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超临界二氧化碳协助制备多组分复合材料及在超级电容器方面的应用

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摘要 采用绿色水热方法合成石墨烯/吡咯气凝胶(G-Py), 原位聚合的方法制备碳纳米管/聚苯胺复合材料(CNT/PANI), 而后通过超临界二氧化碳的协助制备了一系列G-Py和CNT/PANI的复合材料, 并通过红外光谱(FTIR)、X射线衍射(XRD)和Raman光谱研究其结构变化, 电化学工作站测试其电性能, 从而探究超临界二氧化碳对其结构和性能的影响. 研究结果表明, 经过超临界二氧化碳协助一步法得到的复合材料具有最优的电性能. 电化学测试表明其比电容高达373 F/g, 是未经超临界二氧化碳处理制备的复合材料的1.4倍, 说明超临界二氧化碳辅助制备是构筑多组分复合材料的一种有效方法.

关键词
石墨烯凝胶
聚苯胺
碳纳米管
超临界二氧化碳
超级电容器

在过去的几年中, 构建石墨烯的三维结构成为研究的热点[1~4]. 将单个石墨烯片层组合成三维的宏观结构, 对实际应用非常重要. 石墨烯气凝胶具有内部交联的三维贯通网络结构, 具有低密度、较高的电导率、多孔以及比表面积大等优点, 其显著的优点使其应用在超级电容器、柔性电子装置、催化、储氢等领域. 碳材料[5,6]、过渡金属氧化物[7,8]和导电聚合物[9,10]是优异的3大电极材料. 聚苯胺由于其低成本、结构可控、良好的生物相容性以及环境稳定性, 在电化学领域备受关注. 由于掺杂和去掺杂的过程中, 聚苯胺的收缩和溶胀导致其降解困难, 使得基于聚苯胺的超级电容器循环寿命比较短. 为了克服以上缺陷, 将聚苯胺与其他材料如碳材料复合用作电极以获得优异的电性能.

超临界二氧化碳由于低黏度、高扩散性、零表面张力的特性, 常被用来制备纳米复合材料[11~13]. 考虑到软物质理论和超临界二氧化碳的可调性, 通过超临界二氧化碳的协助, 制备可控的结构以及协助纳米粒子可控自组装是一个重要的研究领域[14~16]. 本课题组[17]之前的研究中, 通过简单浸泡的方法将石墨烯/吡咯气凝胶与碳纳米管/聚苯胺组合起来, 碳纳米管/聚苯胺有效阻止了石墨烯片层的聚集; 另外, 在碳管上均匀分散的聚苯胺可有效提高聚苯胺的利用率, 缩短了离子的扩散路径, 从而提高其电性能. 在此基础上, 我们以石墨烯/吡咯凝胶和碳管/聚苯胺为基本单元, 通过超临界二氧化碳的协助, 制备得到一系列不同的复合材料, 通过红外光谱(FTIR)、X射线衍射(XRD)和Raman光谱研究其结构变化, 并通过电化学工作站测试其电性能, 探究超临界二氧化碳对复合材料结构和性能的影响. 该复合材料性能优良, 在质轻柔性储能装置方面有较大的应用潜力.

1 实验与方法

(ⅰ) 原料. 石墨粉(Acros Organics公司); 无水乙醇(分析纯, 国药集团化学试剂有限公司); 苯胺(分析纯, 天津市大茂化学试剂厂); 碳管(北京德科

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Yang H X, Xu Q. Fabrication of hierarchical nanohybrids with assistance of supercritical CO_2 for high-performance supercapacitor applications (in Chinese). Chin Sci Bull, 2015, 60: 2573–2578, doi: 10.1360/N972015-00316

岛金有限公司); 吡咯(pyrrole, Aladdin公司); 过硫酸铵(APS, 分析纯, Sigma Aldrich公司); 二氧化碳(纯度为99.9%, 郑州市双阳气体公司).

(ⅱ) 方法. 根据文献[17]方法制备得到三维石墨烯/吡咯(G-Py)和碳管/聚苯胺(CNT/PANI). G-Py与CNT/PANI通过直接浸泡法制备复合材料GPCP[17]. 作为比较, 制备一系列不同的复合材料: 将G-Py置于乙醇溶液中, 在超临界二氧化碳40℃, 16 MPa的条件下反应2 h, 烘干后得到的样品浸泡到CNT/PANI的乙醇溶液中2 h, 最终烘干, 制备得到复合材料记为SC-G-Py+CNT/PANI. 将CNT/PANI分散在乙醇溶液中, 在超临界二氧化碳40℃, 16 MPa的条件下反应2 h, 而后将G-Py凝胶浸泡到上述CNT/PANI的乙醇溶液中2 h, 最终烘干, 制备得到复合材料记为G-Py+SC-CNT/PANI. 将G-Py的乙醇溶液, 在超临界二氧化碳40℃, 16 MPa的条件下反应2 h, 烘干后得到的样品浸泡到经超临界处理过的CNT/PANI的乙醇溶液中2 h. 最终烘干, 制备得到复合材料记为SC-G-Py+SC-CNT/PANI. 将G-Py浸泡到CNT/PANI的乙醇溶液中, 而后快速转移到超临界二氧化碳中, 在40℃, 16 MPa的条件下反应2 h, 最终烘干, 制备得到复合材料SC-GPCP[18].

(ⅲ) 表征方法. 场发射扫描电子显微镜(SEM, JEOL JSM-6700F, 日本JEOL制造)和透射电子显微镜(FEI, Tecnai G2 20, 美国TEI公司)表征纳米复合材料的形态和结构; 采用红外光谱仪(FTIR, TENSOR 27, 德国Bruker公司)测定红外光谱, KBr压片法, 扫描范围4000~500 cm^{-1}; 采用RM2000型拉曼光谱仪(英国Renishaw公司)测定拉曼光谱, 激光波长514 nm, 扫描范围500~3500 cm^{-1}; 采用D/MAX-IIIB X射线衍射仪(日本RIGAKU公司)测试XRD, Cu Kα射线, λ=0.15418 nm, 扫描范围10°~80°; CHI650D电化学工作站(上海辰华仪器有限公司)分析电化学性能, 采用三电极系统(参比电极为饱和甘汞电极, 对电极为铂片电极, 工作电极为负载有样品的镍泡沫).

2 结果与讨论

如图1所示, 以G-Py和CNT/PANI为基本单元, 通过超临界二氧化碳外场的协助, 制备了一系列的纳米复合材料.

图2(a)为所制得的G-Py凝胶SEM图, 从图上可以看出, G-Py凝胶具有内部相互贯通的大孔结构, 其内

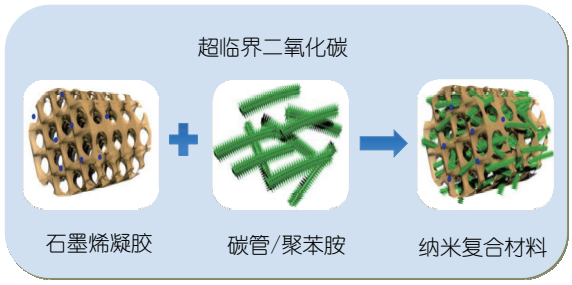


图 1 (网络版彩色)制备不同纳米复合材料的示意图

Figure 1 (Color online) Schematic illustration of the fabrication process of different nanohybrids

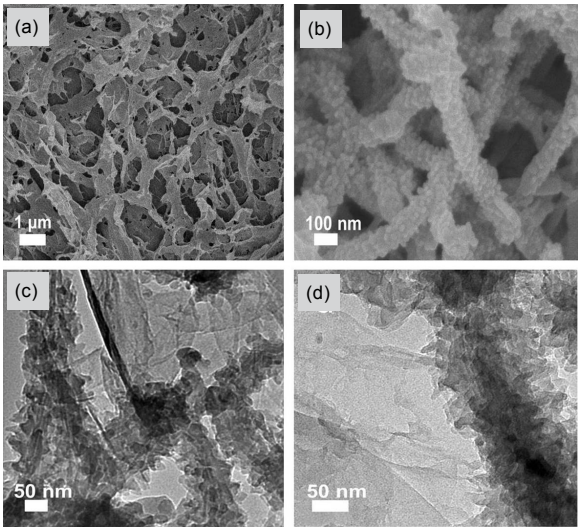


图 2 不同复合材料的SEM和TEM图. (a) G-Py凝胶; (b) CNT/PANI复合材料; (c) 未经超临界二氧化碳处理得到的复合材料GPCP; (d) 超临界二氧化碳协助一步法得到的复合材料SC-GPCP

Figure 2 The SEM and TEM images of different nanohybrids. (a) G-Py aerogel; (b) CNT/PANI nanohybrids; (c) GPCP nanohybrids prepared without the assistant of SC CO_2; (d) SC-GPCP nanohybrids prepared through one step method with the assistance of SC CO_2

部贯穿的网络结构, 有利于缓冲离子以最小的扩散距离从外部电解液扩散到内表面. 图2(b)为苯胺单体浓度为50 mmol/L时CNT/PANI的SEM图, 从图上可以看到聚苯胺垂直生长在碳管的表面, 这是由于碳管的石墨化结构与聚苯胺的芳香环结构之间的π–π相互作用, 使其紧密地结合在一起. 图2(c)是未经超临界二氧化碳处理得到的复合材料GPCP, 图2(d)为超临界二氧化碳协助一步法得到的复合材料SC-GPCP, 两者相比, 说明经过超临界二氧化碳处理后, 样品的微观形貌发生了变化, 棒状聚苯胺的形态更加疏松, 推测这样的形貌更有利于电极和电解液的接触, 从而增强电性能. 另一方面, 由于超临界二氧化碳具有

零表面张力、高扩散性等特性，可将聚合物携带到G-Py凝胶的内部，不仅可以阻止石墨烯片层的聚集，而且有利于发挥多组分的协同效应，提高电性能.

红外光谱的产生来源于分子对入射光子能量的吸收而产生的振动能级的跃迁. 红外吸收光谱主要用于鉴别官能团的存在，并由此测定有机化合物的结构. 如图3所示，样品在1613，1464 cm^{-1}的红外吸收峰，分别对应于变形的醌环和苯环的伸缩振动峰，这是聚苯胺的特征红外峰[19]；在1090 cm^{-1}处的峰是醌环上N原子的伸缩振动，此峰与文献[20]报道的1130 cm^{-1}处的峰相对应，即发生了红移现象，说明聚苯胺与石墨烯存在着强烈的相互作用，这种作用增强了电子在聚苯胺分子链上的离域能力，有利于增强其导电性；在1303 cm^{-1}处的峰是C–N伸缩振动[21]，整体上可以看出复合后的材料具有聚苯胺所有的吸收峰，吸收峰的位置基本保持不变，意味着聚苯胺与石墨烯达到了良好的复合效果，说明通过超临界二氧化碳的协助，成功制备了G-Py与CNT/PANI的复合材料.

图4(a)是不同方法得到的复合材料的XRD谱图，无论超临界二氧化碳处理凝胶G-Py，CNT/PANI，还是两者都经过超临界二氧化碳的处理得到的复合材料，它们的峰形基本一致；图4(b)为不同复合材料的Raman光谱图，1348 cm^{-1}的D峰代表石墨烯边缘的缺陷及无定形结构，1590 cm^{-1}处的G峰对应于碳原子sp^2杂化的面内伸缩振动，代表有序的sp^2键结构，通

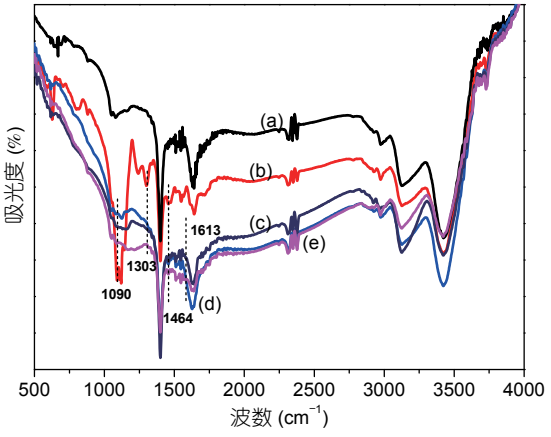


图 3 (网络版彩色)不同方法得到复合材料的FTIR谱图. (a) G-Py; (b) CNT/PANI; (c) G-Py+SC-CNT/PANI; (d) SC-G-Py+CNT/PANI; (e) SC-G-Py+SC-CNT/PANI

Figure 3 (Color online) FTIR spectra of nanohybrids obtained via different methods. (a) G-Py; (b) CNT/PANI; (c) G-Py+SC-CNT/PANI; (d) SC-G-Py+CNT/PANI; (e) SC-G-Py+SC-CNT/PANI

常用D峰和G峰的强度比(I_D/I_G)来表征氧化石墨烯的还原程度[22,23]，对SC-G-Py+CNT/PANI，G-Py+SC-CNT/PANI，SC-G-Py+SC-CNT/PAN而言，其I_D/I_G比值分别为0.944, 0.929, 0.926，说明不同方法得到的复合材料的拉曼光谱吸收强度比值并无太大区别，即不同的处理方法对复合材料结构影响不大.

为了使复合材料应用到超级电容器[24~26]，在三电极体系中，KOH用作电解液时，进一步估测了复合材料用作电极时的电性能. 计算公式如下:

$$C=\frac{1}{mv\Delta V}\int i(V)\mathrm{d}v,$$

式中，m是活性物质的质量，v是扫描速率，ΔV是扫描电压范围，$\int i(V)\mathrm{d}v$是整个曲线的面积.

图4(c)是通过不同复合方法得到的纳米复合材料的循环伏安曲线，从图中可以看出，石墨烯凝胶和苯胺包裹的碳管都经过超临界二氧化碳处理后得到的复合材料SC-G-Py+SC-CNT/PANI，具有更大的面积，说明其比电容较高，同时从图4(d)也可以看出，它具有最长的放电时间，说明其具有优异的电性能，通过下面的表1可以更清楚地看到不同方法得到的复合材料电性能之间的差异.

从表1我们可以看出，经过超临界二氧化碳处理得到的复合材料比电容值均高于未经处理的复合材料GPCP，说明超临界二氧化碳在制备复合材料方面具有明显的优势. G-Py+SC-CNT/PANI的比电容略高于GPCP；但SC-G-Py+CNT/PANI与CPGP相比，其比电容提高了更多，说明超临界二氧化碳对石墨烯凝胶的影响更大. SC-GPCP与其他复合材料相比，可知通过一步法得到的复合材料SC-GPCP具有最优的比电容. 复合材料具有增强的电性能主要是由于聚苯胺和石墨烯的协同效应[27~30]，一方面石墨烯提供较高的比表面积，另一方面聚苯胺插入到石墨烯的层间增加复合材料的导电性，并且有利于电解离子的传输和电子在电极材料内的传输. 通过超临界二氧化碳的协助，采用不同的方法得到复合材料的电性能均有所提高.

由于超临界二氧化碳具有零表面张力、高扩散性、强溶解力、快的传质速度与抗溶剂等特性，通过超临界二氧化碳的协助，可获得一系列的复合材料，SC-G-Py+CNT/PANI, G-Py+SC-CNT/PANI, SC-G-Py + SC-CNT/PANI, SC-GPCP，进而实现石墨烯气凝胶的功能化. 超临界二氧化碳协助得到的复合材料，均具

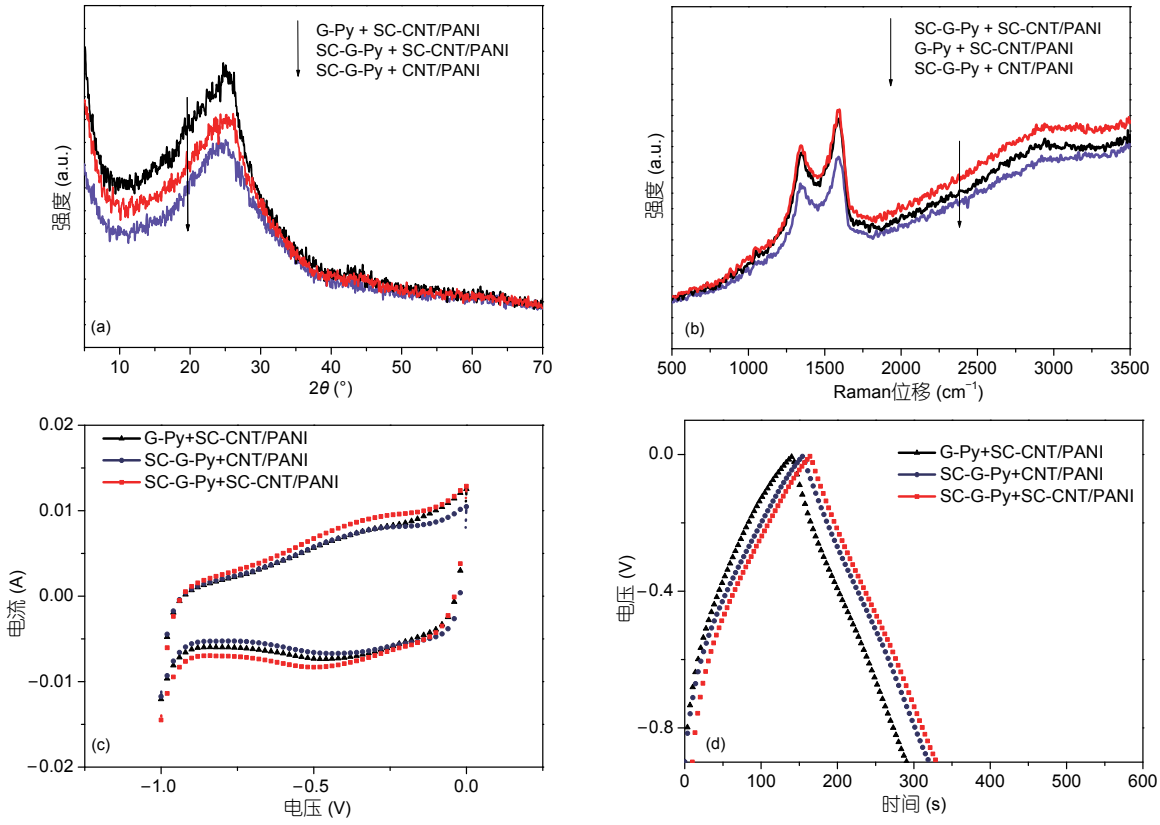


图 4 (网络版彩色)复合材料的(a) XRD谱图, (b) Raman光谱图, (c) 循环伏安曲线(扫描速率为 10 mV/s), (d) 恒流充放电曲线(电流密度为 1 A/g)

Figure 4 (Color online) (a) XRD, (b) Raman spectra, (c) cyclic voltammetry curves at 10 mV/s, (d) galvanostatic charge/discharge curves at a current density of 1 A/g of nanohybrids obtained via different methods

表 1 不同复合材料的比电容对比

Table 1 Comparison of specific capacitance of different nanohybrids

复合材料	C(F/g)
GPCP[17]	263
G-Py+SC-CNT/PANI	278
SC-G-Py+CNT/PANI	326
SC-G-Py+SC-CNT/PANI	310
SC-GPCP[18]	373

有较优异的性能, 主要归因于以下两方面的原因: (1) 经过超临界处理后, 棒状聚苯胺的形态更加疏松, 有利于电解液离子的传输, 从而提高电性能; (2) 通过超临界二氧化碳的协助, 不仅可以将溶胀的聚合物携带到多孔G-Py凝胶的表面, 也可以将其携带到多孔G-Py凝胶的内部, 发挥多组分的协同效应, 从而提高电性能, 因此, 通过一步法得到的复合材料具有更优的电性能.

3 结论

本文以G-Py和CNT/PANI为基本单元, 通过超临界二氧化碳的协助制备了SC-G-Py+CNT/PANI, G-Py+SC-CNT/PANI, SC-G-Py+SC-CNT/PANI, SC-GPCP一系列的复合材料, 研究了不同的处理方法对复合材料结构及电性能的影响, 研究结果表明通过超临界二氧化碳协助一步法得到的复合材料具有最优的电性能, 因此相关制备的复合材料在超级电容器电极材料等能源储存和转化领域具有潜在的应用.

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Fabrication of hierarchical nanohybrids with assistance of supercritical CO_2 for high-performance supercapacitor applications

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Graphene, a novel one-atom-thick two-dimensional (2D) nanomaterial, has attracted much attention, owing to its outstanding chemical and physical properties. In order to expand the application of graphene-based materials in environment, energy, biological and sensing fields, it is necessary to assemble 2D graphene sheets into three-dimensional (3D) architectures. It may furnish graphene materials with higher specific surface areas, stronger mechanically strengths and faster mass and electron transport kinetics because of the combination of 3D porous structure and the outstanding intrinsic properties of graphene. Building 3D graphene-based hybrid nanostructures with anticipated function has become one of the most active research fields. Considering the single-phased nanomaterials always have their intrinsic defects, scientists are inclined to combine unique properties of individual nanostructures and explore their synergistic effect. Considering its low viscosity, high diffusivity, zero surface tension, and plasticization to polymer, supercritical CO_2 ($scCO_2$)has been applied in the fabrication of nanomaterials. In view of the soft matter theory and the great tunabililty of $scCO_2$, it is anticipated that nanocomposites of tailored structure and controlled assembly of nanoparticles can be achieved with the help of $scCO_2$. Graphene-pyrrole (G-Py) aerogel was prepared by a green hydrothermal route, while carbon nanotube/polyaniline (CNT/PANI) composite dispersion was obtained via *in-situ* polymerization method. Then a series of nanohybrids were successfully prepared with the assistance of $scCO_2$. The obtained nanohybrids were characterized by FTIR, X-ray diffraction, Raman, and their electrochemical performance were further evaluated. It was fascinating to observe that the nanohybrid prepared through one step method with the assistance of $scCO_2$ had superior performance. Such hybrid materials exhibit significant specific capacitance of up to 373 F g^{-1}, which is 1.4 times that of the nanocomposite without the assistance of $scCO_2$ electrode. The experimental results are a proof of concept that $scCO_2$ is an efficient method to help achieve hierarchical multi-component nanohybrids and as well as it may guide the way for designing new functional materials that can be used as electrode materials for lightweight and flexible energy storage device in the near future.

graphene aerogel, polyaniline, carbon nanotube, supercritical CO_2, supercapacitor

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