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Electrochemical pulse deposition of Ni nanoparticles on the 3D graphene network to synthesize vertical CNFs as the full-carbon hybrid nanoarchitecture for supercapacitors

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ABSTRACT

In this study, a pulse-mode electrochemical deposition technique was employed to deposit dense and homogeneous Ni nanoparticles on the three-dimensional graphene network (3DGN) as the catalysts for growing the vertical aligned one-dimensional carbon nanofibers (CNFs) to fabricate the full-carbon hybrid nanoarchitecture of CNFs/3DGN for the supercapacitors. When tested as electrode for a supercapacitor, the CNFs/3DGN hybrid nanoarchitecture demonstrated to possess a large surface area and showed an excellent specific capacitance of 59.28 F g^{-1} at a current density of 0.17 mA cm^{-2}, also displayed good cycle stability with capacitance retention of 93.9% after 10,000 cycles in 6 M KOH electrolyte.

1. Introduction

Electrochemical capacitors (also known as supercapacitors) are considered as promising candidates for the important energy storage device for a wide variety of applications [1,2]. Electric double-layer capacitors (EDLCs) are categorized as one kind of the important supercapacitor; in general, the capacitances of EDLCs utilize the high surface area of carbonaceous materials for constructing an electric double-layer at the interface between the electrode and electrolyte [1,2]. The excellent chemical and physical properties of carbonaceous materials such as large specific surface area, high conductivity, good temperature stability, and relatively low cost make them superior candidates for the electrode of EDLCs [3–7].

In order to achieve high-performance EDLCs, the selections of carbonaceous nanomaterials with nanoscale morphologies have been considered as the most effective strategies, because the maximized specific surface area boost the electrochemical reactions. Especially for one-dimensional (1D) carbon nanotubes or carbon nanofibers, and two-dimensional (2D) graphene nanostructures which possess the largest theoretical and experimental surface area [4,5]. On the other hand, in order to improve the capability and efficiency of carbonaceous nanomaterials for electrochemical devices, constructed three-dimensional (3D) carbon hybrid nanoarchitecture by incorporating 1D carbon nanofibers and 2D graphene is an intensively studied field currently [4–7]. However, these previously reported hybrid structure of 1D carbon nanomaterials on the graphene used the PVD equipment to deposit metal catalyst for CNT growth on the single side of electrode [4] or used graphene oxide with binder-paste as a rather non-ideal substitute for graphene [5–7].

In terms of the above considerations, in present work, a pulse-mode electrochemical deposition (Pulse-ECD) technique was employed to deposit dense and homogeneous Ni nanoparticles (NiNPs) on the 3D graphene network (3DGN) as the catalysts to directly grow the vertical aligned 1D CNFs for the fabrication of the full-carbon hybrid nanoarchitecture of CNFs/3DGN for the supercapacitors. Additionally, there were several advantages in this work: (i) The Pulse-ECD method provided a simple process to synthesis NiNPs on the whole surface of 3DGN. (ii) The directly growth of binder-free CNFs/3DGN hybrid nanoarchitecture provided strong adhesion to the substrate with low internal resistance. (iii) This strategy of CNFs directly grown on 3DGN dramatically increased the surface area and provided a simple and scalable approach for constructed 3D carbon hybrid nanoarchitecture.

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2. Experimental

The 3DGN was initially synthesized by thermal chemical vapor deposition (CVD) method. In brief, nickel foam was loaded into a quartz tubular furnace and heated to 900 °C under H_2 atmosphere, then C_2H_2/H_2 gas mixture (8/16 sccm) was introduced into the reaction tube. After 20 min reaction, the quartz tube was then cooled down to ambient temperature to remove the specimen. Afterwards the NiNPs were deposited on the 3DGN as the catalyst for CNFs growth, which performed by using pulse-ECD method. The 3DGN was subjected into a plating bath containing an Ar-saturated aqueous precursor solution (0.01 M solution of $NiSO_4{\cdot}6H_2O$ and 0.1 M H_3BO_3 in deionized water). The pulse-ECD method was utilized a potentiostat/galvanostat (PGSTAT 302 N, Autolab, EcoChemie, Netherlands) in a three-electrode configuration at 30 °C under an ambient pressure. A graphite plate and a saturated calomel electrode (SCE) were served as the counter and reference electrodes, respectively. The pulse potential was applied in $-0.5\ V_{SCE}$ and $-1.0\ V_{SCE}$, and the pulse cycle was performed in 200 scan cycles. Finally, the specimen of as-deposited NiNPs on 3DGN was loaded into a quartz tube furnace chamber to synthesize the CNFs/3DGN via the CVD method. In brief, the specimen was loaded into a quartz tube furnace chamber, heated to 600 °C in an Ar/H_2 (320/70 sccm) gas mixture and annealed for 5 min. Acetylene (C_2H_2, 10 sccm) was then introduced to trigger the growth of CNFs for 15 min, and subsequently cooled to room temperature under Ar atmosphere.

A three-electrode electrochemical working station (CH Instruments, 1140B, USA) was used in the all electrochemical measurements and employed in 6 M KOH aqueous solution. The as-prepared 3DGN and CNFs/3DGN samples were served as the working electrode, while the platinum wire and SCE were the counter electrode and the reference electrode, respectively.

3. Results and discussion

Fig. 1(a)–(d) and (e)–(h) showed the FESEM images of as-deposited NiNPs on 3DGN and CNFs/3DGN, respectively. The NiNPs were uniformly and densely deposited on the surface of 3DGN by the pulse-ECD method, the size of NiNPs was around 200 nm. The dense and homogeneous CNFs were synthesized via the CVD process, the CNFs were of uniform diameter of around 220 nm and length of vertical fibers were approximatively 5 μm with forest-like structures on the surface of 3DGN.

The HRTEM provided direct evidence of our CVD-synthesized graphene of 3DGN, which revealed that the number of layers of graphene was approximately five layers and the interlayer distance of the graphene is 0.34 nm (Fig. 2(a) and (c)). Fig. 2(d) presented the interface between the NiNP and graphite sheets, and it was clearly shown that CVD-synthesized CNFs was an extremely graphitic nanofiber.

Raman spectroscopy was also employed to further confirm the presence of graphene layers under CNFs (Fig. S1). The I_{2D}/I_G ratio and the intensity of the 2D peak indicated that the fabricated graphene consisted of 4–6 layers of graphene [4], which was coincided with the HRTEM results.

The capacitive performance of CNFs/3DGN electrode was evaluated by using cyclic voltammetry (CV) and chronopotentiometry (charge-discharge (CD)) measurements. The specific capacitance of the electrode from CV curves by integrating the area of the profiles according to Eq. (1):

$$C = \int I(V)dV/m \times S \times \Delta V \tag{1}$$

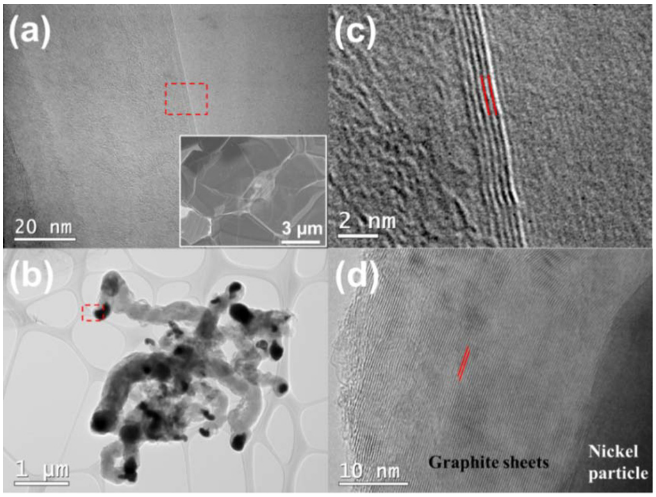

Fig. 2. TEM images of (a) few-layer graphene and (b) CNFs, the inset of (a) is the FESEM image of graphene; (c) and (d) were zoomed-in HRTEM images of regions indicated by red dashed rectangles in (a) and (b), respectively. The solid lines marked in (c) and (d) showed the interlayer distance of 0.34 nm.

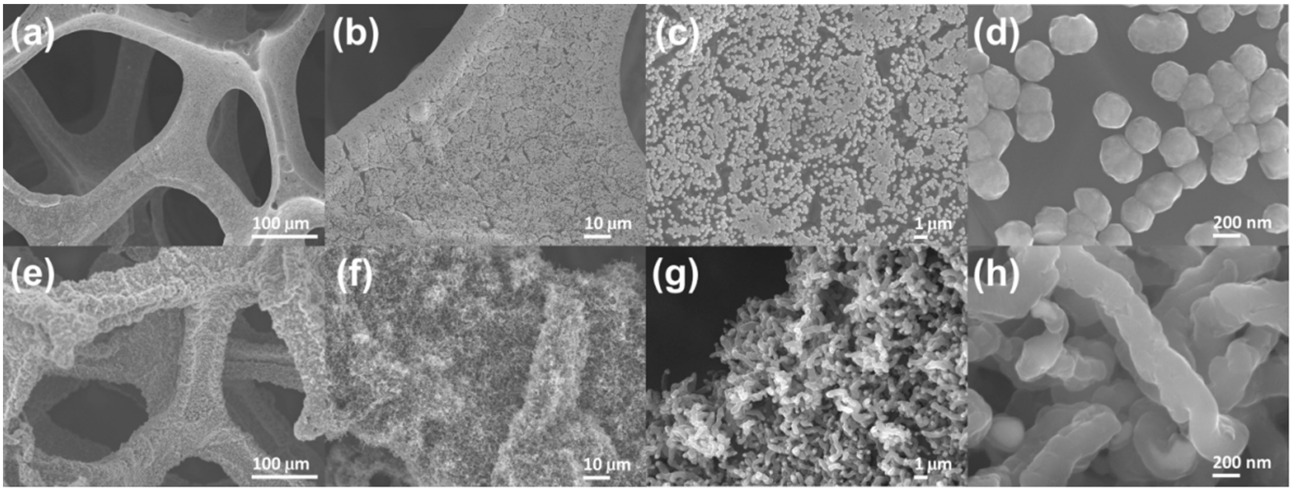

Fig. 1. FESEM images of (a)–(d) NiNPs on 3DGN and (e)–(f) CNFs/3DGN from the low through high magnification, respectively.