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ON-CHIP SUPERCAPACITOR ELECTRODE BASED ON POLYPYRROLE DEPOSITED INTO NANOPOROUS AU SCAFFOLD

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Abstract. On-chip supercapacitors hold the potential promise for serving as the energy storage units in integrated circuit system, due to their much higher energy density in comparison with conventional dielectric capacitors, high power density and long-term cycling stability. In this study, nanoporous Au (NP-Au) film on-chip was employed as the electrode scaffold to help increase the electrolyte-accessible area for active material. Pseudo-capacitive polypyrrole (PPY) with high theoretical capacitance was deposited into the NP-Au scaffold, to construct the tailored NP-Au/PPY hybrid on-chip electrode with improved areal capacitance. Half cell test in three-electrode system revealed the improved capacitor performance of nanoporous Au supported PPY electrode, compared to the densely packed PPY nanowire film electrode on planer Au substrate (Au/PPY). The areal capacitance of 37 mF/cm²~10 mV/s, 32 mF/cm²~50 mV/s, 28 mF/cm²~100 mV/s, 16 mF/cm²~500 mV/s, were offered by NP-Au/PPY. Also, the cycling performance was enhanced via using NP-Au scaffold. The developed NP-Au/PPY on-chip electrode demonstrated herein paves a feasible pathway to employ dealloying derived porous metal as the scaffold for improving both the energy density and cycling performance for supercapacitor electrodes.

1. Introduction

supercapacitor has been attracting tremendous interest owing to its advantage in high power density and long cycling stability [1]. Recently, the promising application of supercapacitor in micro-electro-mechanical-system (MEMS) has been posed and acknowledged as a feasible route to replace the widely used micro-battery that is suffering poor cycling life and low charge/discharge rate [2]. On-chip supercapacitor device therefore becomes the focal point in energy storage field.

At the current stage, one main obstacle in the further development of on-chip supercapacitors is their insufficient energy density [3]. The mainly employed carbon-based active electrodes for on-chip supercapacitors store energy based on double layer mechanism, of which the areal capacitance is still low ranging from several hundred μ F to several mF [4]. To use pseudo-capacitive active materials with high theoretical capacitance for on-chip supercapacitors has been regarded as one effective route to energy enhancement. PPY, one typical conductive polymer has been well studied as pseudo-capacitive material and successfully used in on-chip supercapacitor device [5]. In this study, we demonstrated nanoporous Au film on-chip was used as the electrode scaffold to help increase the electrolyte-accessible area for PPY, and thus realize a high areal capacitance on-chip supercapacitor electrode.



2. Experimental

Alloy thin films ($\sim\text{Au}_{0.3}\text{Cu}_{0.7}$) with the given thickness of 750 nm were deposited on the silicon wafers via co-sputtering of Au (DC-model, 35 W) and Cu (RF-model, 200 W) using a AJA sputter. To selectively etch Cu component, the alloy films coated silicon wafers were dipped in concentrated nitric acid (70 vol%) at room temperature for 3 hours. Afterwards, the thoroughly cleaned porous Au film coated Si wafer was used as the substrate for deposition of active material PPY. The electrochemical deposition of PPY was performed in three-electrode setup, at a constant current density of 1 mA/cm^2 for 10 min, in the plating bath: 0.2 M phosphate buffer (pH = 6.86) containing 0.2 M pyrrole and 0.02 M p-toluenesulfonate acid.

Conventional three-electrode system was employed to study the supercapacitor performance. Pt counter electrode, and Ag/AgCl (in saturated KCl) reference electrode were used for test. A Zahner IM6 electrochemical workstation was used for electrochemical measurements. Cyclic voltammograms (CV) were conducted in 1 M Na_2SO_4 electrolyte. Electrochemical impedance spectra (EIS) were measured over the frequency range from 100 kHz to 100 mHz with an AC perturbation of 10 mV at the open circuit potential. The areal specific capacitance of the on-chip electrodes was calculated by integrating the CVs.

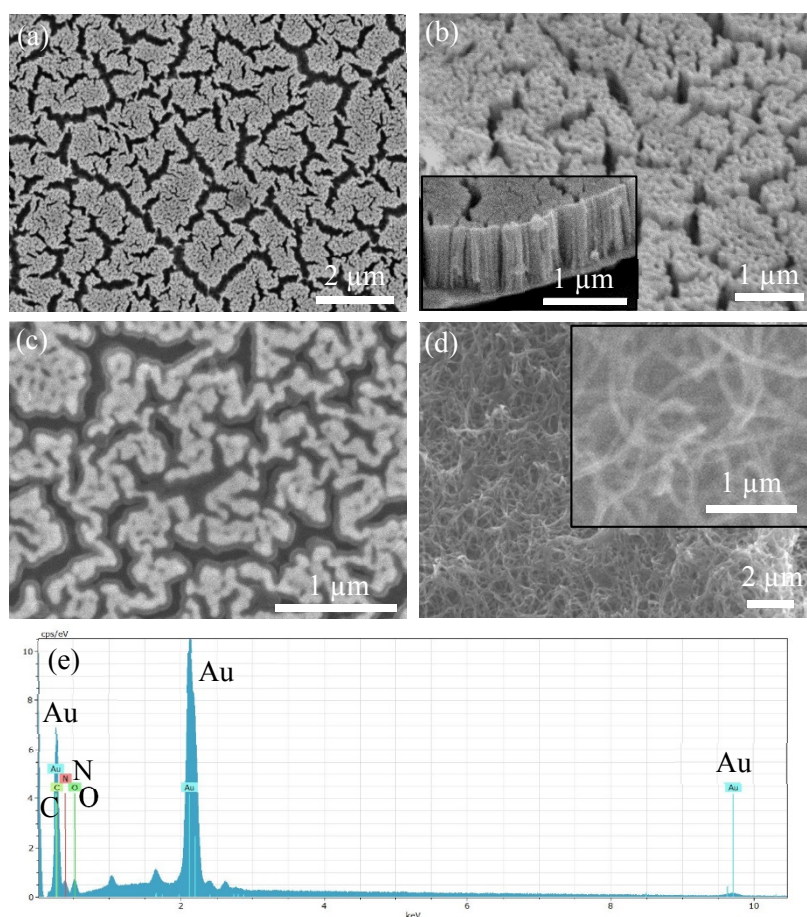


Figure 1. SEM images of (a-b) NP-Au, (c) NP-Au/PPY, (d) Au/PPY. (e) EDX result of NP-Au/PPY

3. Results and discussion

Figure 1(a-b) are SEM images of the obtained NP-Au film after selective etching of Cu component in the alloy film. It can be found that hierarchical porous Au scaffold with both macropores ($> 50 \text{ nm}$) and mesopores ($2\sim 50 \text{ nm}$) was obtained. From the inset SEM image in Figure 1b, the real thickness was estimated to be 700–800 nm, in accordance with the given thickness ($\sim 750 \text{ nm}$) in the sputtering operation. When employed as electrode scaffold, the nanoporous structure could endow large surface areas and favourable pathways for electrolyte ion diffusion. After electro-deposition, the PPY coating

with the thickness less than 10 nm was grown into the nanopores of NP-Au scaffold, as shown in Figure 1c. The successful growth of PPY can also be confirmed by the EDX (energy dispersive X-ray) analysis, shown in Fig. 1e. Besides the Au signal, C, N, O elements can also be detected. C, N signals are the main element components of PPY, while the O element is from the doped anions in PPY matrix. Without the NP-Au scaffold, densely aggregated PPY nanowires are formed on the flat Au film, as shown in Figure 1d, with the diameter of 50~100 nm (see inset).

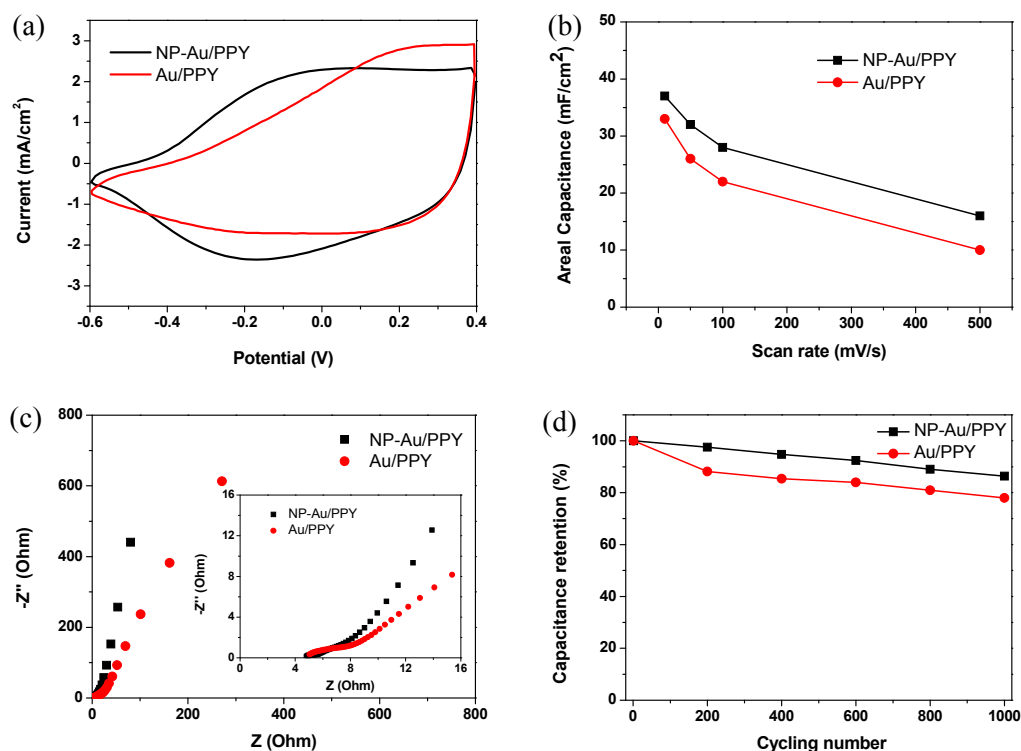


Figure 2. Supercapacitor performance of NP-Au/PPY and Au/PPY: (a) CV at a scan rate of 50 mV/s, (b) Capacitance at varying scan rates, (c) EIS study, and (d) cycling performance at 100 mV/s

Half cell test in three-electrode system revealed the improved supercapacitor performance of NP-Au/PPY compared to the densely stacked PPY nanowire electrode on planer Au substrate. The pseudo-capacitive character of PPY was displayed by Figure 2a, characterized by the existence of prominent redox peaks that is distinct from the carbon-based electric double layer electrode. The larger enclosed CV area of NP-Au/PPY than that of Au/PPY also indicated the larger capacitance can be realized by NP-Au/PPY electrode. As for on-chip supercapacitors, areal capacitance and volumetric capacitance should be the most valuable indicator to evaluate their capacitance, rather than gravimetric capacitance. Therefore, only the capacitance data per unit area and volume are presented herein. The calculated areal capacitance at varying scan rates is presented in Figure 2b. The areal capacitance of 37 mF/cm²~10 mV/s, 32 mF/cm²~50 mV/s, 28 mF/cm²~100 mV/s, 16 mF/cm²~500 mV/s, were offered by NP-Au/PPY. While Au/PPY electrode delivered the areal capacitance of 33 mF/cm²~10 mV/s, 26 mF/cm²~50 mV/s, 22 mF/cm²~100 mV/s, 10 mF/cm²~500 mV/s. Considering the thickness of Au scaffold part (~750 nm), very high volumetric capacitance can be attained by NP-Au/PPY (493 F/cm³~10 mV/s, 213 F/cm³~500 mV/s). The employed NP-Au scaffold can help increase the electrolyte-accessible area for active materials, and thus led to the capacitance enhancement. EIS study (Figure 2c) was employed to illustrate the improved supercapacitor performance of NP-Au/PPY compared to Au/PPY. The quasi semi-circle part in the high-frequency range of Nyquist plot characterizes the charge transfer resistance at the electrode/electrolyte interface. The smaller charge transfer resistance was achieved by NP-Au/PPY. This is benefiting from the hierarchical porous structure with both macropores and mesopores, which can help improve the ionic conductivity [6]. Also the more favourable ion-diffusion realized by porous

conductive scaffold can also be revealed by larger slope of Nyquist plot in the low-frequency range. It is well known that the volume of PPY dramatically varies during the doping and de-doping of electrolyte ions when applied as supercapacitor electrode, which leads to the poor cycling performance. This problem can be alleviated by using NP-Au scaffold that can provide the buffer zone for volume expansion and help avoid the pulverization of PPY. As shown in Figure 2d, after charging/discharging for 1000 cycles at 100 mV/s, the NP-Au/PPY exhibited a 87% capacitance retention, better than the retention ratio of 78% for Au/PPY.

4. Conclusions

We demonstrated the nanoporous Au fabricated by dealloying of sputtered Au-Cu alloy films can be employed as an effective scaffold to develop high performance on-chip supercapacitor electrode. Pseudo-capacitive PPY as the active materials was deposited into the NP-Au scaffold by electrochemical plating method. The hierarchical porous structure of NP-Au with both macropores and mesopores is beneficial for shortening the ion diffusion path and decreasing the ionic resistance, thus led to improved performance of NP-Au/PPY compared with Au/PPY. A high areal capacitance of 37 mF/cm² and volumetric capacitance of 493 F/cm³ can be realized. More significantly, the use of metal scaffold on-chip would readily facilitate the integration of supercapacitor with other MEMS energy harvesting systems through metal-metal bonding technique.

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