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Nanostructures of Pd–Ni alloy deposited on carbon fibers for sensing hydrogen

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ABSTRACT

Pd–Ni alloy nanofilm and nanoparticles with various sizes have been electrodeposited on carbon fibers through controlling potential pulses. The two types of Pd–Ni alloy nanostructures can be used to detect hydrogen gas at room temperature. The dependence of H_2 sensing behavior on sizes of the nanofilm and nanoparticle has been discussed. The results show that response time decreases with hydrogen concentration increasing. In the two ranges of 0–2.8% and 3.6–6% H_2 gas surroundings, response of nanofilm increases with hydrogen concentration, but slightly decreases after exposure to 2.8–3.6% H_2 due to rearrangement of the particles in the nanofilm sensor. For nanoparticles sensor, response increases with hydrogen concentration between 0% and 6%. Both of them display good stability and reversibility. H_2 sensing by the Pd–Ni alloy nanostructures depends on the synthesis of volume expansion of the particles or film, the change of energy barrier at the interface and formation of Pd–H in H_2 gas. The recovery time is shorter in air due to the presence of oxygen than in pure argon.

1. Introduction

Recently, owing to the hot wave of "hydrogen economics", palladium nanomaterials have been extensively studied in the hydrogen-related fields due to their remarkable perm-selectivity for hydrogen and excellent catalytic properties. For example, Pd nanofilms, nanowires and nanoparticles [1–3] have been widely applied in hydrogen sensors. Many methods have been applied to prepare of different nanostructures, including thermal evaporation [4], electroless technique [5], electrochemical step-edge decoration [6,7], self-assembly [8], sputter deposition [9], and so on. There are many types of hydrogen sensors applied the Pd nanomaterials based on different mechanisms, such as fiber optic type [10], electrochemical type [11], hot wire type [12], resistance type [13]. Hydrogen sensors of resistance type have received interests and attention due to low power consumption, low operating temperature, high hydrogen selectivity, high sensitivity and long service life. Luongo and co-workers [14] reported a novel, resistance-based porous silicon sensor with Pd nanostructures as hydrogen sensing layer. This sensor was tested in the range of 0–1.5% hydrogen. It was observed that the sensor demonstrated a significant decrease in resistivity with respect to time when exposed to hydrogen. Kiefer et al. [15] developed a single nanotrench by focused ion beam milling in an evaporated palladium microwire. In the presence of H_2, the trench displayed electrical connection of the initially separated parts of the wire due to the volume increase of the material. Therewith, an electrical current can be switched through the wire.

Despite the superior sensitivity of Pd-based hydrogen sensors, they have several drawbacks. For example, volume expansion by hydrogen absorption causes changes in the structure of Pd thin film and results in hysteresis behavior in electrical resistance [16]. The concentration range of hydrogen adsorption on pure palladium is limited. In addition, the phase transition from α phase of Pd to the "hydride" β phase occurs at fairly low hydrogen partial pressures, and this transition leads to irreversible structural changes in Pd [17,18]. These obstacles can be avoided if adding other metals to form palladium alloy such as Pd–Mg [19], Pd–Au [20], Pd–Ag [21], and Pd–Ni [22–24]. Among these Pd alloys, the Pd–Ni alloy can be used to make excellent H_2 sensors, which respond rapidly and reversibly at room temperature and resist poisoning by H_2S.

Carbon fiber (CF) is a very attractive substrate for electrical signal transduction in miniaturized electrochemical sensors due to the unique advantageous features such as the small dimensions (5–30 μm), low capacitive current, good biocompatibility, low cost, high abundance. Thus, the use of CF-based heterostructures along with that of 1-D metal oxides over Pt- or other noble metal-based electrodes could be a great promising direction to effectively fabricate the electrochemical devices or sensors with high catalytic activity owing to the easy enhancements of their chemical, mechanical, electrical, and optical properties compared to their own physicochemical properties. Tonezzer et al. [25] reported zinc oxide nanowires on carbon microfiber as flexible gas sensor. Im et

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al. [26] reported that Glucose-sensing electrodes were constructed from carbon fibers by electrospinning and heat treatment. Hsiao [27] reported a single carbon fiber for sensing the thermomechanical behavior of an epoxy during the cure cycle. By recording and analyzing the electrical resistance and temperature history of a carbon fiber embedded inside an epoxy specimen during the cure cycle, the interaction between the carbon fiber and the surrounding polymer can be revealed. This embedded carbon fiber sensor approach successfully detects the glass transition zone covering the final transition temperature, the main transition temperature, and the starting transition temperature. Kang and co-workers [28] reported highly efficient electrocatalytic activities of single crystalline RuO_2 nanorods grown on carbon fiber.

In this work, Pd–Ni alloy nanofilm and nanoparticles synthesised on carbon fibers via electrodeposition have been studied for hydrogen gas sensing applications at room temperature. Scanning electron microscopy is applied to characterize the as-prepared samples and energy dispersive X-ray spectrometer is applied to measure the Ni content of the Pd–Ni alloy nanostructures. The response time and response are measured in hydrogen with various concentrations. The effect of air as desorption gas is also studied.

2. Experimental section

2.1. Preparation of carbon fiber template

The polyacrylonitrile carbon fiber obtained by carbonizing polyacrylonitrile was applied as template material to deposit nanostructures. It is a kind of fasciculus which consists of thousands of single carbon fibers with 7 μm diameter of each. Compared with other template materials such as Highly Oriented Pyrolytic Graphite (HOPG) and Anodic Aluminum Oxide (AAO), the use of carbon fiber as substrate can solve the problem in electrical connection and the sensor fabrication. Electrodeposition method is easier to implement than aforementioned methods and the size of the nanostructure can be well controlled. Pretreatment of polyacrylonitrile carbon fiber is necessary before electrodeposition since there are many contaminants on the surface of carbon fibers. If the pretreatment is unsuccessful, the residual contaminants can result in poor adhesion between deposits and carbon fibers. Some contaminants on carbon fibers are removed in alcohol. Burning of polyacrylonitrile carbon fiber in air for a short time is an effective way to remove contaminants, and the burned carbon fibers are soaked in sulfuric acid solution containing some oxidation agent to roughen surface of carbon fiber and enhance surface hydrophilicity.

Briefly, the pretreatment steps included: firstly, carbon fibers were burned in a muffle at 380 °C for 30 min for ungluing; secondly, the burned carbon fibers were soaked in alcohol for 20 min for degreasing; thirdly, the cleaned carbon fibers were pickled in 200 g dm^{-3} $(NH4)_2S_2O_8$ + 100 cm^3 dm^{-3} H_2SO_4 for 35 min for coarsening surface; finally, distilled water was used for rinsing the treated carbon fibers. The SEM image of the prepared carbon fiber is presented in Fig. 1.

2.2. Fabrication of Pd–Ni alloy nanofilm and nanoparticles

A solution composed of 70 mmol dm^{-3} $Pd(NH_3)_4Cl_2$ + 30 mmol dm^{-3} $NiSO_4 \cdot 6H_2O$ + 0.2 mol dm^{-3} NH_4Cl, pH 8.5 was used as electrolyte for deposition of Pd-Ni alloy nanostructure. All of potential values mentioned in this paper were referred versus saturated calomel electrode. Three potential pulses were applied to deposit nanofilm: an oxidation pulse of +0.8 V for 5 s, a negative reducing nucleation pulse of −1.0 to −1.5 V for milliseconds and a growth pulse of −0.3 to −0.45 V for several minutes. Oxidation potential pulse optimized carbon fiber surface, nucleation resulted in highly dense Pd–Ni alloy tiny crystal nanoparticles on the surface, and slow growth connected the tiny isolated nanoparticles to form nanofilm, and then a compact thin nanofilm was obtained. Single potential pulse was applied to deposit nanoparticles at −0.4–−0.5 V for several hundreds seconds. Nanoparticles could be fabricated on the carbon fiber surface and gradually grew bigger.

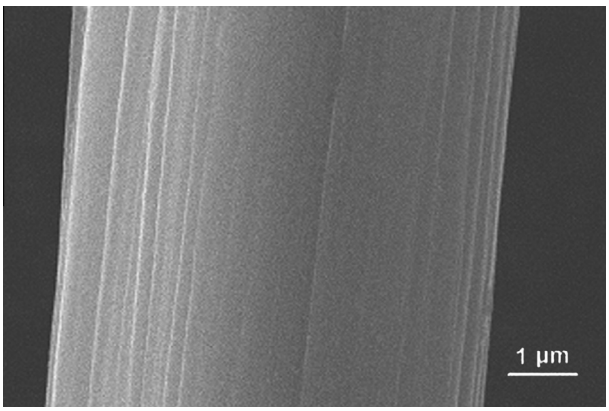

Fig. 1. Surface morphology of carbon fiber with step edges.

2.3. Hydrogen sensing

Three carbon fibers were picked out from those carbon fibers deposited Pd–Ni alloy nanostructure, then placed two Cu electrodes on the three elected carbon fibers with a gap of ~5 mm, and made sure the carbon fibers were parallel to one another. Original electrical resistance of three carbon fibers without electrodeposition is about 790 Ω. The device was placed into a 2.5 cm^3 sealed glass chamber with gas inlet/outlet ports, and the whole experimental setup for hydrogen measurement is displayed in Fig. 2. In this article, to avoid interference of complex gas and study behaviors of Pd–Ni alloy nanofilm and nanoparticles in H_2, we chose argon as the carrier gas like many researchers' choice [3,23,29]. The concentration of hydrogen in argon was adjusted from 0% to 10% (V/V) by blending commercially standard H_2–Ar mixture with pure argon through a gas-blending system. At first, pure argon passed through the sample chamber and a steady baseline current signal appeared. Subsequently, the adjusted H_2–Ar gas let into the sample chamber till a steady response current occurred. Stopped the adjusted gas and started to input pure argon again till the original baseline current recovered. The above operation was repeated to test sensitive performance of sensors in various hydrogen concentrations.

While the gas was flowing through the sample chamber in measurement system, a 5 mV potential was applied to the two terminals of carbon fibers with Pd–Ni alloy nanostructures using a CHI 660B electrochemical workstation controlled by a computer. All experiments were operated at room temperature (~25 °C). The response current was measured through the nanostructures with or without absorption of hydrogen at fixed 5 mV in voltage and the resistance value was calculated according to Ohm's law.

3. Results and discussion

3.1. Electrodeposition of nanofilm and nanoparticles

Using two electrodeposition methods of three potential pulses and single potential pulse can get two Pd–Ni alloy nanostructures of nanofilm and nanoparticles on carbon fibers respectively. Previous work in our group [30] has proved that on HOPG piece continuous nanowires could be obtained under three potential pulses, while on carbon fibers thin Pd–Ni alloy nanofilm was obtained with this method. Fig. 3a shows the SEM image of the nanofilm with thickness of about 400 nm synthesised under three potential pulses of +0.8 V oxidation for 5 s, −1.2 V nucleation for 20 s and −0.35 V growth for 300 s. The Ni content of the Pd–Ni alloy nanofilm is about 8.5 wt.%. Nucleation produces large numbers of Pd–Ni alloy nuclei on the surface of carbon fiber. Then the tiny particles expand their size through growth. As a result, the nanofilm looks continuous, but a lot of small gaps exist in it.

Fig. 3b shows the SEM image of the nanoparticles synthesised under single potential pulse of −0.5 V for 300 s. Many nanoparticles distribute on the surface of carbon fiber, the average particle diameter is about 250 nm, and the Ni content is about 8.5 wt.%.

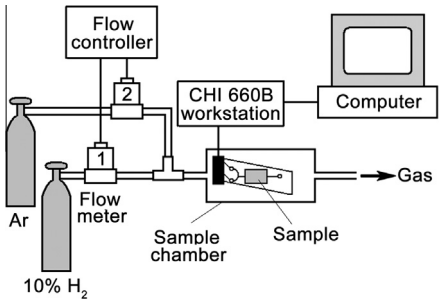

Fig. 2. Block diagram of the experimental setup of hydrogen detection.