双光束激光干涉制备布基石墨烯仿生表面

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摘要 提出一种利用双光束激光干涉系统制备多级石墨烯仿生表面的方法. 利用Nd:YAG激光的双光束干涉系统在不同织物基底上对石墨烯氧化物薄膜进行干涉烧蚀, 激光脱氧还原的同时产生石墨烯微纳结构. 基底织物表面粗糙结构增大了石墨烯仿生薄膜表面粗糙度. 布基的粗糙基底、激光烧蚀石墨烯微纳结构的双重作用形成多级结构的石墨烯仿生表面. 这种石墨烯仿生表面不仅具有超疏水润湿性, 还由于石墨烯微纳结构周期性而展现一定彩虹结构色.

关键词 双光束激光干涉, 织物布基, 石墨烯, 超疏水, 结构色

石墨烯材料这种厚度只有0.34 nm的二维单原子层碳材料^[1,2], 由于其独特的物理化学特性, 自从被发现以来引起材料界的广泛关注, 并且在物理^[3,4]、化学^[5]、机械^[6]、医疗^[7]等领域都有着广泛应用. 然而基于石墨烯这种单原子层材料, 虽然其具有良好导电性, 但是想要将其器件化仍面临着很多挑战. 其中将石墨烯材料微纳结构化一直是一个难题. 原因在于石墨烯材料与其衍生物材料是单原子层材料, 比较容易形成无序的层状堆叠结构, 传统的微纳加工技术如自组装、纳米压印和光刻都很难实现对其微纳结构的可控制备^[8-10]. 现有的对石墨烯仿生功能性的研究主要是依赖石墨烯材料的制备方法, 利用材料的无序堆叠和化学气相沉积(CVD)生长基底的粗糙表面, 而制得的具有粗糙结构的石墨烯膜或者是三维石墨烯泡沫结构^[11,12]. Korarkar课题组^[13]报道了利用不同溶剂改性的方法, 制备具有超亲性和超疏性可调的石墨烯结构化表面. Lin等人^[14]介绍了通过冷冻干燥石墨烯氧化物的水的分散液, 通过离心石墨烯氧化物气凝胶浓

度进行疏水角的一个调节. 表面的多孔结构和含氧官能团的去除都是影响结构化石墨烯疏水的关键因素. 前两种化学制备方法得到的结构化石墨烯表面微纳结构都是无序的、杂乱的, 然而利用模板光掩膜法, 如紫外灯的光热效应^[15]、照相机闪光灯的光热效应^[16]都是既得到图案, 又能结构化其表面.

想要制得有序的、周期性的、可控的石墨烯仿生结构则需要依赖新的微纳加工技术. 激光微纳加工技术, 允许材料的增材和减材加工, 可以实现高精度、高空间分辨率、真三维加工, 其适用于多种材料体系^[17,18]. 本文利用Nd:YAG激光双光束干涉系统在具有粗糙表面的织物布基上制备石墨烯仿生表面, 激光脱氧还原降低表面能和激光烧蚀微纳结构增大粗糙度叠加的双重效应, 使得制备的仿生表面不仅具有超疏水润湿性还由于周期性微纳结构的存在, 使多级结构表面有彩虹结构色. 这种仿生表面和自然界中同样拥有超疏水浸润性和彩虹结构色的蝴蝶翅膀表面相类似.

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1 样品制备与性能表征

1.1 双光束激光干涉系统

Nd:YAG激光双光束干涉系统在加工过程中不需要掩模,因此省去了昂贵的掩模制备成本;光路简单、光学元件便宜;一次性曝光大视场,可较容易地实现大面积周期图形的制备;相对于飞秒激光直写等单点扫描的、用于加工条纹的方法,效率高^[19,20].主要是依赖多光束在样品表面相干叠加作用,从而引起的材料表面的形貌变化^[21,22].这里我们制备石墨烯微纳结构表面主要是利用双光束干涉系统.

实验中用到是一个三倍频、Q开关、单模的Nd:YAG激光.激发波长是355 nm,频率是10 Hz,在加工过程中脉冲持续时间是10 ns.为了使辐照到样品表面的光束能量均匀,通过一组扩束镜系统和光阑调整出射激光的光束直径.然后在经过一个反射镜和一个半反半透镜的作用将一束激光分成能量、光强、亮度均相等的两束激光.这两束激光再经过两个反射镜的作用,在光屏上相应的位置进行相干叠加作用,光强较强位置作用最强,光强较弱的地方作用较弱,最后在样品表面形成周期性的光栅结构.调整光路得到相应光栅结构周期.石墨烯仿生表面制备过程如图1所示.将利用Hummers法^[23]制备好的溶

度为3 mg/mL石墨烯氧化物水溶液,涂覆在3种不同的织物丝绸、棉布、尼龙基底上.然后让溶剂蒸发晾干.通过原子力显微镜(AFM)和扫描电子显微镜(SEM)测试,石墨烯氧化物薄膜的厚度是~1 μm ,3种织物基底的厚度分别为100, 600, 250 μm (图S1).3种织物基底表面的粗糙度和涂覆石墨烯氧化物的粗糙度在表S1中给出.将制备好的石墨烯氧化物薄膜样品放置在光屏上,激光共聚焦显微镜的形貌测试(图S2)表明,在织物表面涂覆的石墨烯氧化物膜是比较均匀的.石墨烯氧化物薄膜表面的形貌由于激光的烧蚀和还原作用而改变,经过激光一次干涉作用,不仅烧蚀出平行梳子状的光栅微纳结构,同时还脱除掉一部分含氧官能团起到还原作用.为了使制备的石墨烯微纳结构表面的粗糙度更大,我们再将一次干涉样品旋转90度再一次干涉,制备二维光栅结构.制备的石墨烯微纳结构的高度并不受石墨烯氧化物水溶液的浓度和涂覆次数的影响,即石墨烯氧化物膜的厚度对激光同等烧蚀条件下产生的结构高度影响不大(图S3).

1.2 制备的石墨烯多级结构表面形貌特征

将激光作用之后的石墨烯多级结构表面进行SEM表征.通过测试发现,经过双光束激光一次干涉后的石墨烯氧化物样品表面形成了大面积均匀的梳子状光栅结构,如图2(a)所示.实际上,光栅结构形貌是随光强作用的变化而分布的.很显然,在高强度区域,石墨烯氧化物被还原的比较彻底,烧蚀的也比较彻底,形成光栅结构的沟槽部分.而在低强度区域,未被还原的石墨烯氧化物被保留下来,并且由于激光的切割作用在微米光栅顶层上形成了向上向外翻卷的石墨烯纳米碎片.也是由于激光的烧蚀作用和石墨烯氧化物材料自身的材料特性,在光强最强和最弱的中间区域形成了层状纳米结构.在织物基底上形成的多级石墨烯光栅微纳结构,在脱氧还原的基础上又增加了表面的粗糙度.这种粗糙度的增加对表面浸润性的影响很大.

调试实验参数,激光功率在0.3~0.6 W是制备石墨烯多级结构比较好的脱氧功率,形成的光栅结构层次很丰富,结构很完整.如果两次干涉的激光功率较低,如为0.15 W,则会形成如图2(b)所示的情况,激光切割烧蚀作用比较弱,难以形成光栅的沟槽部分,并且结构层次也不够丰富,没有次级纳米结构.同时,激光功率过低对石墨烯氧化物材料的还原不

图1 (网络版彩色)双光束干涉系统及石墨烯仿生表面制备过程
Figure 1 (Color online) Two-beam laser interference system and schematic illustration of the fabrication of biomimetic graphene surface

图2 石墨烯多级结构的SEM图像。(a) 一次激光干涉形成的梳子状石墨烯光栅结构SEM图像; (b) 激光功率为 0.15 W形成的石墨烯结构的SEM图像; (c) 激光功率为 0.8 W形成的石墨烯结构的SEM图像; (d)–(g) 激光功率为 0.4 W形成的石墨烯结构的SEM图像

Figure 2 SEM images of multilevel-structured graphene surface. (a) SEM image of combed graphene grating structure by one time laser interference; (b) SEM image of graphene structure with 0.15 W laser power; (c) SEM image of graphene structure with 0.8 W laser power; (d)–(g) SEM images of graphene structure with 0.4 W laser power

彻底;而激光功率过大,如0.8 W,则会对样品表面过度加工,形成的结构间距比较大,次级结构被烧蚀掉,这种情况大大降低了结构表面的粗糙度,如图2(c)所示。图2(d)中制备石墨烯多级结构表面的激光功率为0.4 W,该功率是相对合适的,形成的结构形貌也比较丰富。进一步通过高倍SEM测试表征其微观形貌特征,图2(e)表明两次激光干涉烧蚀后形成了格子状周期为 $\sim 1.5 \mu\text{m}$ 的结构,并且在微米结构上还有很多次级的纳米层状结构和绒毛结构,这一点在图2(f), (g)中也展示出来了。

1.3 制备的石墨烯多级结构表面材料特性

Raman光谱是表征石墨烯类材料杂化性质最基础的测试手段^[24,25]。可以通过测试结果判定样品表面碳原子石墨化的程度。为了表征激光对石墨烯氧化物材料烧蚀还原作用,我们对没有经过激光作用的石墨烯氧化物(GO)表面和激光作用之后的还原后石墨烯氧化物(RGO)表面分别进行拉曼(Raman)光谱测试。测试结果(图3)表明,在宽谱范围内,1354和1599 cm^{-1} 有2个特征峰,分别对应D峰和G峰。G峰代表 sp^2 键合碳原子的震动引起的一种 E_{2g} 模式的石墨化,而D峰则代表缺陷,表示非石墨化的碳原子悬挂在无序平面上的碳原子。经过激光还原前后的石墨烯样品的D峰和G峰有着微小变化。Raman图谱中得

图3 (网络版彩色)GO和RGO样品的Raman光谱

Figure 3 (Color online) Raman spectrum of GO and RGO

到GO和RGO的D/G峰值比率分别为0.99和0.98。理论上,激光作用石墨烯氧化物样品表面,还原作用脱除掉含氧官能团,相当于减少一部分缺陷,应该得到一个更高的 sp^2 杂化碳的比率,但是激光的烧蚀和剪切作用使得之前一部分 sp^2 碳被破坏,相当于引入了新的缺陷在石墨烯碎片中,这种作用导致D峰升高。综合激光在样品表面还原和剪切作用,拉曼光谱结果展示了不太明显的变化。

2 石墨烯多级结构表面仿生特性

通过SEM形貌表征得到,双光束激光作用使得

样品表面产生周期性的微纳结构,增大样品表面的粗糙度,激光作用也使石墨烯结构表面脱出大量的含氧官能团,降低了表面能.微纳结构的存在和含氧官能团的脱出使石墨烯薄膜表面的几何形貌和化学组分都发生了改变,使其成为具有超疏水特性结构薄膜^[26].我们制备的石墨烯多级结构薄膜借助3种不同质地的织物基底,这种多级结构薄膜的浸润性也依赖基底的结构形貌和质地.图4(a)中给出了丝绸、棉布、尼龙表面的浸润性,这3种织物表面与水相液滴接触角分别为110°,136°,150°(测量选取的是5 μL的液滴).而在3种织物基底上的石墨烯多级结构表面测量的接触角则分别为140°,152°,156°.3种不同织物基底的石墨烯多级结构表面的浸润性有着明显差别,主要是由3种不同织物的不同质地和表面结构引起的.图4(b)展示了3种不同织物基底的石墨烯多级结构表面的宏观照片,也观察到3种织物表面形貌是有一定的区别的.

由于石墨烯多级结构表面存在周期性的结构,存在一定的散射和衍射现象.当一束白光辐照到石墨烯多级结构表面时,我们会在结构表面观察到结构色,这种结构色类似彩虹的颜色,可以通过调整观察角度,观察到从赤到紫变换的7种不同丰富色彩,如图4(c)所示.这种彩虹色的结构色,就是光栅结构的衍射现象,可以通过下式表示:

$$m\lambda = d(\sin\theta_0 - \sin\theta_1), \quad (1)$$

其中, m 是衍射级, d 是光栅周期, θ_0 和 θ_1 分别为衍射和入射角^[27].

3 总结

本文首次在纺织物的基底上制备石墨烯的仿生结构表面.利用激光的双光束干涉系统制备石墨烯微纳多级结构.选取合适的激光加工功率(0.4 W),2次干涉织物基底石墨烯氧化物薄膜制备格子状的周期性结构.激光的烧蚀和切割作用不仅可以制备出微米量级的光栅结构,同时还能制备出层状的石墨烯纳米片和纳米绒毛结构.激光作用不仅可以增大石墨烯表面粗糙度,制备微纳米结构,还可以将石墨

图4 (网络版彩色)3种不同织物基底石墨烯多级结构表面仿生特性.(a) 3种织物和在3种基底上石墨烯多级结构表面的浸润性;(b) 3种结构表面照片;(c) 结构表面彩虹结构色

Figure 4 (Color online) Biomimetic properties of multilevel-structured graphene surface on three different fabric bases. (a) Wettabilities of three different fabric base and multilevel-structured graphene surface on three different fabric bases; (b) photographs of multilevel-structured graphene surface on three different fabric base; (c) structural color of multilevel-structured graphene surface

烯氧化物表面一部分含氧官能团脱除,降低其表面能.然而,激光的还原作用和切割作用在还原前后的Raman光谱结果差别并不是很明显.但是制备的石墨烯多级结构表面由于其几何形貌和化学组分的变化,使其表面浸润性呈现超疏水状态.3种不同织物基底的质地和结构影响了石墨烯多级结构表面的浸润性,其中以尼龙基底表面的疏水角最大(156°).表面周期性结构的存在,会在石墨烯结构表面发生衍射和散射作用,使其表面呈现彩虹结构色.相信这种石墨烯多级仿生结构表面在光电显示、可穿戴器件和仿生领域都能为研究者带来新的思考与启迪.

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Summary for “双光束激光干涉制备布基石墨烯仿生表面”

Fabrication of biomimetic graphene films on fabric base by two-beam laser interference

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Through millions of years of evolution and natural selection, various biological species own unique physiological structure and amazing functionality. Biomimetic fabrication demonstrate remarkable trend of development, artificial biomimetic materials and intelligent functional surfaces have been extensively studied by scientists both theoretically and experimentally. In general, traditional biomimetic materials consisting of metal, metal oxides, carbon materials and some other polymer materials, which make outstanding contribution to the generation and development of engineering bionics science and interface chemistry analysis. However, simpleminded traditional materials are not capable to deal with the presence of intelligent driving control and micro nano device applications in artificial biomimetic science. It is well established that the combination of novel materials and novel biomimetic technology may lead to promote progress and development of fabrication with smart integration of multifunctional biomimetic devices.

More recently, a kind of carbon nanomaterials with an atomic layer thickness which named graphene has attracted most widely attention due to its excellent properties, for instance ultrahigh carrier mobility, good electrical conductivity, high transmittance and biocompatibility since it has been founded by mechanical stripping adhesive tape, it becomes a new star of materials scientific fields. Its stable physical/chemical properties make it widely applied in electronic devices, optical devices, biochips, and even intelligent robots. Based on graphene's distinctive material properties, micronano-structured graphene surfaces with special wettability may be fabricated in a biomimetic manner that not only contribute to the experimental research but also bring about a new revolution of graphene-devices.

A method of fabrication of biomimetic graphene surface with multilevel-structures by two-beam laser interference system has been proposed. Graphene oxide films on different fabric bases have been reduced and ablated by Nd:YAG laser interference system. Periodic graphene micronano-structures with grating-like micro structures and additional nanoscale structures have been produced during laser processing process with appropriate laser power (0.4 W), which resulted in deoxidization of abundant hydrophilic oxygen containing groups (OCGs) on GO sheets. To original GO film, the reduced GO (RGO) surface not only exhibited more rough geometry, but also owned lower surface energy. Raman spectroscopy has been characterized, the result of the D and G band peaks of RGO show neglectable changes contrast GO. The reason is that the laser cutting and ablation can bring additional new defects on the edges of graphene sheets, which leads to the increase of D band peak. As a result, the spectra show unobvious changes. Roughness of the fabric surface (silk, cotton, nylon) further increased the surface roughness of biomimetic graphene surface. Graphene biomimetic surface with multi-structures has been formed by the double action of rough fabric base and graphene micronano-structure. The graphene bionic surface with nylon substrate has the largest hydrophobic angle, $\sim 156^\circ$. The biomimetic graphene surface not only possesses superhydrophobic wettability, but also exhibits rainbow structural color due to the existence of periodic graphene micronano-structures. We believe that the biomimetic graphene surface on fabric substrate will not only have important application prospects in the field of bionics, but also be a major exploration and breakthrough in the future research of optoelectronic and wearable devices.

two-beam laser interference, fabric base, grapheme, superhydrophobicity, structural color

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