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# Bimetallic nanoparticles: Preparation, properties, and biomedical applications

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## Abstract

Many studies of non-supported bimetallic nanoparticle (BMNP) dispersions, stabilized by ligands or polymers, and copolymers, were started only about 10 years ago. Several preparative procedures have been proposed, and full characterizations on BMNPs have been approved. Studies on BMNPs received huge attention from both scientific and technological communities because most of the NPs' catalytic activity depends on their structural aspects.

In this study, we focus on the preparation, properties, and bio-application of BMNPs and introduction of the recent advance in these NPs.

**Keywords:** bimetallic, bio-application, nanoparticles, catalytic activity

## Introduction

Bimetallic nanoparticles (BMNPs) involving Au-Pd, Au-Ag, and Au-Pt have been produced in a single step by a sol-gel process and stabilized in liquid and solid matrix. BMNPs have four types of integration patterns: core-shell NPs, sub-cluster NPs, alloy NPs, and multishell NPs (Turkevich et al. 1951). Alloying of metals is a method of developing novel materials that have technological usefulness than their starting substances. Alloy NPs show various structural and physical properties than bulk samples (Couchman and Jesser 1977, Ceylan et al. 2006).

Ongoing extensive studies on non-supported BMNP dispersions, stabilized by polymers or ligands, were started only 10 years ago. Studies on BMNPs received huge attention from both scientific and technological communities, because most of the NPs' catalytic activity depends on their structural aspects (Toshima and Yonezawa 1998). In bulk metals, atoms are arranged in diverse geometries, each metal having its own atomic position. The follow-on crystal structure is typically simple and depends on the identity of the metal and other factors such as temperature. BMNPs

can exist in another type of structure, in which the distribution of each metal element is not the same as that found in the bulk (Thulasiramaraju et al. 2014). Layered core-shell silver-gold BMNPs were arranged by coating Au layers over Ag seeds using a seed-growth technique. The arrangement of  $\text{Ag}_{100-x}\text{Au}_x$  particles can vary from  $x = 0$  to 30 (Cui et al. 2006). Nano-sized materials serve as an ideal candidate for diverse applications due to their extraordinarily small size and correspondingly large surface-to-volume ratio. Additionally, their properties may be modified by changing their size, shape, and composition using synthetic methods (Van Hying and Zukoski 1998, Adair and Suvaci 2000, Jana et al. 2001, Velikov et al. 2003, D'Souza et al. 2004).

## Synthesis

Several studies show that the stability and size of nanoscale colloidal particles effectively depend on the technique and the experimental conditions followed. The novel Ag/Ag-Au BMNPs were produced by the replacement reaction between Ag NPs and  $\text{HAuCl}_4$ . Au-Ag NPs were synthesized by method of reduction of changeable mole fractions of  $\text{HAuCl}_4$  and  $\text{AgNO}_3$  using sodium borohydride in the presence of sodium citrate, in water. The exchange of Ag-NPs into Ag/Ag-Au BMNPs involved numerous sequential processes (Lu et al. 2007, Chen et al. 2006, Park et al. 2009):

1. oxidative dissolution of Ag atoms,
2. reduction of  $\text{AuCl}_4^-$ , and
3. deposition of Au atoms.

Metal NPs can be produced in two different ways, that is, by subdivision of bulk metals (a physical method) and by the growth of particles obtained from metal atoms, which are from molecular or ionic precursors (a chemical method) (Figure 2).

## Core-shell

Core-shell and multishell Au-Ag BMNPs have been produced by successive reduction of metal salts with ascorbic acid on

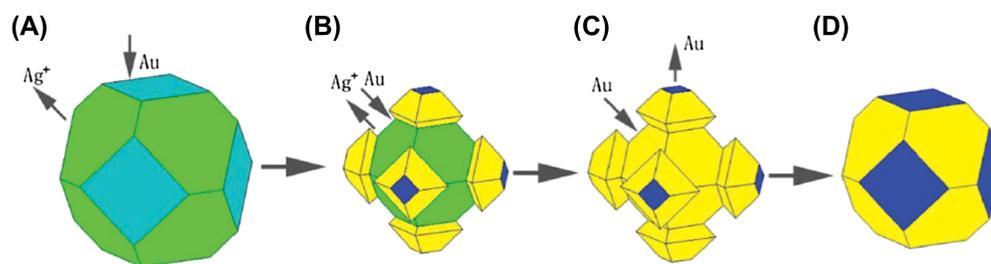


Figure 1. Schematic picture showing the shape and composition progress of Ag/Ag-Au metal core/alloy shell BMNPs. The green and cyan planes signify the {111} and {100} forms of silver, respectively; the yellow and blue planes denote the {111} and {100} forms of gold-silver alloy and pure gold, respectively (Zhang et al. 2008).

pre-made seeds in the presence of a cationic surfactant, cetyltrimethylammonium bromide. In thickness-prescribed synthesis of core-shell structured Au/Ag or Ag/Au NPs, the external metal surface can be tuned as a performance of the internal metal surface, provided that the outer shell is thin enough (Rodriguez-Gonzalez et al. 2005, Cao et al. 2001, Rivas et al. 2000, Daniel and Astruc 2004, Ferrer et al. 2007, Kim et al. 2005) (Figure 1).

### Co-reduction

The co-reduction of Au and Ag precursors is the simplest method of preparing Au-Ag alloy NPs. Since two metal precursors are involved in the reduction reactions, the influence of synthesis conditions on the rates of precursor reduction, and the nucleation and growth of the alloy NPs are more complex than in the case of monometallic NPs (Wang et al.

2009, Wilson et al. 2005, Kim et al. 2003, Mallin and Murphy 2002, Chen and Chen 2002, Link et al. 1999, Hostetler et al. 1998, Han et al. 1998).

### Biogenic synthesis

One of the biological synthesis methods for Au-Ag NPs is by using the leaf extract of *S. mahogani* Jacq. The role of the leaf extract is reduction and stabilization of Au and Ag for the quick arrangement of stable metal NPs with different compositions, shapes, sizes, and also with high monodispersities. Au/Ag BMNPs produced by this technique have prospect for biomedical applications in the future (Mondal et al. 2011).

### Laser-assisted synthesis of Au-Ag alloy NP

One of the simple and convenient methods for synthesizing Au-Ag BMNPs is "laser irradiation" method, which is a bottom-up approach comparable with the approach of laser ablation of bulk materials in solution for producing NPs. Spherical shapes and crystallized NPs can effortlessly be obtained in one-step procedures with no succeeding heat-treatments, due to high energetic state of irradiated species without production of by-products (Takami et al. 1999) (Figure 2).

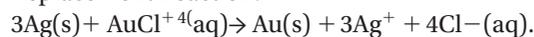
### Replacement reactions

Replacement reaction is a simple method to prepare Ag-Au BMNPs, which occurs between Ag-NPs and HAuCl<sub>4</sub> at elevated temperatures (Sun et al. 2002, Liang et al. 2005, Sun and Xia 2004).

This technique takes advantage of the rapid interdiffusion of Au and Ag atoms in the reduced dimension of NPs, high temperature of the process, and the plenty of interfacial vacancy defects created by the reaction.

The main advantage of this method is that the size and composition of the alloy NPs are separately tunable and that the particles can be formed in high concentrations (good process scalability) (Zhang et al. 2007).

Replacement Reaction:



The produced atomic gold would then alloy with the unreacted silver under suitable situation to form homogeneous alloy NPs (Link et al. 1999) (Figure 3).

### Properties

Properties of BMNPs are influenced by both the metals; they provide excessive ordinary metallic NPs, which is an

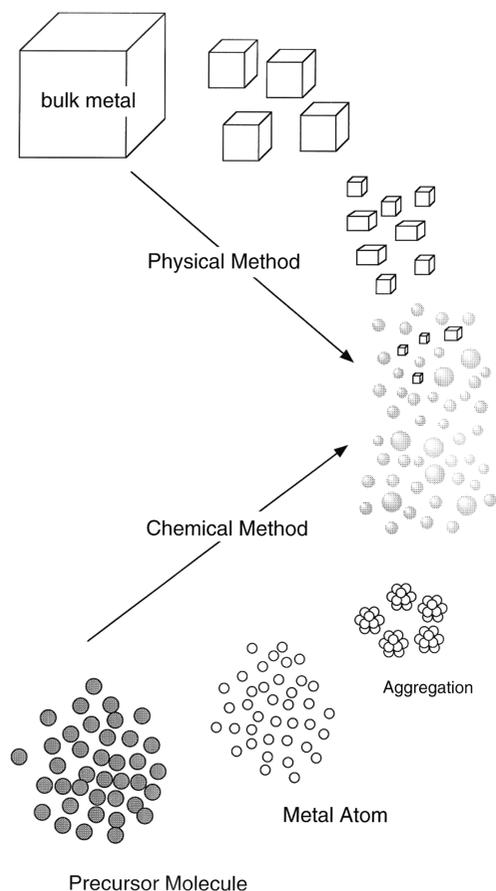


Figure 2. Schematic design of preparative methods of metal NPs.

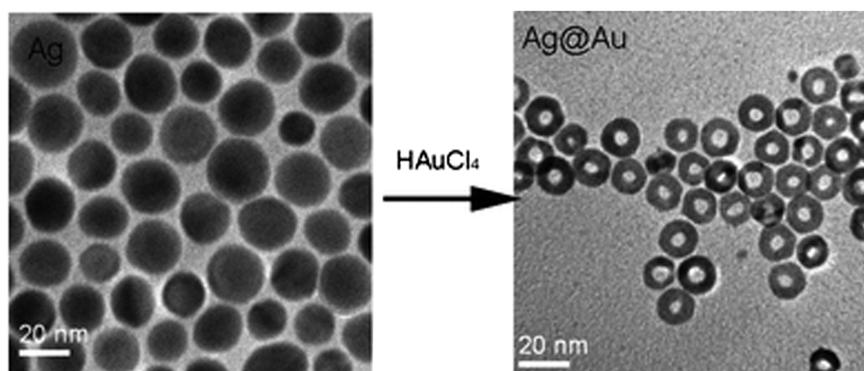


Figure 3. Synthesis of core/shell NPs by the replacement reaction between Ag NPs and  $\text{HAuCl}_4$ . (Zhang et al. 2008).

advantage (Mohl et al. 2011, Huang et al. 2006). The properties of alloy NPs can be extremely different from those of the elemental monometallic nanoparticles (Mohamed et al. 2000).

### Optical properties of Au–Ag

Plasmonic coupling between NPs is one of the most interesting optical properties; the characteristic improvement of local optical field at particle–particle interface is extremely useful for numerous sensing applications (Lee and El-Sayed 2006, Wang et al. 2007). Monometallic Ag and Au NPs have relatively monotonous optical properties due to surface plasmon resonance (SPR); the SPR properties of Ag–Au alloy NPs are incessantly tunable because of the possibility of composition changes. SPR excitation within the gold and silver nanostructures greatly enhances the local electric field (Cheng et al. 2008, Wang et al. 2006). The absorption and dispersion of light in NPs rely on the characteristic of the metals, including their chemical composition, morphology, and size. NPs of noble metals, for instance gold and silver, with a size smaller than the wavelength of visible light powerfully scatter and absorb light because of SPR. Au–Ag BMNPs show diverse optical responses for alloy and core–shell configurations, even when they have the same Au and Ag contents (Kim et al. 2005, Kreibing and Vollmer 1995).

### Antibacterial properties

Au–Ag BMNPs show high-quality antibacterial activity against Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Klebsiella pneumoniae*. BMNPs at the concentration of 1:3 exhibit areas of inhibition against the pathogenic bacteria, for example, *Staphylococcus aureus* and *Klebsiella pneumoniae* (Ramakritinan et al. 2013).

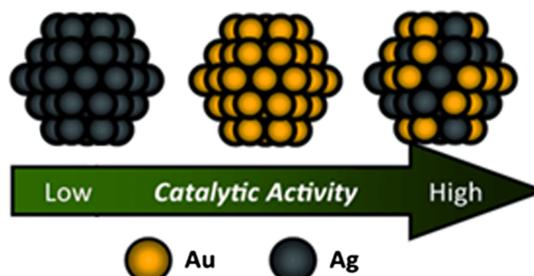


Figure 4. Schematic picture of catalytic activity of Au, Ag, and Au–Ag BMNPs.

### Catalytic properties

A novel group of materials for catalysis have been densely studied, that is, “bimetallic nanoparticles”. Metal NP catalysts comprising two (or more) different metal components have received attention from both technological and scientific points of view for improving the quality or properties of catalyst (Menezes et al. 2013).

Although the size of Au–NPs is smaller than that of Ag–NPs and AuAg–NPs, equal atomic concentrations of Au–NPs, Ag–NPs, and AuAg–NPs are applied for the catalytic reaction due to their enhanced surface areas and decreased densities (Shin et al. 2012).

### Applications

#### Photothermal cancer therapy

Au–Ag BMNPs can be used as nanomaterials in several in vitro and in vivo cancer therapies, Raman scattering development, and catalytic reactions using extremely well-organized photothermal ablation, large resistive heat generation, and tunable near-IR absorption (Liu et al. 2014). Ru-Shi Liu et al. found that oral cancer cells without NPs were not hurt after exposure to laser irradiation for 5 min (see Figure 5a). On the contrary, cells with added NPs experienced significant cell death after laser exposure for 1 min (see Figure 5b and c).

#### Catalytic application

The application of BMNPs as catalysts is one of the most active areas of nanoscience (Discuss and Jellinek 2008). BMNPs act as catalysts in chemical reactions and in environmental remediation. Differential metal components of Au with other metals, such as Ag, Cu, Pt, and Pd, were found to have reduced put on compared with that of net Au associates at the expense of higher cost (Xiong and Manthiram 2005, Shah et al. 2012) (Figure 4).

#### Electroplating and fabrication

BMNPs allow more than one metal to be used for establishing contact, with or without the expense and complexity of integrating Au alloy into the microelectromechanical systems) switch fabrication process (Mallin and Murphy 2002, Wang et al. 2006).

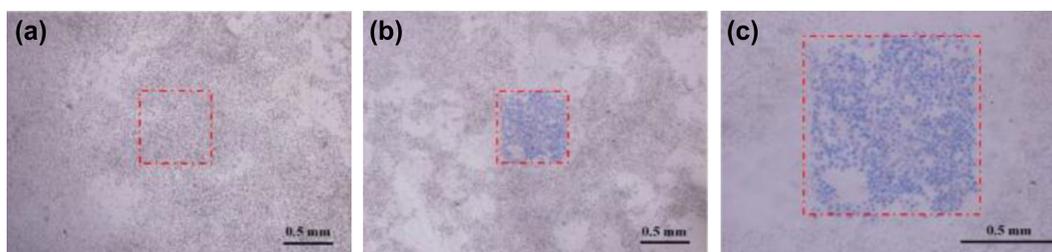


Figure 5. Microscopic image of cells stained using trypan blue after laser irradiation. (a) SAS cancer cells with no NPs, (b-c) cancer cells incubated with gold-silver (10:1 ratio) BMNPs (orange dotted). Squares signify the irradiation zone.

### Potential applications

BMNPs surrounding the surface regions of glass are of great interest because of their potential application (Kim et al. 2007, Wiederrecht 2004). Ag-Au NPs in silica glasses with linear and nonlinear optical properties have been achieved (Ditlbacher et al. 2000). Later, nonlinear field enrichment relying on the laser polarization of single Ag nanobars and nanorice was also reported (Wiley et al. 2007).

### Thermal conductivity

It has been demonstrated that nanofluids, consisting of Ag-Au in water, enhances the thermal conductivity of the fluids (Zhong et al. 2006, van Dijk 2007).

### Conclusion

The BMNPs with core-shell structures can offer unique physical and optical properties inaccessible to monometallic systems. These nanoparticles have been utilized in many areas of research including chemical catalysis, surface-enhanced Raman spectroscopy, and photothermal therapy. This review article provides a comprehensive overview of BMNP systems consisting of gold and silver; it is based on the recent advances in wet-chemical synthetic methodologies, the characterization of size- and shape-dependent optical properties, and various optically driven applications including catalysis, signal-enhancing devices, and biomedical purposes.

### Authors' Contributions

EA and HTN conceived the study and participated in its design and coordination. AA, SD, and MK participated in the sequence alignment and drafted the manuscript. All authors read and approved the final manuscript.

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### Declaration of interest

The authors report no declarations of interest. The authors alone are responsible for the content and writing of the paper.

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