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质谱技术在新能源领域的应用

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摘要：当前，全球能源短缺、气候变化问题日益严重，开发和利用环境友好型能源迫在眉睫。质谱技术能够快速识别多组分物质、鉴定未知化合物结构，在光催化反应、电催化反应以及电化学储能装置开发等能源研究领域得到了广泛应用。本文介绍了液相色谱-质谱（LC-MS）、气相色谱-质谱（GC-MS）、基质辅助激光解吸电离质谱（MALDI-MS）、微分电化学质谱（DEMS）和电喷雾电离质谱（ESI-MS）等技术在反应瞬态中间体、产物检测和反应机理推测方面的应用，并对质谱技术在光催化降解、光催化合成、电催化还原、电催化合成、锂离子电池以及锂硫电池等领域面临的挑战和发展趋势进行展望。

关键词：质谱；产物检测；反应中间体；反应机理；光催化；电催化；储能装置
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Application of Mass Spectrometry in New Energy Fields

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Abstract: The development and utilization of environment-friendly energy is imminent with global energy shortage and climate change becoming increasingly serious. The advancement and utilization of environment-friendly energy, including photocatalytic hydrogen production, electrocatalytic pollutant removal, and the development of electrochemical energy storage devices, have emerged as prominent research topics. A variety of modern analysis techniques provide strong support in these related studies, such as X-ray absorption spectroscopy (XAS) for investigating the active site geometry and electronic structure of photocatalysts, synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) for real-time monitoring of interatomic electron excitation and transfer in photocatalysts, *in situ* electron paramagnetic resonance spectroscopy (EPR) for the detection of free radicals in photocatalysis reactions, Raman spectroscopy (RS) for analyzing the interfacial structure of electrochemical reactions, and *in situ* transmission electron microscopy (TEM) for studying catalyst structure and reactivity in photocatalytic reactions. While these techniques provide abundant information for the mechanistic aspects of the associated chemical processes, it remains challenging to conduct further identification and structural analysis of the reaction intermediates at a molecular level. Due to the ability in rapid identification of the components in complex system, mass

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spectrometry (MS) has been widely used in the new energy fields such as photocatalytic reaction, electrocatalytic reaction, and the development of electrochemical energy storage devices. This review introduced the application of mass spectrometry techniques, including liquid chromatography-mass spectrometry (LC-MS), gas chromatography-mass spectrometry (GC-MS), matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), differential electrochemical mass spectrometry (DEMS), and electrospray ionization mass spectrometry (ESI-MS), in the detection of transient intermediates and products as well as the exploration of reaction mechanisms. Modern mass spectrometry offers critical support for the mechanism analysis of photocatalytic reactions aimed at the mineralization of organic pollutants, hydrogen generation, CO_2 reduction, N_2 fixation, and organic synthesis. It also provides distinct advantages for real-time product monitoring, isotopic labeling analysis, and the capture and identification of short-lived intermediates in electrocatalytic processes, such as hydrogen evolution, oxygen evolution, CO_2 reduction, N_2 reduction, and organic synthesis. By analyzing reaction products and intermediates in electrochemical energy storage devices through mass spectrometry, it is possible to elucidate the nature of energy storage and conduct rational design of high-performance materials. Modern mass spectrometry facilitates both offline detection of products and online identification of reaction intermediates, enhancing the understanding of reaction kinetics and elucidating mechanisms when combined with theoretical calculations. Thus, modern mass spectrometry has become a powerful tool for the study of reaction mechanisms. The challenges and prospects of mass spectrometry in the fields of photocatalytic degradation, photocatalytic synthesis, electrocatalytic reduction, electrocatalytic synthesis, lithium-ion batteries, and lithium-sulfur batteries were also discussed in this review. While current mass spectrometry techniques can detect transient intermediates, challenges persist in identifying the reaction intermediates with lower concentrations and reduced stability. Therefore, optimizing the sampling systems and mass analyzers is crucial to improve the sampling speed, transfer efficiency, and analysis throughput. Understanding complex reaction mechanisms requires correlating reaction intermediates with various conditions, such as reaction time, radiation wavelength, and potential. This necessitates a spatial integration between the reactor and the mass spectrometer to preserve the true form of intermediates and ensure accurate signal transmission that reflects the pertinent reaction parameters. Integrating mass spectrometry to analyze the morphology and structure of reaction intermediates and products with theoretical calculations may enable the construction of a comprehensive, multi-dimensional reaction theory system. Ultimately, employing this theoretical framework to advance experimental research could represent a novel idea in the research filed.

Key words: mass spectrometry (MS); product detection; reaction intermediates; reaction mechanisms; photocatalysis; electro-catalysis; energy storing device

随着全球能源需求的增加，能源短缺问题日益严重，同时，化石燃料资源消耗导致的气候变化和生物多样性丧失等问题也亟待解决[1]。开发和利用环境友好型能源，如光催化制备氢能[2]、电催化除污染物和电化学储能装置的开发[3]等已成为研究热点。在环境友好型能源研究过程中，多种分析技术提供了有力支撑，如 X 射线吸收光谱（XAS）用于研究光催化剂上活性位点的几何结构和电子结构[4-5]，同步辐射 X 射线光电子能谱（SR-XPS）用于实时观察光催化剂上原子间的电子激发和转移[6]，原位电子顺磁共振光谱（EPR）用于识别光催化反应中自由基的形成和演化[7]，拉曼光谱（RS）用于识别电化学反应的界面结构，原位透射电子显微镜（TEM）用于探究催化剂结构和反应性的关系[8-9]等。这些技术手段可以满足对反应机理的探索需求，但难以进一步

在分子水平上进行反应中间体的识别和结构分析。

质谱作为最直观、最灵敏的技术之一，在环境友好型能源开发领域得到广泛应用[10-11]。液相色谱-质谱（LC-MS）[12-13]、气相色谱-质谱（GC-MS）[14]、基质辅助激光解吸电离质谱（MALDI-MS）[15]、微分电化学质谱（DEMS）[16]和电喷雾电离质谱（ESI-MS）[17]等技术在识别多组分物质和鉴定未知物结构方面发挥着重要作用，其可以在光催化反应、电催化反应和电化学储能装置的开发中对产物进行离线检测或对反应中间体进行在线识别，为揭示反应机理和研究反应动力学提供了支撑。

本文将介绍近年来质谱技术在光催化反应、电催化反应和电化学储能研究中进行反应产物监测和中间体捕获鉴定的应用。

1　用于光催化的质谱分析技术

光催化作为解决能源短缺和环境污染问题的有效手段之一已得到广泛研究[18-20]。质谱技术在有机污染物矿化[21]、水分解析氢[22]、CO_2 还原[23-24]、N_2 固定[25]和有机合成[26]等光催化方向中得到应用。

1.1　有机污染物矿化

高灵敏度、高分辨率、没有挥发性或热稳定性限制的液相色谱（LC）被认为是最通用的色谱技术[10]。液相色谱与质谱联用可以实现对稳定反应产物和瞬态反应中间体的定性和定量分析。

Zhou 等[27]采用超高效液相色谱-串联三重四极杆质谱（HPLC-MS/MS）技术对 AgI/三氯氧铋（$Bi_{12}O_{17}Cl_2$）光催化磺胺二甲嘧啶（SMZ）的降解中间体进行鉴定，并提出了 SMZ 的光催化机理。

Mu 等[28]通过捕获实验和高效液相色谱-单四极杆质谱（HPLC-MS）技术得到了负载 $Bi_4O_5I_2$ 的锐钛矿-TiO_2（B）双相纳米线复合催化剂光催化降解对乙酰氨基酚（ACE）过程中可能的反应中间体结构，提出了该过程可能的反应路径，并认为反应的关键活性物质是 O˙H。

Liang 等[29]采用高效液相色谱-串联三重四极杆质谱（HPLC-MS/MS）技术分析反应中间体和产物，提出了在中空管状 g-C_3N_4 上抗生素盐酸四环素（TCH）3 种可能的光催化降解途径。机理分析表明，活性物质 H^+和$^{\bullet}O_2^-$在光降解体系中起主导作用。此外，LC-MS 在多种化学物质（如四环素（TC）[30-37]、恩诺沙星（ENFX）[38-39]、环丙沙星（CIP）[40-41]、左氧氟沙星（LEV）[42-44]等）的光催化降解反应机理分析方面提供了技术支持。

1.2　水分解析氢

光催化析氢是解决日益严重能源危机的一项技术。开发先进的、有合适带隙和催化功能的光催化剂极具挑战[45]。质谱可以满足产物来源的验证、复杂反应机理的确认等多种研发需求。

Yang 等[46]通过同位素实验的四极杆质谱分析，验证了环金属化的 Ir（III）二亚胺络合物 $[Ir(NBI)_2(phen)]PF_6$（NBI=1,8-萘并咪唑，phen=1,10-菲咯啉）作光敏剂、$[Co(dmgH)_2(py)Cl]$（dmgH=丁二肟，py=吡啶）作析氢催化剂、*N*,*N*-二甲基对甲苯胺（DMT）作单电子供体的三组分体系活化水制氢过程中的质子源来源于水，并结合瞬态吸收光谱等技术分析此体系活化水制氢的气体产物以及可能的反应机理，示于图 1。

此外，在线三重四极杆质谱在金属硫化物光催化制氢的反应机理验证中发挥着重要作用[47]。Ye 等[22]采用原位傅里叶变换红外光谱（FT-IR）和在线三重四极杆质谱（MS/MS）对 ReS_2/CdS 光催化制氢机理进行研究，探明了氢的来源和牺牲试剂的转化路径，为构建新型高效光催化剂提供了新见解，促进其在能源开发中的应用。

1.3　CO_2 还原

在解决碳排放和能源危机的全球局势下，二氧化碳捕获并转化为高价值碳氢化合物成为研究热点[48-49]。其中，利用太阳能生产碳化合物极具吸引力[50]。Chen 等[23]通过高分辨率基质辅助激光解吸/电离飞行时间质谱（MALDI-TOF MS）分析出 138 核 3d-4f 团簇 $[Ni_{36}Gd_{102}(OH)_{132}(mmt)_{18}(dmpa)_{18}(H_2dmpa)_{24}(CH_3COO)_{84}(SO_4)_{18}(NO_3)_{18}(H_2O)_{30}]\cdot Br_6(NO_3)_6\cdot(H_2O)_x\cdot(CH_3OH)_y$（Hmmt=甲基巯基噻二唑，$H_3$dmpa=2,2-二羟甲基丙酸，$x$≈130，$y$≈60）在甲醇溶液中具有较高的稳定性，为后续团簇催化 CO_2 还原为 CO 过程提供了支持，示于图 2。

Zu 等[24]利用基于同步辐射加速器的真空紫外光电离质谱（SVUV-PIMS）揭示了在 BiO_2CO_3 纳米片上光催化 CO_2 还原为 CO 的反应过程中，紫外线照射有助于加速 CO 的解吸过程。

1.4　有机合成

光催化已成为在温和条件下合成多种有机

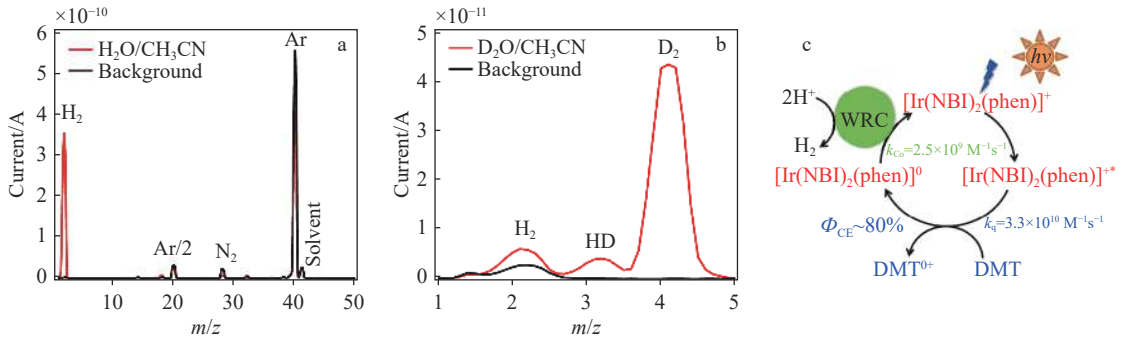

图 1 2.2×10^{-4} mol/L [Ir(NBI)$_2$(phen)]PF$_6$、2.2×10^{-4} mol/L [Co(dmgH)$_2$(py)Cl]和 0.07 mol/L DMT 在 CH$_3$CN/H$_2$O(2:1, *V*/*V*)(a)和 CH$_3$CN/D$_2$O(1:1, *V*/*V*)(b)混合物中产生气体的质谱图以及析氢反应可能的光催化循环机理(c)[46]

Fig. 1 Mass spectra of gas produced of 2.2×10^{-4} mol/L [Ir(NBI)$_2$(phen)]PF$_6$, 2.2×10^{-4} mol/L [Co(dmgH)$_2$(py)Cl], and 0.07 mol/L DMT in the mixtures of CH$_3$CN/H$_2$O (2:1, *V*/*V*) (a) and CH$_3$CN/D$_2$O (1:1, *V*/*V*) (b), and proposed photocatalytic cycle for hydrogen evolution (c)[46]

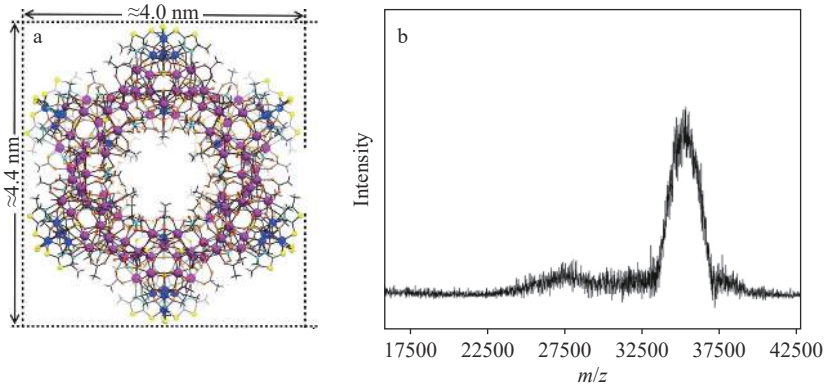

图 2 {Ni$_{36}$Gd$_{102}$}阳离子核中 138 个金属离子的排列透视图(a), 团簇在 CH$_3$OH 溶液中的高分辨率 MALDI-TOF 质谱图(b)[23]

Fig. 2 Perspective view of the hexagonal molecule and the arrangement of 138 metal ions in {Ni$_{36}$Gd$_{102}$} core (a), and high resolution MALDI-TOF mass spectrum of cluster in CH$_3$OH solution (b)[23]

化合物的绿色工具。Wu 等[26]利用非接触式高通量纳米静电喷雾电离(nESTASI)技术与发光二极管(LED)激光器联合, 构建了用于同步反应和质谱分析的双功能光化学微反应器, 示于图 3。该平台可实现低于 1.5 min/次的反应速度、低至皮摩尔级反应量的光催化反应高通量筛选的要求。这种基于质谱开发的快速检测平台为优化光催化过程提供了有力支持。

2 用于电催化的质谱分析技术

电催化技术在清洁能源转换方面发挥着重要作用, 为未来的技术实现提供了许多可持续的过程储备[51]。质谱技术在电催化过程(如析氢反应、析氧反应、CO_2 还原、N_2 还原和有机合成)的产物实时监测、同位素标记分析、短寿命中间体捕获鉴定等方面展现了特有的优势。

2.1 析氢反应

氢能是一种清洁能源, 电化学水分解制氢是一种有前景的制氢途径, 其高度依赖于析氢反应(HER)电催化剂的电活性[52-54]。由于副反应(如表面氧化物还原)的重叠, HER 在非贵金属材料上的动力学和机理参数很难从法拉第电流中获得[55-56]。为解决这一问题, Díaz-Coello 等[57]提出了一种利用微分电化学质谱(DEMS)分析电化学介质中动力学和反应机理的方案, 即利用 DEMS 的离子电流来处理在相同电位内发生的几个电化学反应。通过碱性介质中钨基催化剂上 *m*/*z* 2 信号的变化规律, 可以得到准确的析氢

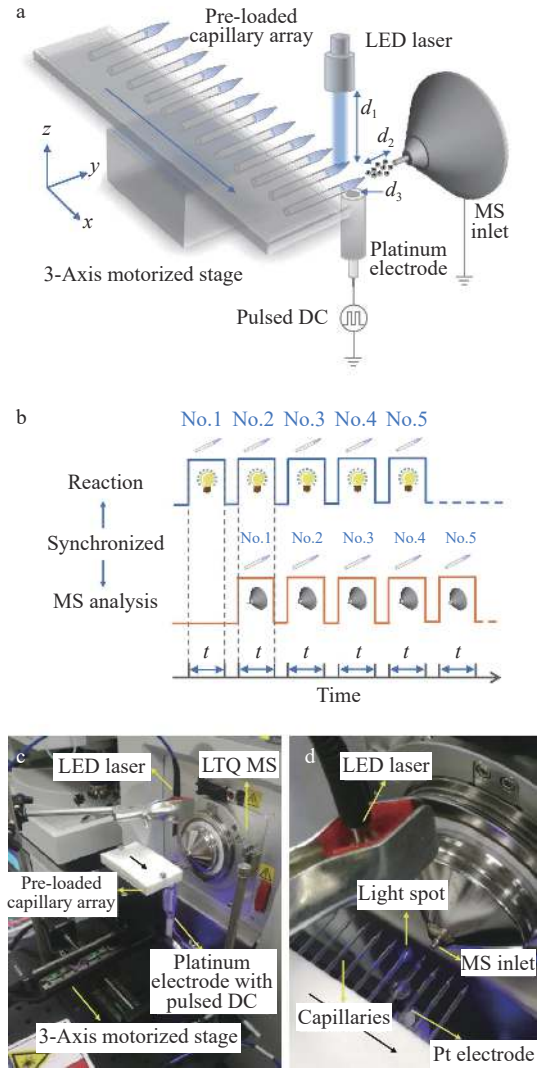

图 3　nESTASI-MS 光催化筛选平台示意图(a)，反应筛选过程中每个毛细管的可见光照射和质谱分析的时间序列(b)，筛选平台模块的整体照片(c)，光催化和质谱分析的同步照片(d)[26]

Fig. 3　Schematic illustration of the nESTASI-MS based photocatalytic screening platform (a), time sequences of the visible light irradiation and MS analysis for each capillary during the reaction screening (b), photographs of the modules of the platform (c), and enlarged view of the simultaneous light irradiation and mass spectrometric detection of reactions in two capillaries (d)[26]

反应 Tafel 斜率。这种检测方式不需要对非贵金属进行预还原处理就可获得精确的 Tafel 斜率、速率确定步骤(RDS)以及反应动力学和反应机制。Bazan-Aguilar 等[58]使用 DEMS 技术分析得到泡沫镍电极上析氢反应准确的起始电位、动力学和机制参数。同时，结合 DEMS 和电化学拉曼光谱(EC-Raman)技术分析研究镍基电极上 HER 的电极-电解质界面行为，阐明了 HER 的反应机理。

2.2　析氧反应

电化学 HER 和析氧反应(OER)是基础电化学和应用电化学中最重要的 2 个反应。由于 OER 在可能的反应机理研究方面更复杂，且在典型反应电位下会出现表面不稳定性，所以关于 OER 的研究较少[59-61]。设计用于四电子 OER 过程兼具高性能和低成本的电催化剂仍是一大挑战[62-65]。

Huang 等[66]通过计时电位法测试和电感耦合等离子体质谱(ICP-MS)分析发现，Co_3O_4/CeO_2 纳米复合材料表现出与 Co_3O_4 相当的析氧反应活性和更好的开路稳定性(即催化剂稳定性)，从而解决了活性和稳定性的取舍问题。Lin 等[67]采用与同位素标记法相结合的原位微分电化学质谱(DEMS)技术对析氧反应产物进行原位监测，充分证明了 Ru/MnO_2 催化剂在析氧反应过程中遵循氧化物路径机制(OPM)[68]。

未来，对 OER 的研究应依赖于结合原位质谱分析的多种互补的表征技术[69]，以比较各种类型催化剂的结构-活性相关性，有利于理解 OER 机制。此外，应深度结合原位表征与理论计算，以确定 OER 活性中心并全面掌握 OER 机理，从而有助于设计高效、稳定的 OER 催化剂。

2.3　CO_2 还原

电催化将二氧化碳还原为燃料和化学品是帮助封闭人为碳循环和储存间歇性可再生能源(电力)的理想途径[70-71]。与 HER 和 OER 不同，CO_2 还原反应(CO2RR)会产生大量产物，涉及不同数量的转移电子和反应中间体[70]。质谱技术不仅可以定量分析产物，还可以探究反应机理，从而提升 CO_2 还原的研究维度。

Bondue 等[72-73]使用 DEMS 与电解池相结合，通过 DEMS 上离子电流与电化学析出的 CO 量成比例的关系，实现了在线检测 CO_2 还原反应中 CO_2 消耗量、还原形成的氢气和 CO 的量，进而发现增加 CO_2 分压可以提高 CO_2 的还原速率，并抑制质子还原产生氢气，使法拉第效率接近 100%。对 CO_2 反应产物的定量分析可以优化电化学反应条件，推动 CO_2 还原的工业化进程。

Wang 等[74]通过电化学质谱对铜基纳米催化剂(CuO_xNP)在 CO_2/CO 共同进料生产乙烯进行

工艺和机理研究，使用 DEMS 的乙烯离子电流（C_2H_4-H^+产生量）分析循环伏安电极电势扫描期间 C_2H_4 的产率，发现 CO_2/CO 共同进料在阴极和阳极扫描方向上产生了最大增强的乙烯离子电流，并在较宽的电压范围内，CO_2/CO 共同进料具有更高的乙烯生产率。此外，根据 DEMS 测量的同位素实验，可以准确评估每种机制的乙烯动力学起始电位，得到每种机制的动力学特征。在 $^{12}CO_2$/^{12}CO 共进料和 $^{12}CO_2$ 进料下的阴极乙烯产生曲线重合，表明乙烯主要来源于 CO_2 还原后的 *CO（表面吸附 CO）在阴极扫描上的二聚。因此，DEMS 不仅可以检测产物量，优化反应工艺，还可以探究反应机理，根据 CO_2 和 CO 存在不同的表面吸附位点这一思路，为多组分 CO2RR 电催化剂的设计提供指导。

2.4 N_2 还原

电化学氮还原（eNRR）因其使用可再生能源和环境友好性成为生产氨的一种制备工艺[75-76]。尽管已经对 eNRR 催化剂进行了广泛研究，但迄今为止还没有得到最佳的催化剂。依靠质谱技术分析挥发性中间体和产物，进而揭示氮还原的反应机理，是加速 eNRR 催化剂设计开发的重要手段。Yao 等[77]使用 Bi 基金属-有机框架（Bi-MOF）作为前体（预催化剂）研究 eNRR 的机制，使用在线 DEMS 原位测定挥发性电化学反应中间体 N_2H_2 和产物 NH_3，确定了零价铋催化剂上存在还原和分解两步机制。

2.5 有机物合成

高级化学品的电催化合成已成为有机合成的重要分支。Cheng 等[78]将钯电极插入纳米电喷雾电离质谱（nano-ESI-MS）的电喷雾源中，利用 nano-ESI-MS 的固有电化学能力和钯电极的皮摩尔级阳极腐蚀来产生和评估用于温和电催化的高效阳离子催化剂，示于图 4a。在没有外部氧化剂和添加剂的条件下，这种在线筛选电化学过渡金属催化的新型集成平台在室温下几分钟内即可实现电解钯催化的 Suzuki 偶联和电化学 C—H 芳基化，示于图 4b～4f。

此外，质谱在探究有机合成机理中也发挥着重要作用。Tu 等[79]通过原位 DEMS 同位素跟踪实验，揭示了尿素氧化反应（UOR）中分子内 N—N 键偶联机制。

3 用于电化学储能装置的质谱分析技术

与物理储能和化学储能相比，电化学储能在可扩展性、使用寿命、灵活性等方面具有更多优势[80]。近 20 年来，已开发了多种电化学储能装置，包括碱金属离子电池（如锂离子电池、钠离子电池和钾离子电池（KIBs））、超级电容器和锂硫电池[81]。通过质谱技术分析电化学储能装置中的反应产物和反应中间体，可以探索材料的储能本质，为提高材料的储能性能提供了设计原理。

3.1 锂离子电池

自电池商业化以来，锂离子电池（LIBs）一直是便携式电子设备中最主要的电源[82-83]。三元正极材料镍钴锰酸锂因其综合性能高、成本低而逐步超越磷酸铁锂和锰酸锂成为锂离子电池的主流技术路线。对于锂离子电池中储能材料的开发和储能机理的探索已经成为研究热点。

Zhang 等[84]开发了滴定质谱（TMS），并准确量化与氧相关的阴离子氧化还原反应（锂离子电池和镍钴锰（NCM）/富锂阴极）、碳酸盐沉积和分解（空气暴露降解和电解质氧化）以及死锂的形成（锂金属电池和过放电石墨阳极）。在使用 TMS 测定 NCM 中碳酸盐和氧化晶格氧的过程中发现，碳酸盐的电化学分解速率超过了在 $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$（NCM111）上充电超过 4.5 V 之后电解质分解衍生的产生速率，在低含量 $Ni^{3/4+}$、高含量 $Co^{3/4+}$的 NCM 表面电催化/分解目标往往集中在阴极电解质界面（CEI）上，示于图 5。因此，开发抗氧化 CEI（如引入牺牲添加剂以促进 CEI 结构）是限制 NCM111 可逆容量的有效策略。TMS 不仅可获取有关产物的关键信息（如氧化晶格氧和固体电解质相（SEI）/阴极电解质相（CEI）成分的定量），还可以推测出更多提高锂离子电池储能的有力策略。

Zhou 等[85]使用原位液体二次离子质谱（liquid-SIMS）研究了锂离子电池（电解液为溶有双（氟磺酰基）酰亚胺锂（LiFSI）的 1,2-二甲氧基乙烷（DME））中固体电解质界面（铜电极）的形成机制。研究表明，在初始充电过程中，Li^+会引导电解质-溶剂分子的自组装，在电极和电解质之间形成界面双电层。同时，使用原位液体二次离子质谱法结合分子动力学模拟，探究了锂离子电池中 SEI 的形成过程。因而，liquid-SIMS 已成为锂离子电池机理研究的有力工具。

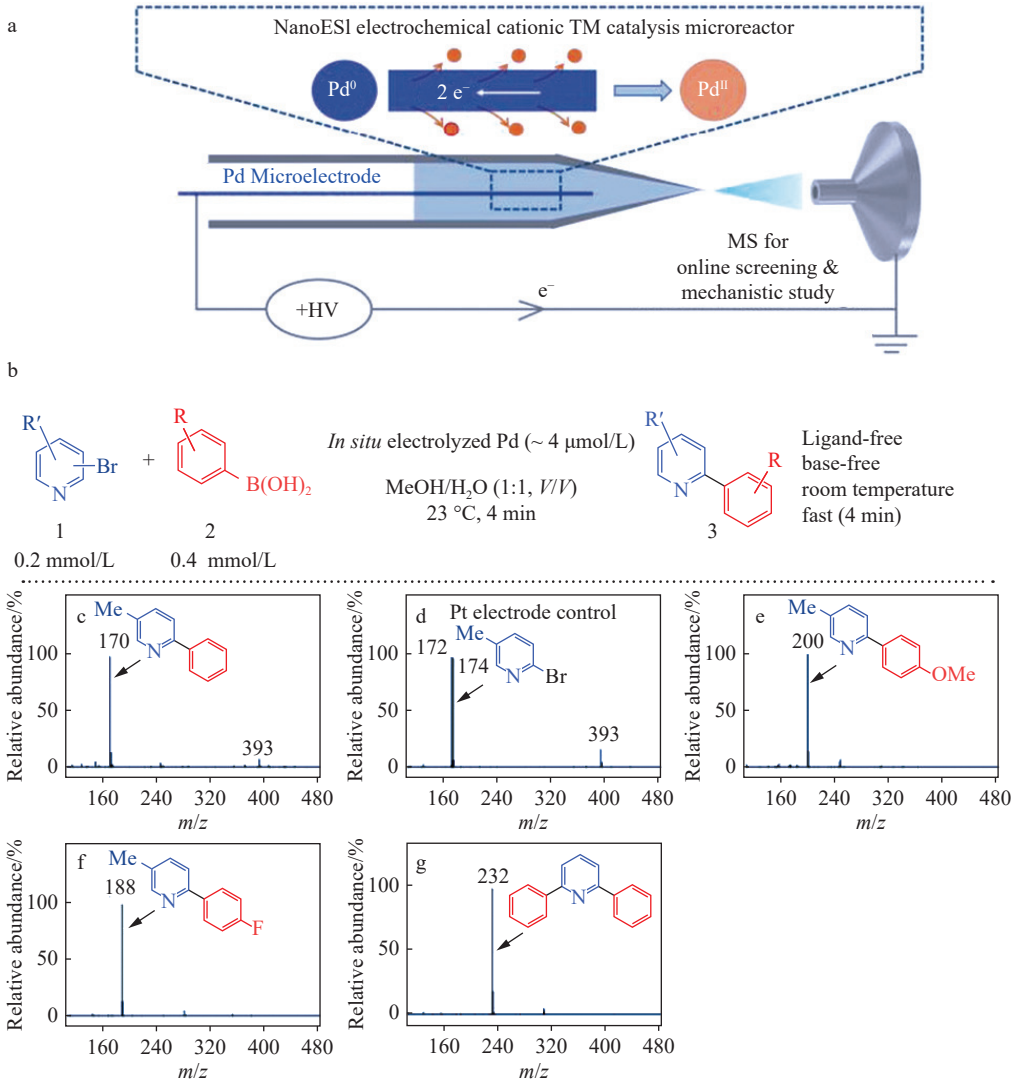

图 4　纳米 ESI 发射极中阳离子 Pd 催化的温和 C—H 官能化反应的过渡金属电化学催化平台示意图(a)，ESI 测得的电解钯催化的无配体和无碱 Suzuki 偶联的反应(b)，反应时间为 4 min 时所测得的质谱图：2-溴-5-甲基吡啶与苯基硼酸的原位电解 Pd 催化的 Suzuki 偶联(c)，用 Pt 电极代替 Pd 电极进行 2-溴-5-甲基吡啶和苯基硼酸反应的对照实验(d)，2-溴-5-甲基吡啶与 4-甲氧基苯基硼酸的反应(e)，2-溴-5-甲基吡啶与 4-氟苯基硼酸的反应(f)，2,6-二溴吡啶与苯基硼酸的反应(g)[78]

Fig. 4　Schematic diagram of the electrochemical transition-metal catalysis platform for cationic Pd-catalyzed mild C—H functionalization reactions in a nano-ESI emitter (a), and reactions for ESI electrolyzed Pd-catalyzed ligand- and base-free Suzuki coupling (b), and mass spectra showing *in situ* electrolyzed Pd-catalyzed Suzuki coupling of 2-bromo-5-methylpyridine with phenylboronic acid (c), and mass spectrum of a control experiment for 2-bromo-5-methylpyridine and phenylboronic acid reaction by replacing Pd electrode with Pt electrode (d), and mass spectrum of 2-bromo-5-methylpyridine with 4-methoxyphenylboronic acid (e), and 2-bromo-5-methylpyridine with 4-fluorophenylboronic acid (f), and 2,6-dibromopyridine with phenylboronic acid (g)[78]

3.2　超级电容器

与传统储能设备相比，超级电容器具有长循环寿命、高比功率和高能量的特点，填补了普通电容器和蓄电池的应用空白[86-87]。碳基材料(如活性炭(AC)、碳纳米管(CNT)、三维分级多孔碳(HPCX)等)具有低成本、易加工、电化学惰性、孔隙率可控和多种活性位点的特性，广泛应用于功率输送要求高的超级电容器中[88]。

Zhang 等[89]在探究以碳前驱体(SP_x)为原料制备的三维分级多孔碳(HPCX)材料在超级电容

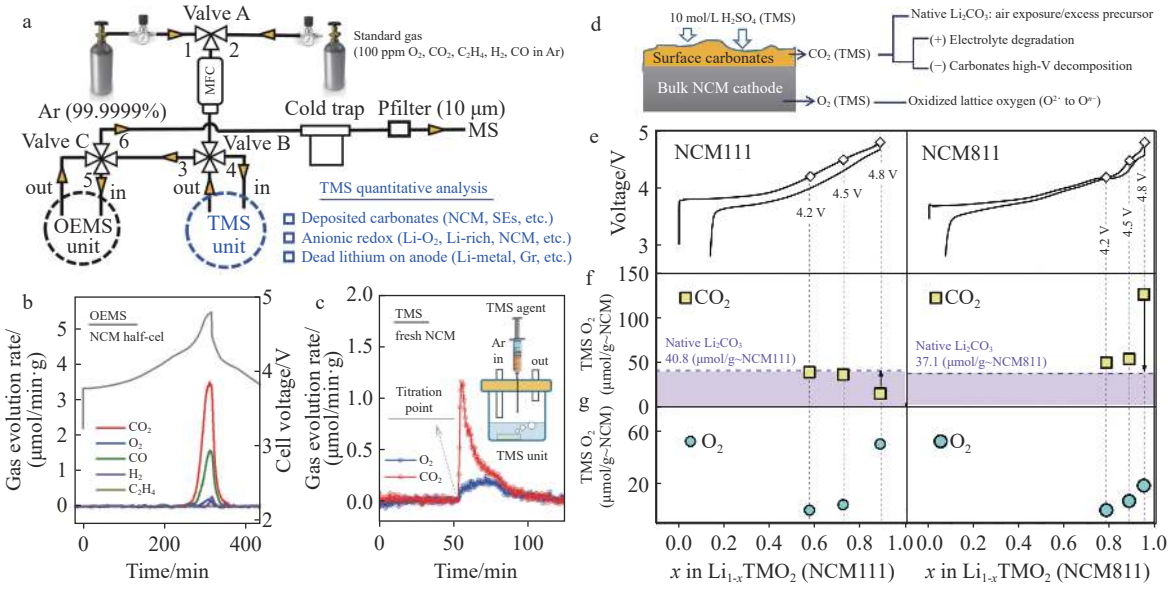

图 5 基于 TMS 和在线电化学质谱(OEMS)的气体分析装置示意图(a),在 NCM 半电池初始循环期间采集的 OEMS 谱图(b),从 NCM 中采集的 TMS 谱图(c),在 NCM 阴极上使用 TMS 分析的机理示意图(d),NCM 初始循环的恒流充放电电压曲线(e),在 4.2、4.5 和 4.8 V 电压下的 TMS 谱图(f, g)[84]

Fig. 5 Schematic of the TMS and online electrochemical mass spectrometry (OEMS)-based gas analysis system (a), OEMS results collected during the initial cycle of the NCM half-cell (b), and TMS results collected from fresh NCM (c), schematic illustration for the mechanism of TMS employed on the charged NCM cathode (d), the galvanostatic charge-discharge voltage profiles of the initial cycles of NCM (e), and the TMS results on specific voltages at 4.2, 4.5 and 4.8 V (f, g)[84]

器中的性能时,使用气相色谱-质谱(GC-MS)和静电场轨道阱质谱(Orbitrap MS)在分子水平上探明了碳前驱体的具体组成,揭示了碳前驱体中的含氮和含氧化合物有助于提高容量、表面极性和导电性的规律,表明高分辨质谱可以统计并挖掘碳材料样品的分子特征,便于比较各样品之间的差异,为揭示反应本质提供了有效手段。

3.3 锂硫电池

锂硫(Li-S)电池因其理论能量密度高和储藏资源丰富的优势而被认为是高研究价值的电池系统[90-91]。然而,可溶性多硫化物的穿梭效应和缓慢的转化阻碍了锂硫电池的实际应用[92-93]。Yu 等[94]通过电化学与质谱联用技术(EC-MS)直接观察到锂硫电池中不稳定的多硫化物中间体,并估计不同电压下多硫化物的相对丰度分布。结合 EC-MS、循环伏安法(CV)和计算模拟,可以探索硫的阴极反应路径,揭示硫的氧化还原动力学特征,为克服可溶性多硫化物锂的穿梭效应、提高锂硫电池性能提供了手段和理论基础。利用质谱技术可以深入了解硫阴极氧化还原反应的机理,为设计新型高性能的阴极提供指导,促进硫的氧化还原动力学的发展。

4 总结与展望

近年来,质谱技术因灵敏度高、直观性好以及可快速检测反应瞬态中间体和反应产物的能力,已成为研究反应机理的有力工具。本文介绍了质谱技术在光催化、电催化和储能装置中反应机理研究的应用。尽管目前质谱技术可以检测瞬态中间体,但在检测浓度较低、稳定性较差的反应中间体时仍是挑战。对此,还需要优化采样系统、缩短采样时间、提高采样效率,以及进一步优化质量分析器的设计,提高质量精度、传输效率和分析速度。未来,对于复杂反应机理的研究,获取反应中间体与反应条件(反应时间、反应波长、反应电位等)的对应关系是重要基础。因此,反应器与质谱之间既要有维持中间体真实形态的空间连接,还要具备准确反映反应参数的信号传输,以降低反应机理的研究难度。另外,采用质谱技术分析反应中间体和产物的形态

和结构等初级信息时，还应结合理论计算，多维度、全方位地构建反应理论体系，推动理论指导实验的交互进程。

参考文献：

[1] WANG Y, LIU Y, XU Z, YIN K, ZHOU Y, ZHANG J, CUI P, MA S, WANG Y, ZHU Z. A review on renewable energy-based chemical engineering design and optimization[J]. Renewable and Sustainable Energy Reviews, 2024, 189: 114 015.

[2] ZHANG L, LIU L, PAN Z, ZHANG R, GAO Z, WANG G, HUANG K, MU X, BAI F, WANG Y, ZHANG W, CUI Z, LI L. Visible-light-driven non-oxidative dehydrogenation of alkanes at ambient conditions[J]. Nature Energy, 2022, 7(11): 1 042-1 051.

[3] LV J, XIE J, MOHAMED A G A, ZHANG X, WANG Y. Photoelectrochemical energy storage materials: design principles and functional devices towards direct solar to electrochemical energy storage[J]. Chemical Society Reviews, 2022, 51(4): 1 511-1 528.

[4] FRENKEL A I, RODRIGUEZ J A, CHEN J G. Synchrotron techniques for *in situ* catalytic studies: capabilities, challenges, and opportunities[J]. ACS Catalysis, 2012, 2(11): 2 269-2 280.

[5] FRENKEL A I, WANG Q, MARINKOVIC N, CHEN J G, BARRIO L, SI R, CÁMARA A L, ESTRELLA A M, RODRIGUEZ J A, HANSON J C. Combining X-ray absorption and X-ray diffraction techniques for *in situ* studies of chemical transformations in heterogeneous catalysis: advantages and limitations[J]. The Journal of Physical Chemistry C, 2011, 115(36): 17 884-17 890.

[6] JIAO Z, SHANG M, LIU J, LU G, WANG X, BI Y. The charge transfer mechanism of Bi modified TiO_2 nanotube arrays: TiO_2 serving as a “charge-transfer-bridge” [J]. Nano Energy, 2017, 31: 96-104.

[7] XIAO J, XIE Y, RABEAH J, BRÜCKNER A, CAO H. Visible-light photocatalytic ozonation using graphitic C_3N_4 catalysts: a hydroxyl radical manufacturer for wastewater treatment[J]. Accounts of Chemical Research, 2020, 53(5): 1 024-1 033.

[8] TAO F F, CROZIER P A. Atomic-scale observations of catalyst structures under reaction conditions and during catalysis[J]. Chemical Reviews, 2016, 116(6): 3 487-3 539.

[9] TAHERI M L, STACH E A, ARSLAN I, CROZIER P A, KABIUS B C, LaGRANGE T, MINOR A M, TAKEDA S, TANASE M, WAGNER J B, SHARMA R. Current status and future directions for *in situ* transmission electron microscopy[J]. Ultramicroscopy, 2016, 170: 86-95.

[10] 杨建正, 周涛, 张见营. 质谱在纳米材料成分及粒径分析中的应用[J]. 质谱学报, 2023, 44(6): 721-738.
YANG Jianzheng, ZHOU Tao, ZHANG Jianying. Application of mass spectrometry in component and particle size analysis of nanomaterials[J]. Journal of Chinese Mass Spectrometry Society, 2023, 44(6): 721-738(in Chinese).

[11] 葛喜洋, 尹伊颜, 欧阳津, 那娜. 基于常压质谱技术的化学反应中间体监测研究进展[J]. 质谱学报, 2024, 45(1): 31-43.
GE Xiyang, YIN Yiyan, OUYANG Jin, NA Na. Recent development on the detection and monitoring of chemical intermediates by ambient mass spectrometry[J]. Journal of Chinese Mass Spectrometry Society, 2024, 45(1): 31-43(in Chinese).

[12] MEJÍA-CARMONA K, SOARES Da SILVA BURATO J, BORSATTO J V B, de TOFFOLI A L, LANÇAS F M. Miniaturization of liquid chromatography coupled to mass spectrometry[J]. TrAC Trends in Analytical Chemistry, 2020, 122: 115 735.

[13] VARGAS MEDINA D A, MACIEL E V S, de TOFFOLI A L, LANÇAS F M. Miniaturization of liquid chromatography coupled to mass spectrometry[J]. TrAC Trends in Analytical Chemistry, 2020, 128: 115 910.

[14] AYALA-CABRERA J F, MONTERO L, MECKELMANN S W, UTESCHIL F, SCHMITZ O J. Review on atmospheric pressure ionization sources for gas chromatography-mass spectrometry. Part I: current ion source developments and improvements in ionization strategies[J]. Analytica Chimica Acta, 2023, 1 238: 340 353.

[15] MA C, XIE L, WANG X, LIANG K, KONG B. Interfacial assembly of functional mesoporous nanomatrices for laser desorption/ionization mass spectrometry[J]. Nano Today, 2022, 42: 101 365.

[16] KIM S, KIM H S, KIM B, KIM Y J, JUNG J W, RYU W H. *In situ* gas analysis by differential electrochemical mass spectrometry for advanced rechargeable batteries: a review[J]. Advanced Energy Materials, 2023, 13(39): 2 301 983.

[17] HU B, YAO Z P. Electrospray ionization mass spectrometry with wooden tips: a review[J]. Analytica Chimica Acta, 2022, 1 209: 339 136.

[18] HE Y, CHEN K, LEUNG M K H, ZHANG Y, LI L, LI G, XUAN J, LI J. Photocatalytic fuel cell-a review[J].

Chemical Engineering Journal, 2022, 428: 131 074.

[19] MECHA A C, CHOLLOM M N. Photocatalytic ozonation of wastewater: a review[J]. Environmental Chemistry Letters, 2020, 18(5): 1 491-1 507.

[20] YANG L, FAN D, LI Z, CHENG Y, YANG X, ZHANG T. A review on the bioinspired photocatalysts and photocatalytic systems[J]. Advanced Sustainable Systems, 2022, 6(5): 2 100 477.

[21] LI Y, YU B, HU Z, WANG H. Construction of direct Z-scheme SnS_2@$ZnIn_2S_4$@kaolinite heterostructure photocatalyst for efficient photocatalytic degradation of tetracycline hydrochloride[J]. Chemical Engineering Journal, 2022, 429: 132 105.

[22] YE L, MA Z, DENG Y, YE Y, LI W, KOU M, XIE H, XU Z, ZHOU Y, XIA D, WONG P K. Robust and efficient photocatalytic hydrogen generation of ReS_2/CdS and mechanistic study by on-line mass spectrometry and *in situ* infrared spectroscopy[J]. Applied Catalysis B: Environmental, 2019, 257: 117 897.

[23] CHEN W P, LIAO P Q, JIN P B, ZHANG L, LING B K, WANG S C, CHAN Y T, CHEN X M, ZHENG Y Z. The gigantic$\{Ni_{36}Gd_{102}\}$hexagon: a sulfate-templated "star-of-David" for photocatalytic CO_2 reduction and magnetic cooling[J]. Journal of the American Chemical Society, 2020, 142(10): 4 663-4 670.

[24] ZU X, ZHAO Y, LI X, CHEN R, SHAO W, WANG Z, HU J, ZHU J, PAN Y, SUN Y, XIE Y. Ultrastable and efficient visible-light-driven CO_2 reduction triggered by regenerative oxygen-vacancies in Bi_2 O_2 CO_3 nanosheets[J]. Angewandte Chemie (International Ed in English), 2021, 60(25): 13 840-13 846.

[25] WANG L, XIA Y, YU J. Hydrogen-bond activation of N_2 molecules and photocatalytic nitrogen fixation[J]. Chem, 2021, 7(8): 1 983-1 985.

[26] WU L, WAN Q, NIE W, HAO Y, FENG G, CHEN M, CHEN S. High-throughput nano-electrostatic-spray ionization/photoreaction mass spectrometric platform for the discovery of visible-light-activated photocatalytic reactions in the picomole scale[J]. Analytical Chemistry, 2021, 93(43): 14 560-14 567.

[27] ZHOU C, LAI C, XU P, ZENG G, HUANG D, ZHANG C, CHENG M, HU L, WAN J, LIU Y, XIONG W, DENG Y, WEN M. *In situ* grown AgI/$Bi_{12}O_{17}Cl_2$ heterojunction photocatalysts for visible light degradation of sulfamethazine: efficiency, pathway, and mechanism[J]. ACS Sustainable Chemistry & Engineering, 2018, 6(3): 4 174-4 184.

[28] MU R, AO Y, WU T, WANG C, WANG P. Synthesis of novel ternary heterogeneous anatase-TiO_2 (B) biphase nanowires/$Bi_4O_5I_2$ composite photocatalysts for the highly efficient degradation of acetaminophen under visible light irradiation[J]. Journal of Hazardous Materials, 2020, 382: 121 083.

[29] LIANG Q, LIU X, WANG J, LIU Y, LIU Z, TANG L, SHAO B, ZHANG W, GONG S, CHENG M, HE Q, FENG C. *In-situ* self-assembly construction of hollow tubular g-C_3N_4 isotype heterojunction for enhanced visible-light photocatalysis: experiments and theories[J]. Journal of Hazardous Materials, 2021, 401: 123 355.

[30] HAO C C, TANG Y B, SHI W L, CHEN F Y, GUO F. Facile solvothermal synthesis of a Z-scheme 0D/3D CeO_2/$ZnIn_2S_4$ heterojunction with enhanced photocatalytic performance under visible light irradiation[J]. Chemical Engineering Journal, 2021, 409: 128 168.

[31] LI S, CAI M, WANG C, LIU Y. Ta_3N_5/CdS core-shell S-scheme heterojunction nanofibers for efficient photocatalytic removal of antibiotic tetracycline and Cr(VI): performance and mechanism insights[J]. Advanced Fiber Materials, 2023, 5(3): 994-1 007.

[32] LI S, WANG C, LIU Y, CAI M, WANG Y, ZHANG H, GUO Y, ZHAO W, WANG Z, CHEN X. Photocatalytic degradation of tetracycline antibiotic by a novel $Bi_2Sn_2O_7$/Bi_2MoO_6 S-scheme heterojunction: performance, mechanism insight and toxicity assessment[J]. Chemical Engineering Journal, 2022, 429: 132 519.

[33] LUO Y, ZHENG A, LI J, HAN Y, XUE M, ZHANG L, YIN Z, XIE C, CHEN Z, JI L, HONG Z, XIE X. Integrated adsorption and photodegradation of tetracycline by bismuth oxycarbonate/biochar nanocomposites[J]. Chemical Engineering Journal, 2023, 457: 141 228.

[34] PAN T, CHEN D, XU W, FANG J, WU S, LIU Z, WU K, FANG Z. Anionic polyacrylamide-assisted construction of thin 2D-2D WO_3/g-C_3N_4 Step-scheme heterojunction for enhanced tetracycline degradation under visible light irradiation[J]. Journal of Hazardous Materials, 2020, 393: 122 366.

[35] TANG Y, LI T, XIAO W, HUANG Z, WEN H, SITU W, SONG X. Degradation mechanism and pathway of tetracycline in milk by heterojunction N-TiO_2-Bi_2WO_6 film under visible light[J]. Food Chemistry, 2023, 401: 134 082.

[36] YANG R, ZHU Z, HU C, ZHONG S, ZHANG L, LIU B, WANG W. One-step preparation (3D/2D/2D) $BiVO_4$/$FeVO_4$@rGO heterojunction composite photocatalyst for the removal of tetracycline and hexavalent chromium ions in water[J]. Chemical Engineering Journal, 2020,

390: 124 522.

[37] GUO F, HUANG X, CHEN Z, CAO L, CHENG X, CHEN L, SHI W. Construction of Cu_3P-$ZnSnO_3$-g-C_3N_4 p-n-n heterojunction with multiple built-in electric fields for effectively boosting visible-light photocatalytic degradation of broad-spectrum antibiotics[J]. Separation and Purification Technology, 2021, 265: 118 477.

[38] HUANG J, LI D, LI R, ZHANG Q, CHEN T, LIU H, LIU Y, LV W, LIU G. An efficient metal-free phosphorus and oxygen Co-doped g-C_3N_4 photocatalyst with enhanced visible light photocatalytic activity for the degradation of fluoroquinolone antibiotics[J]. Chemical Engineering Journal, 2019, 374: 242-253.

[39] CAI M, LIU Y, WANG C, LIN W, LI S. Novel $Cd_{0.5}Zn_{0.5}S/Bi_2MoO_6$ S-scheme heterojunction for boosting the photodegradation of antibiotic enrofloxacin: degradation pathway, mechanism and toxicity assessment[J]. Separation and Purification Technology, 2023, 304: 122 401.

[40] WEN X J, NIU C G, ZHANG L, LIANG C, GUO H, ZENG G M. Photocatalytic degradation of ciprofloxacin by a novel Z-scheme CeO_2-Ag/AgBr photocatalyst: influencing factors, possible degradation pathways, and mechanism insight[J]. Journal of Catalysis, 2018, 358: 141-154.

[41] HUNGE Y M, YADAV A A, KANG S W, LIM S J, KIM H. Visible light activated MoS_2/ZnO composites for photocatalytic degradation of ciprofloxacin antibiotic and hydrogen production[J]. Journal of Photochemistry and Photobiology A: Chemistry, 2023, 434: 114 250.

[42] HE Y, QIAN J, WANG P, WU J, LU B, TANG S, GAO P. Acceleration of levofloxacin degradation by combination of multiple free radicals via MoS_2 anchored in manganese ferrite doped perovskite activated PMS under visible light[J]. Chemical Engineering Journal, 2022, 431: 133 933.

[43] LI S, WANG C, CAI M, YANG F, LIU Y, CHEN J, ZHANG P, LI X, CHEN X. Facile fabrication of TaON/Bi_2MoO_6 core-shell S-scheme heterojunction nanofibers for boosting visible-light catalytic levofloxacin degradation and Cr(VI) reduction[J]. Chemical Engineering Journal, 2022, 428: 131 158.

[44] LUO D, ZHU P, DUAN M, LIU M, LU H, HUANG Z. Mechanism and degradation pathways insight of photocatalytic oxidation antibiotics by geometrical Ag/$AgNbO_3$/$BiVO_4$ plasmon Z-type heterojunction[J]. Separation and Purification Technology, 2023, 311: 123 287.

[45] IDRISS H. Hydrogen production from water: past and present[J]. Current Opinion in Chemical Engineering, 2020, 29: 74-82.

[46] YANG M, YARNELL J E, EL ROZ K, CASTELLANO F N. A robust visible-light-harvesting cyclometalated Ir(III) diimine sensitizer for homogeneous photocatalytic hydrogen production[J]. ACS Applied Energy Materials, 2020, 3(2): 1 842-1 853.

[47] HUANG J, LI X, JIN X, WANG L, DENG Y, SU F, WONG P K, YE L. High-efficiency and stable photocatalytic hydrogen evolution of rhenium sulfide co-catalyst on $Zn_{0.3}Cd_{0.7}S$[J]. Materials Advances, 2020, 1(3): 363-370.

[48] ZHAO Y, WATERHOUSE G I N, CHEN G, XIONG X, WU L Z, TUNG C H, ZHANG T. Two-dimensional-related catalytic materials for solar-driven conversion of CO_x into valuable chemical feedstocks[J]. Chemical Society Reviews, 2019, 48(7): 1 972-2 010.

[49] TERHOLSEN H, HUERTA-ZERÓN H D, MÖLLER C, JUNGE H, BELLER M, BORNSCHEUER U T. Photocatalytic CO_2 reduction using CO_2-binding enzymes[J]. Angewandte Chemie (International Ed in English), 2024, 63(16): e202319313.

[50] CHEN G, WATERHOUSE G I N, SHI R, ZHAO J, LI Z, WU L Z, TUNG C H, ZHANG T. From solar energy to fuels: recent advances in light-driven C(1) chemistry[J]. Angewandte Chemie (International Ed in English), 2019, 58(49): 17 528-17 551.

[51] SEH Z W, KIBSGAARD J, DICKENS C F, CHORKENDORFF I, NØRSKOV J K, JARAMILLO T F. Combining theory and experiment in electrocatalysis: insights into materials design[J]. Science, 2017, 355(6 321): eaad4998.

[52] KRISHNAN A, AJITH A, KRISHNAN A V, SAJI R E, SYAMLI S, SHIBLI S M A. Ni-based electro/photo-catalysts in HER-a review[J]. Surfaces and Interfaces, 2023, 36: 102 619.

[53] YIN H, RONG F, XIE Y. A review of typical transition metal phosphides electrocatalysts for hydrogen evolution reaction[J]. International Journal of Hydrogen Energy, 2024, 52: 350-375.

[54] ZHAO X, HE D, XIA B Y, SUN Y, YOU B. Ambient electrosynthesis toward single-atom sites for electrocatalytic green hydrogen cycling[J]. Advanced Materials, 2023, 35(14): e2210703.

[55] DÍAZ-COELLO S, AFONSO M M, PALENZUELA J A, PASTOR E, GARCÍA G. Composite materials from transition metal carbides and ionic liquids as electrocatalyst for hydrogen evolution in alkaline media[J]. Journal of

Electroanalytical Chemistry, 2021, 898: 115 620.

[56] DÍAZ-COELLO S, PALENZUELA J A, AFONSO M M, PASTOR E, GARCÍA G. WC modified with ionic liquids for the hydrogen evolution reaction in alkaline solution[J]. Journal of Electroanalytical Chemistry, 2021, 880: 114 878.

[57] BAZAN-AGUILAR A, GARCÍA G, PASTOR E, RODRÍGUEZ J L, BAENA-MONCADA A M. *In-situ* spectroelectrochemical study of highly active Ni-based foam electrocatalysts for hydrogen evolution reaction[J]. Applied Catalysis B: Environmental, 2023, 336: 122 930.

[58] DÍAZ-COELLO S, GARCÍA G, ARÉVALO M C, PASTOR E. Precise determination of Tafel slopes by DEMS. Hydrogen evolution on tungsten-based catalysts in alkaline solution[J]. International Journal of Hydrogen Energy, 2019, 44(25): 12 576-12 582.

[59] ZHANG K, ZOU R. Advanced transition metal-based OER electrocatalysts: current status, opportunities, and challenges[J]. Small, 2021, 17(37): 2 100 129.

[60] YU H, KE J, SHAO Q. Two dimensional Ir-based catalysts for acidic OER[J]. Small, 2023, 19(48): 2 304 307.

[61] O'M BOCKRIS J, SHAMSHUL HUQ A K M. The mechanism of the electrolytic evolution of oxygen on platinum[J]. Proceedings of the Royal Society of London Series A, 1956, 237(1 209): 277-296.

[62] ANANTHARAJ S, KUNDU S, NODA S. "The Fe Effect": a review unveiling the critical roles of Fe in enhancing OER activity of Ni and Co based catalysts[J]. Nano Energy, 2021, 80: 105 514.

[63] KARMAKAR A, KARTHICK K, SANKAR S S, KUMARAVEL S, MADHU R, KUNDU S. A vast exploration of improvising synthetic strategies for enhancing the OER kinetics of LDH structures: a review[J]. Journal of Materials Chemistry A, 2021, 9(3): 1 314-1 352.

[64] SHAHZAD A, ZULFIQAR F, ARIF NADEEM M. Cobalt containing bimetallic ZIFs and their derivatives as OER electrocatalysts: a critical review[J]. Coordination Chemistry Reviews, 2023, 477: 214 925.

[65] ZENG F, MEBRAHTU C, LIAO L, BEINE A K, PALKOVITS R. Stability and deactivation of OER electrocatalysts: a review[J]. Journal of Energy Chemistry, 2022, 69: 301-329.

[66] HUANG J, SHENG H, ROSS R D, HAN J, WANG X, SONG B, JIN S. Modifying redox properties and local bonding of Co_3O_4 by CeO_2 enhances oxygen evolution catalysis in acid[J]. Nature Communications, 2021, 12(1): 3 036.

[67] LIN C, LI J L, LI X, YANG S, LUO W, ZHANG Y, KIM S H, KIM D H, SHINDE S S, LI Y F, LIU Z P, JIANG Z, LEE J H. *In-situ* reconstructed Ru atom array on α-MnO_2 with enhanced performance for acidic water oxidation[J]. Nature Catalysis, 2021, 4(12): 1 012-1 023.

[68] SONG F, BUSCH M M, LASSALLE-KAISER B, HSU C S, PETKUCHEVA E, BENSIMON M, CHEN H M, CORMINBOEUF C, HU X. An unconventional iron nickel catalyst for the oxygen evolution reaction[J]. ACS Central Science, 2019, 5(3): 558-568.

[69] ZHANG Q, XIAO W, FU H C, LI X L, LEI J L, LUO H Q, LI N B. Unraveling the mechanism of self-repair of NiFe-based electrocatalysts by dynamic exchange of iron during the oxygen evolution reaction[J]. ACS Catalysis, 2023, 13(22): 14 975-14 986.

[70] NITOPI S, BERTHEUSSEN E, SCOTT S B, LIU X, ENGSTFELD A K, HORCH S, SEGER B, STEPHENS I E L, CHAN K, HAHN C, NØRSKOV J K, JARAMILLO T F, CHORKENDORFF I. Progress and perspectives of electrochemical CO_2 reduction on copper in aqueous electrolyte[J]. Chemical Reviews, 2019, 119(12): 7 610-7 672.

[71] GAO D, ARÁN-AIS R M, JEON H S, ROLDAN CUENYA B. Rational catalyst and electrolyte design for CO_2 electroreduction towards multicarbon products[J]. Nature Catalysis, 2019, 2(3): 198-210.

[72] BONDUE C J, KOPER M T M. A DEMS approach for the direct detection of CO formed during electrochemical CO_2 reduction[J]. Journal of Electroanalytical Chemistry, 2020, 875: 113 842.

[73] BONDUE C J, GRAF M, GOYAL A, KOPER M T M. Suppression of hydrogen evolution in acidic electrolytes by electrochemical CO_2 reduction[J]. Journal of the American Chemical Society, 2021, 143(1): 279-285.

[74] WANG X, de ARAÚJO J F, JU W, BAGGER A, SCHMIES H, KÜHL S, ROSSMEISL J, STRASSER P. Mechanistic reaction pathways of enhanced ethylene yields during electroreduction of CO_2-CO co-feeds on Cu and Cu-tandem electrocatalysts[J]. Nature Nanotechnology, 2019, 14(11): 1 063-1 070.

[75] KUMAR J, MOHAN N G, GURUSAMY T, GORANTLA S M N V T, RAVICHANDRAN P, MONDAL K C, RAMANUJAM K. Electrochemical dinitrogen to ammonia reduction at a nickel(ii) site: an easy access to an air-stable catalyst[J]. Journal of Materials Chemistry A, 2024, 12(8): 4 473-4 483.

[76] YAO Y, ZHU S, WANG H, LI H, SHAO M. A spectro-

scopic study of electrochemical nitrogen and nitrate reduction on rhodium surfaces[J]. Angewandte Chemie (International Ed in English), 2020, 59(26): 10 479-10 483.

[77] YAO D, TANG C, LI L, XIA B, VASILEFF A, JIN H, ZHANG Y, QIAO S Z. *In situ* fragmented bismuth nanoparticles for electrocatalytic nitrogen reduction[J]. Advanced Energy Materials, 2020, 10(33): 2 001 289.

[78] CHENG H, YANG T, EDWARDS M, TANG S, XU S, YAN X. Picomole-scale transition metal electrocatalysis screening platform for discovery of mild C–C coupling and C–H arylation through *in situ* anodically generated cationic Pd[J]. Journal of the American Chemical Society, 2022, 144(3): 1 306-1 312.

[79] TU Z, LIU X, XIONG D, WANG J, GONG S, XU C, WU D, CHEN Z. Ultrafast room-temperature activation of nickel foams as highly efficient electrocatalysts[J]. Chemical Engineering Journal, 2023, 475: 146 253.

[80] LV Z, LI W, YANG L, LOH X J, CHEN X. Custom-made electrochemical energy storage devices[J]. ACS Energy Letters, 2019, 4(2): 606-614.

[81] CAI W, YAN C, YAO Y X, XU L, XU R, JIANG L L, HUANG J Q, ZHANG Q. Rapid lithium diffusion in Order@Disorder pathways for fast-charging graphite anodes[J]. Small Structures, 2020, 1(1): 2 070 001.

[82] LI S, WANG K, ZHANG G, LI S, XU Y, ZHANG X, ZHANG X, ZHENG S, SUN X, MA Y. Fast charging anode materials for lithium-ion batteries: current status and perspectives[J]. Advanced Functional Materials, 2022, 32(23): 2 200 796.

[83] WANG X X, GUAN D H, MIAO C L, LI J X, LI J Y, YUAN X Y, MA X Y, XU J J. Boundary-free metal-organic framework glasses enable highly stable all-solid-state lithium-oxygen battery[J]. Advanced Energy Materials, 2024, 14(5): 2 303 829.

[84] ZHANG H, CHEN J, HONG Y, WU X, HUANG X, DAI P, LUO H, ZHANG B, QIAO Y, SUN S G. Titration mass spectroscopy (TMS): a quantitative analytical technology for rechargeable batteries[J]. Nano Letters, 2022, 22(24): 9 972-9 981.

[85] ZHOU Y, SU M, YU X, ZHANG Y, WANG J G, REN X, CAO R, XU W, BAER D R, DU Y, BORODIN O, WANG Y, WANG X L, XU K, XU Z, WANG C, ZHU Z. Real-time mass spectrometric characterization of the solid-electrolyte interphase of a lithium-ion battery[J]. Nature Nanotechnology, 2020, 15(3): 224-230.

[86] ZHU Y, MURALI S, STOLLER M D, GANESH K J, CAI W, FERREIRA P J, PIRKLE A, WALLACE R M, CYCHOSZ K A, THOMMES M, SU D, STACH E A, RUOFF R S. Carbon-based supercapacitors produced by activation of graphene[J]. Science, 2011, 332(6 037): 1 537-1 541.

[87] ZHANG L L, ZHAO X S. Carbon-based materials as supercapacitor electrodes[J]. Chemical Society Reviews, 2009, 38(9): 2 520-2 531.

[88] FRACKOWIAK E. Carbon materials for supercapacitor application[J]. Physical Chemistry Chemical Physics, 2007, 9(15): 1 774.

[89] ZHANG X, SUN B, FAN X, BAI H, LIANG P, ZHAO G, SAIKIA B K, WEI X. Building relationships between molecular composition of carbon precursor and capacitance of a hierarchical porous carbon-based supercapacitor[J]. ACS Applied Energy Materials, 2021, 4(1): 985-995.

[90] FENG S, FU Z H, CHEN X, ZHANG Q. A review on theoretical models for lithium-sulfur battery cathodes[J]. InfoMat, 2022, 4(3): e12304.

[91] HE J, MANTHIRAM A. A review on the status and challenges of electrocatalysts in lithium-sulfur batteries[J]. Energy Storage Materials, 2019, 20: 55-70.

[92] CHEN Z X, ZHAO M, HOU L P, ZHANG X Q, LI B Q, HUANG J Q. Toward practical high-energy-density lithium-sulfur pouch cells: a review[J]. Advanced Materials, 2022, 34(35): e2201555.

[93] WANG J, HAN W Q. A review of heteroatom doped materials for advanced lithium-sulfur batteries[J]. Advanced Functional Materials, 2022, 32(2): 2 107 166.

[94] YU Z, SHAO Y, MA L, LIU C, GU C, LIU J, HE P, LI M, NIE Z, PENG Z, SHAO Y. Revealing the sulfur redox paths in a Li-S battery by an *in situ* hyphenated technique of electrochemistry and mass spectrometry[J]. Advanced Materials, 2022, 34(7): e2106618.

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