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Effective Electrocatalytic Oxidation of Glucose at Platinum Nanoparticle-based Carbon Electrodes

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The effective direct electrocatalytic oxidation of glucose in alkaline solution at electrochemically deposited Pt nanoparticle-modified glassy carbon electrode is reported, for the first time. Catalytic oxidation of glucose was observed and comparison to a previously reported system based on gold nanoparticles showed a significant positive catalytic effect of the prepared electrodes in the current study: a considerable shift of the oxidation peak potential by ca. 280 mV was found. *I–t* measurements revealed that only a very minute Pt loading as small as ca. 9.2×10^{-3} mg cm^{-2} is required to obtain comparable current densities with those at Au nanoparticles.

The electrocatalytic oxidation of glucose, especially for its potential applications in the field of fuel cells, has been examined extensively in the literature particularly on gold substrates,[1–4] to which much attention has been paid so far. On the other hand, the use of nanoparticles of different metal substrates to fabricate highly active electrodes has attracted great interest owing to its wide range of electrochemical applications.[5–7] In this respect, we have introduced in a previous work Au nanoparticle-modified HOPG electrodes as a potential candidate for the effective electrocatalytic oxidation of glucose.[3] In the current study, a far better catalyst in alkaline solution that is based on electrochemically fabricated Pt nanoparticles (PtNPS) is reported for the first time, to the best of our knowledge, having different catalytic activity than bulk Pt as we discussed in previous works.[1,2]

A glassy carbon (GC) electrode ($\phi = 3$ mm) purchased from BAS Inc., Japan was firstly polished with the help of a micro cloth using aqueous slurries of alumina paste to a mirror-like finish, then sonicated in ultrapure water (Milli-Q 18.2 MΩ cm, Millipore System Inc.) for 10 min. Prior to electrochemical measurements, electrolytic solutions were purged with high-purity nitrogen for at least 20 min, and during measurements the nitrogen flow was kept uninterrupted. PtNPS were then electrodeposited onto GC electrodes from a (0.05 M H_2SO_4 + 1 mM $PtCl_4$) solution by applying a 300 s potential step from 0.5 to 0.1 V vs. Ag|AgCl|KCl (sat).[8] The prepared electrodes were then removed from the solution and washed thoroughly with Milli-Q water. Ag|AgCl|KCl (sat) electrode and a Ptplate served as reference and counter electrodes, respectively.

The morphology of the prepared PtNPS was investigated using scanning electron microscopy (SEM) analysis, conducted with a (JSM-6060LV, JEOL Ltd., Japan) scanning electron microscope.

The observed catalytic activities were studied using voltammetric measurements performed using a CV-50W voltammetric analyzer (Bioanalytical Systems, Inc.).

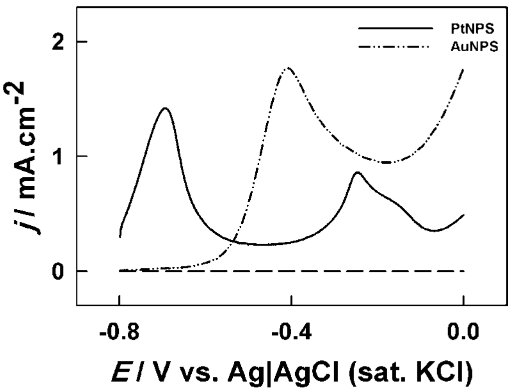

Figure 1. Voltammetric curves measured in N_2-saturated (10 mM glucose + 0.1 M NaOH) solutions at 50 mV s^{-1}.

In order to compare with the catalytic activity of AuNPS-based electrodes, GC electrodes were also modified with AuNPS electrodeposited from a (0.5 M H_2SO_4 + 1 mM $HAuCl_4$) solution via a 300 s potential step from 1.1 to 0 V vs. Ag|AgCl|KCl (sat).

Figure 1 shows characteristic voltammograms at both PtNPS- and AuNPS-deposited GC electrodes in N_2-saturated (10 mM glucose + 0.1 M NaOH) solutions. At the latter, the oxidation of glucose at the potential of interest in the present work conditions occurs via a two-electron oxidation reaction to yield gluconolactone.[1–3] An eye-catching feature in Figure 1 is the significant positive catalytic effect observed when PtNPS were used as catalyst, as is shown by a ca. 280 mV negative shift of the oxidation peak potential comparing PtNPS- and AuNPS-electrodeposited GC electrodes from ca. −410 to ca. −690 mV, respectively.

According to several reports, the oxidation process at Pt catalysts is rather complicated and is believed to be behind some controversial reports in the literature in the past. The voltammetric shape and the linear relation between the peak current and the scan rate suggest that the reaction process corresponds to the oxidation of adsorbed glucose onto the PtNPS catalyst in agreement with reports at Pt electrode showing three steps in this process, two are chemical and one electrochemical,[9] as follows (Where GH denotes glucose):

$$\mathrm{GH} \rightarrow \mathrm{GH_{ads}} \qquad \text{(Fast)} \qquad (1)$$

$$\mathrm{GH_{ads}} \rightarrow \mathrm{G_{ads}} + \mathrm{H_{ads}} \qquad \text{(Slow)} \qquad (2)$$

$$\mathrm{H_{ads}} \rightarrow \mathrm{H^+} + \mathrm{e^-} \qquad \text{(Fast)} \qquad (3)$$

Where eq 2 is the rate-determining step. The final oxidation product at this very negative potential is probably gluconolactone (GL) by either disproportionation reaction

$$2\mathrm{G_{ads}} \rightarrow \mathrm{GL} + \mathrm{GH} \qquad (4)$$

or the further oxidation of the adsorbed species of glucose at

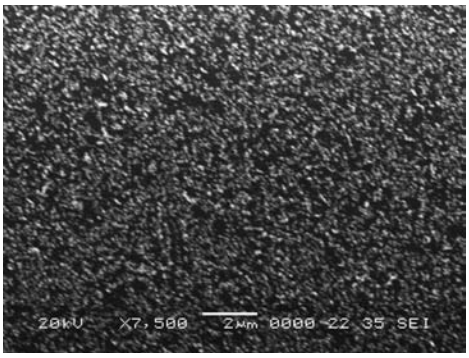

Figure 2. SEM image of electrodeposited PtNPS onto GC electrode via 300 s potential from a (0.05 M H_2SO_4 + 1 mM $PtCl_4$) solution.

more positive potentials, judging from the peak current and that the main oxidation product obtained by electrolysis at Pt electrode at −0.35 V was gluconolactone.

The examination of the SEM micrograph for the as-prepared PtNPS-modified GC electrode (cf. Figure 2) shows very nicely dispersed PtNPS with an average particle size of ca. 100 nm covering the whole substrate electrode's surface. The calculated total charge Q_{cal} obtained by integration of the I–t curves recorded during the potential step measurements for PtNPS electrodeposition gives an estimation of the amount of deposited PtNPS to be ca. 9.2×10^{-3} mg cm^{-2}, with the assumption that Pt$^{\mathrm{IV}}$ (i.e. of the electrolytic solution) reduces to Pt metal with a 100% current efficiency. This amount is very interestingly tenfold lower than what is required to fabricate one of the best effective catalytic electrodes, that is based on AuNPS, for glucose electrocatalytic oxidation at the same experimental conditions for both GCE (ca. 9.05×10^{-2} mg cm^{-2}) and HOPG[3] (ca. 8.88×10^{-2} mg cm^{-2}) electrodes. Furthermore, the obtained current densities in the present work (i.e. ca. 1.42 mA cm^{-2}) are greatly higher compared to the electrocatalytic oxidation of glucose at another reported PtNPS-based catalyst in similar alkaline media,[10] which is an important criterion for practical applications.

The data obtained in the current work make it possible to investigate the direct electrocatalytic oxidation of glucose at PtNPS-modified electrode without the need to use expensive metal substrate as base electrode. It also constitutes a good alternative to overcome the problem encountered with the UPD technique, where Pt adatoms failed to deposit on the electrode surface.[1,11] The observed catalytic activities in the current study are in good agreement with the expected behavior based on our previous work at various metal substrate electrodes where Pt was shown to be the best catalyst in terms of oxidation peak potential.[1,12] Moreover, the current study offers an easy, controllable, and far cheaper method to utilize the platinum catalyst.

These findings represent an interesting key point for fuel cells applications, though several steps are still required for the real battery design and preparation. Nevertheless, we have attempted first trial battery performance measurements based on the obtained data in the present study. For this, since practical fuel cells require higher currents (i.e. in the order of mA), we designed an anode catalyst system based on modified carbon felt (CF) electrodes ($\phi = 1.5$ cm) which is well known for its large surface area. Prior to PtNPS electrodeposition, the CF electrode was treated in a 1 M nitric acid solution by carefully heating for around 2 h at 250 °C then sonicating in Milli-Q water for 30 min. This manipulation tremendously decreased the water repellency of the CF electrode to the extent that the prepared electrodes were totally submerged in solution at the end this pretreatment. This enables us to gain in terms of active surface area for the nanoparticles electrodeposition. The CF electrode was then modified with PtNPS as described earlier and Pt catalyst was allowed to be electrodeposited for 15 min in this case (ca. 0.41 mg cm^{-2}). The as-prepared PtNPS-deposited CF electrode was then combined with a highly efficient air electrode of a Panasonic® zinc–air battery, constituting the cathode of the proposed fuel cell. These two electrodes were then sandwiched into a conventional fuel cell set, and a (0.3 M NaOH + 200 mM glucose) solution was used as fuel. The measured preliminary data are very promising, with an open circuit voltage of ca. 0.79 V, a short circuit current of ca. 17 mA cm^{-2} and a maximum output power of ca. 1.47 mW cm^{-2}. The current practical disadvantage, however, is the limited working time of this system since current decreases drastically with time. In this respect, the output current and, by consequence, the maximum output power decreased by ca. 70% within one hour time. We are currently working on the improvement of the prepared catalyst, and more detailed investigations are under way, aiming at elucidation of the real oxidation product at very negative potential on the PtNPS-modified electrode to understand the reaction mechanism in more details and to make open the reaction sites on the Pt surface (occupied by G_{ads}) to continuous oxidation of glucose.

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