



Short communication

Bi-modified palladium nanocubes for glycerol electrooxidation



Anna Zalineeva, Stève Baranton, Christophe Coutanceau*

Université de Poitiers, IC2MP, Laboratoire de Catalyse et Milieux Non-Conventionnels, UMR CNRS 7285, 4 Rue Michel Brunet, 86022 Poitiers, France

ARTICLE INFO

Article history:

Received 24 June 2013

Received in revised form 12 July 2013

Accepted 12 July 2013

Available online 19 July 2013

Keywords:

Adatoms

Bismuth

Glycerol oxidation

Nanocubes

Nanospheres

Palladium

ABSTRACT

Syntheses, surface modification by bismuth adatoms and activity towards glycerol electro-oxidation of preferentially-shaped Pd nanoparticles are described. High activity of {100} surface nanodomains is demonstrated, as well as changes in activity and selectivity induced by the presence of Bi adatoms.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The electrochemical conversion of glycerol gains more and more attention because glycerol is a by-product of biofuel industries, and for its potency for electric energy or hydrogen and added-value-chemical cogeneration [1]. Due to complex oxidation pathways a large number of useful chemicals may be produced [2]. The control of activity and selectivity can be provided by the electrode potential and the formulation of electrocatalysts. In alkaline medium, palladium is a catalytic metal active for the electrooxidation of small organic molecules [3–5]. Many electrocatalytic reactions on Pd surface are known to be structure-sensitive [6,7]. The activity and selectivity of Pd catalysts can also be tuned by modification with p-group atoms, such as Bi [8–10]. Here, the synthesis of preferentially-shaped Pd nanoparticles and their surface modification by spontaneous bismuth adsorption are described, as well as their activity towards glycerol electro-oxidation.

2. Experimental

Pd nanocubes and nanospheres were synthesized by a colloidal method derived from that developed by Xia et al. [11]. K_2PdCl_4 (Premion® 99.99%, Alfa Aesar) was dissolved in ultrapure water (18.2 M Ω , Milli-Q, Millipore), with PVP (polyvinylpyrrolidone, Mw ~ 55,000, Sigma-Aldrich) as stabilizer agent, and reduced with ascorbic acid (Reagent grade, Sigma-Aldrich) with KBr for nanocubes, without for nanospheres. The mixture was heated at 80 °C and the reaction was performed for 3 h. To remove the surfactant molecules,

the solution was dispersed in water and the nanoparticles were re-precipitated by addition of NaOH pellets (BioXtra, purity \geq 98 %, Sigma-Aldrich). A high shape selectivity and a narrow size distribution were obtained (10–12 nm edge length for Pd nanocubes and ca. 5 nm diameter for Pd nanospheres, Fig. 1a). Electrochemical experiments were conducted in 10^{-1} M NaOH (Semiconductor Grade 99.99%, Aldrich) or $5 \cdot 10^{-1}$ M H_2SO_4 (suprapur, Merk) supporting electrolyte in ultrapure water, deaerated by N_2 bubbling (U-quality, L'Air Liquide). The working electrode was a gold support with clean nanoparticles deposited from a suspension in water, the reference electrodes were reversible hydrogen electrodes (RHE). Before glycerol oxidation experiments, the Pd nanoparticle surface was checked by recording cyclic voltammograms (CVs) from 0.1 to 0.6 V vs RHE; these potential limits were chosen in order to avoid alteration of the surface structure through hydrogen evolution and absorption reactions, and Pd surface oxide formation.

3. Results and discussion

Voltammetric profiles recorded in acidic and alkaline media on Pd nanocubes and nanospheres (Fig. 1b) show redox peaks in the hydrogen adsorption/desorption and oxidation/reduction regions which could be assigned to different surface arrangements and surface oxidation states. These experiments highlight the influence of surface structure on hydrogen under potential deposition (H-UPD) profiles. The reversible peak recorded at ca. 0.25 V in acidic medium, less defined and reversible between 0.25 and 0.50 V in alkaline medium, is related to hydrogen adsorption/desorption on {100} surface nanodomains. It is more reversible and sharper in the case of nanocubes, which are expected to exhibit mainly {100} surface nanodomains, as observed

* Corresponding author. Tel.: +33 5 49 45 48 95; fax: +33 5 49 45 35 80.
E-mail address: christophe.coutanceau@univ-poitiers.fr (C. Coutanceau).

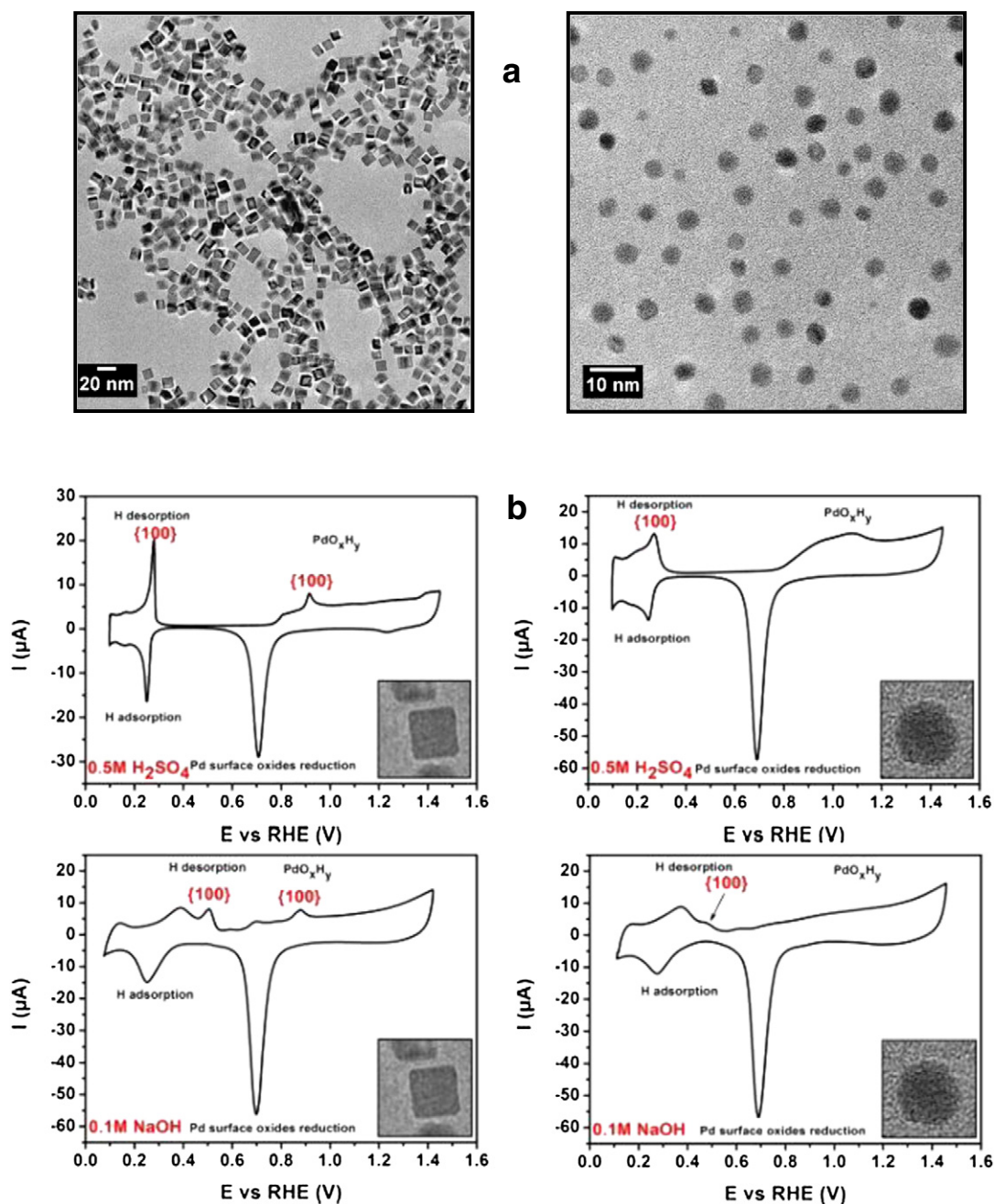


Fig. 1. (a) TEM images and (b) cyclic voltammograms of Pd nanocubes and nanospheres (scan rate = 5 mV s^{-1}).

for Pt nanocubes [12,13]. The onset potential of Pd surface oxidation occurs between 0.60 and 0.75 V, at lower potentials in alkaline medium than in acidic one. In the potential region of Pd surface oxide formation a sharp peak related to {100} facets is observed at 0.9 V in both acidic and alkaline electrolytes. After correction of the background current, the active surface areas calculated from the H desorption region in voltammograms recorded in acidic medium were 1.8 cm^2 and 1.3 cm^2 for Pd nanospheres and Pd nanocubes, respectively. This was confirmed by calculating the active surface areas from the Pd surface oxide reduction peak, assuming that a PdO monolayer is formed for an upper potential limit of 1.45 V vs RHE, leading to 2.1 cm^2 and 1.2 cm^2 for Pd nanospheres and Pd nanocubes, respectively.

Nanocubes are more active for the electrooxidation of 10^{-1} M glycerol in alkaline medium than nanospheres from ca. 0.55 V to 1.0 V as higher current densities are recorded over this potential range

(Fig. 2a). The glycerol electrooxidation voltammograms display the same general shape for both materials: a shoulder from 0.55 to 0.85 V and a main peak for higher potentials. The shoulder is more pronounced for nanocubes exhibiting higher density of {100} extended surface domains. We propose that the oxidation process occurring in this potential range is related to interactions between {100} surface domains and adsorbed species from glycerol.

At low glycerol concentrations (10^{-2} M and 10^{-3} M), three oxidative contributions are observed on Pd nanocubes (Fig. 2b). At 10^{-1} M glycerol, the oxidation peaks are shifted towards higher potentials, due to higher surface poisoning by species from glycerol adsorption. Indeed, for the lowest glycerol concentration, a current peak becomes visible in the 0.3 V to 0.4 V range corresponding to the first H desorption peak in the CV of Fig. 1b: the surface coverage by species from glycerol adsorption is lower. Moreover, the feature corresponding to H

Download English Version:

<https://daneshyari.com/en/article/6601582>

Download Persian Version:

<https://daneshyari.com/article/6601582>

[Daneshyari.com](https://daneshyari.com)