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Sensors

NICKEL-PALLADIUM NANOPARTICLES FOR NONENZYMATIC METHANOL DETECTION

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Silicon microchannel plates (MCP) modified by nickel-palladium nanoparticles (Ni-Pd|Si-MCP) have highly ordered microchannels with uniform diameters and lengths isolated and parallel to one another and are excellent sensors for the determination of methanol in alkaline solutions. The 3D ordered Si MCP is fabricated by electrochemical etching used as the backbone, and the Ni-Pd nanoparticles are sensitive materials for detecting methanol that was obtained by an electroless plating method. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and electrochemical methods were employed to characterize the Ni-Pd|Si-MCP structure. An electrochemical workstation was used to monitor the sensing characteristics of the Ni-Pd|Si-MCP electrode. As a result of the synergetic effects rendered by the MCP and Ni-Pd nanoparticles, these sensors present a high sensitivity of 0.168 mA mM^{-1}, and the detection limits was 12 μM. In particular, since the fabrication process is compatible with conventional silicon technology, the structure has immense potential as an efficient, nonenzymatic, and integrated methanol sensors.

Keywords: Nanocomposites; Porous materials; Semiconductors; Sensors

INTRODUCTION

Methanol has widespread applications but is toxic if ingested therefore, it is important to develop a reliable and selective methanol sensor. Traditionally, detection of methanol is accomplished by Fourier transform infrared (FTIR), chromatography and electrochemical methods (Bangalore et al. 1994; Qin and Cadet 1997; De Paula et al. 1999). Electrochemical techniques are the most popular due to high sensitivity, rapid turnaround, and low cost and most electrochemical methods utilize

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enzyme electrodes (Liu and Kirchhoff 2007; Wu et al. 2007; Guo and Dong 1997; Zhang et al. 1999; Konash and Magner 2005). Although some of these prototype sensors exhibit low detection limit, excellent sensitivity, and high stability, the instability of enzymes under harsh conditions such as high temperature or presence of toxic chemicals poses practical concerns. An electrocatalyst with higher activity and low cost is one of the key components in electrochemical sensors. To solve this problem, there are two major strategies. The first approach involves the use of new non-platinum catalyst materials to pare cost in mass production such as Ag, Ni, or Co (Sawai and Suzuki 2004; Coutanceau et al. 2006) and the second means is to utilize catalytic supporting materials to achieve high dispersion, utilization, activity, and stability. Owing to the inherent advantages of silicon-based nanomaterials having unique semiconducting, mechanical, and optical properties, as well as chip integration capability with other electronic components, many small-scale prototype sensors have been produced by silicon-based microfabrication techniques. Silicon nanowires were popular used as the backbone in this field, silicon nanowires as support for metal nanocatalysts in electrode materials exhibits excellent performance in electro-oxidation of alcohol. However, due to the bound-like structure, it is difficult, or perhaps even unrealistic, to achieve fast redox couples, faradaic currents which depend significantly on the active area of the 3-dimensional (3D) structure.

Silicon microchannel plates (MCP) consist of many closely packed channels with a common diameter. It had been reported that Silicon microchannel (Si-MCP) having better performance than conventional porous materials for their macro-porous and ordered channel. Modification of the silicon MCP inner wall with metals can improve the humidity sensing behavior drastically (Miao et al. 2010a). The channels are ordered and parallel to each other thereby providing effective pathways for gas transport. In addition, the high aspect ratio leads to beneficial surface properties which appeal to integrated microfluidics, fuel cell, optoelectronics, sensors, and actuators.

In this paper, we report the dispersion of nickel-palladium nanopaticles on silicon MCP and evaluate the methanol sensing capability in alkaline media. In order to minimize silicon corrosion, nickel is deposited by electroless plating. The synergetic effects of the Ni-Pd nanoparticles and silicon MCP give rise to excellent methanol sensing capability.

EXPERIMENTAL

P-type <100> silicon wafers were used as the substrate to fabricate the MCPs. Details of the electrochemical process can be found in references 8 and 9. Namely, the wafer was first thermally oxidized to form a SiO_2 layer and then patterned using lithography to define square open regions on the front side. Etch the windows by hydrofluoric acid buffered solution. Create pyramidal notches by tetramethyl ammonium hydroxide etching. At last, the silicon MCPs was formed by photo-assisted electrochemical etching. Silicon MCPs with a depth of about 150 μm and side length of each channel of about 5 μm were plated with nickel-palladium nanoparticles by electroless plating (Chen et al. 2008; Lin et al. 2009; Tao et al. 2009). The entire surface of the silicon MCP was uniformly coated

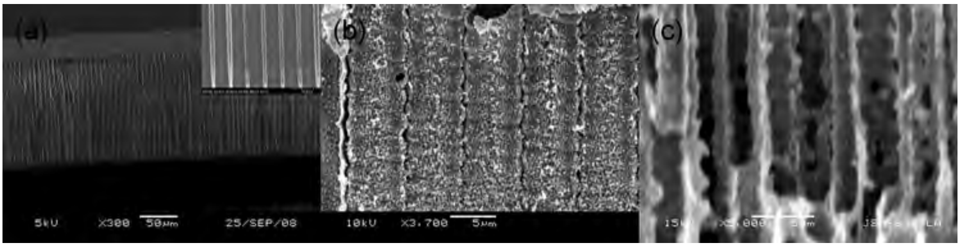

Figure 1. (a) SEM images of the microstructure of the Si-MCP, (b) Cross-sectional SEM images of the Ni-Pd/Si-MCP, and (c) Cross-sectional SEM images of the microstructure of the Ni-Pd/Si-MCP after electrochemical measurement.

with nickel-palladium particles by immersion in a plating bath for 25 min. An LK3200A electrochemical workstation (Tianjin, China) was used to monitor the sensing characteristics of the Ni-Pd/Si-MCP electrode. The measurement was carried out by the successive injection of different concentrations of methanol to the electrolyte. All the chemicals were analytical grade and the experiments were performed at around 25°C.

RESULTS AND DISCUSSION

Figure 1(a) depicts the SEM image of the silicon MCP, the magnify cross-section of MCP was shown in the inset. Figure 1(b) is the corresponding magnified picture of the cross-sectional image after electroless nickel-palladium plating. The silicon MCP and Ni-Pd/Si-MCP which possess highly ordered microchannels with uniform diameter and length are well isolated and parallel to one another. After electroless plating, a thin nickel/palladium layer was formed on the silicon MCP surface. Figure 1(c) is the magnified picture of the cross-sectional SEM image after electrochemical measurement and shows that the microstructure and morphology are not altered much. Thus, it can be inferred that the Ni-Pd/Si-MCP structure is stable in alkaline media. The EDS results in Fig. 2 show that the layer on the sidewall of the

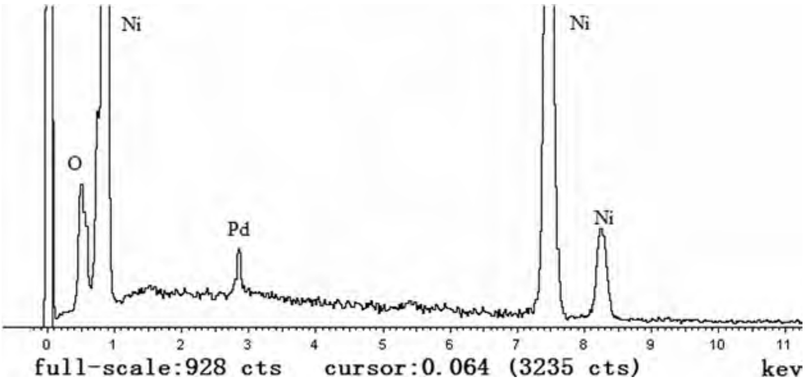

Figure 2. Corresponding EDS image of the structure in Fig. 1(b).

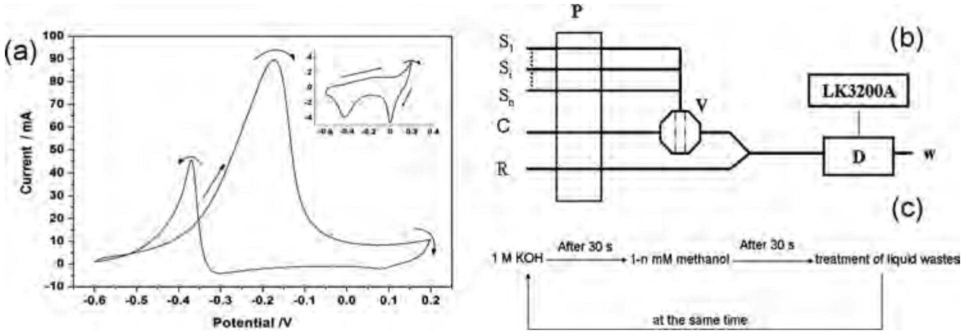

Figure 3. (a) Cyclic voltammograms of the Ni-Pd/Si-MCP in 1 M methanol and 1 M KOH acquired at a scanning rate of $50\,\mathrm{mVs}^{-1}$ [without methanol shown in inset of Fig. 3(a)]. (b) Schematic diagram of the methanol sensing detection system, where $S_1,\ldots,S_n$, represent the solutions with different concentrations of methanol (1 mM, 2 mM, 3 mM, 4 mM, ...), C is the electrolyte of 1 M KOH solution, R is deionized water, V is the 6-channel valve, P is the peristaltic pump, D is the tri-electrode cell, and W is the channel of bleed waste liquor. (c) Injection order of the electrolyte solution.

channel consists of mainly Ni and Pd with some O and reveal that the surface on all channels is fully covered by Ni-Pd.

Figure 3(a) shows the cyclic voltammograms of the Ni-Pd/Si-MCP composite in 1 M methanol and 1 M KOH at a scanning rate of $50\,\mathrm{mVs}^{-1}$. The cyclic voltammograms of the Ni-Pd/Si-MCP electrode in 1 M KOH in the absence of methanol is shown in the inset of Fig. 3a.

In the CV obtained in the 1 M KOH solution, the hump observed from the Ni-Pd/Si-MCP electrode in the potential region from −0.2 to 0 V has a broad shoulder, and two reduction peaks exist at potentials −0.42 V and 0 V, respectively. Multiple scans of the shape showed no change, which indicate the electrode is very stable. After 1 M methanol was added in the potential range of $-0.6\,\mathrm{V} \sim 0.2\,\mathrm{V}$, the CV exhibited two well-defined current peaks in the forward and reverse scans. The Ni-Pd/Si-MCP electrode showed electro-oxidation of methanol starting at −0.55 V and a maximum peak at −0.17 V. After reaching the maximum, the current density decreased due to the formation of oxide on the catalyst surface and the catalyst activity was degraded. Another current density peak was observed at −0.36 V during reverse scanning and it signified desorption of CO generated by methanol oxidation (Bhaskaran et al. 2009). The negative onset potential and magnitude of the peak current in the forward scan suggested better electrocatalytic activity for methanol in the alkaline medium. The peak in the anodic sweep was more sensitive than that in the cathodic sweep, and so the potential corresponding to the peak in the anodic sweep was chosen in our subsequent experiments to evaluate the efficacy of methanol determination by using various concentrations of methanol.

Figure 3(b) shows the schematic diagram of the methanol sensing detection system. During the experiments, different concentrations of methanol were injected through S by the peristaltic pump P. The current was continuously monitored at a potential of −0.1 V and the injection order is shown in Fig. 3 (c).

Figure 4 shows the catalytic current versus methanol concentration. The current increased with higher methanol concentration and the electrode also responded

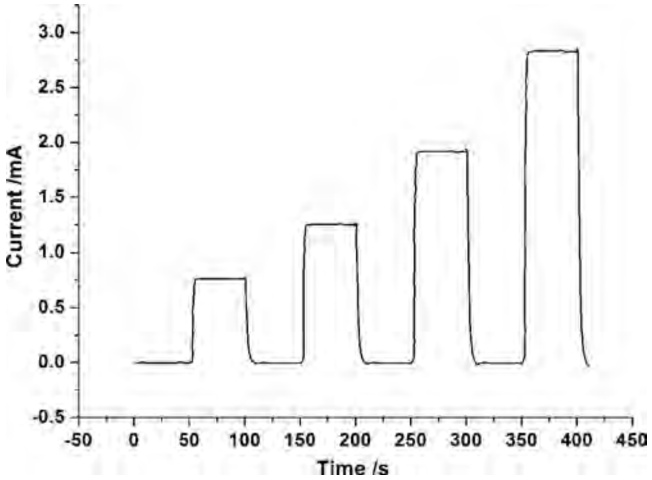

Figure 4. Relationship between the catalytic current and methanol concentration.

quickly to the addition of methanol. The response time and recovery time measured from the Ni-Pd/Si-MCP nanocomposite were about 7 s and 9 s, respectively, as indicated in Fig. 5. The good linear relationship between the current and methanol concentration is presented in Fig. 6. The fitted equation has the form of $J = 0.2553 + 0.16804x$ with a relative correlation coefficient of 0.998. The sensitivity calculated from the calibration curve was 0.168 mA mM^{-1} and the lowest concentration of glucose that can be detected was 12 μM.

Additional measurements were conducted by placing the Ni-Pd/Si-MCP nanocomposite in an electrolyte solution of 1 M KOH together with 5 mM methanol to assess the stability and the chrono-amperometric response was monitored. No obvious decay was observed from the peak current even after 500 cycles. Furthermore,

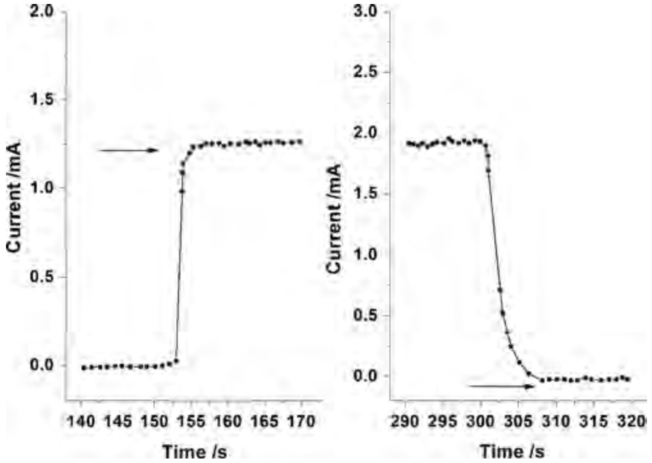

Figure 5. Response time and recovery time of the Ni-Pd/Si-MCP.

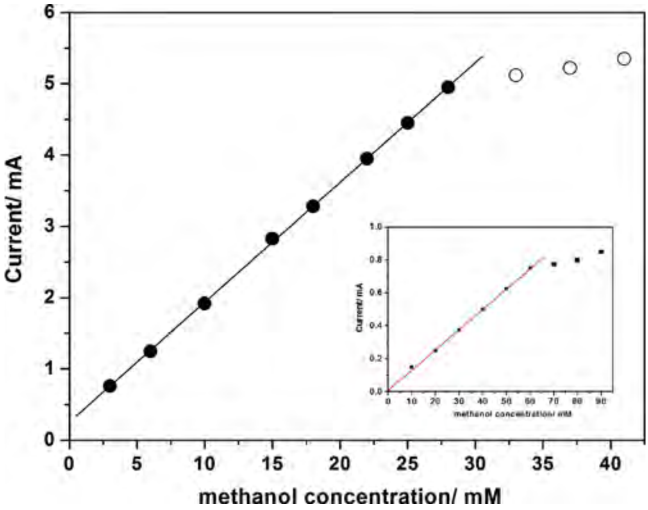

Figure 6. Relationship between the current and methanol concentration. (Figure available in color online.)

the reproducibility measured similarly at a fixed potential of –0.2 V. The relative standard deviation (RSD) was 2.8%, which can be inferred that the Ni-Pd/Si-MCP electrode has excellent electrochemical stability.

Our results reveal that the Ni-Pd/Si-MCP electrode had sensitivity to methanol. This can be attributed to the synergetic effects of the Ni-Pd nanoparticles and silicon MCP (Miao et al. 2010a). First of all, the Ni-Pd nanoparticles serve as a good catalyst in methanol oxidation. Secondly, the silicon MCP acts as a backbone to provide a large area of active surface while bearing the weight of the Ni-Pd sensing materials. Last, but not least, the composite Ni-Pd/Si-MCP electrode prevents silicon corrosion in alkaline media.

CONCLUSION

A Ni-Pd/Si-MCP array electrode is constructed by electrochemical etching and electroless plating. The sensor responds sensitively to methanol and has good stability, reproducibility, as well as short response and recovery time. These merits suggest that the Ni-Pd/Si-MCP electrode is a promising nonenzymatic methanol sensor, and the compatibility of the fabrication process with microelectronics enables easy and large-volume industrial adoption.

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