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Non-aqueous nanoporous gold based supercapacitors with high specific energy

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ABSTRACT

In this study, we report that the supercapacitor performance of polypyrrole (PPy) in non-aqueous electrolytes can be dramatically improved by highly conductive nanoporous gold which acts as both the support of active PPy and the current collector of supercapacitors. The excellent electronic conductivity, rich porous structure and large surface area of the nanoporous electrodes give rise to a high specific capacitance and low internal resistance in non-aqueous electrolytes. Combining with a wide working potential window of ~2 V, the non-aqueous PPy-based supercapacitors show an extraordinary energy density and power density.

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1. Introduction

The electrochemical energy storage devices play a critical role in green energy innovation for energy harvesting and power delivery [1–4]. Among various electrochemical energy storage devices, electrochemical supercapacitors have drawn increasing attention for environment-friendly applications, such as portable electronics, hybrid electric vehicles and memory backup systems because of their high power density, rapid charge/discharge rate and high specific capacitance [5–7]. On the basis of the mechanisms of charge storage, the electrochemical supercapacitors can be divided into two types. One is the electrochemical double layer capacitors (EDLC) which store energy by non-Faradic surface ion adsorption [8,9]. The other is the pseudocapacitors which realize high energy storage through fast Faradic redox reactions and intercalation of ions at interfaces between active electrode materials, such as conducting polymers [10,11] and transition metal oxides [12,13], and electrolytes. Although the pseudocapacitors have a relatively high capacitance compared to EDLC, the energy density of pseudocapacitors is still much lower than that of Li-ion batteries, which is limited by their narrow working potentials in aqueous solutions and/or insufficient utilization of pseudocapacitive reactions in non-aqueous electrolytes.

The energy density (E) of a supercapacitor is determined by the equation: $E = 0.5C_sV^2$, where C_s is the specific capacitance of the supercapacitor and V is the working potential of the cell [14]. Usually, supercapacoitors have a narrow potential window, which is lower than 1.2 V in aqueous solutions due to the restriction of thermodynamic potential of water electrolysis. Hence, a non-aqueous solution with large stable working potential is expected to enlarge the energy storage capacity of pseudocapacitors [15,16]. Recently, room temperature ionic liquids (RTILs) have been investigated as non-aqueous solutions for a high working potential of supercapacitors, which are promising electrolytes owing to their high electrochemical and thermal stability, wide liquid-phase range, low vapor pressure and non-flammability.

Among many pseudocapacitive materials, polypyrrole (PPy) has attracted considerable attentions as a promising electrode material own to its low material costs, high theoretical capacitance, environmental friendliness and easy synthesis [17,18]. Similar to other pseudocapactive materials, the energy densities of PPy-based capacitors are largely limited by a narrow working potential window in aqueous solutions. Since conducting polymers usually have a lower electric conductivity and lower specific capacitance than transition metal oxides in non-aqueous solutions, there are very few attempts on non-aqueous PPy-based supercapacitors [14,19,20]. Although these non-aqueous supercapacitors have an enlarged operation voltage window, the improvement in the energy density of the PPy-based supercapacitors is minimal because of high internal resistance and decreased specific capacitance. Therefore, enhancing the electric conductivity and specific capacitance of PPy-based electrodes in non-aqueous electrolytes is essential to realize the high energy density.

Dealloyed nanoporous metals with a high electrical conductivity, large specific surface area and excellent affinity with active materials have recently been utilized as both supports of pseudocapacitive

materials and current collectors of supercapacitors and actuators [8,13, 21–24]. The metal based three-dimensional electrodes can obviously enhance the specific capacitance of poor-conductive active materials and effectively reduce the device weight and volume, simultaneously. In the context of our previous work in preparing high-conductive PPy-nanoporous gold (NPG) hybrid composites with a high specific capacitance [25,26], in this study we developed PPy-NPG based non-aqueous supercapacitors with a wide operation voltage window and high energy density by using RTIL as electrolytes.

2. Experimental section

2.1. Synthesis of NPG and PPy-NPG hybrid composites

All the chemicals were of analytical grade and used without further purification. Nanoporous gold (NPG) films with a thickness of about 100 nm were fabricated by free chemical corrosion using commercial $Au_{35}Ag_{65}$ (at. %) alloy leaves in a concentrated HNO_3 solution (wt. 69%) for 6 h at room temperature. Deionized water (18.2 MΩ·cm) was utilized to rinse as-prepared NPG for three times in order to remove the residual chemical substances within pore channels after the nanoporous structure of NPG was taken away from the acid solution. The as-prepared NPG films were then fixed to polyethylene terephthalate (PET) plates by annealing NPG/PET at the temperature of 80 °C for convenient handling as flexible electrodes

PPy-NPG composites were prepared by an electrochemical plating method [25,27]. 1.382 mL Pyrrole (99.0% Wako Pure Chemical Industries) and 1.6 mL $HClO_4$ (Kanto Chemical Co., Inc.) were dissolved in 200 mL distilled water to form a 0.1 M Pyrrole/$HClO_4$ solution. The NPG/PET plates were immersed into the electrolyte at room temperature. The electroplating was performed in a standard three-electrode system with a platinum sheet as the counter electrode, Ag/AgCl as the reference electrode, and an NPG/PET plate as the working electrode. The anodic oxidation synthesis of pyrrole on NPG was conducted by a cyclic voltammetry (CV) method with a potential window ranging from −0.2 V to 0.9 V. The loading amount of PPy was controlled by the cycling number of plating. The mass of deposited PPy was determined based on the equation: $m = QM/zF = QM_M/(2 + y)F$, where m is the mass of the deposited PPy, Q is polymerizing charge, y is a stoichiometric factor evaluating the PPy insertion degree (=0.2, based on Ref. [28]), and F is the faradic constant [29]. M_M is the molecular weight of the polymer monomer unit ($M_M = M_{Py} - 2$), and M_{Py} is pyrrole molecular weight.

2.2. Microstructure characterization

The microstructure of the as-synthesized PPy-NPG composites was characterized by a JEOL JIB-4600F scanning electron microscope (SEM) and a JEOL JEM-2100F transmission electron microscope (TEM) equipped with double spherical aberration correctors.

2.3. Assembly of PPy-NPG supercapacitors and electrochemical measurements

Two-electrode supercapacitor devices were constructed with two PPy-NPG/PET plates as the electrodes separated by a thin cotton paper (~40 μm in thickness, BemlieseTM). The electrochemical properties and capacitive performances of the PPy-NPG supercapacitors were investigated using a standard two-electrode electrochemical system. The CV and charge/discharge curves were measured at different scan rates and current densities using an electrochemical station (Ivium Technology). Three kinds of RTIL were chosen as electrolytes in this study, including 1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMI-FSI), 1-Ethyl-3-methylimidazolium Dicyanamide (EMI-DCA) and N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI).

3. Results and discussion

Fig. 1(a) exhibits the top view SEM image of 1-cycle plated PPy-modified NPG with an open nanoporous structure. The average size of pore channels and gold ligaments of as-prepared NPG were measured to be ~40 nm using a rotational fast Fourier transform method [30]. The thickness of the NPG current collector is about 100 nm. The ultra-thin current collector provides excellent rate performance by eliminating the slow diffusion of the RTIL electrolytes in nano-sized pore channels. The bright-field TEM image shows that the PPy coating forms a core-shell structure in which the conducting polymer layer displays bright contrast as the shell that uniformly covers the internal surface of the dark-contrast metal ligaments (Fig. 1(b)). The core-shell structure with open porosity promises the good conductivity of the PPy-NPG composite and the effective rapid ion transport of electrolytes within the porous electrodes. A high-resolution TEM (HRTEM) image (Fig. 1(c)) reveals the well-bonded PPy/Au interface and the deposited PPy has an amorphous structure without any well-defined periodic lattice. By tuning the cycle number of the electrochemical plating, the loading amount and the layer thickness of PPy can be well controlled. The loading amount of PPy gradually increases with the cycling number from 1 to 5. As shown in Fig. S1(a–e), the samples plated for 1 to 3-cycles exhibit open structure which is similar to pure NPG due to the weak contrast of PPy in the SEM images. When the cycle number increases to 4 and 5, some nanopores are blocked by the excess PPy which grows on the external surface of the NPG films. Quantitative measurements indicate the nearly linear dependence of the loaded PPy amount with the plating cycle (Fig. S1(f)).

The PPy-NPG composites were assembled into a two-electrode supercapacitor for electrochemical measurements. Two PPy-NPG films were used as working electrode and counter electrode, respectively. A piece of cotton paper was utilized as separator between two PPy-NPG electrodes for preventing short circuit and free mobility of cations and anions from non-aqueous electrolytes. Since the capacitive Performance of the PPy-NPG supercapacitors shows the strong dependence on the loading amount of PPy, the capacitance performance of the electroplated NPG with different PPy loading amounts was first investigated to optimize the loading amount of PPy. Fig. S2(a–c) reveal the CV curves
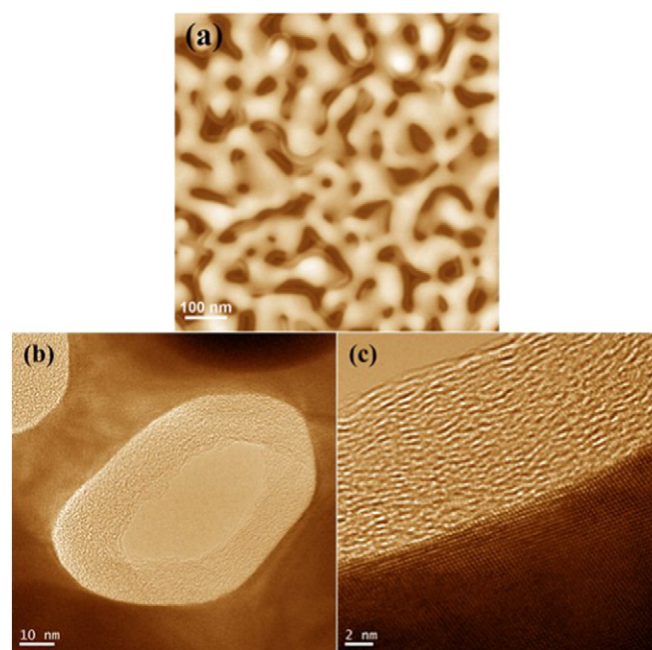

Fig. 1. (a) Representative SEM and (b) TEM images of the PPy-NPG composite with electroplated PPy. (c) HRTEM image showing the interfacial structures of the PPy-NPG composite.