



Bare palladium nano-rosettes for real-time high-performance and facile hydrogen sensing

Jianli Zou, Lee J. Hubble¹, K. Swaminathan Iyer*, Colin L. Raston**

Centre for Strategic Nano-Fabrication, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA 6009, Australia

ARTICLE INFO

Article history:

Received 24 March 2010
Received in revised form 19 June 2010
Accepted 30 June 2010
Available online 3 August 2010

Keywords:

Palladium nanoparticles
Hydrogen sensing
Microfluidics
Process intensification

ABSTRACT

Surfactant free reduction of palladium using hydrogen gas at ambient pressure under continuous flow results in nano-rosettes of palladium built of 6 nm particles. These palladium nano-rosettes are effective real-time sensors of hydrogen gas via a simple drop cast technique.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The ever-growing relevance of hydrogen gas in modern technologies has initiated research towards the development of high-performance sensors with fast response times. Indeed, detecting and monitoring hydrogen gas with precision and accuracy is becoming an increasingly important issue for applications in chemical and petroleum refining, fuel cells and rocket fuels for spacecrafts. Furthermore, hydrogen in breath has also been reported as an important indicator in disease monitoring such as fructose malabsorption [1], fibromyalgia [2] and neonatal necrotizing enterocolitis [3,4]. Palladium has emerged as an important candidate for hydrogen gas sensing because of its ability to absorb high quantities of hydrogen and its highly selective response. In particular, palladium nanomaterials based chemical sensors have gained momentum recently due to their miniaturization potential and real-time monitoring capabilities. Additionally, rapid response times are observed due to the low energy barriers associated with

the diffusion of hydrogen into the high surface area to volume ratio nanomaterials. Sensing herein is based on the well-established principle that palladium spontaneously absorbs H₂ gas as atomic hydrogen which diffuses into the lattice to form palladium hydride, PdH_x, resulting in a α to β phase transition and a corresponding change in the lattice spacing. The change in phase and lattice spacing leads to a measurable resistance change of palladium material. The range of palladium nanomaterials reported for hydrogen sensing by monitoring the aforementioned change include Pd nanowires [5], Pd meso-wires [6], Pd films [7,8], Pd/carbon nanotube hybrids [9,10] and Pd/titania nano-hybrids [11]. While a few of the recently reported Pd-based sensors demonstrate impressive response times in milliseconds, they suffer drawbacks due to the limitations in scalability, reproducibility and multi-step assembly processes. A facile method which can overcome these issues, at the same time incorporating high-performance and fast response, is important for this technology to become viable. To this end we have developed a scalable method to fabricate surfactant free palladium nano-rosettes under continuous flow using a microfluidic platform and hydrogen gas as a reducing agent. We demonstrate that the high surface area of these unprotected, bare palladium nano-rosettes facilitate sensing hydrogen gas with high efficiency in real-time. Also of significance is that this involves a simple and inexpensive drop casting approach.

There are a few reports detailing the synthesis of Pd nanoparticles in aqueous solution with size and shape control in the presence of a surfactant or a capping agent [12,13]. However, for application in a hydrogen sensor a passivated Pd surface in the presence of a surfactant or a capping agent would result in a lag in response time and would lower the sensor the detection limits because of the

* Corresponding author at: Centre for Strategic Nano-Fabrication, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, M313, 35 Stirling Highway, Crawley, WA 6009, Australia. Tel.: +61 8 6488 4470; fax: +61 8 6488 1005.

** Corresponding author at: Centre for Strategic Nano-Fabrication, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, M313, 35 Stirling Highway, Crawley, WA 6009, Australia. Tel.: +61 8 6488 3045; fax: +61 8 6488 8683.

E-mail addresses: swaminatha.iyer@uwa.edu.au (K.S. Iyer), colin.raston@uwa.edu.au (C.L. Raston).

¹ CSIRO Materials Science and Engineering, Lindfield, NSW 2070, Australia.

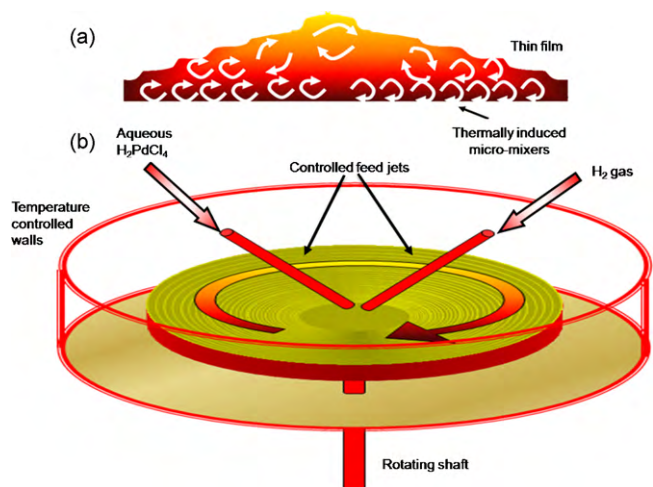


Fig. 1. Schematic representation of (a) the hydrodynamics of the fluid flow over a spinning surface and (b) a spinning disc processor (SDP).

reduction in active surface available for hydrogen adsorption [7,14]. A scalable fabrication technique devoid of surfactants will generate bare palladium nanoparticles with high surface area to volume ratio that would be poised for applications in sensing hydrogen in real-time. Hydrogen gas has been used as a reducing agent to produce Pd nanomaterials, from palladium(II) salts, albeit with long reaction times, and involving the use of surfactants and operating under high pressure [15–17]. Bubbling a solution of H₂PdCl₄ with hydrogen in a round bottom flask results in precipitation of large micron sized Pd particles that are colloidally unstable in water in the absence of a surfactant (see Supporting Information Fig. S1). “Process Intensification” offers alternative routes to preparing nanoparticles alleviating the obstacles of the relaxed fluid dynamic regime associated with conventional batch processes. The demand for intensified processing, of which spinning disc processing (SDP) is a subset, has led to the design and development of a range of reactors that offer operating conditions with rapid heat and mass transfer under continuous flow conditions with residence times reduced to seconds rather than minutes or hours. SDP offers a novel avenue for intensified nano-fabrication *via* exploiting the high centrifugal acceleration to generate thin films which provide rapid heat and mass transfers, Fig. 1a and b. The geometry and key elements of a SDP are illustrated in Fig. 1. The key components of SDP include: (i) a 100 mm rotating disc with controllable speed (up to 3000 rpm) and (ii) feed jets located at a radial distance of 5 mm from the centre of the disc. SDP generates a very thin fluid film (1–200 μm) on a rapidly rotating disc surface, within which nanoparticle formation occurs. Following injection, where the reagents contact close to the centre of the spinning disc, the fluid film initially experiences an increase in radial flow velocity whereupon the liquid is moving close to the disc velocity. The flow here becomes similar to the Nusselt model [18]. The shear forces and viscous drag between the moving fluid layer and the disc surface create turbulence and ripples which give rise to highly efficient turbulent mixing within the thin fluid layer. The turbulent waves thus generated can be a combination of circumferential waves moving from the disc centre to the disc periphery, and helical waves, depending on the operating parameters. The wavy thin film generated on a rotating disc surface in the presence of a gas, notably H₂, offers the ability to control the size of the ensuing particles by controlling the delivery of H₂ to the thin film. Recent reports highlight that waves generated in the fluid film over a moderately spinning disc speed clearly enhance the gas adsorption into the liquid [19–21]. The flow is accompanied by non-linear waves, which strongly influence the diffusion

boundary that develops beneath the surface of the film. The progressive waves are generated in the region of active micromixing and hence offer the proposed control necessary to synthesize bare Pd nanoparticles, Fig. 1a.

To the best of our knowledge, this is the first report detailing the use of H₂ gas as a reducing agent to make colloidally stable Pd nanoparticles in an aqueous thin fluid film. The technology offers a realistic route towards large-scale synthesis of bare Pd nanoparticles for applications in hydrogen sensing, in the present case.

2. Experimental

2.1. The synthesis and characterization of palladium nano-rosettes

In a typical synthesis of palladium nano-rosettes, the H₂PdCl₄ solution (0.6 mmol L⁻¹) was bubbled with argon 30 min and then was fed from one jet at the feed rate of 0.7 mL s⁻¹. Hydrogen gas was fed from another jet to reduce palladium(II) to palladium nanoparticles. The speed of the spinning disc was set at 1500 rpm. The as-synthesized nano-rosettes were washed using MilliQ water (>18 MΩ-cm) three times and re-dispersed in water before any further test. The size and morphology of the samples were determined using transmission electron microscopy (TEM, JEOL 3000F and JEOL 2000 FX II) operating at 300 and 80 kV, respectively. The powder XRD pattern of the palladium nano-rosettes was measured using an Oxford Diffraction Gemini-R CCD diffractometer (using Cu Kα = 1.54178 Å radiation).

2.2. The set-up and characterization of hydrogen gas sensor

In a 300–350 μm thick Si <1 0 0> n-doped wafer used in the sensor device was covered by a 300 nm insulating Si₃N₄ layer deposited using Plasma Enhanced Chemical Vapour Deposition. The interdigitated electrode pattern was transferred by using photolithography, which was followed by depositing a 5 nm chromium binding layer and a 50 nm gold layer using an in-house built metal evaporator system (more details about IDE see Supporting Information). The palladium nanoparticle solution was drop cast onto the surface of each IDE using aliquots of 0.02 μL from a 0.5 μL glass syringe which were subsequently air-dried. The test procedure involved alternating nitrogen gas (20 min) and varying concentrations of hydrogen gas (4 min). The change of the current was monitored at the same time. The total flow rate of gas was 1000 mL min⁻¹. The voltage applied between electrodes was 100 mV dc. The images of the sensors were recorded using a scanning electron microscope (SEM, Zeiss 1555 VPSEM) operating at an accelerating voltage of 10 kV.

3. Results and discussions

3.1. Characterization of palladium nano-rosettes

A typical representation of the Pd nanoparticles obtained using the above technique can be seen from Fig. 2a. Interestingly, the Pd nanoparticles show a rosette structure which is comprised of many smaller nanoparticles in an ordered agglomeration pattern. The size of the individual Pd nanoparticles which construct the rosette is about 6 nm, Fig. 2b. The crystallinity of the nano-rosettes was confirmed using high-resolution transmission electron microscopy (TEM), Fig. 2c. Additionally, the XRD pattern of the palladium nano-rosettes measured with a CCD diffractometer (using Cu Kα = 1.54178 Å radiation) agreed with the Pd Card (JCPDS card No. 05-0681), Fig. 2d, which indicated a high crystallinity of the palladium nanoparticles synthesized using SDP. We believe that in the absence of a capping agent, the high surface free energy pal-

Download English Version:

<https://daneshyari.com/en/article/740970>

Download Persian Version:

<https://daneshyari.com/article/740970>

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