Aerobic Oxidation Catalyzed by Gold Nanoclusters as *quasi*-Homogeneous Catalysts: Generation of Hydrogen Peroxide using Ammonium Formate

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Gold(0) nanocluster with d_{av} = 1.3 ± 0.3 nm stabilized by poly(N-vinyl-2-pyrrolidone) (**Au:PVP-1**) showed high catalytic activity toward the generation of hydrogen peroxide in water under ambient conditions using ammonium formate as a reductant. Generation of hydrogen peroxide was monitored by tracking the conversion of o-tolylboronic acid to o-cresol. In the presence of excess ammonium formate, o-cresol was obtained from o-tolylboronic acid with ~60% yield within 24 hours at 300 K. In order to investigate the dependence of the reactivity on cluster size, monodispersed gold nanoclusters (**Au:PVP-n**; n=2-4) with average diameters up to ~5 nm were prepared by the seed-mediated growth method using Na_2SO_3 as a reductant. Smaller cluster showed superior catalytic activity compared to larger clusters, suggesting that molecular oxygen species preferentially adsorbed on small Au clusters played an essential role in the formation of hydrogen peroxide.

Key words: Gold Nanocluster, Aerobic Oxidation, Hydrogen Peroxide Generation

1. INTRODUCTION

The use of hydrogen peroxide, H_2O_2, in oxidation processes has generated great interest because of increasing environmental concerns: the co-product of such reactions is water, which is environmentally benign. However, the conventional method of H_2O_2 preparation involves autoxidation of hydroanthraquinone in complex organic solvents [1]. In addition, the transport, storage, and handling of explosive H_2O_2 are quite hazardous. Thus, it is of scientific and practical importance to develop methods for in-situ liquid-phase generation of H_2O_2 [2,3] by use of inexhaustible molecular oxygen.

The discovery of gold-catalyzed CO oxidation by Haruta and coworkers [4] has opened up a new application of gold nanoclusters, namely as oxidation catalysts using O_2 [5-15]. For example, the generation of H_2O_2 from O_2 and gaseous H_2 has been reported for many heterogeneous Au cluster catalysts [5-8]. Thus, one can anticipate that H_2O_2 can be generated in aqueous media by utilizing Au nanoclusters in a *quasi*-homogeneous state. Previously, we have reported that small gold(0) nanoclusters (d_{av} = 1.3 ± 0.3 nm) stabilized by a water-soluble polymer, poly(N-vinyl-2-pyrrolidone) (**Au:PVP-1**) showed excellent catalytic activity in water under ambient conditions toward the following aerobic oxidations: oxidative homo-coupling reaction of arylboronic acids (eq. 1) [16] and oxidation of benzylic alcohols (eq. 2) [17]. In the former reaction, phenol derivatives were also obtained as by-products. Phenols may not have been produced by direct Au-catalyzed processes but by the oxidation of arylboronic acids with H_2O_2 generated in the coupling reactions. Indeed, the generation of H_2O_2
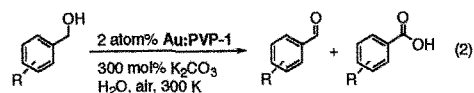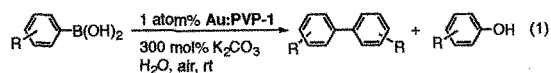
was confirmed by the iodo-starch reaction in the latter process (eq. 2). In other words, the Au:PVP clusters acted as *quasi*-homogeneous catalysts for H_2O_2 generation using an arylboronic acid or benzylic alcohol as a reductant. These results have prompted us to develop more efficient processes of H_2O_2 generation by the Au:PVP clusters through an appropriate choice of reductant.

In order to achieve this objective under aerobic conditions in water, ammonium formate (HCO_2NH_4) was used as a reductant in place of H_2 in the present study. Ammonium formate is readily soluble in water, easy to handle, and has often been utilized for the transition-metal-catalyzed hydrogenations [18]. We show below that HCO_2NH_4 works as a good reductant for the Au-nanocluster-catalyzed generation of H_2O_2. The mechanism of H_2O_2 formation is discussed on the basis of cluster-size dependent catalytic activity.

2. EXPERIMENTAL

2.1 Preparation and characterization of Au:PVP clusters

All chemicals were commercially available and used without further purification. The water used in the preparation was of Milli–Q grade with specific resistance above 18 MΩ·cm.

Details of the preparation procedure of **Au:PVP-1**

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have been described elsewhere [16]. Briefly, $AuCl_4^-$ (1 mM, 50 mL) was reduced by $NaBH_4$ (0.1 M, 5 mL) at 273 K in the presence of PVP (K-30, 555.5 mg). The resulting hydrosol was further dialyzed overnight to remove inorganic impurities. The **Au:PVP-1** clusters were characterized by transmission electron microscopy (TEM); UV-vis absorption spectroscopy; X-ray diffraction (XRD); X-ray absorption near-edge structure (XANES); and extended X-ray absorption fine structures (EXAFS); and X-ray photoelectron spectroscopy (XPS).

The larger Au:PVP clusters were prepared by the seed-mediated growth method [17]. Typically, a mixture (2 mL) of $AuCl_4^-$ and Na_2SO_3 was quickly added to the **Au:PVP-1** hydrosol (0.5 mM, 20 mL) deaerated by freeze-pump-thaw cycles. The concentrations of $AuCl_4^-$ were 15, 45, and 90 mM for **Au:PVP-n** (n = 2–4), respectively. The mixture was stirred for an additional 3 hours under N_2. The hydrosol was further dialyzed by centrifugal ultrafiltration (MWCO=10 kDa). The **Au:PVP-n** (n = 2–4) clusters thus formed were characterized by TEM and UV-vis spectroscopy.

All of the Au:PVP samples were stored as solutions below 2 °C. They were used within a week although we did not observe any sign of degradation of the clusters thus stored for longer periods.

2.2 General procedure for the generation of hydrogen peroxide

The reaction was carried out using an organic synthesizer (EYELA, PPS-2510). An aqueous solution of Au:PVP (0.5 mM, 4 mL, 1 atom%) was added to a test tube containing o-tolylboronic acid (27.2 mg, 0.2 mmol), ammonium formate (37.8 mg, 0.6 mmol), and H_2O (2 mL), and the mixture was stirred vigorously (1,300 rpm) at 300 K. After stirring for 24 h at 300 K, the reaction was extracted with ethyl acetate. The formation of hydrogen peroxide was monitored by tracking the conversion of o-tolylboronic acid to o-cresol (eq. 3). The organic phase extracted was separated, dried over Na_2SO_4, and then diluted to 100 mL. The yield of o-cresol was determined by gas chromatography (Shimadzu, GC-2014).

(3)
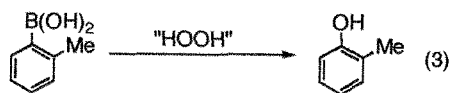
3. RESULTS AND DISCUSSION

3.1 Size distributions of Au:PVP-n (n = 1–4)

Figures 1 and 2 show the UV-vis spectra and typical TEM images with cluster size distributions of **Au:PVP-n** (n = 1-4), respectively. As described in our previous paper [16], the rigorous characterization of **Au:PVP-1** by various analyses has revealed that fcc Au(0) nanocrystals

with a diameter of 1.3 ± 0.3 nm were formed in the PVP matrix. The surface-plasmon bands well known for large Au particles (>2 nm) were clearly visible at ~520 nm in the optical spectra of **Au:PVP-n** (n = 2–4), whereas a small shoulder was barely discernible for **Au:PVP-1** (Figure 1). The intensity of the plasmon band increased with n, suggesting the formation of larger gold clusters. Indeed, the average core sizes of **Au:PVP-n** (n = 2-4) were determined to be 2.3 ± 0.4, 3.3 ± 0.5, 4.3 ± 0.6 nm for n = 2, 3, and 4, respectively (Figure 2). These results demonstrated that the seed-mediated growth approach provided a powerful method for the size-selective preparation of polymer-stabilized gold clusters. In this method, Na_2SO_3 could reduce the $Au(III)Cl_4^-$ ions to Au(0) only in the presence of **Au:PVP-1**. This observation suggested that the Au(0) atoms were formed near the cluster surface and that these Au atoms tended to be deposited on the cluster. Under such conditions, all the Au:PVP clusters grew in size synchronously so that the resulting clusters were monodispersed.
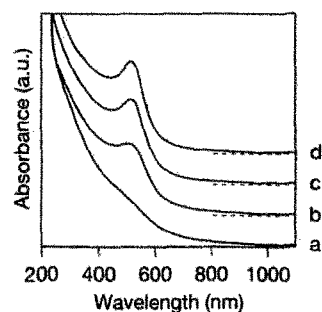
Fig. 1: UV-vis spectra of **Au:PVP-n**; (a) n = 1, (b) n = 2, (c) n = 3, and (d) n = 4.
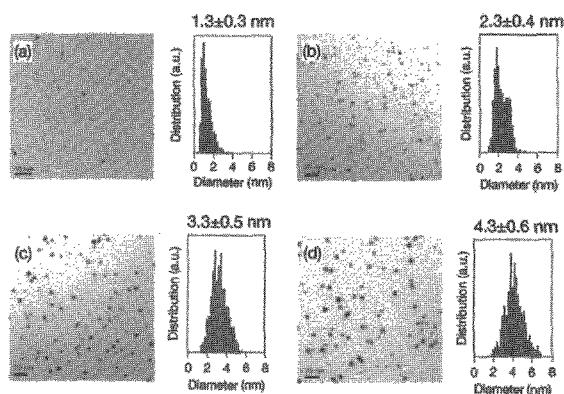
Fig. 2: TEM images and cluster size distributions of **Au:PVP-n**; (a) n = 1, (b) n = 2, (c) n = 3, and (d) n = 4.

3.2 Catalytic activities of Au:PVP-n for generation of hydrogen peroxide

In-situ formation of H_2O_2 was monitored via the oxidation of o-tolylboronic acid to o-cresol (eq. 3) because of the following reasons: (1) It is well known

that organoboron compounds are readily oxidized by H_2O_2 quantitatively to give the corresponding hydroxy compounds; and (2) The methyl group at the *ortho* position effectively suppresses the homocoupling reaction due to steric hindrance [16]. The yields of *o*-cresol for **Au:PVP-*n*** are listed in Table 1 together with the core sizes of the corresponding clusters. Entry (1) shows that the oxidation reaction (3) was catalyzed by **Au:PVP-1**. The oxidation by **Au:PVP-1** was suppressed under anaerobic conditions and gave a small amount of homocoupling product (~4% yield) in the absence of H_2O_2 [16]. These results clearly indicated that *the Au:PVP clusters catalyzed the formation of H_2O_2 from HCO_2NH_4 and O_2.*

The catalytic activity was higher for the smaller Au:PVP clusters as shown in Table 1. Similar size dependences have been observed in the homocoupling of arylboronic acids [16] and alcohol oxidation [17], and thus our results can also be ascribed to the well-known fact that molecular oxygen is adsorbed only on the smaller clusters [19]. It has been believed concerning supported gold catalysts that electron transfer from the substrate activates the cluster so that molecular oxygen is adsorbed. This explanation cannot be applied to our Au:PVP clusters because the PVP interacts only weakly with the gold clusters [20]. Recently, it has been theoretically predicted that water molecules attached to the surfaces of the gold clusters promote O_2 absorption through hydrogen bond interactions [21]. Although the mechanism for O_2 absorption is not clear at this moment, the superoxo-like species formed on the surfaces of the smaller clusters are intimately involved in the formation of H_2O_2. Unfortunately, our optical measurements (Figure 3) showed growth and/or aggregation of the clusters during the reaction. In particular, the most active **Au:PVP-1** clusters degraded to the greatest extent; the brownish color of the **Au:PVP-1** hydrosol became purple after the reaction, whereas the others appeared red throughout the reaction. Further efforts are necessary to develop more appropriate stabilizers for practical use.

Table 1. Yields of oxidation of *o*-tolylboronic acid to *o*-cresol

entry	catalyst	*d* (nm)	yield (mol%)
1	**Au:PVP-1**	1.3 ±0.3	57
2	**Au:PVP-2**	2.3±0.4	32
3	**Au:PVP-3**	3.3±0.5	34
4	**Au:PVP-4**	4.3±0.6	22

3.3 Competition between homocoupling and hydroxylation of phenylboronic acid

As reported previously, **Au:PVP-1** catalyzes the

Fig. 3: UV-vis spectra of **Au:PVP-*n*** before (full line) and after (dotted line) the reaction; (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, and (d) $n = 4$.

oxidative homocoupling reaction of arylboronic acid, yielding the corresponding biaryl derivatives [16]. In contrast, the homocoupling process is greatly suppressed in the presence of HCO_2NH_4. That is, $PhB(OH)_2$ is transformed to Ph-Ph and PhOH in 72 and 23% yield, respectively in the **Au:PVP-1** catalyzed reaction in K_2CO_3 solution (eq. 4), while PhOH is obtained in 92% yield in HCO_2NH_4 solution along with the Ph-Ph in 8% yield (eq. 5). In eq. 4, PhOH is likely to be formed via oxidation of the C-B bond of $PhB(OH)_2$ by H_2O_2 arising from boron peroxide and water [16]. The high yield of PhOH in eq. 5 indicates that Au-cluster-catalyzed H_2O_2 formation in HCO_2NH_4 solution proceeds much faster than the transmetalation of $PhB(OH)_2$.

4. SUMMARY

The present study demonstrated the high potentiality of Au(0) nanoclusters as *quasi*-homogeneous catalysts for the generation of H_2O_2 under ambient conditions in aqueous HCO_2NH_4 solution. Smaller clusters showed superior catalytic activity to larger clusters, suggesting that the activation of molecular oxygen adsorbed on small Au clusters played an essential role in the formation of H_2O_2. Since aqueous H_2O_2 has been frequently used as a safe oxidant in both industrial and laboratory processes including practical organic syntheses such as alkene epoxidation, the present method is expected to help realize direct utilization of aerobic oxidation for various organic transformations via in-situ H_2O_2 generation.

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