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原子掺杂对不同配体中碳点光致发光性能的影响研究

谭超,汪克威,胡永俊
(广东工业大学材料与能源学院,广东 广州 510006)

摘要: 碳点具有光学性质可调及光稳定性好的特性,被广泛应用于各种工业领域,特别是光致发光领域。碳点的光致发光与碳源的分子结构密切相关,其中碳点自身分散性会影响发光强度。为研究碳点在不同配体中的光致发光性能,采用掺杂合成-溶液透析法,制备了3种分子结构的碳点材料,掺杂碳点NCDs、共掺杂碳点NSCDs及混合碳点NCDs+NSCDs。利用扫描电子显微镜、透射电子显微镜和X射线衍射表征了其显微形貌,利用紫外可见光谱仪测试了其吸光强度,配置了乙醇、有机溶液进行紫外和自然光照射发光测试,研究了3种碳点的分散性及发光性能。研究结果表明,NCDs呈二维细片状形貌,NSCDs的掺杂原子负载在其表面,而NCDs+NSCDs的掺杂原子团具有强的单分散性。3种碳点均为均匀分布的纳米颗粒,尺寸大小约1.8 nm。以NCDs的碳特征峰为初始位置基准,NSCDs的特征峰明显向左发生了偏移,NCDs+NSCDs的特征峰也发生了向左偏移,但显著程度低于NSCDs。其主要原因是掺杂原子团的引入使晶面间距发生变化,影响了碳点晶面间距的大小,表明掺杂原子已引入碳点中。3种碳点在自然光照射下均发出绿色荧光,且随着激发波长越长偏向蓝移,其中NCDs+NSCDs荧光发光颜色最深,表明其具有更强的亲水性和分散性。分散性的增强会使碳点的发光强度增强,NCDs+NSCDs在不同配体中的发光强度最强,表明其分散性强,增强了其光致发光性能。本研究为碳点发光性能在光致发光及其他领域的应用提供了参考。

关键词: 碳点;原子掺杂;光致发光性能;表面修饰;分散性;配体;发光强度;荧光发光
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0　引言

碳点是基于纳米科技技术,改变分子结构及尺寸,使颗粒尺寸在0—20 nm之间的一类零维碳纳米材料[1-3]。2003年,Science杂志把量子点的发现列为十大科学突破之一。早期的量子点大多数含有对人体有害的重金属元素(如Cd、Pb、Hg等),在当今社会号召环保的前提下制约了量子点的发展,从而促使人们进一步开发了一些不含污染元素的量子点(如碳量子点、石墨烯量子点、黑鳞量子点、硫量子点等)。由于碳点的性能独特,被广泛地应用于各领域中,如在生物医学领域中主要应用于人类的疾病诊断和治疗,表现为传感器制造、药物载体输送[4-8]等。另外,碳点还具有可调的光学性质,并且光稳定性好,也被应用于光致发光领域中。

碳点的光致发光与其分子结构有密切的关系,而碳源的取自决定了碳点的结构和发光特性[9]。有学者[10-12]研究证明,通过调控苯二胺的三种异构体,碳点可以发出红、蓝、绿光,说明碳源决定了碳点的最终结构和发光颜色。根据光学性能,可开发新的碳点合成方法,从而调控碳点的电子结构。随着碳点合成工艺的成熟,碳点作为添加剂与石墨烯复合被应用于光电器件中,尤其在提高钙钛矿太阳能电池的效率和稳定性方面,研究发现了碳点的光致发光与石墨烯之间的电荷转移关系,这是因为石墨烯的二维结构为扩展量子点体系提供了丰富的原子空位缺陷,从而使碳点大量嵌入复合材料中[13-14]。最初发现的大多数量子点其实是含金属或重金属元素,而且大部分被用在半导体材料中的光子发射器中[15],应用体现在量子传感、量子信息分布、量子光子学、量子密码学、量子自旋光子界面等技术

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作者简介:谭超,硕士研究生,研究方向为碳材料的设计合成及其在锂硫电池中的应用。E-mail:ctan826@163.com。

中[16-19]。碳点的光致发光产率及高电荷离子迁移率与引入其他电子缺陷有很大关系,如碳纳米管晶格中引入sp^3缺陷而诱导新的电子态使光致发光红移[20]。然而,重金属量子点带有剧毒性,毫无疑问会造成环境污染,如镉量子点浸入人体会使人体造成骨质疏松而损害人体健康[21]。于是,许多的研究者再次力举推进碳点的研发,通过自下而上的方法制备了多种碳点,并且应用在各个领域中[2]。同样,碳点的光致发光性能也得到了广泛的研究。Ding等[22]采用一锅水热法制备了高产量碳点,该碳点能稳定发出不同颜色的光,充分体现了其优异的发光性能。

本文通过掺杂合成-溶液透析的方式,制备了碳点(NCDs)、碳点(NSCDs)及混合碳点(NCDs+NSCDs),并且对其合成机理、掺杂类别进行了分析,研究了他们在不同配体中的光致发光性能。同时,利用可见紫外光对3种碳点的分散性进行了分析。本研究为碳点发光特性在其他领域中的应用提供了参考。

1 实验部分

1.1 试剂

实验所用试剂包括:柠檬酸(纯度≥99.5%)、尿素(纯度为99%)、L-半胱氨酸(纯度为99%),均购自麦克林公司;丙酮(分析纯),广州化学剂厂生产;氨水(AR,25%—28%)、N,N-二甲基甲酰胺(纯度>99.9%),均购自阿拉丁公司;甲醇(分析纯),华光科技公司生产。实验所用的透析袋(小包装品牌Biovake),产自美国生物医学公司Biomed Instruments Inc。

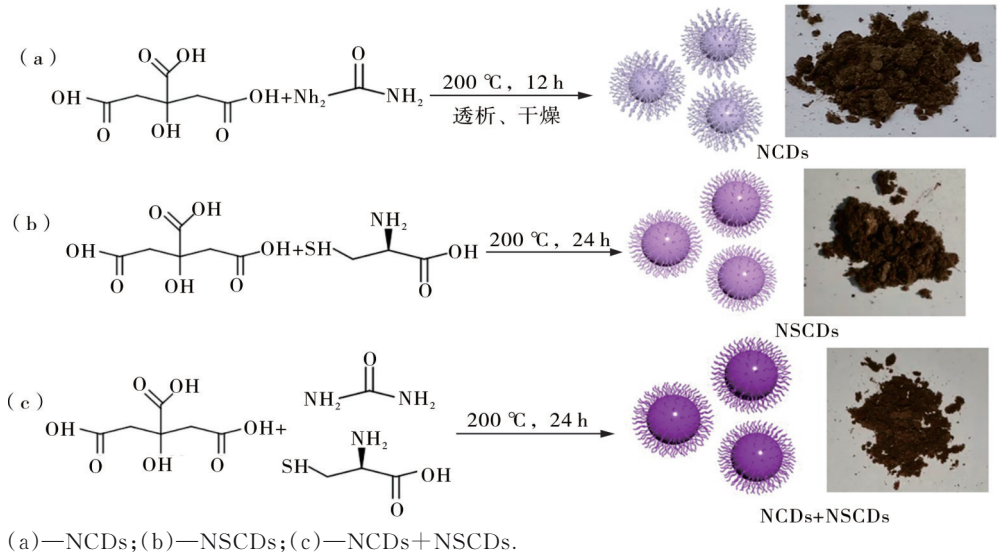
1.2 方法

根据文献[23-24]对碳点的报道,设计出实验方案。首先,将3 g的柠檬酸和2 g的尿素加入到100 mL的超纯水中,在60 ℃下搅拌10 min后再超声10 min。然后,将溶液倒入不锈钢反应釜内,在马弗炉内程序升温(升温速率5 ℃·min^{-1})至200 ℃后恒温加热8 h。最后,将溶液冷却至室温后透析2 d,经干燥后得到碳点(NCDs)。同样,碳点(NSCDs)和混合碳点(NCDs+NSCDs)也是采取类似的方法制备。将3 g的柠檬酸、2 g的尿素和0.5 g的半胱氨酸加入到100 mL的超纯水中,按照上述的制备步骤可得到碳点(NSCDs)和混合碳点(NCDs+NSCDs)。

2 结果与讨论

2.1 碳点的合成机理及形貌表征

图1为NCDs、NSCDs和NCDs+NSCDs的制备流程示意图。从图1可见,所制备的3种碳点均伴有软柔的特征。从尿素的结构式可看到,其具有丰富的氨基官能团,该官能团经过复杂的氧化还原反应后被引入碳点中,成为碳点的氮掺杂原子。从半胱氨酸结构式可看到,其既含有氨基基团又含有巯基基团,所以半胱氨酸是碳点中氮、硫掺杂的主要来源[25]。通常将没有杂原子前驱体引入的碳点认为是纯碳点,所以从狭义的角度出发,碳点可分为纯碳点(CDs)、掺杂碳点(XCDs)和共掺杂碳点(XYCDs)。同时,也说明碳点具有丰富的功能基团、成份可控、后续可设计性强的特点。



(a)—NCDs;(b)—NSCDs;(c)—NCDs+NSCDs.

图1 3种掺杂碳点的合成示意图

Figure 1 Schematic diagram of synthesis for three doped carbon dots

2.2 碳点的SEM、TEM、XRD表征

图2为3种碳点的SEM图和TEM图。从图2可见：单从表面观察分散在乙醇溶液中的3种碳点，其中碳点（NCDs）的形貌呈二维细片状，而氮硫掺杂碳点（NSCDs）的杂原子负载在碳点表面，氮硫共掺杂的碳点（NCDs＋NSCDs）更具有团聚的特点，掺杂原子团具有强的单分散性；3种碳点均呈纳米颗粒状且均匀分布，尺寸大小约为1.8 nm，表明碳点成功合成。

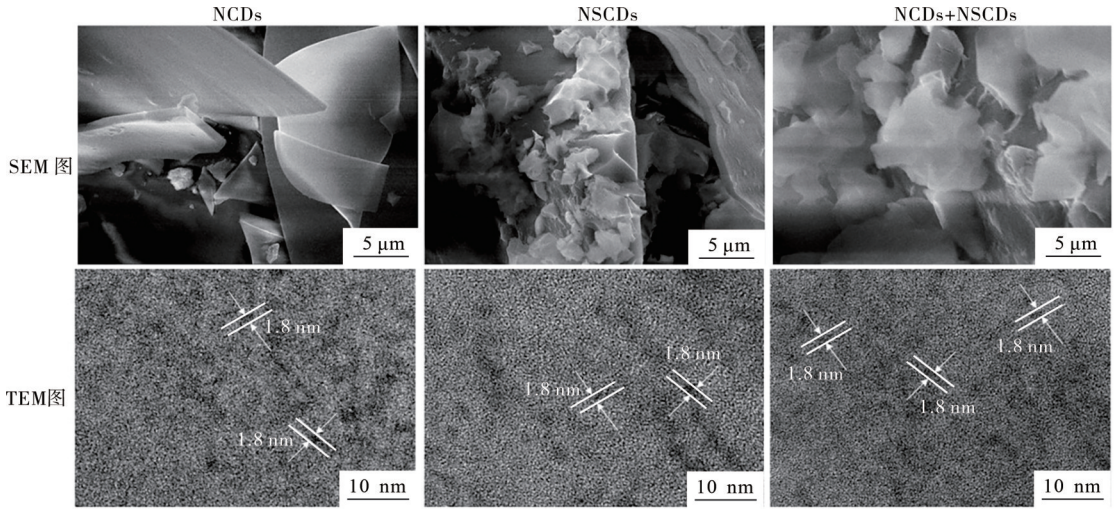


图2 碳点的SEM图TEM图

Figure 2 Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of carbon dots

对3种含不同掺杂原子的碳点进行了X射线衍射仪（XRD）图谱测试，结果如图3所示。从图3可见，NCDs、NSCDs和NCDs＋NSCDs均在2θ＝30—35°处存在碳的特征峰，以NCDs的碳特征峰为初始位置基准，NSCDs的特征峰明显向左发生了偏移，而NCDs＋NSCDs的特征峰也发生了向左偏移，但没有NSCDs那么明显。这是由于在合成碳点的过程中，伴有掺杂原子团的引入，从而使晶面的间距发生变化，碳点晶面间距的大小变化造成碳的特征峰左偏移。

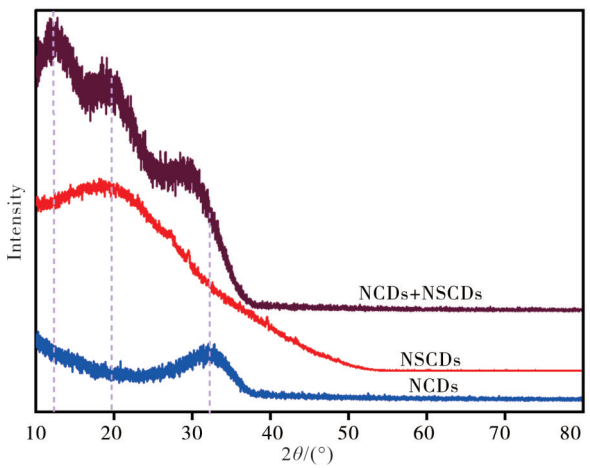
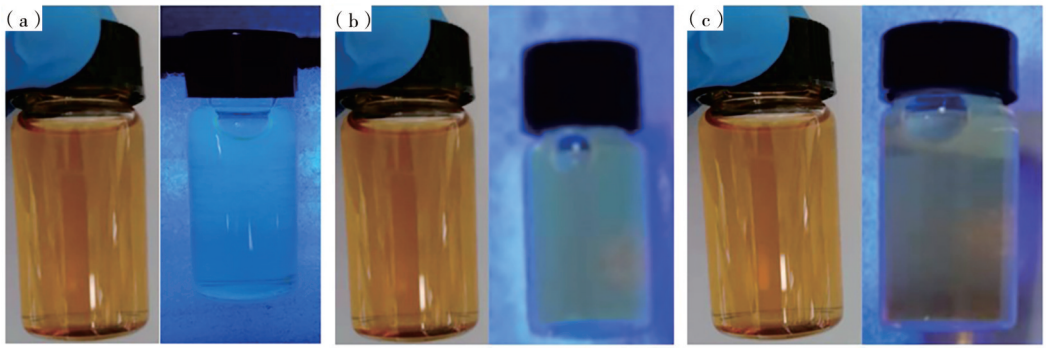


图3 碳点的X射线衍射（XRD）图

Figure 3 X-ray diffractometer (XRD) plot of carbon dots

2.3 碳点在不同配体中的发光性及分散性

碳点是一类具有可调控性的纳米材料，不同的碳点会发出不同颜色的光，或者以不同配比制备出来的碳点也会影响碳点发光的颜色和强度。将3种碳点分别配成浓度为1 mg·mL^{-1}的乙醇溶液，然后在365 nm紫外灯照射下，观察瓶身的发光情况，结果如图4所示。从图4可见，在自然光的照射下，3种碳点均发出绿荧光；在波长为365 nm紫外灯照射下，随着激发的波长越长碳点溶液的颜色偏向蓝移，其中混合碳点溶液的颜色最深。由于掺杂原子功能基团具有极强的吸附能力，其不仅可以改变纳米粒子的晶面间距，还能促进原子核增大，使碳点具有丰富的活性位点，从而增强了碳点的亲水性，而亲水性的增强会使分散性增强，分散性的增强会使发光强度增强[25]。分散性越强的溶液色度就会越浓，颜色加深代表碳点发光性能增强。其中，混合碳点的荧光发光的颜色最深，说明掺杂原子多的碳点具有更强的功能性[26]。



(a)—NCDs;(b)—NSCDs;(c)—NCDs+NSCDs。

图4 碳点在自然光照下(左)和波长365 nm紫外灯下的显示光学照片

Figure 4 Carbon dots under natural light (left) and under a 365 nm UV lamp display optical photographs

为了进一步分析3种碳点对可见紫外光谱的吸收强度,将3种碳点分别配成浓度为1 mg·mL^{-1}的乙醇溶液,然后在365 nm紫外灯照射下比较他们的吸光强度,结果如图5所示。从图5可见,混合碳点(NCDs+NSCDs)的吸光强度最强、共掺杂碳点(NSCDs)次之、纯碳点(NCDs)最弱,表明掺杂的碳点具有较强的分散性。

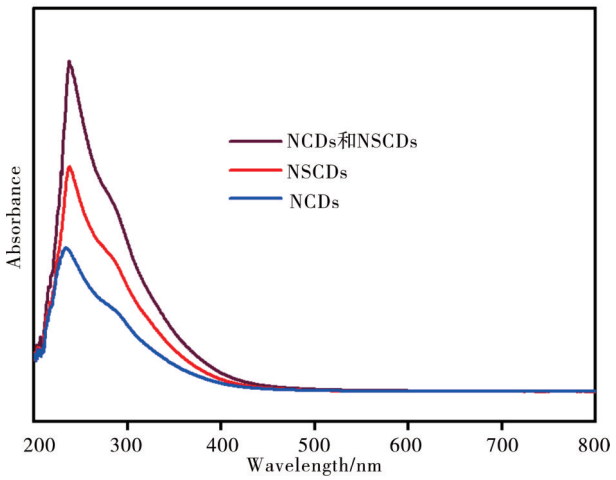
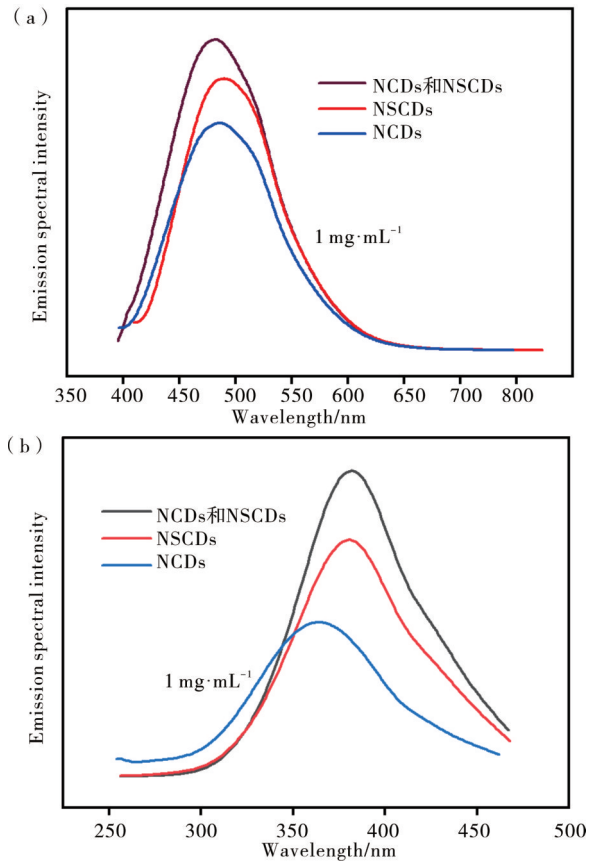


图5 碳点的紫外-可见光谱(UV-vis)测试

Figure 5 Ultraviolet-visible spectrum test for carbon point (1 mg·mL^{-1} ethanol solution)

对3种碳点(NCDs、NSCDs、NCDs+NSCDs)进行荧光分光光度计测试,结果如图6所示。从图6可见:3种碳点在波长487 nm左右处均存在强发射峰,其中碳点(NCDs+NSCDs)的发射光谱强度最强;另外,碳点(NCDs+NSCDs)的激发光谱强度也是3种碳点中最强的。

除了对碳点在乙醇溶液中进行荧光发光测试外,碳点还能在许多有机配体中显示良好的分散性。借助碳点对酸(pH=3、4)、碱(pH=8、9)性的



(a)—发射光谱图;(b)—激发光谱图。

(a)—emission spectra;(b)—excitation spectra.

图6 碳点的发射光谱图和激发光谱图

Figure 6 Emission and excitation spectra of carbon dots, respectively

敏感程度及光致发光效应,来检测污水中所含污染源的种类[27-28]。图7为碳点在不同有机配体中(浓度0.5 mg·mL^{-1})在自然光照下(左)和在365 nm紫外灯下的光学照片。从图7可见,碳点在醚类配体中也具有良好的分散性,其中混合碳点NCDs+

NSCDs溶液的颜色较深，显示其具有良好的分散性。碳点具有良好的分散性，特别是掺杂原子碳点，其可作为最佳的电解液添加剂，其丰富的功能基团对负极锂离子具有引导性的作用，促进了锂离子在电化学过程中均匀沉积，减少了枝晶的生长，保护了整个电池的回路[29]。其实，碳点对锂离子的均衡引导，是碳点光致发光带来的功能。

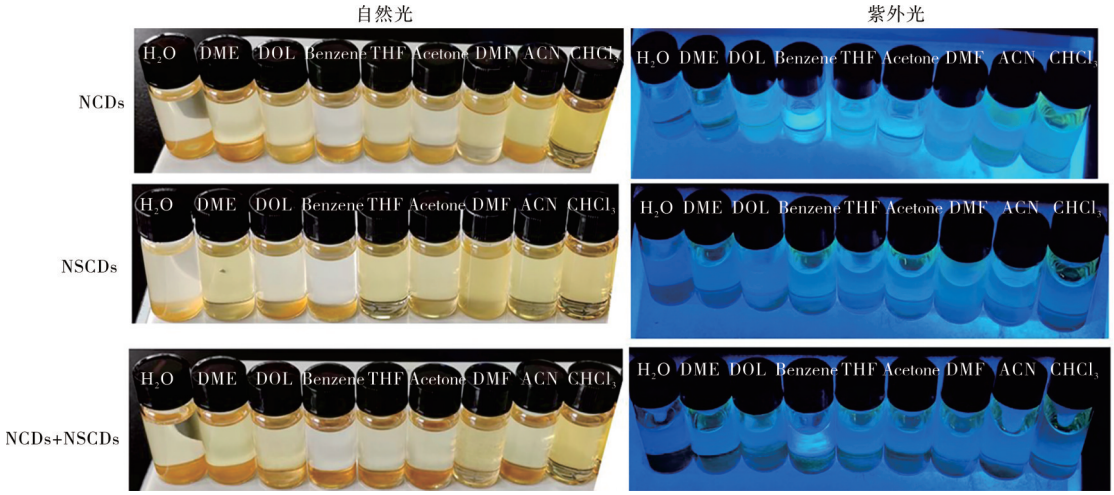


图7 碳点在不同配体中在自然光照(左)和在365 nm紫外灯下的显示光学照片

Figure 7 Optical photographs of carbon dots in different organic solvents under natural light (left) and under a 365 nm UV lamp

3 结论

碳点的光致发光性能受环境、浓度、配体等因素影响，其自身的分散性会影响浓度的变化，从而导致了分散液的彩色变化。3种碳点在合成时，因前驱体的比例不同，引起碳点晶体结构发生变化，其中碳点(NSCDs)和(NCDs+NSCDs)的特征峰向左偏移，说明掺杂碳点给分散液提供了更丰富的缺陷空位，增强了碳点的生物相容性，使碳点发挥更优异的发光性能。

碳点作新一代碳材料，推动了医学领域、催化领域、电池领域等各项事业的发展。扩宽了人类对碳材料进一步的科学认识。目前，碳点依旧处于研究中，还需更深入去探索。比如，对碳点的制备趋于人类食用化，制备出来的碳点富有绿色化食品特点，可以作为治病药物注入到人体血液当中，从而使碳点真正成为对人类有用的新材料。

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Study on Photoluminescence Characteristics of Carbon Dots in Different Ligands

TAN Chao, WANG Kewei, HU Yongjun
(College of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, China)

Abstract: Carbon dots are widely used in various fields especially in the field of photoluminescence due to their adjustable optical properties and good optical stability. The photoluminescence of carbon dots is closely related to the molecular structure of carbon sources, in which the dispersion of carbon dots affects their luminescence intensity. In order to study the

photoluminescence properties of carbon dots in different ligands, carbon dots NCDs, NSCDs and NCDs+NSCDs were prepared by doping synthesis and solution dialysis , the morphologies of the three carbon dots were observed by scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. The light absorption intensity of the three carbon dots was measured by UV-vis. The dispersion and luminescence properties of the three carbon points were also studied. The results show that the morphology of carbon dots NCDs is two-dimensional fine sheet, the heteroatoms of carbon dots NSCDs are loaded on its surface , and the doped atomic groups of carbon dots NCDs+NSCDs have strong monodispersion. The three carbon dots are uniformly distributed as nanoparticles with a size of about 1.8 nm. Taking the carbon characteristic peak of NCDs as the initial position reference, the characteristic peak of NSCDs has obviously shifted to the left , and the characteristic peak of NCDs+NSCDs also shifted to the left, but it is not as obvious as NSCDs. This is because the introduction of doping atomic groups changes the crystal face spacing, thus affecting the size of the crystal face spacing of carbon dots, which shows that doping atoms have been introduced into the carbon dots. The three carbon dots all emit green fluorescence under natural light , and tend to shift to blue with the longer excitation wavelength , among which the mixed carbon dots have the deepest fluorescence color , indicating that the carbon dots of NCDs+NSCDs have stronger hydrophilicity and dispersion, and the enhancement of dispersion will enhance the luminous intensity of carbon dots. The emission intensity of NCDs+NSCDs carbon dots in different ligands is the strongest, indicating that its dispersion is enhanced , thus enhancing its photoluminescence performance. As a new generation of carbon materials, carbon dots have promoted the development of various fields and further understanding of carbon materials.

Keywords: carbon dots; atom doping; photoluminescence; surface modification; dispersivity; ligand; luminous intensity; fluorescence

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