



基于第一性原理计算的低维功能材料分子设计

吕海峰, 武晓君*

中国科学技术大学化学与材料科学学院, 合肥微尺度物质科学国家研究中心, 合肥 230026

* 联系人, E-mail: xjwu@ustc.edu.cn

2023-07-16 收稿, 2023-10-02 修回, 2023-10-13 接受, 2023-10-24 网络版发表

国家杰出青年科学基金(2225301)、国家自然科学基金(22073087, 12147105)、中国科学院稳定支持基础研究领域青年团队(YSBR-004)、中国科学院先导科技专项(XDB0450101)和中部学校基础研究基金(20720220007)资助

摘要 低维材料具有高比表面积以及独特的物理化学特性, 是未来能源、信息等技术领域的重要研究内容, 但如何实现特定结构和功能是其实际应用的基础. 分子是保持化学结构和特性的最小单元, 从分子基元出发, 可以实现低维材料结构预测以及功能导向的理论设计. 本文综述了低维功能材料理论设计方面的研究进展, 结合分子设计策略和第一性原理电子结构计算方法, 针对特定结构和性能开展理论设计, 预测了复杂二维单质晶体结构以及一系列低维新型光催化材料和自旋电子学材料, 并揭示了低维材料功能和分子基元物性之间的对应关系, 总结和展望了低维功能材料分子设计的优势与挑战.

关键词 低维功能材料, 分子设计, 第一性原理, 光解水, 室温磁性

先进材料是新一代高新技术的先导和物质基础. 与体相材料相比, 低维材料中至少一个维度位于原子尺度, 包括二维纳米片、一维纳米线或纳米管、零维的纳米团簇等^[1-3]. 由于显著的量子尺寸效应, 低维材料的能级结构会由连续变为离散, 表现出丰富、新颖的力学、电子、磁学、光学、热学和催化等物理化学特性^[4-7], 逐步发展成为未来信息、能源技术领域的重要物质基础, 被广泛应用在半导体器件、自旋电子器件、光/电催化、能源存储和转换器件等^[8-12]. 因此, 发展具有特定结构、特殊功能的低维材料是材料科学研究领域需要长期关注的问题.

低维材料具有丰富的微观结构, 电子、自旋、轨道等多种量子态的耦合, 以及力、电、磁、光等外场下的响应行为^[13-15]. 为满足低维材料的实际应用, 需要在原子尺度上控制材料的形貌, 精准表征结构和物性, 并研究其在实际应用过程中的动态变化, 并评估量子转换效率^[16-18]. 实现上述过程可以进一步优化实验技

术和设备, 同时可以借助于材料的理论计算和模拟^[19,20]. 与实验研究不同, 基于第一性原理的理论计算与模拟不仅可以获得低维材料的结构、物性特征, 同时可以构建材料结构-物性、物性-环境之间的内在关联, 结合物理化学基本原理针对设计特定功能的材料体系^[21,22]. 因此, 如何理论构建成分-结构-物性-功能之间的映射关系, 实现功能导向的低维材料理论设计和物性调控是低维材料研究的核心问题.

分子是保持化学和结构特性的最小结构单元, 同时具有丰富的结构和物理化学特性、易于合成, 可以作为结构单元进行有序组装获得多功能低维材料^[23-25]. 与从原子出发的设计策略相比, 分子基元组装需要根据分子的对称性和化学成键规则, 可以有效地降低势能面的复杂性, 设计获得具有特定结构的低维材料^[26-28]. 此外, 低维材料可以“继承”或“集成”分子基元的物理化学特性, 实现具有特定功能低维材料的定向设计^[29-31]. 同时, 分子设计策略还可以利用自组装或

引用格式: 吕海峰, 武晓君. 基于第一性原理计算的低维功能材料分子设计. 科学通报, 2023, 68: 4448-4456

Lü H F, Wu X J. Molecular design of low-dimensional functional materials based on first-principles calculation (in Chinese). Chin Sci Bull, 2023, 68: 4448-4456, doi: 10.1360/TB-2023-0696

者缩聚等反应方法预合成其中的初级结构单元,实现低维材料的模块化合成^[32,33]。

近几十年来,结合材料理论模拟方法和分子设计策略,实现了一系列基于分子的低维功能材料,包括共价有机框架材料、金属有机框架材料以及分子晶体等,被广泛应用于气体分离、存储和感应、能源储存、电/热传输介质、发光器件、自旋电子器件、多铁、催化以及生物相关等技术领域^[34~39],上述应用的定向设计与优化依赖于构建分子基元和低维材料之间的对应关系。本文从理论模拟角度出发,综述了低维功能材料分子设计方面的研究进展,包括结构和功能。第一部分通过二维双层硼烯结构理论设计说明低维材料结构的分子设计策略及限域生长机制。第二部分侧重于研究分子-低维材料之间的对应关系,阐述了新型低维光催化材料和自旋电子学材料的分子设计策略。最后总结和展望了低维功能材料分子设计的优势与未来挑战。

1 低维材料结构预测

材料性能决定于结构,而如何高效、准确地获得低维材料的全局结构是低维材料设计的核心挑战之一。解决上述挑战一是需要开发高效的全局结构搜索算法,可以通过元素种类、配比等信息遍历体系的多维势能面,从原子出发寻找全局最优结构;二是结合物理化学成键原则和拓扑构型,从分子水平上直接设计得到低维材料。

近年来,已有多种全局结构搜索算法用于材料科学研究,包括遗传算法、粒子群优化算法、差分进化算法等,其中,分别基于粒子群优化算法和遗传算法开发的CALYPSO和USPEX已经被广泛用于自由状态以及受限状态下低维材料的结构预测^[43,44],理论设计获得许多具有特殊结构和物性的材料,比如电池负极、高温超导体、自旋电子学材料、负泊松比等^[45~49],为实验合成指定结构和功能的低维材料提供了理论支持。其中一个典型的案例为二维单层硼烯结构预测。硼是第五号元素,比碳少一个价电子,因此具有多中心-两电子的复杂成键特征,可能形成丰富的二维平面结构,一直是相关理论和实验研究的热点。借助于粒子群优化算法,本课题组^[40]从化学组分出发预测得到34种稳定的二维单层硼烯结构并计算了相对稳定性和电子结构,证实了二维单层硼烯的多晶型特点,如图1(a)所示。随后,通过原子气相沉积方法,成功在银衬底上制备得到理论预测的二维单层硼烯 β_{12} 和 χ_3 ,并且

和衬底限制下的结构预测结果一致^[50]。接下来,基于全局结构搜索方法,预测衬底限制下二维硼烯结构,如图1(b)所示。由上可知,全局结构搜索算法能够实现特定结构和功能低维材料的理论设计,但是受限于计算资源和势能面的复杂度,结构搜索通常局限于几十个原子的体系,无法实现原子较多情况下的结构搜索。

从分子出发的低维材料设计可以结合分子成键特点和拓扑构型,有效地降低势能面维度,获得低维材料的势能空间和稳定的晶体构型,同时这种“自下而上”的单元组装特性为低维材料的模块化合成提供了实验可行性。这里,通过二维双层硼烯结构预测为例说明通过分子设计策略获得二维双层硼烯结构。如图1(c)所示,选取二维单层硼烯 β_{12} 中的结构单元构建二维双层硼烯,通过结构单元扩展的方式获得上、下两层“之字形” β_{12} 硼烯结构,然后根据硼的多中心成键特点,选取上、下层硼烯中的四配位硼原子形成两层之间的硼硼键,从而得到二维双层硼烯的复杂晶体结构(包含366个硼原子)。接下来,利用第一性原理电子结构计算方法,得到了铜衬底上二维双层硼烯的STM模拟图像,与实验表征结果具有相同的亮、暗分布条纹。能带结构和态密度计算表明双层硼烯为金属性,和实验中STS表征吻合^[41]。

基于上述工作,本课题组^[42]进一步研究了铜衬底单层硼烯上硼团簇的存在形式。首先,实验观测到铜表面被单层硼烯全覆盖后,硼原子进一步沉积会形成亮度均一、周期性排列的亮斑,其尺寸大小约为 5 ± 0.5 Å,高度约为60 pm,同时硼团簇会选择吸附在单胞中的特定位置。依据上述表征,选取适当尺寸的硼团簇 $B_n(n=3\sim 12)$,计算不同硼团簇在铜衬底单层硼烯上的吸附能,结果表明 B_5 团簇具有最大的吸附能,同时STM模拟图像与实验吻合,电荷分布计算表明铜衬底单层硼烯的电荷分布决定了 B_5 团簇的形成和周期性排列。 B_5 团簇紧密堆积形成全覆盖之后,将表现出类似“多米诺骨牌效应”的结构转变,团簇从“立式”变为“躺式”,团簇之间形成硼硼键,全覆盖的 B_5 团簇会自发转变为第二层硼烯,如图1(d)所示,证实了实验中硼团簇覆盖度增加并最终得到双层硼烯的动态演变过程,阐明了双层硼烯的分子基元扩展生长机制。

综上所述,二维双层硼烯结构构建表明分子设计不仅可以获得大体系低维材料晶体结构,同时能够表征低维材料的生长机制,为低维材料的制备提出有效策略。同样,应用分子设计概念,基于磷双原子、三

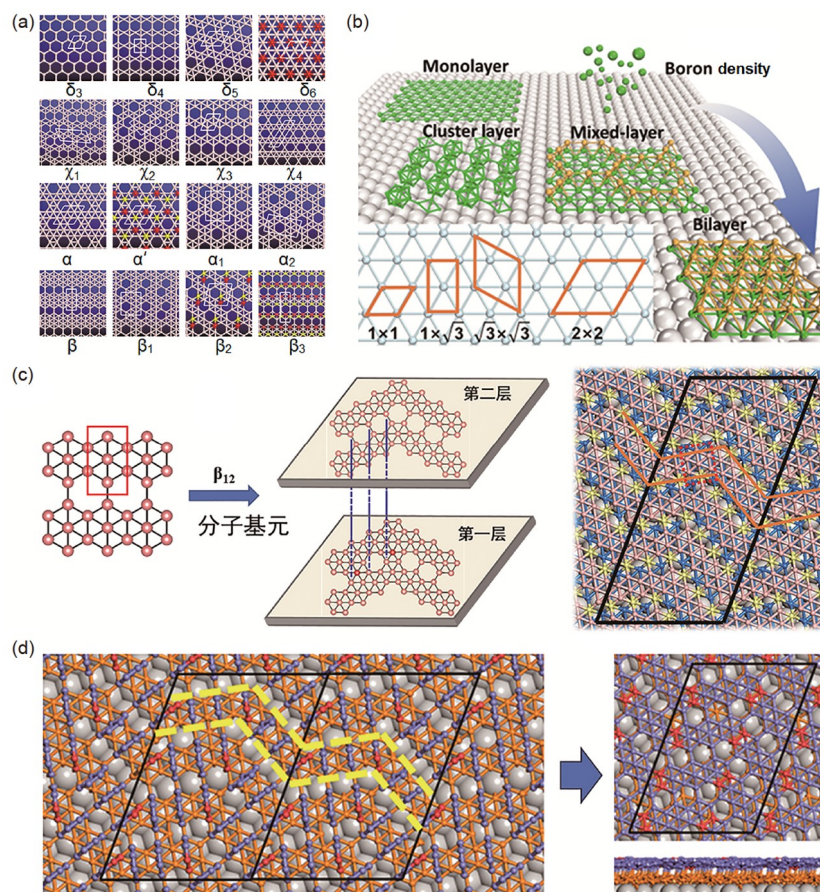


图1 (网络版彩色)二维硼烯结构分子设计。(a) 二维单层硼烯全局结构搜索^[40]。(b) 衬底限制下二维硼烯结构搜索。(c) 基于 β_{12} 单元组装得到二维双层硼烯^[41]。(d) 单层硼烯上 B_5 团簇全覆盖向双层硼烯的结构转变^[42]

Figure 1 (Color online) The molecular design of two-dimensional borophene. (a) Different kinds of 2D boron structures obtained by global structure search^[40]. (b) Different kinds of 2D boron structures obtained by substrate-constrained global structure search. (c) The two-dimensional bilayer borophene obtained by assembly of β_{12} unit^[41]. (d) Structural transition from full coverage of B_5 clusters on monolayer borophene to bilayer borophene^[42]

原子、四原子、六原子等结构单元进行组装可以获得21种二维磷单质结构^[51]。基于碳杂环分子进行脱氢组装可以得到一种具有近零泊松比和高载流子迁移率的二维单层碳半导体材料^[52]。近来,多个实验组报道了一种二维富勒烯材料^[53,54],可以看作是由富勒烯分子单元组装得到,实验表明其为半导体,说明可以通过分子设计策略实现具有新颖结构和物性的低维材料。

2 特定功能低维材料的分子设计

低维材料理论设计的核心挑战是建立功能与结构之间的映射关系,实现特定功能材料的定向设计。分子基元组装不仅可以获得新颖构型的低维材料,同时低维材料也可以“集成”或者“继承”分子基元的物理化学特性。基于上述分子设计策略,构建了新型低维光催化

材料和自旋电子学材料。

2.1 低维光催化材料分子设计

能源和环境问题是现代社会的重要议题,其中利用可见光将水分解为氢气和氧气是解决上述问题的一个有效途径。为实现可见光全解水,对光催化材料的基本要求是带隙大于1.23 eV,低于约3 eV,同时导带底和价带顶需要跨越析氢和析氧反应的氧化还原电位。低维材料具有较长的载流子弛豫时间、高比表面积以及多样的电子结构,是可见光全解水的重要载体之一。目前,实验和理论提出了众多的候选材料,主要包括低维无机材料,如过渡金属氧化物、硫化物、氮化物等,以及低维有机材料,如共轭有机框架体系^[18]。其中,共轭有机框架材料主要由非金属元素碳、氮、氢等组成,

同时具有分子组装特性, 电子结构丰富多样, 是一类有潜力的光催化材料. 但目前报道的大部分高分子光催化材料仅能进行析氢半反应, 需要借助牺牲剂或助催化剂实现析氧, 可见光全解水材料鲜有报道.

针对上述问题, 本课题组^[56]从理论计算角度出发, 揭示了二维共轭有机框架材料可见光全解水的机制为同时具备析氢和析氧的活性位点, 同时光生载流子可以同时驱动水的氧化、还原反应, 设计得到一类含炔基的体系. 第一性原理电子结构计算结合反应过程自由能计算表明炔基可以调控体系的带边位置, 同时体系中同时包含析氢和析氧的活性位点, 实现了单一非金属高分子材料吸收可见光催化全解水, 并提出了单位点和双位点两种析氧反应机理. 实验合成的含有1,3-二炔基的二维共轭高分子材料证实可以利用可见光实现全解水, 全光谱测量的太阳能到氢气的转换效率达0.6%.

基于上述工作, 本课题组^[55]进一步提出了功能分子单元组装设计全解水高分子光催化材料的策略(图2

(a)), 筛选具有光催化析氢和析氧活性的功能分子, 结合成键规则和空间拓扑构型, 设计得到具有适宜能级位置、同时具有分离的氧化、还原活性中心的低维光催化材料. 分子设计策略可以有效利用分子之间的相互作用调控低维光催化材料的电子结构, 同时集成分子单元的功能性.

应用此方法, 本课题组^[55]从理论上提出了12种碳、氮基的二维共轭有机框架体系, 自由能计算表明其中3种可以实现利用可见光全分解水生成氢气和氧气. 进一步, 通过实验合成了其中的一种材料, I-TST, 并研究其光解水活性, 在不添加催化剂的条件下, 实现了产氢和产氧. 基于庚炔框架实现了一类可以利用可见光全解水制备过氧化氢的二维庚炔有机框架, 太阳能到化学能的转换效率为0.78%. 接下来, 如图2(b)所示, 结合机器学习和第一性原理计算, 理论构建了分子能级位置和二维共轭有机框架材料带边位置的对应关系, 实现了定向设计特定电子结构的低维高分子催化材料.

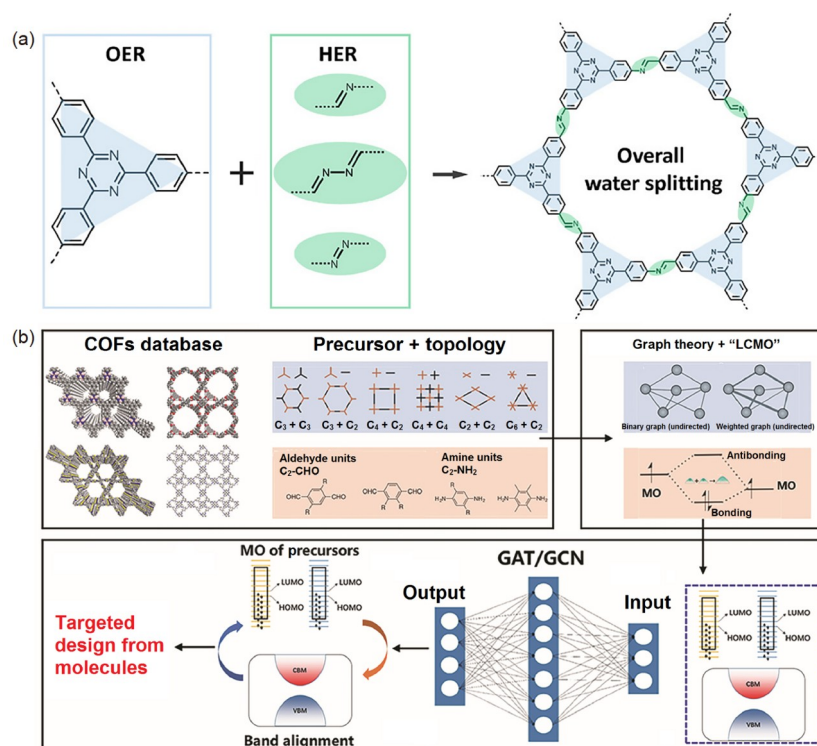


图2 (网络版彩色)二维共价有机框架材料分子设计. (a) 基于功能分子拓扑序设计利用可见光全分解水的二维共轭高分子材料^[55]. (b) 基于分子轨道构建预测二维高分子材料带边位置 workflow

Figure 2 (Color online) Molecular design of two-dimensional covalent organic frameworks. (a) Design of two-dimensional covalent organic frameworks toward visible light-driven overall water splitting based on functional molecular units^[55]. (b) Construction of workflow for predicting band-edge positions of two-dimensional covalent organic frameworks based on the molecular orbitals of precursors

2.2 低维自旋电子学材料分子设计

自旋电子器件可以同时利用电子的电荷和自旋自由度实现信息的传递、存储和处理, 具有响应速度快、能耗低、存储密度高等特点. 实现自旋自旋器件需要解决3个关键的科学问题, 即自旋极化载流子的产生和注入、自旋的长程传输以及自旋方向的调控和探测. 解决上述问题依赖于设计新型自旋电子学材料. 低维磁性材料具有丰富的电学和磁学特性, 是纳米自旋电子器件的重要物质载体之一. 为构筑可在不低于室温下工作的纳米尺度自旋电子器件, 高居里温度、高自旋极化率和大磁晶各向异性能是对低维磁性材料的基本要求.

由于具有潜在的高磁晶各向异性能, 一维纳米线是低维磁性体系的候选材料, 前期理论工作表明可以通过金属原子和其他结构单元组装构建一维磁性纳米线, 包括 $3d(\text{TM} = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn})$ 金属原子和苯环交替组成的一维 $[\text{TM}(\text{Bz})]_{\infty}$ ^[57], 钒原子与茂基(Cp)、同时与茂基和苯环、与蒽基(Ant)组成的一维 $[\text{V}(\text{Cp})]_{\infty}$ 、一维 $[\text{V}(\text{Bz})\text{V}(\text{Cp})]_{\infty}$ 、 $[\text{V}_2(\text{Ant})]_{\infty}$ 以及钒、铁原子与茂基形成的一维 $[\text{V}(\text{Cp})\text{Fe}(\text{Cp})]_{\infty}$ ^[58], 锰原子与并茂基形成的一维 $[\text{Mn}_2(\text{Pn})]_{\infty}$ ^[59], 双金属与萘基组成的 $[(\text{Np})_2\text{V}_2\text{TM}_2]_{\infty}$ ^[60], 双金属与茂基组成的一维 $[(\text{Cp})\text{TM}_1(\text{Cp})\text{TM}_2]_{\infty}$ ($\text{TM}_1 = \text{Ti}, \text{Cr}, \text{Fe}; \text{TM}_2 = \text{Sc}-\text{Co}$)^[61], 镧系元素与环辛四烯组成的 $\text{Ln}_n\text{COT}_{n+1}$ ($\text{Ln} = \text{Eu}, \text{Ho}$)^[62]等, 这些磁性纳米线具有丰富的磁学和电学性质, 可以形成一维磁性金属、半导体以及半金属等. 基于上述分子单元组装策略, 本课题组^[63]采用了 MH_3 分子($\text{M} = \text{Sc}, \text{Cr}, \text{Mn}$ 和 Co)的限域组装得到稳定的一维纳米线结构, 金属的 d 轨道在桥连氢原子配体形成的晶体场中发生分裂, 电子占据情况决定了体系的磁基态, 其中 CoH_3 为半金属, 具有100%的自旋极化率. 氢配位的一维纳米线金属原子键长接近其体相键长, 具有较强的链内磁交换耦合. 同时, 一维 CoH_3 纳米线在沿轴方向与其正交方向的磁晶各向异性能差大约为1 meV, 因此可以有效地稳定其长程磁序, 如图3(a)所示.

二维磁性材料具有自旋、电荷之间的相互作用, 可以作为纳米自旋电子器件的载体材料. 其中, 分子组装是一种构建二维磁性材料有效策略. 早期理论研究工作包括, $3d$ 过渡金属($\text{TM} = \text{Cr}-\text{Zn}$)酞菁分子组装得到二维磁性材料 TMPc , 其中二维 MnPc 为铁磁半导体^[65], 过渡金属 Cr 与卟啉可以组装得到二维铁磁材料,

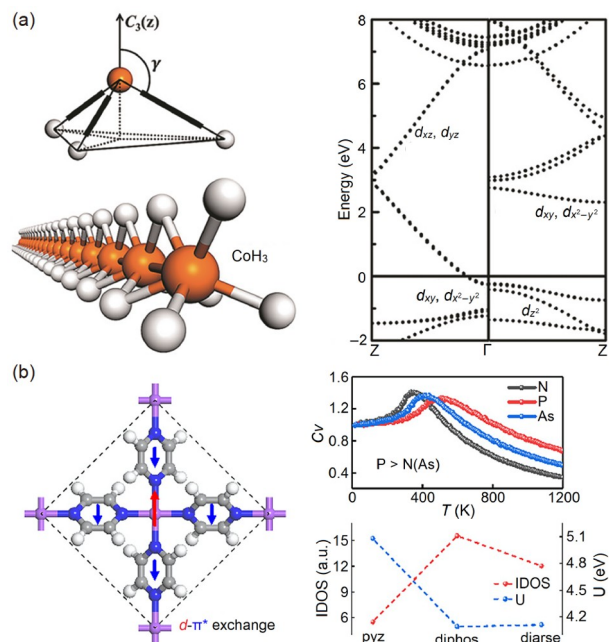


图3 (网络版彩色)低维自旋电子材料分子设计. (a) 一维磁性半金属 CoH_3 分子纳米线, 具有100%自旋极化率^[63]. (b) 室温磁性二维金属有机框架分子设计策略^[64]

Figure 3 (Color online) Molecular design of low-dimensional spintronics. (a) One-dimensional half-metallic CoH_3 nanowire with 100% spin polarization^[63]. (b) The design strategy of two-dimensional metal-organic frameworks with room-temperature magnetism^[64]

居里温度为187 K^[66], 以实验合成 $\text{Ni}_3\text{C}_{12}\text{S}_{12}$ 为二维模板得到居里温度为450 K的二维 $\text{Mn}_3\text{C}_{12}\text{N}_{12}\text{H}_{12}$ ^[67], 居里温度为209 K的二维 $\text{Zn}_3\text{C}_{12}\text{O}_{12}$ ^[68]等. 近来理论研究工作表明可以在过渡金属阳离子和有机阴离子之间引入一种较强的 $d-p$ 直接亚铁磁性交换相互作用, 如二维金属有机框架磁性材料 $\text{Cr}(\text{pentalene})_2$ 和 $\text{Cr}(\text{DPP})_2$ ^[35,69], 将过渡族金属 Cr 与对称反演破缺的连接体可以得到二维多铁体系^[37,70]等. 同样基于上述 $d-p$ 直接交换相互作用, 本课题组^[71]理论设计了一系列具有高居里温度的二维金属有机框架半导体体系. 首先, 在实验上已经合成的金属有机材料 $\text{Li}_{0.7}[\text{Cr}(\text{pyz})_2]\text{Cl}_{0.7} \cdot 0.25(\text{THF})(\text{pyz}, \text{吡嗪}; \text{THF}, \text{四氢呋喃})$ 的基础上, 进一步通过理论预测了二维 $\text{Cr}(\text{pyz})_2$ 单层材料, 表现出本征的双极磁性半导体特征, 居里温度达到342 K, 并明确了其高居里温度来源于中心金属原子和配位之间形成的 $d-p$ 直接交换作用. 进一步, 基于 sql 拓扑构型, 构建3种二维金属有机框架体系 $\text{Cr}(\text{pyz})_2$ 、 $\text{Cr}(\text{diphos})_2$ 和 $\text{Cr}(\text{diarse})_2$, 如图3(b)所示, 第一性原理计算表明3种二维金属有机框架体系的磁基态均为亚铁磁态, 金属之间磁矩为同向排列, 金属和分子

配体之间为反向排列。分子配体均由一个电子填充到反键 π 轨道, 形成一个单占据轨道, 从而配位和中心金属之间形成直接磁交换耦合作用^[64]。基于蒙特卡洛的数值模拟方法, $\text{Cr}(\text{pyz})_2$ 、 $\text{Cr}(\text{diphos})_2$ 和 $\text{Cr}(\text{diarse})_2$ 的磁临界温度(T_c)分别为344、512和437 K, 这与中心金属原子Cr和配体分子之间的轨道杂化强度呈正相关并提出了金属原子Cr的 d 轨道和分子配体的反键轨道 π^* 在费米能级附近占据态的重叠积分作为轨道杂化强度的描述因子。在分子单元组装策略基础上, 进一步调控拓扑序和轨道序, 理论提出了一种同时具有 p 轨道磁性与费米狄拉克半金属特性的二维过渡金属过氧化物晶体。

3 总结和展望

低维材料展现出丰富的物理化学特性, 在信息、能源等技术领域有着广泛的应用前景, 但其核心问题为特定结构和功能的定向实现。结合分子设计策略和第一性原理计算, 理论揭示了二维双层硼墨烯的结构特征和生长机制, 并针对特定的光解水和自旋电子器件应用, 提出了二维高分子全光解水材料和低维磁性材料, 构建了低维材料功能性和分子基元物性之间的对应关系。接下来, 结合数据驱动的人工智能模型, 针对特定功能, 进一步构建结构基元和材料物性之间的映射关系, 同时研究其在服役环境下的量子效率, 实现低维功能材料的定向设计并为相关实验提供理论基础。

参考文献

- 1 Zhuo Z J, Lü H F, Wan Y Y, et al. Towards rational design of low-dimensional material: From structure prediction to molecular engineering (in Chinese). *Sci Sin Chim*, 2018, 48: 998–1014 [卓之问, 吕海峰, 万阳阳, 等. 低维纳米材料的理性设计: 从结构预测到分子设计. 中国科学: 化学, 2018, 48: 998–1014]
- 2 Cheon G, Duerloo K A N, Sendek A D, et al. Data mining for new two- and one-dimensional weakly bonded solids and lattice-commensurate heterostructures. *Nano Lett*, 2017, 17: 1915–1923
- 3 Butler S Z, Hollen S M, Cao L, et al. Progress, challenges, and opportunities in two-dimensional materials beyond graphene. *ACS Nano*, 2013, 7: 2898–2926
- 4 Gjerding M N, Taghizadeh A, Rasmussen A, et al. Recent progress of the Computational 2D Materials Database (C2DB). *2D Mater*, 2021, 8: 044002
- 5 Seh Z W, Kibsgaard J, Dickens C F, et al. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science*, 2017, 355: eaad4998
- 6 Lü J. Atomic lego catalysts synthesized by atomic layer deposition. *Acc Chem Res*, 2022, 3: 358–368
- 7 Lü H, Niu Y, Wu X, et al. Electric-field tunable magnetism in van der Waals bilayers with A-type antiferromagnetic order: Unipolar versus bipolar magnetic semiconductor. *Nano Lett*, 2021, 21: 7050–7055
- 8 Novoselov K S, Geim A K, Morozov S V, et al. Electric field effect in atomically thin carbon films. *Science*, 2004, 306: 666–669
- 9 Geim A K, Novoselov K S. The rise of graphene. *Nat Mater*, 2007, 6: 183–191
- 10 Yang H, Valenzuela S O, Chshiev M, et al. Two-dimensional materials prospects for non-volatile spintronic memories. *Nature*, 2022, 606: 663–673
- 11 Lin J, Lü H, Wu X. Enhanced oxygen reduction on graphene via Y_5Si_3 electride substrate: A first-principles study. *Chin J Chem Phys*, 2018, 31: 649–654
- 12 Gao S, Wang T, Jin M, et al. Bifunctional Nb-N-C atomic catalyst for aqueous Zn-air battery driving CO_2 electrolysis. *Sci China Mater*, 2023, 66: 1013–1023
- 13 Lü H F, Wu X J. Theoretical design and regulation of low-dimensional spintronics (in Chinese). *Chin Sci Bull*, 2018, 63: 3442–3452 [吕海峰, 武晓君. 低维自旋电子材料的理论设计与调控. 科学通报, 2018, 63: 3442–3452]
- 14 Li X, Yang J. First-principles design of spintronics materials. *Natl Sci Rev*, 2016, 3: 365–381
- 15 Falin A, Holwill M, Lü H, et al. Mechanical properties of atomically thin tungsten dichalcogenides: WS_2 , WSe_2 , and WTe_2 . *ACS Nano*, 2021, 15: 2600–2610
- 16 Lü H F, Wu X J, Chen L. Synthesis and ordered assembly of boron magic number clusters (in Chinese). *Physics*, 2023, 52: 269–271 [吕海峰, 武晓君, 陈岚. 成功实现硼幻数团簇的合成和有序组装. 物理, 2023, 52: 269–271]
- 17 Wang L, Wan Y, Cheng H, et al. Unraveling the photocatalytic water dissociation pathways on two-dimensional conjugated polymers. *ChemCatChem*, 2019, 11: 6236–6243
- 18 Fu C, Wu X, Yang J. Material design for photocatalytic water splitting from a theoretical perspective. *Adv Mater*, 2018, 30: 1802106
- 19 Freeman A J, Wimmer E. Density functional theory as a major tool in computational materials science. *Annu Rev Mater Sci*, 1995, 25: 7–36

- 20 Butler K T, Davies D W, Cartwright H, et al. Machine learning for molecular and materials science. *Nature*, 2018, 559: 547–555
- 21 Zunger A. Inverse design in search of materials with target functionalities. *Nat Rev Chem*, 2018, 2: 0121
- 22 Kim B, Lee S, Kim J. Inverse design of porous materials using artificial neural networks. *Sci Adv*, 2020, 6: eaax9324
- 23 Mishra A, Ma C Q, Bäuerle P. Functional oligothiophenes: Molecular design for multidimensional nanoarchitectures and their applications. *Chem Rev*, 2009, 109: 1141–1276
- 24 Wan C, Duan X, Huang Y. Molecular design of single-atom catalysts for oxygen reduction reaction. *Adv Energy Mater*, 2020, 10: 1903815
- 25 Jeong D S, Shin H S, Yang J. Influence of the molecular structure of metal-phthalocyanine on electrocatalytic reactions. *Sci China Mater*, 2022, 65: 3324–3333
- 26 Albaugh A, Boateng H A, Bradshaw R T, et al. Advanced potential energy surfaces for molecular simulation. *J Phys Chem B*, 2016, 120: 9811–9832
- 27 Manzhos S, Carrington Jr T. Neural network potential energy surfaces for small molecules and reactions. *Chem Rev*, 2021, 121: 10187–10217
- 28 McCammon J A. Computer-aided molecular design. *Science*, 1987, 238: 486–491
- 29 Lan Y, Han X, Tong M, et al. Materials genomics methods for high-throughput construction of COFs and targeted synthesis. *Nat Commun*, 2018, 9: 5274
- 30 Furukawa H, Cordova K E, O’Keeffe M, et al. The chemistry and applications of metal-organic frameworks. *Science*, 2013, 341: 1230444
- 31 Whitesides G M, Mathias J P, Seto C T. Molecular self-assembly and nanochemistry: A chemical strategy for the synthesis of nanostructures. *Science*, 1991, 254: 1312–1319
- 32 Carlucci L, Ciani G, Proserpio D M, et al. Entangled two-dimensional coordination networks: A general survey. *Chem Rev*, 2014, 114: 7557–7580
- 33 Huang N, Wang P, Jiang D. Covalent organic frameworks: A materials platform for structural and functional designs. *Nat Rev Mater*, 2016, 1: 16068
- 34 Zhou S, Shekhah O, Ramirez A, et al. Asymmetric pore windows in MOF membranes for natural gas valorization. *Nature*, 2022, 606: 706–712
- 35 Li X, Yang J. Realizing two-dimensional magnetic semiconductors with enhanced curie temperature by antiaromatic ring based organometallic frameworks. *J Am Chem Soc*, 2019, 141: 109–112
- 36 Ji X, Ge L, Liu C, et al. Capturing functional two-dimensional nanosheets from sandwich-structure vermiculite for cancer theranostics. *Nat Commun*, 2021, 12: 1124
- 37 Yang Y, Ji J, Feng J, et al. Two-dimensional organic–inorganic room-temperature multiferroics. *J Am Chem Soc*, 2022, 144: 14907–14914
- 38 Jin E, Asada M, Xu Q, et al. Two-dimensional sp^2 carbon-conjugated covalent organic frameworks. *Science*, 2017, 357: 673–676
- 39 Fortea-Pérez F R, Mon M, Ferrando-Soria J, et al. The MOF-driven synthesis of supported palladium clusters with catalytic activity for carbene-mediated chemistry. *Nat Mater*, 2017, 16: 760–766
- 40 Wu X, Dai J, Zhao Y, et al. Two-dimensional boron monolayer sheets. *ACS Nano*, 2012, 6: 7443–7453
- 41 Chen C, Lü H, Zhang P, et al. Synthesis of bilayer borophene. *Nat Chem*, 2022, 14: 25–31
- 42 Lü H, Chen C, Li W, et al. Selective binding and periodic arrangement of magic boron clusters on monolayer borophene. *Proc Natl Acad Sci USA*, 2023, 120: e2215131120
- 43 Wang Y, Lü J, Zhu L, et al. CALYPSO: A method for crystal structure prediction. *Comput Phys Commun*, 2012, 183: 2063–2070
- 44 Glass C W, Oganov A R, Hansen N. USPEX—Evolutionary crystal structure prediction. *Comput Phys Commun*, 2006, 175: 713–720
- 45 Yu T, Zhao Z, Sun Y, et al. Two-dimensional PC_6 with direct band gap and anisotropic carrier mobility. *J Am Chem Soc*, 2019, 141: 1599–1605
- 46 Song B, Zhou Y, Yang H M, et al. Two-dimensional anti-van’t Hoff/Le Bel array AlB_6 with high stability, unique motif, triple dirac cones, and superconductivity. *J Am Chem Soc*, 2019, 141: 3630–3640
- 47 Gou J, Xia B, Li H, et al. Binary two-dimensional honeycomb lattice with strong spin-orbit coupling and electron-hole asymmetry. *Phys Rev Lett*, 2018, 121: 126801
- 48 Huang C, Feng J, Wu F, et al. Toward intrinsic room-temperature ferromagnetism in two-dimensional semiconductors. *J Am Chem Soc*, 2018, 140: 11519–11525
- 49 Wang Y, Li F, Li Y, et al. Semi-metallic Be_3C_2 monolayer global minimum with quasi-planar pentacoordinate carbons and negative Poisson’s ratio. *Nat Commun*, 2016, 7: 11488
- 50 Feng B, Zhang J, Zhong Q, et al. Experimental realization of two-dimensional boron sheets. *Nat Chem*, 2016, 8: 563–568
- 51 Zhuo Z, Wu X, Yang J. Two-dimensional phosphorus porous polymorphs with tunable band gaps. *J Am Chem Soc*, 2016, 138: 7091–7098
- 52 Zhuo Z, Wu X, Yang J. Me-graphene: A graphene allotrope with near zero Poisson’s ratio, sizeable band gap, and high carrier mobility. *Nanoscale*, 2020, 12: 19359–19366
- 53 Hou L, Cui X, Guan B, et al. Synthesis of a monolayer fullerene network. *Nature*, 2022, 606: 507–510
- 54 Meirzadeh E, Evans A M, Rezaee M, et al. A few-layer covalent network of fullerenes. *Nature*, 2023, 613: 71–76
- 55 Wan Y, Wang L, Xu H, et al. A simple molecular design strategy for two-dimensional covalent organic framework capable of visible-light-driven

- water splitting. *J Am Chem Soc*, 2020, 142: 4508–4516
- 56 Wang L, Wan Y, Ding Y, et al. Conjugated microporous polymer nanosheets for overall water splitting using visible light. *Adv Mater*, 2017, 29: 1702428
 - 57 Xiang H, Yang J, Hou J G, et al. One-dimensional transition metal-benzene sandwich polymers: Possible ideal conductors for spin transport. *J Am Chem Soc*, 2006, 128: 2310–2314
 - 58 Wang L, Cai Z, Wang J, et al. Novel one-dimensional organometallic half metals: Vanadium-cyclopentadienyl, vanadium-cyclopentadienyl-benzene, and vanadium-anthracene wires. *Nano Lett*, 2008, 8: 3640–3644
 - 59 Wu X, Zeng X C. Double metallocene nanowires. *J Am Chem Soc*, 2009, 131: 14246–14248
 - 60 Zhang X, Han J, Liu Y, et al. Structural, electronic, and magnetic properties of one-dimensional organic bimetal-naphthalene sandwich nanowires. *J Phys Chem C*, 2012, 116: 5414–5419
 - 61 Zhang X, Tian Z, Yang S W, et al. Magnetic manipulation and half-metal prediction of one-dimensional bimetallic organic sandwich molecular wires $[\text{CpTM}_1\text{CpTM}_2]_\infty$ ($\text{TM}_1 = \text{Ti, Cr, Fe}$; $\text{TM}_2 = \text{Sc-Co}$). *J Phys Chem C*, 2011, 115: 2948–2953
 - 62 Zhang X, Ng M F, Wang Y, et al. Theoretical studies on structural, magnetic, and spintronic characteristics of sandwiched $\text{Eu}_n\text{COT}_{n+1}$ ($n = 1-4$) clusters. *ACS Nano*, 2009, 3: 2515–2522
 - 63 Li X, Lü H, Dai J, et al. Half-metallicity in one-dimensional metal trihydride molecular nanowires. *J Am Chem Soc*, 2017, 139: 6290–6293
 - 64 Lü H, Li X, Wu D, et al. Enhanced curie temperature of two-dimensional Cr(II) aromatic heterocyclic metal-organic framework magnets via strengthened orbital hybridization. *Nano Lett*, 2022, 22: 1573–1579
 - 65 Zhou J, Sun Q. Magnetism of phthalocyanine-based organometallic single porous sheet. *J Am Chem Soc*, 2011, 133: 15113–15119
 - 66 Tan J, Li W, He X, et al. Stable ferromagnetism and half-metallicity in two-dimensional polyporphyrin frameworks. *RSC Adv*, 2013, 3: 7016–7022
 - 67 Liu J, Sun Q. Enhanced ferromagnetism in a $\text{Mn}_3\text{C}_{12}\text{N}_{12}\text{H}_{12}$ sheet. *ChemPhysChem*, 2015, 16: 614–620
 - 68 Wu M, Wang Z, Liu J, et al. Conetronics in 2D metal-organic frameworks: Double/half Dirac cones and quantum anomalous Hall effect. *2D Mater*, 2017, 4: 015015
 - 69 Li X, Yang J. Toward room-temperature magnetic semiconductors in two-dimensional ferrimagnetic organometallic lattices. *J Phys Chem Lett*, 2019, 10: 2439–2444
 - 70 Li X, Liu Q B, Tang Y, et al. Quintuple function integration in two-dimensional Cr(II) five-membered heterocyclic metal organic frameworks via tuning ligand spin and lattice symmetry. *J Am Chem Soc*, 2023, 145: 7869–7878
 - 71 Li X, Lv H, Liu X, et al. Two-dimensional bipolar magnetic semiconductors with high Curie-temperature and electrically controllable spin polarization realized in exfoliated $\text{Cr}(\text{pyrazine})_2$ monolayers. *Sci China Chem*, 2021, 64: 2212–2217

Summary for “基于第一性原理计算的低维功能材料分子设计”

Molecular design of low-dimensional functional materials based on first-principles calculation

Haifeng Lü & Xiaojun Wu*

*Hefei National Research Center for Physical Sciences at the Microscale, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China** Corresponding author, E-mail: xjwu@ustc.edu.cn

In recent decades, low-dimensional materials have encountered great advances in scientific research and practical applications, which have attracted much attentions from researchers worldwide. Due to the significant quantum confinement effect, low-dimensional materials usually exhibit superior physical and chemical properties to their bulk counterpart, rendering them great potential in many applications, such as catalysts, nanoelectronics, spintronics, and energy, but how to realize specific structures and functionalities is the basis for their practical applications. Theoretical simulation of low-dimensional materials is of particular interest for the discovery of new materials because it provides an effective approach to create a direct relationship between their structural information and physical properties (especially the electronic structure of low-dimensional materials) at the atomic level by using modern computational methods, mainly represented by first-principles calculations. In past decades, substantial efforts have been devoted to the theoretical design of low-dimensional materials, providing some hints for experimental studies to accelerate the discovery of new materials, such as global structure prediction, multiscale simulation, and machine-learning based material design. However, it is a major challenge to predict/design the structure of low-dimensional materials with targeted functionalities merely starting from their composition. One major hinderance is the extremely complicated potential surface, with its complexity increasing exponentially with the number of atoms, resulting in huge computational effort to predict the global stable structures of materials and establish a reliable structure/property relationship only from their composition to directly design materials with targeted functionalities. In addition, the theoretical design of low-dimensional materials with targeted functionalities starting from their compositions, i.e., element and number of atoms, usually requires building an explicit structure with specific atoms, raising great challenges to experimental synthesis and postprocessing methods at the nanoscale. Molecule is the basic unit of substance with complete chemical properties of that substance that can be used as building block to develop low-dimensional materials, feature spanning chemical space, controllable synthesis, porosity, multifunctional properties, and various postsynthetic methods. Compared with building low-dimensional material with atoms, the complexity of the potential energy surface can be significantly reduced if building low-dimensional materials with molecules, of which the structures are constrained by the basic bonding theory between molecular building blocks. Additionally, the basic chemical function of molecules can be integrated into low-dimensional materials, providing a practical strategy to design low-dimensional materials with targeted functionalities with specific molecular building blocks. Meanwhile, polycondensation and self-assembly reactions provide synthetic methods to construct molecule-based low-dimensional materials using predesigned primary and high-order structures, leading to modular synthesis. In past decades, increasing attention has been devoted to molecule-based low-dimensional materials, with wide applications in gas adsorption or separation, luminescence, sensors, energy storage, transport media, catalysis, magnets, and biomaterials. The rational design of low-dimensional materials based on molecular building blocks with specific configurations and functionalities has also attracted theoretical interest to describe the interactions between molecule-based units, and create a relationship between low-dimensional materials and molecular building blocks to realize the inverse design of low-dimensional materials with targeted functionalities. This paper aims to provide an overview of low-dimensional material design based on the joint molecular design strategy and first-principles electronic structure calculation method from theoretical aspects, including the structural prediction of two-dimensional allotropic crystals, a series of low-dimensional photocatalysts, and low-dimensional spintronics, in which the interplay between the properties of molecules and functionalities of low-dimensional materials is emphasized. We conclude with the benefits and challenges of molecule-based low-dimensional materials and outline the efforts to bridge the molecules and low-dimensional materials.

low-dimensional functional materials, molecular design, first-principles calculation, photocatalytic water splitting, room-temperature magnetismdoi: [10.1360/TB-2023-0696](https://doi.org/10.1360/TB-2023-0696)