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Development of Nanoporous Gold- Based Supercapacitor

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Abstract. In light of excellent power density and extended cycling stability, supercapacitors have been recognized as the advanced energy storage in the future. Nanoporous gold with a large internal surface and excellent conductivity, is a promising electrode material for supercapacitors. This article reviews latest progress in capacitive application of nanoporous gold and nanoporous gold-based composite.

1. Introduction

Owing to general concerns about limited oil storage and global warming situation, there is growing demand for alternative green energy storage and conversion systems including batteries, fuel cells, and supercapacitors [1-4]. Electrochemical supercapacitors(SCs) have attracted particular attention in light of their excellent power density and extended cycling stability[5]. Typically the SCs exhibit 20–200times larger capacitance per unit volume or mass than conventional capacitors [6]. In general, supercapacitor system contains electrode, electrolyte and separator. Numerous efforts have been made to develop advanced electrode materials for high-performance SCs by making use of surface ion adsorption, referred as double-layer capacitance, and surface redox reactions, referred as pseudo-capacitance [7].

Nanoporous gold is a corrosion-derived nanostructured material. It is generated by the corrosion of an alloy comprised of Au and a less noble metal, such as Ag, Cu or Al. The electrochemical removal (dealloying) of the less noble constituent results in an open bicontinuous nanoporous network of interconnected ligaments comprised almost entirely gold[8]. The difference in the compositions of the precursor alloys, the dealloying conditions and subsequent thermal annealing of dealloyed materials will result in remarkble dissimilarity of pore sizes, which may effect the capacitive property of electrode. Furthermore, the plastic deformation of nanoporous gold under compressive stress was studied by depth-sensing nanoindentation[9]. NPG with a relative density of 42% exhibit a mean hardness of 145(±11)MPa and aYoung's modulus of 11.1(±0.9) Gpa, potentially opening a door to a class of high yield strength—low-density materials,such as supercapacitor electrodes.

2. NPG-based supercapacitors.

2.1 NPG for electric double-layer capacitors (EDLCs)

Electric double-layer capacitors are based on the accumulation of ions of opposite charges in a double layer at electrodes. The charging and discharging process does not give rise to any chemical phase and composition change, and thus the EDLCs have relatively much better cyclability. In recent years, carbon material such as graphene and carbon nanotubes as well as activated cabon has been widely reported as electrode for EDLCs [10]. On the other hand, porous metals with a large internal surface and excellent conductivity are also promising electrode for supercapacitors, which have not been well investigated.

X.Y. Lang et al. fabricated nanoporous gold(NPG) sheets with a thickness of 30μm by delloying $Ag_{65}Au_{35}$ (at.%) ribbons(as shown in Fig.1[11]). The dealloying process was performed by free corrosion in a 70% HNO_3 solution for 24h at room temperature, followed by pure water quenching. The dealloyed samples have quasi-periodic nanoporous channels and gold ligaments with average size of ~40nm. After synthesizing NPG sheets into SC device, electrochemical experiments were carried out using a classic two-electrode configuration in a 2M KOH aqueous solution and a N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl) imide (DEME-TFSI) room temperature ionic liquid (RTIL), repectively. The calculated energy density of the SC device was determined to be 16.5–21.7 mWh cm^{-3}, which is 2–4 times higher than those with the KOH solution (4.89–8.31 mWh cm^{-3}), mainly because of the higher operation voltage given by low ionic mobility of the ionic liquid.

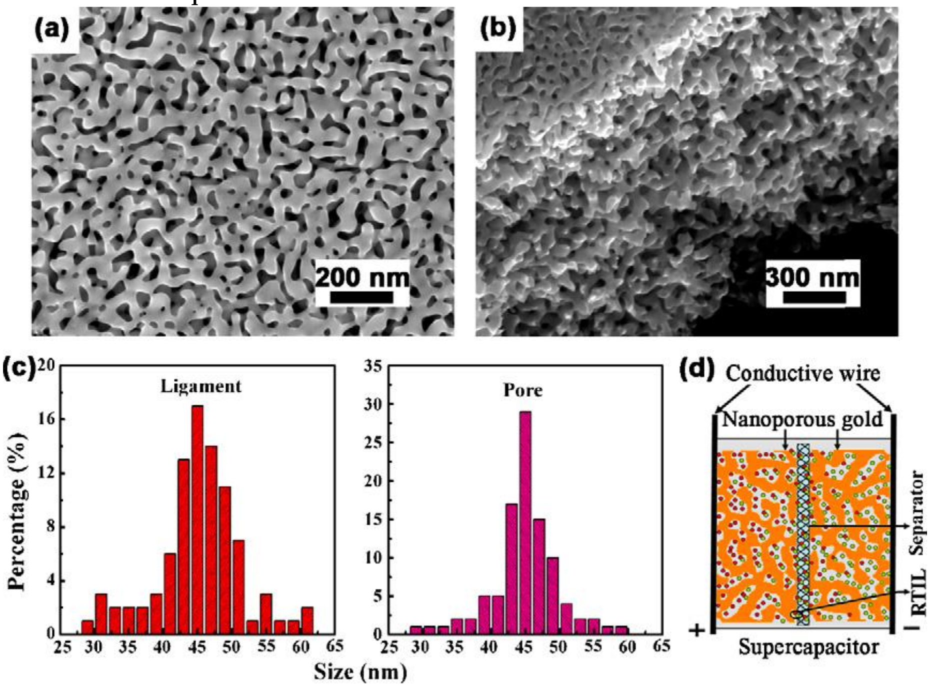

Fig. 1 Representative (a) top view and (b) cross-section SEM images of a NPG electrode. (c) Size distributions of gold ligaments and nanoporous channels of the NPG sample. (d) Schematic diagram of the supercapacitor assembled with NPG as both electrodes and current collectors, and a piece of cotton paper as separator [11]

2.2 NPG for pesudocapacitors

To overcome the low energy density of electrochemical double-layer capacitors, great efforts have been devoted to studying transition metal oxides (RuO_2 [12], MnO_2 [13], NiO [14], CoO_x [15]) and conductive polymers (PPy, PANI) which exhibit typical pseudocapacitance. Thus make the pesudocapacitors display much higher specific capacitance than double-layer capacitors, where the mechanism of fast and Faradic surface redox reaction offers the high energy storage. On the other hand ,the poor conductivity and anomalous structure essentially limits the practical uses of pseudocapacitors. Accordingly, nanoporous gold with bicontinuous structure, uniform pore size and excellent conductivity is a promising substrate and current collector for electrode-active materials.

MnO_2 has attracted intense attention because of its low cost, environmental friendliness, and high theoretical capacitance (1,370 F g^{-1}). Designing composite materials by depositing MnO_2 onto a conductive substance is a feasible strategy to address the poor electrical conductivity of MnO_2. Henghui Xu et al. reported on fabrication of NPG@MnO_2 composite electrode (as shown in Fig.2 [16]). The electrodeposition of MnO_2 was carried out with a three-electrode system, where the NPG was used as the working electrode and a mixed solution of 0.1 M $Mn(CH_3COO)_2$ and 0.1 M Na_2SO_4 as electrolyte. The loading of MnO_2 can be easily adjusted by changing the deposition time and constant current density. The charge–discharge storage capacity of the hybrid NPG@MnO2 electrode was measured in 1 M aqueous Na_2SO_4 solution. When the current density was increased from 0.5 to8 mA cm^{-2}, the areal capacitance decreased from 45 to37.2 mF cm^{-2}, corresponding to a decrease in mass capacitance from 839.4 to 690.1 F g^{-1}, which shows a better capacitive property than other reported MnO_2-based nanostructures like MnO_2/carbon nanotube (~385.4 F g^{-1})[17], MnO_2/polyaniline(~415 F g^{-1})[18] and MnO_2/nanotube/PEDOT-poly(styrenesulphonate) ternary composites (~427 F g^{-1})[19].

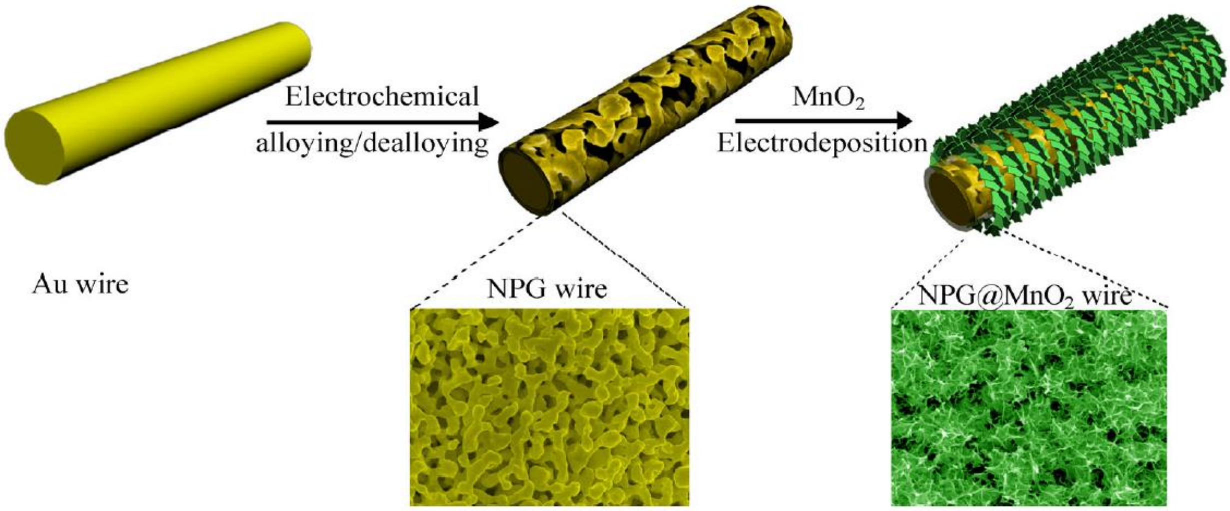

Fig. 2 Schematic illustration of the synthesis and morphology of the NPG@MnO2 electrode[16].

Among many types of metal oxides,nickel hydroxide($Ni(OH)_2$) has been widely researched due to its potential for high energy density[20]. Sun-I Kim et al.[21]have developed an outstanding supercapacitor with high capacitance, high energy density, and semipermanent lifetime using the $Ni(OH)_2$/NPG electrode. By synthesizing a hierarchical structure of Ni $(OH)_2$ on a porous 3D-current collector, the capacitance per gram and per volume has been maximized to reach 3168F g^{-1} and 2223F cm^{-3}, respectively. The low resistance metal-semiconductor contact effectively decreased the loss of capacitance by lowering the dead volume at the interface between the Ni $(OH)_2$ and NPG. By maintaining the volume of inner pores, the effects of the nanochannels were enhanced in the unique structure of the porous electrode, which dramatically improved the capacitive properties and cycle stability.

In Xingyou Lang's study[22] , three-dimensional bicontinuous NPG/PANI composite electrodes have been fabricated by electrochemical polymerization. The freestanding and flexible composite films have been demonstrated a volumetric capacitance up to~1500 F cm^{-3} at the current density of~1 A cm^{-3}, 10 times higher than that of graphene/PANI composites (~150 F cm^{-3}), which make this composite a promising electrode material for high-performance aqueous and all-solid-state supercapacitors with ultrahigh power density, high energy density.The good capacitive behaviors of the NPG/PANI SC devices arise from the ion and electron transports enhanced by unique bicontinuous nanostructure, where the nanoporosity facilitates the fast ion diffusion, and provides the large PANI/electrolyte interface to ensure the sufficient redox reaction of PANI during charge/discharge processes. The three-dimensional interconnected Au network with ultrahigh electrical conductivity harnesses the electron transport by remarkably decreasing the internal resistance of assembled devices.

3. Conclusion and prospect

In conclude, NPG with quasi-periodic nanoporous channels, a large internal surface and excellent conductivity shows promising application prospect in supercapacitor electrodes. There has been some progress in nanoporous gold-based supercapacitor such as combining different transition metal oxides and conductive polymers with NPG for optimized capacitive property. More work could be done to improve NPG electrode performance by controlling the nanoporosity due to the convenient access to pore size control. Flexible NPG can also be optimized for further application in wearable device with appropriate electrolyte.

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