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Short communication

Ultrahigh capacitance of nanoporous metal enhanced conductive polymer pseudocapacitors

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HIGHLIGHTS

► NPG-PPy hybrid electrodes are fabricated by combining dealloying and electropolymerization.
► Nanoporous hybrid structure facilitates charge transport and thus has low internal resistance.
► Ultrahigh energy densities of ~100 Wh kg^{-1} in a 3-electrode configuration, comparable to NiMH batteries, can be achieved.
► High power density of ~57 kW kg^{-1} is retained along with ultrahigh capacitance.
► The hybrid electrodes keep up to 85% the maximum capacitance after 3000 cycles.

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ABSTRACT

A high energy density is critical for supercapacitors to supersede conventional batteries for the applications where both high power and high energy are demanded. Here we report nanoporous metal/conductive polymer hybrid electrodes fabricated by electrochemically plating conductive polypyrrole into nanoporous channels of a dealloyed nanoporous metal. The low electric resistance and open porosity of the nanoporous metal give rise to excellent conductivity of electrons and ions and hence dramatically improved electrochemical performances of the pseudocapacitive polypyrrole. Supercapacitors based on the hybrid electrodes show an ultrahigh energy density of ~100 Wh kg^{-1} in a three-electrode, comparable to NiMH batteries, as well as high power density of ~57 kW kg^{-1}. Cycling stability measurements demonstrate that the hybrid electrode can retain 85% of the maximum capacitance after 3000 cycles and the degeneration is mainly caused by the dissolution of polypyrrole during charge/discharge cycling.

1. Introduction

With the rapid development of the economy and the exhaustion of fossil fuels, electrochemical energy storage and conversion systems, such as batteries, fuel cells and supercapacitors, with both high power density and energy density are highly demanded as alternative energy sources of electric and hybrid electric vehicles in green energy innovation. [1–5] Among these energy devices, supercapacitors are expected to bridge the gap between conventional capacitors with high power density but low energy density and batteries that have high energy density but low power density [6–11] because there is still a large space for supercapacitors to further improve their energy density with retaining high power density. There are two mechanisms for the charge storage of supercapacitors. One is so called electrochemical double-layer capacitance by non-Faradic surface ion adsorption; [6,7,12,13] and the other is the pseudocapacitance by fast Faradic redox reactions at electrode/electrolyte interfaces [14–16] These two mechanisms can work separately or together, depending on the electrode materials used in supercapacitors [4,17,18] Conductive porous materials with large surface areas, such as active carbon and nanoporous metals, [1,9,10,19,20] are desired electrodes for electrochemical double-layer supercapacitors. In general, electrochemical double-layer supercapacitors have obvious advantages in power density and lifetimes, but their energy density is still much lower than that of batteries [2,9,18,21] Therefore, it has been the recent topic of intense research to search for new electrode materials that can provide high energy density, comparable to batteries. It has been known that transition

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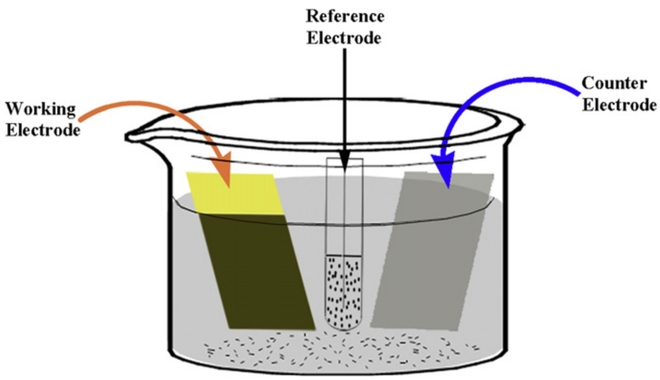

Fig. 1. Schematic illustration of the three-electrode system for capacitance measurements in this study.

metal oxides, such as MnO_2 and RuO_2, and conductive polymers, such as polyaniline (PANI) and polypyrrole (PPy), have high theoretical capacitance values for pseudocapacitors [3,22–25] However, their capacitive performances are limited by high electric resistance and low cycling stability. Particularly, the attainable energy density is often an order of magnitude lower than their theoretical assessment. Recently, by utilizing the excellent conductivity, large internal surfaces and open porosity of nanoporous gold (NPG), Lang et al. successfully incorporated pseudocapacitive MnO_2 and PANI into NPG and fabricated novel hybrid electrodes for supercapacitors with a high energy density [26,27]. Meng and Ding also documented the fabrication of an ultrathin, flexible, all-solid-state supercapacitor based on PPy-decorated NPG [28] In this study, we developed a PPy/NPG hybrid electrode that offers an ultrahigh energy density of ~100 Wh kg^{-1} in a three-electrode mode, comparable to NiMH batteries, and retained high power density of ~57 kW kg^{-1} as well as good cycling stability.

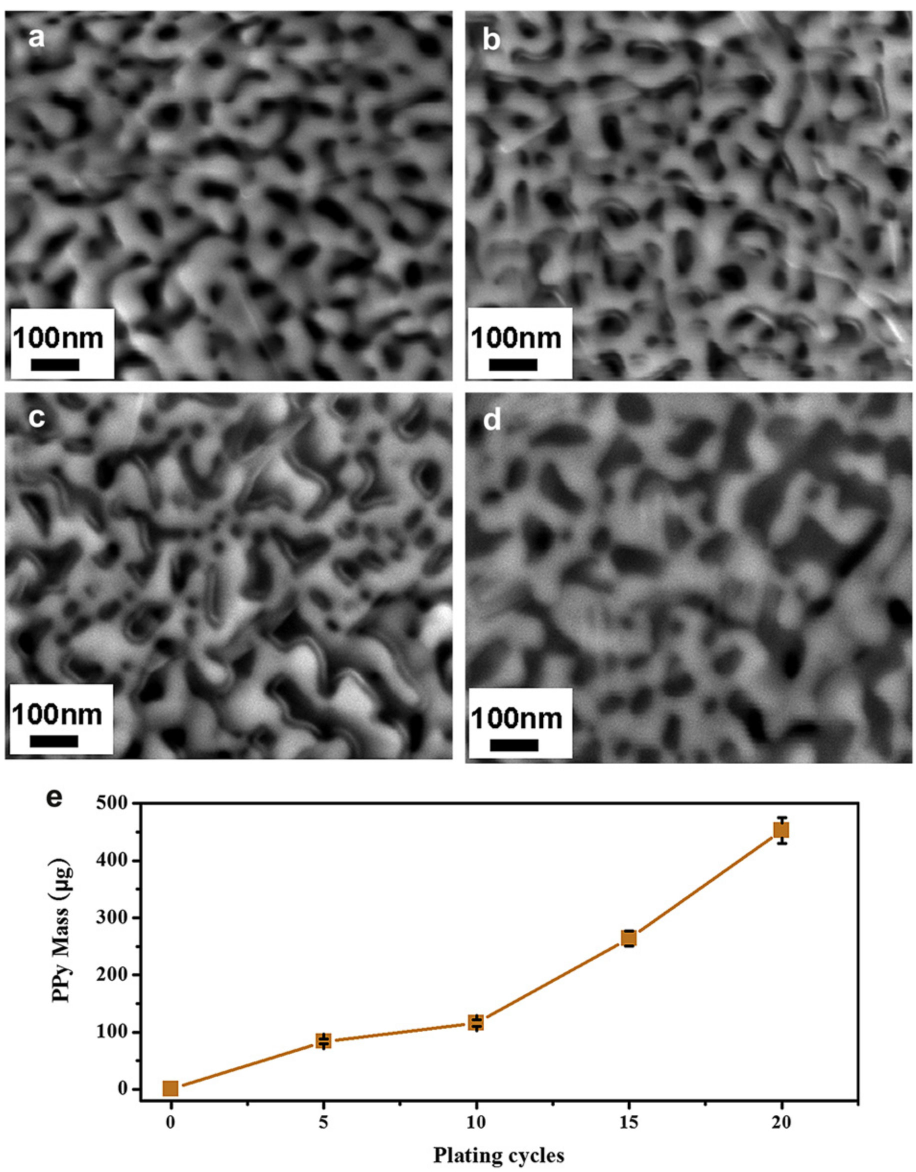

Fig. 2. . SEM images of PPy/NPG composites with different plating cycles: (a) 5 cycles; (b) 10 cycles; (c) 15 cycles; and (d) 20 cycles. (e) The relationship between plating cycles and PPy loading amounts.