晶态钛氧簇合物的制备与性能研究进展

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摘要 太阳能在可持续能源的供应和环境污染物的处理方面起着非常重要的作用. 纳米二氧化钛由于其低成本、高效能以及环境友好的特征, 被认为是太阳能转化和环境治理中很有潜能的光催化剂. 然而, 这类纳米颗粒材料也具有一些不容忽视的缺点, 包括结构非精确性、粒径不均一、无机-有机界面信息不明确以及表面成分不确定等. 这些因素极大阻碍了对这类重要光催化材料的深入研究, 比如催化机理的探讨、电荷转移路径的确定、界面的理性修饰以及构效关系探索等. 作为纳米二氧化钛材料结构和催化性能的分子模型化合物, 具有明确结构的晶态钛氧簇合物逐渐成为研究者关注的焦点. 其精确的原子层面结构信息、明确的配体-簇核连接方式、可调控的簇核尺寸以及较好的溶解性都为深入研究它们的功能导向结构设计, 最终优化其催化应用提供了可能. 本文详细介绍了钛氧簇合物的研究背景、合成方法、结构多样性及其性能, 并总结了其在功能材料方面的最新应用.

关键词 钛氧簇合物, 溶剂热合成, 能带结构, 光催化, 复合材料

金属氧簇化学是无机化学和结构化学中非常重要的研究领域, 相关的研究已有近两百年的历史. 随着科学技术的不断发展和人们认识问题的逐步深入, 金属氧簇化学已成为当前发展最快的交叉学科之一, 与金属有机化学、高分子化学、物理化学、材料科学、催化化学等研究领域紧密结合, 在人类进步和经济发展中扮演着非常重要的作用^[1-5]. 金属氧簇化合物不仅具有丰富的结构多样性, 而且在催化、光电磁材料、荧光传感等方面具有十分广泛的潜在应用, 吸引了诸多研究者的兴趣^[6-9]. 基于金属氧簇的诸多优点, 包括可调控的簇核尺寸、易于精准修饰、多功能性(酸性、光电催化、氧化还原性)、低温高活性、低毒和低腐蚀性等, 它被视为实现催化剂的人工设计最合适的材料之一, 在催化领域的研究中受到广泛重视^[10-12]. 目前, 金属氧簇在催化领域的研究中取得了许多进展, 包括金属氧簇的酸催

化、氧化催化、双功能催化、活化二氧化碳合成碳酸酯等, 甚至部分已经实现了工业化应用, 充分显示了它们在现实生活中的应用价值.

能源问题和环境问题是当今世界面临的两大挑战. 当前以煤炭和石油等化石燃料为主的国家, 已经面临严重的环境污染, 加上化石燃料存在枯竭危险, 开发和利用绿色可再生能源已成为关乎人类可持续发展的关键问题. 太阳能是一种绿色、高效、来源丰富、成本低廉的可再生能源^[13-16]. 在太阳能的利用上比较关键的是如何模拟绿色植物的光合作用, 如利用太阳能分解水产生氢气和氧气. 在这个过程中需要用到催化剂, 其中纳米二氧化钛(TiO_2)由于其丰富的储量、稳定的化学性质以及无毒廉价的优点成为目前应用最为广泛的光催化剂^[17,18]. 纳米二氧化钛的光生空穴具有非常强的氧化性, 可以将大多数的有毒有机污染物氧化为二氧化碳, 可大量用于土

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Gao M Y, Zhang L, Zhang J. Preparation and properties of polyoxo-titanium clusters (in Chinese). Chin Sci Bull, 2018, 63: 2731-2744, doi: 10.1360/N972018-00502

壤、水和空气的净化. 1972年, Fujishima和Honda^[19]首次将二氧化钛作为光催化剂进行光裂解水产氢的研究. 然而, 这类纳米材料具有很大程度的非精确特性, 包括原子位置不明晰、粒径不均一以及无机-有机界面信息不明确等. 这些不确定性极大阻碍了对这类重要光催化材料的基础研究, 如催化机理、电荷转移以及表界面改性等^[18,20-23].

作为纳米二氧化钛材料结构和反应的模型化合物, 具有明确结构信息的晶态钛氧簇合物逐渐成为研究者关注的焦点^[24-26]. 随着近代X射线单晶衍射技术和结构解析软件的发展, 越来越多的研究者投身到晶态钛氧簇合物这一新兴研究领域, 取得了系列进展^[26,27]. 钛氧簇合物精确的原子位置信息、明确的配体-簇核连接方式、可调控的簇核尺寸, 以及较好的溶解性为理解其构效关系以及拓宽其功能应用提供了可能, 同时也为相关二氧化钛表面改性的分子模拟和理论计算提供极佳的研究平台^[28-31]. 随着合成技术的不断发展, 新颖的合成路线不断开发, 研究者正致力于合成更多结构新颖的钛氧簇合物.

综上所述, 通过调控钛氧簇合物的合成策略以实现其结构多样性, 包括尺寸、对称性和核数, 不仅有利于理解其结构和性能之间的构效关系, 还能为进一步拓宽其在功能材料领域的应用提供帮助.

1 钛氧簇合物的合成方法

众所周知, 四价钛离子在水中易快速自发水解, 产生二氧化钛沉淀, 结晶程度差, 这就给晶态钛氧簇合物的制备造成了很大困难. 通过研究者的不懈努力, 探索出一系列合成方法来提高钛氧簇合物材料的结晶度.

1.1 强酸性水相合成

少量 $\text{Ti}(\text{OR})_4$ 就会在水中产生大量的沉淀, 因此它在水相合成中的应用在很大程度上是受限的. 在水中合成钛氧簇合物的一个可行的方法是水溶液酸化法以抑制其快速水解, 这是传统的合成金属氧簇的主要方法^[32]. 除了 $\text{Ti}(\text{OR})_4$ 外, 也可以使用 TiCl_4 或 TiOSO_4 作为钛源, 因为它们比较容易溶解在水中形成酸性透明溶液, 在水相合成反应中表现出潜在的应用^[33]. 山东大学王一峰课题组^[34-36]采用此种方法在水溶液中得到一系列钛氧簇合物. 这种绿色溶剂的应用对化学与环境的和谐发展有着重要的意义.

1.2 严格的情性条件合成

由于 $\text{Ti}(\text{OR})_4$ 易水解, 所以在早期的合成过程中严格控制无水、无氧条件. Schubert课题组^[37,38]在氩气氛围中, 使用手套箱技术来实现钛氧簇合物的制备. 甚至一些测试也要在装有闭路循环系统的手套箱中来除去湿气和氧气^[39,40]. 此法合成条件苛刻、操作繁琐、成本较高, 因此只有少部分课题组采用此种方法.

1.3 溶剂热合成

在水热合成法的基础上, 用醇类或者乙腈等有机溶剂取代水而形成的合成方法, 在反应自发产生的压力条件下, 通过原料的自组装来得到钛氧簇合物^[41-43]. 此法适用于合成常温常压下难合成的钛氧簇合物、功能化配体修饰的钛氧簇合物以及异金属掺杂的钛氧簇合物. 随着溶剂热合成钛氧簇合物方法的不断优化, 设备仪器的持续更新, 越来越多结构和性质多样化的钛氧簇合物被成功制备. 利用溶剂热合成方法制备钛氧簇合物受到诸多因素的影响, 如反应的温度、溶剂、pH、反应时间等, 其合成机理仍需要研究者进一步的研究和探索, 以期实现目标结构的理性合成. 此法以其操作简单、易于控制、省时省力等优点, 在合成钛氧簇合物领域得到最广泛的应用. 在这一方法基础上, 本课题组^[27]利用溶剂热条件下的羧酸与醇的酯化反应来原位产生水分子, 从而实现反应体系的水量控制, 成功合成系列高核钛氧团簇.

1.4 两步合成法

相对于原位合成法, 两步合成法因具有较高的可控性而得以快速发展. 此方法是将钛氧簇合物用作前驱体和钛源, 实现配体的进一步修饰和替换. Coppens课题组^[31]采用 Ti_7 簇合物作为前驱体和钛源, 通过两步法将其连接得到更高核钛氧簇合物 $\text{Ti}_{34}\text{O}_{50}\text{O}^{\text{Pr}}_{30}\text{DMABA}_6$. 此法在诱导形成高核的钛氧簇合物, 以及形成簇基金属有机框架物(MOF)材料中具有潜在的应用.

1.5 离子热合成

离子热合成法是一种合成分子筛和配位聚合物的新方法. 离子液体相对于其他溶剂, 具有双重作用, 不仅可以用作溶剂, 而且可以用作模板剂^[44-47]. 最近, 本课题组^[48]成功将离子热合成应用于制备钛

氧簇合物, 利用此种方法获得的钛氧簇合物的簇核高达28核, 更为重要的是还可将具有较大共轭的有机配体引入到钛氧簇中. 研究表明, 阴离子在合成大的钛氧簇合物方面扮演着非常重要的角色. 由于此法比溶剂热法污染更小, 溶解能力更强, 操作更方便而深受研究者的喜爱. 尽管它在合成钛氧簇合物方面尚处于起步阶段, 但是它作为环境友好型合成方法具有非常长远的研究意义.

2 钛氧簇合物的新颖结构

得益于合成策略的发展, 近几年来一些新型钛氧簇合物相继被报道. 2016年, 本课题组^[41]采用温和的溶剂热反应, 通过调控钛酸酯在异丙醇溶剂中的水解聚合, 以及反应温度、pH和反应时间, 成功制备出首例具有类富勒烯结构的高核钛氧簇合物 $H_6[Ti_{42}(\mu_3-O)_{60}(O^iPr)_{42}(OH)_{12}](Ti_{42})$, 如图1所示. 在该钛氧簇合物中, 按照配位环境的不同, 42个钛原子可以分为两类: 12个七配位的钛原子形成 Ti_{12} 正二十面体和30个五配位的钛原子形成 Ti_{30} 三十二面体, 使整个结构具有最高的分子对称性 I_h . 同时, 该 Ti_{42} 分子也是当时所报道的最高核钛氧簇合物, 其簇核尺寸达到了1.5 nm; 质谱和液态紫外可见吸收光谱测试表明 Ti_{42} 簇合物具有非常高的溶液稳定性, 从而能够通过逐层液相外延生长法将其组装分散到多孔MOF薄膜的孔道中. 这项研究成果不仅丰富了富勒烯型分子的组成, 而且也拓宽了新型高核高对称性钛氧簇合物材料的研究思路.

同年, 本课题组^[42]继续采用低温溶剂热合成法,

图1 (网络版彩色) 钛氧簇合物 Ti_{42} 的分子结构^[41]

Figure 1 (Color online) Molecular structure of cluster TOF-1. Adapted with permission from Ref. [41]. Copyright (2016) American Chemical Society

运用分步式层扩展思路, 从带状 Ti_6 簇合物出发, 通过移除有机位阻配体的策略合成 Ti_{17} 簇合物, 进一步提高组装的浓度成功得到了目前最高核的钛氧簇合物 $Ti_{52}(\mu-OH)_2(\mu-O)_{14}(\mu_3-O)_{50}(\mu_4-O)_8(PA)_{34}(O^iPr)_{28}(Ti_{52})$, 其簇核尺寸达到了3.6 nm, 如图2所示. 这些钛氧簇合物材料都具有很高的空气和水溶液稳定性, 可以在pH 3~13范围内保持结构不变. 此外, 紫外光照射条件下的水分解产氢测试证实, 这一系列钛氧簇合物都具有较好的光催化活性和稳定性, 而且还表现出有趣的簇核尺寸效应, 其中 Ti_{52} 簇合物的光解水产氢速率为 $398 \mu mol h^{-1} g^{-1}$, 约是 Ti_6 簇合物产氢速率

图2 (网络版彩色) $\{Ti_6\}$ (a), $\{Ti_{17}\}$ (b), $\{Ti_{52}\}$ (c)的晶体结构. 上面一行表示分子结构; 下面一行表示多面体图, 并且标示了其核的尺寸^[42]

Figure 2 (Color online) Crystal structures of $\{Ti_6\}$ (a), $\{Ti_{17}\}$ (b), and $\{Ti_{52}\}$ (c). The above array displays their molecular structures. The below array represents the polyhedral drawing of the $\{Ti_6\}$, $\{Ti_{17}\}$, and $\{Ti_{52}\}$ clusters, with their core diameters highlighted. Adapted with permission from Ref. [42]. Copyright (2016) American Chemical Society

的2倍. 该研究成果不仅为高核钛氧簇分子的构建提供了行之有效的方案, 同时也为钛氧簇合物结构-催化性能构效关系的研究提供了宝贵的经验.

随后, 山东大学王一峰课题组^[34]利用控制溶解度的方法来调控水溶胶的预成核过程从而实现钛氧簇合物的结晶, 获得一系列含有 $\{\text{Ti}_{18}\text{O}_{27}\}$ 簇核的三层五棱柱类型的钛氧簇合物, 如图3所示. 这些钛氧簇合物的簇核外围被硫酸盐和水基配体包裹, 在水和乙腈等多种溶剂中表现出较好的溶解性和稳定性, 并且可以通过质谱、振动光谱和 ^{17}O NMR进行溶液态化学的研究. 该成果所报道的一系列新的钛氧簇合物为研究材料的液相均相催化和表面改性提供了新思路.

除了直接法合成钛氧簇合物, 后功能化法是另外一种合成羧酸修饰钛氧簇合物的新方案. 王一峰课题组^[49]采用 TiI_4 和 $\text{Ti}(\text{O}^i\text{Pr})_4$ 作为前驱体, 通过溶剂热反应首先合成了包含碘和OH的 $\{\text{I}@\text{Ti}_{22}\text{O}_{32}\}$ 笼状钛氧簇合物, 然后经过后功能化处理成功合成了特戊酸修饰的钛氧簇合物 $\{\text{I}@\text{Ti}_{22}\text{O}_{32}(\text{tBuCOO})_9\}$ (tBuCOOH , 特戊酸)和3,5-二-叔丁基邻苯二酚(H_2DTBC)修饰的钛氧簇合物 $\{\text{I}@\text{Ti}_{22}\text{O}_{32}(\text{DTBC})\}$, 如图4所示. 此工作

图3 (网络版彩色) $[\text{Ti}_{18}\text{O}_{27}(\text{OH}_2)_{30}(\text{SO}_4)_6]^{6+}$ 的晶体结构. (a) 侧视图; (b) 俯视图; (c) 18个钛原子的三层排列; (d) $[\text{Ti}_{18}\text{O}_{27}(\text{OH}_2)_{30}(\text{SO}_4)_6]^{6+}$ 结构中存在的 $\{\text{Ti}(\text{Ti}_5)\}$ 五边形构筑单元^[34]

Figure 3 (Color online) Crystal structures of $[\text{Ti}_{18}\text{O}_{27}(\text{OH}_2)_{30}(\text{SO}_4)_6]^{6+}$. (a) Side and (b) top views, (c) the triple-deck arrangement of the 18 Ti atoms, and (d) the $\{\text{Ti}(\text{Ti}_5)\}$ pentagonal building unit in the structure of $[\text{Ti}_{18}\text{O}_{27}(\text{OH}_2)_{30}(\text{SO}_4)_6]^{6+}$. Adapted with permission from Ref. [34]. Copyright (2016) American Chemical Society

图4 (网络版彩色) $\{\text{I}@\text{Ti}_{22}\text{O}_{32}(\text{tBuCOO})_9\}$ 和 $\{\text{I}@\text{Ti}_{22}\text{O}_{32}(\text{DTBC})\}$ 的形成过程^[49]

Figure 4 (Color online) Formation process of $\{\text{I}@\text{Ti}_{22}\text{O}_{32}(\text{tBuCOO})_9\}$ and $\{\text{I}@\text{Ti}_{22}\text{O}_{32}(\text{DTBC})\}$. Adapted with permission from Ref. [49]. Copyright (2016) American Chemical Society

不仅为研究钛纳米材料表面配体交换以及电子和空穴的传输提供基础, 而且更好地阐述了在溶剂热过程中钛氧簇纳米晶的形成机理.

虽然乙二醇可以用来修饰金属氧簇^[50,51], 但是目前还没有乙二醇修饰的钛氧簇合物的报道. 厦门大学郑南峰课题组^[52]首次采用乙二醇和一元羧酸配体结合作为表面配体, 与钛前驱体(钛酸丁酯)共组装得到一系列孔径为8.3 Å的大环状钛氧簇合物 $\text{Ti}_{32}\text{O}_{16}(\text{C}_2\text{H}_4\text{O}_2)_{32}(\text{RCO}_2)_{16}(\text{C}_2\text{H}_5\text{O}_2)_{16}$, 如图5所示. 该簇合物整体为电中性, 具有固有的微孔多孔特征. 该团簇的 $\{\text{Ti}_{32}\text{O}_{16}\}$ 骨架是由8个结构相同的 $\{\text{Ti}_4\}$ 四面体结构单元连接而成. $\{\text{Ti}_4\}$ 四面体笼由1个六配位的Ti和1个七配位的Ti分别通过2个消除双质子的乙二醇和一个羧酸桥联形成闭合的大环. 另外的2个Ti均为六配位, 通过羧酸和消除单质子的乙二醇修饰. 有趣的是, 环与环之间通过丰富的分子间弱相互作用排列形成完美的一维纳米管, 纳米管进一步堆积形成多孔网络骨架. 调节表面羧酸配体的尺寸不仅可以改变纳米管的排列方式(四方或六方排列), 而且还可以调控微孔钛氧簇合物对 CO_2 气体的吸附焓. 高分辨质谱分析表明, 在溶液相中, 表面单齿配位的乙二醇配体具有较高的交换活性, 8 min即可完成交换反应. 通过亲水的丙三醇和疏水的高氟代辛醇分别与乙二醇交换, 可以有效调节钛氧簇薄膜的亲疏水性.

本课题组^[48]首次采用低共熔溶剂热法实现了钛氧簇合物的合成, 得到的4例化合物最高核达到了28核, 而且表现出不同的光解水产氢活性, 如图6所示.

图5 (网络版彩色)CTOC-1 的球棍模型(a); 空间填充模型的俯视图(b); 空间填充模型的侧视图(c). N_2 在 77 K 时的吸附/解吸等温线(d)和DFT 计算的CTOC-1 的孔径尺寸(内插图)^[52]

Figure 5 (Color online) Top view of the individual CTOC-1 in balls and sticks (a), space filling (b), side view in space filling (c). N_2 adsorption/desorption isotherm at 77 K (d) and DFT calculated pore size (d, inset) of CTOC-1. Adapted with permission from Ref. [52]. Copyright (2016) American Chemical Society

最重要的是这4例化合物均是通过共轭配体(1,10-菲罗啉或2,2'-联吡啶)修饰, 形成了一种核壳结构的模型. 这样的共轭结构使这4例化合物具有较高的水稳定性和不同的分散性. 1,10-菲罗啉修饰的 Ti_6 簇合物比2,2'-联吡啶修饰的 Ti_6 簇合物具有更快的分散速度以及更高的光解水产氢速率(相差3.6倍).

3 钛氧簇合物的性能调控

钛氧化物半导体光催化材料在光伏电池、太阳能驱动水分解/二氧化碳还原以及环境污染物降解方面的应用十分广泛, 但是由于其较大的禁带宽度, 只能接受紫外光激发, 而太阳光谱中紫外光只占据太阳辐射总能量的非常少的一部分, 这严重限制了它们的实际应用, 因此如何提高他们的可见光响应是该领域亟待解决的关键科学问题^[53-56]. 为解决这一关键科学问题, 通常采用的方法是对此类材料进行配体功能化修饰以及金属/非金属掺杂来调控它们的

能带结构以增强可见光吸收, 实现快速有效的电子和空穴的分离和转移^[30,35,57-60].

2014年, 英国剑桥大学Wright课题组^[54,55,57]采用乙醇溶剂热的合成方法制备出一系列过渡金属离子掺杂的钛氧簇合物, 如 $[MnTi_{14}(OEt)_{28}O_{14}(OH)_2](MnTi_{14})$, $[FeTi_{14}(OEt)_{28}O_{14}(OH)_2](FeTi_{14})$, $[GaTi_{14}(OEt)_{28}O_{15}(OH)](GaTi_{14})$, $[(GaCl)_2Ti_{14}(OEt)_{20}O_{20}]((GaCl)_2Ti_{14})$ 和 $[Ti_{27}MnKO_{35}(OH)_2(OEt)_{39}]_{0.33}[Ti_{28}MnKO_{37}(OH)(OEt)_{40}]_{0.67}([Ti_{27}Mn]_{0.33}[Ti_{28}Mn]_{0.67})$, 其晶体结构如图7所示. 该工作的目的是为了研究掺杂过渡金属离子对钛氧簇合物的能带结构产生的影响, 并将其用于模拟过渡金属掺杂的体相二氧化钛纳米材料^[58]. 研究结果表明, Mn, Fe和Ga掺杂对目标产物的能带结构存在一定程度的影响, 但是文章重点指出了利用Kubelka-Munk方法鉴定能带宽度时可能面临的挑战, 如钛氧簇合物共结晶的杂质会导致测定结果的不准确, 另外其自身的结构不稳定性也会造成测试结果的误差.

本课题组通过使用有机配体和过渡金属离子的修饰成功地调控了钛氧簇合物的禁带宽度. 采用有机膦酸配体组装出结构非常稳定的 $\{Ti_6P_2\}$ 簇^[61], 该结构与Schubert课题组^[59]合成的 $[Ti_6O_4(O^iPr)_{10}(O_3PR)_2]^{2+}$ 簇核非常相似. 如图8所示, 该簇核的两侧分别具有3个活性配位点, 在保证 $\{Ti_6P_2\}$ 簇核不变的前提下, 使用14种不同含氧的有机配体对其进行修饰, 研究表明随着钛氧簇合物配体中吸电子基团的增多, 极性增大, 相应的钛氧簇合物的禁带宽度呈现出变小的趋势. 然而钛氧簇合物材料的吸收波长仍然处于紫外区. 进一步通过吡啶-羧酸类双功能配体:

图6 (网络版彩色) Ti_{28} 簇合物的簇核结构(a)和分子结构(b)^[48]

Figure 6 (Color online) The Ti_{28} core structure (a) and molecular structure (b) of Ti_{28} cluster. Reproduced by permission from Ref. [48]. Copyright (2016) The Royal Society of Chemistry

图7 (网络版彩色)钛氧簇合物的球棍模型. (a) MnTi_{14} , FeTi_{14} 和 GaTi_{14} 的晶体结构; (b) 钛氧簇合物 $(\text{GaCl})_2\text{Ti}_{14}$ 的晶体结构; (c) 钛氧簇合物 $[\text{Ti}_{27}\text{Mn}]_{0.33}[\text{Ti}_{28}\text{Mn}]_{0.67}$ 的晶体结构^[58]

Figure 7 (Color online) Ball-and-stick representations of titanium-oxo clusters. (a) MnTi_{14} or FeTi_{14} or GaTi_{14} , (b) $(\text{GaCl})_2\text{Ti}_{14}$, and (c) $[\text{Ti}_{27}\text{Mn}]_{0.33}[\text{Ti}_{28}\text{Mn}]_{0.67}$. Reproduced by permission from Ref. [58]. Copyright (2016) The Royal Society of Chemistry

图8 (网络版彩色){ Ti_6P_2 }簇核通过活性配位点导致的结构演变图示(配体取代和金属掺入)^[61]

Figure 8 (Color online) Illustration of the structural evolution (ligand substitution and metal incorporation) of the $\{\text{Ti}_6\text{P}_2\}$ cluster core, through the labile coordination sites. Reproduced by permission from Ref. [61]. Copyright (2016) John Wiley and Sons

异烟酸或四氮唑乙酸的引入, 将过渡金属离子同时引入到 $\{\text{Ti}_6\text{P}_2\}$ 结构中, 成功地将其光谱响应范围调控至可见光区, 并进一步通过改变过渡金属离子的配位环境, 实现了其可见光吸收的调控。

在氧化钛材料体系中, 铜离子是有效的用来提高其光解水产氢速率的掺杂剂^[62-66]。最近, 本课题组^[61,67]系统研究了钛氧簇合物的铜卤素簇掺杂, 成功合成了一系列通过铜卤素簇连接的一维链、二维层和三维diamond构型的钛氧簇基材料。这些材料的连

接单元为 $\{\text{Ti}_6\}$, 铜卤素簇单元分别是 $\{\text{Cu}_2\text{X}_2\}$, $\{\text{Cu}_4\text{X}_4\}$ 和 $\{\text{Cu}_4\text{X}_4\text{-DABCO-Cu}_4\text{X}_4\}$ 。实验表明, 这种多金属和多维掺杂的方法成功实现了晶态钛氧簇材料的光吸收和能带结构调控, 如图9所示。另外, 由于铜离子和氮之间强的吸附力, 还可通过这一方法制备含有无色钛氧核和有色铜卤壳层的杂化材料。

苏州大学戴洁课题组^[9,68-73]在提升钛氧簇的光电响应效果方面做出了很多的工作, 尤其制备了一系列生色团(例如: 9-蒽甲酸、邻苯二酚、二茂铁甲酸、

图9 (网络版彩色)基于 $\{Ti_6\}$ 和不同的铜卤素的多维材料图^[67]

Figure 9 (Color online) Photos of multi-dimensional materials based on $\{Ti_6\}$ and different copper halides. Adapted with permission from Ref. [67]. Copyright (2017) American Chemical Society

水杨酸和四硫富瓦烯二羧酸)修饰的钛氧簇合物^[74~78]。其中比较典型的例子是采用二茂铁甲酸和异丁酸制备的两例同构的钛氧簇合物 $[Ti_6O_6(O^iPr)_6(O_2C^iBu)_6]$ (**1**)和 $[Ti_6O_6(O^iPr)_6(O_2C^iBu)_6]$ (**2**)(O_2C^iBu , 二茂铁甲酸根; O_2C^iBu , 异丁酸根), 如图10所示^[78]。光电流测试结果表明, 随着所加电压的增加, 光电流响应效果加强。比较有趣的是含二茂铁甲酸配体的钛氧簇合物的光电流测试效果要好于含异丁酸配体的钛氧簇合物。主要原因是电荷会从二茂铁甲酸配体转移钛离子上, 而二茂铁甲酸配体的存在提升了电子的激发和电荷分离的效率。

4 钛氧簇合物的材料应用

钛氧簇合物作为晶态材料, 它本身有一些突出的特点, 如结构可剪裁性、可溶解性以及光催化活性^[30,41,43]。为了探索钛氧簇合物的潜在应用, 研究者

开展了大量的研究工作。

4.1 光催化产氢

为了提高钛氧簇合物的稳定性和光吸收特性, 中国科学技术大学刘波课题组^[79]合成出了一种在酸碱溶液中具有超高稳定性的铜掺杂的钛氧簇合物: $Ti_{12}In_6O_{18}(O_2C^iBu)_6(POTi_{12}In_6)$, 如图11所示。这种钛氧簇合物在可见光的激发下, 表现出明显的光电流信号和污染物降解性质。此外, 在可见光光照且不使用助催化剂的情况下具有光催化产氢性能。同年, 刘波课题组^[80]又合成出了铬掺杂的钛氧簇合物: $Ti_{12}Cr_6O_{18}(O_2C^iBu)_6(POTi_{12}Cr_6)$ 。它在全波段的太阳光下, 仍然表现出较好的光解水产氢性能。尤其在近红外光条件下的光解水制氢性能与大多数催化剂的催化效果相媲美。

钛氧簇合物不仅可以用于掺杂体系中, 三元复合材料的研 究也受到了广泛关注。近年来, 本课题组^[81,82]成功设计了一系列基于钛氧簇合物的三元复合光催化材料体系, 如图12所示。具体实施过程中通过三步溶剂热反应, 分别把CdS纳米颗粒和钛氧簇合物原位自组装到多孔MOF材料MIL-101中, 从而制备出了具有较好可见光响应的三元PTC/CdS/MIL-101催化剂。同时, 由于三组分之间较好的协同效应, 在可见光光照且无添加贵金属作助催化剂的条件下, 此三元材料的光解水产氢速率比CdS/MIL-101二元材料有了较大的提高。更有趣的是增加钛氧簇合物上修饰的有机配体的共轭基团可以进一步提高这类

图10 (网络版彩色) $[Ti_6O_6(O^iPr)_6(O_2C^iBu)_6]$ (a)和 $[Ti_6O_6(O^iPr)_6(O_2C^iBu)_6]$ (b)的分子结构^[78]

Figure 10 (Color online) Molecular structures of $[Ti_6O_6(O^iPr)_6(O_2C^iBu)_6]$ (a) and $[Ti_6O_6(O^iPr)_6(O_2C^iBu)_6]$ (b). Adapted with permission from Ref. [78]. Copyright (2016) American Chemical Society

图 11 (网络版彩色)(a) POTi₁₂In₆的晶体结构; (b) 在可见光激发下(>400 nm), I₂/NaI的乙腈溶液中POTi₁₂In₆的光电流信号; (c) POTi₁₂In₆对甲基橙的光降解的时间分布; (d) 在可见光激发下, 在含有 10 mL H₂O和 0.1 mL三乙胺的溶液中, 20 mg的POTi₁₂In₆的产氢量随时间的变化; 插图为 POTi₁₂In₆在可见光激发下的光解水产氢的循环测试^[79]

Figure 11 (Color online) (a) Crystallographic structure of POTi₁₂In₆. (b) Transient photocurrent responses of POTi₁₂In₆ in I₂/NaI CH₃CN solution under visible irradiation (>400 nm). (c) Temporal profile of the photo-degradation of methyl orange (MO) over POTi₁₂In₆. (d) Time course of the hydrogen production yield over 20 mg of POTi₁₂In₆ ($\lambda > 400$ nm) from an aqueous solution containing 10 mL H₂O and 0.1 mL triethylamine under visible-light irradiation. Insert: cycling tests of watersplitting H₂ evolution under visible light illumination on POTi₁₂In₆. Reproduced with permission from Ref. [79]. Copyright (2017) The Royal Society of Chemistry

图 12 (网络版彩色)不同光催化剂在可见光(>420 nm)激发下的产氢量随时间的变化图(a)和产氢速率图(b)^[81]

Figure 12 (Color online) Time course of H₂ evolution under visible-light (>420 nm) irradiation (left) and production rates (right) by different photocatalysts. Reproduced by permission from Ref. [81]. Copyright (2017) John Wiley & Sons

三元催化剂的催化活性, 最终产氢速率达到 $94.9 \text{ mmol g}_{\text{CdS}}^{-1} \text{ h}^{-1}$, 较二元材料提高了近50倍. 电化学和光谱分析表明, 在这个三元PTC/CdS/MIL-101复合体系中, 钛氧簇合物可以作为电子传递媒介, 将光生电子从CdS颗粒分散到MIL-101表面, 从而促进电荷-空穴分离, 最终提高了光解水产氢效率. 这项研究成果不仅建立了基于钛氧簇合物的高效可见光驱动产氢催化体系, 同时也从分子层面提供了调控并优化其催化活性的有效工具.

4.2 催化水氧化

除了用作光催化产氢催化剂, 钛氧簇合物在水氧化方面也有相关报道. 厦门大学龙腊生课题组^[83]报道了一系列镧系金属掺杂的钛氧簇合物 $[\text{Ln}_8\text{Ti}_{10}(\mu_3\text{-O})_{14}(\text{tbba})_{34}(\text{Ac})_2(\text{H}_2\text{O})_4(\text{THF})_2] \cdot 2\text{Htbba}$ ($\text{Ln} = \text{Eu}, \text{Sm}, \text{Gd}$; $\text{Htbba} = 4$ -叔丁基苯甲酸), 如图13所示. 该系列钛氧簇合物具有较好的化学稳定性和高效的光驱动水氧化性能, 催化转化数和催化转化频率都相对较高. 尤其是含Eu的化合物在反应3 h后的产氧速率达到 $509.8 \text{ mmol g}^{-1}$, 比P25的产氧速率 (75.7 mmol g^{-1}) 高6倍多.

4.3 识别和分离

基于金属有机框架物(MOFs)材料的一系列优点, 也可以将钛氧簇合物和MOFs材料复合构建新的功能材料. 但受限于MOFs材料有限的窗口尺寸, 与孔道尺寸匹配的钛氧簇分子直接负载到MOFs孔结构中是一个极具挑战性的难题. 本课题组与德国Christof

Wöll课题组^[84,85]合作巧妙地采用改进的逐层式液相外延生长的方法将手性的 $\text{Ti}_4(\text{OH})_4(\text{R/S-BINOL})_6$ 簇(BINOL=1,1'-联-2-萘酚)负载到HKUST-1薄膜的孔道中, 如图14所示. 该方法不仅能够非常高效地将 $\text{Ti}_4(\text{OH})_4(\text{R/S-BINOL})_6$ 簇有序排列在HKUST-1薄膜的孔道结构中, 而且能够按功能导向负载目标钛氧簇分子, 并且成功实现了乳酸甲酯对映体的高效识别和分离. 这种液相外延生长法不仅可以具有特殊功能的钛氧簇合物有效地负载到多孔MOF材料的孔道中得到具有复合功能的薄膜材料, 同时拓宽了从合成纳米颗粒到合成有序的亚晶(metacrytal)或者晶态原子级别颗粒的研究方法.

5 讨论和结论

综上所述, 本文详细介绍了晶态钛氧簇合物的研究背景、合成方法、结构、性能及其在新型材料方面的应用. 得益于近代X射线单晶衍射硬件和软件的发展以及各种新颖的合成策略, 越来越多具有不同结构和簇核的晶态钛氧簇合物被制备并表征. 此外, 各类晶态钛氧簇合物在光驱动水分解、污染物降解以及二元/三元复合材料的构建方面也受到了广泛的关注和发展. 尽管如此, 相比于传统的多金属氧酸盐, 钛氧簇合物的研究仍然处于起步阶段. 因此, 在结构新颖钛氧簇合物的设计合成、金属离子的掺杂、光电性能的优化、新型复合材料的构筑等领域仍然有很大的发展空间. 除此之外, 目前钛氧簇合物的制备大多依赖于配位自组装的方法, 如何准确深入地解读其生长机理以最终实现可控合成也非常具有挑战性和必要性.

图13 (网络版彩色) (a) $[\text{Eu}_8\text{Ti}_{10}(\mu_3\text{-O})_{14}(\text{tbba})_{34}(\text{Ac})_2(\text{H}_2\text{O})_4(\text{THF})_2] \cdot 2\text{Htbba}$ 结构的球棍模型; (b) 化合物和P25的光电催化产氧量^[83]
Figure 13 (Color online) (a) Ball-and-stick view of the molecular structure of $[\text{Eu}_8\text{Ti}_{10}(\mu_3\text{-O})_{14}(\text{tbba})_{34}(\text{Ac})_2(\text{H}_2\text{O})_4(\text{THF})_2] \cdot 2\text{Htbba}$. (b) Photoelectrocatalytic amount of O_2 of compounds and P25. Adapted with permission from Ref. [83]. Copyright (2017) American Chemical Society

图14 (网络版彩色)手性钛氧簇负载型金属有机框架薄膜。(a) R-Ti-MOC簇的结构;(b) 负载有Ti-MOC的HKUST-1的胶囊状结构的示意图;(c) 液相外延法(LPE)原位生长对映体Ti-MOC负载的HKUST-1薄膜的逐层生长示意图^[85]

Figure 14 (Color online) Chiral Ti-oxo-cluster loaded HKUST-1 thin film. (a) Structure of the used R-Ti-MOC cluster. (b) Schematic presentation of the encapsulation of Ti-MOC by HKUST-1. (c) Schematic presentation of *in situ* layer-by-layer growth of enantiopure Ti-MOC-loaded HKUST-1 thin film using the liquid phase epitaxy (LPE) approach. Adapted with permission from Ref. [85]. Copyright (2016) American Chemical Society

参考文献

- Long D L, Burkholder E, Cronin L. Polyoxometalate clusters, nanostructures and materials: From self assembly to designer materials and devices. *Chem Soc Rev*, 2007, 36: 105–121
- Wang E B, Hu C W, Xu L. Introduction of polyoxometalates chemistry (in Chinese). Beijing: Chemical Industry Press, 1997 [王恩波, 胡长文, 许林. 多酸化学导论. 北京: 化学工业出版社, 1997]
- Chen F W, Hu C W. Research advance of on catalysis of polyoxometalates (in Chinese). *Prog Chem*, 2011, 23: 19–41 [陈发旺, 胡长文. 多金属氧簇催化研究进展. 化学进展, 2011, 23: 19–41]
- Cini M, Bradshaw T D, Woodward S. Using titanium complexes to defeat cancer: The view from the shoulders of titans. *Chem Soc Rev*, 2017, 46: 1040–1051
- Zheng K, Setyawati M I, Leong D T, et al. Antimicrobial silver nanomaterials. *Coord Chem Rev*, 2018, 357: 1–17
- Zheng S T, Yang G Y. Recent advances in paramagnetic-TM-substituted polyoxometalates (TM=Mn, Fe, Co, Ni, Cu). *Chem Soc Rev*, 2012, 41: 7623–7646
- Katsoulis D E. A Survey of applications of polyoxometalates. *Chem Rev*, 1998, 98: 359–387
- Zheng X Y, Xie J, Kong X J, et al. Recent advances in the assembly of high-nuclearity lanthanide clusters. *Coord Chem Rev*, 2017, doi: 10.1016/j.ccr.2017.10.023
- Zou D H, Wang P, Luo W, et al. Fluorescent hydrogel generated conveniently from a perylene tetracarboxylate derivative of titanium(IV) alkoxide. *Inorg Chem*, 2018, 57: 1623–1629
- Du P, Eisenberg R. Catalysts made of earth-abundant elements (Co, Ni, Fe) for water splitting: Recent progress and future challenges. *Energy Environ Sci*, 2012, 5: 6012–6021
- Zheng H, Du M H, Lin S C, et al. Assembly of wheel-like $\text{Eu}_{24}\text{Ti}_8$ cluster under the guidance of high resolution electrospray ionization mass spectrometry. *Angew Chem Int Ed*, 2018, doi: 10.1002/anie.201806757
- Li H, Sun Y, Yuan Z Y, et al. Titanium phosphonate based metal-organic frameworks with hierarchical porosity for enhanced photocatalytic hydrogen evolution. *Angew Chem Int Ed*, 2018, 57: 3222–3227
- Lewis N S. Toward cost-effective solar energy use. *Science*, 2007, 315: 798–801
- Mao C, Zuo F, Hou Y, et al. *In situ* preparation of a Ti^{3+} self-doped TiO_2 film with enhanced activity as photoanode by N_2H_4 reduction. *Angew Chem Int Ed*, 2014, 53: 10485–10489

- 15 Dong S, Ding X, Guo T, et al. Self-assembled hollow sphere shaped $\text{Bi}_2\text{WO}_6/\text{RGO}$ composites for efficient sunlight-driven photocatalytic degradation of organic pollutants. *Chem Eng J*, 2017, 316: 778–789
- 16 Dong S, Cui Y, Wang Y, et al. Designing three-dimensional acicular sheaf shaped $\text{BiVO}_4/\text{reduced graphene oxide}$ composites for efficient sunlight-driven photocatalytic degradation of dye wastewater. *Chem Eng*, 2014, 249: 102–110
- 17 Schrauzer G N, Guth T D. Photolysis of water and photoreduction of nitrogen on titanium dioxide. *J Am Chem Soc*, 1977, 99: 7189–7193
- 18 Kubacka A, Fernandez-Garcia M, Colon G. Advanced nanoarchitectures for solar photocatalytic applications. *Chem Rev*, 2012, 112: 1555–1614
- 19 Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, 238: 37–38
- 20 Tan H, Zhao Z, Niu M, et al. A facile and versatile method for preparation of colored TiO_2 with enhanced solar-driven photocatalytic activity. *Nanoscale*, 2014, 6: 10216–10223
- 21 Yang H G, Liu Q, Qiao S Z, et al. Solvothermal synthesis and photoreactivity of anatase TiO_2 nanosheets with dominant {001} facets. *J Am Chem Soc*, 2009, 131: 4078–4083
- 22 Zhao Z, Zhang X, Zhang G, et al. Effect of defects on photocatalytic activity of rutile TiO_2 nanorods. *Nano Res*, 2015, 8: 4061–4071
- 23 Zuo F, Bozhilov K, Dillon R J, et al. Active facets on titanium(III)-doped TiO_2 : An effective strategy to improve the visible-light photocatalytic activity. *Angew Chem Int Ed*, 2012, 51: 6223–6226
- 24 Du Y, Yang H, Wan S, et al. A titanium-based porous coordination polymer as a catalyst for chemical fixation of CO_2 . *J Mater Chem A*, 2017, 5: 9163–9168
- 25 Benedict J B, Freindorf R, Trzop E, et al. Large polyoxotitanate clusters: Well-defined models for pure-phase TiO_2 structures and surfaces. *J Am Chem Soc*, 2010, 132: 13669–13671
- 26 Coppens P, Chen Y, Trzop E. Crystallography and properties of polyoxotitanate nanoclusters. *Chem Rev*, 2014, 114: 9645–9661
- 27 Fang W H, Zhang L, Zhang J. Synthetic strategies, diverse structures and tuneable properties of polyoxo-titanium clusters. *Chem Soc Rev*, 2018, 47: 404–421
- 28 Sokolow J D, Trzop E, Chen Y, et al. Binding modes of carboxylate- and acetylacetonate-linked chromophores to homodisperse polyoxotitanate nanoclusters. *J Am Chem Soc*, 2012, 134: 11695–11700
- 29 Gao M Y, Chen S, Hu L X, et al. Synthesis and photocatalytic H_2 evolution properties of four titanium-oxo-clusters based on a cyclohex-3-ene-1-carboxylate ligand. *Dalton Trans*, 2017, 46: 10630–10634
- 30 Gao M Y, Fang W H, Wen T, et al. Connecting titanium-oxo clusters by nitrogen heterocyclic ligands to produce multiple cluster series with photocatalytic H_2 evolution activities. *Cryst Growth Des*, 2017, 17: 3592–3595
- 31 Steunou N, Kickelbick G, Boubekeur K, et al. A new polyoxo-alkoxo titanium cluster of the Keggin family: Synthesis and characterization by X-ray diffraction and NMR spectroscopy. *J Chem Soc Dalton Trans*, 1999, (21): 3653–3655
- 32 Randall W J, Weakley T J R, Finke R G. Oxidation resistant inorganic-porphyrin analog polyoxometalates. 3. Synthesis and X-ray crystallographic characterization of a new heteropolyoxoanion structural type, the diruthenium-oxo-bridged bimetallic inorganic-porphyrin analog $\text{KLi}_{15}[\text{O}\{\text{Ru}^{\text{IV}}\text{Cl}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2] \cdot 2\text{KCl} \cdot 60\text{H}_2\text{O}$. *Inorg Chem*, 1993, 32: 1068–1071
- 33 Reichmann M G, Hollander F J, Bell A T. Structure of $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$. *Acta Crystallogr C*, 1987, 43: 1681–1683
- 34 Zhang G, Liu C, Long D L, et al. Water-soluble pentagonal-prismatic titanium-oxo clusters. *J Am Chem Soc*, 2016, 138: 11097–11100
- 35 Hu J, Zhan L, Zhang G, et al. Effects of substitutional dopants on the photoresponse of a polyoxotitanate cluster. *Inorg Chem*, 2016, 55: 8493–8501
- 36 Zhang G, Hou J, Tung C H, et al. Small titanium oxo clusters: Primary structures of titanium(IV) in water. *Inorg Chem*, 2016, 55: 3212–3214
- 37 Artner C, Koyun A, Schubert U. A heterobimetallic copper-titanium oxo cluster with a new structural motif. *Monatsh Chem*, 2015, 146: 1777–1780
- 38 Czakler M, Artner C, Schubert U. Titanium oxo/alkoxo clusters with both phosphonate and methacrylate ligands. *Monatsh Chem*, 2015, 146: 1249–1256
- 39 Eslava S, Goodwill B P R, McPartlin M, et al. Extending the family of titanium heterometallic-oxo-alkoxy cages. *Inorg Chem*, 2011, 50: 5655–5662
- 40 Eslava S, Hengesbach F, McPartlin M, et al. Heterometallic cobalt(II)-titanium(IV) oxo cages: Key building blocks for hybrid materials. *Chem Commun*, 2010, 46: 4701–4703
- 41 Gao M Y, Wang F, Gu Z G, et al. Fullerene-like polyoxotitanium cage with high solution stability. *J Am Chem Soc*, 2016, 138: 2556–2559
- 42 Fang W H, Zhang L, Zhang J. A 3.6 nm Ti_{52} -oxo nanocluster with precise atomic structure. *J Am Chem Soc*, 2016, 138: 7480–7483

- 43 Wang J F, Fang W H, Li D S, et al. Cocrystal of $\{\text{Ti}_4\}$ and $\{\text{Ti}_6\}$ clusters with enhanced photochemical properties. *Inorg Chem*, 2017, 56: 2367–2370
- 44 Morris R E. Ionothermal synthesis—Ionic liquids as functional solvents in the preparation of crystalline materials. *Chem Commun*, 2009, (21): 2990–2998
- 45 Nakamura D, Gunjishima I, Yamaguchi S, et al. Ultrahigh-quality silicon carbide single crystals. *Nature*, 2004, 430: 1009–1012
- 46 Zhang J, Wu T, Chen S, et al. Versatile structure-directing roles of deep-eutectic solvents and their implication in the generation of porosity and open metal sites for gas storage. *Angew Chem Int Ed*, 2009, 48: 3486–3490
- 47 Smith E L, Abbott A P, Ryder K S. Deep eutectic solvents (DESs) and their applications. *Chem Rev*, 2014, 114: 11060–11082
- 48 Narayanam N, Fang W H, Chintakrinda K, et al. Deep eutectic-solvothermal synthesis of titanium-oxo clusters protected by pi-conjugated chromophores. *Chem Commun*, 2017, 53: 8078–8080
- 49 Hou J, Hu J, Sun Q, et al. A Post-functionalizable iso-polyoxotitanate cage cluster. *Inorg Chem*, 2016, 55: 7075–7078
- 50 Song T Q, Dong J, Gao H L, et al. Three coordination polymers based on M_2 ($\text{M}=\text{Co}$, Ni and Zn) clusters: Structures, magnetic and fluorescent properties. *Inorg Chim Acta*, 2017, 466: 393–397
- 51 Xiao H, Zhou J, Liu X. Two new 3-D cadmium bromoplumbates: The only example of heterometallic bromoplumbate based on crown $[\text{Cd}(\text{Pb}_4\text{O}_4)\text{Br}_2]$ clusters. *Dalton Trans*, 2018, 47: 4833–4839
- 52 Zhao C, Han Y Z, Dai S, et al. Microporous cyclic titanium-oxo clusters with labile surface ligands. *Angew Chem Int Ed*, 2017, 56: 16252–16256
- 53 Chen X, Li C, Gratzel M, et al. Nanomaterials for renewable energy production and storage. *Chem Soc Rev*, 2012, 41: 7909–7937
- 54 Matthews P D, King T C, Wright D S. Structure, photochemistry and applications of metal-doped polyoxotitanium alkoxide cages. *Chem Commun*, 2014, 50: 12815–12823
- 55 Eslava S, McPartlin M, Thomson R I, et al. Single-source materials for metal-doped titanium oxide: Syntheses, structures, and properties of a series of heterometallic transition-metal titanium oxo cages. *Inorg Chem*, 2010, 49: 11532–11540
- 56 Assi H, Mouchaham G, Steunou N, et al. Titanium coordination compounds: From discrete metal complexes to metal-organic frameworks. *Chem Soc Rev*, 2017, 46: 3431–3452
- 57 Lv Y, Du W, Ren Y, et al. An integrated electrochromic supercapacitor based on nanostructured Er-containing titania using an Er(III)-doped polyoxotitanate cage. *Inorg Chem Front*, 2016, 3: 1119–1123
- 58 Lv Y, Cheng J, Matthews P D, et al. A study of the optical properties of metal-doped polyoxotitanium cages and the relationship to metal-doped titania. *Dalton Trans*, 2014, 43: 8679–8689
- 59 Czakler M, Artner C, Schubert U. Acetic acid mediated synthesis of phosphonate-substituted titanium oxo clusters. *Eur J Inorg Chem*, 2014, 12: 2038–2045
- 60 Lv H T, Li H M, Zou G D, et al. Titanium-oxo clusters functionalized with catecholate-type ligands: Modulating the optical properties through charge-transfer transitions. *Dalton Trans*, 2018, doi: 10.1039/c8dt01844h
- 61 Liu J X, Gao M Y, Fang W H, et al. Bandgap engineering of titanium-oxo clusters: Labile surface sites used for ligand substitution and metal incorporation. *Angew Chem Int Ed*, 2016, 55: 5160–5165
- 62 Xu S, Ng J, Zhang X, et al. Fabrication and comparison of highly efficient Cu incorporated TiO_2 photocatalyst for hydrogen generation from water. *Int J Hydrog Energy*, 2010, 35: 5254–5261
- 63 Lee W P C, Tan L L, Sumathi S, et al. Copper-doped flower-like molybdenum disulfide/bismuth sulfide photocatalysts for enhanced solar water splitting. *Int J Hydrog Energy*, 2018, 43: 748–756
- 64 Du J, Wang J, Ji L, et al. A Highly active and robust copper-based electrocatalyst toward hydrogen evolution reaction with low overpotential in neutral solution. *ACS Appl Mater Interfaces*, 2016, 8: 30205–30211
- 65 Sun Q, Dong Y, Wang Z, et al. Synergistic nanotubular copper-doped nickel catalysts for hydrogen evolution reactions. *Small*, 2018, 14: e1704137
- 66 Zhang Y, Ma Y, Chen Y Y, et al. Encased copper boosts the electrocatalytic activity of N-doped carbon nanotubes for hydrogen evolution. *ACS Appl Mater Interfaces*, 2017, 9: 36857–36864
- 67 Fang W H, Wang J F, Zhang L, et al. Titanium-oxo cluster based precise assembly for multidimensional materials. *Chem Mater*, 2017, 29: 2681–2684
- 68 Wu Y Y, Luo W, Wang Y H, et al. Titanium-oxo-clusters with dicarboxylates: Single-crystal structure and photochromic effect. *Inorg Chem*, 2012, 51: 8982–8988
- 69 Wang P, Wu Y Y, Wu J, et al. Perylene carboxylate-modified titanium-oxide gel, a functional material with photoswitchable fluorescence properties. *J Mater Chem C*, 2013, 1: 7973–7978
- 70 Wang S, Su H C, Yu L, et al. Fluorescence and energy transfer properties of heterometallic lanthanide-titanium oxo clusters coordinated

- with anthracenecarboxylate ligands. *Dalton Trans*, 2015, 44: 1882–1888
- 71 Zhang G L, Wang S, Hou J L, et al. A lanthanide-titanium (LnTi_{11}) oxo-cluster, a potential molecule based fluorescent labelling agent and photocatalyst. *Dalton Trans*, 2016, 45: 17681–17686
- 72 Guo Y, Hou J L, Luo W, et al. Effects of co-coordinated auxiliary ligands on the photoelectrochemical behaviour of titanium-alkoxide-dyes. *J Mater Chem A*, 2017, 5: 18270–18275
- 73 Yang S, Su H C, Hou J L, et al. The effects of transition-metal doping and chromophore anchoring on the photocurrent response of titanium-oxo-clusters. *Dalton Trans*, 2017, 46: 9639–9645
- 74 Wu Y Y, Wang P, Wang Y H, et al. Metal-phenanthroline fused Ti_{17} clusters, a single molecular source for sensitized photoconductive films. *J Mater Chem A*, 2013, 1: 9862–9868
- 75 Wu Y Y, Lu X W, Qi M, et al. Titanium-oxo cluster with 9-anthracenecarboxylate antennae: A fluorescent and photocurrent transfer material. *Inorg Chem*, 2014, 53: 7233–7240
- 76 Hou J L, Luo W, Wu Y Y, et al. Two Ti_{13} -oxo-clusters showing non-compact structures, film electrode preparation and photocurrent properties. *Dalton Trans*, 2015, 44: 19829–19835
- 77 Yin J X, Huo P, Wang S, et al. A tetrathiafulvalene-grafted titanium-oxo-cluster material: self-catalyzed crystal exfoliation and photocurrent response properties. *J Mater Chem C*, 2015, 3: 409–415
- 78 Hou J L, Luo W, Guo Y, et al. Titanium oxo cluster with six peripheral ferrocene units and its photocurrent response properties for saccharides. *Inorg Chem*, 2017, 56: 6451–6458
- 79 Liu S, Hu W, Nath J K, et al. $[\text{Ti}_{12}\text{In}_6\text{O}_{18}(\text{OOCCH}_3)_{30}]$: A multifunctional hetero-polyoxotitanate nanocluster with high stability and visible photoactivity. *Dalton Trans*, 2017, 46: 678–684
- 80 Zhang J, Hu W, Zhang J, et al. Stable heteropolyoxotitanate nanocluster for full solar spectrum photocatalytic hydrogen evolution. *J Phys Chem C*, 2017, 121: 18326–18332
- 81 Jiang Z, Liu J, Gao M, et al. Assembling polyoxo-titanium clusters and cds nanoparticles to a porous matrix for efficient and tunable H_2 -evolution activities with visible light. *Adv Mater*, 2017, 29: 160339
- 82 Férey G, Mellot-Draznieks C, Serre C, et al. A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science*, 2005, 309: 2040–2042
- 83 Lu D F, Kong X J, Lu T B, et al. Heterometallic lanthanide-titanium oxo clusters: A new family of water oxidation catalysts. *Inorg Chem*, 2017, 56: 1057–1060
- 84 Chui S S Y, Lo S M F, Charmant J P H, et al. A chemically functionalizable nanoporous material $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$. *Science*, 1999, 283: 1148–1150
- 85 Gu Z G, Fu H, Neumann T, et al. Chiral porous metacrystals: Employing liquid-phase epitaxy to assemble enantiopure metal-organic nanoclusters into molecular framework pores. *ACS Nano*, 2016, 10: 977–983

Summary for “晶态钛氧簇合物的制备与性能研究进展”

Preparation and properties of polyoxo-titanium clusters

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Effectively harvesting solar energy plays a crucially important role in supplying sustainable energy and addressing the environmental pollutants. Titanium dioxide (TiO_2) nanoparticles are recognised as the best promising photocatalysts for solar energy conversion, photovoltaic cells and degradation of organic pollutants, due to its advantages of low cost, high efficiency and environmental friendliness. The strong oxidative potential of the photogenerated holes TiO_2 nanoparticles can oxidize water to create hydroxyl radicals and oxidize most organic pollutants into carbon dioxide. “Honda-Fujishima effect” was described firstly by Fujishima and Honda in 1972, that promote the field of photocatalysis extensively. The first example that TiO_2 nanoparticles was used for photocatalyst of photocatalytic hydrogen production under UV excitation, was published in 1977. However, the defects of strong imprecise structural information at the atomic level, including uncertain surface composition, uneven sizes, and unclear inorganic-organic interface information, have led to a great limitation for deeper research on such vital photocatalytic materials. Therefore it would be a great challenge to investigate the theoretical catalytic mechanism, explore the charge transfer path, modify the surface as well as understand the structure-property relationship at the molecular level. Serving as the structure and reactivity model, crystalline titanium-oxo clusters (TOCs) with accurate structures have attracted considerable attention in recent decades. A growing numbers of TOCs with various structures have been synthesized attributed to the rapid development of single-crystal X-ray diffraction analysis. As a most special class of oxo-clusters-based materials between molecular compounds and nanoparticles, it did have made tremendous progress, although there is still large space for the development of TOCs, compared with polyoxometalate clusters like polyoxomolybdate complexes and polyoxotungstate compounds. Accurate atomic location, clear ligand-nuclearity connectivity, highly tunable cluster size and high solubility of TOCs give great chances to investigate the optimal reaction condition through simply varying the synthesized conditions of solution-based prepared methods, and analyze the structure-property relationship at the molecular level, as well as provide an excellent research platform for the molecular simulation and theoretical calculation of the surface modification of TOCs.

This review is directed to cover the main advances on the development of TOCs. Firstly, the representative synthetic and design approaches are classified and discussed including the conventional and latest successful synthetic routes, such as strict inert condition synthesis, solvothermal synthesis, two-step synthesis, ionothermal synthesis, etc. In addition, a large proportion of TOCs with diverse novel structures are reviewed, as the result of successful synthetic and design methods, for example, the first fullerene-like Ti_{42} cluster, the highest nuclearity of Ti_{52} cluster, microporous cyclic Ti_{32} clusters, etc. Moreover, tunable properties are also outlined by modifying different coordinating ligands and doping metals or non-metals. They contribute to get rid of UV-light dependence and enhance their visible-light absorption. Furthermore, applications in a variety of different fields, e.g. photocatalytic hydrogen generation, photoelectrochemical water oxidation, recognition and separation, are also discussed.

titanium-oxo clusters, solvothermal synthesis, bandgap, photocatalysis, composite

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