CHEMISTRY OF MATERIALS
Communication

*Chem. Mater.* **2010,** *22,* 1273–1275 1273
DOI:10.1021/cm902948v

# Low-Temperature Synthesis of Ultrathin Rhodium Nanoplates via Molecular Orbital Symmetry Interaction between Rhodium Precursors

Kwonho Jang,[†] Hae Jin Kim,[‡] and Seung Uk Son*[,†]

[†]*Department of Chemistry and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea and* [‡]*Korea Basic Science Institute, Daejeon 350-333, Korea*

*Received September 22, 2009*
*Revised Manuscript Received November 18, 2009*

Shape-controlled synthesis of nanomaterials has become an important issue to synthetic material scientists because new physical and chemical properties can be obtained through the evolution of unprecedented shapes.[1] Diverse methods for shape control of nanomaterials have been developed on the basis of the template method,[2] growth of intrinsic anisotropic crystals,[3] use of shape directing catalysts,[4] and oriented attachment mechanism,[5] as well as the low-temperature, kinetically controlled growth of nanomaterials.[6]

Recently, the Xia and Yang groups demonstrated the growth of gold nanowires in amine solution at low temperature (even at room temperature), which is an interesting example of kinetically controlled synthesis.[7] The cubic phase of the resultant nanowires indicates that the low-temperature growth has the potential to produce unprecedented nanomaterials. Interestingly, the relatively weak Au−Au aurophilic interaction[8] in solution played a key role in the assembly of precursors and the resultant shape evolution.

Similar to the aurophilic interaction, a weak metal−metal interaction between the group 9 metals with an oxidation state of +1 was observed by Gray and coworkers, which has been attributed to a molecular orbital symmetry interaction of the filled $\sigma$-metal−metal bonding and $\sigma^*$-antibonding orbitals with the empty $p_z$ $\sigma$ and $\sigma^*$ orbitals (Figure 1).[9] This interaction stabilized the filled orbitals and destabilized the empty orbitals. Despite its relative weakness, the resultant interaction is strong enough to induce the assembly of complexes, even in solution.[9] Very recently, our research group disclosed the Rh(I)−Rh(I) interaction of square planar $Rh(CO)_2Cl$(amine) complexes to form molecular wires.[10] In the present study, we report the preparation of unprecedented ultrathin (1.3 nm thickness) rhodium nanoplates at 50 °C via metal−metal interaction between Rh(I) precursors.

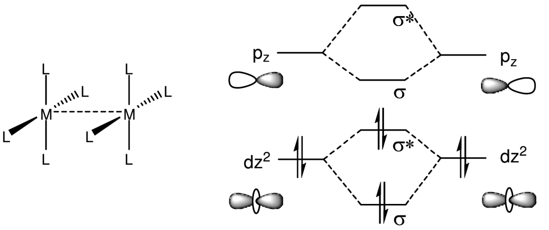

**Figure 1.** Molecular orbital symmetry interaction between $d^8$-metal complexes.

The shape-controlled synthesis of rhodium nanoparticles has been extensively studied because it is a very important metallic catalyst for diverse organic transformations.[11] However, the shape-controlled synthesis of rhodium nanomaterials has focused on the isotropic structure due to rhodium's face-centered cubic (fcc) structure. As far as we are aware, no report has been published on anisotropic rhodium nanomaterials such as 2D nanoplates.

In the typical synthetic procedure for rhodium nanoplates, rhodium carbonyl chloride dimer, $[Rh(CO)_2Cl]_2$ (39 mg, 0.10 mmol) was dissolved in oleylamine (10 mL) at room temperature. The resultant solution was heated at 50 °C for 10 days without stirring. In contrast, when the solution was stirred, no nanomaterials were obtained. As the reaction proceeded, black precipitates were formed on the wall of the vial. The mother liquid was decanted and the precipitates on the wall of the vial were collected and washed with methanol several times. When the reaction temperature was above 70 °C, a significant amount of isotropic nanomaterials was mixed. At room temperature, no nanomaterials were formed. The resultant precipitates were dispersed in methylene chloride. Figure 2a and Figure S1 in the Supporting Information showed the typical transmission electron microscopy (TEM) image of the top view of nanoplates (vide infra).

---

*Corresponding author. E-mail: sson@skku.edu.

(1) Peng, X.; Manna, U.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.

(2) Liang, Y.; Zhen, C.; Zou, D.; Xu, D. *J. Am. Chem. Soc.* **2004**, *126*, 16338.

(3) Park, K. H.; Choi, J.; Kim, H. J.; Oh, D.-H.; Ahn, J. R.; Son, S. U. *Small* **2008**, *4*, 945.

(4) Dong, A.; Yu, H.; Wang, F.; Buhro, W. E. *J. Am. Chem. Soc.* **2008**, *130*, 5954.

(5) (a) Tang, Z.; Kotov, N. A.; Giersig, M. *Science* **2002**, *297*, 237. (b) Cho, K.-S.; Talapin, D. V.; Gaschler, W.; Murray, C. B. *J. Am. Chem. Soc.* **2005**, *127*, 7140.

(6) Park, K. H.; Choi, J.; Chun, J.; Kim, H. J.; Son, S. U. *Chem. Commun.* **2008**, 1659.

(7) (a) Lu, X.; Yavuz, M. S.; Tuan, H.-Y.; Korgel, B. A.; Xia, Y. *J. Am. Chem. Soc.* **2008**, *130*, 8900. (b) Huo, Z.; Tsung, C.-K.; Huang, W.; Zhang, X.; Yang, P. *Nano Lett.* **2008**, *8*, 2041.

(8) Dziwok, K.; Lachmann, J.; Wilkinson, D. L.; Müller, G.; Schmidbaur, H. *Chem. Ber.* **1990**, *123*, 423.

(9) (a) Mann, K. R.; Gordon, J. G.II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553. (b) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G.II. *Inorg. Chem.* **1978**, *17*, 828.

(10) Jang, K.; Jung, I. G.; Nam, H. J.; Jung, D.-Y.; Son, S. U. *J. Am. Chem. Soc.* **2009**, *131*, 12046.

(11) (a) Zhang, Y.; Grass, M. E.; Kuhn, J. N.; Tao, F.; Habas, S. E.; Huang, W.; Yang, P.; Somorjai, G. A. *J. Am. Chem. Soc.* **2008**, *130*, 5868. (b) Hoefelmeyer, J. D.; Niesz, K.; Somorjai, G. A.; Tilley, T. D. *Nano Lett.* **2005**, *5*, 435. (c) Park, K. H.; Jang, K.; Kim, H. J.; Son, S. U. *Angew. Chem., Int. Ed.* **2007**, *46*, 1152.

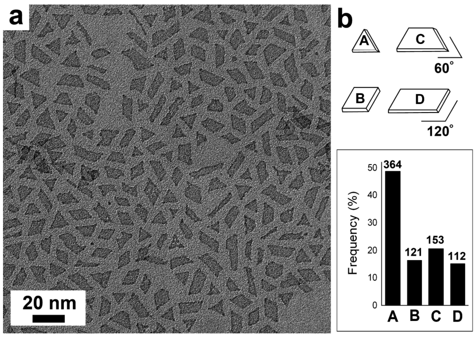

**Figure 2.** (a) TEM image of the top view of the prepared nanoplates, (b) shape distribution diagram by investigating 750 plates.

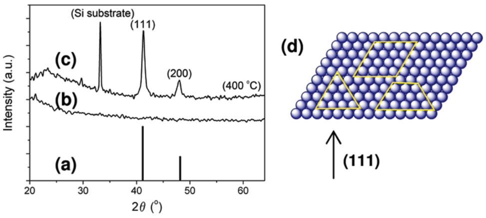

**Figure 3.** Powder X-ray diffraction patterns of (a) metallic rhodium in literature, (b) the as-prepared nanoplates, and (c) the heat-treated sample at 400 °C. (d) Illustration of the shape evolution of ultrathin nanoplates.

Interestingly, the top view of plates varied from triangle to qudrangle (trapezoid, rhombus). The distribution of these shapes was statistically analyzed by counting 750 plates (Figure 2b). The triangular nanoplates were observed as major shape. Interestingly, all the observed shapes have 60 or 120° angles and square shape was not detected. This observation can be a clue for understanding the crystal plane of plates (vide infra). The powder X-ray diffraction (XRPD) studies of the as prepared materials showed no valuable information due to the ultrathin thickness of plates (Figure 3a,b). However, when the isolated nanomaterials were heated at 400 °C under argon for 12 h, two distinct peaks were observed, which were indexed as metallic rhodium (JCPDS # 01−1214) (Figure 3c). Unfortunately, X-ray photoelectron spectroscopy (XPS) of the as-prepared samples showed no reliable rhodium peaks due to the ultrathin thickness of materials and the coating of organic materials on surface of nanoplates (Figure S5 in the Supporting Information). Energy-dispersive X-ray spectroscopy (EDS) of the as prepared samples showed a trace amount of chlorine (4 atomic% chlorine to rhodium), which supports the theory that the major materials are not rhodium chloride species. Electron diffraction (ED) pattern of as prepared nanoplates matched well with that of metallic rhodium (see Figure S2 in the Supporting Information).

The evolution of the observed shapes can be rationalized by understanding the crystal structure of the nanomaterials. The top plane of nanoplates is (111) plane of metallic rhodium based on high resolution-TEM study (vide infra) and triangular and qudraangular shapes having 60 and 120° angles can be generated as illustrated in Figure 3d.

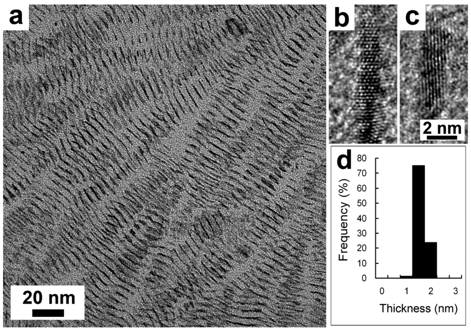

**Figure 4.** (a) TEM image, (b,c) HRTEM images, and (d) thickness distribution diagram of the obtained rhodium nanoplates.

Recently, diverse metallic nanoplates, including Au and Ag, with an fcc phase have been prepared. However, the thickness of these nanoplates was relatively thick in the range of 5−100 nm.[12] By slowly evaporating the hexane solvent of sample solution, the side view of the packed nanoplates were observed in TEM investigation (Figure 4).

As shown in panels a and d in Figure 4, the prepared rhodium nanoplates in this study were ultrathin with an average thickness of only $1.3 \pm 0.2$ nm (counting 176 plates). The prepared nanoplates exhibited a self-assembled packing structure in range of tens of micrometers (see Figure S3 in the Supporting Information).

The side view of nanoplates was further analyzed by high resolution-TEM. (Figure 4b,c) The average distance of parallel crystal planes to the plates was 0.222 nm, which was assigned to the distance of the (111) crystal plate (0.220 nm, JCPDS # 01−1214). The distance of the vertical crystal planes to plates was 0.233 nm, which was assigned to the 1/3 (422) crystal plane (the known distance between the 1/3 (422) crystal plane, 0.234 nm, JCPDS # 01−1214). Actually, all known Ag, Au, and Pd nanoplates with fcc phase have the same structure.[12]

It is quite noteworthy that the rhodium nanoplates were prepared at unusually low temperature, 50 °C. To investigate the formation process of nanoplates, we studied the precursor solution by UV−visible (UV/vis) absorption spectroscopy. The color of the precursor solution was dramatically changed from reddish yellow to black depending on the concentration (Figure 5). In 1975, the metal−metal interaction between the Rh(I) complexes was characterized via UV/vis spectroscopy by Gray.[9] The proof of the metal−metal interaction in solution was a sudden observation of the new strong and broad absorption bands across the visible-light range with a maximum absorption at 568 nm. The appearance of these bands was quite dependent on the complex concentration.

In this study, similar behavior was observed in the UV/vis spectra of the precursor solution (also, see the detail characterization of metal−metal interaction of Rh(CO)$_2$Cl(amine) complexes in ref 10). As shown in Figure 5b, a new broad shoulder band started to appear at 500 nm in the 5 mM solution. The intensity was increased

---

[12] (a) Busbee, B. D.; Obare, S. O.; Murphy, C. J. *Adv. Mater.* **2003**, *15*, 414. (b) Cui, X.; Li, C. M.; Bao, H.; Zheng, X.; Zang, J. C.; Ooi, P.; Guo, J. *J. Phys. Chem. C* **2008**, *112*, 10730. (c) Xiong, Y.; McLellan, J. M.; Chen, J.; Yin, Y.; Li, Z.-Y.; Xia, Y. *J. Am. Chem. Soc.* **2005**, *127*, 17118.

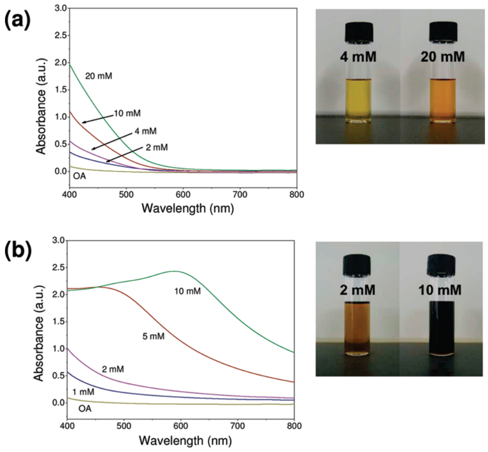

**Figure 5.** Concentration-dependent UV−visible spectroscopy and photographs of oleylamine solution of (a) $RhCl_3$ and (b) $[Rh(CO)_2Cl]_2$.

with increasing solution concentration. The solution was clearly homogeneous but very dark in the 10 mM solution. In the UV/vis spectrum, a very strong and broad absorption band appeared across the visible-light range. In this study, the synthesis of rhodium nanoplates was conducted with a 10 mM solution of precursor. The color change was quite reversible and the dilution of 10 mM solution to 2 mM resulted in the disappearance of the absorption peak at 585 nm. Through reaction of $[Rh(CO)_2Cl]_2$ with equivalent of oleylamine, the resultant complex, $Rh(CO)_2Cl$(oleylamine) was isolated and characterized by $^1H$, $^{13}C$ NMR and elemental analysis. Similar with $Rh(CO)_2Cl$(alkylamine),[10] the compound showed the reversible concentration dependent color change in solution and assembly behavior in solid state through the metal−metal interaction.

Although the other rhodium precursors were screened, the formation of rhodium nanoplates was only observed by using $[Rh(CO)_2Cl]_2$. In the case of $[Rh(COD)Cl]_2$, $\{Rh[P(OPh)_3]_2Cl\}_2$ and $RhCl_3$, the color of 10 or 20 mM solutions in oleylamine was reddish-yellow and the new peak in range of 500 to 700 nm was not observed (Figure 5a). It is noteworthy that Rh(COD)Cl(amine) and $Rh[P(OPh)_3]_2Cl$(amine) did not show the metal−metal interaction due to the steric effect of ligands.[10] Also, it has been well-known that the molecular orbital symmetry interaction has been observed in $d^8$−$d^8$ or $d^{10}$−$d^{10}$ systems. In this context, Rh(III) having $d^6$ electron configuration showed no metal−metal interaction in solution. Even after 10 days at 50 °C, the original color of the solution of these precursors was maintained and no nanomaterials were observed in TEM studies.

According to IR studies on 10 mM oleylamine solution of $[Rh(CO)_2Cl]_2$, CO ligands in this complex were gradually deligated in oleylamine solution during the nanoplate forming process. The amine-induced reduction process in the synthesis of zero-valence nanomaterials has been well-documented.[13] The excess amine gradually reduced the Rh (I) via electron transfer to form cationic radical, which abstracted the Cl from the precursors. Considering observations above, the speculated growth mechanism was described as shown in Figure 6. On the basis of the chain structure of $Rh(CO)_2Cl$(methylamine),[10] the coordinated oleylamines would be located up and down of 1D chains. The chains interact each other via van der Waals interaction between alkyl groups to form lamellar structure. Finally, the gradual deligation and reduction of Rh(I) to zero-valence Rh would form the 2D plates with shape evolution to triangle or quadrangle.

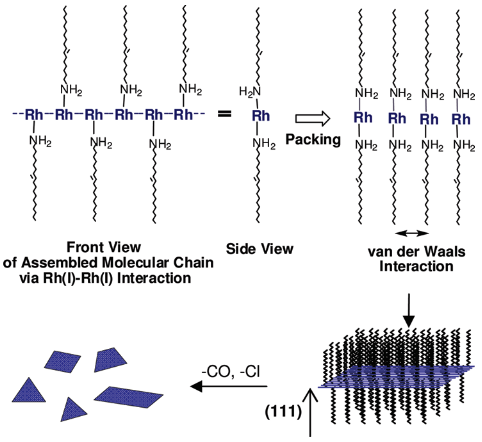

**Figure 6.** Suggested growth mechanism of rhodium nanoplates.

Considering the suggested formation mechanism in Figure 6, two-dimensional shape evolution would be quite dependent on the van der Waals interaction between the coordinated oleylamines. This hypothesis was supported by the following observations. When the length of alkylchains was gradually reduced to dodecyl, octyl, and butyl, the relative number of the observed 2D plates to 1D rods was significantly reduced (Figure S4 in the Supporting Information).

In conclusion, the unprecedented ultrathin rhodium nanoplates were successfully prepared via kinetically controlled growth at low temperature. The metal−metal interaction between the rhodium precursors in the solution was observed via UV/vis spectroscopy, which induced the assembly of precursors and the anisotropic shape evolution of rhodium. This approach can be extended to other square planar transition complexes having $d^8$ electronic configuration. Also, we believe that these ultrathin rhodium plates can be easily adhered on solid support for catalytic applications.

**Acknowledgment.** H.J.K. thanks the Hydrogen Energy R&D Center, a 21st century Frontier R&D Program. This work was supported by grants NRF-20090094024 (Priority Research Centers Program) and R31-2008-000-10029-0 (WCU program) through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology.

**Supporting Information Available:** Experimental general, synthetic procedure of Rh nanoplates, synthesis and characterization of $Rh(CO)_2Cl$(Oleylamine), additional TEM images and ED patterns (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(13) Newman, J. D. S.; Blanchard, G. J. *Langmuir* **2006**, *22*, 5882.