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Nonenzymatic Glucose Detection Using Mesoporous Platinum

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Roughness of nanoscopic dimensions can be used to selectively enhance the faradaic current of a sluggish reaction. Using this principle, we constructed mesoporous structures on the surfaces of pure platinum electrodes responding even more sensitively to glucose than to common interfering species, such as L-ascorbic acid and 4-acetamidophenol. Good sensitivities, as high as $9.6 \mu\text{A cm}^{-2} \text{mM}^{-1}$, were reproducibly observed in the presence of high concentration of chloride ion. The selectivities, sensitivities, and stabilities determined experimentally have demonstrated the potential of mesoporous platinum as a novel candidate for nonenzymatic glucose sensors.

Over the past decades, numerous studies have been performed to overcome or alleviate the drawbacks of enzymatic glucose sensors. The most serious problem of such sensors is their lack of stability due to the intrinsic nature of enzymes. To address this problem, earlier studies attempted to determine the glucose concentration without using enzymes.^{1–9} Amperometric measurements allow observation of the electrochemical oxidation of glucose on a bare platinum (Pt) surface.^{1–3} However, even state-of-the-art technology for glucose sensors using Pt electrodes is not free from poisoning by adsorbed intermediates,¹⁰ low sensitivity, and poor selectivity. Such drawbacks have been partly overcome by Pt–Pb alloy (Pt₂Pb) electrodes.⁸ Compared with pure Pt surfaces, glucose is electrochemically oxidized on Pt₂Pb surfaces at remarkably negative potentials. Thus, Pt₂Pb is relatively insensitive to interfering species, such as L-ascorbic acid (AA),

uric acid, and 4-acetamidophenol (AP). Moreover, Pt₂Pb generates more stable and larger responses than pure Pt. However, despite these valuable advantages, surface poisoning by chloride ion remains a serious problem. For example, the amperometric signal diminishes rapidly in the presence of 0.01 M NaCl and eventually almost disappears. Efforts have also been made to modify Pt surfaces with other materials. Although Pt surfaces modified with Ti, Pb, Bi, or WO₃^{4–7} have reportedly shown catalytic activity in terms of glucose oxidation, the dissolution of metal ions and the toxicities of the heavy metal elements involved prevent these methods from being put to practical use.

The key idea behind the present study is based on the fact that the roughness of mesoporous electrodes is even smaller than the scale of the chronoamperometric diffusion field in most cases. Since the diffusion layers extend several micrometers away from the electrode surface in milliseconds, reactants inside the mesopores (2–50 nm in diameter)¹¹ are depleted in diffusion-controlled electrochemical systems, as illustrated in Figure 1A. As a result, the faradaic currents of rapidly oxidizable or reducible reactants are proportional to the apparent geometric area of the electrode, regardless of its mesoporous roughness.¹² On the other hand, faradaic currents associated with kinetic-controlled electrochemical events are sensitive to the nanoscopic surface area of the electrode, rather than to its geometric area (Figure 1B). Deeper and denser mesopores on an electrode surface generate larger roughness factors, that is, the ratio of nanoscopic surface area to the geometric surface area. Highly enlarged electrode areas, in nanoscale terms, boost the faradaic currents of the sluggish reaction exclusively as depicted in Figure 1C.

The fabrication method and the properties of mesoporous Pt films have been previously reported upon.^{11,13–23} Attard et al.

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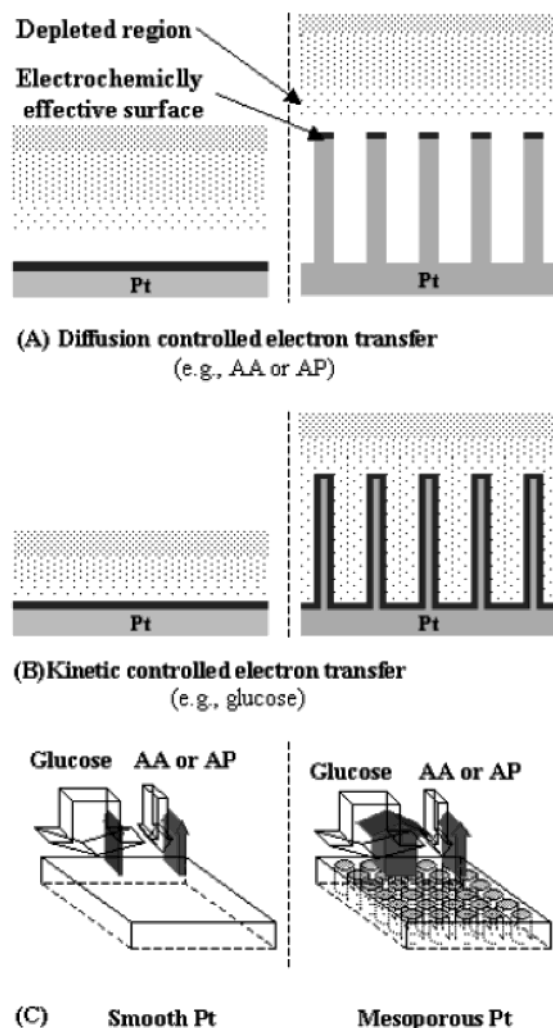


Figure 1. Schematic representation of the effect of pore structure on electrochemical reactions.

initially reported that mesoporous Pt film could be produced by electrodeposition from a hexagonal (H_1) liquid crystalline phase composed of the nonionic surfactant (octaethylene glycol monohexadecyl ether, $C_{16}EO_8$)²³ and found that the electrodeposited Pt film, with cylindrical hexagonally arrayed pores (pore diameter, 2.5 nm; pore–pore distance 5.0 nm), was adherent and shiny. The first application of a mesoporous electrode to an analytical purpose was reported by Evans et al.¹⁷ According to them, mesoporous Pt films electrodeposited onto microelectrodes¹⁶ showed tremendous improvements in terms of hydrogen peroxide detection sensitivity, as compared with bare Pt.

The normal physiological level of glucose is 3–8 mM, which is much higher than those of AA and AP, ~0.1 mM. However, these two interfering species generate oxidation currents that are comparable to that of highly concentrated glucose, because their electron transfer rates are considerably faster than that of glucose. Therefore, the direct oxidation of glucose is a suitable subject for

the application of mesoporous Pt films. The present study reports on discriminatively enhanced amperometric responses to glucose and on the performance of nonenzymatic glucose sensors based on mesoporous Pt structures.

EXPERIMENTAL SECTION

Reagents. Octaethylene glycol monohexadecyl ether $C_{16}EO_8$ (Fluka), hydrogen hexachloroplatinate hydrate (Aldrich), sulfuric acid, D-(+)-glucose (Sigma), L-ascorbic acid (Aldrich), and 4-acetamidophenol (Sigma) were used without purification.

Instruments. Electrochemical experiments were performed using an electrochemical analyzer (model CH660, CH Instruments Inc., Austin, TX 78733). Ag/AgCl (3 M KCl) and a platinum wire were used as reference and counter electrodes, respectively. A platinum rod electrode (0.020 cm²) was used as a substrate electrode for the mesoporous platinum film. Another Pt disk electrode was polished with alumina (0.3 μ m) and then used as a smooth Pt electrode. Small-angle X-ray diffraction was measured using a small-angle X-ray scattering unit fitted with general area detector diffraction (Bruker, Germany).

Preparation of Liquid Crystals. $C_{16}EO_8$ (0.42 g), distilled water (0.29 g), and hydrogen hexachloroplatinate hydrate (0.29 g) were mixed, and the temperature was raised to 80 °C, at which point the mixture became transparent and homogeneous. Electrodes were then inserted into the homogeneous mixture, and the temperature was lowered to room temperature (~23–26 °C). At this stage, the mixture became a highly viscous liquid crystalline material.

Electrodeposition of Mesoporous Platinum. Platinum deposition was carried out on a polished platinum rod electrode at constant potential (–0.06 V vs Ag/AgCl). The resulting mesoporous platinum electrode was placed in distilled water for 1 h to extract the $C_{16}EO_8$, and the extraction procedure was repeated 3–4 times. The electrode was then electrochemically cleaned using a cycling potential between +1.0 and –0.45 V versus Ag/AgCl in 0.5 N sulfuric acid until reproducible cyclic voltammograms were obtained.

Electrochemical Experiments. All electrochemical measurements were done in a three-electrode system. The surface areas of the Pt electrodes were determined by measuring the areas under the hydrogen adsorption/desorption peaks of the cyclic voltammograms (scan rate, 0.2 V sec^{–1}) in 0.5 N sulfuric acid solution. A conversion factor of 210 μ C cm^{–2} was used to determine the electrode area.²⁴ The diffusion characteristics of the mesoporous Pt were compared with that of smooth Pt by measuring the cyclic voltammograms of both Pt's in 1.0 mM potassium ferricyanide solution and checking the peak currents and peak separations. The mesoporous platinum electrode was evaluated as a glucose sensor in aerated 0.1 M phosphate buffered saline (PBS) solution containing 0.15 M NaCl and in a temperature-controlled cell containing 10 mL of PBS (pH 7.4, 37.2 \pm 0.2 °C). NaN_3 was not used because it blocks the oxidation of glucose. Amperometric curves were obtained in a quiescent solution a few seconds after stopping the stirring that was required to mix the materials added (i.e., glucose, AA, and AP). Current changes 100 s after adding glucose to concentrations of 1, 3, 6, 10, 15, and 20 mM were treated as specific responses to the glucose in the

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solution. The signals for AA and AP were measured by adding 0.1 mM of AA and AP sequentially and reading the current changes 100 s later. We confirmed that the AP signal was unaffected by the presence of AA. The platinum electrode was electrochemically cleaned before each measurement.

RESULTS AND DISCUSSION

Fabrication and Characterization of Mesoporous Pt. Mesoporous Pt was electrodeposited in a $C_{16}EO_8$ -based liquid crystalline phase using the method described by Attard et al.^{20,23} The Pt films as obtained were characterized by checking the typical features of the mesoporous Pt.^{11,16,20,23} (1) The Pt films showed high specific surface areas and roughness factors (e.g., a specific area of 37 m²/g for a H₁-ePt film with a roughness factor of 72, assuming a faradaic efficiency of $\sim 30\%$ ¹¹). Similar specific area and roughness factors have been already reported for mesoporous Pt by Gollas et al.¹¹ (2) Bright surfaces were observed as a result of their excellent flatness. The measured roughness of the mesoporous Pt was reportedly 20 ± 5 nm over a 1 mm² area of a 300-nm-thick film.^{20,23} (3) A single X-ray diffraction peak appeared at 1.68 Å (2θ) corresponding to a pore–pore distance of 6.1 nm (for a hexagonal structure). Gollas et al. found a pore–pore distance of 5.9 nm by low-angle X-ray diffraction.¹¹ (4) The Pt film showed diffusion characteristics similar to those of a well-polished Pt (Pt-s) surface. When the cyclic voltammograms were recorded in a ferricyanide solution with the mesoporous and well-polished Pt electrodes, the apparent voltammetric behavior from the two electrodes was similar to each other (see Supporting Information available). For example, the cyclic voltammograms exhibit not only the same separations between the cathodic and anodic peaks but also comparable peak currents normalized by geometric area (not by nanoscopic area). The similarity in the diffusion behavior of mesoporous and smooth Pt electrodes was previously reported by Elliott et al.¹⁶

These features of the resulting Pt film almost coincide with those already reported for mesoporous Pt. This characterization confirmed that the Pt films electrodeposited in this study had the mesoporous structure of H₁-ePt with hexagonal cylindrical mesopores of ~ 2.5 -nm diameter and a wall thickness of ~ 2.5 nm.²³ Hereafter, the electrodeposited Pt film in this study will be also referred to H₁-ePt.

Amperometric Response to Glucose. In cyclic voltammetry measurements using H₁-ePt, the oxidation peaks of glucose, AA, and AP appeared at 0.14, 0.13, and 0.42 V versus Ag/AgCl, respectively (Supporting Information available). Amperometric measurements were performed at 0.4 V versus Ag/AgCl, which was positive enough to oxidize glucose and AA. Figure 2 shows the amperometric responses of H₁-ePt (roughness factor, 72) and of Pt-s (roughness factor, 2.6) to glucose, AA, and AP in aerated phosphate-buffered saline (PBS) solution containing 0.15 M NaCl (pH 7.4, 37.2 ± 0.2 °C). Pt-s was very sensitive to AA and AP, but responded only negligibly to glucose. On the other hand, the H₁-ePt surface responded to glucose with linear dependence (R value, 0.999) in the glucose concentration range of 0–10 mM with a sensitivity of $9.6 \mu A cm^{-2} mM^{-1}$, as demonstrated in Figure 3.

H₁-ePt electrodes with various roughness factors were formed by electroplating by controlling the charge passed during the deposition process. These electrodes were then used to measure

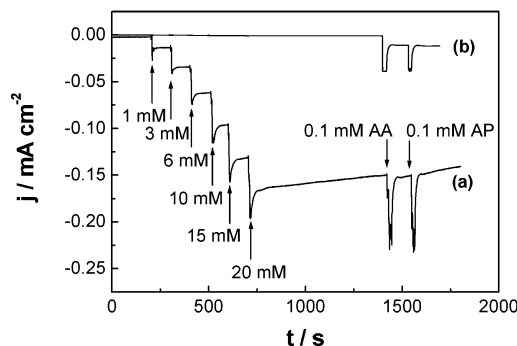


Figure 2. Current density vs time curves showing the responses of (a) H₁-ePt (roughness factor, 72) and (b) Pt-s (roughness factor, 2.6) to glucose, AA, and AP at +0.4 V vs Ag/AgCl in aerated PBS (pH 7.4, 37.2 ± 0.2 °C). Glucose, AA, and AP were added at the points indicated by arrows to the concentrations mentioned. Current spikes immediately after additions were due to stirring for a few seconds.

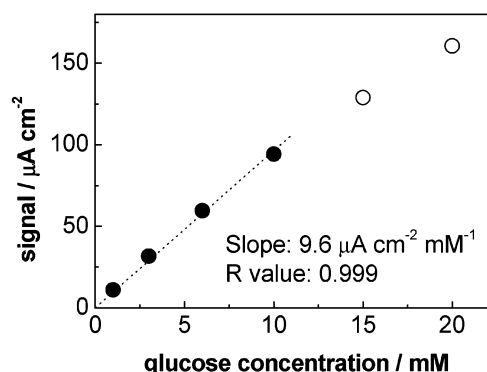


Figure 3. Calibration curve for the H₁-ePt signal (roughness factor, 72) to glucose in aerated PBS solution (pH 7.4) at $37.2 (\pm 0.2)$ °C. When the glucose was added, the solution was stirred for a few seconds only. Signals were recorded in the quiescent solution 100 s after the glucose addition.

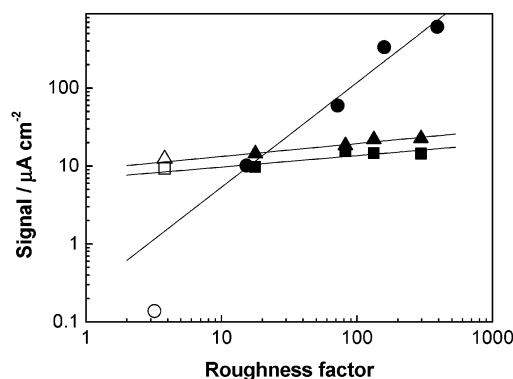


Figure 4. Effect of the roughness factors of H₁-ePt (solid) and Pt-s (open) on the signals for 6 mM glucose (circle), 0.1 mM AA (triangle), and 0.1 mM AP (square). The signals were determined in quiescent solutions 100 s after adding glucose, AA, or AP.

the signals for glucose (6 mM), AA (0.1 mM) and AP (0.1 mM). Figure 4 unequivocally shows selective signal amplification by the mesoporous surfaces. The close to unity slope of the graph in logarithmic scale indicated the linear dependence of the responses of H₁-ePt to glucose on the roughness factors (Figure 4, solid circle). On the other hand, the responses of H₁-ePt to AA (Figure 4, solid triangle) and AP (Figure 4, solid square) were little affected. Consequently, the effective electrode area enlarged specifically

enhanced the faradaic current so that selectivity to glucose over AA and AP was remarkably improved. The response of Pt-s to glucose (Figure 4, open circle) deviated from linearity between the currents and the roughness factors. This implies that such a specific sensitivity does not stem solely from the increased roughness factor. It is unclear at present what causes the signal enhancement, other than surface roughness.

CONCLUSIONS

The mesoporous surface of H₁-ePt offers a number of attractive features that have not been reported previously. First, it provides nonenzymatic selectivity over representative interfering species. Although Sun et al.⁸ reported that the Pt₂Pb alloy electrode is insensitive to interfering materials, this insensitivity was achieved by simply lowering the potential, and therefore, the interfering materials were not oxidized. However, selectivity in the present study was evaluated at a potential that allowed the oxidation of such interfering materials. In view of the physiological level of glucose (3–8 mM) and that of the interfering agents (0.1 mM), the selectivity of H₁-ePt appears to be good enough for clinical application without enzyme or an additional outer membrane. Second, the mesoporous surface retains sufficient sensitivity in the presence of chloride ion, even at a PBS level of 0.15 M. Most of the electrochemical sensors based on novel metals for nonenzymatic glucose detection almost entirely lose their activity because of poisoning by the chloride ion, which is abundant in nature, particularly in physiological fluids. The excellent performance of this simple system encourages us to find new applica-

tions for enzyme-free chemical sensors. Finally, H₁-ePt is mechanically and chemically stable, and its surface can be easily regenerated by electrochemical cleaning. As a possible application, H₁-ePt can be embedded inside the microchannels on sophisticatedly engineered chips and be combined with microfluidics. Further detailed work on the properties and practical applications of mesoporous surfaces is in progress.

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SUPPORTING INFORMATION AVAILABLE

Cyclic voltammograms of H₁-ePt and Pt-s in 0.5 N H₂SO₄, in 1.0 mM potassium ferricyanide. Voltammetric responses of H₁-ePt and Pt-s for AA, AP, and various concentrations of glucose. Small-angle X-ray pattern of H₁-ePt. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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