Enhancement of the electrocatalytic activity of gold nanoparticles *via* $NaBH_4$ treatment†

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We report on the enhancement of the electrocatalytic activity of Au nanoparticles after $NaBH_4$ treatment and its application to H_2O_2 detection.

Electrocatalysis is one of the most important areas of electrochemistry, with many practical applications in devices such as sensors[1] and fuel cells.[2] Thus, much research has been devoted to improving the electrocatalytic activity of electrodes. These efforts have generally focused on electrode modification (especially with nanomaterials)[3] and/or electrode activation (by means of electrochemical,[4] thermal,[5] or chemical[6] treatments).

Electrochemical[4,7] and thermal treatments[5] of metal electrodes allow a high level of electrocatalytic activity. However, when an electrode is covered with a sensing layer, electrochemical treatment by applying a high potential or thermal treatment at high temperatures may damage that layer. This damage can be minimized if a mild chemical treatment is employed. Therefore, in some cases chemical electrode activation is preferred.

Au is an inert metal and exhibits relatively weak adsorption properties. In general, hydrogen is neither adsorbed on nor absorbed into Au when the metal comes in contact with hydrogen gas.[7a] The reason for this is that Au does not catalytically cleave the chemical bond of the hydrogen molecule.[8] However, a large amount of hydrogen is absorbed/adsorbed when the gas is evolved electrochemically.[9] This cathodic treatment permits the activation of Au electrodes,[7b,c] which is believed to be associated with adsorbed/absorbed hydrogen species[7d] or a metastable surface state.[10] Nevertheless, the exact mechanism remains unclear. Hydride transfer to the Au nanoparticles in an $NaBH_4$-containing solution has been commonly applied to achieve the catalytic reduction of organic molecules,[11] which suggests that the $NaBH_4$ treatment may have the same effect as the cathodic treatment.

Hydrogen peroxide (H_2O_2) detection is of great importance in oxidase-based biosensors and in monitoring oxidative stress, food, and environment.[12] Prussian Blue has been widely adopted as an electron mediator to achieve H_2O_2 reduction at potentials more positive than that of the O_2 reduction reaction.[12a] On the other hand, Pt electrodes have been used for the electrochemical oxidation of H_2O_2.[13] Generally, this oxidation process takes place less readily (and is less reproducible) on Au electrodes than on Pt ones.[13] Although Au nanomaterials have been employed for H_2O_2 detection, these have only been used for the electrochemical reduction of the peroxide, not for the oxidation process.[14]

Here, we report on the enhancement of the electrocatalytic activity of Au nanoparticles for the electrooxidation of H_2O_2, glucose and formic acid after $NaBH_4$ treatment. The mechanism of this enhancement was investigated in terms of the hydrogen species adsorbed/absorbed on the Au nanoparticles, and the kinetics of the processes of activation and deactivation of these nanoparticles were assessed. In addition, we applied the enhanced electrocatalytic activity of the obtained Au structures to the detection of H_2O_2.

Au nanoparticles were adsorbed onto an indium tin oxide (ITO) electrode modified with amine-terminated dendrimers[15] by simply dropping an Au-nanoparticle-containing solution onto the electrode (see Scheme S1 of ESI†). The ITO electrode provides low background currents because of its poor electrocatalytic activity[16] for the electrooxidation of H_2O_2. To evaluate the effect of the $NaBH_4$ treatment on the electrochemical process, we recorded cyclic voltammograms of the Au-nanoparticle- and dendrimer-modified ITO electrodes before and after $NaBH_4$ treatment (see Fig. 1(a)). The anodic current in the cyclic voltammogram obtained on the Au-nanoparticle-modified electrode before the $NaBH_4$ treatment [curve (ii) in Fig. 1(a)] is low and only somewhat higher than that measured on the dendrimer-modified ITO electrode [curve (i) in Fig. 1(a)]. Considering that the electrooxidation of H_2O_2 is very slow at ITO electrodes, the increased current must be related to Au nanoparticles adsorbed on the ITO electrode. However, the current enhancement is not significant, which indicates that the electrooxidation of H_2O_2 is slow on the untreated Au nanoparticles. A large anodic peak was observed at less than 0.3 V [see curve (iii) in Fig. 1(a)] after the $NaBH_4$ treatment. This peak

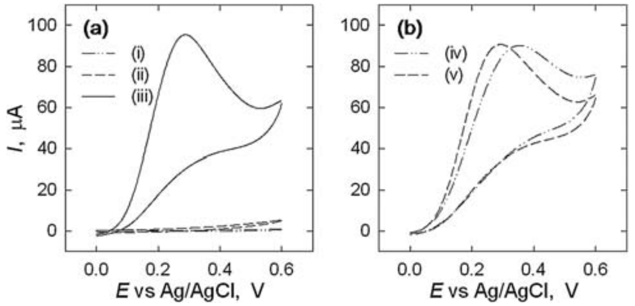

Fig. 1 Cyclic voltammograms obtained at (i) dendrimer-modified ITO electrodes and (ii–v) Au-nanoparticle- and dendrimer-modified ITO electrodes in a carbonate buffer solution containing 1 mM H_2O_2 (at a scan rate of 50 mV s^{-1}) (ii) before and after (iii) $NaBH_4$ treatment, (iv) cathodic treatment, or (v) $NaBH_4$ treatment followed by a *p*-benzoquinone treatment.

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† Electronic supplementary information (ESI) available: Experimental details, activation of Au electrodes, SEM images, cyclic voltammograms for glucose and formic acid, *etc.* See DOI: 10.1039/b806984k

current was very high and reproducible. Plain Au electrodes also show enhanced electrocatalytic activity for the electrooxidation of H_2O_2 after $NaBH_4$ treatment (see Fig. S1 of ESI†), although the enhancement is less significant and reproducible than that of the Au-nanoparticle-modified ITO electrodes. These results clearly show that the $NaBH_4$ treatment of Au-nanoparticle-modified ITO electrodes significantly enhances their electrocatalytic activity for the electrooxidation of H_2O_2. Interestingly, there was no significant difference between the SEM images of Au-nanoparticle-modified ITO electrodes that were obtained before $NaBH_4$ treatment, after $NaBH_4$ treatment, and after $NaBH_4$ treatment followed by the electrooxidation of H_2O_2 (see Fig. S2 of ESI†). This indicates that there is no significant change in the shape of Au nanoparticles during $NaBH_4$ treatment and the electrooxidation of H_2O_2.

An enhanced electrocatalytic activity has also been reported for cathodically treated Au electrodes.[7c] Thus, we also checked the electrocatalytic activity of our Au nanoparticles after a cathodic treatment, which was carried out by applying a potential of −0.6 V (for 10 min) in 0.1 M H_2SO_4. The cyclic voltammogram obtained after the cathodic treatment [curve (iv) in Fig. 1(b)] is similar to that recorded after the $NaBH_4$ treatment [curve (iii) in Fig. 1(a)], indicating that the enhanced electrocatalytic activity is almost the same in both cases. These results show that $NaBH_4$ treatment has the same effect as cathodic treatment.

The enhanced electrocatalytic activity of Au nanoparticles after $NaBH_4$ treatment is not only observed in case of the electrooxidation of H_2O_2, but also for glucose and formic acid (see Fig. S3 of ESI†). This observation is very interesting because the electrocatalytic oxidation of glucose is very important in terms of electrochemical glucose sensors[17] and the electrocatalytic oxidation of formic acid is crucial in its application to fuel cells.[18]

Cathodic treatment allows the adsorption/absorption of hydrogen on/into Au electrodes.[9] Likewise, $NaBH_4$ treatment could permit the adsorption/absorption of hydrogen on/into Au nanoparticles. An anodic peak is observed at about 0.25 V in the cyclic voltammogram obtained in a PBS solution after $NaBH_4$ treatment [curve (i) in Fig. 2(a)]. However, this peak is not observed during the second scan [curve (ii) in Fig. 2(a)]. Instead, the cyclic voltammogram obtained during this second scan [curve (ii) in Fig. 2(a)] coincides well with that recorded before the $NaBH_4$ treatment [curve (iii) in Fig. 2(a)]. A similar anodic peak is observed at around 0.2 V in the cyclic voltammogram obtained after cathodic treatment of the electrode [curve (v) in Fig. 2(b)]. The intensity of this peak, which can be attributed to the electrooxidation of adsorbed/absorbed hydrogen species,[4,7a] decreased during the second scan. These results indicate that hydrogen is adsorbed/absorbed on/into the Au nanoparticles during the $NaBH_4$ treatment.

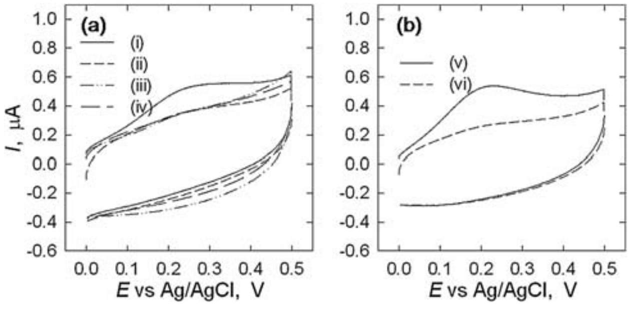
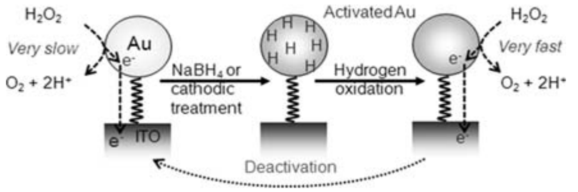


Fig. 2 Cyclic voltammograms obtained at Au-nanoparticle-modified ITO electrodes in (a) a PBS solution (at a scan rate of 10 mV s^{-1}) after (i, ii) and before (iii) $NaBH_4$ treatment, (v, vi) cathodic treatment, or (iv) $NaBH_4$ treatment followed by a *p*-benzoquinone treatment. The voltammograms represent either (i, iii, iv, v) the first scan or (ii, vi) the second one.

The adsorbed/absorbed hydrogen species may affect the electrocatalytic activity of the Au nanoparticles. To test this possibility, we compared the electrocatalytic activities of the treated electrodes toward the electrooxidation of H_2O_2 before and after removing the hydrogen species from the Au nanoparticles. The adsorbed/absorbed species was removed by dipping the $NaBH_4$-treated electrode for 20 min into a PBS solution containing *p*-benzoquinone. No anodic peaks were observed during the first scan in the cyclic voltammogram [see curve (iv) in Fig. 2(a)]. The reason for this is that *p*-benzoquinone oxidizes the adsorbed/absorbed hydrogen species. However, the enhanced electrocatalytic activity of the electrode remained unchanged, even after treatment with *p*-benzoquinone [see curve (v) in Fig. 1(b)]. The enhanced electrocatalytic activity was also maintained after the first anodic scan, while the adsorbed/absorbed hydrogen species were oxidized and removed. These results clearly show that the enhanced electrocatalytic activity is not directly related to the adsorbed/absorbed hydrogen species.

It is well known that hydrogen adsorption/absorption generates strain in the lattices of metals, especially Pd.[10a,19] Some studies suggest that this strain-induced structural change results in the activation of metal electrodes.[10] However, this hypothesis has not been clearly proved. In any case, it is evident that an activated state is formed after the adsorption/absorption of hydrogen. The hydrogen-loaded (and even hydrogen-depleted) Au nanoparticles show a highly enhanced electrocatalytic activity, with the activated state offering much faster electron-transfer kinetics at the Au nanoparticles. Pd nanoparticles have been reported to absorb more hydrogen than the bulk metal.[19a,20] Similarly, Au nanoparticles are expected to absorb more hydrogen species than bulk Au, which may result in much enhancement of the electrocatalytic activity for the electrooxidation of H_2O_2.

The electrocatalytic activity of the Au nanoparticles increased with increasing $NaBH_4$-treatment time, until a maximum value was reached (see Fig. S4a of ESI†). A 15-min $NaBH_4$ treatment was enough to obtain maximum electrocatalytic activity. The enhanced electrocatalytic activity decreased with increasing incubation time in air (see Fig. S4b of ESI†) and phosphate buffer solution (see Fig. S5 of ESI†). Importantly, the enhanced activity was recovered after retreatment with $NaBH_4$ [see curve (iv) in Fig. S4b of ESI†]. This result indicates that a cyclic conversion between the hydrogen-induced activated state and the hydrogen-free original state is possible. Interestingly, there was still some enhanced electrocatalytic activity in air after one month [see curve (iii) in Fig. S4b of ESI†], indicating that the activated state is retained for a long time. This deactivation behavior reveals that the activated state slowly returns to the original state after the adsorbed/absorbed hydrogen species have been removed. Oxidation current corresponding to the adsorbed/absorbed hydrogen species decreased significantly 12 h after the $NaBH_4$ treatment (see Fig. S6 of ESI†), whereas the Au nanoparticles



Scheme 1 Schematic representation of the cyclic conversion occurring during the activation and deactivation of Au nanoparticles.

still showed enhanced electrocatalytic activity, even one month after the treatment [see curve (iii) in Fig. S4b of ESI†].

Scheme 1 illustrates the mechanism of the cyclic conversion occurring during the activation and deactivation of Au nanoparticles. Both the $NaBH_4$ treatment and the cathodic treatment allow extensive adsorption/absorption of hydrogen species on/into the Au nanoparticles, thereby forming an activated state which remains even after the hydrogen species have been removed.

Fig. 3(a) and S7 of ESI† show the dependence of linear-sweep voltammograms on the concentration of H_2O_2. The voltammograms were obtained after $NaBH_4$ treatment of Au-nanoparticle-modified ITO electrodes. Fig. 3(b) and S8 of ESI† show the dependence of the anodic current at 0.25 V on the concentration of H_2O_2. At a concentration of 100 nM, the current is (1.84 ± 0.05) μA (mean ± standard deviation), which is clearly higher than that measured in the absence of H_2O_2, namely (1.47 ± 0.04) μA. Accordingly, the detection limit of the sensor is 100 nM, which is very low and comparable to that of a Prussian-Blue-based detection method.[21] H_2O_2 could be detected at concentrations ranging from 100 mM to 100 nM.

In conclusion, we have shown that high electrocatalytic activity for the electrooxidation of H_2O_2, glucose and formic acid can be achieved by means of the chemical treatment of Au nanoparticles with $NaBH_4$. This treatment allows the adsorption/absorption of large amounts of hydrogen species on/into the Au nanoparticles, thereby forming an activated state that remains even after the hydrogen species have been removed, and then returns slowly to the original state. A more detailed study is required to elucidate the exact mechanism of the enhanced electrocatalytic activity of the Au nanoparticles. We believe that the simple chemical treatment could be applied to the enhanced electrooxidation of various organic molecules.

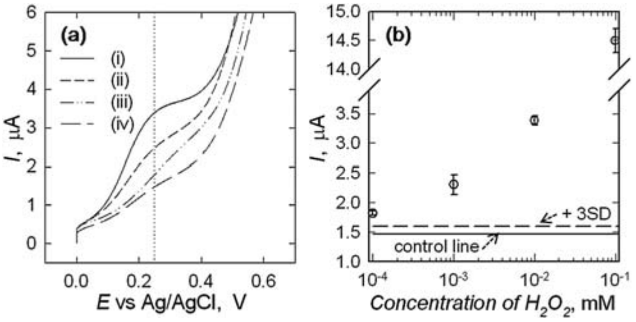


Fig. 3 (a) Concentration dependence of linear-sweep voltammograms in a carbonate buffer solution containing different concentrations of H_2O_2 ((i) 10 μM, (ii) 1 μM, (iii) 100 nM and (iv) 0 nM) at a scan rate of 50 mV s^{-1}. (b) Dependence of the anodic current at 0.25 V on the concentration of H_2O_2. The control line corresponds to the mean current in the absence of H_2O_2.

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