**Preparation of Ag_{core}/Au_{shell} Bimetallic Nanoparticles from Physical Mixtures of Au Clusters
and Ag Ions under Dark Conditions and Their Catalytic Activity for Aerobic Glucose
Oxidation**

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ABSTRACT:

AgAu bimetallic nanoparticles (BNPs), one of the most extensively studied bimetallic systems in the literatures, could have various structures and compositions depending on their preparation conditions. In the present work, catalytically highly active PVP-protected Ag_{core}/Au_{shell} BNPs of about 2.5 nm in diameter were fabricated from physical mixtures of aqueous dispersions of Au nanoparticles and Ag⁺ ions under dark conditions without using any reducing agents. The prepared Ag_{core}/Au_{shell} BNP colloidal catalysts, which possessed a high activity for aerobic glucose oxidation, were characterized by Ultraviolet-visible spectrophotometry (UV-Vis), Inductive coupled plasma emission spectrometer (ICP), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Energy disperse spectroscopy (EDS) in High-resolution scanning transmission electron microscopy (HR-STEM). The highest activity (11,360 mol-glucose·h⁻¹·mol-metal⁻¹) was observed for the BNPs with the Ag/Au atomic ratio of 1/9, the TOF value of which is about two times higher than that of Au nanoparticles with the particle size of 1.3 nm. The enhanced catalytic activity of the prepared Ag_{core}/Au_{shell} BNPs compared to Au NPs can be ascribed to the presence of negatively charged Au atoms resulted from electron donations from neighboring Ag atoms and PVP due to electronic charge transfer effects. XPS measurements as well as electronic structure calculation based on the density functional theory have revealed that the Au atoms are indeed negatively charged.

Keywords: A. Metals, A. Nanostructures, B. Chemical synthesis, D. Catalytic properties.

1. Introduction

Colloidal dispersions of metallic nanoparticles are currently attracting much attention as catalysts. Metal nanoparticles without inorganic supports indeed have some advantages over their supported counterparts [1]. For example, the intrinsic properties of metal nanoparticles can be elucidated without the effect of the metal-support interaction, and more uniform particle sizes can be obtained in the dispersed systems than in the supported cases, especially under conditions of high metal concentration. Colloidal metal dispersions can be easily obtained through liquid chemical reduction processes under the protection of water-soluble polymers, such as poly(N-vinyl-2-pyrrolidone) (PVP) [2–5].

Bimetallic nanoparticles (BNPs) have been extensively investigated with the aim of improving their preparative procedures as well as controlling their catalytic activity and selectivity [6-13]. Colloidal BNP catalysts can be prepared by simultaneous reduction of two types of metal ions with or without a protective reagent (usually a polymer or a surfactant) or by successive reduction of one metal over the nuclei of another. Co-reduction of two types of metal ions often resulted in alloyed nanoparticles, although core-shell structures could also be formed [11]. On the other hand, successive reduction of one metal after another was generally employed to produce a core-shell structure [12-13].

Recently, extensive researches have been directed toward synthesis and characterization of alloy and core/shell structured Ag/Au BNPs to understand the influence of bimetalization on their catalytic, electronic and optical properties [11, 14-16]. Layered core-shell bimetallic silver-gold colloids were prepared by the seed-growth method and analyzed with transmission electron microscopy (TEM) images and electron diffraction patterns [14]. Additionally, bimetallic gold and silver particles, a core/shell structure, were prepared by a UV-photoactivation technique [15].

Although a number of methods have been reported for the preparation of Ag/Au BNPs [11, 14-16], the synthesis of Ag/Au BNPs with controlled compositions and sizes on a large scale is still difficult because Ag^+ ions readily form precipitates when they are used as a starting material in combination with a HAuCl_4 precursor (one of the most widely used source precursors for Au). In a previous paper [17], we have reported on the synthesis of catalytically highly active PVP-protected Ag/Au BNPs with sizes less than 2 nm from physical mixtures of aqueous dispersions of Au NPs with Ag^+ ions in natural light. The precipitation of silver halide (such as AgCl) could be avoided since the mixing of Ag^+ ions and Au NPs was carried out after the synthesis of the Au NPs and the chlorides arising from the Au precursor were completely removed in advance by the ultra-filtration. The photoexcited state of Au NPs and the presence of the UV in the natural light could be ascribed to the reduction of Ag^+ ions in the mixing process.

In the present paper, we report on an unexpected finding that the presence of natural light might not be necessary for the preparation of Ag/Au BNPs. $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs with sizes of about 2.5 nm were fabricated under dark conditions by physically mixing Au NP dispersions and Ag^+ ion solutions at room temperature (rt) for 2 h. To our knowledge, there have been no reports on the synthesis of PVP-protected $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs under dark conditions without using any reductants. As-prepared $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs were analyzed by Ultraviolet-visible spectrophotometry (UV-Vis), dark field scanning transmission electron microscopy (DF-STEM), Energy dispersion X-ray spectroscopy (EDS), TEM, and X-ray photoelectron spectroscopy (XPS), and their catalytic activities as a function of their compositions investigated for the aerobic glucose oxidation. In addition, density functional theory (DFT) calculations were carried out to investigate electronic structures of Ag and Au atoms in the as-prepared $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs.

2. Experimental section

Materials

Hydrogen tetrachloroaurate (III) tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.9%) purchased from Tokyo Kasei Kogyo, Ltd., and silver perchlorate (AgClO_4 , 99.99%), sodium borohydride (NaBH_4 , 99.0%), and PVP (poly(*N*-vinyl-2-pyrrolidone, K30, molecular weight about 40,000) purchased from Wako Pure Chemical Industries Ltd. were used directly without further purification. All glasswares and Teflon-coated magnetic stirring bars were cleaned with aqua regia, followed by copious rinsing with purified water. Water was purified with a Millipore Milli-RX 12 plus water system.

Preparation of PVP-protected Au NPs by rapid injection of NaBH_4

Monodispersed and PVP-protected Au NPs were prepared by rapid injection of NaBH_4 into $\text{AuCl}_4^-/\text{PVP}$ aqueous solutions as detailed below [11]: An aqueous solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (25 mL, 0.44 mmol L^{-1}) was added to an aqueous PVP (50 mL, 44 mmol L^{-1} in monomer unit) solution followed by stirring at 0°C for 30 min. Then, an aqueous solution of NaBH_4 (6.67 mL, 16.5 mmol L^{-1} , 0°C) was rapidly injected into the mixed solution under vigorous stirring. The molar ratio of PVP monomer units to the total metal ions (R_{PVP}) was 100, and the molar ratio of NaBH_4 to the total metal ions (R_{NaBH_4}) was 5. The addition time of rapid injection of NaBH_4 into $\text{AuCl}_4^-/\text{PVP}$ was within 5 s. Finally, the transparent and brownish colloidal dispersions obtained were filtered by an ultrafilter membrane with a cutoff molecular-weight of 10,000 (Toyo Roshi Kaisha LTD.) and washed twice with water and then once with ethanol under nitrogen to remove extra agents and byproducts. The residual ethanol of PVP-protected Au colloids was removed by using a rotary evaporator at 40°C . PVP-protected Au NPs were finally obtained by vacuum drying at 40°C for 48 h. The UV-Vis spectra, the TEM micrographs and size distribution histograms of the Au NP dispersion prepared by rapid injection of NaBH_4 were reported in one of our previous papers [11].

The spectrum of the starting Au NPs exhibits a very weak plasmon absorbance at 520 nm, indicating the formation of enough small NPs. The average diameter based on the size distribution is about 1.1~1.4 nm for the Au NPs.

Preparation of Ag/Au BNPs from simultaneous physical mixture of Au NP aqueous dispersions and Ag⁺ ions under dark conditions

We tried to prepare Ag/Au BNPs via simultaneously and physically mixing Au NP aqueous dispersions and Ag⁺ ions under dark conditions. Aqueous solutions of AgClO₄ were added to the as-synthesized Au NP aqueous colloidal dispersions with continuous stirring at room temperature for 2 h in darkness to prepare a series of catalysts, and the detailed compositions and processing conditions are shown in Table 1. For example, Ag₅₀Au₅₀ BNPs were prepared as follows (Hereafter, the numbers in the subscript stand for the synthetic feeding ratios of the two metals.): An aqueous solution of AgClO₄ (25mL, 0.44 mmol L⁻¹) was added to an as-prepared Au NP colloidal dispersion (25 mL, 0.44 mmol L⁻¹) with continuous stirring at room temperature for 2 h in a N₂ atmosphere. The Ag/Au BNPs were obtained using the same washing, evaporation and drying procedures as those used for Au NPs.

Characterization of BNPs

UV–Vis absorption spectra within 200–800 nm were recorded using a Shimadzu UV-2500PC recording spectrophotometer using a quartz cell with 10 mm of optical path length.

TEM images were taken by using a JEOL TEM 1230 at accelerated voltage of 80 kV. The specimens were obtained by dropping one or two droplets of the Ag/Au colloidal ethanol solutions onto a thin amorphous carbon film-covered copper microgrid and evaporating ethanol in air at room temperature. Prior to the specimen preparation, the colloidal ethanol solutions were sonicated for 10 min to obtain a better particle dispersion on the microgrid. Image analysis was performed with

iTEM software (Olympus Soft Imaging Solution GmbH). For each sample, generally at least 200 particles from different parts of the grid were used to estimate the mean diameter and size distribution of particles. High resolution TEM (HR-TEM) and DF-STEM observations were performed using a JEOL TEM 2010F microscope at accelerated voltage of 200 keV in the UBE Scientific Analysis Laboratory. EDS was carried out using a NORAN UTW type Si(Li) semiconducting detector with about 1 nm beam diameter attached to the HR-TEM.

Metal contents in the PVP-protected Ag/Au BNPs were determined by optical emission spectroscopy with inductive coupled plasma (ICP-OES, Varian 720-ES). For this purpose the samples were solubilized in aqua regia (HCl/HNO₃) in advance.

XPS measurement was performed using a Quantum 2000 spectrometer (PHILIPS) under Al K α radiation ($E = 1486.6$ eV). Binding energies (BE) were normalized by the C(1s) binding energy of adventitious carbon contamination taken to be 284.6 eV. The analyses of Au and Ag were based on the Au 4f_{7/2} and Ag 3d_{5/2} peaks.

Glucose oxidation at controlled pH

The catalytic performances of all catalysts were evaluated by glucose oxidation as a model reaction. The reactions were carried out at 60 °C in a 50-mL glass beaker settled in a thermostat (about 2000 mL). During the experiment, the pH of the reaction suspensions was kept constant at 9.5 by addition of a 1 mol L⁻¹ NaOH solution using an automatic potentiometric titrator (Kyoto Electronics MFG. CO. Ltd., Japan). Oxygen was bubbled through the suspensions with a flow rate of 100 mL min⁻¹ at an atmospheric pressure. The suspensions were vigorously stirred with a magnetic stirrer. The starting concentration and volume of glucose solution were 0.264 mol L⁻¹ and 30 mL, respectively, and the charged weight of catalyst was about 2 mg. The catalytic reactions were automatically carried out for 2 h. The activity (mol-glucose·s⁻¹·mol-metal⁻¹) for glucose

oxidation of the BNPs was calculated from the slope of a straight line fitted with the NaOH amount vs reaction time data. The specific activity related to the metal content of the catalysts was used to compare catalysts with different gold contents, and the maximum activity was calculated for comparison. A typical NaOH amount vs time diagram with the fit line is shown in Figure S1. The slope of the fit line reflects the maximum activity of the catalyst. Catalytic activities of all the samples were measured at least twice under the same conditions and the mean value of the measuring results was used for comparison.

DFT Calculation

The structure and properties of the M_{55} clusters were calculated using the DMol³ DFT package. In these calculations, an all-electron relativistic core treatment and a doubled numerical basis set with polarization functions were employed. The rPBE functional was used for the DFT calculations. For all calculations, the spin restricted SCF calculations were carried out with a convergence criterion of 10^{-5} a.u. for the total energy and the electron density. We used the convergence criteria of 0.004 hartree/A on the force parameters, 0.005 Å on the displacement parameter, and 2×10^{-5} hartree on the total energy in the geometry optimization. The Mulliken population analysis was used for the investigation of the atomic charges of the targeted clusters. For these calculations, the rPBE functional and DNP basis sets were used.

3. Results and discussion

Plasmon absorption enhancements of Au NPs by addition of Ag ions.

In a previous paper [17], we reported the preparation of Ag/Au BNPs from the physical mixture in natural light, UV–Vis absorbance spectra were recorded as a function of time to monitor the formation of the Ag/Au BNPs prepared by mixing the colloidal dispersions of Au NPs and Ag^+ ions

in natural light. The results showed that only one surface plasmon peak was observed in all the UV-Vis spectra of the Ag/Au colloidal dispersions obtained after 0 ~ 2 h mixing. Moreover, the peak intensity at 520 nm was dramatically increased after addition of Ag^+ ion without appearance of Ag NP surface plasmon resonance peak expected at ca. 400 nm. We consider that the presence of the UV light in the natural light and the photoexcited state of Au NPs could play important roles in the formation of Ag/Au BNPs via the physical mixture route.

In this work, we tried to prepare the Ag/Au BNPs by mixing the colloidal dispersions of Au NPs and Ag^+ ions under dark conditions. We also recorded the UV-Vis spectra at various stages during the mixing process. The UV-Vis absorbance spectra as a function of mixing time of the $\text{Ag}_{30}\text{Au}_{70}$ BNPs (Figure 1a), along with the relationship between the mixing time and the absorbance of the plasmon by taking the absorbance of the original Au NP dispersion as 0 in darkness (Figure 1b), clearly demonstrates that the present phenomena tended to be similar to those in the case of Ag/Au BNPs prepared by physical mixture in natural light [17]. In order to reinforce the dependence of the addition of Ag^+ ions on the change of absorbance intensity of the prepared Ag/Au BNPs, a series of Ag/Au BNPs with various Ag contents were prepared by physical mixing at room temperature for 2 h under dark conditions. All the UV-Vis spectra of the Ag/Au BNPs colloidal dispersions with various Ag/Au ratios prepared in the dark, are shown as a function of mixing time in Figures S2-S4, revealing the same phenomena. In the case of $\text{Ag}_{50}\text{Au}_{50}$ BNPs, however, their surface plasmon peaks indicate much lower intensities compared with other samples, which is considered to arise from the dilution by the large amount of Ag^+ solution added ($\text{Ag}^+/\text{Au}=1/1$, v/v).

The drastic increase in absorbance occurred during the mixing period under dark conditions, suggesting the change of composition, structure or size occurred in the starting Au NPs. Otherwise, the absorbance intensity of the mixture dispersion would be kept at the same level. We do not think

that the absorbance intensity increase could be ascribed to the aggregation of the Au NPs since it is well accepted that aggregated Au NPs will result in a clear red-shift of the UV plasmon resonance peak. To investigate the effect of the particle aggregation on the UV-Vis spectrum of Au NPs, we prepared two series of PVP-protected Au NPs with large average sizes by alcohol reduction (Figure S5 showing the TEM images and UV-Vis spectra of well-isolated and aggregated Au NPs.) since the UV resonance peak of tiny Au NPs cannot be clearly characterized. Figure S5a shows a representative TEM image of the series Au NPs without particle aggregation, all the NPs are spherical and well-isolated, mainly distributed within the range from about 3 to 40 nm, and the average sizes ($\pm$ standard deviation) of the NPs based on the TEM images are 9.8 ± 3.6 nm. Another series Au NPs with particle aggregation showing in Figure S5b, demonstrated an average size of 23.6 ± 9.1 nm for comparison. The UV-Vis spectra of the two series Au NPs (Figures S5c-S5d) indicated that the series Au NPs without particle aggregation showed an adsorption peak at *ca.* 530 nm which can be assigned to the surface plasmon absorption from the gold. However, for the aggregated series of Au NPs (Figures S5d), a wide adsorption peak around 650 nm was observed. This clear red-shift of the UV absorption peak can be ascribed to the presence of the particle aggregation. It should be pointed out that no clear red-shift of the UV absorption peak could be observed in the present Ag/Au BNPs prepared by physical mixture under the conditions without any light and reductants.

UV-Vis spectroscopy is an efficient tool to study the geometric structure of Ag/Au BNPs. It is well known that Au_{core}/Ag_{shell} BNPs usually have two SPR bands in the UV-Vis profile near the Ag and Au SPR bands [10, 18], and Ag/Au alloy BNPs have only one plasmon band, where the wavelength at the maximum absorbance shifts in a linear fashion depending on the composition [19]. Figure 2 shows the UV-Vis spectra of Au and Ag NP dispersions, and Ag/Au BNP dispersions

with various compositions prepared by the physical mixture method in darkness, indicating that only one plasmon peak was observed and that clear red shift or blue shift of the plasmon peak was not observed for all the BNPs with various contents of Ag. These results suggested that the formed BNPs prepared by the present physical mixture route should have an $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ structure. Otherwise, the SPR band near about 520 nm in Figures 2 would shift to lower wavelength with increasing of the Ag contents.

During the evolution of the Ag/Au BNPs from Au NP dispersions and Ag^+ ions via the present physical mixture route, we also recorded the particle size changes of the Ag/Au BNPs at different mixing stages using TEM. The TEM images and the evolution of the size changes of the Ag/Au BNPs formed after various mixing time are shown in Figure 3. These results indicate that the average particle sizes of the prepared Ag/Au BNPs increase with increasing the mixing time. For example, for the $\text{Ag}_{50}/\text{Au}_{50}$ BNPs, the starting Au NPs were well dispersed with an average size of 1.1 ± 0.3 nm. When Ag^+ ions were added to the Au NP dispersions, however, the average diameter of the particles after mixing became larger than that of the starting Au NPs. The size distribution analysis (Figure S6) based on the TEM images gives the average diameter of 2.8 ± 0.7 nm and 3.0 ± 0.5 nm, respectively, for particles obtained from the physical mixture after 5 and 60 min mixing. Similar phenomena were also observed in the Au NPs prepared with various Ag^+ ion species in a reproducible fashion as shown in Figure 3b. All the TEM images in Figure 3 show that no aggregation occurred during the process of the physical mixing.

UV-Vis spectra and the relationship between particle sizes and mixing time of the prepared Ag/Au BNPs suggest that the added Ag^+ ions were reduced to Ag atoms in the presence of Au NPs in the present work. In order to further confirm the presence of Ag in the final BNPs, the chemical compositions of the prepared Ag/Au BNPs were obtained from ICP analysis as shown in Table 2,

indicating a representative set of results by comparing Ag atomic% in the final BNPs and that in the feeding metal precursors. The feeding atomic Ag ratios in the synthetic solutions are approximately proportional to the resulting Ag atomic ratios in the final BNPs.

Structure and catalytic activity for glucose oxidation of Ag/Au BNPs

TEM images of Ag/Au BNPs prepared from physical mixture in the dark using Au NP dispersions and Ag^+ ions as starting materials are shown in Figure 4. The prepared Ag/Au particles were well dispersed, but their average diameters became larger with increasing of AgClO_4 . The average particle sizes are about 2.4 ± 1.0 nm, 2.4 ± 1.1 nm, 2.5 ± 0.9 nm, 2.6 ± 1.2 nm, and 3.0 ± 2.2 nm for $\text{Ag}_{10}\text{Au}_{90}$, $\text{Ag}_{20}\text{Au}_{80}$, $\text{Ag}_{30}\text{Au}_{70}$, $\text{Ag}_{40}\text{Au}_{60}$, and $\text{Ag}_{50}\text{Au}_{50}$ nanoparticles, respectively. These results indicated that the final average particle sizes of the prepared Ag/Au BNPs increase with increasing the Ag contents, suggesting that Ag^+ ions were indeed reduced using the present method. The increment in the diameters might be caused by an ingress of Ag atoms into Au nanoparticles after reduction of Ag^+ ions, which could be considered as one of the reasons for the surface plasmon enhancement.

In order to further examine whether a core-shell structure was obtained from the present mixing process, EDS on as-prepared BNP was obtained. Figure 5 presents together a typical HR-STEM image (a) and EDS (b) of Ag/Au BNPs prepared by addition of AgClO_4 aqueous solutions to PVP-protected Au NP colloidal dispersions under dark conditions. Since the size of EDS electron beam is 1 nm in diameter, the compositions of different parts of a nanoparticle can be examined independently. Interestingly, the EDS results revealed the co-existence of Ag and Au in the center of the nanoparticle and the presence of only Au in the edge of the nanoparticle, confirming the core/shell (Ag/Au) structure of the $\text{Ag}_{10}\text{Au}_{90}$ BNPs. For example, the compositions of particle 2 were Ag (0%) and Au (100%) in the edge, and Ag (5%) and Au (95%) in the central part of the

nanoparticle as shown in the insert table of Figure 5. These results indicated that Au atoms were not present in the center of the particle, but were concentrated on the edge of the particle ($\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ structure). The reason for the appearance of Ag in edge may be due to the diffusion of the incident electron. The incident electron may diffuse into the central part of the particle and emit the characteristic X-ray of Ag. To the knowledge of the authors, this is the first report on the formation of the PVP-protected $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ -like BNPs with sizes of about 2 nm via the physical mixture route using Au NP dispersions and Ag^+ ions as starting materials under the condition without any lights and reductants. At present time, the reason for the formation of the $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs and the plasmon enhancement of the mixture of Au NP dispersion and Ag^+ ion solution in the dark is still unclear, although the protective polymer PVP might have worked as a reducing agent in the present case, which is being investigated and the results will be reported in a future publication.

It is well-known that composition plays an important role in the catalytic activity of BNPs. In order to get more information on the effect of compositions upon the catalytic activities, all the Ag/Au BNPs with various atomic ratios were used as the colloidal dispersion catalysts for aerobic glucose oxidation in solution. The catalytic activity varies with the compositions of the BNPs as shown in Figure 6. The highest catalytic activity was achieved for the samples of $\text{Ag}_{10}\text{Au}_{90}$ BNPs, whose activity is $11,360 \text{ mol-glucose}\cdot\text{h}^{-1}\cdot\text{mol-metal}^{-1}$. The activity of the $\text{Ag}_{10}\text{Au}_{90}$ BNPs is about two times higher than that of pure Au NPs ($6230 \text{ mol-glucose}\cdot\text{h}^{-1}\cdot\text{mol-metal}^{-1}$) even though the former have a larger particle size (2.4 nm) than the latter (1.4 nm).

Correlation between negatively charged Au atoms and catalytic activities of Ag/Au BNPs

The higher catalytic activity of Ag/Au BNPs compared to Au NPs can be explained by the effects of electronic charge transfer between different kinds of adjacent elements which were used before to explain the high catalytic activities of BNPs and TNPs in several cases [20-23]. In the case of the

Au/Ag BNPs, the ionization potential values of Au and Ag are 9.22 and 7.58 eV, respectively. As a result, electronic charges would transfer from Ag atoms to Au atoms, leading to an increase in the electron density on the Au, which could act as catalytically active sites, activating molecular oxygen by donating excess electronic charge to the antibonding orbital and resulting superoxo- or peroxo-like oxygen and then promotes glucose oxidation [24].

In order to examine the electronic properties of the catalytically active BNPs, and to confirm the electronegativity of the above-mentioned Au atoms, DFT calculations were carried out to study the electronic states of the Au atoms in present Ag/Au NPs. At the present stage, it is still impossible for us to make a large scale calculation for the large NPs, such as M_{147} and M_{309} , etc. Hence DFT calculations of a M_{55} model NP (core/shell-structured $Ag_{13}Au_{42}$) were examined for understanding the correlation between the electronic states and catalytic activity of the BNPs for aerobic glucose oxidation. The calculation results are shown in Figure 7a. The most important result was that all the Au atoms located at the shell are indeed negatively charged, while the Ag atoms have positive charges. These results support the presence of the electronic charge transfer from the Ag atoms to Au atoms in as-prepared Ag_{core}/Au_{shell} BNPs.

Apart from the electron charge transfer from Ag to Au atoms, PVP could transfer electron to Au atoms in the as-prepared PVP-protected Ag_{core}/Au_{shell} BNPs. In order to confirm the electron charge effect of PVP, DFT calculation on the electronic structures of the Ag_{core}/Au_{shell} BNPs protected by PVP were also carried out for comparison. Figure 7b shows that the Mulliken charges of some Au atoms in core/shell-structured $Ag_{13}Au_{42}$ BNPs protected by N-ethylpyrrolidone (EP) as a simple model of PVP are calculated to be as low as -0.044. It should be pointed that, for the BNPs without PVP as a stabilizer, the lowest Mulliken charges of -0.025 for the Au atoms were observed in the core/shell-structured $Ag_{13}Au_{42}$ BNPs. The more negative Mulliken charges of the Au atoms in

EP-protected $\text{Ag}_{13}\text{Au}_{42}$ BNPs than that of $\text{Ag}_{13}\text{Au}_{42}$ BNPs without EP indicate that PVP indeed donates electronic charge to the Au atoms. This result provides crucial evidence that PVP not only acts as a stabilizer but also plays a direct role in regulating the electronic structures of the Ag/Au BNPs. The possible electronic charge transfer effects in Ag/Au BNPs are illustrated in Figure 8. From the results of DFT calculation, we can conclude that the Au atoms in BNPs are indeed negatively charged, as a result of the charge transfer from the Ag atoms and from the PVP molecules, and these negatively charged Au atoms would act as crucial active sites for the aerobic glucose oxidation. Above all, the higher catalytic activity of the prepared $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs than the corresponding Ag and Au NPs may be ascribed to the following factors: 1) the small average diameter, about 2 nm, and 2) the negatively charged Au atoms in the $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs acting as catalytically active sites for the glucose oxidation.

4. Conclusion

In summary, we have found that core/shell-structured Ag/Au BNPs of about 2.4 nm in diameter can be prepared from physical mixture of Au NP dispersions and Ag^+ ions under dark conditions without using any reductants. The prepared $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs with the composition of Ag/Au (1/9) had the highest catalytic activity for glucose oxidation among those BNPs with various composition ratios and Au NPs. The activity of the core/shell-structured $\text{Ag}_{20}\text{Au}_{80}$ BNPs is about two times higher than that of pure Au NPs, even though the $\text{Ag}_{20}\text{Au}_{80}$ BNPs have a larger particle size than Au NPs. The high catalytic activity of the Ag/Au BNPs could be ascribed to the presence of negatively charged Au atoms caused by electronic charge transfer effects from Ag atoms and PVP molecules to Au atoms in the PVP-protected $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ BNPs. The electronic charge transfer effects are supported by the DFT calculation of model $\text{Ag}_{13}/\text{Au}_{42}$ clusters.

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Table captions

Table 1 Detailed preparation conditions of Ag/Au BNPs using physical mixtures of Ag⁺ ions and Au NPs under dark conditions

Table 2 Comparison of theoretical and ICP results of Au and Ag contents in the final Ag/Au series BNPs prepared from physical mixtures at room temperature for 2 h under dark conditions.

Figure captions

Figure 1. (a) UV-Vis spectra of Au NPs and Ag⁺ ions dispersions as a function of mixing time. (b) Absorbance increment ratios as a function of mixing time using the absorbance of the original mixture of Au NPs (before Ag⁺ ion addition) as the reference. When an aqueous dispersion of Au NPs (35mL, 0.44 mmol L⁻¹) and an aqueous solution of AgClO₄ (15 mL, 0.44 mmol L⁻¹) were mixed at room temperature under dark conditions (Ag⁺/Au =30/70, atomic ratio; The absorbance intensities of 520 nm were used for calculation.)

Figure 2. UV-Vis spectra of dispersions of Au and Ag NPs, and Ag_{core}/Au_{shell} BNPs with various compositions prepared from physical mixtures of Au NPs and AgClO₄ solution at room temperature for 2 h under dark conditions.

Figure 3. Evolution of particle sizes and mixing time of Ag_{core}/Au_{shell} BNPs prepared from physical mixtures under dark conditions

Figure 4. TEM images of the final Ag_{core}/Au_{shell} BNPs prepared from physical mixtures at room temperature for 2h under dark conditions .

Figure 5. HR-STEM image (a) and EDS results (b) of core/shell-structured Ag₂₀Au₈₀ BNPs prepared from physical mixtures at room temperature for 2h under dark conditions.

Figure 6. Catalytic activities toward glucose oxidation of the final Ag_{core}/Au_{shell} BNPs with various

contents of Ag.

Figure 7. DFT calculations of electronic structure of core/shell-structured $\text{Ag}_{13}\text{Au}_{42}$ and EP-protected $\text{Ag}_{13}\text{Au}_{42}$ BNPs (Yellow: Au; Blue: Ag; Attached substance: EP molecule. The data shown in Figure 7 indicate the Mulliken charges of Au, and Ag in the BNPs.)

Figure 8. Schematic illustration of possible electronic charge transfer effects from Ag atoms and PVP molecule in the core/shell-structured $\text{Ag}_{20}\text{Au}_{80}$ BNPs.

Table 1

Code	Preparation conditions of Au NPs				Mixing conditions		Compositions
	T / °C	Time / h	R_{PVP}	R_{NaBH_4}	T / °C	Time / h	
AgAu- D1	0	1	100	5	-		Au
AgAu- D2	0	1	100	5	RT	2	Au/Ag=9/1
AgAu- D3	0	1	100	5	RT	2	Au/Ag=8/2
AgAu- D4	0	1	100	5	RT	2	Au/Ag=7/3
AgAu- D5	0	1	100	5	RT	2	Au/Ag=6/4
AgAu- D6	0	1	100	5	RT	2	Au/Ag=5/5
AgAu- D7	Ag NPs prepared with the same conditions for Au NPs						Ag

(R_{PVP} : The molar ratio of PVP monomer units to the Au^{3+} ions; R_{NaBH_4} : The molar ratio of NaBH_4 to the Au^{3+} ions)

Table 2

Ag/Au BNPs	Au, atom %		Ag, atom %	
	theoretical	ICP results	theoretical	ICP results
AgAu- D1	100	-	0	-
AgAu- D2	90	87.7	10	12.3
AgAu- D3	80	75.2	20	24.8
AgAu- D4	70	69.5	30	30.5
AgAu- D5	60	62.5	40	37.5
AgAu- D6	50	50.6	50	49.4
AgAu- D7	0	-	0	-

(a) UV-Vis spectra

(b) Absorbance intensity increasing ratios

Figure 1

Figure 2

(a) TEM images of $\text{Ag}_{50}/\text{Au}_{50}$

Compositions, atomic	Particle sizes, nm	
	Ag^+/Au , 5 min	Ag^+/Au , 60 min
$\text{Ag}^+/\text{Au} = 20/80$	2.0 ± 0.4	2.4 ± 1.1
$\text{Ag}^+/\text{Au} = 50/50$	2.8 ± 0.7	3.0 ± 2.2

(b) Evolution of size change

Figure 3

Figure 4

(a) HR-STEM

Particles	spot	Chemical compositions, atom%	
		Ag	Au
1	center	11	89
	edge	5	95
2	center	5	95
	edge	0	100

(b) EDS-STEM results of the particles in Figure 5 (b)

Figure 5

Figure 6

(a) $\text{Ag}_{13}\text{Au}_{42}$ BNPs

(b) EP-protected $\text{Ag}_{13}\text{Au}_{42}$ BNPs

Figure 7

Ag/Au = 20/80

Figure 8

Graphical Abstract

TOC graphic

The synthesis, characterization and catalytic activities for glucose oxidation of AgAu bimetallic nanoparticles (BNPs) with size of less than 2 nm are reported.

The catalytic activity of $\text{Ag}_{10}\text{Au}_{90}$ BNPs was about two times higher than that of Au NPs, even the BNPs have a larger particle size than that of Au NPs.