掺硫多孔石墨烯对典型VOCs的光催化性能

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摘要 燃料燃烧、交通运输、化工生产等过程产生的挥发性有机污染物(volatile organic compounds, VOCs)是导致城市灰霾和光化学烟雾的重要物质。多相光催化反应因条件温和、直接利用太阳光驱动等优点而成为一种理想的VOCs降解技术。本研究采用密度泛函理论, 计算掺杂非金属硫原子的单层多孔石墨烯(porous graphene, PG)的光催化性能, 包括能带结构、能带边缘位置、分波态密度和前线轨道(highest occupied molecular orbital-lowest unoccupied molecular orbital, HOMO-LUMO)以及它的光学吸收谱, 对O₂、H₂O和VOCs分子的吸附性能等, 以探讨光催化降解VOCs的可能性。掺杂硫原子后, PG材料能带的带隙大幅降低, 对O₂分子的吸附能显著提高, 结合能带边缘位置的结果, 表明PG材料能产生更多的光生电子, 并且提高了产生超氧自由基的能力。对比原始PG材料, 硫掺杂PG(S-doped PG)材料的光学响应向红外区偏移, 光吸收波长阈值增大, 表明硫原子的掺杂大大提高了原始PG材料对可见光的吸收。此外, 对VOCs较大的吸附能也表明S-doped PG是一种很有前途的降解VOCs的光催化剂, 多维度的计算分析将为多孔石墨烯在光催化中的实际应用提供理论指导。

关键词 多孔石墨烯, 光催化降解, 硫掺杂, 挥发性有机污染物, 密度泛函理论

近10年来, 城市化建设的成功带动了经济腾飞, 但随之而来的是一些不容忽视的环境问题, 人民安居乐业的同时, 越来越关注环境的保护。其中一类危害较大的污染物: 挥发性有机化合物(volatile organic compounds, VOCs)引起了人们的关注。VOCs是一类含有机成分的易挥发物质, 主要来源于燃料燃烧、交通运输、化工生产等工业过程。作为众多新型、毒性更强的二次污染物前驱体, 它们能引发光化学烟雾等大气环境问题^[1-3], 同时人体的危害也不容小觑, 接触VOCs会刺激皮肤、眼睛和呼吸道等, 长此以往暴露在高浓度VOCs环境中将引发一系列疾病甚至死亡^[4-6]。

目前已有多种处理VOCs的技术, 包括生物降解^[7]、燃烧^[8]、吸附^[9-12]以及低温^[13,14]或光催化氧

化^[15]。在这些技术中, 可再生太阳能驱动的光催化技术具有资源丰富、技术经济^[16]、反应条件温和、深度矿化净化、不产生二次污染等优点而成为一种理想的VOCs降解技术^[17,18]。自1972年发现“本多-藤岛效应(Honda-Fujishima effect)^[19]后, 利用半导体实现高效光催化技术得到了迅速发展^[20]。其中, 大比表面积和高表面活性中心密度使得二维半导体材料具有丰富的吸附和反应活性位点, 且相较于块体材料, 它可以直接在表面产生光生载流子, 缩短电荷的扩散途径, 从而加快电荷的界面传输过程^[21-25]。因此, 二维半导体纳米材料能够在众多光催化剂中脱颖而出。然而, 目前基于二维半导体的光催化技术还存在各种各样的问题使其在实际应用中受到极大的限制^[26]。例如, 二维石墨烯材料因优

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异的光学透过率和与吸附剂良好的界面接触等优点使其自问世便引起极大关注^[27,28],但其零带隙的特点导致它通常只能作为载体与其他光催化材料复合^[21,29-31]。如利用光降解亚甲基蓝,Zhang等人^[29]采用二氧化钛与石墨烯复合制光催化剂。在光催化制氢方面,Xiang等人^[30]发现石墨烯偶联g-C₃N₄材料可大大促进该过程。因此,选择一种高效的光催化剂将使光催化反应事半功倍。一般来说,对可见光具有较大的光响应范围是高效可见光催化剂的首要条件,以保证其良好的光吸收效率。除此之外,一定的光催化活性也是必不可少的^[32,33]。然而,这些条件往往很难同时在一种催化剂上实现。为了解决这些问题,研究者对光催化剂的结构和组成进行了改进,使得光催化剂具有更为合适的能带结构等。因此,我们关注于多孔石墨烯(porous graphene, PG),作为石墨烯的衍生物,因其具有较高的比表面积和多孔孔道,可用于分子的运输或存储,成为应用最广泛的多孔材料^[34]。相比于零带隙的二维石墨烯,已有研究表明PG是一类具有带隙的半导体材料^[35,36],这些优点均为其在光催化领域的应用提供了可能。但PG的能带带隙偏高,这是因为PG结构中连接环的单个碳-碳键隔离了它们的芳香单元,使得共振 π 键难以形成,最终影响光生电子的产生^[34]。因此,通过改性手段调控PG材料的能带带隙变得十分必要。

目前,半导体材料主要依赖负载贵金属^[37]、半导体复合^[38,39]或碳材料复合^[40,41]、掺杂调控元素^[42,43]等方法提高光催化活性。其中,掺杂非金属元素因能有效调节材料的带隙宽度而成为了光催化材料改性的热门手段^[44-47]。例如2001年,Asahi等人^[44]发现利用氮原子取代部分二氧化钛材料的氧原子后,其光催化活性有了极大的改善。随后,Zhang等人^[47]发现多孔石墨相氮化碳(g-C₃N₄)材料被氧原子掺杂后带隙显著变窄,可见光响应范围极大提高。因此,可以预见对PG材料进行掺杂修饰必将有利于调控材料至适合的能带带隙和带边位置而应用于光催化反应中。近年来,掺杂型碳材料由于其丰富多样的结构以及优异的催化性能^[48-50]占据了掺杂改性手段的半壁江山。研究发现,在碳材料上掺杂非金属元素如氮、硼、磷、硫等,非金属原子与碳原子由于原子大小等性质不同将发生sp²杂化,电负性的差异将改变电子原本的密度分布形势,从而打破碳材料的电中性特性来提升其催化性能^[51]。因此,无论将富电子(如氮)还是缺电子(如硼)的杂原子掺进碳材料,都能极大提升碳材料的氧还原反应性能,而电中性碳材

料不具有催化活性^[52]。同时,在实际应用中,以各种含硫的化合物作为硫源,已经通过许多不同的方法合成了掺硫碳材料^[53,54]。例如, Ma等人^[55]利用流化床技术获得了具有良好孔隙比例的硫掺杂多孔石墨烯(S-doped PG)。目前, S-doped PG主要应用于电化学领域,包括电池储能、超级电容器^[56]、电催化氧化还原反应^[57]以及温和条件下有机物氧化^[58],鉴于在这些领域中的优异表现,推断其可能在光催化领域也具有不错的性能。因此,研究在实际应用中容易制备的S-doped PG是否具有较好的光催化降解VOCs的性能具有重要意义。

本文使用密度泛函理论(density functional theory, DFT)研究多孔石墨烯在掺杂非金属硫原子前后光催化性能的变化,包括它们的几何结构、能带结构、能带边缘位置、分波态密度和前线轨道(highest occupied molecular orbital-lowest unoccupied molecular orbital, HOMO-LUMO)等确定其电子特性,以及S-doped PG的光学吸收谱,以分析其在实际应用中的光响应性能等,并通过计算它们对典型VOCs气体的吸附能,探讨其降解VOCs的可能性。本研究将为开发高效光催化降解VOCs的多孔石墨烯催化剂提供理论指导,并阐明S-doped PG光催化降解VOCs领域的应用前景。

1 计算方法

本研究采用基于DFT计算的Materials Studio软件中的CASTEP模块和Dmol³模块。对VOCs、O₂或者H₂O分子的吸附和轨道性质计算由DMol³模块执行^[59-61],其余计算因为涉及电子性质等更为精细的计算分析,所以另行采用了CASTEP模块执行^[62]。其中,所有计算的交换关联泛函均采用了广义梯度近似(generalized gradient approximation-Perdew-Burke-Ernzerhof, GGA-PBE)泛函^[63],同时采用双数值极化函数基组(double numeric plus polarization, DNP)^[60]。为保证计算结果的准确性,所有自洽迭代能量收敛标准均为1.0×10⁻⁵ Ha(1 Ha=27.2114 eV),原子间最大的相互作用力和位移的收敛标准分别为0.002 Ha/Å和0.005 Å,并且计算精度全部采用Fine等级。同时,考虑到层间相互作用力的影响,将计算模型的真空层统一设置为20 Å,超晶胞设置为6×6×1,所有的原子都允许被弛豫,所有计算中的电荷转移数都可通过Hirshfeld分析得到。

在DMol³模块中,考虑到范德华力的弱相互作用,采用了基于OBS(Ortmann-Bechstedt-Schmidt)的DFT-D

校正方法^[64]. 核心电子处理采用了全电子方法, 该方法考虑了系统中的所有电子. k 点(k -point)设置为 $20 \times 20 \times 1$. 在CASTEP模块中, 对范德华力的校正采用的是基于TS(Tkatchenko-Scheffler)的DFT-D方法^[63,65], 平面波截断能设置为680 eV, k 点设置为 $6 \times 6 \times 1$. 在计算能带结构和态密度时, 为了更加精确地比较光催化剂的性质, 我们测试了两种泛函(GGA-PBE以及HSE06杂化泛函)对计算结果的影响^[62,66]. 对VOCs、O₂或者H₂O分子吸附在PG或者S-doped PG上的吸附能 E_{ads} 或非金属原子掺杂在S-doped PG上的结合能 E_b 可定义为

$$E_{\text{ads/b}} = E_{\text{A-B}} - E_{\text{A}} - E_{\text{B}}, \quad (1)$$

式中, $E_{\text{A-B}}$ 为体系(吸附分子或掺杂原子与基底材料构成的体系)的总能量, E_{A} 为吸附分子(VOCs, O₂或者H₂O)或掺杂原子的能量, E_{B} 为单独的S-doped PG或单层PG材料的能量.

2 结果与讨论

2.1 S-doped PG的几何结构与电子性质

图1(a)所示为PG材料顶、侧面结构示意图, 图中红色的数字1和2分别代表可供硫原子掺杂的位点, 在进行几何优化后计算硫原子在位置1和2掺杂的结合能, 分别为-0.620和-0.170 eV, 因此硫原子在位置1得到最为稳定的S-doped PG结构(图1(b)). 掺杂硫原子之后, 比较两者的侧面图可以很明显地发现, PG基底发生了较为强烈的形变, 硫原子引起了周围原子的凸起. 这与之前的研究Al掺杂在PG材料引起的形变类似^[67,68], 在该项工作中形变引起基底的电学性质也发生较大改变, 所以S-doped PG的电学性质也可能发生了变化, 通过计算PG和S-doped PG的能带结构、分波态密度以及

图1 PG(a)和S-doped PG(b)结构的顶、侧面结构示意图
Figure 1 Schematic diagram of top and side structures of PG (a) and S-doped PG (b)

HOMO-LUMO等来分析掺杂硫原子前后电子性质的差别, 结果分别绘制于图2和3.

在计算能带结构时, 首先测试了两种交换相关泛函对计算结果的影响. 如图2所示, 无论是PG还是S-doped PG, GGA-PBE泛函计算出的能带带隙值均小于杂化泛函HSE06计算出的结果. 这可能是因为GGA-PBE泛函通常在预测材料的色散性质时误差偏大, 从而影响计算, 导致低估材料的带隙值^[62,66]. 并且杂化泛函HSE06计算出的PG带隙值(3.050 eV)更接近文献^[35]的数值(3.200 eV), 因此我们认定杂化泛函HSE06能更加精确地描述能带的相关性质. 同时可以发现, 硫原子的掺杂导致能带带隙大幅降低, 从3.050 eV(PG)减小为2.127 eV(S-doped PG), 这将极大改善材料的光催化性能, 因为带隙值越小, 意味着其禁带宽度也更小, 从而保证了电子从价带跃迁到导带所需的能量也更少.

如图3所示, HOMO-LUMO在PG材料上原本分布均匀, 掺杂硫原子之后, 产生了离域化的电子态, 导致HOMO-LUMO聚集在掺杂的硫原子附近, 这将使得材料分离或者转移光生电子空穴对变得更为容易. 然而, 对于高效光催化材料来说, 仅仅具备合适的能带带隙还不足以决定光催化性能, 半导体材料的能带边位置同样至关重要. 因此, 结合上文对泛函测试的结果, 我们继续选用能更加精确地描述交换相关的杂化泛函HSE06来计算其能带边位置.

2.2 S-doped PG的能带边缘位置

利用光催化降解污染物的过程中, 最关键的一步就是产生具有强氧化能力的活性氧物种如羟基自由基($\cdot\text{OH}$)或超氧自由基($\text{O}_2^{\cdot-}$), 它们能够有效攻击污染物VOCs, 将其矿化成二氧化碳和水. 所以, 只有当光催化剂的价带边跨过超氧自由基的电势, 或导带边跨过羟基自由基的电势才能产生活性氧物质高效降解污染物. 因此, 可以利用功函数计算PG和S-doped PG材料相对于标准电极电势计算出的价带带边最大值(valence band maximum, VBM)和导带带边的最小值(conduction band minimum, CBM):

$$E_{\text{VBM}}(\text{eV}) = -\Phi + 0.5E_g, \quad (2)$$

$$E_{\text{CBM}}(\text{eV}) = -\Phi - 0.5E_g, \quad (3)$$

$$E'_{\text{CBM/VBM}}(\text{V}) = -E_{\text{VBM/CBM}} - 0.5E_g, \quad (4)$$

式中, Φ 为材料的功函数, E_g 为材料的带隙值, $E'_{\text{CBM/VBM}}$ 为相对于标准电极电势(normal hydrogen electrode,

图 2 PG和S-doped PG的能带结构(a)以及分波态密度(b)
Figure 2 The calculated band structure (a) and partial density of states (b) of PG and S-doped PG

图 3 PG和S-doped PG的前线轨道(LUMO-HOMO)图. 红色和蓝色的区域分别代表了分子轨道波函数的正负相位
Figure 3 LUMO and HOMO of PG and S-doped PG. The red and blue areas represent the positive and negative phases of the molecular orbital wave function, respectively

NHE)(pH 7.0 V vs. NHE $\approx$ -4.5 eV)计算出的电势值. 通过HSE06泛函计算PG和S-doped PG材料的功函数以及

导带和价带带边位置, 得到如图4(a), (b)所示的功函数值分别为5.999 eV(PG)和4.823 eV(S-doped PG). 可以发现掺杂后功函数值明显降低, 根据式(2)和(3)可知两者的带边位置肯定也发生了较大改变. 图4(c)比较了两种材料所对应的导带和价带带边位置的差异, 不难发现对于PG材料而言, 其价带位置高于 $\text{H}_2\text{O}/\bullet\text{OH}$ 电极电位, 而导带位置低于 $\text{O}_2/\text{O}_2^{\bullet-}$ 电极电位, 说明其原本具有产生羟基自由基的可能性. 在掺杂硫原子后, PG材料的带边位置整体上移, 与羟基自由基的相对电势电位已相去甚远, 使得S-doped PG的价带位置低于 $\text{H}_2\text{O}/\bullet\text{OH}$ 电极电位, 而导带位置高于 $\text{O}_2/\text{O}_2^{\bullet-}$ 电极电位. 这说明掺杂硫原子之后, PG材料反而具有产生超氧自由基的可能性. 虽然两种自由基都可以用于降解污染物, 但S-doped PG的带隙更窄, 产生光生电子空穴对相对而言更加容易, 所以可以预见掺杂后PG材料的光催化潜能更大.

2.3 S-doped PG对氧气和水的吸附

在光催化反应中, 利用太阳光促使氧气或水分解来生成活性自由基是十分有前途的^[18]. 在此, 我们全面考虑了O₂分子和H₂O分子在平行与垂直两个方向上的吸附模型, 探讨PG在掺杂硫原子之后对它们的吸附变化. 从图5所示的吸附构型可以看出, H₂O分子在PG材料掺杂硫原子前后的吸附构型并没有明显变化, 都是吸附在孔洞的附近, 只是对S-doped PG而言会靠近硫原子, 但依然保持着依靠范德华力吸附的状态. 然而, O₂分子从原本悬在PG材料上空, 转变为与S-doped PG中的硫原子键合形成硫-氧键. 这或许说明O₂分子与硫原子发生了强相互作用, 然而几何构型不足以证明这种猜想, 还需要从吸附能再验证硫原子掺杂前后的吸

附变化. 表1汇总了O₂分子和H₂O分子在硫原子掺杂PG材料前后的吸附能、键长和电荷转移量. 就H₂O分子的吸附情况而言, 不难发现PG材料在掺杂硫原子之后, 对H₂O分子的吸附能差别不大, 其他电子结构特征如O—OH键长以及电子转移数也并无明显变化, 结合几何吸附构型, 可以确定硫原子的掺杂对H₂O分子的吸附几乎无影响, 仅仅只是相对羟基自由基的电势电位变化了. 然而, PG材料在掺杂之后对O₂分子的吸附能明显提高(从-0.590 eV增至-2.462 eV), O=O键长(从1.218 Å拉伸至1.418 Å)以及电子转移数(从0.024e增至0.545e)也都有所提高. 这都说明O₂分子被掺杂的硫原子成功激活, 再结合上一节中带边位置的结果, 可以确定S-doped PG可以产生超氧自由基.

图4 PG(a)和S-doped PG(b)的功函数, 以及相应的导带、价带的带边缘位置(c)

Figure 4 The work function of PG (a) and S-doped PG (b), and the related band edge position (c) of their CBM and VBM

图5 O₂分子(a)和H₂O分子(b)分别吸附在原始PG单分子层和S-doped PG单分子层的最佳吸附构型

Figure 5 Optimal adsorption configurations of O₂ (a) and H₂O (b) molecules on the original PG monolayer and S-doped PG monolayer, respectively

表 1 O_2 分子和 H_2O 分子吸附在原始 PG 和 S-doped PG 上的最佳吸附构型下的几何和电子参数

Table 1 Geometrical and electronic parameters of the optimal adsorption configurations of O_2 and H_2O molecules on original PG and S-doped PG

	参数 ^{a)}	PG	S-doped PG
O_2	$E_{\text{ads}}(\text{eV})$	-0.590	-2.462
	$d_{\text{O-O}}(\text{\AA})$	1.218	1.418
	$q(\text{e})$	-0.024	-0.545
H_2O	$E_{\text{ads}}(\text{eV})$	-1.408	-1.315
	$d_{\text{O-OH}}(\text{\AA})$	0.981	0.981
	$q(\text{e})$	0.049	0.056

a) E_{ads} 为相应的吸附能, d 为 $\text{O}=\text{O}$ 键或 $\text{O}-\text{OH}$ 键的键长, q 为气体分子的电荷转移量

2.4 S-doped PG 对典型 VOCs 的吸附

VOCs 具有很多种类, 它们的危害性也不尽相同. 我国城市地区的 VOCs 主要来源一般为机动车尾气、工业污染排放、油品挥发泄漏等. 因此, 选取了几种较为典型的有毒 VOCs: 甲醛(formaldehyde)、苯(benzene)、甲苯(toluene)和苯乙烯(styrene), 探讨 PG 和 S-doped PG 对它们的吸附性能. 图 6 汇总了甲醛、苯、甲苯和苯乙烯吸附在原始 PG 单层和 S-doped PG 单层上的最佳构型, 发现除了吸附位点有所不同, VOCs 在 S-doped PG 上主要吸附在硫原子的附近, 4 种 VOCs 被吸附的构型在两种材料上几乎没有差别. 同时, 计算获得了 4 种 VOCs 在 PG 和 S-doped PG 上的吸附能, 分别为

-1.328/-1.154 eV(甲醛)、-2.145/-2.183 eV(苯)、-2.653/-2.615 eV(甲苯)和-2.878/-2.904 eV(苯乙烯), 发现它们在两种材料上的吸附能相差不大, 都属于化学吸附的范畴, 这是 S-doped PG 成为降解 VOCs 催化剂的前提条件, 并且以往的研究已经证实 PG 材料对 VOCs 具有良好的吸附能^[67], 所以 S-doped PG 有望成为降解 VOCs 的高效光催化剂.

2.5 S-doped PG 的光学性质

上述研究已经表明 S-doped PG 一旦接收可见光的照射, 就能够高效地产生超氧自由基, 是一种有前景的光催化材料. 所以在此基础上, 还需要研究 S-doped PG 的可见光响应性来做最后的验证工作. PG 和 S-doped PG 对可见光的吸收范围和能力曲线如图 7 所示, 可以发现 PG 材料在掺杂硫原子后, 吸收曲线的面积没有较大变化, 但可见光响应范围有些许向红外区偏移的趋势. 另外, 根据康普顿效应(波长 $\lambda=1240/\text{带隙值 } E_g$)计算, 得到 S-doped PG 以及原始 PG 的光吸收波长阈值分别为 583 和 406 nm, 这表明硫原子的掺杂大大提高了原始 PG 材料对可见光的吸收响应. 综上所述, S-doped PG 具有良好的可见光吸收响应性, 具备更强的产生光生电子的能力, 进而在光催化降解 VOCs 方面被赋予更高的期望.

3 结论

本研究采用 DFT 计算方法, 研究了 PG 在掺杂非金

图 6 甲醛(a)、苯(b)、甲苯(c)、苯乙烯(d)分别吸附在原始 PG 单分子层和 S-doped PG 单分子层上的顶部与侧面视图

Figure 6 Top and side views of formaldehyde (a), benzene (b), toluene (c), and styrene (d) adsorbed on the original PG monolayer and S-doped PG monolayer, respectively

图7 PG和S-doped PG的光吸收曲线
Figure 7 Light absorption curves of PG and S-doped PG

属硫原子前后光催化性能的变化,以探讨S-doped PG是否能应用在光催化降解典型VOCs方面。首先在对掺杂结构的结果进行全面比较后,分析了最稳定的S-

doped PG结构的电子特性,包括能带结构、能带边缘位置、分波态密度和HOMO-LUMO。硫原子掺杂后,PG材料的能带带隙从3.050 eV降低至2.127 eV,大幅的下降利于S-doped PG产生更多的光生电子,同时,带边位置的降低使得S-doped PG提高了原始PG单层产生超氧自由基的能力。计算了S-doped PG对O₂分子、H₂O分子以及VOCs分子的吸附性能,PG材料在掺杂硫原子之后对O₂分子的吸附作用明显提高,这一发现与其带边位置的结果进一步说明了超氧自由基的产生。并且,S-doped PG对4种典型VOCs的吸附性能都属于化学吸附范畴,是其有望降解VOCs催化剂的基本条件。最后,计算了S-doped PG的光学吸收谱来分析其光响应性能,向红外区偏移的光吸收曲线和增大的光吸收波长阈值都表明硫原子的掺杂大大提高了原始PG材料对可见光的吸收响应。综上所述,S-doped PG是一种有前途的降解VOCs的光催化剂,且多维度的计算分析将为PG在光催化中的实际应用提供理论指导。

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Summary for “掺硫多孔石墨烯对典型VOCs的光催化性能”

Photocatalytic degradation of typical VOCs on sulfur-doped porous graphene

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Volatile organic compounds (VOCs), one type of the most harmful pollutants, which mainly from fuel combustion, transportation and chemical industry or other industrial processes, have aroused great concern. Because they are important substances lead to urban haze and photochemical smog, long-term exposure to high concentration of VOCs will stimulate human skin, eyes, and respiratory tract and finally cause a series of diseases even death. Nowadays, a variety of VOCs treatment technologies are available, including biodegradation, combustion, adsorption, and low temperature or photocatalytic oxidation. Among these technologies, the renewable solar-driven multiphase photocatalytic technology has the advantages of rich resources, technical economy, mild reaction conditions, deep mineralized purification, no secondary pollution and so on, becoming an ideal VOCs degradation technology. Due to the large specific surface area and high active center density, semiconductor is often used as a catalyst to realize efficient photocatalysis. Therefore, understanding the performance of semiconductor photocatalyst is of great significance to develop an effective photocatalyst for VOCs degradation from a theoretical perspective.

In this study, we calculated the photocatalytic properties of monolayer porous graphene (PG) doped with nonmetallic sulfur using density functional theory (DFT) calculations. The electronic properties of the most stable S-doped PG structure including the energy band structure, the band edge positions, the partial density of states (PDOS), and the highest occupied and the lowest occupied orbitals (HOMO-LUMO) were analyzed first after a comprehensive comparison of doping results. The results manifest that after doping the sulfur atom, the band gap of PG material decreases from 3.050 to 2.127 eV, which is conducive to the generation of more photogenerated electrons in S-doped PG. At the same time, the reduction of band edge position makes S-doped PG improve the ability of superoxide free radical generation than the original PG monolayer. Then, the adsorption performance of S-doped PG on O₂, H₂O and VOCs molecules was calculated. The results show that the adsorption energy of PG material for O₂ molecule is significantly increased (from -0.590 to -2.462 eV) after doping single atom S, the O=O bond length (from 1.218 to 1.418 Å) and electron transfer number (from 0.024e to 0.545e) greatly enhanced, all indicating that the O₂ molecule is successfully activated. Combined with the results of band edge position, it can be confirmed that S-doped PG can generate superoxide radicals. In addition, the adsorption performance of S-doped PG on four typical VOCs belongs to the category of chemical adsorption, which provides an important prerequisite for the degradation of VOCs catalyst. Finally, the optical absorption spectrum of S-doped PG was calculated to analyze its optical response properties. The optical absorption curve shifted to the infrared region, the wavelength threshold increased, and according to Compton effect calculation, the light absorption wavelength threshold of S-doped PG and original PG is 583 and 406 nm respectively, all of these indicating the doped sulfur atom tremendously promoted the absorption response of visible light compared to the original PG material.

In summary, our work indicates that S-doped PG is a promising photocatalyst for VOCs degradation, and multidimensional calculation and analysis will provide theoretical guidance for the practical application of porous graphene in photocatalysis.

porous graphene, photocatalytic degradation, sulfur doped, volatile organic compounds, density functional theory

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