



# Pd-modified TiO<sub>2</sub> electrode for electrochemical oxidation of hydrazine, formaldehyde and glucose

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## ABSTRACT

The electrocatalysis of the oxidation of hydrazine, formaldehyde and glucose on a nanoporous Pd-modified TiO<sub>2</sub> electrode, prepared by the hydrothermal process, was investigated in 0.1 M NaOH solutions. The electrocatalytic activity of the Pd-modified TiO<sub>2</sub> electrode for the electrochemical oxidation of hydrazine, formaldehyde and glucose is characterized by the low onset potentials of  $-0.80$ ,  $-0.70$  and  $-0.85$  V (vs Ag, AgCl), respectively. Compared to the oxidation of formaldehyde and glucose, the hydrazine oxidation on the Pd-modified TiO<sub>2</sub> presents the highest anodic oxidation current densities, showing that the Pd-modified TiO<sub>2</sub> electrode is more electro-active for the hydrazine oxidation than for the oxidation of formaldehyde and glucose. Chronoamperograms at different concentrations of hydrazine and formaldehyde showed that the Pd-modified TiO<sub>2</sub> electrode is a promising electrochemical sensor for the detection of hydrazine with a sensitivity of  $0.554 \text{ mA cm}^{-2} \text{ mM}^{-1}$  and a detection limit of  $0.023 \text{ mM}$ , and for the detection of formaldehyde with a sensitivity of  $0.20667 \text{ mA cm}^{-2} \text{ mM}^{-1}$  and a detection limit of  $0.015 \text{ mM}$ . However, it was found from the chronoamperometric responses at various glucose concentrations that a linear plot of the anodic oxidation current density versus glucose concentration developed only in the range of 7–35 mM glucose while an obvious deviation from the linear relationship was observed at both low and large glucose concentrations. Results show that the prepared Pd-modified TiO<sub>2</sub> electrode could be applied to the direct liquid (hydrazine, formaldehyde, and glucose) fuel cells as an effective anodic catalyst, in addition to be a promising electrochemical sensor for the detection of hydrazine and formaldehyde.

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## 1. Introduction

Electrochemical oxidation of hydrazine has been extensively investigated with regard to its promising application to direct fuel cells and to hydrazine detection. Platinum and Pt-containing materials have been paid much attention because of their effective electroactivity towards hydrazine oxidation. Both polycrystalline platinum [1,2] and single-crystal platinum surfaces [3–6] presented electrocatalytic activity for hydrazine oxidation in acidic or alkaline solutions. Nickel and modified nickel electrodes were also applied to amperometric determination of hydrazine [7,8]. In addition, electro-oxidation of hydrazine was performed at various modified glassy carbon and carbon nanotube electrodes [9–15], and silver or silver nanoparticles [16,17]. Gold electrodes, including Au nanoparticles and nanoparticle–polypyrrole nanowire modified glassy carbon [18,19], and gold electrode modified with iron phthalocyanine complex linked to mercaptopyrindine self-assembled monolayer [20] etc, also exhibited attractive electroactivity for hydrazine oxidation. Palladium and palladium alloys were applied to electro-oxidation of hydrazine as

effective electrocatalysts in view of their less anodic over-potentials for hydrazine oxidation, and they included Pd particles on poly(vinylferrocene) [21], Pd/WO<sub>3</sub> film [22], Pd nanoparticles decorated ionic liquid-modified carbon electrode [23], Pd/TiO<sub>2</sub> nanotubes [24], Pd nanoparticles on carbon nanotubes, and Pd nanoparticles supported on boron-doped diamond [25,26]. These Pd-containing electrodes presented appreciable electrocatalytic activity towards hydrazine oxidation when compared with the related studies.

Knowledge of the reactivity of formaldehyde in an electrochemical environment is important for various applications including fuel cells and electrochemical detection. Therefore, electrochemical oxidation of formaldehyde at various electrocatalysts has been receiving much attention [27]. Copper and copper alloys have been studied for decades as anode catalysts for the formaldehyde oxidation [28–30]. In addition, electro-oxidation of formaldehyde at Pt, binary Pt–Au and Pt–Ru electrocatalysts has also been investigated in both acidic and alkaline media [27,31–37]. Cyclic voltammetric responses showed that the Pt–Ru alloy increases the current for HCHO oxidation in alkaline media by more than one order of magnitude with respect to the pure metals [35]. Other noble metal electrocatalysts utilized for the formaldehyde oxidation include polycrystalline palladium [27], gold [27], palladium nanoparticles electrodeposited on carbon ionic liquid composite electrode [38], and palladium nanoparticles on

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functional multi-walled carbon nanotubes which exhibited a lower onset potential and higher anodic current densities for formaldehyde oxidation than Pd nanoparticles on carbon [39]. Ni and Ni based electrodes have also gained considerable interest in the electrochemical oxidation of formaldehyde [40,41].

Glucose electro-oxidizing anodes have been studied not only because of their importance in medical and food industries as glucose sensors, but also in the context of glucose–air fuel cells [42–45]. Platinum and gold electrodes have been proved to exhibit effective electroactivity for glucose oxidation [46–50]. Enhancement of electrocatalytic activity of gold electrodes for the glucose oxidation is usually actualized by dispersing gold into small or even nano-scale sized particles [51–57]. Ag modified Au electrodes were reported to act as good catalysts for glucose oxidation, and show the best improvement compared to the bare Au(1 1 1) and Au(1 0 0) single-crystal electrodes [58–60]. Further, Sulak et al. prepared a gold-deposited polyvinylferrocene film on Pt electrode and examined its electrochemical properties as an amperometric glucose biosensor [61]. Different behaviors in the glucose electro-oxidation on polycrystalline gold electrodes, after various treatments including annealing, alumina polishing, and amalgamation, were investigated by Cho et al. [62].

Nanoporous electrocatalysts have three-dimensional (3D) network textures which present both considerable surface areas and high stability of the catalysts particles, showing high electrocatalytic activity for some specific electrochemical reactions [63–65]. In previous works, we fabricated the nanoporous Pd particles modified titanium electrode using a simple hydrothermal process and this electrocatalyst presented significantly high electrocatalytic activity for formic acid oxidation in acidic solutions [66]. The present paper aims to examine its electrocatalytic properties towards the oxidation of hydrazine, formaldehyde and glucose in alkaline solutions.

## 2. Experimental details

All chemicals used in this work were analytical grade products and used without further purifications. Palladium chloride, hydrazine, formaldehyde, glucose and sodium hydroxide were purchased from Sinopharm Group Chemical Reagent Co. Ltd. Pure water (18.2  $\Omega$  cm) was obtained from doubly distilled water that has been subjected to the treatment of ion exchange resins. Titanium pieces were of 99.2% purity.

Electrochemical measurements were carried out with a computer controlled AutoLab PGSTAT30/FRA electrochemical system (Netherlands). Morphological structure of the sample was examined using scanning electron microscopy (SEM) taken on a JEOL 5900LV. A conventional three-electrode cell was used with a silver chloride electrode (Ag/AgCl, 3 M KCl) as reference, large platinum foil as counter electrode and the prepared nanoporous Pd-modified TiO<sub>2</sub> as working electrode. The Pd-modified TiO<sub>2</sub> electrode was prepared by the hydrothermal deposition of nanoporous palladium particles on the surface of titanium plates using the formaldehyde as the reduction agent, as described as our previous works [66]. At first, Ti plates with the size of 10 mm  $\times$  5 mm were etched in 10% HCl at 85  $^{\circ}$ C for 10 min to obtain a clean and rough Ti surface. Then, the Ti plates were washed with pure water and subsequently subjected to ultrasonic treatment for 5 min. Finally, the pretreated Ti plates were transferred to a Teflon container lined autoclave containing 5% formaldehyde (CH<sub>2</sub>O) and 5 mmol/L PdCl<sub>2</sub>, and heated at 180  $^{\circ}$ C for 10 h. After cooling to room temperature, the coated Ti substrates were removed, air dried, then rinsed with the pure water. This process resulted in the synthesis of the Pd nanoparticles-modified TiO<sub>2</sub> electrode, which presented a nanoporous texture with a considerable surface active area. According to the SEM image (not shown) of the cross section of the Pd-modified TiO<sub>2</sub> electrode, the Pd layer thickness of the Pd-modified TiO<sub>2</sub> electrode is reckoned to be ca. 0.5 to 0.8  $\mu$ m because of the porous

surface structure. Prior to electrochemical measurements, the prepared Pd-modified TiO<sub>2</sub> electrode was subjected to a successive cycling potential scanning between  $-0.80$  and  $+0.80$  V (vs Ag/AgCl, 3 M KCl) at a scan rate of 100 mV/s in 0.1 M NaOH solution until a stable voltammogram was obtained. All potentials reported in this paper were referred to the Ag/AgCl which was positioned as close to the working electrode as possible by means of a Luggin capillary. Before experiments, pure nitrogen gas (99.99%) was bubbled through the solution to remove the dissolved oxygen in the solution. During measurements, N<sub>2</sub> was continuously flushed over the surface of the solution. All experiments were carried out at ambient temperature ( $24 \pm 2$   $^{\circ}$ C).

## 3. Results and discussion

### 3.1. Morphological characterization

The surface morphology of the prepared Pd-modified TiO<sub>2</sub> electrode was examined by scanning electron microscopy (SEM). SEM image of Fig. 1 shows a good coverage of Pd catalyst particles on the surface of Ti substrate. The catalyst particles with the sizes of ca. 140 to 170 nm are connected with each other to form a three-dimensional texture. This porous structure provides stable immobilization of the palladium particles on the Ti surface.

### 3.2. Electro-oxidation of hydrazine

Electrocatalytic activity of the Pd-modified TiO<sub>2</sub> electrode towards hydrazine oxidation was examined by cyclic voltammetry (CV). Fig. 2 presents CV responses of the Pd-modified TiO<sub>2</sub> at different hydrazine concentrations from 0 to 60 mM. It is observed from the CV profiles of Fig. 2 that hydrazine oxidation at the Pd-modified TiO<sub>2</sub> electrode commences at a potential of ca.  $-0.80$  V, showing a low overpotential compared with other reported electrocatalysts such as platinum electrodes [6], Ag nanoparticles on carbon nanotubes [17] and Pd nanoparticles supported on a boron-doped diamond electrode [26]. In addition, significant oxidation currents of hydrazine at the Pd-modified TiO<sub>2</sub> were also found and a limiting current plateau for the positive potential scan appears in the range of 5–30 mM hydrazine. With the increment of hydrazine concentration, the limiting current increases while its corresponding potential span becomes narrower or even fades away.

The change of the limiting current plateau with the hydrazine concentration illustrates that the anodic oxidation of hydrazine at the Pd-modified TiO<sub>2</sub> electrode is a mass-transfer controlled process. According the SEM image of the Pd-modified TiO<sub>2</sub> as shown in Fig. 1, its nanoporous texture provides considerable numbers of active

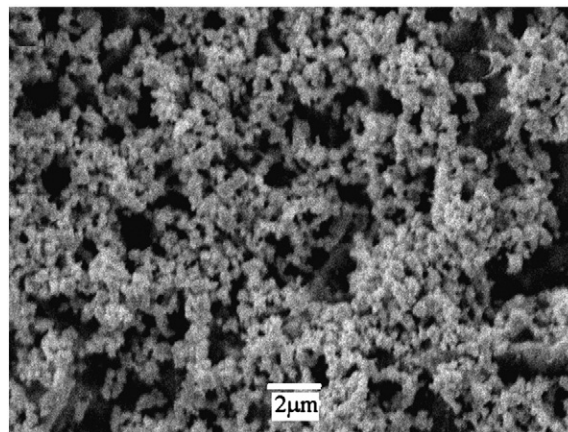


Fig. 1. SEM image of the Pd-modified TiO<sub>2</sub> electrode.

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