 1-pentyl isocyanide as surfactant. From the observation of TEM image, synthesized nanoparticles have tetrahedral structure with 28 nm (Figure 3). The size of tetrahedral nanoparticles was 10 times bigger than that of previously prepared sphere ones. The hydrogen storage volume showed 0.34 mass% at 10 MPa and rt.

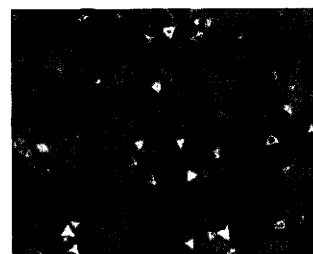


Figure 3. TEM image of tetrahedral palladium nanoparticles

3. Vanadium-palladium nanoparticles

Vanadium stored six times hydrogen compared to palladium. Because vanadium metal on surface is oxidized easily, synthesis of vanadium nanoparticles is difficult. I examined stabilization of vanadium by doping vanadium to palladium nanoparticles. Synthesized nanoparticles contained 10 % of vanadium and formed alloy structure from the observation of lattice spacing in TEM image. Hydrogen storage volume showed 0.47 mass% at rt and 10 MPa.

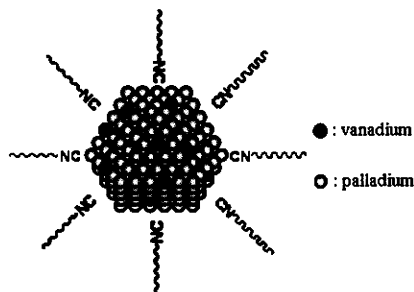


Figure 4. vanadium-palladium alloy nanoparticle

Conclusion

I synthesized porous palladium nanoparticle assemblies using tetrakis(terpyridine) bridging ligands. Nanoparticles aggregated with the distance estimated by the size of the ligand between nanoparticles. I succeeded to control the network structure of palladium nanoparticles by bridging ligands.

Next, I synthesized isocyanide protected palladium tetrahedral nanoparticles with larger size. The size of nanoparticles was 10 times compared to previous ones and hydrogen storage volume was larger than small ones. In addition, the tetrahedral structure is unique structure and expected possibilities for bridging structure.

Finally, I synthesized vanadium-palladium alloy nanoparticles. It formed alloy structure and hydrogen storage volume was 0.47 mass% which was larger than that of palladium nanoparticles. If I prepared alloy nanoparticles with larger ratio of vanadium, the hydrogen storage properties would be changed compared to this result.