石墨烯/碳纳米管复合材料的制备及其电化学电容性能

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摘要 以化学气相沉积(CVD)法生长的石墨烯作为基体, 采用原位复合方法制备出三维石墨烯/碳纳米管纳米复合材料. 使用扫描电子显微镜(SEM)和透射电子显微镜(TEM)对复合材料的微观形貌和结构进行表征, 并运用循环伏安、交流阻抗等技术对纳米复合材料的超级电容性能进行研究. 实验结果表明, 石墨烯/碳纳米管纳米复合材料作为超级电容器电极材料, 在1.5 mol/L Li_2SO_4 体系中的最大比电容为289.8 F/g, 经2000次循环后, 其容量保持92%, 表现出优异的比容量和循环稳定性.

关键词 石墨烯, 碳纳米管, 复合材料, 超级电容性能

超级电容器作为一种介于传统电容器与可充电电池之间的新型储能装置^[1~5], 因其比容量大、功率密度高、循环寿命长和对环境无污染等特点而备受人们的关注. 作为新型绿色环保产品, 超级电容器能提供高于传统电容器的能量密度, 虽然低于电池的能量密度, 但其相比于二次电池具有更加优异的功率密度和循环寿命. 因此, 超级电容器有望应用于移动通讯、电动汽车、微电子器件等领域, 具有广阔的应用前景^[4~9]. 在超级电容器中, 电极材料是关键因素, 其性能直接决定着超级电容器的主要性能指标.

石墨烯(graphene)作为一种新型的二维纳米材料, 已受到研究者的广泛关注^[10~12]. 石墨烯由于具有导电性良好、电荷迁移率高^[13]、比表面积高^[14]等许多优异的性质, 使其能应用于高分子复合材料^[10]、场效应晶体管^[15]、液晶显示^[16]、能量存储等诸多领域. 因此, 具有优良导电性和高比表面积的石墨烯将是超级电容器的理想电极材料^[17], 有望进一步提高超级电容器的功率密度和能量密度. 石墨烯作为超级电容器电极材料的相关报道已有不少^[18~21], 如Du

等人^[22]采用热剥离法制备得到石墨烯纳米片, 以30%(质量分数)KOH作为电解液时测得其比电容为150 F/g. Ekchand研究组^[23]采用剥离制备的石墨烯作为电极材料, 在1 mol/L H_2SO_4 电解液中测得最大比电容达117 F/g.

本文以化学气相沉积(CVD)法生长的石墨烯作为原料, 利用原位复合的方法, 在石墨烯表面采用CVD方法沉积碳纳米管(CNTs), 得到石墨烯/碳纳米管三维纳米复合材料, 以期提高超级电容器的比能量和循环稳定性, 并对其超级电容器性能进行研究.

1 实验

(i) 材料制备. 采用CVD法制备石墨烯, 具体步骤为: 将清洗好的泡沫镍片置于高温管式炉的恒温区, 先通入纯Ar 30 min(200 mL/min)除去石英管内的空气, 再通入 H_2/Ar (100/200 mL/min)的混合气体, 以20 °C/min的升温速率升温到850 °C; 升温结束后, 由 H_2/Ar 的混合气体中载入 CH_4 (100/200/10 mL/min), 保温20 min, 进行石墨烯的生长; 生长结束后, 关闭

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CH_4 和 H_2 ,使样品在Ar保护气氛中随炉冷却到室温。

将0.35 g二茂铁溶解于7 mL二甲苯溶液,超声1 h,得到橙红色的均匀溶液,作为碳纳米管生长的催化剂和液相碳源,二茂铁在高温下分解得到纳米尺度的铁颗粒,二甲苯作为液态碳源高温下分解提供碳原子,碳原子被铁颗粒吸附并催化生长出碳纳米管;将沉积石墨烯的泡沫镍片置于高温管式炉中,先通入Ar排除空气,再以 $15\text{ }^\circ\text{C}/\text{min}$ 的升温速率升温到 $750\text{ }^\circ\text{C}$,将气体切换到 H_2/Ar 混合气体($50/350\text{ mL}/\text{min}$),保温10 min;然后将上述混合溶液以 $0.2\text{ mL}/\text{min}$ 的速度注入反应腔体,保持30 min后停止注入,进行石墨烯表面碳纳米管的沉积;沉积结束后,将气体切换为Ar($200\text{ mL}/\text{min}$)并随炉冷却至室温;最后得到表面生长了石墨烯/碳纳米管纳米复合材料的样品,并将生长有石墨烯和碳纳米管的泡沫镍作为工作电极进行电化学电容性能测试。

(ii) 结构与性能表征. 用JEOL JSM-6700F型场发射扫描电子显微镜(FESEM, 操作电压20 kV)和FEI Tecnai G² F30型透射电子显微镜(TEM, 加速电压200 kV)观察样品的微观结构和表面形貌。

采用三电极体系,以饱和甘汞电极为参比电极,铂电极为辅助电极,在CHI 660D电化学工作站上进行循环伏安和交流阻抗(AC impedance)测试. 电解质溶液使用 $1.5\text{ mol}/\text{L}$ Li_2SO_4 溶液,循环伏安测试电压为 $-0.5\sim 0.5\text{ V}$,扫描速率为 $2\sim 40\text{ mV}/\text{s}$;交流阻抗的测试频率为 $0.01\text{ Hz}\sim 100\text{ kHz}$,交流信号振幅为5 mV。

2 结果与讨论

将生长了石墨烯和碳纳米管的泡沫镍置于SEM下进行观察. 图1(a)为在泡沫镍上长有石墨烯和碳纳米管的SEM照片. 从图中可以看到泡沫镍的立体网状结构,而从图1(a)插图可以看到石墨烯/碳纳米管复合材料在金属镍表面密集分布的微观形貌,且分布较为均匀. 从图1(b)可以看出,大量的碳纳米管附着在呈山丘状凸起的石墨烯宏观体表面,且碳纳米管含量较高,其取向性不明显,但具有一定程度的缠绕、弯曲,管径分布比较均匀,表明已在泡沫镍表面制备出石墨烯/碳纳米管三维复合材料。

图2为石墨烯/碳纳米管复合材料的微观形貌. 将生长了石墨烯和碳纳米管的泡沫镍经过盐酸溶液刻蚀后得到石墨烯/碳纳米管复合材料;用去离子水清洗后置于酒精中分散,取少量在TEM下进行观察. 由

图1 石墨烯/碳纳米管复合材料的低倍(a)和高倍(b)SEM照片

Figure 1 Low (a) and high (b) magnification SEM images of graphene/CNT composite

图2 (网络版彩色)石墨烯/碳纳米管复合材料的TEM图((a)~(c))及结构示意图(d)

Figure 2 (Color online) TEM images ((a)~(c)) and structure schematic view (d) of graphene/CNT composite

图2(a)可以看出,碳纳米管相互交叠,且被石墨烯包裹,形成碳纳米管被石墨烯薄膜包夹的夹层结构,说明在第2步生长碳纳米管的过程中,也伴随有石墨烯的生长. 虚线圆圈内可观察到许多碳纳米管具有顶端黑色圆环,这是多根碳纳米管依附于石墨烯表面开始聚集生长的部位,说明复合材料中碳纳米管和石墨烯相互结合良好. 图2(b)是边缘区域石墨烯的TEM照片以及衍射图,可以看到,石墨烯为半透明状,其衍射谱图的衍射斑点呈现出多晶环状,这是由于其层数多,衍射一般就会从单晶衍射点趋向多晶环. 此外,清晰的六环衍射斑点说明得到的是结晶度较好的多层石墨烯. 图2(c)中矩形、椭圆形显示的是石墨烯与碳纳米管的两种结合方式,分别是石墨烯与碳纳米管管壁结合(矩形)、顶部或底部结合(椭圆)。

图2(d)是其对应的结构示意图,而实际的堆叠方式可能不是只有这两种夹心结构.这两种结构可以利用碳纳米管使石墨烯片层分开,防止发生片层间的堆叠现象,同时能够为石墨烯片层间的电子传输搭建桥梁.此外,石墨烯的片层结构及片层间的空隙可以实现活性物质的高密度负载,该特性是单一的石墨烯或碳纳米管所没有的.

图3是石墨烯和石墨烯/碳纳米管复合材料不同扫描速率下的循环伏安曲线.由图3可知,石墨烯和石墨烯/碳纳米管复合材料的循环伏安曲线(CV)中氧化-还原峰不明显,说明在扫描电位范围内,没有发生明显的氧化-还原反应;但曲线显示出超级电容特有的较为对称的矩形轮廓,可逆性良好,总体表现出较好的超级电容性能.由图3(a)和(b)对比可以看到,石墨烯/碳纳米管复合材料比石墨烯的矩形性更好,说明石墨烯/碳纳米管复合材料具有更好的双电层特性.由图3(b)可以看出,随着扫描速率的增加,石墨烯/碳纳米管复合材料的循环伏安曲线矩形性降低,这是因为扫描速率较大时,电化学极化加剧,使得电极活性物质利用率降低;而且在40 mV/s的高扫描速率下曲线仍然保持着较好的矩形对称性,说明其功率性能良好.

图4(a)为石墨烯和石墨烯/碳纳米管复合材料的比电容随扫描速率变化的曲线.根据循环伏安曲线,可以计算比电容值,其计算公式为

$$C_s = \frac{1}{\Delta V s} \int_{v_0}^{v_1} \frac{|I|}{(dV/dr)} dV, \quad (1)$$

其中, ΔV 为电压窗口, s 为工作电极的表面积, v_0 和 v_1 分别表示起始和终止电位, I 为即时电位所对应的电流,

dV/dr 表示电压扫描速度.用式(1)计算得到,在低扫描速率2 mV/s时,两种材料的比电容最大,石墨烯的比电容为150.1 F/g,而石墨烯/碳纳米管复合材料的比电容为289.8 F/g,复合材料的比电容得到了明显提高.即使在扫描速度高达40 mV/s时,复合材料的比电容仍然保持99.1 F/g,这主要是由于石墨烯和碳纳米管的三明治结构,可以有效防止石墨烯片层发生堆叠,增大比表面积,而碳纳米管可以为石墨烯片层间的电子和离子传输搭建桥梁,以实现活性物质的高密度负载,因而双电层电容较高.另外,随着扫描速率的增加,二者的比电容值都呈下降趋势,说明高扫描速率下发生了电化学极化现象,导致比电容降低;当扫描速率增加至40 mV/s时,石墨烯和石墨烯/碳纳米管复合材料的比电容下降率分别为80%和65%,由此可见,随着扫描速度的增大,后者电容的稳定性更好.图4(b)为两种材料在开路电位下的电化学阻抗谱Nyquist曲线.在高频范围,曲线半圆部分的直径代表电荷在电极内的迁移电阻(R_{ct})^[24-26].从图中可以看出,石墨烯/碳纳米管复合材料的电荷迁移电阻比石墨烯小,产生该现象的原因可能是由于碳纳米管的引入,避免了石墨烯的堆叠,增加了材料的比表面积,促进电荷在石墨烯片层上的迁移,从而在一定程度上减小电荷迁移电阻.因此,石墨烯/碳纳米管复合材料具有更优异的电荷转移性能和双电层电容性能.

图5为石墨烯和石墨烯/碳纳米管复合材料在扫描速率为10 mV/s时的循环稳定性曲线,每隔50个循环记录1次.2000次循环的循环稳定性曲线可以看出二者都具有较高的循环稳定性.由图5可知,扫描速度为

图3 (网络版彩色)石墨烯(a)和石墨烯/碳纳米管复合材料(b)在不同扫描速率下的循环伏安曲线
Figure 3 (Color online) CVs of graphene (a) and graphene/CNT composite (b) at different scan rate

图4 (网络版彩色)石墨烯和石墨烯/碳纳米管复合材料在不同扫描速率下的比电容值(a)及交流阻抗图谱(b)

Figure 4 (Color online) Specific capacitance (a) and AC impedance (b) of graphene and graphene/CNT composite at different scan rate

图5 (网络版彩色)石墨烯和石墨烯/碳纳米管复合材料在扫描速度为10 mV/s时的循环稳定性曲线

Figure 5 (Color online) Cycling stability curves of graphene and graphene/CNT composite at the scan rate of 10 mV/s

10 mV/s时, 石墨烯/碳纳米管复合材料的首次比电容为211.9 F/g, 而经过2000次循环后, 比电容仍保持

195.6 F/g, 保持率为92%, 平均每次循环下降0.0038%, 电极比电容衰减很小, 说明复合材料具有良好的超级电容性能和循环稳定性. 而石墨烯的比电容虽然没有明显下降, 但是与碳纳米管复合后的比电容明显比复合前高, 即使2000次循环后有所下降, 也高于单纯石墨烯的比电容, 这说明石墨烯/碳纳米管复合材料将在超级电容器领域具有更广阔的应用前景.

3 结论

采用原位CVD法生长石墨烯, 制备出石墨烯/碳纳米管三维复合材料. 石墨烯/碳纳米管复合材料作为超级电容器电极材料, 具有优异的比电容和循环稳定性, 在1.5 mol/L Li_2SO_4 体系中的最大比电容为289.8 F/g. 扫描速度为10 mV/s时, 经过2000次循环后比电容达195.6 F/g, 比电容保持率为92%.

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Summary for “石墨烯/碳纳米管复合材料的制备及其电化学电容性能”

Preparation and electrochemical capacitive performance of graphene/carbon nanotube composite

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The development of more advanced and environmentally friendly energy storage devices is an urgent request to meet future societal and environmental needs. Supercapacitor is one of the most promising electrochemical energy storage devices owing to its long cycle life, high dynamic propagation, quickly response and low maintenance cost compared to the traditional batteries and capacitors. However, their energy density is far less batteries, which limits their application in energy storage. In order to break through the limitation, exploring novel electrode materials with both high energy densities and power densities is extremely urgent. At present, it is a hot topic to produce composite electrode materials with synergistic effect. Graphene, a one-atom-thick two dimensional single layer of sp^2 -bonded carbon, owing to its unique structural properties, has exhibited many advantages, such as extraordinarily high electrical and thermal conductivity, great mechanical strength and high surface area, making it a potential candidate for applications in energy storage field. Therefore, graphene based composite materials have been utilized in various practical applications, including energy storage and conversion, transparent conducting films, chemical sensors, and actuators, etc. Given the extraordinary properties of graphene, such as the low mass density, good compatibility, highly conductive, large specific surface area and excellent flexibility, it is considered as one of the most suitable substrate materials for preparing supercapacitor electrodes.

In recent years, graphene composites as supercapacitor electrode material have been widely investigated. Here, three-dimensional (3D) graphene/carbon nanotube (CNT) nanocomposites were prepared by *in-situ* compound method using as-synthesized graphene as matrix, which prepared by chemical vapor deposition (CVD). Firstly, graphene was prepared on Ni foam by CVD method using CH_4 as carbon sources and H_2/Ar as buffer gas at $850^\circ C$. Then a solution carbon source was obtained by ultrasonic vibration using a mixture solution of ferrocene and dimethylbenzenes. Finally, 3D graphene/CNT nanocomposite was synthesized by CVD method using Ni foam deposited graphene as supporter substrate at $750^\circ C$ for 30 min. The morphology and microstructure of the resulting samples were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the electrochemical capacitive performance of the samples were investigated using CHI 660D chemical workstation to analyze the cyclic voltammetry and AC impedance.

The results indicated that large amounts of graphenes had been formed on the Ni foam and 3D graphene/CNT nanocomposites also had been synthesized. The 3D lamellar structures between graphenes formed in the synthesis process could densely upload active substance, which was very different in structure and performance with individual graphene. The cyclic voltammetry (CV) curves of 3D graphene/CNT composite exhibited that the electrochemical capacitive performance has good reversibility. The Nyquist plots also displayed that the 3D graphene/CNT composite has excellent performance of electric charge transportation and double layer capacitance. The electrochemical measurements indicated that the maximum specific capacitance of 3D graphene/CNT composite, as the supercapacitor electrode material, exhibited a maximum specific capacitance of 289.8 F/g using $1.5\text{ mol/L Li}_2\text{SO}_4$ as the electrolyte in the system and also showed excellent high-capacity and cycling stability. The specific capacitance of the 3D graphene/CNT composite remains 92% after 2000 cycles.

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