Korean J. Chem. Eng., 36(9), 1417-1420 (2019)
DOI: 10.1007/s11814-019-0337-4

pISSN: 0256-1115
eISSN: 1975-7220

Synthesis RhAg bimetallic composite nanoparticles for improved catalysts on direct synthesis of hydrogen peroxide generation

Yangpil Jang[*,‡], **Hyobin Nam**[**,***,‡], **Joseph Song**[****,*****,‡], **Seungyong Lee**[**,***,†],
Jae-Pyung Ahn[*****,†], **and Taekyung Yu**[*,†]

*Department of Chemical Engineering, College of Engineering, Kyung Hee University, Youngin 17104, Korea
**Materials Architecturing Research Center, Korea Institute of Science and Technology, Seoul 02455, Korea
***Department of Nanomaterials Science and Engineering, Korea University of Science and Technology, Daejeon 34113, Korea
****Department of Material Science & Engineering, College of Engineering, Korea University, Seoul 02841, Korea
*****Nano Materials Analysis Center, Korea Institute of Science and Technology, Seoul 02455, Korea

(*Received 18 April 2019 • accepted 7 July 2019*)

Abstract−This study reports on the aqueous-phase synthesis of rhodium-silver (RhAg) bimetallic composite nanoparticles with a controllable Rh/Ag ratio. Due to the high cost of Rh compared with Ag, the RhAg nanoparticles were synthesized in two steps: the synthesis of Ag nanoparticles and the formation of a Rh-rich RhAg area on the surface of the Ag nanoparticles. Transmission electron microscopy and corresponding elemental mapping analyses exhibited that the synthesized 20 nm-sized quasi-spherical RhAg nanoparticles were composed of Ag-rich and Rh-rich area, respectively. Considering the amount of Rh used and productivity, the RhAg nanoparticles with a Rh content of 0.8% exhibited the best catalytic performance for the direct H_2O_2 generation reaction.

Keywords: RhAg Nanoparticles, Bimetallic, Aqueous-phase Synthesis, Rh-rich Area, H_2O_2 Generation Reaction

INTRODUCTION

High specific surface properties and surface-to-volume ratios make nanosized metals good catalysts for various chemical and electrochemical reactions [1,2]. Noble metal nanoparticles, including platinum (Pt) and palladium (Pd), have been introduced to catalysts for the production of multi-substituted olefins, the oxidation of biomass materials, and oxygen reduction reactions [3-6]. For the synthesis of hydrogen peroxide (H_2O_2), a method of synthesizing H_2O_2 directly from hydrogen (H_2) and oxygen (O_2) using Pd as a catalyst instead of anthraquinone has been attracting attention because of its eco-friendliness and economy [7-9]. Although the use of these noble metals as catalysts is highly effective, their scarcity and high prices limit their use.

Many studies have investigated the use of bimetallic nanoparticles to increase reaction efficiency while reducing the amount of Pt or Pd used. Most research has focused on the synthesis of Pt- or Pd-based alloy nanoparticles, such as PtCu, Pt_3Ni, Pt_3Fe, and Pd_3Fe [10,11]. Alloying with various metals, especially transition metals, could modulate the electronic structure of the alloy, resulting in better catalytic activity while reducing the use of noble metals [12]. Other studies have attempted to reproduce the electronic structure of Pd or Pt using an alloy of two other materials. For example, it was reported that an alloy synthesized by mixing iridium (Ir) and gold (Au), which are in front of and behind Pt on the periodic table, showed an electronic structure similar to that of Pt [13].

In this study, we attempted to create alloy nanoparticles to replace Pd by mixing rhodium (Rh) and silver (Ag), which are in front of and behind Pd on the periodic table. In previous syntheses of RhAg alloy nanoparticles, the alloy nanoparticles were synthesized by co-reduction of Rh and Ag precursor, thus leading to the formation of nanoparticles with homogeneous composition of Rh and Ag in the particles [14,15]. In this case, inefficient nanoparticles were produced in which a large amount of expensive Rh was present in the core area not involved in the catalytic reaction. Because Rh is considerably more expensive than Ag, we developed a new synthetic method to reduce the amount of Rh by using core-shell nanoparticle synthesis techniques. First, pure Ag nanoparticles were synthesized by reducing the Ag precursor in the presence of a stabilizer. When we added the Rh precursor into an aqueous suspension of the Ag nanoparticles, a Rh-rich RhAg area formed on the surface of the Ag nanoparticles, resulting in the synthesis of RhAg bimetallic composite nanoparticles. Thus, by placing low-priced Ag in the core and forming a highly reactive RhAg on the surface, we successfully synthesized bimetallic nanoparticles with high reactivity while minimizing the amount of Rh used. We could easily modulate the Rh/Ag ratio just by changing the concentration of the Rh precursor. Considering the amount of Rh used and productivity, the RhAg nanoparticles with a Rh content of 0.8 at% were the most efficient RhAg bimetallic nanoparticles in the direct H_2O_2 generation reaction.

[†] To whom correspondence should be addressed.
E-mail: jpahn@kist.re.kr, patra@kist.re.kr, and tkyu@khu.ac.kr
[‡] These authors contributed equally to this research

EXPERIMENTAL SECTION

1. Materials

Silver nitrate ($AgNO_3$), rhodium nitrate ($Rh(NO_3)_3$), sodium borohydride ($NaBH_4$), and polyvinyl pyrrolidone (PVP, MW=10,000) were purchased from Aldrich. They were used without any additional purification.

2. Synthesis of Ag Nanoparticles

A total of 5 mg of $NaBH_4$ and 250 mg of PVP was dissolved in 8 mL of water in 20 ml vial at 25 °C. Then, 2 mL of $AgNO_3$ solution (85 mg) was injected into the reacting solution. The final mixture solution was heated at 25 °C for 2 h (Stirring rate was 800 rpm). The product was then collected by centrifugation (9,000 rpm) and washed five times with acetone to remove any remaining chemicals. The RhAg nanoparticles were dispersed in 5 mL of water for further experiments. The concentration of Ag in the final dispersion was 10.3 mg/L, as measured by inductively coupled plasma (ICP).

3. Synthesis of RhAg Composite Nanoparticles

A total of 1 mL of the Ag nanoparticle suspension was injected to 8 mL of an aqueous solution containing 0.2 mg of $NaBH_4$ and 5 mg of PVP. Then, 1 mL of $Rh(NO_3)_3$ solution (7.63×10^{-5} mM for RhAg 0.5, 1.53×10^{-4} mM for RhAg 1, 4.58×10^{-4} mM for RhAg 3, and 7.63×10^{-4} mM for RhAg 5, respectively) was injected into the solution in 20 ml vial. The resulting solution was kept at 25 °C for 30 min (Stirring rate was 800 rpm). The synthesized RhAg composite nanoparticles were collected by centrifugation and washed with acetone water. After washing, the product was well dispersed in water.

4. Synthesis of Rh Nanoparticles

A total of 16.7 mg of $NaBH_4$ and 417 mg of PVP was dissolved in 8 mL of water in 20 ml vial at 25 °C. Then, 2 mL of $Rh(NO_3)_3$ solution (20 mg) was injected into the reacting solution. The final mixture solution was heated at 25 °C for 30 min (stirring rate was 800 rpm). The product was then collected by centrifugation and washed five times with acetone to remove any remaining chemicals. After washing, the product was well dispersed in water.

5. Catalytic Properties of RhAg Composite Nanoparticles for H_2O_2 Generation

Direct synthesis of H_2O_2 was performed in a 24-well plate. The reaction medium (total 2 mL) consisted of ethanol and water (ethanol : water volume ratio=1 : 4) with 0.9 mM sodium bromide (NaBr) and 0.02 M phosphoric acid (H_3PO_4). The weight of the used RhAg nanoparticles was 0.1 mg. O_2 gas flow was 20 mL/min and H_2/Ar (4 : 96 of volume ratio) gas flow was 50 mL/min, respectively. The total flow rate was 70 mL/min ($H_2 : O_2$ volume ratio= 1 : 10). The H_2O_2 generation reaction was carried out at room temperature for 1 h. After the H_2O_2 generation reaction, the concentration of H_2O_2 was measured using a 2,9-dimethyl-1,10-phenanthroline method [16]. 0.3 mL of 48 mM neocuproine ethanol solution and 0.3 mL of 10 mM $CuSO_4$ aqueous solution were mixed with 0.5 mL of buffer solution (pH=7). After addition of H_2O_2 solution obtained above experiments, the intensity change of an absorption peak at 454 nm of the final mixture solution was monitored using UV-vis.

6. Characterization

Transmission electron microscopy (TEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and high-resolution

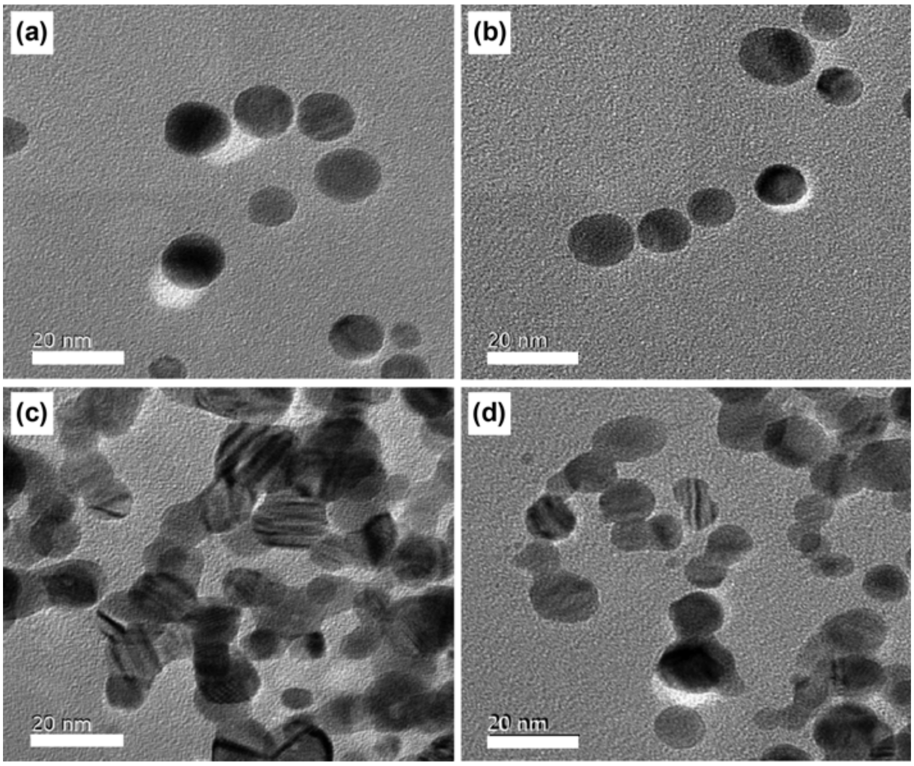


Fig. 1. TEM images of (a) RhAg 0.5, (b) RhAg 1, (c) RhAg 3, and (d) RhAg 5.

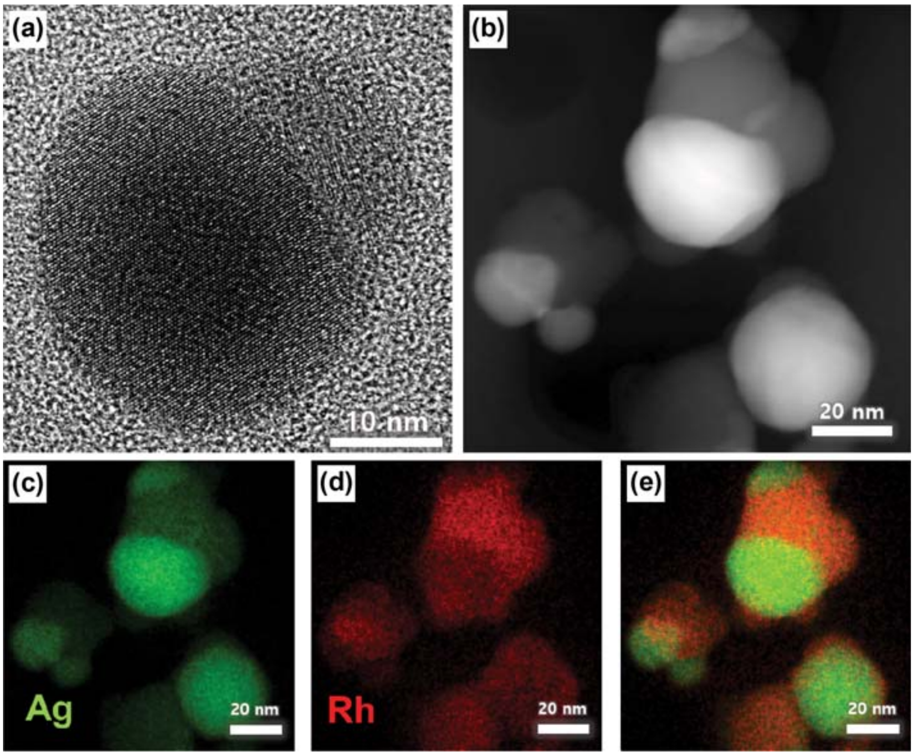


Fig. 2. (a) HRTEM and (b)-(e) HAADF-STEM-EDS mapping images of RhAg 5.

TEM (HRTEM) images were obtained using an FEI Talos microscope (Super-X EDS) at 200 kV. ICP analyses were carried out using a Direct Reading Echelle ICP, LEEMAN.

RESULTS AND DISCUSSION

RhAg composite nanoparticles were synthesized using a two-step method. First, Ag nanoparticles were synthesized by reduction of $AgNO_3$ with $NaBH_4$ at 25 °C. Fig. S1(a) shows a TEM image of the synthesized Ag nanoparticles, indicating the formation of spherical nanoparticles having an average size of 14.7 nm. The powder XRD patterns taken from the Ag nanoparticles exhibit diffraction peaks at 38.1°, 44.3°, 64.7°, 77.4°, and 81.6°, which can be indexed to the (111), (200), (220), (311), and (222) planes of face-centered cubic Ag (Fig. S1(b), *Fm3m*, a=4.086 Å, Joint Committee on Powder Diffraction Standards file no. 04-0783), respectively.

To form a Rh-rich area on the surface of the Ag nanoparticles, the Rh precursor was reduced in the presence of the Ag nanoparticles, similar to the seed-mediated growth method that is typically used for the synthesis of core/shell nanoparticles [17]. The color of the solution containing the RhAg nanoparticles was turbid gray, similar to that of the Ag nanoparticle solution. The synthesized RhAg nanoparticles had quasi-spherical morphology with sizes of approximately 14.9 nm for RhAg 0.5, 15.1 nm for RhAg 1, 14.9 nm for RhAg 3, and 15.2 nm for RhAg 5 (Fig. 1). The amounts of Rh in the RhAg nanoparticles were 0.4 at% for RhAg 0.5, 0.8 at% for RhAg 1, 1.6 at% for RhAg 3, and 2.4 at% for RhAg 5, indicating that the Rh/Ag composition could be controlled by controlling the amount of Rh precursor.

An HRTEM image of RhAg 5 shows that the nanoparticles consisted of a combination of two different areas: a crystalline area with a clearly visible lattice and an amorphous area (Fig. 2(a)). HAADF-STEM images show that these two areas have different elemental compositions (Fig. 2(b)). The Ag/Rh elemental compositions of each area were approximately around 6.4 for the bright area and around 1.4 for the dark area, respectively (Fig. S2). In addition, we also found that the crystalline area contained a small amount of Rh compared with the amorphous area in the nanoparticles. The elemental distribution of the nanoparticles was also measured by energy-dispersive X-ray spectrometry (EDS) mapping, demonstrating that there were two areas with different Rh/Ag compositions: Ag-rich and Rh-rich (Fig. 2(c) to 2(e)). During the reduction of the Rh precursor in the presence of the Ag nanoparticles, we believe that a Rh-rich RhAg bump with an amorphous crystal structure formed on the surface of the Ag nanoparticles, thus forming the RhAg bimetallic nanoparticles.

In a typical direct synthesis of H_2O_2, Pd and AuPd alloy are used as catalysts, but the high cost of the catalyst is one of the factors impeding the industrialization of this H_2O_2 producing method [16]. In this research, the synthesized RhAg nanoparticles had expensive Rh, but used up to only 5%. Therefore, we thought that the nanoparticles were competitive enough to be used as catalysts for the production H_2O_2. Fig. 3 shows the productivity of the RhAg nanoparticles in the reaction: 0.80 ppm for RhAg 0.5, 3.08 ppm for RhAg 1, 2.83 ppm for RhAg 3, and 3.34 ppm for RhAg 5. Pure Ag and Rh nanoparticles did not show any catalytic activity in same experimental conditions. These results demonstrate that mixing Rh and Ag could result in a new catalytic property, similar to a previ-

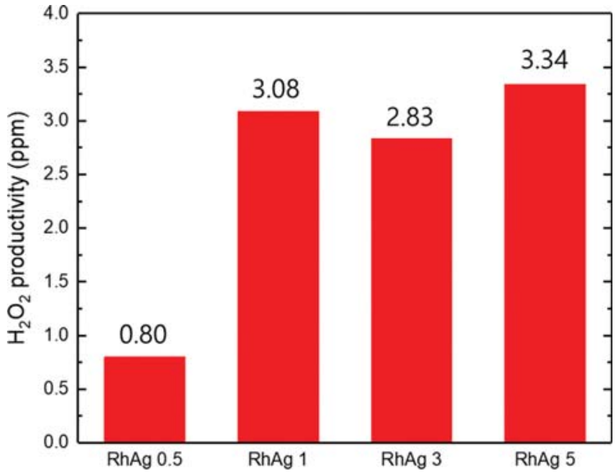


Fig. 3. The H_2O_2 productivity of the catalysts of RhAg bimetallic nanoparticles with different amounts of Rh.

ously reported IrAu system [13]. Interestingly, when the amount of Rh increased to more than 0.8 at%, the productivity of the RhAg nanoparticles was similar, indicating that a sufficiently high productivity could be obtained even by using a small amount of Rh. Considering the amount of Rh used and productivity, the RhAg nanoparticles with Rh content of 0.8 at% were the most efficient RhAg bimetallic nanoparticles in the direct H_2O_2 generation reaction. We believe that the RhAg bimetallic nanoparticles from the present synthesis have a Rh-rich area on the surface of the nanoparticles, thus resulting in higher productivity from only a small amount of Rh. Comparing the cost of catalysts, RhAg nanoparticles with 1 at% of Rh are ten-times cheaper than Pd nanoparticles of the same weight (Rh: 92.92 \$/g, Pd: 43.75 \$/g, and Ag: 0.48 \$/g) [18]. Although the ability of Pd nanoparticles to produce H_2O_2 is superior to that of RhAg, we confirmed that RhAg nanoparticles also had a competitive advantage in terms of cost.

SUMMARY

This study has demonstrated the aqueous-phase synthesis of RhAg bimetallic nanoparticles with both Ag-rich and Rh-rich areas. Due to seed-mediated growth, a Rh-rich area was located on the surface of the nanoparticles, thus leading to high productivity using only a small amount of Rh. The results of our research indicate the possibility of a new catalytic property by mixing two different noble metals. However, Rh is rare and expensive. To reduce the use of rare and expensive Rh, we plan to carry out the following two studies. One is the formation of ultra-thin RhAg alloy layer less than 1 nm on the surface of Ag nanoparticles. The other research is the synthesis of alloy nanocatalysts using a metal having a similar electronic structure as Rh, for example, Ru. Furthermore, the use of expensive noble metals may be reduced by forming a noble metal-rich area on the bimetallic nanoparticles.

ACKNOWLEDGEMENTS

This research was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (NRF-2014R1A5A1009799 and NRF-2016M3D1A1021140).

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

REFERENCES

1. R. M. Mohamed, D. L. McKinney and W. M. Sigmund, *Mater. Sci. Eng. R Rep.*, **73**, 1 (2012).
2. J. Miao, X. Liu, H. Jiang, Y. Liu and R. Chen, *Korean J. Chem. Eng.*, **36**, 385 (2019).
3. Z. Chen, M. Waje, W. Li and Y. Yan, *Angew. Chem. Int. Ed.*, **46**, 4060 (2007).
4. S. J. Yoo, S.-K. Kim, T.-Y. Jeon, S. J. Hwang, J.-G. Lee, S.-C. Lee, K.-S. Lee, Y.-H. Cho, Y.-E. Sung and T.-H. Lim, *Chem. Commun.*, **47**, 11414 (2011).
5. W. He, J. Liu, Y. Qiao, Z. Zou, X. Zhang, D. L. Akins and H. Yang, *J. Power Sources*, **195**, 1046 (2010).
6. E.-Y. Ko, E. D. Park, K. W. Seo, H. C. Lee, D. Lee and S. Kim, *Korean J. Chem. Eng.*, **23**, 182 (2006).
7. G.-H. Moon, M. Fujitsuka, S. Kim, T. Majima, X. Wang and W. Choi, *ACS Catal.*, **7**, 2886 (2017).
8. X. Xiao, T.-U. Kang, H. Nam, S. H. Bhang, S. Y. Lee, J.-P. Ahn and T. Yu, *Korean J. Chem. Eng.*, **35**, 2379 (2018).
9. S. Park, T. J. Kim, Y.-M. Chung, S.-H. Oh and I. K. Song, *Korean J. Chem. Eng.*, **28**, 1359 (2011).
10. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, *J. Phys. Chem. B*, **108**, 17886 (2004).
11. H. Park, K. Kim, H. Kim, D.-K. Kim, Y. S. Won and S.-K. Kim, *Korean J. Chem. Eng.*, **35**, 1547 (2018).
12. C.-X. She, J. Xiang, B. Ren, Q.-L. Zhong, X.-C. Wang and Z.-Q. Tian, *J. Korean Electrochem. Soc.*, **5**, 221 (2002).
13. D.-H. Seo, H. Shin, K. Kang, H. Kim and S. S. Han, *J. Phys. Chem. Lett.*, **5**, 1819 (2014).
14. A. Roy, B. Debnath, R. Sahoo, K. R. S. Chandrakumar, C. Ray, J. Jana and T. Pal, *J. Phys. Chem. C*, **120**, 5457 (2016).
15. S. Gricia, L. Zhang, G. W. Piburn, G. Henkelman and S. M. Humphrey, *ACS Nano.*, **8**(11), 11512 (2014).
16. K. Kosaka, H. Yamada, S. Matsui, S. Echigo and K. Shishida, *Environ. Sci. Technol.*, **32**, 3821 (1998).
17. L. Lu, H. Wang, Y. Zhou, S. Xi, H. Zhang, J. Hu and B. Zhao, *Chem. Commun.*, **2**, 144 (2002).
18. http://www.infomine.com/investment/metal-prices/.

Supporting Information

Synthesis RhAg bimetallic composite nanoparticles for improved catalysts on direct synthesis of hydrogen peroxide generation

Yangpil Jang[*,‡], Hyobin Nam[**,***,‡], Joseph Song[****,*****,‡], Seungyong Lee[**,***,†],
Jae-Pyung Ahn[*****,†], and Taekyung Yu[*,†]

*Department of Chemical Engineering, College of Engineering, Kyung Hee University, Youngin 17104, Korea
**Materials Architecturing Research Center, Korea Institute of Science and Technology, Seoul 02455, Korea
***Department of Nanomaterials Science and Engineering, Korea University of Science and Technology, Daejeon 34113, Korea
****Department of Material Science & Engineering, College of Engineering, Korea University, Seoul 02841, Korea
*****Nano Materials Analysis Center, Korea Institute of Science and Technology, Seoul 02455, Korea

(*Received 18 April 2019 • accepted 7 July 2019*)

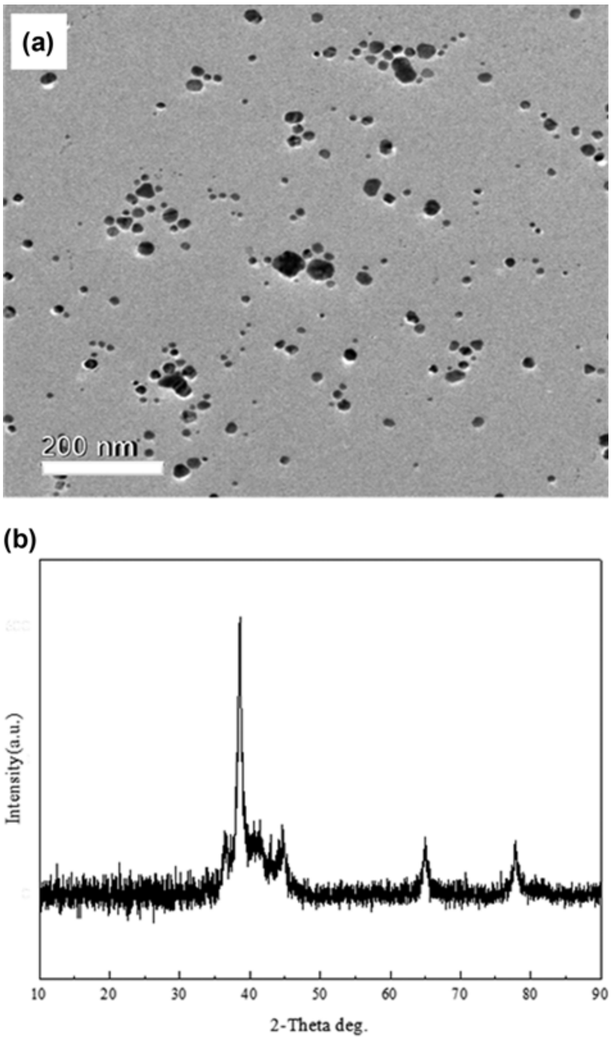
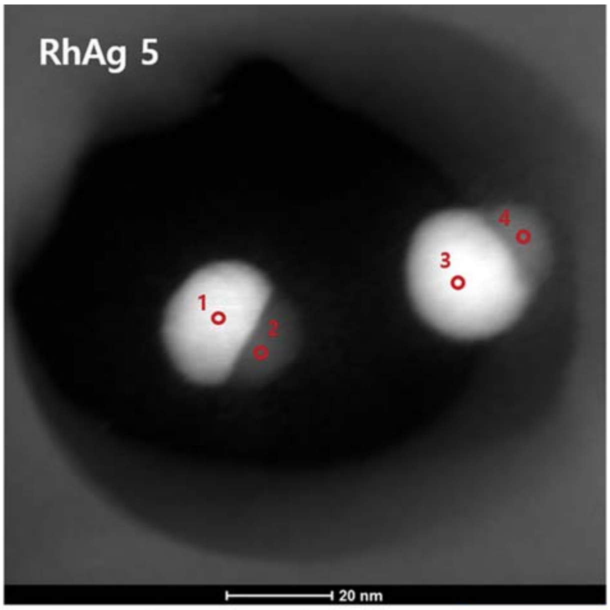


Fig. S1. (a) TEM image and (b) XRD patterns of the Ag nanoparticles.



Point	Rh	Ag	Rh:Ag
1	13.29	86.71	1:6.53
2	40.16	59.84	1:1.49
3	13.69	86.31	1:6.30
4	42.86	57.14	1:1.33

Fig. S2. The HAADF-STEM image and Rh/Ag composition of RhAg 5.

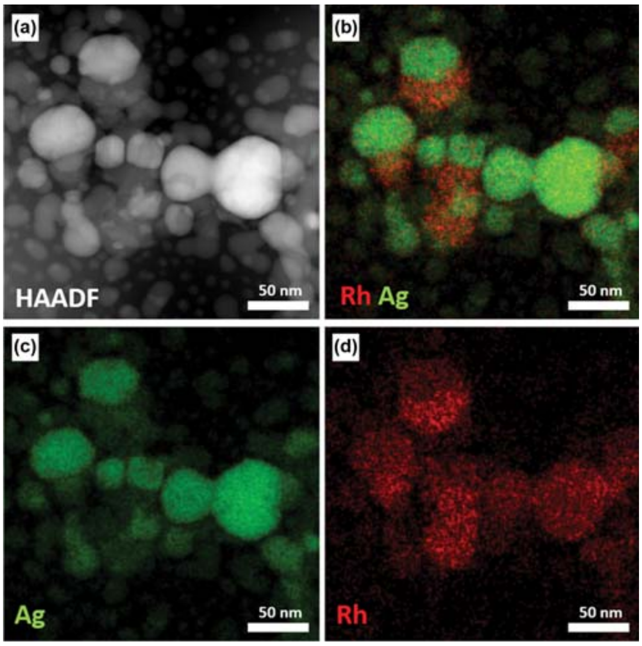


Fig. S3. (a) HRTEM and (b)-(e) the STEM-EDS mapping images of RhAg 0.5.

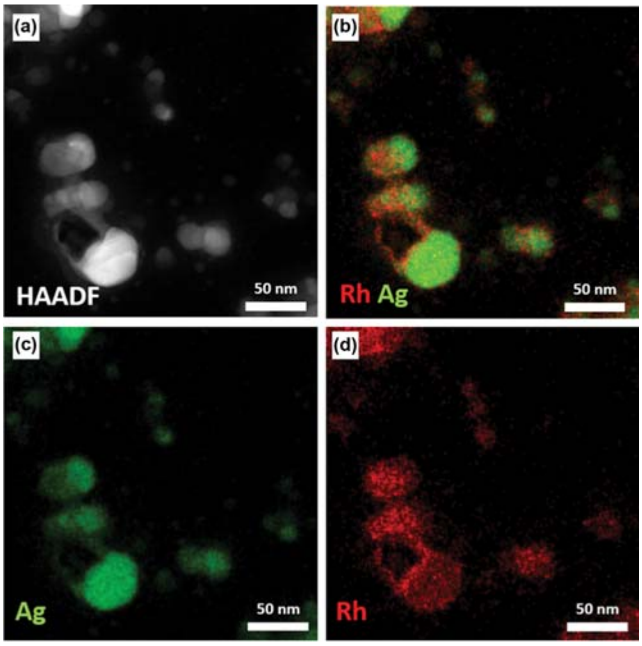


Fig. S5. (a) HRTEM and (b)-(e) the STEM-EDS mapping images of RhAg 3.

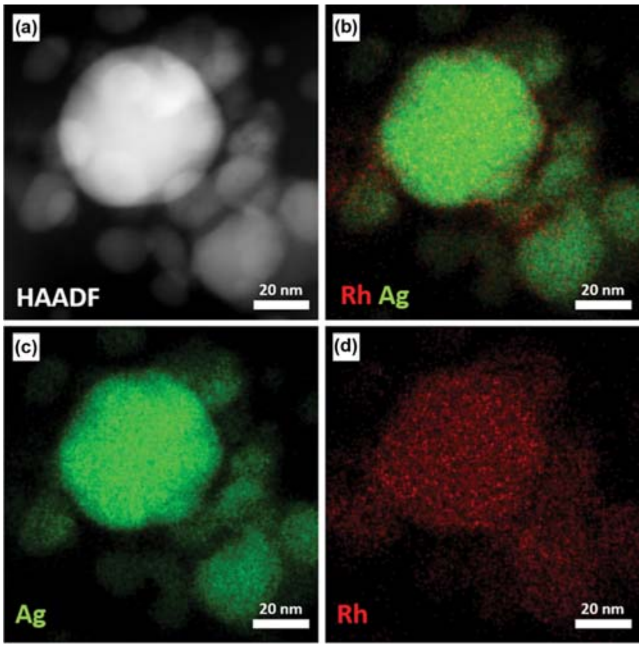


Fig. S4. (a) HRTEM and (b)-(e) the STEM-EDS mapping images of RhAg 1.