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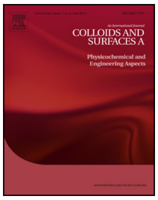

Admixing palladium nanoparticles with tungsten oxide nanorods toward more efficient electrocatalytic oxidation of formic acid

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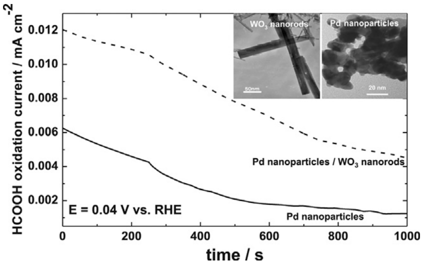
HIGHLIGHTS

- Hybrid electrocatalysis was obtained by combining hexagonal tungsten oxide nanorods and Pd nanoparticles.
- H_xWO_3, WO_{3-y} and Pd nanoparticles are expected to exist at electrocatalytic interface.
- Enhancement of oxidation of formic acid at potential as low as 0.04 V vs. RHE was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

By depositing nanorods of tungsten oxide over catalytic palladium nanoparticles (dispersed onto glassy carbon substrate), enhancement of the overall electrocatalytic activity toward oxidation of formic acid in acid medium was observed. The effect was particularly evident from the increase of chronoamperometric currents at a fairly low potential of 0.04 V vs. RHE. Under such conditions, tungsten oxide nanorods seem to be partially and reversibly reduced not only to nonstoichiometric hydrogen tungsten(VI,V) oxide bronzes (H_xWO_3, $0 < x < 1$) but also substoichiometric lower tungsten (VI,IV) oxides (WO_{3-y}, $0 < y < 1$). Mutual interactions between tungsten oxides with Pd nanoparticles affect electrochemical characteristics of both components. The metal–oxide interactions, as well as high population of hydroxyl groups at the electrocatalytic interface (favoring oxidative removal of passivating CO adsorbates), are most likely responsible for the overall enhancement effect. In comparison to conventional electrodeposited microporous tungsten oxides, WO_3 nanorods, despite their small dimensions, are more robust and less hydrated. Electrochemical diagnostic experiments were supported with microscopic measurements aiming at monitoring morphology of catalytic surfaces with use of transmission (TEM) and scanning (SEM) electron microscopies. The palladium nanoparticles were of the sizes 10–20 nm, and the tungsten oxide nanorods had diameters of 50–70 nm while being approximately 5 μm long.

1. Introduction

There has been growing recent interest in use of formic acid as an organic fuel for low-temperature fuel cells. Formic acid has several advantages that include reduced toxicity, high practical power density and limited crossover through Nafion membrane during operation of the fuel cell [1–5]. Formic acid is probably the simplest organic liquid fuel, and it can serve as a model reactant for

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studies of the electrooxidation of small organic molecules. It has recently been established that palladium nanoparticles are promising (highly active) catalytic nanostructures for electrooxidation of formic acid employed [6,7]. Formic acid is believed to undergo oxidative decomposition on Pd surface according to two mechanisms that are described bellow [8]:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e \quad (1)$$

$$HCOOH \rightarrow CO_{ads} + H_2O \quad (2a)$$

$$CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad (2b)$$

The reaction based on direct oxidation to CO_2 (Eq. (1)) as a main path is obviously more efficient than the two-step process involving formation of carbon monoxide intermediate. Indeed, strongly bonded CO_{ads} species formed in reaction (2a) tend to accumulate slowly on Pd surface and results in the catalyst deactivation. The poison (i.e. CO_{ads} intermediate) can be removed according to reaction (3), but if the reaction is relatively slow or thermodynamicall unfavorable, the CO_{ads} species would completely poison the Pd surface.

The application of various metal oxides (e.g. WO_3 [9,10], TiO_2 [11–15], MoO_x [16], Eu_2O_3 [17]) as components of electrocatalytic materials, in which noble metal nanoparticles are dispersed, has been described. It is reasonable to expect that inorganic oxides can modify the electronic structure of active noble metals as well as they can provide large population of —OH groups at the catalytic interface. It has been reported that Pt and PtRu catalysts supported on WO_3 exhibited high activity toward electrooxidation of methanol [18–20], ethanol [21,22] and formic acid [9,10,23]. Hydrated tungsten oxides can form hydrogen bronzes (H_xWO_3) that effectively facilitate dehydrogenation of small organic molecules. Other important properties of tungsten oxide films in mixed-valent ($W^{VI,V}$) state include high rates of charge (electron and proton) propagation [24,25] and ability to transfer electrons effectively to three-dimensionally distributed catalytic centers [26–28]. The activating role of tungsten oxide is related to the presence of —OH groups on the oxide surface: they facilitate oxidation of poisoning CO intermediates [21,29,30] and the overall increase of the electrochemically active surface area [31].

In the present work, we explore tungsten oxide nanorods [21] as high surface area active additives to dispersed catalytic nanostructured palladium. In addition to the existence of possible interactions between Pd and WO_3 capable of promoting oxidation of HCOOH directly to CO_2 and stabilizing Pd nanoparticles against their agglomeration [10,32,33], we expect additional activity form redox reactions of hexagonal tungsten oxide nanorods [21] leading to the formation of substoichiometric WO_{3-y} $(0 < y < 1)$ coexisting with H_xWO_3 $(0 < x < 1)$ and WO_3 at the electrocatalytic interface. Our electrochemical diagnostic experiments have involved cyclic voltammetric and chronoamperometric measurements in the solutions of formic acid in H_2SO_4 solutions. The results are consistent with the activating role of WO_3 nanorods on dispersed Pd nanoparticles during electrooxidation of formic acid. This observation may be of importance to the development of catalytic anode materials for direct formic acid fuel cells.

2. Experimental

Chemical reagents were analytical grade materials. They were deoxygenated by bubbling with high purity nitrogen. All solutions were prepared using doubly distilled and subsequently deionized (Millipore Milli-Q) water. Measurements were made at room temperature (22 ± 2 °C).

Palladium nanoparticles and Nafion were purchased from Sigma–Aldrich. Sulphuric acid and formic acid were obtained from POCh (Gliwice, Poland). Tungsten oxide (WO_3) hexagonal nanorodes were prepared by hydrothermal method from the solution (mixture) of Na_2WO_4, $2H_2O$, H_2O, C_6H_5—NH_2, HCl and Na_2SO_4 as described earlier [21]. Later 1.0 mg of WO_3 nanorods was dispersed in 0.1 cm^3 of deionized water using an ultrasonic bath for 1 h. To prepare catalytic layers composed of palladium nanoparticles and WO_3 nanorods, first 2 μl of the suspension of palladium nanoparticles (prepared by dispersing 7.1 mg of commercial palladium black via sonication for 120 min in 2.0 cm^3 of deionized water to obtain a homogenous mixture) was dropped onto the glassy carbon (GC) electrode surface and let dry in air at room temperature (22 °C) for 30 min. In the second step, 1 μdm^3 of the suspension of WO_3 was introduced onto the palladium nanoparticles. At the end, the electrode was conditioned by overcoating with 1 μdm^3 of Nafion solution (obtained by dissolving 5% commercial Nafion solution in ethanol at the 1–10 volume ratio). The loading of palladium nanoparticles was equal to 100 μg cm^{-2}.

Electrodeposition of conventional tungsten oxide film [24] was achieved on the GC electrode surface by immersion in 10 mmol dm^{-3} WO_3 + 2 mol dm^{-3} H_2SO_4 solution) and application of 25 full voltammetric potential cycles at 50 mV s^{-1} in the potential range potential from 0.04 to 1.04 V (vs. RHE).

All electrochemical measurements were done using CH Instruments Model 760D workstation (Austin, USA). The electrochemical experiments were performed in a conventional three-electrode cell. A glassy carbon disk electrode (geometric area, 0.071 cm^2) was used as the working electrode. The counter and the reference electrodes were carbon wire and saturated (K_2SO_4) Hg/Hg_2SO_4, respectively. All potentials are expressed vs. the reversible hydrogen electrode (RHE). Before modification, a working electrode was activated by polishing with successively finer grade aqueous alumina slurries (grain size 1–0.05 μm).

Transmission electron microscopy (TEM) images were obtained with JEM 1400 (JEOL Co., Japan, 2008) equipped with energy-dispersive full range X-ray microanalysis system (EDS INCA Energy TEM, Oxford Instruments, Great Britain) and high resolution digital camera (CCD MORADA, SiS-Olympus, Germany).

Scanning electron micrograph (SEM) images were obtained using the LEO 435 VP microscope (Rontec, USA) equipped with EDX analyzer.

3. Results and discussion

3.1. Morphology of WO_3 nanorods and palladium black

Fig. 1 shows the scanning electron micrographs, SEMs (Fig. 1a) and a transmission electron microscopic (TEM) image (Fig. 1b) of palladium black. It is apparent from the SEM and TEM data (Fig. 1a and b) that the Pd nanoparticles are of spherical shape and they exhibit some tendency to form agglomerates. Their sizes range from 10 to 20 nm. Fig. 2 illustrates SEM and TEM images of WO_3 nanorods. The results are consistent with the appearance of rod-like geometries typically of approximately 50–70 nm diameters and roughly 5 μm length.

3.2. Characterization of tungsten oxide in acid medium

Fig. 3 shows cyclic voltammetric responses of (A) the conventional [21] (electrodeposited) WO_3 film and (B) WO_3 nanorods recorded in 0.5 mol dm^{-3} H_2SO_4. As expected for the tungsten oxide electrodeposited system [23,24,26,27] (Fig. 3A), the voltammetric behavior of the conventional largely hydrated (dihydrate [24]) film is predominantly characterized by double reduction