Research Article

Synthesis of Carbon Nanotube/Graphene Composites by One-Step Chemical Vapor Deposition for Electrodes of Electrochemical Capacitors

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To control the packing density of carbon nanotubes (CNTs) and the number of graphene layers, carbon nanotube/graphene composites are directly grown on cobalt (Co) catalysts-coated nickel foam by one-step ambient pressure chemical vapor deposition (CVD) at different temperatures and times. The carbon nanotube/graphene composites grown by one-step CVD at 850°C for 10 min possess the highest specific capacitance. Furthermore, a lower growing temperature leads to a higher packing density of CNTs and a smaller number of layers of graphene. A shorter growing time also leads to a smaller number of layers of graphene.

1. Introduction

Electrochemical capacitors are charge-storage devices which possess a higher power density and a longer cycle life than batteries [1, 2]. Their applications include power sources for hybrid vehicles, starting power for fuel cells, and burst-power generation in electronic devices [3–7]. Electrochemical capacitors are classified into two types, electric double layer capacitors (EDLC) and pseudocapacitors according to the energy-storage mechanisms. The capacitance of an EDLC arises from the separation of charge at the interface between the electrode and the electrolyte. However, pseudocapacitance arises from redox reactions of electroactive materials with several oxidation states [1, 8–12].

CNTs have nanometer size, hollow structure, low ratio of micropores, high accessible surface area, low resistance, and high stability [13]. Graphene has higher accessible specific surface area compared with CNTs as well as activated carbon and higher conductivity compared with activated carbon as well as CNTs [14–16]. These properties make them potentially suitable for fabrication of electrodes in electrochemical capacitors.

The densities of CNTs grown on Fe, Co, and Ni catalysts are 4×10^9 1/cm², 4×10^9 1/cm², and 2×10^9 1/cm², respectively, due to the easy agglomeration of the small sized Ni particles compared with Fe or Co particles [17]. Furthermore, Co catalysts have shown the highest intensity ratio of the C-C stretching mode to the disorder-induced mode of graphite structure for carbon products at lower temperatures [18]. Therefore, in this study, CNTs were grown on Co (catalysts) in order to minimize amorphous carbon formation and achieve a higher density of CNTs, thus producing higher electrochemical stability. The capacitive properties of graphene films depended on the number of graphene layers, and the graphene films with three layers possessed low charge-transfer resistance as well as higher specific capacitance than those of thicker graphene films due to the close attachment of graphene films on the Ni substrate [19]. Too high carbon supply rate leads to increasing defect density of graphene and thicker graphene results from higher growth temperature [20]. Bilayer graphene can be synthesized by CVD on polycrystalline Ni films and the average defect density decreases with the increasing growing time [21]. Thickness of graphene films can be controllably synthesized by chemical

vapor deposition (CVD) on polycrystalline copper and the number of layers of graphene increases with the increasing growing time and temperature [22].

The layer spacing between the graphene nanosheets controlled through interacting function nanocarbons such as CNTs might be crucial for enhancement of the storage capacity [23]. The CNTs can act as the spacer in fabricating a three-dimensional hierarchical structure with graphene sheets, thus enhancing its effective surface area and capacitance performance [24]. The multiwalled carbon nanotubes in the graphene/multiwalled carbon nanotube film can efficiently increase the basal spacing and bridge the defects for electron transfer between graphene sheets, thus increasing electrolyte/electrode contact area and facilitating transportation of electrolyte ion as well as electron into the inner region of electrode [25]. Three-dimensional CNTs/graphene sandwich structures with CNTs pillars grown in between the graphene layers were prepared by CVD and the unique structure possessed the high-rate transportation of electrolyte ions as well as electrons throughout the electrode matrix since the introduction of CNTs can provide diffusion path for electrolyte ions on the surface of graphene and the interconnection of CNTs with graphene can form a conductive network for the transport of electrons [26]. Carbon nanofibers were grown by CVD on graphene sheets synthesized by a modified Hummers method; the carbon nanofibers with many cavities and open tips as well as edges of exposed graphene platelets can be homogeneously distributed in between the graphene sheets as spaces to separate the neighboring graphene and be beneficial for fast ion/electron transfer as well as sufficient contact between active materials as well as electrolyte [27]. Vertically aligned CNTs were directly grown by CVD (60 sccm C_2H_2 , 120 sccm H_2 , and 200 sccm Ar, $750^\circ C$) on graphene paper coated with Fe as well as Al_2O_3 and a higher as well as more stable discharge capacity compared with graphene paper as well as CNTs was achieved [28]. Graphene films were grown on copper foil by low pressure CVD (20 torr, $1000^\circ C$, and 100 sccm CH_4 , 200 sccm H_2 , and 200 sccm Ar), then functionalized with 1-pyrenebutyric acid by drop casting, and coated with multiwalled carbon nanotubes by drop casting after functionalization [29]. Hybrid CNTs and graphene nanostructures were directly grown by ambient pressure chemical vapor deposition (CVD); methane was introduced to form graphene on copper foils at $950^\circ C$, then Fe catalysts were deposited on graphene/copper foils by e-beam evaporation, and ethylene was next introduced to grow pillar CNTs on graphene/copper foil at $750^\circ C$ [30]. The CNTs-graphene hybrid materials were grown by simple one-step ambient pressure CVD on copper foil spin-coated with silicon nanoparticles using ethanol as precursor at different temperatures and the density of CNTs can be controlled by the CVD growth temperature [31]. The CNTs-graphene hybrid materials were synthesized on an oxygen-plasma treated copper film coated with Fe catalysts by e-beam evaporation through a one-step CVD process using a mixture of acetylene and hydrogen at 650 torr for 10 to 20 min [32]. Vertically grown multiwalled CNTs on a single-layer graphene floor were synthesized by a one-step acetylene-CVD process on copper foil (catalysts for graphene growth)

FIGURE 1: The CV curve at a potential scan rate of 100 mV/s in a 6 M KOH solution for carbon nanotube/graphene composites grown by one-step CVD for 10 min at $850^\circ C$.

FIGURE 2: The effects of carbon nanotube/graphene composites grown by one-step CVD for 10 min at different growing temperatures ($850^\circ C$, $900^\circ C$, and $950^\circ C$) on specific capacitance.

coated with Fe (catalysts for multiwalled CNTs growth) by e-beam evaporation [33]. To increase the accessibly specific surface area and the stability as well as conductivity between the carbon nanotube bundles as well as the nickel foam, three-dimensional few layer graphene/multiwalled carbon nanotube architectures were fabricated on oxygen-plasma treated nickel foam coated with Fe catalysts by e-beam evaporation through a one-step ambient pressure CVD process using a mixture of acetylene and hydrogen [34]. Therefore, in order to control the packing density of CNTs and the number of graphene layers, carbon nanotube/graphene composites were fabricated on hydrogen-annealed nickel foam coated with Co catalysts by radio frequency (RF) magnetron sputtering through a one-step ambient pressure CVD process at different temperatures and times in this research.

2. Materials and Methods

Nickel foam with three-dimensional conductive network structure working as template for the growth of graphene facilitated easy access of electrolyte ions to electrode surface and hence increased the active material utilization of the electrode and then the specific capacitance of the electrode with the Ni foam current collector was higher than that with the Ti mesh current collector [35, 36]. The nickel foam ($1 \times 2 \text{ cm}^2$) was degreased ultrasonically in acetone until any surface grease was completely eliminated. Next, it was rinsed

FIGURE 3: Raman spectra of carbon nanotube/graphene composites grown by one-step CVD for 10 min at different growing temperatures ((a) 850°C, (b) 900°C, and (c) 950°C).

with pure deionized water and then oven-dried in air (50°C) to constant weight.

Carbon nanotube/graphene composites were grown by one-step ambient pressure CVD. First, the pretreated nickel foam substrate was heated at 1000°C in H₂ (100 sccm) and Ar (250 sccm) for 10 min to reduce the surface oxide layer. Next, before carbon nanotube/graphene composites growth, the Co catalyst particles were deposited on the pretreated and annealed nickel foam substrate by RF magnetron sputtering from a 3-inch disk Co target (purity: 99.9%, purchased from SCM, INC) in a vacuum chamber with a background pressure of 7×10^{-6} torr. The distance between the target and the substrate was 10 cm. The sputtering power, sputtering pressure, sputtering time, and the volume flow rate of argon were maintained at 50 W, 5 mtorr, 5 min, and 25 sccm, respectively. Finally, carbon nanotube/graphene composites were grown on the annealed as well as Co-coated nickel foam using thermal chemical vapor deposition (CVD) with a gas mixture of C₂H₂ (15 sccm) and H₂ (100 sccm) as well as Ar (400 sccm) at different temperatures (850, 900, and 950°C) as well as times (10, 15, and 20 min) and then by cooling to ambient temperatures at a rate of 10°C min⁻¹ in Ar with the same volume flow rate as carbon nanotube/graphene composites grown.

Electrochemical measurements for the prepared carbon nanotube/graphene composite electrodes were performed

using an electrochemical analyzer (CH Instruments CHI 608B, USA). The three-electrode cell consisted of Ag/AgCl as the reference electrode, Pt as the counter electrode, and the prepared carbon nanotube/graphene composite electrodes as the working electrode. The electrolytes were degassed with purified nitrogen gas before voltammetric measurements and nitrogen was passed over the solution during all the measurements. The solution temperature was maintained at 25°C by means of circulating water thermostat (HAAKE DC3 and K20, Germany). The cyclic voltammetry (CV) was undertaken with a 6 M aqueous electrolyte (KOH) since the high KOH concentration led to high capacitance, low internal resistance, and a narrow voltage window for activated carbon electrodes [37]. A CV scan rate of 100 mV s⁻¹ in the range -1~0 V was used in all measurements except where stated. Capacitance is normalized to 1 g of the carbon nanotube/graphene composites except where stated:

$$C = \frac{1}{m\Delta V S} \int i dV, \quad (1)$$

where m is the mass of the carbon nanotube/graphene composites, ΔV is the potential window, S is the scan rate, and $\int i dV$ is the integrated area of the CV curve.

Chronopotentiometry (CP) was undertaken with varying currents (1, 3, and 5 mA).

FIGURE 4: The FESEM images of carbon nanotube/graphene composites grown by one-step CVD for 10 min at different growing temperatures ((a) 850°C, (b) 900°C, and (c) 950°C).

The packing density of CNTs for carbon nanotube/graphene composites grown at different temperatures as well as times and the thickness of the carbon nanotubes for the carbon nanotube/graphene composite grown for 10 min at 850°C were conducted by field emission scanning electron microscope (FE-SEM: JEOL JSM-6700F, Japan). Furthermore, the I_{2D}/I_G for carbon nanotube/graphene composites grown at different temperatures and times were investigated by microscopes Raman spectrometer (inVia, Renishaw, England).

3. Results and Discussion

The CV curve at a potential scan rate of 100 mV/s in a 6 M KOH solution for carbon nanotube/graphene composites grown by one-step CVD for 10 min at 850°C is shown in Figure 1, which exhibits a nearly rectangular shape.

Figure 2 shows the effects of carbon nanotube/graphene composites grown by one-step CVD for 10 min at different growing temperatures (850, 900, and 950°C) on specific capacitance. Carbon nanotube/graphene composites grown by one-step CVD at 850°C possessed the highest specific capacitance (see Figure 2). The reason behind this behavior may be explained as follows. The lower the growing temperature, the larger the I_D/I_G (see Figure 3) due to a higher packing density of CNTs (possessing more defects than graphene) at a lower growing temperature (see Figure 4 and Table 1). A similar result (the density of CNTs can be controlled by the

FIGURE 5: The effects of carbon nanotube/graphene composites grown by one-step CVD at 850°C for different growing times (10, 15, and 20 min) on specific capacitance.

CVD growth temperature) has been published in previous literature [31]. The I_D/I_G (0.427) for carbon nanotube/graphene composites grown by one-step CVD at 850°C is larger than others (0.388 and 0.206). The larger the I_D/I_G , the more the defect of carbon nanotube/graphene composites [21] and then the higher the surface area of carbon nanotube/graphene composites, which led to increasing the specific capacitance

FIGURE 6: Raman spectra of carbon nanotube/graphene composites grown by one-step CVD at 850°C for different growing times ((a) 10 min, (b) 15 min, and (c) 20 min).

FIGURE 7: The FESEM images of carbon nanotube/graphene composites grown by one-step CVD at 850°C for different growing times ((a) 10 min, (b) 15 min, and (c) 20 min).

TABLE 1: The carbon nanotube packing density (calculated from Figures 4 and 7) of carbon nanotube/graphene composites grown by one-step CVD at different growing temperatures and times.

Carbon nanotube/graphene composites growing conditions	Carbon nanotube packing density, cm^{-2}
One-step CVD at 850°C for 10 min	7.86×10^7
One-step CVD at 900°C for 10 min	9.34×10^6
One-step CVD at 950°C for 10 min	2.80×10^6
One-step CVD at 850°C for 15 min	8.06×10^8
One-step CVD at 850°C for 20 min	8.87×10^8

for carbon nanotube/graphene composites grown by one-step CVD at 850°C . Furthermore, the lower the growing temperature, the larger the I_{2D}/I_G (see Figure 3). The I_{2D}/I_G (0.826) for carbon nanotube/graphene composites grown by one-step CVD at 850°C is larger than others (0.599 and 0.578). The larger the I_{2D}/I_G , the smaller the number of layers of graphene [19] and then the lighter the graphene weight, which also led to increasing the specific capacitance for carbon nanotube/graphene composites grown by one-step CVD at 850°C . A similar result (thicker graphene results from a higher growth temperature) has been published in previous literature [20, 22].

Figure 5 shows the effects of carbon nanotube/graphene composites grown by one-step CVD at 850°C for different growing times (10, 15, and 20 min) on specific capacitance. Carbon nanotube/graphene composites grown by one-step CVD for 10 min possessed the highest specific capacitance (see Figure 5). The reason behind this behavior may be explained as follows. The shorter the growing time, the larger the I_{2D}/I_G (see Figure 6). The I_{2D}/I_G (0.826) for carbon nanotube/graphene composites grown by one-step CVD for 10 min is larger than others (0.735 and 0.568). The larger the I_{2D}/I_G , the smaller the number of layers of graphene [19] and then the lighter the graphene weight, which led to increasing the specific capacitance for carbon nanotube/graphene composites grown by one-step CVD for 10 min. A similar result (thicker graphene results from a longer growth time) has been published in previous literature [22]. Furthermore, the I_D/I_G (0.427) for carbon nanotube/graphene composites grown by one-step CVD for 10 min is a little smaller than others (0.448 and 0.493) since the packing density of CNTs (possessing more defects than graphene) suddenly decreases with the decreasing growing time (see Figure 7 and Table 1) and even the average defect density for graphene increases with the decreasing growing time [21].

Figure 8 shows discharge curves of the carbon nanotube/graphene composite (grown by one-step CVD at 850°C for 10 min) with different currents. The capacitance of the carbon nanotube/graphene composite was calculated from $C = i/[m(dE/dt)]$, where m is the mass of the carbon nanotube/graphene composites, i is the current, and dE/dt is the slope of Figure 8. The capacitances as calculated by the above equation are shown in Figure 9. The lower the current, the higher the capacitance. The reason behind this behavior may be that the lower the current, the longer the discharge

FIGURE 8: Discharge curves of the carbon nanotube/graphene composite (grown by one-step CVD at 850°C for 10 min) with different currents.

time (see Figure 8), leading to higher capacitance due to $C = i/[m(dE/dt)]$.

The I_G/I_{2D} for the carbon nanotube/graphene composite grown for 10 min at 850°C is about equal to 1.21 (see Figure 3(a)). The number of layers of the graphene for the carbon nanotube/graphene composite is about 20 [38]. The thickness of single-layer graphene is about 0.34 nm [39] and the interlayer distance between the graphene sheets is about 0.35 nm [40]. According to the above data, the thickness (13.45 nm) of the graphene for the carbon nanotube/graphene composite can be estimated. The thickness of the carbon nanotubes for the carbon nanotube/graphene composite is about $3.02 \mu\text{m}$ (see Figure 10). So the thickness of the carbon nanotube/graphene composite grown on Ni foam for 10 min at 850°C is about $3.03345 \mu\text{m}$. Furthermore, the area of the substrate (nickel foam) is 2 cm^2 . Then the volume of the carbon nanotube/graphene composite is $6.0669 \times 10^{-4} \text{ cm}^3$. Therefore, the gravimetric capacitance (90.79 F g^{-1} , please see at 850°C and 1000 cycles of Figure 2 of the revised paper) of the carbon nanotube/graphene composite (0.008 g) can be converted into the volumetric capacitance (1197 F cm^{-3}).

4. Conclusions

The lower the growing temperature, the larger the I_D/I_G and then the more the defect, the higher the surface area, which led to increasing specific capacitance. The lower the growing temperature, the larger the I_{2D}/I_G , and then the smaller the number of layers of graphene, the lighter the graphene weight, which also led to increasing specific capacitance. Furthermore, the shorter the growing time, the larger the I_{2D}/I_G , and then the smaller the number of layers of graphene, the lighter the graphene weight, which led to increasing specific capacitance.

FIGURE 9: The effects of CP currents on specific capacitance of the carbon nanotube/graphene composite grown by one-step CVD at 850°C for 10 min.

FIGURE 10: Cross-sectional morphology of the carbon nanotube/graphene composite grown on Co-coated nickel foam by one-step CVD at 850°C for 10 min.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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