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Polymer-Protected and Au-Containing Bi- and Trimetallic Nanoparticles as Novel Catalysts for Glucose Oxidation

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Summary: Polymer-protected metal nanoparticles (NPs) are recognized as a type of complex between a polymer and metal NPs, since the metal NPs are stabilized by coordination to the polymer. Thus, they can work as an effective catalyst in a dispersed state due to their high surface area-to-volume ratio and high stability by protection with poly(N-vinyl-2-pyrrolidone) (PVP). In this study, colloidal dispersions of PVP-protected and Au-containing bi- and trimetallic NPs were prepared and applied to the catalyst for the aerobic oxidation of glucose into gluconic acid in an alkaline solution. The AuAg and AuPt bimetallic NPs were more active than the Au NPs although the Ag and Pt NPs were less active than the Au NPs. The AuAgPt (Au/Ag/Pt = 7/2/1) trimetallic NPs were the most active catalyst for the same reaction. The high activity can be explained by electronic charge transfer from the Ag or Pt to the Au.

Keywords: Ag; Au catalyst; bimetallic nanoparticles; gluconic acid; glucose oxidation; Pt; trimetallic nanoparticles

Introduction

Polymer-protected metal nanoparticles (NPs) can be prepared by the reduction of metal ions coordinated by polymers. The metal atoms on the surface of the prepared NPs are strongly coordinated to the polymer, which makes the polymer-protected metal NPs rather stable in a dispersion and more active as a catalyst.[1–5] If the same metal NPs are protected by low-molecular-weight ligands, such metal NPs do not work as a stable active catalyst, since the reaction substrates cannot attack the surface atoms of the metal NPs. If the metal NPs strongly coordinate to a ligand such as a thiol ligand, the ligand-stabilized metal NPs are not active as a catalyst because the ligands work as poisons by covering the active sites of the metal NPs. If the coordination bond is too weak, then the metal NPs are not well stabilized and form aggregates of the NPs during the reaction, because the weakly coordinated ligands leave the metal NPs by attack of the reaction substrates on the surface of NPs. In the metal NPs protected by a polymer like poly(N-vinyl-2-pyrrolidone) (PVP), a PVP molecule steadily binds to a metal NP at multiple sites on the surface of the NP in spite of the weak coordination as a single bond. The polymer-protected metal NPs can work as an active and stable catalyst because the polymer can still remain near the NP during the attack of the reaction substrates on the surface of the NPs. This situation is illustrated in Figure 1.

The catalytic properties of polymer-protected metal NPs are also affected by the size of the NPs and the type of metal.[6–9] In general, the smaller the size of the NPs, the higher the catalytic activity. In addition,

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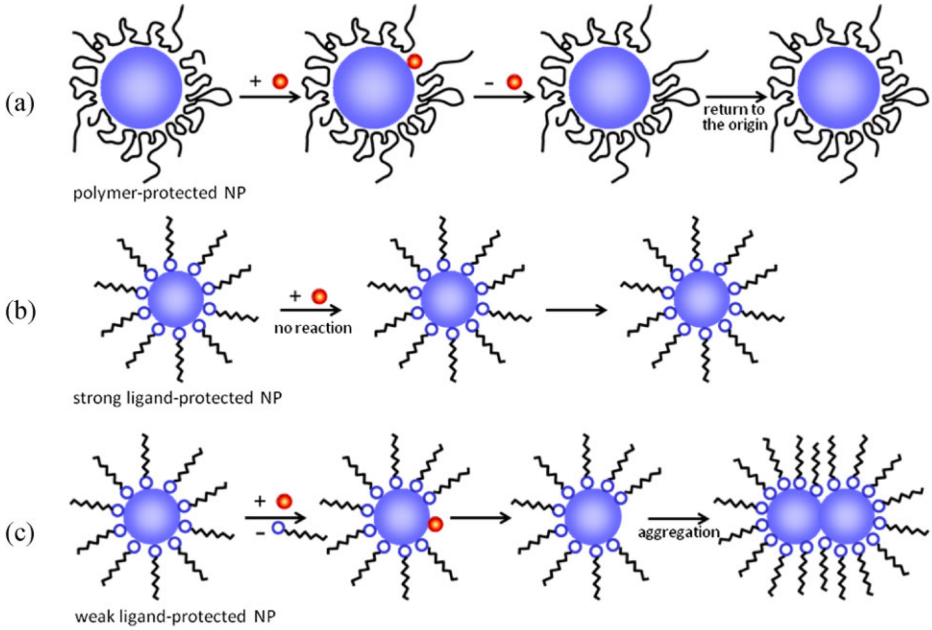


Figure 1.

Schematic illustration of the catalytic action of (a) polymer-protected NPs, (b) strong ligand-protected NPs, and (c) weak ligand-protected NPs on the reaction substrate (small red circle).

the bimetallic or trimetallic NPs, in which the metal atoms at the active sites are adjacent to foreign metal atoms, can have a higher catalytic activity than the original monometallic NPs. The acceleration effects by the adjacent foreign elements are called as electronic and geometric effects.[7]

Gold was known as an inactive metal as a catalyst until Haruta discovered the activity of supported gold catalysts for the oxidation of carbon monoxide at a relatively low temperature.[10] Many gold catalysts have now been reported.[11–14] Based on these studies, it has become clear that gold has a very specific property as a catalyst. That is, gold works as a catalyst for aerobic oxidation at a relatively low temperature, which cannot be achieved by other methods. Recently, colloidal dispersions of PVP-protected gold NPs was reported to have a catalytic activity for the aerobic oxidation of an alcohol to an aldehyde, especially when the size of the NPs is small enough.[15,16] Gold NPs supported on carbon or metal oxide supports were reported to have a high activity for the selective aerobic oxidation of glucose to gluconic acid.[17] Recently, we found that Au/Pt/Ag (70/20/10) trimetallic NPs are much more active as a stable catalyst for selective aerobic glucose oxidation.[18]

We now summarize our recent results regarding the catalyses of gold-containing bimetallic and trimetallic colloidal NPs for glucose oxidation, and detailed processes to achieve these particular trimetallic NPs as the most active catalyst for the aerobic oxidation of glucose.

Experimental Part

Preparation of Polymer-Protected Metal NPs

Dispersions of PVP-protected metal NPs were prepared by reduction of the corresponding metal salts like $HAuCl_4$, H_2PtCl_6 and $AgClO_4$ by $NaBH_4$ in water. For example, $Au_{70}Pt_{20}Ag_{10}$ (R) TNPs (the subscripts of Au, Pt and Ag denote the synthetic feeding ratios of the three metals) were prepared as follows.[18] An aqueous solution of $HAuCl_4 \cdot 4H_2O$ (35 mL, 1.32 mM) and $H_2PtCl_6 \cdot 6H_2O$ (10 mL, 1.32 mM) was added to an aqueous PVP solution (50 mL, 1.32 nM) with vigorous stirring. An aqueous solution of $AgClO_4$ (5 mL, 1.32 mM) was added to the solution and the mixture was stirred for 30 min in an ice-water bath at 0 °C. The molar ratio of the PVP units to the total metal ions (R_{PVP}) was 100, and the molar ratio of $NaBH_4$ to the total metal ions (R_{NaBH4}) was 5. An aqueous solution of $NaBH_4$ (20 mL, 16.5 mM, 0 °C) was then rapidly injected into the mixture under vigorous stirring. The addition time was within 5 s. The colloidal dispersions of the metal NPs were filtered through 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 pressure to remove any extra agents and byproducts. The residual ethanol of the PVP-protected trimetallic NPs was removed using a rotary evaporator at 40 °C. The PVP-protected trimetallic NPs were finally obtained as a powder by drying under vacuum at 40 °C for 48 h.

Characterization of Polymer-Protected Metal NPs

Ultraviolet and visible (UV-vis) spectroscopies were used to check the disappearance of the metal ions during the reaction, and to estimate the size of Au NPs and the structure of the bimetallic and trimetallic NPs containing Au. The metal content of the PVP-protected bimetallic and trimetallic NPs was determined by optical emission spectroscopy with inductive coupled plasma (ICP-OES, Various 720-ES). The polymer content was determined by thermogravimetry (TG Bruder AXS, WS002). The ICP and TG results showed that the metal and polymer compositions in the fine bimetallic and trimetallic NPs were almost the same as those in the starting solution.

Transmission electron microscopy (TEM) images were obtained using a JEOL TEM 1230 at the accelerated voltage of 80 kV. The specimens were obtained by placing one or two drops of the colloidal ethanol dispersion of the polymer-protected metal NPs on a thin amorphous carbon film-covered copper microgrid and dried in air at room temperature. Prior to the specimen preparation, the colloidal dispersions were sonicated for 10 min to obtain a better particle dispersion on the copper grid. The image analysis was performed using iTEM software (Olympus Soft Imaging Solution GmbH) of at least 200 particles.

Aerobic Oxidation of Glucose Using Au-Containing Metal

The catalytic performance of all the catalysts was evaluated by the aerobic glucose oxidation as a model reaction. The reactions were carried out at 60 °C in a 50-mL glass beaker placed in a thermostat. During the experiment, the pH of the reaction mixture was kept constant at 9.5 by the addition of a 1 mol L^{-1} NaOH solution using an automatic potentiometric titration system (Kyoto Electronics MEG. Co., Ltd., Japan), since the oxidation of glucose selectively produced gluconic acid, and the produced gluconic acid consumed an equimolar amount of NaOH as shown in Figure 2. Oxygen was bubbled through the reaction mixtures at the flow rate of 100 mL min^{-1} and atmospheric pressure. The mixture was vigorously stirred by a magnetic stirrer. The starting concentration and volume of the glucose solution was 0.264 mol L^{-1} and 30 mL, respectively. The reactions were automatically carried out for 2 h. The turnover frequency (TOF) was calculated from the slope of the straight line fitted to the NaOH amount vs. reaction time curve.

Catalytic Activity of PVP-Protected Monometallic NPs

The catalytic activity of the PVP-protected monometallic NPs was evaluated by choosing Au and its families (coinage metals) and easily available platinum group metals because Au is known as an active

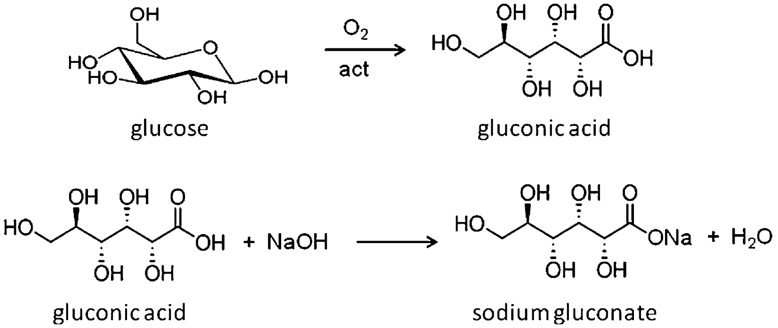


Figure 2.
Reaction scheme of aerobic oxidation of glucose in alkaline solution.

catalyst for glucose oxidation and the Pt group metals are often used as a general catalyst.

Dispersions of the PVP-protected nanoparticles (NPs) were prepared by reduction of the corresponding metal chloride with $NaBH_4$ in water by two different addition methods, i.e., rapid injection and dropwise addition. The isolated metal NPs, after purification by an ultrafilter and drying under vacuum, were examined as a catalyst for glucose oxidation. The results are shown in Figure 3a and 3b. The catalytic activity and average particle size of the PVP-protected monometallic NPs prepared by the dropwise addition of $NaBH_4$ are shown in Figure 3a and those by the rapid injection of $NaBH_4$ in Figure 3b. A comparison of both figures indicates that the Au NPs are the most active among the metal NPs examined in this study. In addition, it was confirmed that the rapid injection method produced metal NPs with a higher catalytic activity than the dropwise addition method, since the rapid injection method produced smaller NPs than the dropwise method as usually observed.

Catalytic Activity of PVP-Protected Bimetallic NPs

We examined the preparation and evaluation of the catalytic activity of the bimetallic NPs containing Au since the catalytic activity of a metal can be often improved by the addition of a small amount of another element.[1] The preparation was

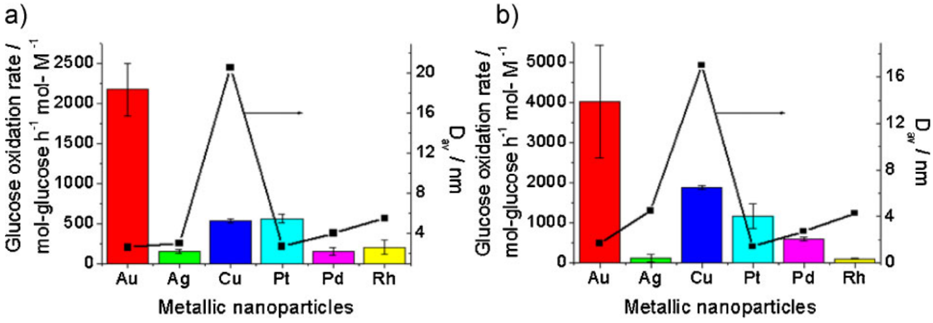


Figure 3.
Comparison of catalytic activities (sticks) and average particle sizes (squares) of monometallic NPs prepared by dropwise addition and rapid injection of $NaBH_4$ in the solution of the corresponding metal salts in water at 0 °C in the presence of PVP ($R_{PVP} = 40$). a) Dropwise addition. b) Rapid injection.

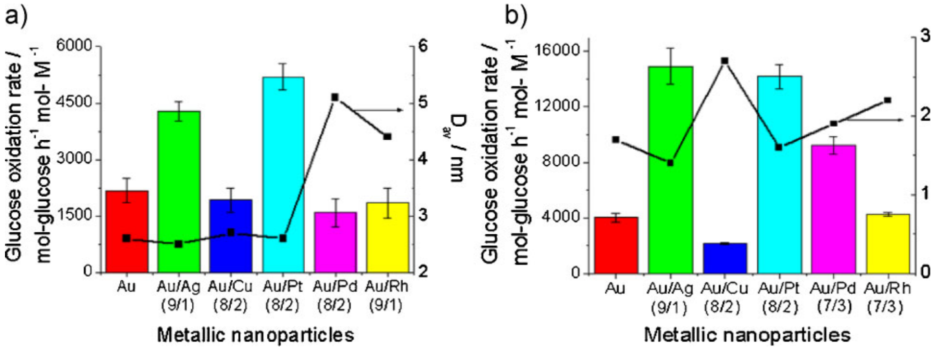


Figure 4.
Comparison of catalytic activities (sticks) and average particle sizes (squares) of bimetallic NPs prepared by dropwise addition and rapid injection of $NaBH_4$ into the solution of the corresponding mixtures of metal salts in water at 0 °C in the presence of PVP ($R_{PVP} = 100$). a) Dropwise addition. b) Rapid injection.

carried out by reduction of the mixtures of $HAuCl_4$ and chloride salts of another element by the dropwise addition or rapid injection of $NaBH_4$ at various molar ratio of metals. Figure 4 summarizes the catalytic activities of the Au monometallic NPs, and AuAg, AuCu, AuPt, AuPd and AuRh bimetallic NPs at the molar ratios of Au/Ag, Au/Cu, Au/Pt, Au/Pd and Au/Rh = 9/1, 8/2, 8/2, 8/2, and 9/1, respectively, in which the highest activity was achieved in each series. The results showed that (1) the rapid injection method of $NaBH_4$ produced smaller sized bimetallic NPs and a higher catalytic activity for the glucose oxidation than the dropwise addition of $NaBH_4$, and (2) the Au/Ag and Au/Pt bimetallic NPs had a higher catalytic activity than the Au nanometallic NPs.

Thus, we precisely carried out the experiments for optimizing the preparation conditions in order to obtain bimetallic NPs with the highest catalytic activity. Figure 5 and 6 compare the catalytic activities depending on the preparation conditions. Based on these comparisons, the optimized preparation conditions were determined as follows: (1) the reduction method; rapid injection of $NaBH_4$, (2) the molar ratio of $NaBH_4$ versus metal, i.e., $R_{NaBH4} = 10$, and (3) the molar ratio of monomer unit of PVP versus metal, i.e., $R_{PVP} = 100$.

In order to understand these differences in the catalytic activity, we precisely characterized the Au/Ag bimetallic NPs. Figure 7 shows the HR-TEM images and size distribution histograms as well as the spot EDS analyses of the bimetallic NPs at the center and the edge of each particle prepared by the dropwise addition (Figure 7a, 7b, and 7c) and rapid injection (Figure 7d, 7e, and 7f) of $NaBH_4$. These results suggest that the NPs prepared by the dropwise addition had a larger average size and wider size distribution than those prepared by the rapid injection. Although both NPs were mixtures of the alloy NPs with various compositions, the Au atoms were rather localized at the edge of each particle in the bimetallic NPs prepared by the rapid injection than in those prepared by the dropwise addition. These differences may be the reason for the difference in the catalytic activities.

Under the best conditions, the effect of the molar contents of silver in the AuAg bimetallic NPs on the catalytic activity and average size were examined and illustrated in Figure 8.

The result revealed that the Ag content of 20%, i.e., Au/Ag = 8/2, provided the highest catalytic activity, although the average size of the NPs at Au or Au/Ag = 9/1 is smaller than that at Au/Ag = 8/2.

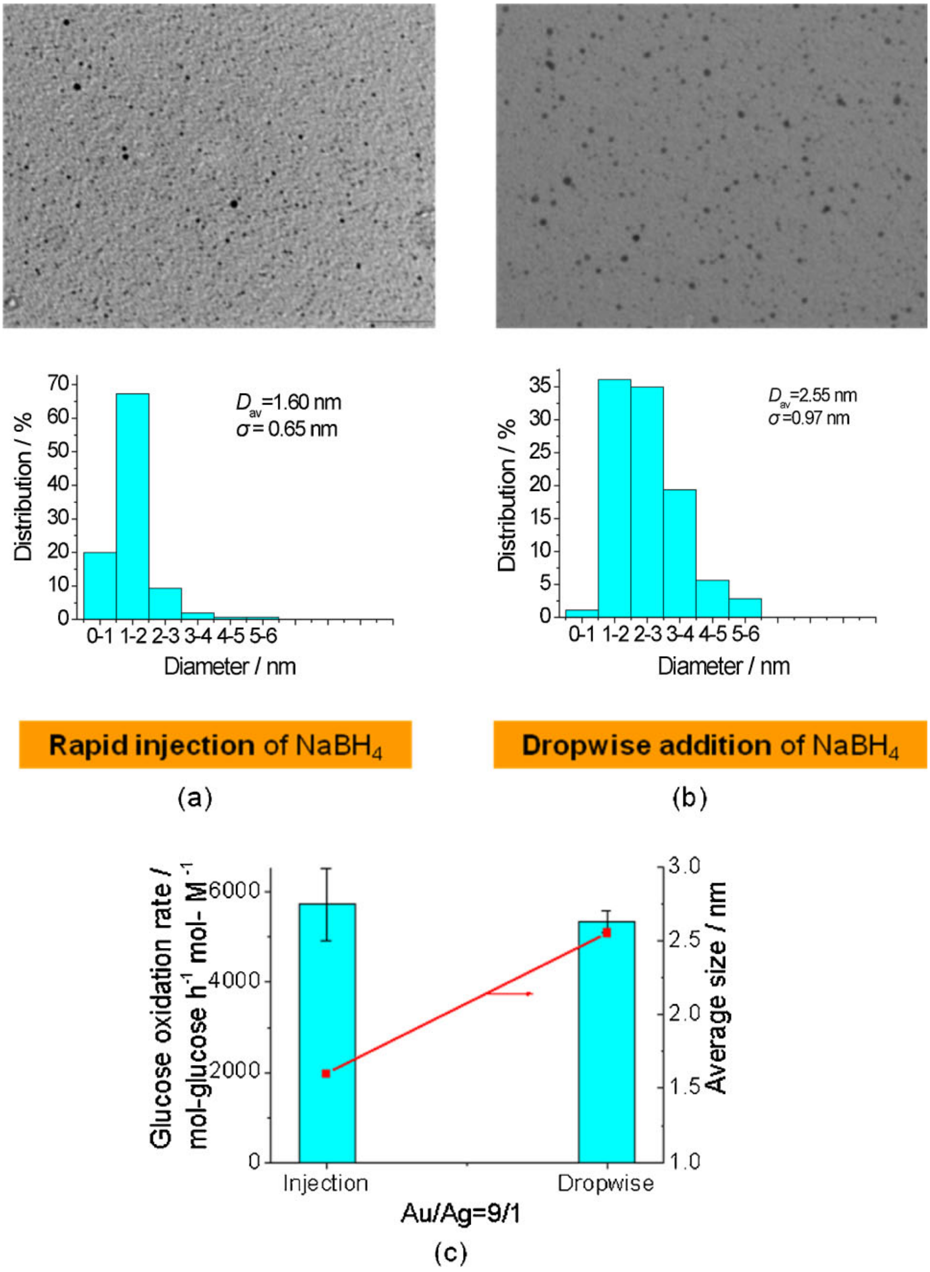


Figure 5.

TEM images and size distribution (a and b), and comparison of catalytic activities (sticks) and average particle sizes (squares) (c) of AuAg (Au/Ag = 9/1) bimetallic NPs prepared by dropwise addition and rapid injection of $NaBH_4$ into the solution of the mixtures of $HAuCl_4$ and $AgClO_3$ in water at 0 °C in the presence of PVP ($R_{PVP} = 100$).

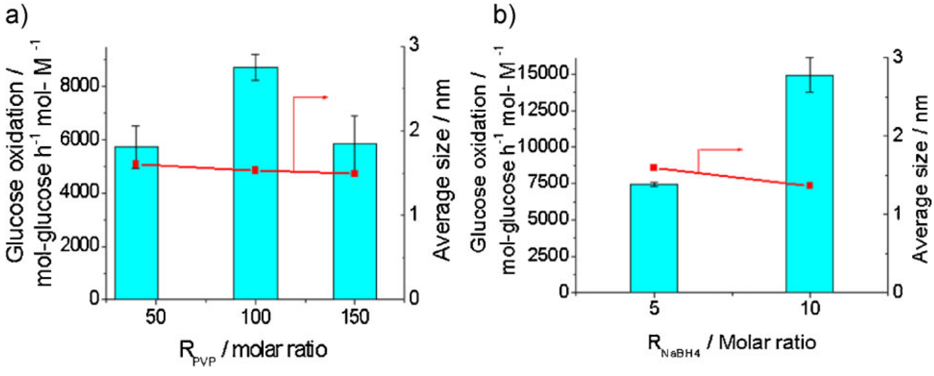


Figure 6.

Effect of R_{PVP} (a) and R_{NaBH4} (b) upon catalytic activities (sticks) and average particle sizes (squares) of AuAg (Au/Ag = 9/1) bimetallic NPs prepared by rapid injection of $NaBH_4$ into the solution of the corresponding mixtures of salts in water (1.32 mM for (a) and 0.44 mM for (b)) at 0 °C in the presence of PVP (R_{PVP} = 5 and 100 for (a) and (b), respectively).

The NPs at Au/Ag = 8/2 has a rather Ag-core/Au-shell structure, which is suggested based on the HR-TEM and EDS analyses.[19] A typical data are shown in Figure 9.

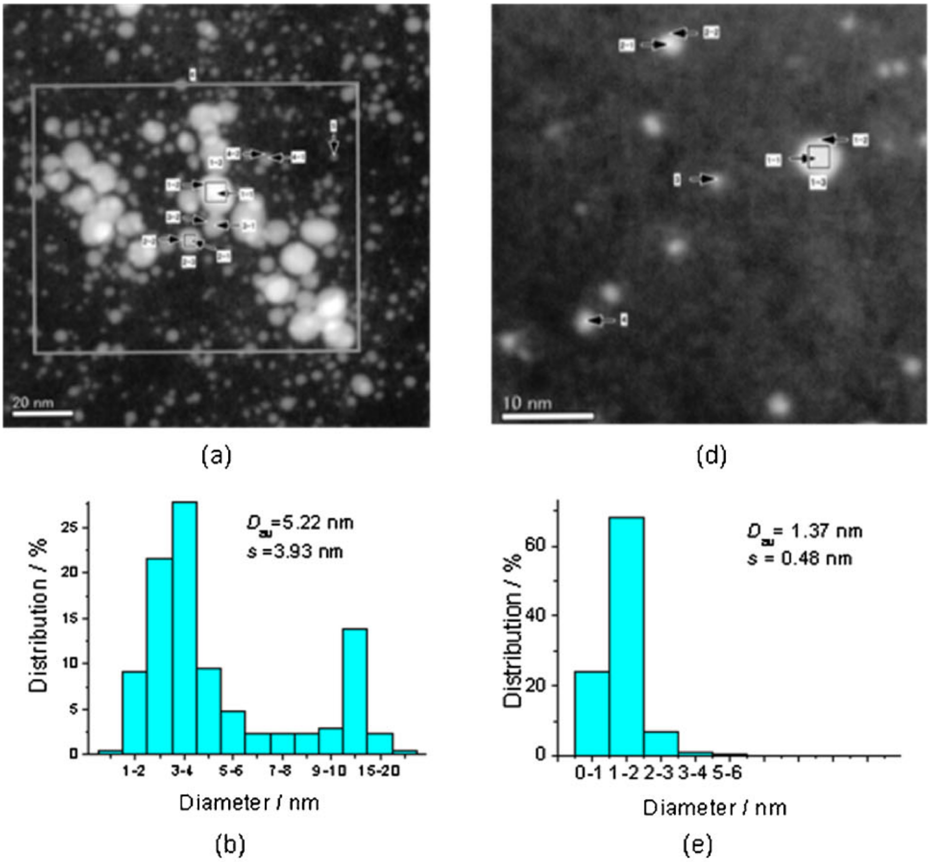
For the AuPt bimetallic NPs, optimization of the preparation conditions to obtain bimetallic NPs with the highest catalytic activity was carried out by a method similar to that of the Au/Ag bimetallic NPs. The effects of (a) the additive method of $NaBH_4$, (b) the concentration of metal ions, and (c) the R_{PVP} (molar ratio of PVP monomer unit against metal) on the catalytic activity of the obtained AuPt bimetallic NPs were examined and the results are shown in Figure 10.

The catalytic activity of the PVP-protected AuPt (Au/Pt = 8/2) bimetallic NPs prepared by reduction with the rapid injection of $NaBH_4$ in the presence of PVP (R_{PVP} = 150) and at the metal concentration of 1.32 mM is shown in Figure 3 with other NP catalysts for comparison. Surprisingly, the AuPt bimetallic NPs with a high catalytic activity have a rather Au-core/Pt-shell structure based on the HR-TEM and EDS analyses. Since the Pt NPs have a low activity, the results suggest that only a small amount of Au in the surface may be active as the catalyst. These details will be published elsewhere.

It is worth noting that the Ag and Pt atoms are much more effective than other elements like Cu, Pd, and Rh to improve the catalytic activity of Au NPs by forming the bimetallic NPs. The electron-donating property of the Ag and Pt atoms to Au atoms may be suggested to be the driving force for the high activity of the AuAg and Au/Pt bimetallic NPs. A reviewer pointed out why Cu, Pd, and Rh do not effectively improve the catalytic activity of the Au NPs. Unfortunately, we do not have an answer but a possible explanation may be due to the crystallinity of the bimetallic systems.

Catalytic Activity of PVP-Protected Trimetallic NPs

Since the Ag and Pt elements very effectively improve the catalytic activity of the Au NPs in the bimetallic system as described in the previous session, we examined the catalytic activity of the AuPtAg trimetallic NPs at various Au/Pt/Ag ratios. These results are shown in Figure 11, which reveals that the trimetallic NPs at the molar ratio of Au/Pt/Ag = 70/20/10 have the highest activity among the examined trimetallic NPs.[18] We do not exactly know which Au/Pt/Ag ratio gives the best results. However, the ratio Au/Pt/Ag = 70/20/10 gave the highest activity



EDS	Site	Composition/atom%	
		Ag	Au
Spot 1-1	center	1.3	98.7
Spot 1-2	edge	9	91
Spot 2-1	center	1.6	98.4
Spot 2-2	edge	3.5	96.5
Spot 3-1	center	9.4	90.6
Spot 3-2	edge	4.9	95.1
Spot 4-1	center	1.9	98.1
Spot 4-2	edge	4.2	95.8
Spot 5	all	4.0	96.0
Area 1-3	-	6.2	93.8
Area 2-3	-	0	100
Area 6	-	15.7	84.3

(c)

EDS	Site	Composition/ atom%	
		Ag	Au
Spot 1-1	center	50.3	49.8
Spot 1-2	edge	9.0	91
Spot 2-1	center	4.4	95.6
Spot 2-2	edge	3.5	96.5
Spot 3	-	0	100
Spot 4	-	0	100
Area 1-3	-	2.4	97.6

(f)

Figure 7.
HR-TEM images (a and d), size distribution histograms (b and e), and EDS compositions (c and f) of AuAg bimetallic NPs prepared by dropwise addition (a, b, and c) and rapid injection (d, e, and f) of $NaBH_4$.

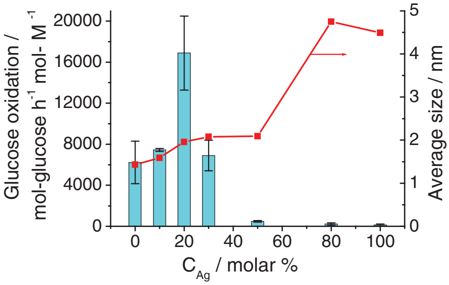


Figure 8.
Comparison of catalytic activities (sticks) and average particle sizes (squares) of AuAg bimetallic NPs of various compositions prepared by rapid injection of $NaBH_4$ ($R_{NaBH4}=10$) in the 0.44 mM solution of the corresponding mixtures of metal salts in water at 0 °C in the presence of PVP ($R_{PVP}=100$).

among the examined AuPtAg trimetallic NPs. The molar ratio mentioned here is the feeding ratio of the starting solution. As shown in the experimental section, the ICP results showed that the metal ratios of the final NPs are almost the same as those of the starting solution. In addition, the catalytic activity for the first run of this trimetallic NPs did not significantly decrease in the repeated batches (2–4).

The electron charge transfer effect between the adjacent elements in bimetallic NPs was often reported for the reason of the high catalytic activities.[20] Since the trimetallic NPs have a random alloy structure,[18] this surprisingly high catalytic activity could be attributed to the electron charge transfer effect of the adjacent elements (Pt and Ag) on the Au atoms, The electron charge transfer effect can be illustrated as shown in Figure 11. In addition to the electron charge transfer from Pt to Au and Ag to Au, a sequential electron charge transfer from Ag to Pt and then subsequently from Pt to Au may occur in the system. These effects effectively play their roles to improve the catalytic activity.

Conclusion

We have carried out a series of experiments involving the preparation and catalytic activity evaluation of various monometallic NPs and Au-containing bi- and trimetallic NPs by using aerobic glucose oxidation as the measure. When compared to the monometallic NPs, the Au NPs gave the best results compared to the other examined metals. However, the combination of Au with Ag and Pt resulted in an excellent improvement in the catalytic activity, although the Ag and Pt monometallic NPs have much less activity than the Au NPs. In addition, the AuPtAg trimetallic NPs resulted in a much higher activity especially at the molar ratio of Au/Pt/Ag = 70/20/10. These results showed that the electron charge transfer may be the most important factor to improve the

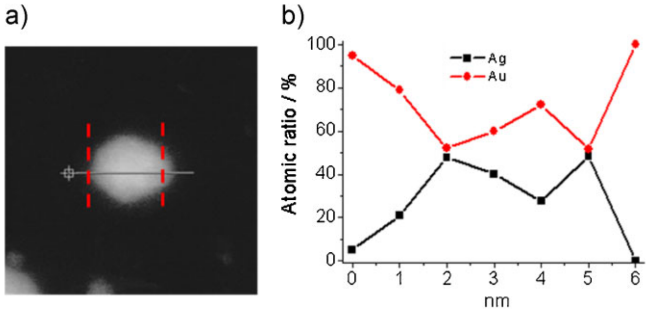


Figure 9.
The HR-TEM (a) and EDS line analysis (b) of a AuAg bimetallic NP prepared by rapid injection of $NaBH_4$ at $R_{PVP}=100$, $R_{NaBH4}=10$, and 0.44 mM.

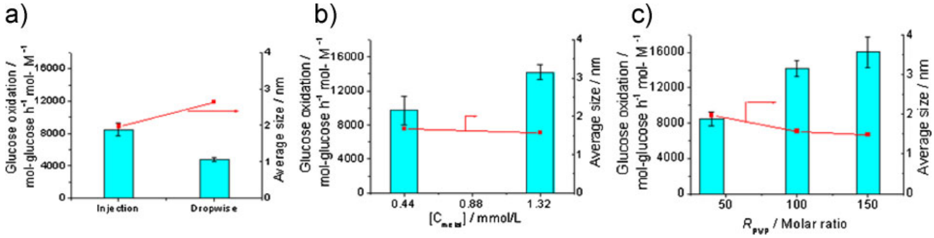


Figure 10.
Effect of the addition method of $NaBH_4$ (a), the concentration of metal salts in water (b), and the PVP ratio, i.e., R_{PVP} (c) on the catalytic activities (sticks) and average particle sizes (squares) of the AuPt (Au/Ag = 8/2) bimetallic NPs.

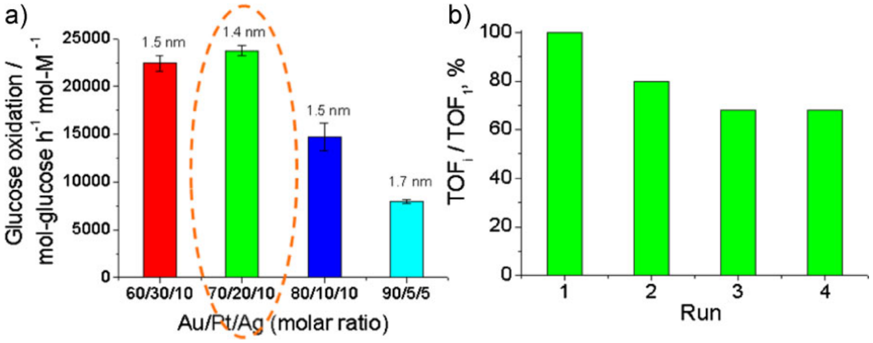


Figure 11.
The catalytic activities of AuPtAg trimetallic NPs at various molar ratios of the three elements (a) and those of AuPtAg (Au/Pt/Ag = 70/20/10) for the repeated runs (b).

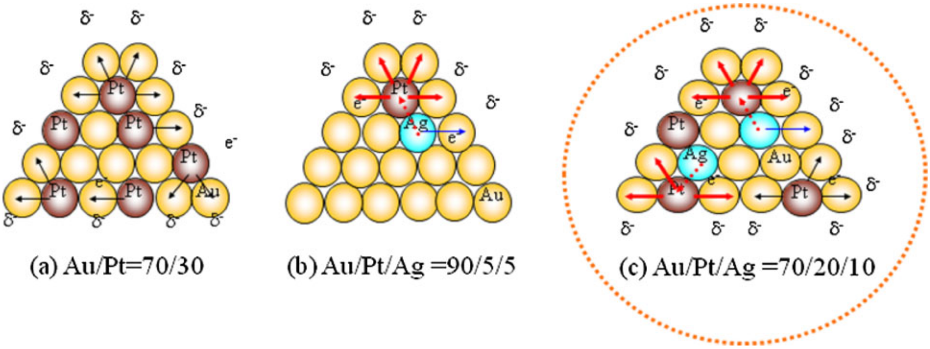


Figure 12.
Schematic illustration of electron charge transfer of (a) AuPt (Au/Pt = 70/30) bimetallic NPs, and AuPtAg trimetallic NPs at the molar ratio of (b) Au/Pt/Ag = 90/5/5 and (b) Au/Pt/Ag = 70/20/10.

catalytic activity of Au. In this particular case, the precise core/shell structure is not necessary, but even the random alloy structure could be effective for the electron charge transfer. In other words, the simplest preparation method, i.e., the rapid injection of $NaBH_4$ into the mixtures of the metal salts is useful for the preparation of the catalytically active colloidal dispersion of the Au-containing metal NPs.

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