



# Fabrication of catalytically active AgAu bimetallic nanoparticles by physical mixture of small Au clusters with Ag ions

Haijun Zhang<sup>a</sup>, Naoki Toshima<sup>b,c,\*</sup>

<sup>a</sup> College of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei Province 430081, China

<sup>b</sup> Department of Applied Chemistry, Tokyo University of Science Yamaguchi, SanyoOnoda-shi, Yamaguchi 756-0884, Japan

<sup>c</sup> CREST, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan

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## ABSTRACT

Catalytically highly active PVP-protected AgAu bimetallic nanoparticles (BNPs) less than 2 nm in diameter were fabricated by simultaneous physical mixture of aqueous dispersions of Au clusters with Ag<sup>+</sup> ions. The prepared AgAu BNPs, the dispersion of which was stably kept for more than 2 months under ambient conditions, were characterized by UV–vis, ICP, HR-TEM, and EDS in HR-STEM. The prepared BNP colloidal catalysts possessed a high activity for aerobic glucose oxidation. The highest activity of 3.77 mol–glucose s<sup>−1</sup> mol–metal<sup>−1</sup> was observed for the BNPs prepared with Ag/Au atomic ratio of 2/8, which was more than two times higher than that of Au nanoparticles with nearly the same particle sizes.

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## 1. Introduction

Bimetallic nanoparticles (BNPs) are important catalysts because they usually possess enhanced catalytic activity and selectivity compared with those of the corresponding monometallic nanoparticles (MNP) [1–9]. AgAu BNPs having various structures and varying Ag/Au ratios are one of the most widely studied bimetallic systems in the literatures [10]. These materials show interesting optical properties that are dependent not only on the composition but also on the geometrical structure, specially a random alloy or has a core/shell structure.

AgAu alloy BNPs are usually synthesized by the simultaneous reduction of both salts in solutions, while core/shell-structured AgAu BNPs are traditionally synthesized by controlled deposition of the shell metal onto a seed of the core metal. Core/shell BNPs with apparent well-defined interfaces between the two metals have been reported by several authors via successive reduction of the different metals [11–16]. Mulvaney et al. deposited gold onto radiolytically prepared silver seeds by irradiation of KAu(CN)<sub>2</sub> solutions [11]. Treguer et al. prepared layered nanoparticles (NPs) by radiolysis of mixed Au(III)/Ag(I) solutions [13]. Silver colloids covered with gold in the surface layer were prepared by mixing a solution of HAuCl<sub>4</sub> with a silver colloid and addition of

a reductant (*p*-phenylenediamine) in the second step [14]. Layered core/shell bimetallic AgAu colloids have been prepared by the seed-growth method and analyzed with transmission electron microscopy (TEM) images and electron diffraction patterns [15]. Additionally, bimetallic Au and Ag particles with a core/shell type structure have been prepared by a UV-photoactivation technique [16].

Although there are several methods reported for the preparation of AgAu BNPs [11–31], it has been believed that synthesis of AgAu BNPs with controlled compositions and sizes on a large scale is difficult because Ag<sup>+</sup> ions easily form precipitates with halide ions in aqueous solutions when Ag<sup>+</sup> ions were used as a starting material in combination with a HAuCl<sub>4</sub> precursor (a most widely used starting materials for Au). Moreover, it is still a challenge to prepare AgAu BNPs with sizes of less than 2 nm. We have already reported the formation of core/shell structured BNPs with various combinations of metal elements by simultaneous reduction [21–23], sacrificial hydrogen reduction [24], and self-organization by mixing two colloidal dispersions in solutions at room temperature [25,26]. In a previous paper [27], we report on a novel synthetic method of AgAu BNPs by a simple procedure of mixing Ag<sup>+</sup> ions with Au NPs dispersed in an aqueous solution at room temperature. In this system, the problem of precipitation of silver halide (such as AgCl) can be well solved since the mixing of Ag<sup>+</sup> ions and Au NPs is performed after the Au precursor is completely reduced to form Au NPs and the ionic impurities such as chloride are removed by the ultra-filtration in advance. However, the prepared AgAu BNPs

\* Corresponding author. Tel.: +81 836 88 4561; fax: +81 836 88 4567.  
E-mail address: [toshima@rs.tus.ac.jp](mailto:toshima@rs.tus.ac.jp) (N. Toshima).