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High volumetric electrochemical performance of ultra-high density aligned carbon nanotube supercapacitors with controlled nanomorphology

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ABSTRACT

The superior electrical conductivity and parallel ion pathways formed by aligned carbon nanotubes (A-CNTs) make them attractive for the nanoporous electrodes of supercapacitors. To achieve high volumetric energy and power densities, the low volume density of the as-synthesized A-CNT (<5%) should be densified. In this paper, we demonstrate a mechanical densification method that allows the density of A-CNTs to be tuned precisely over a broad range while preserving the straight ion pathway between A-CNTs. The supercapacitors fabricated from 40% volumetric fraction (Vf) of A-CNTs as the electrodes with the thickness of 0.8 mm exhibit a power density of 25 kW L^{-1} (50 kW kg^{-1}), which is much higher than that of the A-CNTs electrodes with similar thickness fabricated by other methods and that of activated carbon electrodes.

1. Introduction

Supercapacitors, which store charges through electrical double layers (EDL), bridge the gap of power and energy between batteries and dielectric capacitors [1–5]. Although batteries can store a large quantity of energy, they release energy in a slow rate, resulting in a very low power density with a limited lifetime [6,7]. On the other hand, dielectric capacitors can be charged and discharged at high rate and hence possess very high power density, but their energy density is low [1,8]. With relatively high power, mid-high energy density and long cycle lifetime, supercapacitors are attractive for many applications, such as in grid scale renewable energy storage and in hybrid electric vehicles where high energy, high power and reasonable lifetime are all required [9–12]. For these advanced applications, it is highly desirable to further improve the volumetric power and energy density of supercapacitors.

Recent advances in aligned carbon nanotubes (A-CNTs) have demonstrated many attractive features of A-CNTs as the nanoporous electrodes for supercapacitors. The superior electrical conductivity of the A-CNTs and the parallel ion pathways formed by the A-CNTs reduce the electric resistance and improve the ion transport, as schematically illustrated in Fig. 1a with a comparison with randomly arranged nanoporous electrodes, such as those constructed from the activated carbons, which possess tortuous ion transport pathways [13–19]. Consequently, supercapacitor cells with A-CNTs exhibit much less equivalent series resistance (ESR) values and have the potential to achieve much higher power and energy density than the supercapacitors fabricated from activated carbons and randomly packed CNTs [20,21].

However, as-synthesized A-CNT forests have a low nanotube volume fraction (<5%) and direct use of the A-CNT forests for the supercapacitor electrodes will lead to low volumetric electrochemical performance because of the low volumetric specific electrode surface area. Therefore, A-CNTs should be densified to reach higher CNT number per unit area in order to fully realize high volumetric power and energy density of the devices which are critical for a broad range application in electric and electronic systems which require compact device size and increased functions within a limited device volume [5].

In the past decade, several groups have worked on approaches to densify the as-grown A-CNTs to high CNT density in order to achieve high volumetric capacitance, energy density, and power

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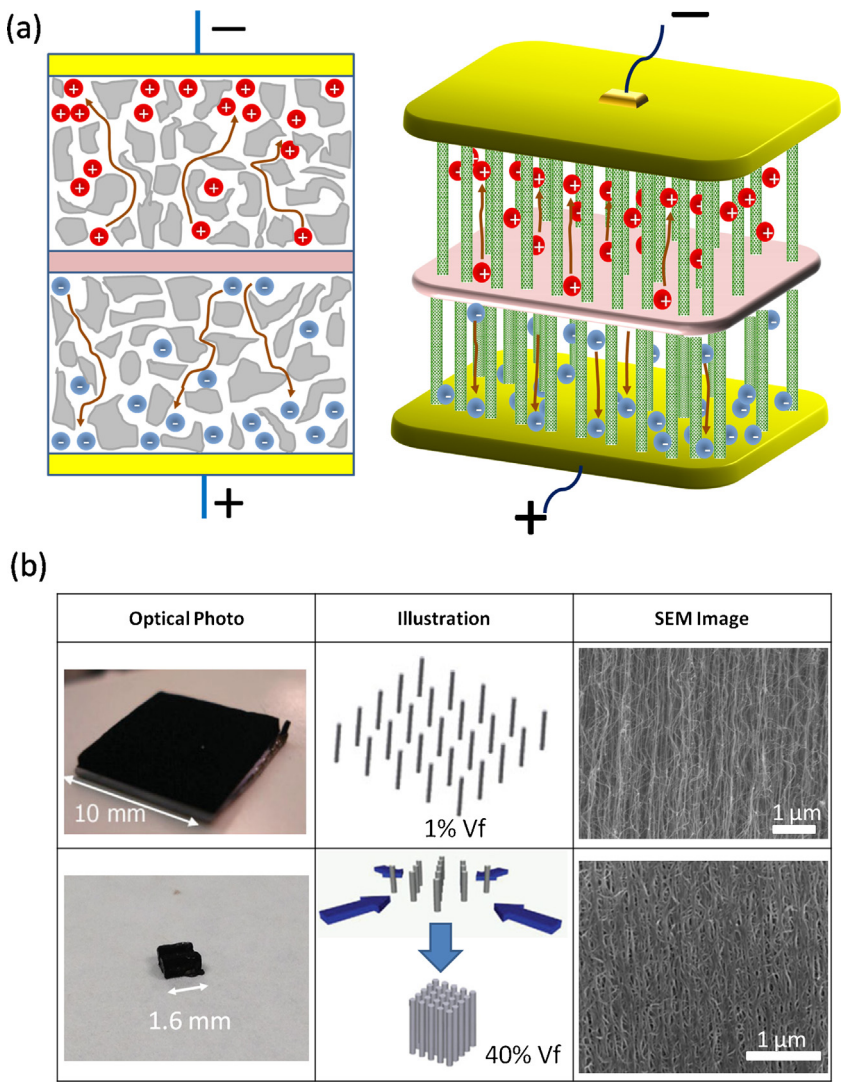

Fig. 1. (a) Schematic of the tortuous ion transport paths in nanoporous electrodes formed, for example, from the activated carbons, and parallel ion pathways in the A-CNTs. (b) Optic images, schematic of mechanical densification process, and SEM images of 1% Vf and 40% Vf A-CNTs.

density. For example, Futaba et al. introduced a liquid collapsing method to densify A-CNTs in which the surface tension of liquid forces the A-CNTs to collapse to a high density [22]. Compared with the liquid-induced collapse densification method, the mechanical densification method introduced in this paper for fabricating high volume fraction (Vf) A-CNT electrodes offers several advantages, including the ability to tune the density of the A-CNTs precisely, ranging from the original 1% Vf A-CNTs to more than 40% Vf, while maintaining the nanomorphology of the A-CNTs. Hence this method provides a realistic approach for large scale manufacturing of supercapacitors employing A-CNTs with desired volume fraction while preserving the nanomorphology of the easy ion transport pathways.

In this paper, we report the investigation of supercapacitors fabricated from A-CNTs in the volume fraction from 1% to 40%. The supercapacitor cells based on A-CNTs with high volume fraction exhibit excellent electrochemical performance using the unique mechanical densification method. As a result, the supercapacitors fabricated from A-CNTs with 40% Vf A-CNTs exhibit volumetric and gravimetric power densities of 25 kW L^{-1} and 50 kW kg^{-1}, respectively, for the capacitor cell with 0.8 mm thick A-CNT electrodes, compared with 1.1 kW L^{-1} and 2.5 kW kg^{-1} for the capacitor cell with 0.8 mm thick activated carbon electrodes and 13.4 kW L^{-1} and 24 kW kg^{-1} for the supercapacitors using smaller 0.5 mm thick A-CNTs densified by the liquid collapsing method [22].

2. Experimental

The A-CNTs in this study were synthesized via a modified chemical vapor deposition (CVD) method on silicon substrates using iron (Fe) on alumina as a catalyst [23]. The as-grown A-CNT forests have a 1% volume fraction (Vf) of CNTs with densities of 10^9–10^{10} CNTs cm^{-2}. The average diameter of these CNTs is 8 nm with 3–5 shells of walls and the CNT-CNT spacing is approximately 80 nm in the as-grown A-CNT forest. For the high volume fraction A-CNT fabrication, the CNT forests were released from the silicon substrate and then subjected to a mechanical biaxial densification process in two orthogonal directions as illustrated in Fig. 1b. In this method, the released A-CNT forests were placed in a specially designed sample holder. The height of the sample holder was the same as the height of the A-CNT forest so that the top and bottom of the forest remained flat during the densification process. The A-CNT forest was densified along one direction first (see Fig. 1b) to a fixed amount using a mechanical bar, and then another mechanical bar in the orthogonal direction was used to press the A-CNT forest to