

表面化学修饰调控无机二维纳米材料的磁性及其应用

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摘要 无机固体材料中的电子自旋态是决定其磁学行为的核心因素, 同时也是实现高效磁能转化和灵敏磁响应的重要基础. 近年来, 由于具有新奇自旋结构和维度降低带来的新奇量子态, 二维纳米材料, 特别是单层和寡层无机二维材料, 其磁学性能引起了广泛研究, 极有希望应用于下一代自旋电子器件中. 二维纳米材料具有极高比表面积使得表面态非常重要, 因而化学修饰策略能应用于调制其本征物性. 本文概述了近年来发展的利用表面化学修饰对无机二维纳米材料本征磁性调控的系列进展, 并基于此将该类材料广泛应用于磁电阻、磁热效应等.

关键词 表面化学修饰, 无机二维纳米材料, 磁性能调控, 磁阻效应, 磁热

由于维度的降低, 二维无机纳米材料如石墨烯、氮化硼、过渡金属氧化物和过渡金属硫化物等, 表现出许多新奇的物理性质和结构特点, 在电子器件, 如晶体管、自旋阀和传感器等许多方面展示出很大的应用前景^[1~6]. 先进纳米电子器件中对纳米材料的磁学性质提出了更高的要求, 以能够实现在更多的外环境参数下, 如施加外电场、弹性应力或光辐照等条件下进行自旋可控操作^[7~9]. 然而, 大部分二维无机纳米材料本身是本征非磁的^[10~12], 这就对如何在二维无机纳米材料中进行磁性能的诱导与调控, 设计出新的磁性二维无机纳米材料提出了更高的要求. 针对这个问题, 目前发展的包括过渡金属磁性原子掺杂策略、缺陷工程等实验手段能够实现二维纳米材料中磁性诱导产生, 但是仍不能满足实际器件中对磁性材料具有稳定和可调控的磁性需求^[10~12]. 因此, 如何实现基于二维无机纳米材料进行可控和精准的磁性调控是一个有意义但亟待解决的挑战.

无机二维纳米材料表面原子的化学修饰是对其本征磁性进行可控和精准调控的有效方法. 二维纳米材料, 通常仅有几个原子厚度, 暴露出大量的表面

原子, 拥有极高的比表面积, 这些结构特点使得无机二维纳米材料的表面态同材料体态具有同等重要性^[13]. 尽管在三维块材固体中, 表面修饰方法已有应用, 但对三维块材进行表面的处理难以对其体相具有的本征自由度(如电子、电荷和自旋)造成决定性影响. 与块材不同, 比表面积大的超薄二维纳米结构, 在外加电场或不同溶液、气体环境等外界因素的影响下能够有效改变其表面电子的整体电荷和自旋态, 有望实现对其磁学性质、电子性质甚至结构等本征属性的有效调节^[14,15]. 例如, 非磁性的超薄 MoS_2 纳米片经过表面氢化处理后表现出铁磁性^[16]; 通过阴离子固溶法在二维 TiTe_2 超薄纳米材料中实现巨磁阻效应^[17]. 由此可见, 一方面, 表面化学调控为实现二维纳米材料本征磁性的引入和调控提供了有效策略; 另一方面, 无机二维纳米材料为调节材料本征磁性的表面修饰方法提供了良好的材料平台, 并为实现二维超薄纳米片磁性的可控和准确调控提供了可能^[13]. 具体而言, 由于二维材料的低维特性和拥有大量表面原子, 在化学反应位点上表现出巨大优势. 此外, 二维材料的二维量子限域效应使得电子间有

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较强的相互作用,从而促使二维无机纳米材料自旋、电荷、晶格间的耦合更加强烈。例如,晶格结构中含有过渡金属元素的无机二维纳米材料通常具有特殊的电学性质——如超导性、电荷密度波及Mott转变,这些性质意味着电子之间强相互作用的存在^[18,19]。因此,表面化学修饰可以通过对超导、金属态、半金属态及半导体态等电子结构形态进行改变,从而引发电子转移或晶格变化来改变自旋状态。界面应变、辐射、原子吸附会引起表面结构畸变、悬键、电子注入效应都能实现二维材料整体磁性能的有效调控。更为重要的是,这类引发表面电子转移或局部晶格畸变的化学修饰方式不会破坏材料结构的完整性,因此成为引入无机二维纳米材料磁性的有效方法。总而言之,掺杂、吸附、缺陷调控等表面化学修饰方法是在不破坏无机二维固体纳米材料结构的基础上调节其本征物理性质的有效途径,也是将这类非磁性无机二维纳米材料发展为新式自旋电子器件至关重要的一步。

本文将综述近期通过表面化学修饰调控无机二维纳米材料磁性的系列方法,重点介绍在不影响二维纳米材料原有二维晶格骨架结构的基础上调制其本征磁学性能,涉及表面悬键引入、表面原子结构调控、表面非磁性粒子嵌入等表面化学手段。基于电荷和自旋属性实现无机二维纳米材料的能带结构、本征磁性等调控,构筑新型二维磁性材料体系并展望高效磁能转化和自旋电子器件的可能应用。

1 表面化学修饰调控二维纳米材料磁性

1.1 表面氢化引入悬键调控二维纳米材料磁性

最近,具有磁有序结构的铁磁性二维纳米材料由于表现出极大的潜力被应用于自旋电子器件而受到广泛关注^[20,21]。迄今为止,为发展具有3d电子构型的铁磁性二维纳米材料研究已经取得长足进展^[22,23],但是具有s/p电子构型的铁磁性二维非金属纳米材料,得益于它们可以呈现出相对较弱的自旋-轨道耦合效应并且具有更长的自旋弛豫时间,更适合应用于未来的自旋电子器件^[24]。然而,非金属材料一般缺少有序的自旋结构,这大大阻碍在其二维结构中实现铁磁性行为,因此在二维非金属纳米材料中实现铁磁耦合的调制是迫切需要解决的问题。

近年来,氢化提供了一种新方法来调节材料的电子结构^[25],同时也为在二维非金属超薄纳米片中

产生与自旋相关的信息提供了新的设计思路。理论计算表明,氢化石墨烯可能引发铁磁性行为^[26,27]。但是把氢原子引入到表面的碳原子面上,使得碳平面结构从 sp^2 杂化轨道转变为 sp^3 杂化轨道,需要克服一个巨大的能垒^[28]。然而,与石墨结构类似的C-N层间弱堆积的 $g-C_3N_4$,显示出了在氢化方面的可能性。在 $g-C_3N_4$ 中,只有1个 sp^2 杂化的C原子上有1个未成对电子,而孤对电子或更多的电子存在于 sp^2 杂化或 sp^3 杂化的N原子上。因此,从实验角度来看,在 $g-C_3N_4$ 超薄纳米片上引入氢悬键比较容易。本课题组^[29]通过理论计算分析表明,在 $g-C_3N_4$ 超薄纳米结构中通过引入氢悬键可以实现磁性耦合的调制(图1(a)),同时在实验上通过表面氢化的方法在 $g-C_3N_4$ 超薄二维结构上引入氢悬键,成功实现磁性铁磁耦合,并且随着氢悬键含量的增多可以调控 $g-C_3N_4$ 的饱和磁化强度(图1(b))。伴随着氢悬键含量增多, $g-C_3N_4$ 超薄纳米结构可以呈现出比较大的饱和磁化强度,室温下饱和磁化强度可以高达0.015 emu/g,相应的矫顽力约为87 Oe。从实验上证实氢悬键的引入可调控二维非金属 $g-C_3N_4$ 的自旋耦合强度。

1.2 表面分子吸附诱导结构畸变在二维纳米材料诱导铁磁性

超导和磁性之间的相互作用关系一直都是固体材料的研究热点^[30~33]。在超导体里,由于铁磁态会破坏超导库珀对的自旋单态,使得超导和铁磁相互竞争和抑制,二者几乎很难共存^[34~36]。目前能够实现同时观察到这两种竞争电子态的手段大部分是依靠构建复合结构,也就是将具有铁磁性的基元材料和超导的基元材料复合来实现超导和铁磁共存^[35,37]。构建二者复合结构的策略推动了超导和铁磁共存的研究^[37~40],但在单一纳米材料中实现超导和铁磁共存将会进一步推动对超导和铁磁共存的理解和认识。

本课题组^[41]提出表面分子吸附策略,利用静电相互作用,促使极性分子吸附到超导二维材料NbSe₂表面,导致Nb-Se键轻微的伸长变形,减弱Nb和Se之间的共价相互作用,引发自旋极化,使得NbSe₂二维超导纳米片表现出短程的铁磁性(图2)。表面吸附的胍分子(N₂H₄)是一个强极性气体分子(1.83德拜),并且具有很强的还原性。通过锂插层液相剥离制备的纳米片表面带有负电荷,与强极性的N₂H₄分子之间的静电作用力使其容易吸附在NbSe₂二维超导纳米片

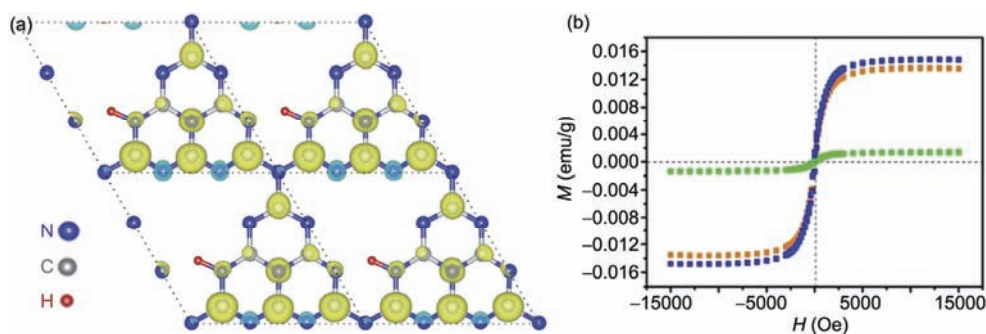


图1 (网络版彩色)氢化悬键在二维g-C₃N₄中引入铁磁性. (a) 氢化g-C₃N₄的自旋态密度分布; (b) 不同氢化程度g-C₃N₄的磁化曲线(*M-H*)
Figure 1 (Color online) Hydrogen dangling bonds induce ferromagnetism in two-dimensional graphitic-C₃N₄. (a) Spin density distribution of ultrathin g-C₃N₄ nanosheets with hydrogen dangling bonds; (b) *M-H* curves of g-C₃N₄ nanosheets with different contents of hydrogen dangling bonds

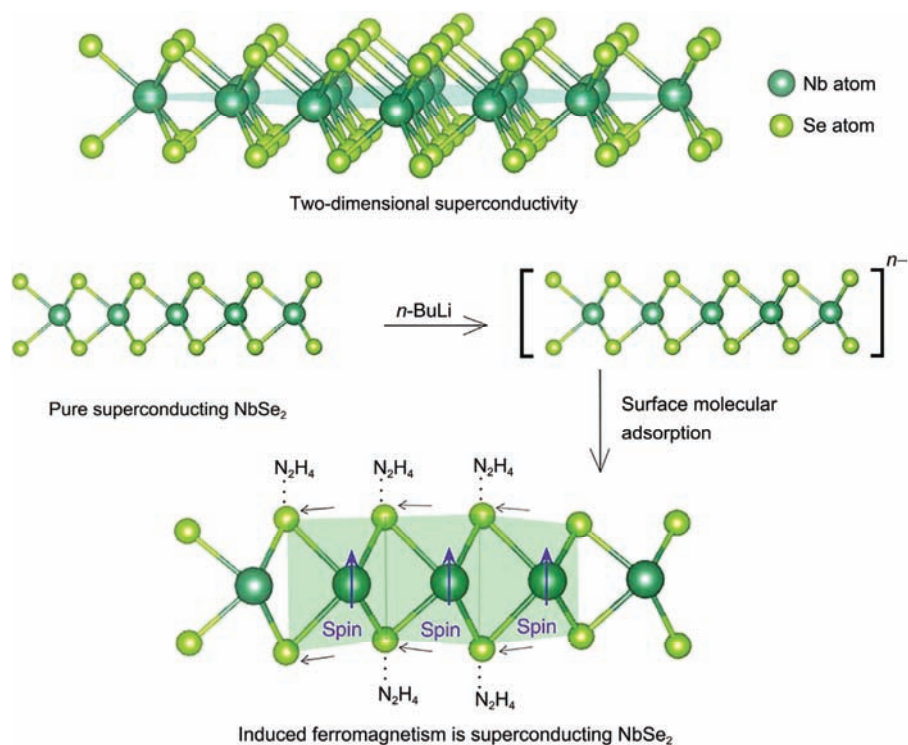


图2 (网络版彩色)极性分子吸附在NbSe₂二维结构表面的示意图, 在具有超导性质的NbSe₂二维材料体系中引入铁磁性
Figure 2 (Color online) Schematic illustration of the coexistence of superconductivity and ferromagnetism in two-dimensional NbSe₂

表面之上, 同时N₂H₄分子的强还原性保证在分子吸附过程中NbSe₂纳米片的稳定性. 表面分子吸附策略保证二维NbSe₂原有结构的完整性, 并且又引入铁磁性, 为在超导二维纳米材料中实现可控自旋极化调控带来新的思路.

1.3 表面分子辅助制备铁磁和电荷密度波共存的二维纳米材料

在过去的几年中, 由于原子层厚度的石墨烯具

有特殊的物理化学性质, 因此受到广泛关注^[42~44]. 同时, 二维纳米材料, 特别是只有单个原子层或几个原子层厚度的过渡金属硫属化合物超薄纳米片, 由于其特殊的电子结构及丰富的物理性质也引起了研究者极大兴趣, 并能应用于能源存储及转换、传感、光电器件及自旋电子器件等领域^[45]. 代表性的过渡金属硫属化合物TiS₂, TiSe₂, MoS₂, MoSe₂, WS₂, WSe₂, VS₂的超薄纳米片在近几年已经取得突破性的进展^[46~51]. 但是, 将新奇电学行为和自旋性质整合

在一个二维(2D)的过渡金属硫属化合物超薄纳米片材料中至今仍是巨大挑战。

本课题组^[22]报道了一种基于水溶液体系表面分子(甲酰胺)辅助合成 VSe_2 的方法,并将其拓展成为一种合成硒化物的普适性策略,如图3(a)所示.此外,还通过液相剥离的方法成功获得只有4~8个Se-V-Se原子层厚度的 VSe_2 超薄二维纳米结构.通过第一性原理计算及原子结构分析,认为在 VSe_2 结构中,沿着 a 轴和 b 轴的无限 V^{4+} - V^{4+} 原子链会在2D a - b 平面内形成一个 V^{4+} - V^{4+} 的网状结构,所有相邻的 V^{4+} - V^{4+} 之间的强相关联电子作用会引起其金属态的行为及原型的电荷密度波态,而且 V^{4+} 的 $3d^1$ 电子构型同样会带来丰富的相关自旋信息.因此,伴随着 $3d^1$ 电子构型和它们之间的强相关联电子作用, VSe_2 超薄纳米片成为一种同时拥有奇特电学性质和自旋性质的新型的2D过渡金属硫属化合物材料.正如, VSe_2 超薄纳米片薄膜的电阻率随温度的变化(图3(b))和在300 K的 M - H 曲线(图3(c))所示,表面甲酰胺辅助合成制备的 VSe_2 超薄纳米片铁磁和电荷密度波共存。

2 基于表面化学修饰调控无机二维纳米材料的磁学应用

2.1 表面拓扑化学策略获得超顺磁石墨烯,实现室温低场巨磁阻效应

近年来,自旋电子器件,一种基于操纵电子自旋自由度运算而有望突破摩尔定律物理极限的新型逻辑器件,引起人们广泛研究和发展的热潮^[3,52].石墨烯超薄的物理结构特点、长的室温自旋相干长度和相干时间,在应用于自旋电子器件方面展示出非常大的潜力^[53~55].但纯净的石墨烯是本征抗磁性,发展不同的自旋调控手段以得到具有可控磁电性能的石墨烯,是目前石墨烯自旋电子学领域的研究热点^[56~58].目前,主要通过将石墨烯裁成纳米带或引入杂质原子的手段形成铁磁或反铁磁有序的结构,以制备在低温高场下具有大磁阻效应的石墨烯.但获取在室温低场的情况下具有对高灵敏磁场调控的石墨烯材料依然存在很大的挑战。

本课题组^[59]提出通过表面拓扑化学策略获得具

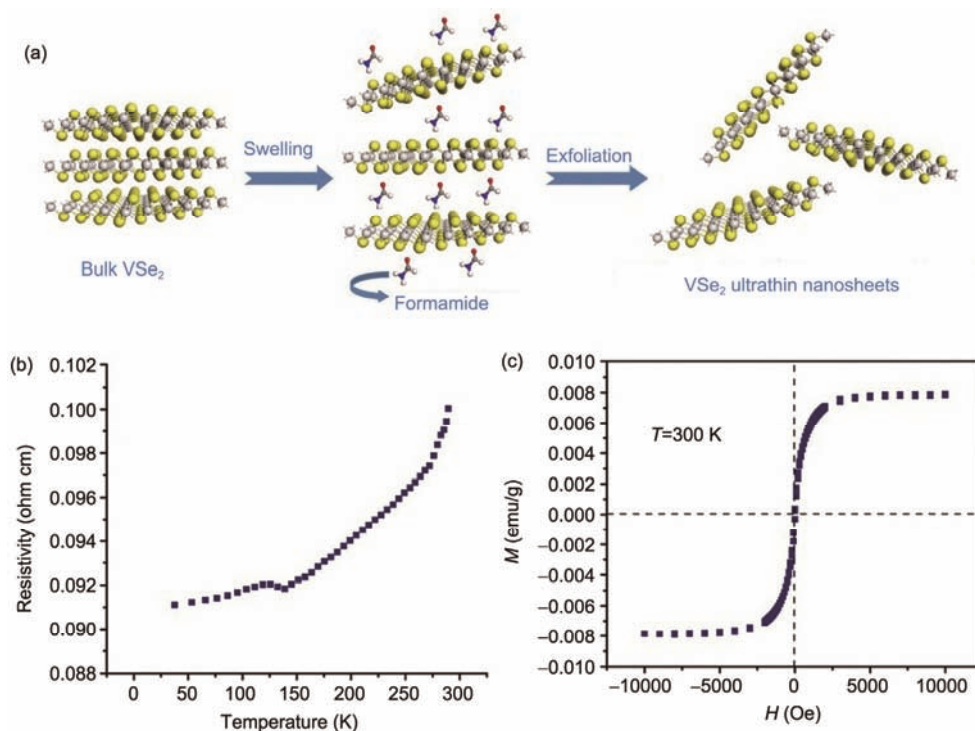


图3 (网络版彩色)表面分子辅助合成二维 VSe_2 纳米片。(a) 将块材 VSe_2 剥离成超薄纳米片的示意图;(b) 制备的 VSe_2 超薄纳米片薄膜的电阻率随温度的变化;(c) 制备的 VSe_2 超薄纳米片薄膜在300 K的 M - H 曲线

Figure 3 (Color online) Surface-molecule assisting synthesis of two-dimensional VSe_2 nanosheets. (a) Schematic illustration of exfoliating bulk VSe_2 into ultrathin nanosheets; (b) temperature-dependent resistivity of as-obtained ultrathin nanosheets; (c) M - H curve of assembled VSe_2 thin film at 300 K

有超顺磁性能的石墨烯结构,并且在室温低磁场下表现出的巨磁阻效应.如图4(a)所示,通过表面官能团拓扑取代的手段,利用巯基的还原性,将巯基诱导净磁矩的铁磁石墨烯经过温和的氧化处理,通过控制巯基含量调控石墨烯的磁畴大小,制备出磁畴之间相互作用非常弱的超顺磁石墨烯.铁磁石墨烯由于磁畴之间相互作用强,在未加磁场时自旋已经排列整齐,自旋相干散射弱,在加外磁场时磁阻效应较弱.而超顺磁石墨烯由于磁畴之间相互作用弱,零场时自旋排列杂乱,而在低磁场下磁畴实现自旋翻转,表现出明显的负磁阻效应.如图4(c)所示,在300 K的温度下,这种超顺磁石墨烯在外磁场为500 Oe时的负磁阻值达到8.6%.理论计算表明,这种石墨烯结构的磁性来源主要是巯基,而且不同结构的巯基室温下对氧的稳定性不同,使得部分处于不稳定结构的巯基脱附,而其余的巯基贡献剩余的磁性,由于磁矩的尺寸发生改变,氧化后的石墨烯表现出超顺磁性.该实验结果实现了超高的室温低场磁阻,有望应用于石墨烯实现自旋电子器件中.

2.2 阴离子固溶实现二维纳米材料的巨磁阻效应

基于电子自旋自由度调控的巨磁阻材料,能实

现信息高密度存储和高速读写,是整个信息产业的核心^[60,61].随着人们对电子器件高集成度和小型化日益增长的需求,在更小的材料尺度实现磁阻效应成为追求目标^[62,63].以石墨烯为代表的二维纳米材料具备独特的形貌和优异的物性特征,为实现纳米自旋电子器件提供了重要的材料基础^[64~67].因此,在二维纳米材料中实现自旋的本征调控和磁阻效应,是近年来该领域的研究热点.由于大部分二维材料是本征非磁的,如何在二维材料中引入本征净磁矩成为开发二维自旋电子器件的关键^[68,69].

本课题组^[17]提出阴离子固溶新方法,通过低价卤族取代硫族元素克服了阳离子掺杂形成插层化合物而难以剥离的缺点.在二维纳米材料(TiTe_2)中,引入本征自旋和调控能带结构,实现自旋相关散射电子输运,构建了基于二维过渡金属硫属化合物的巨磁阻器件.通常认为,磁性粒子掺杂是一种常用方法来向非磁性材料中引入磁性;然而,从微观结构和合成的角度来看,在二维过渡金属硫族元素化合物中直接使用磁性阳离子磁掺杂法并非最佳选择.在层状三明治结构中,带负电荷的硫族元素离子在外表面;当带正电荷的磁性离子掺杂进入时,它们倾向于在静电作用下向层间空隙聚集,从而形成二维纳米

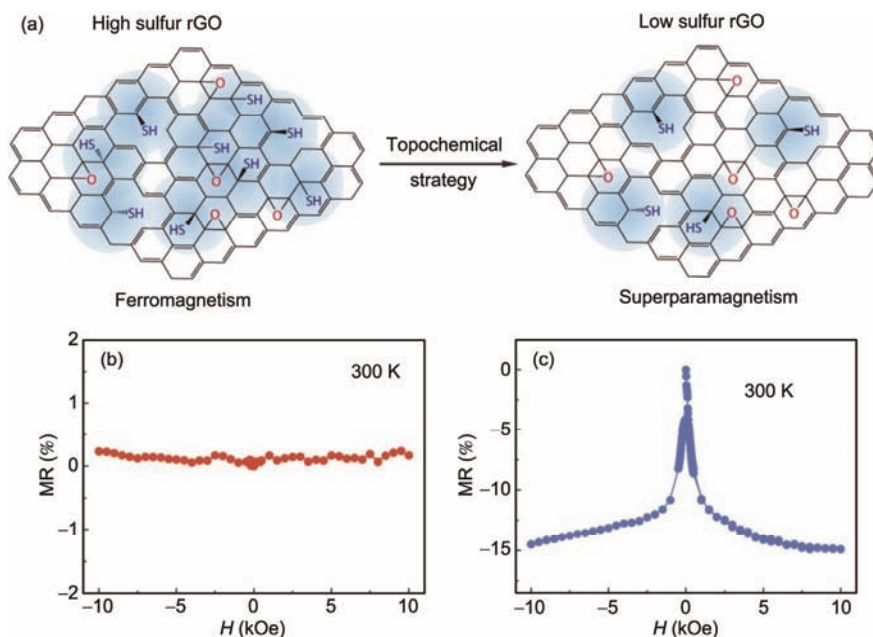


图4 (网络版彩色)表面拓扑化学策略获得超顺磁石墨烯,实现室温低场巨磁阻效应. (a) 示意图; 铁磁石墨烯(b)和超顺磁石墨烯(c)在300 K的磁阻随磁场的变化关系

Figure 4 (Color online) Surface topochemical strategy obtaining superparamagnetic reduced graphene oxide with large magnetoresistance. (a) Schematic illustration; magnetic-field dependence of the magnetoresistance for ferromagnetic r-GO (b); and superparamagnetic r-GO (c)

结构的插入式结构,不利于通过剥离法形成超薄结构.如图5(a)所示,基于过渡金属硫属化合物 TiTe_2 ,该工作通过设计阴离子碘固溶法,成功地获得 TiTeI 超薄纳米片,并将原本金属态的 TiTe_2 超薄纳米片能带打开,得到半导体态的 TiTeI 超薄纳米片. Ti^{3+} 局域磁阻的自旋阻挫构形导致电子自旋相关散射(图5(b)),使得 TiTeI 超薄纳米片在外加磁场的情况下表现出负磁阻.随着外加磁场的增大, TiTeI 超薄纳米片的负磁阻越来越大(图5(c)).该实验结果实现了,二维纳米材料体系最大的本征负磁阻效应,−85% (10 K, 5 T).

2.3 空间限域生长石墨烯基超晶格结构增强磁热效应

众所周知,超晶格材料由于其特殊的界面电子结构能够带来奇特的物理性质,近年来引起了越来越

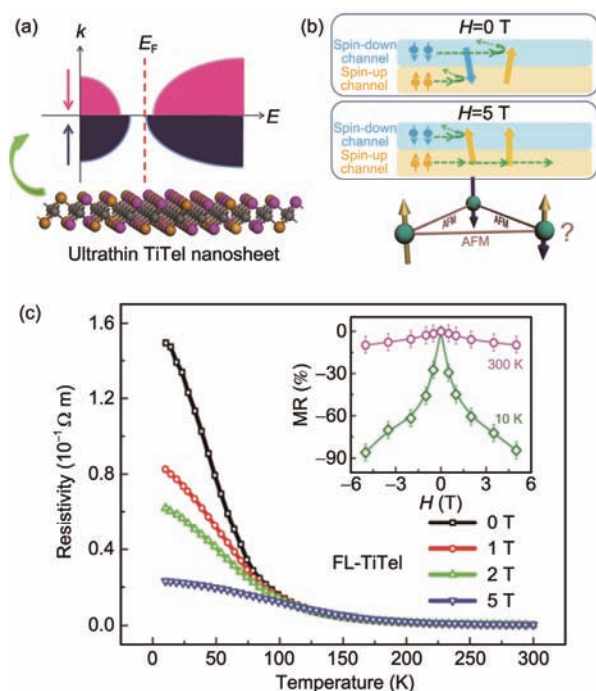


图5 (网络版彩色)阴离子固溶实现二维 TiTeI 纳米片的巨磁阻效应. (a) 阴离子碘固溶实现二维 TiTeI 能带打开; (b) Ti^{3+} 局域磁阻的自旋阻挫构形导致电子自旋相关散射; (c) 超薄 TiTeI 纳米片在不同磁场下的负磁阻效应,插图是在10和300 K下,磁阻随磁场强度变化的曲线

Figure 5 (Color online) Large negative magnetoresistance induced by anion solid solution in two-dimensional TiTeI . (a) Density of states of TiTeI ultrathin nanosheets indicating the band gap opening; (b) schematic diagram of the spin-dependent scattering between the conducting electrons and the local Ti^{3+} magnetic moment in the ultrathin TiTeI ; (c) temperature-dependent resistivity under various magnetic fields for ultrathin TiTeI . Inset: magnetic field dependence of the magnetoresistance at 10 and 300 K

越广泛的研究兴趣^[70~72].然而传统的超晶格材料通常是借助昂贵的脉冲激光沉积或分子束外延生长获得,这也意味着后续的实际应用需要经过复杂的过程将所获得的超晶格从生长衬底上转移^[73].与此同时,最新的研究结果表明,石墨烯具有独特的双极电子特性,当与其他材料复合时,可作为电子给体或电子受体来有效调节材料的电子结构,因此石墨烯基超晶格材料由于糅合了超晶格特殊的界面性质及石墨烯独特的电子结构,有可能带来一系列传统材料不存在的新性能^[74~78].

针对上述挑战,谢毅课题组^[79]提出一种新的空间限域生长策略成功制备石墨烯基超晶格材料的方法,获得了完美堆垛结构(图6(a)),克服了传统生长超晶格材料的缺点.在这种石墨烯基超晶格材料中,石墨烯不仅可以作为一个独特的空间限域反应器使钒氧层沿着石墨烯面二维生长,而且可以作为电子给体,引起钒氧层结构的结构重组,降低生成高对称性钒氧骨架的生成能.同时,借助同步辐射X射线吸收精细结构谱对该超晶格的精细结构进行了详细表征.结果表明,超晶格中的钒氧层的对称性明显大于在自由空间得到的 $\text{VO}_2(\text{B})$,并导致了一级可逆相转变的出现及由之产生的磁热效应,这种相转变类似于 $\text{VO}_2(\text{M})$ - $\text{VO}_2(\text{R})$ 相变过程中对称性由高到低的转变.由于超晶格中二维的单畴结构和石墨烯层的应力作用,这个转变过程中的磁熵变值相比于 $\text{VO}_2(\text{M})$ - $\text{VO}_2(\text{R})$ 相变的磁熵变值提高了8倍.在单层石墨烯-单层氧化钒-单层石墨烯的超晶格结构中,夹层的电子转移与应力会导致氧化钒晶格结构的重排,从而赋予超晶格纳米片磁学性质.由于V-V链中钒原子的d轨道电子共用产生的导向作用,空间限域法合成的纳米片超晶格结构的磁性随温度上升阶梯式增长(图6(b)).如图6(c)所示,上述方法制备得到的石墨烯基超晶格磁化强度随外加磁场变化的曲线也证实了材料磁性以及阶梯式增长对磁热效应的作用.

2.4 异质自旋掺杂引起局域结构扭曲实现高效电催化析氢

氢气由于其高的能量密度和极低的环境污染,被认为是一种理想的可持续清洁能源的载体.电催化析氢被认为是一种高效产生氢气的方式,近年来受到广泛研究和关注.众所周知,为了提高产氢效率,这些电催化过程都需要催化剂来降低反应的过

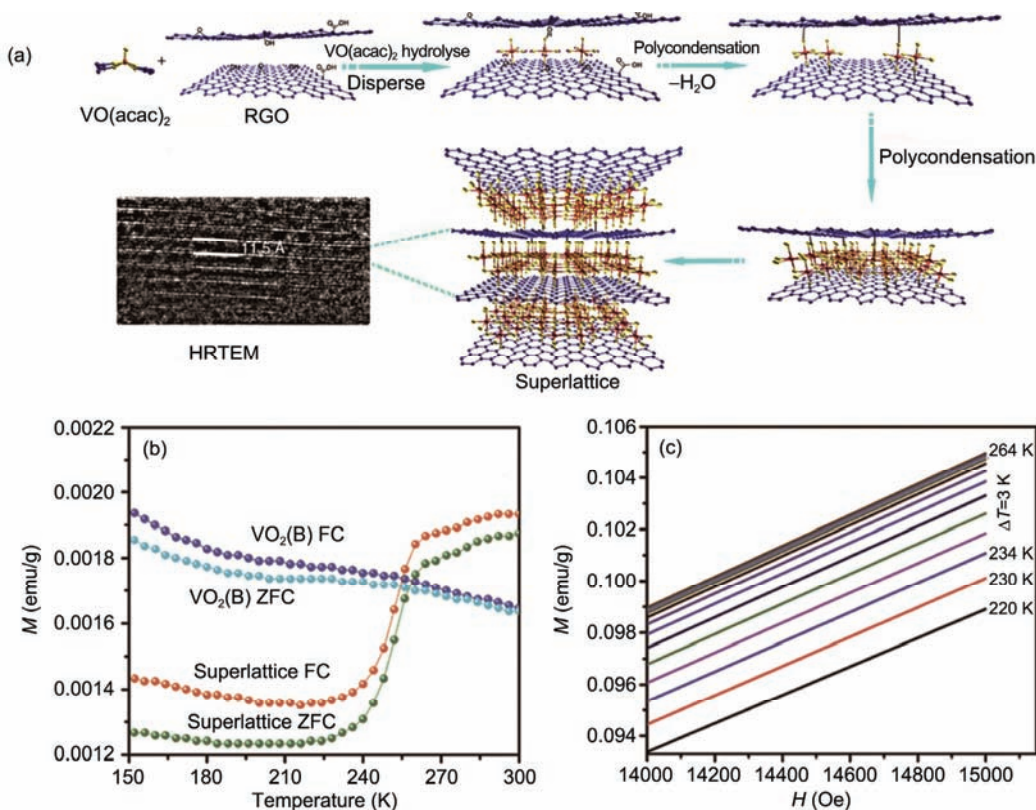


图6 (网络版彩色)空间限域生长石墨烯基超晶格结构增强磁热效应. (a) 空间限域生长石墨烯基超晶格结构的示意图; (b) 石墨烯基超晶格和 $\text{VO}_2(\text{B})$ 在零场冷却与场冷却条件下磁化强度随温度变化曲线; (c) 石墨烯基超晶格在相变温度下磁化强度随外加磁场的变化曲线

Figure 6 (Color online) Magnetocaloric effects in graphene-based superlattice synthesized with a spatially confined reaction. (a) Schematic illustration of the space-confined nanoreactor strategy for the synthesis of graphene based superlattice; (b) zero-field cooling and field cooling M - T curves for the superlattice nanosheets and $\text{VO}_2(\text{B})$; (c) field-dependent magnetization plots at transition temperatures for the superlattice nanosheets

电位^[80,81]. 尽管一些贵金属电催化如Pt表现出优越催化性能, 但其丰度低、不易获取等特点限制了其在电催化析氢进一步的广泛应用. 因此, 如何设计高效、经济的非贵金属电催化剂成为目前的一个重要挑战. 在众多的非贵金属电催化剂中, 第八族过渡金属硫属化合物 ME_2 (M 代表Fe, Co或Ni, E 代表S或Se)由于其高丰度、高稳定性和其本征的电催化活性吸引着材料学家的广泛关注. 但是, 对其本征的活性位点和电催化动力学的调控仍显不足, 这样极大限制其电催化性能的进一步优化. 第八族过渡金属硫属化合物 ME_2 这类催化剂的活性位点通常被认为是位于边缘的硫属原子^[82], 因此, 暴露出更多的边缘位点是优化这类电催化剂活性位点的主要思路. 在二维原子平面内构建微小无序能够在保证原有的二维电子共轭的前提下, 同时有效地增加边缘的活性位点, 是增加活性位点的理想模型. 由于异相自旋也就是异质原子掺杂能够在二维平面内产生不平衡的库仑作用,

这种微小的不平衡的库仑作用能够为构建微小扭曲提供驱动力. 同时, 通过调节掺杂量为调节无序度(边缘活性位点)提供了便利^[83]. 另外, 引入异相自旋不可避免地会调控催化剂的电子结构, 从而能为降低电催化析氢反应的反应能垒提供可能. 基于以上的分析, 掺杂异相自旋是在原子排布和电子结构层面上协同优化第八族过渡金属硫属化合物 ME_2 的活性位点和动力学过程的有效策略, 为提高这类催化剂电催化析氢性能提供了可能.

以金属性的 CoSe_2 为例^[83], 通过改进的液相剥离的方法获得了Mn掺杂的 CoSe_2 超薄片. 通过 M - H 测试, 证明了 Mn^{2+} 的异质自旋成功引入到 CoSe_2 超薄片, 见图7(a). 通过高分辨透射电子显微镜(HRTEM)照片(图7(a)), 能清楚地观察到晶格的微小扭曲. 如图7(c)所示, 晶格的微小扭曲是在不平衡的库仑作用力和Mn-Se与Co-Se之间不匹配的Jahn-Tell畸变. 同时通过快速傅里叶转换(fast Fourier transform, FFT)

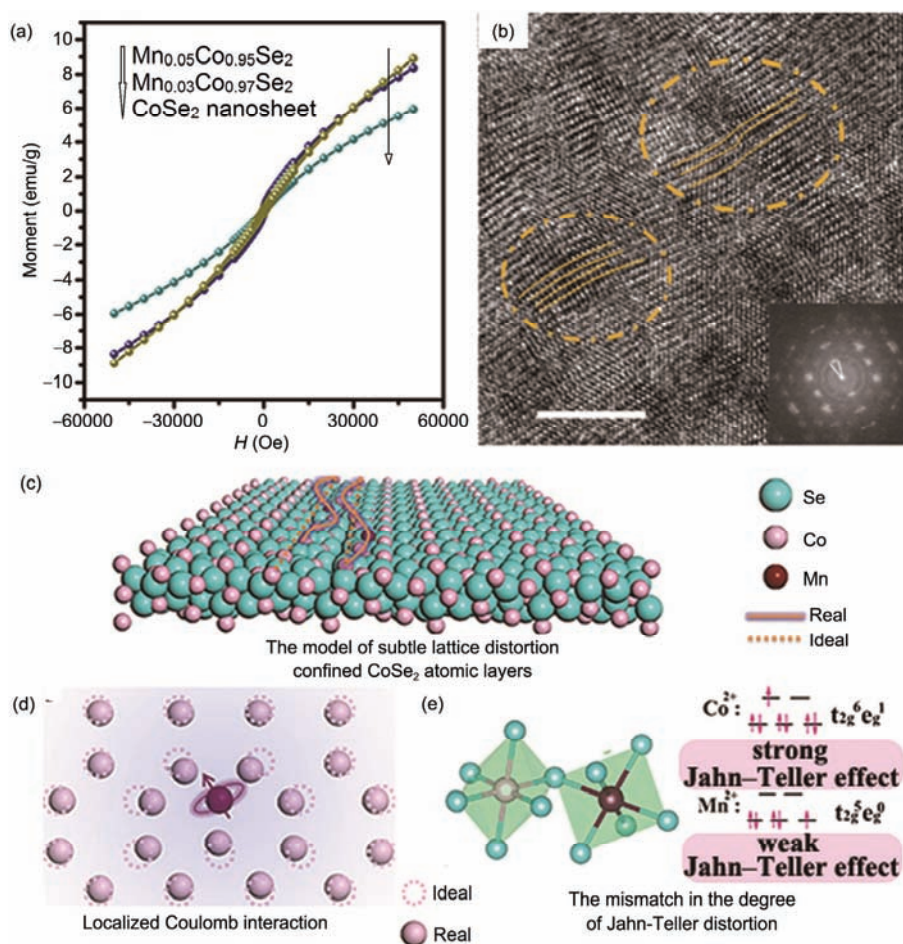


图7 (网络版彩色)异质自旋掺杂引起局域结构扭曲实现高效电催化产氢. (a) 300 K下的磁化曲线; (b) HRTEM照片观察到异相自旋引入诱发局域结构扭曲; (c)~(e) 微小结构扭曲形成示意图

Figure 7 (Color online) Heterogeneous spin states induce subtle lattice distortion, triggering highly-efficient hydrogen evolution. (a) Magnetic field dependence of magnetization (M - H) curves at 300 K; (b) induced local distortion in heterogeneous spin incorporated CoSe_2 nanosheets revealed by HRTEM; (c)~(e) schematic illustrations of the formation mechanism for the subtle distortion of atomic rearrangement

定性计算 CoSe_2 , $\text{Mn}_{0.03}\text{Co}_{0.97}\text{Se}_2$ 和 $\text{Mn}_{0.05}\text{Co}_{0.95}\text{Se}_2$ 的无序度分别为4.6%, 11.6%和23.3%, 与通过电化学方法测试的电化学活性位点结果一致, 说明通过异相掺杂诱导的晶格微小扭曲能够获取更多的边缘活性位点. 另外, 利用第一性原理计算了掺杂后的 CoSe_2 电催化过程, 发现掺杂后吸附的H原子转化为 H_2 的能量明显降低, 也就是异相的自旋掺杂降低了电催化析氢的反应能垒. 基于对电催化剂活性位点和动力学能垒的协同调控, 异质自旋掺杂的 CoSe_2 二维纳米片的电催化析氢性能(过电位, 极化电流密度和Tafel斜率)相对于未掺杂薄片得到了显著增强. 更重要的, 基于本工作提出的这种异相自旋掺杂来优化活性位点和动力学过程的策略为进一步优化非贵金属电催化剂提供了一个有效手段.

3 总结与展望

作为一种基于无机二维纳米材料结构特点发展的调控手段, 表面化学修饰能够实现在不破坏原有的二维骨架结构基础上进行磁性能调控, 将推进其在电子器件、晶体管和自旋电子器件等方面的应用. 本文概括了近期研究中为实现二维纳米材料本征磁性调控而发展的系列表面化学修饰方法, 包括表面氢化引入悬键实现非金属自旋电子的耦合作用, 表面分子吸附诱发结构畸变引入短程铁磁有序, 表面拓扑转化实现超顺磁石墨烯, 以及基于磁性能优化应用于磁阻、磁热和催化等方面的进展. 表面化学修饰方法的合理选择可以实现对二维纳米材料本征物理性质的调控, 为设计新型自旋电子器件材料带来新的思路.

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Summary for “表面化学修饰调控无机二维纳米材料的磁性及其应用”

Surface chemical-modification of inorganic two-dimensional nanomaterials for engineering the intrinsic magnetic properties and related applications

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Recently, due to the novel spin structures and unique magnetic states, the magnetic properties of two-dimensional (2D) nanomaterials, especially monolayer or few-layer inorganic ultrathin nanosheets, exhibit great promise for the next-generation spintronics. As is known, practical application usually requires materials with magnetic properties which can be deliberately regulated by external control parameters, such as, applied electric fields, elastic stress or light. However, most of the 2D inorganic nanomaterials are intrinsically non-magnetic. To tackle this challenge, tremendous efforts have been dedicated to effectively tuning the magnetic properties of two-dimensional nanomaterials, such as, transitional metal atoms doping and point defects, which provide feasible ways of magnetic modulation to induce magnetism. Unfortunately, compared with the high demands of practical magnetic application, there is still way to inducing magnetism in two-dimensional nanomaterials in a precise and controlled manner. In this regard, how to effectively obtain magnetic two-nanomaterials remains a great but noteworthy challenge.

Atomic-scale-thickness 2D nanomaterials possess extremely large specific surface area, making their surface phase as important as bulk counterparts. Compared to bulk counterparts, the ultrathin nanosheets with outmost atom layers exposed are more vulnerable to the surface modification, which has been theoretically and experimentally confirmed. Therefore, surface chemical modification of inorganic 2D nanomaterials offers a novel way to engineer intrinsic magnetic properties of 2D nanomaterials. Furthermore, the exposed high specific surface area and quantum confinement of electrons in the two-dimensional nanomaterials endow the surface chemical modification strategies to regulate the intrinsic magnetic properties in a controllable and precise manner. In this review, we focus on recent research about regulation strategies of magnetic behaviors, especially concerning surface chemical modification strategies, which bring about novel magnetic inorganic two-dimensional materials. For instance, introducing hydrogen dangling bonds into graphitic carbon nitride nanosheets successfully inducing ferromagnetism; surface adsorption of hydrazine molecules onto two-dimensional NbSe₂ nanosheets triggering the distortion of Nb-Se covalent bond, which results in the spin polarization; surface molecules meditating synthesis of ultrathin VSe₂ nanosheets which display ferromagnetism and charge density wave. Benefiting from regulated magnetic properties, inorganic two-dimensional nanomaterials deliver promising magnetic energy conversion and magnetic response applications, which ranges from the giant magnetoresistance, magnetocaloric effect to efficiently hydrogen evolution. Surface-chemical modification of two-dimensional nanomaterials has seen the advance for regulating their intrinsic magnetic properties.

surface chemical-modification, two-dimensional inorganic nanomaterials, magnetic property regulation, magnetic energy conversion, magnetic response

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