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Reprint of "Synergetic combination of an enzyme and gold catalysts for glucose oxidation in neutral aqueous solution"☆

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ABSTRACT

Glucose oxidation by enzyme takes place in neutral aqueous solution at room temperature, producing gluconic acid in equilibrium with gluconate, while gold catalysts exhibit much higher catalytic activity but in alkali solution to produce sodium gluconate. The combination of glucose oxidase with selected gold catalysts such as Au/ZrO_2 and Au/NanoDiamond led to improved catalytic performance in neutral solution at room temperature. Gold nanoparticles supported on ZrO_2 decomposed hydrogen peroxide (H_2O_2) formed by the oxidation of glucose and depressed the damage of glucose oxidase by H_2O_2. In addition, Au/ZrO_2 utilized H_2O_2 produced by the enzyme to oxidize glucose to gluconic acid. In contrast, gold nanoparticles supported on NanoDiamond were active only for the decomposition of H_2O_2, while the presence of NanoDiamond itself could encourage glucose oxidase for the selective oxidation.

1. Introduction

Catalytic transformation of biomass derived natural resources to valuable compounds is becoming of immense importance for the sustainable development of chemical industry [1]. Ethanol (C2 compound) is produced from cones, sugar canes, and cellulose in an amount of 81.40 million tons a year in 2011 in the world [2] and occupies the majority of its commercial production. Glycerol (C3 compound) which is by-produced in the production of biodiesel oil is produced in an amount of 0.75 million tons/year [3]. Glucose (C6 compound) is also an important chemical resource which is produced from starch in an amount of 20 million tons/year. In the transformation of these biomass derived resources to valuable compounds, chemical processes have a lot of advantages, for example, higher purity and shorter reaction time, over the biological ones using microorganisms [1].

Gold nanoparticles (hereafter denoted as NPs) supported on base metal oxides, carbon, and polymers exhibit unique and useful catalytic performance leading to green sustainable chemistry [4–6]. For biomass derived resources, supported gold catalysts show interesting catalytic performance. Ethanol can be selectively transformed into acetic acid in aqueous solution on $Au/MgAl_2O_4$ catalyst [7] and into acetaldehyde by the gas phase oxidation on Au/La_2O_3 and Au/MoO_3 catalysts with molecular oxygen [8,9]. The hydrogenolysis of glycerol on Au/Al_2O_3 at 423 K selectively produces 1,2-propane diol [10]. The aerobic oxidation of glucose in strong aqueous alkali solution can produce sodium gluconate with extremely high rate of reaction on Au/ZrO_2. Turnover frequency per surface exposed gold atoms (TOF) reached 45 s^{-1} [11].

Glucose oxidation can also be performed using a biocatalyst, namely glucose oxidase (GOx), which gives low initial rate (1.7×10^{-6} mol L^{-1} s^{-1}) but a high TOF of 145 s^{-1}. Glucose oxidase can work in neutral solution at room temperature and can produce gluconic acid [12]. Gluconic acid is used as a complexing agent in industrial cleaning of metal surfaces and as a food additive. Since gluconic acid is a mild acid, it is in equilibrium with alkali gluconate under reaction conditions. The amount of strong acid required to obtain gluconic acid can be minimized if the reaction proceeds in neutral or acidic solution. In contrast, supported gold catalysts give much higher initial rate (1.4×10^{-4} mol L^{-1} s^{-1}) but in alkali solution at higher temperature [11,13–15].

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Our attempt is to combine glucose oxidase as a biological catalytic system with supported gold NPs as an artificial catalytic system to seek for synergetic improvement in catalytic performance. Vennestrøm et al. have recently reported the combination of glucose oxidase with titanium silicalite-1 to utilize the by-product of one reaction (H_2O_2) for the second one (epoxidation of allyl alcohol) [16]. Our idea, which can be expressed by "a hybrid of an enzyme catalyst with artificial catalysts for the same reaction", has come out from the instructive and inspiring review article presented by Professor Bernard Delmon [17]. He has proposed a bridged system between man-made functional solids and enzyme. We hope that this paper could present a preliminary example of his concept.

2. Experimental

2.1. Materials

The majority of metal oxide supports used were commercially available metal oxide powders: Al_2O_3 (Sumitomo Chemical, AKP-GO15, 148 $m^2\,g^{-1}$), SiO_2 (Fuji Silysia Chemical, CARiACT Q-10, 300 $m^2\,g^{-1}$), TiO_2 (Nippon Aerosil, P-25, 50 $m^2\,g^{-1}$), ZnO (Hakusui Tech, ZINCOX SUPER F-2, 14 $m^2\,g^{-1}$), ZrO_2 (Dai-ichi Kigenso Kagaku Kogyo, RC-100, 80–120 $m^2\,g^{-1}$), SnO_2 (Sigma–Aldrich, nanopowder, <100 nm), and CeO_2 (Dai-ichi Kigenso Kagaku Kogyo, 166 $m^2\,g^{-1}$). Two types of carbon supports were used, namely, NanoDiamond (ND) (NanoCarbon Research Institute, NanoAmando, 4–5 nm) and KetjenBlack (KB) (Lion, CARBON ECP, 780 $m^2\,g^{-1}$). Reagent grades, NH_4VO_3, $MnCl_2{\cdot}4H_2O$, $KMnO_4$, $Fe(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, Na_2CO_3, NaOH, glucose were used as received. As gold precursors, dimethyl Au^{III} acetylacetonate ($Me_2Au(acac)$) was purchased from Tri Chemical Laboratories Inc. Glucose oxidase (from *Aspergillus niger*, 240,000 units g^{-1}) was purchased from Wako Pure Chemical Industries.

2.2. Preparation of metal oxide supports

V_2O_5 was prepared by calcination of NH_4VO_3 in air at 300 °C for 4 h. For the preparation of MnO_2, an aqueous solution (30 mL) of $MnCl_2{\cdot}4H_2O$ (50 mmol) was added slowly to an aqueous solution (100 mL) of $KMnO_4$ (37 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. The precipitate was repeatedly washed with distilled water until the pH reached a steady value of around 4. The precipitate was collected by filtration, dried at 120 °C overnight, and then calcined in air at 300 °C for 4 h.

Fe_2O_3, Co_3O_4, NiO, CuO and La_2O_3 were prepared by the neutralization method. An aqueous solution of metal nitrate (0.1 M L^{-1}) was rapidly added into an aqueous solution of Na_2CO_3 (1.2 equiv., 0.1 M L^{-1}) at 70 °C. After stirring for 1 h, the suspension was centrifuged and the precipitate was repeatedly washed with distilled water until the pH reached a steady value of around 6. The precipitate was filtrated, dried at 120 °C overnight, and then calcined in air at 300 °C for 4 h.

2.3. Deposition of gold NPs on carbons and metal oxides

All gold catalysts were prepared by the solid grinding (SG) method [18]. Briefly, dimethyl gold acetylacetonate, $Me_2Au(acac)$, (8.3 mg) and support (1.0 g) were ground in an agate mortar for 20 min. The mixture was calcined in air at 300 °C for 4 h or reduced in 20 vol% H_2/N_2 stream at 120 °C for 2 h. The gold loading was 0.5 wt%.

2.4. Characterization

Transmission electron microscope (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) observations were carried out by using a JEOL JEM-3200FS operating at 300 kV. At least 140 particles of gold were observed to estimate the mean diameters and the standard deviation.

Table 1
Aerobic oxidation of glucose catalyzed by GOx combined with supported gold NPs.[a]

Entry	Catalyst		Initial rate ($mol_{glucose}\,L^{-1}\,s^{-1}$)[b]	Conv. after 1 h (%)[c]
1	GOx	Au/ZrO_2	$(7.4 \pm 1.4) \times 10^{-5}$	98 ± 2
2	GOx	Au/NanoDiamond	$(5.6 \pm 1.6) \times 10^{-5}$	98 ± 2
3	GOx	Au/La_2O_3	5.2×10^{-5}	98
4	GOx	Au/Al_2O_3	$(5.4 \pm 1.6) \times 10^{-5}$	96 ± 2
5	GOx	Au/CeO_2	6.2×10^{-5}	95
6	GOx	Au/SnO_2	6.8×10^{-5}	94
7	GOx	Pt/ZrO_2	$(4.9 \pm 0.5) \times 10^{-5}$	93 ± 5
8	GOx	Au/MnO_2	6.5×10^{-5}	91
9	GOx	Au/Co_3O_4	5.8×10^{-5}	91
10	GOx	–	$(4.8 \pm 1.5) \times 10^{-5}$	90 ± 3
11	GOx	Au/Fe_2O_3	4.2×10^{-5}	88
12	GOx	Au/SiO_2	$(4.5 \pm 0.5) \times 10^{-5}$	87 ± 2
13	GOx	Au/TiO_2	5.8×10^{-5}	86
14	GOx	Au/ZnO	4.5×10^{-5}	84
15	GOx	Au/V_2O_5	2.9×10^{-5}	83
16	GOx	Au/NiO	4.5×10^{-5}	73
17	GOx	Au/CuO	3.9×10^{-5}	42
18	GOx	Au/KetjenBlack	2.5×10^{-5}	76
19	GOx	NanoDiamond	4.2×10^{-5}	93
20	GOx	ZrO_2	3.6×10^{-5}	79
21	GOx	Al_2O_3	3.6×10^{-5}	85
22	GOx	KetjenBlack	2.3×10^{-5}	62
23	–	Au/ZrO_2	6.5×10^{-6}	4
24	–	Au/Al_2O_3	9.7×10^{-6}	3

[a] Reaction conditions: 2 wt% aqueous glucose solution (31 mL), GOx (0.13 g L^{-1}), 0.5 wt% Au loading catalyst (8.0 mg), glucose/Au = 15,000 (mol/mol), O_2 (60 mL min^{-1}), 30 °C, pH 7.
[b] Calculated from a straight line fitted to the conversion–time curve.
[c] The pH of the solution was kept at 7 by the titration with 1 M NaOH aqueous solution. Conversion after 1 h was calculated by the amount of NaOH added.

2.5. Catalytic tests

Glucose oxidation was carried out by using 2 wt% glucose aqueous solution (31 mL), 0.13 g L^{-1} of GOx and 8.0 mg of inorganic catalyst by bubbling O_2 (60 mL min^{-1}) at atmospheric pressure. The aqueous dispersion was stirred at 30 °C under controlled pH of 7 (±0.5) by titrating with 1 M L^{-1} NaOH aqueous solution. The conversion of glucose was calculated from the total amount of NaOH added. The reaction mixture was filtrated to remove the catalyst and the filtrate was evaporated. The residue was analyzed by ^1H NMR (JEOL 300 MHz, D_2O) to compare with authentic sample of sodium gluconate.

3. Results and discussion

3.1. Combination effect of enzyme and gold catalysts on glucose oxidation

Table 1 shows the catalytic activity of glucose oxidase combined with gold NPs supported on a variety of metal oxides and on carbons. The initial rate, which was calculated from the slope of the straight part of conversion vs reaction time, shows the initial catalytic activity, whereas the conversion of glucose after 1 h reaction reflects the stability property of the catalytic systems. In

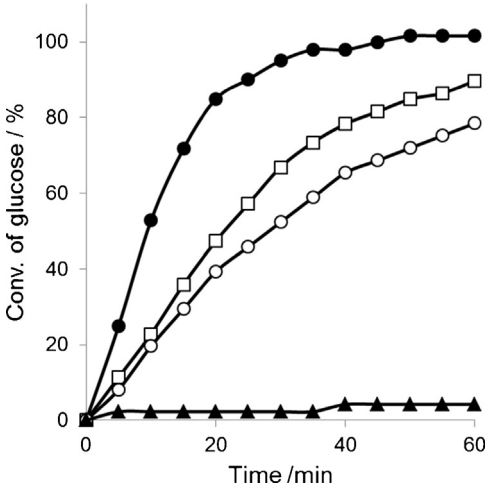

Fig. 2. Conversion–time curves for glucose oxidation in neutral aqueous solution at 30 °C with GOx and Au/ZrO_2. Reaction conditions: 2 wt% aqueous glucose solution (31 mL), GOx (0.13 g L^{-1}), 0.5 wt% Au loading catalyst (8.0 mg), glucose/Au = 15,000 (mol/mol), O_2 (60 mL min^{-1}), 30 °C, pH 7. The pH of the solution was kept at 7 by the titration with 1 M NaOH aqueous solution. Conversion was calculated by the amount of NaOH added. (●) GOx + Au/ZrO_2; (□) GOx; (○) GOx + ZrO_2; (▲) Au/ZrO_2.

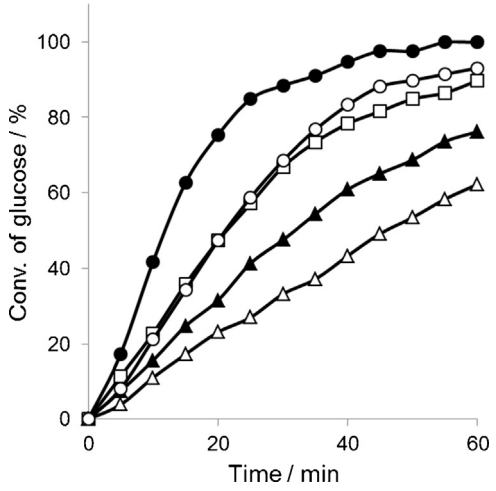

Fig. 1. Conversion–time curves for glucose oxidation in neutral aqueous solution at 30 °C with GOx and Au/carbon supports. Reaction conditions: 2 wt% aqueous glucose solution (31 mL), GOx (0.13 g L^{-1}), 0.5 wt% Au loading catalyst (8.0 mg), glucose/Au = 15,000 (mol/mol), O_2 (60 mL min^{-1}), 30 °C, pH 7. The pH of the solution was kept at 7 by the titration with 1 M NaOH aqueous solution. Conversion was calculated by the amount of NaOH added. (●) GOx + Au/ND; (○) GOx + ND; (□) GOx; (▲) GOx + Au/KB; (△) GOx + KB.

Table 2
The decomposition of H_2O_2 by gold and platinum catalysts.[a]

Entry	Catalyst	Rate of O_2 generation (mL min^{-1})[b]
1	Au/ZrO_2	0.13
2	Pt/ZrO_2	0.12
3	Au/Al_2O_3	0.10
4	Au/NanoDiamond	0.10
5	Au/KetjenBlack	0.09
6	ZrO_2	0.09
7	Al_2O_3	0.07
8	NanoDiamond	0.08
9	KetjenBlack	0.08
10	blank	0.04

[a] Reaction conditions: 0.3 wt% H_2O_2 aqueous solution (10 mL), catalyst (2.7 mg), 30 °C, pH 7.
[b] Measured by soap-film flow meter.

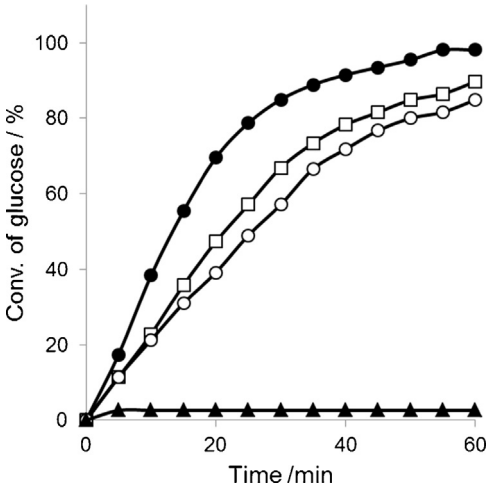

Fig. 3. Conversion–time curves for glucose oxidation in neutral aqueous solution at 30 °C with GOx and Au/Al_2O_3. Reaction conditions: 2 wt% aqueous glucose solution (31 mL), GOx (0.13 g L^{-1}), 0.5 wt% Au loading catalyst (8.0 mg), glucose/Au = 15,000 (mol/mol), O_2 (60 mL min^{-1}), 30 °C, pH 7. The pH of the solution was kept at 7 by the titration with 1 M NaOH aqueous solution. Conversion was calculated by the amount of NaOH added. (●) GOx + Au/Al_2O_3; (□) GOx; (○) GOx + Al_2O_3; (▲) Au/Al_2O_3.

Table 3
The effect of H_2O_2 on aerobic glucose oxidation by gold and platinum catalysts.[a]

Entry	Catalyst	Conv. after 1 h (%)[b]	
		O_2	$O_2 + H_2O_2$
1	Au/ZrO_2	4	12
2	Au/Al_2O_3	3	5
3	Pt/ZrO_2	0	0
4	Au/NanoDiamond	0	0
5	Au/KetjenBlack	0	4
6[c]	GOx	86	67

[a] Reaction conditions: 2 wt% aqueous glucose solution (31 mL), 0.5 wt% Au loading catalyst (8.0 mg), glucose/Au = 15,000 (mol/mol), O_2 (60 mL min^{-1}) or O_2 (60 mL min^{-1}) and 0.3 wt% H_2O_2 aqueous solution, 30 °C, pH 7.
[b] The pH of the solution was kept at 7 by the titration with 1 M NaOH aqueous solution. Conversion after 1 h was calculated by the amount of NaOH added.
[c] GOx (0.13 g L^{-1}).

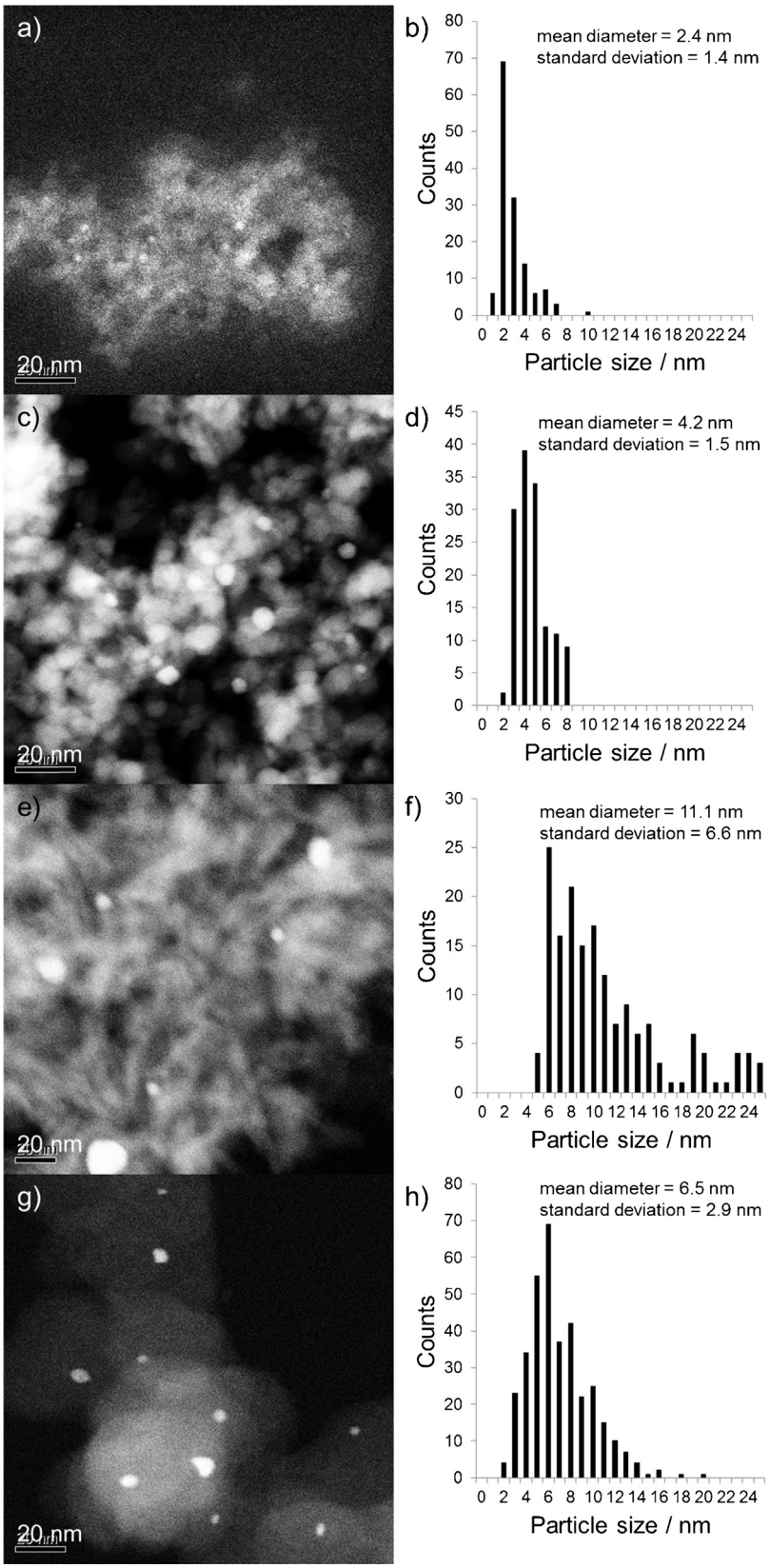

Fig. 4. HAADF-STEM images of (a) Au/ND, (c) Au/ZrO_2, (e) Au/Al_2O_3, (g) Au/KB, and distribution of the diameter of gold NPs in (b) Au/ND, (d) Au/ZrO_2, (f) Au/Al_2O_3, and (h) Au/KB.

the case of several representative gold catalysts, they were prepared by 2–5 times by the same method under the same conditions and were subjected to glucose oxidation (entries 1, 2, 4, 7, 10 and 12).

Supported gold NPs catalysts can be classified into two groups. The first one showed increases in both initial rate of reaction and conversion of glucose after 1 h reaction by the combination with glucose oxidase. They are, in the order of decreasing catalytic

activity, Au/ZrO_2, Au/ND, Au/La_2O_3, Au/Al_2O_3, Au/CeO_2, Au/SnO_2, Au/MnO_2, and Au/Co_3O_4 (entries 1–9). The second one showed decreases in both initial rate of reaction and conversion after 1 h and is composed of Au/Fe_2O_3, Au/SiO_2, Au/TiO_2, Au/ZnO, Au/V_2O_5, Au/NiO, Au/CuO, and Au/KB (entries 11–18). There seems to be no clear correlations between the kind of metal oxide supports and the enhancing effect on the catalytic activity for glucose oxidation. It is likely that synergy between supported gold catalysts and glucose oxidase may depend on the biological compatibility rather than on physicochemical properties of the support materials.

It is interesting to note that two carbon materials show opposite effect on the catalytic activity. Gold NPs deposited on KetjenBlack having mesopores reduced the initial oxidation rate with glucose oxidase by half, while gold NPs on NanoDiamond which were non-porous enhanced the initial rate by 17%. Among supports alone without gold deposition, ND, ZrO_2, Al_2O_3, and KB, only NanoDiamond presented higher conversion of glucose after 1 h reaction (entries 19–22).

Fig. 1 shows that glucose oxidase alone could not attain 100% conversion because of the deactivation by H_2O_2 formed during reaction. The combination with KB without gold deposition yielded lower conversions than with Au/KB, suggesting that gold NPs could facilitate the decomposition of H_2O_2. In fact, Table 2 shows that deposition of gold NPs or Pt NPs on ZrO_2, Al_2O_3, ND, and KB increased the rate of H_2O_2 decomposition (entries 1–9). In contrast, the combination with ND without gold deposition yielded a little higher conversion than glucose oxidase alone. Because H_2O_2 decomposition on ND was moderately fast similar to KB, it can be assumed that the co-presence of ND enhances gluconic acid production by glucose oxidase. Deposition of gold NPs on ND enabled glucose oxidase to transform glucose with 100% conversion. This is probably because Au/ND decomposes H_2O_2 more rapidly and avoids deactivation of glucose oxidase.

Figs. 2 and 3 show that Au/ZrO_2 and Au/Al_2O_3 which exhibited the highest catalytic activity for the aerobic oxidation of glucose in strong alkali solution were not active at all under neutral conditions (Table 1, entries 23 and 24). However, the combination with glucose oxidase appreciably increased the catalytic activity both in terms of initial rate and conversion attained after 1 h reaction though the combination of their supports alone with glucose oxidase showed negative effect.

3.2. Characterization of the catalysts

Although gold NPs could not be observed by a high-resolution TEM, the diameters of primary particles of ND could be estimated to be 5–10 nm for Au/ND. Fig. 4a shows a HAADF-STEM image as well as a distribution of the diameter of gold NPs in Au/ND. By this technique even tiny gold NPs could be observed because the contrast was intensified by the second power of the atomic weight of the element, namely, $[197(Au)/12(C)]^2 = (16.4)^2$. Obviously, gold NPs were highly and almost homogeneously dispersed. The mean diameter and standard deviation of gold NPs were calculated to be 2.4 nm ± 1.4 nm from about 30 images taken by a HAADF-STEM (Fig. 4b).

The diameters of primary particles of ZrO_2 were estimated to be 5–10 nm by HR-TEM. A HAADF-STEM image for Au/ZrO_2 which exhibited the most efficient combination effect is shown in Fig. 4c. The mean diameter of gold NPs on ZrO_2 was calculated to be 4.2 nm ± 1.5 nm (Fig. 4d). In the case of Pt/ZrO_2, platinum NPs could not be observed even by a HAADF-STEM. It is probable that platinum NPs were too small and below 2 nm in diameter. The Au/Al_2O_3 catalyst was composed of a mixture of 20–50 nm particles and needles of Al_2O_3. Gold NPs could be found but they were dispersed with a small population density (Fig. 4e). The gold particles are 11.1 nm ± 6.6 nm in diameter (Fig. 4f). This feature is different from that of a typical active gold catalyst. Accordingly, there is a large room to improve the catalytic activity of Au/Al_2O_3. In Au/KB, the diameters of primary particles of KB are 20–50 nm. The mean diameter of gold NPs on KB was 6.5 nm ± 2.9 nm (Fig. 4h).

3.3. Decomposition of H_2O_2 by gold catalysts

Table 2 shows the decomposition of H_2O_2 on supported gold catalysts and on support materials without gold deposition. All materials show a certain degree of catalytic activity for H_2O_2 decomposition which avoids the deactivation of enzyme catalysts. In the cases of Au/ZrO_2, Au/ND, Au/Al_2O_3, Pt/ZrO_2 and ND, the combination with glucose oxidase showed positive effect as expected. In contrast, in the cases of Au/KB, ZrO_2, Al_2O_3 and KB, they showed negative effect. In particular, Au/KB highly depressed glucose oxidation by glucose oxidase even though the deposition of noble metals increased the rate of H_2O_2 decomposition. The fact means that the co-presence of KB itself caused the depression of the enzyme activity (Fig. 1). Therefore the compatibility of support materials with glucose oxidase is one of the key factors for synergy effect as well as the ability for H_2O_2 decomposition.

3.4. Effect of H_2O_2 on glucose oxidation with O_2

Table 3 lists glucose conversion with O_2 alone and with O_2 and H_2O_2. On glucose oxidase, the conversion with O_2 alone was higher than with O_2 and H_2O_2, indicating that the co-presence of H_2O_2 depressed the oxidation reaction. On Au/ZrO_2, the conversion was appreciably increased from 4 to 12%. This may partly explain why the combination of enzyme with Au/ZrO_2 catalyst exhibits enhanced catalytic activity. The gold catalyst utilizes H_2O_2 produced by glucose oxidation with the enzyme to gluconic acid and at the same time it decomposes H_2O_2 to avoid the deactivation of enzyme by H_2O_2.

4. Conclusions

Aerobic oxidation of glucose has been conducted in neutral aqueous solution at room temperature to produce acid-rich gluconate by using a hybrid system of a biological catalyst like an enzyme and artificial catalysts like supported gold catalysts. Gold catalysts were chosen because they exhibit higher catalytic activity at around room temperature than other metal catalysts.

1) Gold NPs supported on a variety of base metal oxides and carbons showed positive synergy by the combination with glucose oxidase, in particular, Au/ZrO_2, Au/Al_2O_3, and Au/NanoDiamond.
2) In the case of Au/ZrO_2 and Au/Al_2O_3, the combination with their supports alone showed negative effect whereas the gold catalysts showed positive synergy caused by the following: they decompose H_2O_2 produced by glucose oxidase and protect the enzyme from oxidative damages by H_2O_2 and furthermore utilize H_2O_2 for glucose oxidation to gluconic acid.
3) In the case of Au/ND which is active for H_2O_2 decomposition but not active for the glucose oxidation with O_2 and with O_2 and H_2O_2, it can only prevent glucose oxidase from the oxidative deactivation by H_2O_2. However, the presence of ND does not cause the negative effect to glucose oxidase, in other words, glucose oxidase is compatible with ND.

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