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## 一步法制备氧化石墨烯/聚苯胺/Au 复合材料及电化学性能\*

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摘 要: 以改进的 Hummers 法制备的氧化石墨烯为基底,以氯金酸为氧化剂和金源,原位聚合苯胺单体,一步制得氧化石墨烯/聚苯胺/金(GO/PANI/Au)三元复合材料。形貌和成分分析结果表明,氯金酸成功地将苯胺氧化成聚苯胺,并被还原生成金纳米颗粒。电化学性能测试结果表明,随着氧化剂用量的增加,三元复合材料的比电容呈现先增大后减小的趋势,当氧化剂加入量为 0.03~mmol~bl,所制备的三元复合材料比电容最大,在 1~A/g电流密度、 $1~mol/L~H_2SO_4$ 电解液中比容量达 327~F/g,在 15~A/g电流密度下容量保持率也高达 81%。

关键词: 氧化石墨烯;聚苯胺;纳米金;电化学性能

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## 0 引 言

超级电容器是一种介于电池和传统电容器之间的一种新型的能量存储装置,它具有功率密度高,工作温度范围宽,循环寿命长,良好的环境稳定性等优点,被广泛应用于电动汽车,移动设备及航空航天等领域污迹,聚苯胺作为一种典型的导电聚合物,由于其独特的掺杂/去掺杂特性,良好的环境稳定性及成本低廉等优点而被广泛用作超级电容器电极材料[4-5]。但聚苯胺作为电极材料在多次充放电过程中易发生膨胀,致使在大的电流密度下,比容量衰减速度加快,倍率性能变差[6-7]。复合材料是改善这一问题的有效途径,一方面可以通过调控复合材料的结构和形貌,增加电解质与电活性物质之间的浸润效果和接触面积,提高自合材料的电化学利用率[8-9];另一方面复合材料可提升电极材料的电导率,较高的电导性可以加速电子的转移速率,有利于电化学能量的存储[10-11]。

氧化石墨烯(GO)作为石墨烯的衍生物,在电子器件,生物医学及功能性复合材料等领域均有广泛应用[12-16]。Liu<sup>[17]</sup>等在石墨烯片层表面原位聚合苯胺,制备了二元石墨烯/聚苯胺复合材料,其比容量为237 F/g;Sun等<sup>[16]</sup>通过 Pickering 乳液聚合制备了聚苯胺/氧化石墨烯复合材料,同时研究了其电化学性能,结果表明,在聚合物纳米颗粒表面附着氧化石墨烯片,改善了聚合物链的膨胀和收缩现象,其电化学性能也得到了提升。然而,氧化石墨烯表面含有大量的功能性基团,如羟基、羧基、羰基和环氧基团等,势必会降低复合材料的电导性,影响电化学性能。纳米金由于

其具有良好的电子传递性能及高的电导率,且其化学性能稳定,可以用于提升电极材料电子传输能力。 Tan 等 [18] 制备了 Nano-Au@PANI 蛋黄空心结构复合材料,在电流密度为 0.5~A/g 时,比容量为 79~F/g; Shayeh 等 [19] 制备了 PANI/rGO/AuNPs 三元复合材料,对比 PANI 与 PANI/rGO/AuNPs 二者的电化学性能,三元复合材料之间的协同优势使得复合材料的电化学性能更为优异,在  $1~mol/L~H_2SO_4$  电解液中比容量可达 303~F/g。

本文以氧化石墨烯为基底,以氯金酸为氧化剂和金源,原位聚合苯胺单体,一步制得 GO/PANI/Au 三元复合材料。利用氧化石墨烯较大的比表面积、聚苯胺的赝电容特性和金纳米粒子优良的导电性及环境稳定性改善复合材料的电化学性能。并研究了氧化剂用量对复合材料电化学性能的影响规律。

### 1 实验

#### 1.1 试剂与仪器

苯胺 (An,分析纯),天津市大茂试剂厂;盐酸 (HCl,分析纯),白银良友化学试剂有限公司;天然石墨,优级纯,青岛天源达石墨有限公司;浓硫酸 ( $H_2SO_4$ ,分析纯)、过氧化氢( $H_2O_2$ ,分析纯),天津市富宇精细化工有限公司;氯金酸( $HAuCl_4$ ,分析纯),天津市迈思科化工有限公司;实验室用水为自制二次蒸馏水。

JSM-2010 型透射电子显微镜(TEM),日本电子公司;S-4800 型场发射扫描电子显微镜(SEM);D8/ADVANCE型X射线衍射仪(XRD),德国布鲁克公

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司; NEXUS-670 型傅里叶变换红外光谱仪(FT-IR), 美国尼高力公司; CHI660C 电化学工作站, 上海辰华 仪器公司。

#### 1.2 GO/PANI/Au 复合材料的制备

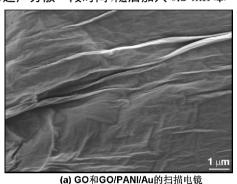
参照文献[20]制备 GO,具体过程如下:首先称取 2 g鳞片石墨,在冰水浴中缓慢加入到 50 mL 98%的浓 硫酸中,反应 30 min 后将 8 g KMnO4 缓慢加入到上 述混合液中,在温度为 35 ℃条件下继续搅拌反应 120 min,加入一定量蒸馏水稀释后,将反应温度升至 90 ℃,继续反应 0.5 h 后加入一定量 5% 的  $H_2O_2$ ,所 得产物经离心分离后,蒸馏水洗涤至中性后干燥备用。

称取上述已制备 GO 100 mg 分散于蒸馏水中,加入 一定量浓盐酸后,超声分散一段时间,随后加入 0.2 mL 苯 HAuCl<sub>4</sub>,冰水浴下反应 24 h 后,所得产物经离心干 燥,得到 GO/PANI/Au 复合材料,将所得产物分别标 记为 GO/PANI/Au-0.02, GO/PANI/Au-0.03, GO/ PANI/Au-0.04,GO/PANI/Au-0.05.

## 结果与讨论

### 2.1 形貌分析

图 1(a) 为 GO 的 SEM 照片。从图 1(a) 可以看 出,氧化石墨烯表面有波浪形褶皱存在,结合图 1(c) 的氧化石墨烯 TEM 照片可以看出,GO 片层呈半透明 纱状结构。



(b) GO和GO/PANI/Au的扫描电镜



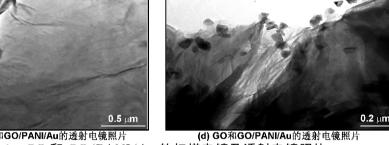


图 1 GO和 GO/PANI/Au 的扫描电镜及透射电镜照片

Fig 1 SEM and TEM images of GO and GO/PANI/Au

经一步法制备的 GO/PANI/Au 三元复合材料的 SEM 照片如图 1(b) 所示, 从照片中可以看出白色的亮 点,并且GO的层与层之间有絮状物质。三元复合材 料的 TEM 照片中(图 1(d))也可以清楚的看到直径 20~40 nm 的小颗粒附着在片层的表面,并且对比图 1(c)及(d),GO 片层颜色加深、厚度增加。上述结果 表明,经氯金酸氧化苯胺单体后,形成了石墨烯、金纳 米颗粒和聚苯胺三元复合材料。在 GO/PANI/Au 三 元复合材料的形成过程中,氯金酸将苯胺氧化成聚苯 胺,苯胺的氨基将氯金酸还原为金纳米颗粒,这里氯金 酸既是氧化剂又同时是金源[21]。

## 2.2 红外光谱分析

图 2 为 GO 和 GO/PANI/Au 的红外谱图。从 GO 的红外谱图中可以看出,在 3 447 cm<sup>-1</sup> 处强的特 征峰可能归属于GO和吸附水上的—OH振动。 1 636 cm<sup>-1</sup>处代表 GO 羧基中 C ─O 的伸缩振动。 1 395 cm<sup>-1</sup>处的振动峰为氧化石墨烯的─OH 的弯曲 振动峰,而  $1~127~\mathrm{cm}^{-1}$  处的吸收峰 C-O 键的吸收 峰[22]。

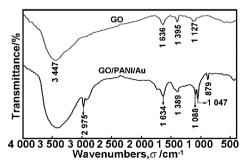


图 2 GO和 GO/PANI/Au 的红外谱图

Fig 2 FT-IR curves of GO and GO/PANI/Au 对比 GO/PANI/Au 的红外谱图,出现了聚苯胺 的吸收峰 $,2~975~cm^{-1}$ 对应于 C—H 键的特征峰, 1 088,1 047 和 879 cm<sup>-1</sup> 处的特征峰分别对应于聚苯

胺中苯环和醌环的骨架振动及 C—H 键的面外弯曲振动<sup>[23-24]</sup>,这表明氯金酸成功地将苯胺单体氧化成聚苯胺。

#### 2.3 X 射线衍射分析

图 3 为 GO 和 GO/PANI/Au 的 XRD 谱图。

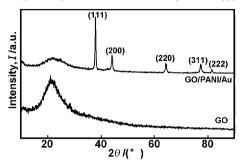


图 3 GO和GO/PANI/Au的XRD谱图

Fig 3 XRD patterns of GO and GO/PANI/Au

从图 3 可以看出,在  $2\theta = 21.06$ °附近出现一宽的特征衍射峰,对应于 GO 的(002)晶面,在  $2\theta = 37.94$ , 44.12,64.34,77.36 及 81.52°处的特征峰,分别对应于 (111),(200),(220),(311)及(222)晶面,与纳米金的

面心立方结构相对应。此外,三元复合材料中,在  $2\theta$  = 21.06°处的特征衍射峰,峰形变宽,强度减弱,可能是非晶态的聚苯胺掩盖了 GO 的衍射峰所致。

#### 2.4 电化学性能分析

所制备的 GO/PANI/Au 三元复合材料,由于其独特的片层结构及各组分间的协同作用,有望成为优良的超级电容器的电极材料。图 4(a) 为不同氧化剂浓度下复合材料的循环伏安曲线。从图 4(a) 可以看出,所有样品的循环伏安曲线形状基本相同,在电压窗口 $-0.2\sim0.8$  范围内有氧化还原峰存在,主要是由于聚苯胺不同掺杂状态的变化导致的 $[^{25]}$ 。从不同样品的循环伏安曲线可以看出 GO/PANI/Au-0.03 的积分面积较大,其比电容相对较好。在不同扫描速率下GO/PANI/Au-0.03 的循环伏安曲线如图 4(b) 所示,随着扫描速率从 5~mV/s 增至 50~mV/s,其曲线形状未发生明显的扭曲,表现出良好的倍率性能。GO/PANI/Au 三元复合材料的恒流充放电曲线如图 4(c) 所示,从图 4(c) 可以看出,电压与时间的关系为非线性的,表明复合材料的赝电容特性。

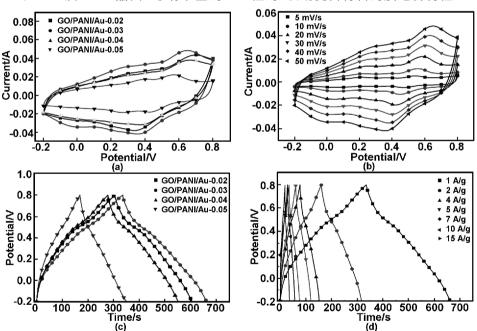


图 4 (a) GO/PANI/Au 复合材料在扫描速率为 5 mV/s 时的循环伏安曲线;(b) GO/PANI/Au-0.03 在 5  $\sim$  50 mV/s 时的循环伏安曲线;(c) GO/PANI/Au 复合材料在电流密度为 1 A/g 时的充放电曲线;(d) GO/PANI/Au-0.03 在  $1\sim$ 15 A/g 时的充放电曲线

Fig 4 (a) CV curves of GO/PANI/Au composites at a scan rate of 5 mV/s; (b) CV curves of GO/PANI/Au-0.03 at 5-50 mV/s; (c) GCD curves of GO/PANI/Au composites at a current density of 1 A/g; (d) GCD curves of GO/PANI/Au-0.03 at 1-15 A/g

根据充放电曲线利用式(1)可计算出复合材料的比电容[26]

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

式中,C 为比电容,F/g;I 为为恒定电流值,A; $\Delta t$  为放电时间,s;m 为活性物质的质量,g; $\Delta V$  代表电位窗口,V。通过计算,在电流密度为 1 A/g 时 GO/PA-

NI/Au-0.02、GO/PANI/Au-0.03、GO/PANI/Au-0.04、GO/PANI/Au-0.05 的比容量分别为 302,327,276 和 182 F/g。GO/PANI/Au-0.03 三元复合材料在不同电流密度下的充放电曲线如图 4(d) 所示,在 1 A/g 电流密度下,样品的充放电曲线基本呈现几何对称,表明其电容性能良好,所有的充放电曲线均出现充放电平台,在  $0.8\sim0.45$  V 电位区间的曲线与双电层电容有

关,在 0.45 V 以下的曲线主要是由于电极材料表面发生了氧化还原反应而引起的赝电容<sup>[27-28]</sup>。

GO/PANI/Au 三元复合材料的阻抗谱图如图 5 (a) 所示, 所有样品的阻抗曲线呈现相似的形状, 均由 高频区的半圆和低频区的斜直线构成,半圆与实轴的 交点代表有效内阻  $R_s$  的数值,主要包括电活性物质的 内阻,集流体的内阻及电解液的内阻[29]。从图 5 可以 看出,GO/PANI/Au 三元复合材料的  $R_s$  为 0.5  $\Omega$ ,表 明复合材料具有较低的内阻,半圆的直径和斜直线分 别代表电化学转移阻抗  $R_{ct}$ 及 Warburg 阻抗[30-31],对 比发现,GO/PANI/Au-0.03 具有较小的电化学转移 阻抗和 Warburg 阻抗。图 5(b)为 GO/PANI/Au 复 合材料的倍率性能曲线图。从图 5(b)可以看出,比容 量随着电流密度的增大逐渐减小,主要原因是因为当 电流密度较大时,电解液与电活性物质之间接触不充 分而导致比电容的下降。当电流密度在 1 A/g 时, GO/PANI/Au-0.02,GO/PANI/Au-0.03,GO/PANI/ Au-0.04 和 GO/PANI/Au-0.05 的比电容分别为 302, 327,276 和 182 F/g, 当电流密度增大至 15 A/g 时(初 始电流密度的 15 倍),比电容为 201,264,203 和 123 F/g,复合材料的容量保持率可达 66%,81%, 73%和67%,表明复合材料具有良好的倍率性能。随 着复合材料中氧化剂用量的增大,复合材料的比容量 呈现先增大后减小的趋势。当氧化剂氯金酸用量过低 时,复合材料中金和聚苯胺的量过低,导致复合材料的 电活性物质较少,从而导致电化学性能一般。当氯金 酸用量过高时可能致使聚苯胺出现过氧化,从而使聚 苯胺的电化学性能下降。

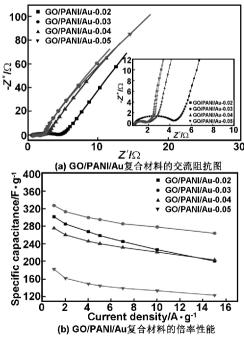


图 5 (a)GO/PANI/Au 复合材料的交流阻抗图;(b) GO/PANI/Au 复合材料的倍率性能

Fig 5 (a) Nyquist plots of GO/PANI/Au; (b) rate performance of GO/PANI/Au

## 3 结 论

以氯金酸为氧化剂和金源,氧化石墨烯为模板,成功地通过一步法制备出 GO/PANI/Au 三元复合材料。在苯胺的聚合过程中,苯胺中的胺基可以将氯金酸原位还原成金纳米颗粒。随着氧化剂用量的增加,复合材料的比电容呈现先增加后减小的趋势,比电容最高可达 327 F/g,当电流密度达到初始电流密度的15 倍时,容量保留率为 81%。氧化石墨烯片层的褶皱结构可能改善了聚苯胺在充放电过程中的膨胀收缩,而金纳米粒子不仅加速了电子传导,还可能改善了整个电极的质子扩散,使得三元复合材料具有较优异的倍率性能,同时也保留了赝电容材料高的比容量特性。

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# Effect of hydrothermal time on hemocompatibility of three-dimensional graphene

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Abstract: Three-dimensional graphene were produced via the ethylenediamine hydrothermal reduction method by using the two-dimensional graphene. And in this experiment, the hole's diameter of three-dimensional graphene was adjusted by the hydrothermal reaction time. In order to characterize the surface topography, the chemical characteristics and components of three-dimensional graphene, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used. The protein absorption rate and the platelet conglutination rate of three-dimensional graphene were also contrasted by protein electrophoresis test, platelet conglutination test and hemolysis test. The hole's diameter of three-dimensional graphene decreased from 340 to 230 μm with the increasing of hydrothermal reaction time. The introduction of nitrogen into the three-dimensional graphene formed new chemical bonds. When the hydrothermal time was extended from 6 to 24 h, the bovine serum albumin absorption rate of three-dimensional graphene was improved from 2.6% to 16.8% and the hemolysis ratio was decreased from 2.2 % to 0.3 %. In addition, the capability of resist platelet conglutination of three-dimensional graphene was increased. With the increasing of hydrothermal reaction time, the hole's diameter of three-dimensional graphene was reduced and the specific surface area was increased. The ability of BSA absorption and the capability of resist platelet conglutination were also improved. Furthermore, the hemolysis ratios were decreased. Therefore, the increasing of hydrothermal reaction time was conducive to enhance the hemocompatibility of three-dimensional graphene.

Key words: three-dimensional graphene; hydrothermal time; hemocompatibility; protein absorption; platelet conglutination; hemolysis ratio

# One-step preparation of graphene oxide/polyaniline/Au composites and electrochemical properties

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Abstract: The graphene oxide/polyaniline/gold (GO/PANI/Au) ternary composites were prepared successfully by one step method. The graphene oxide prepared by the modified Hummers method was used as the substrate, and the aniline monomer was polymerized in situ by using chloroauric acid as the oxidant and the gold source. The morphology and composition analysis showed that chloroauric acid successfully oxidized aniline to polyaniline and was reduced to gold nanoparticles. The electrochemical performance test showed that the specific capacitance of the ternary composites increased first and then decreased with the increase of the amount of oxidant. When the oxidant was added in an amount of 0.03 mmol, the prepared ternary composite had the largest specific capacitance. The specific capacity is 327 F/g at a current density of 1 A/g in 1 mol/L H<sub>2</sub>SO<sub>4</sub> electrolyte. When the current density reached at 15 A/g, the capacity retention rate was still as high as 81% compared with initial current density.

Key words: graphene oxide; polyaniline; nano gold; electrochemical performance