Chemistry Letters Vol.33, No.10 (2004)

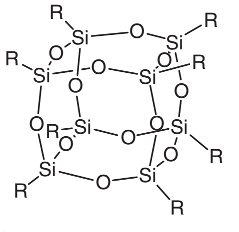
Self-organized Wire-like Aggregates of Palladium Nanoparticles with Poly(amidoamine)dendrimer

Kensuke Naka,* Hideaki Itoh, and Yoshiki Chujo*
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Katsura, Nishikyo-ku, Kyoto, 615-8510

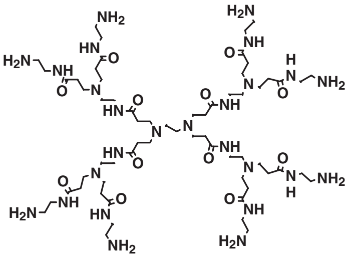
(Received July 20, 2004; CL-040847)

Wire-like aggregates of palladium nanoparticles with a length up to several micrometer were produced by stirring palladium(II) acetate with the G1.0 poly(amidoamine) (PAMAM) dendrimer in methanol at room temperature via self-organized wire-like templates of palladium ions and the PAMAM dendrimer.

Metal nanoparticles have drawn increasing interest because of their novel properties, which are caused by size and surface effects and are different from those of bulk or molecular materials, and because of their potential applications in catalysis and nonlinear optics, and as electronic, magnetic, or other advanced materials.[1] The realization of technologically useful nanoparticle-based materials depends not only on the quality of the nanoparticles (e.g., size and shape) but also on their spatial orientation and arrangement. The development of practical strategies for the assembly of metal nanoparticles into order structure is thus an area of considerable current interest. Many efforts focus on the formation of organized two-dimensional (2-D) and three-dimensional (3-D) structures of metal nanopartices. However, the organization of nanoparticles in one-dimensional (1-D) assemblies has met with limited success. The most successful route for the preparation of 1-D assemblies of metal nanoparticles requires using templates, such as DNA,[2,3] mesoporous silica,[4] steps or edges supported on solid substrates.[5,6] However, few papers have reported the fabrication of 1-D nanocomposites of nanoparticles without templates.[7,8] It is still desirable to design a simple self-assembly process for preparation of 1-D structure of the metal nanoparticles.



1 : R = $CH_2CH_2CH_2NH_3^+Cl^-$



G1.0 PAMAM dendrimer

Recently we have reported the self-organization of palladium nanoparticles.[9] Uniform spherical aggregates of palladium nanoparticles with a mean diameter of 70 nm were produced by stirring palladium(II) acetate with octa(3-aminopropyl)-octasilsesquioxane octahydrochloride (**1**) in methanol at room temperature via self-organized spherical templates of palladium ions and **1**. The structure and the multifunctionality of **1** may play a predominant role for the formation of the uniform spherical aggregates. Our goal is to control the size and the shape of aggregates of metal nanoparticles. We used here the G1.0 poly(amidoamine)(PAMAM) dendrimer instead of **1**. We observed the self-assembling of the metal nanoparticles into wire-like aggregates using the G1.0 PAMAM dendrimer. It is worth pointing out that the wire-like aggregates are formed spontaneously without any external force and templates described above.

When an acidic methanol solution (50 mL) (containing 5.0×10^{-3} mmol of HCl) of the G1.0 PAMAM dendrimer (1 mg, 7.0×10^{-4} mmol) and palladium(II) acetate (10 mg, 4.4×10^{-2} mmol) was stirred at room temperature, the solution immediately became turbid. This suggests microscopic aggregate formation. The solutions gradually turned from yellow to black with increasing reaction time, indicating the reduction of palladium ions and the formation of palladium nanoparticles.

After 24 h reaction, one drop of the solution containing the obtained product was placed on a copper grid and allowed to evaporate the solvent under atmospheric pressure at room temperature. The transmission electron microscopy (TEM) investigation showed the wire-like aggregates (Figure 1). The most length of the wire-like aggregates was more than 0.5 μm. These wire-like aggregates were clearly composed of dark spots. These dark spots were individual palladium nanoparticles. Every nanoparticles, with a size of 4.0 ± 0.8 nm, appeared as a discrete entity in the aggregates. The scanning electron microscopy investigation also indicated that the obtained products were wire-like structure.

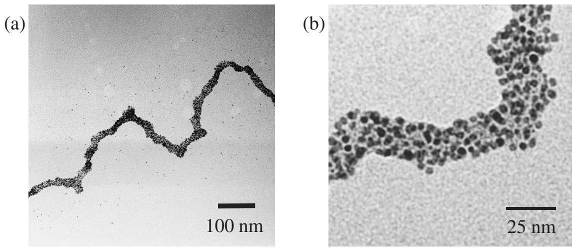


Figure 1. TEM images of (a) the wire-like aggregate of palladium nanoparticles and (b) enlarged image.

X-ray diffraction (XRD) is a strong method to investigate the solid structure of metal nanoparticles. The XRD pattern of the obtained product showed the characteristic diffraction peaks of the palladium face-centered cubic (fcc) phase, indicating the formation of metallic Pd. The average size of particles was about 4.0 nm calculated by Scherrer formula from half-widths of the diffraction peaks. The calculated value from XRD pattern is in good agreement with the result by the TEM image.

Some insight into the formation mechanism of the wire-like aggregates has been obtained by examining TEM images. After addition of PAMAM dendrimers into a methanol solution of pal-

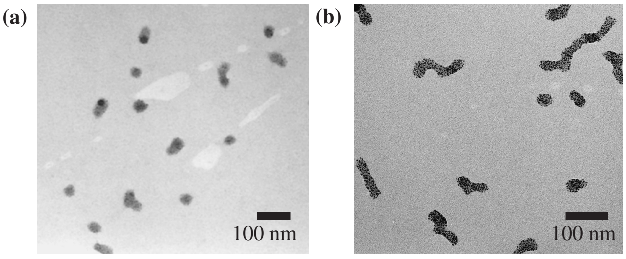


Figure 2. TEM images of the reaction mixture after (a) 10 min and (b) 6 h from addition of the G1.0 PAMAM dendrimer.

ladium(II) acetate and the resulting mixture was stirred at room temperature for 10 min, one drop of the solution was placed on a carbon grid for TEM analysis. Only spherical colloids with low contrast were observed (Figure 2a). No individual palladium nanoparticles were identified as black dots. After an aging time of 6 h, the spherical colloids stuck together and started directed aggregation growth (Figure 2b). A careful look at the aggregates enables to distinguish individual palladium nanoparticles as a black dot, indicating that reduction of the palladium ions proceeded in the colloids. When the aging time was further prolonged to 24 h, the wire-like assemblies consisted of palladium nanoparticles were observed. These results indicate that the primary colloids consisting of PAMAM dendrimers and palladium ions with a diameter of 40 nm were formed at the early stage of the reaction and aggregated into wire-like assemblies in a directional manner. The reduction of the palladium ions by methanol proceeded slowly in the colloids. The shape of the wire-like assemblies was kept during the reduction process of palladium ions. Consequently, the palladium nanoparticles were incorporated into the wire-like colloids composed of PAMAM dendrimers.

Addition of $NaBH_4$ as a strong reducing agent to a freshly prepared methanol solution of palladium(II) acetate and PAMAM dendrimers resulted in the immediate change of color from yellow to black, which is characteristic for formation of palladium nanoparticles. The TEM investigation of the obtained product showed no wire-like aggregates but irregular aggregates of palladium nanoparticles. It is assumed that the wire-like colloids were destroyed during the rapid collision of metal atoms. This result indicates that the weak reducing agent such as methanol is a prerequisite for the formation of the wire-like colloids of the palladium nanoparticles.

Effect of different added amount of HCl to methanol solution before adding PAMAM dendrimers and palladium acetate was observed. The amount of HCl to methanol solution was varied from 0 to 15×10^{-3} mmol. When the amount of HCl was from 0 to 1.0×10^{-3} mmol, uniform spherical aggregates with a diameter of 50 nm composed of palladium nanoparticles was observed. In contrast, when the amount of HCl was higher than 1.0×10^{-3} mmol, the wire-like aggregates of palladium nanoparticles were observed (Figure 1). However, in the case of 15×10^{-3} mmol of HCl, the wire-like aggregates tended to interconnect forming network aggregates. That is because the morphology of aggregates of palladium nanoparticles changes from spherical to wire-like or network with increasing the added amount of HCl. These experimental results suggest that the added amount of HCl to methanol solution has a significant influence on the morphology of aggregates of palladium nanoparticles.

The formation of the wire-like aggregation could be interpreted through the simulation results of particle growth by irreversible aggregation of particles.[10] Since exposed ends of clusters of the particles grow more rapidly than the interior, the resulting cluster has a chainlike structure.

From the fact that the addition of HCl to the solution resulted in the wire-like aggregates, the driving force for assembly could be electrostatic interaction and hydrogen bonding between ammonium groups of the dendrimer and $PdCl_4^{2-}$ anion formed by ligand exchange.[11,12] Two control experiments were carried out. Addition of HBr instead of HCl also showed the same result like using HCl. In contrast, addition of HNO_3 showed no wire-like aggregates. This would be due to the lack of palladium anions (PdX_4^{2-}, X = ligand). These results support that the hydrogen bonding between halogen anions and the ammonium groups play an important role in this system.

In conclusion, we have demonstrated the self-organization of the metal nanoparticles into wire-like aggregates by dendrimers. The present method offers unique possibilities for designing new synthetic routes of controlled organized structure based on the metal nanoparticles. The investigations for fine-tuning of the product structure by controlling experimental conditions and different generation of the dendrimers will be reported. We hope that this concept represents a powerful and general strategy for the creation of highly structured multifunctional materials.

References

1 M. A. El-Sayed, *Acc. Chem. Res.*, **34**, 257 (2001).
2 E. Braun, Y. Eichen, U. Sivan, and G. Ben-Yoseph, *Nature*, **391**, 775 (1998).
3 J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke, and H. K. Schackert, *Adv. Mater.*, **12**, 507 (2000).
4 Y. J. Han, J. M. Kim, and G. D. Stucky, *Chem. Mater.*, **12**, 2068 (2000).
5 T. Oku and K. Suganuma, *Chem. Commun.*, **1999**, 2355.
6 T. Teranishi, A. Sugawara, T. Shimizu, and M. Miyake, *J. Am. Chem. Soc.*, **124**, 4210 (2002).
7 J. H. Zeng, J. Yang, Y. Zhu, Y. F. Liu, Y. T. Qian, and H. G. Zheng, *Chem. Commun.*, **2001**, 1332.
8 O. Vidoni, T. Reuter, V. Torma, W. Meyer-Zaika, and G. Schmid, *J. Mater. Chem.*, **11**, 3188 (2001).
9 K. Naka, H. Itoh, and Y. Chujo, *Nano Lett.*, **2**, 1183 (2002).
10 L. M. Sander, *Nature*, **322**, 789 (1986).
11 D. I. Svergun, M. B. Kozin, P. V. Konarev, E. V. Shtykova, V. V. Volkov, D. M. Chernyshov, P. M. Valetsky, and L. M. Bronstein, *Chem. Mater.*, **12**, 3552 (2000).
12 L. M. Bronstein, S. N. Sidorov, A. Y. Gourkova, P. M. Valetsky, J. Hartmann, M. Breulmann, H. Cölfen, and M. Antonietti, *Inorg. Chim. Acta*, **280**, 348 (1998).

Published on the web (Advance View) August 28, 2004; DOI 10.1246/cl.2004.1236