

河南省本科高校青年骨干教师考核报告

支撑材料

项目名称：基于喹啉酮的锌离子荧光传感器的机理及其在生化体系中的应用研究

起止时间：2021 年 9 月至2026 年 8 月

培养对象姓名：姜松 专业技术职务：副教授

学 校：河南农业大学

目录

一、教学科研项目	1
1. 河南省自然科学基金项目	1
2. 河南省科技副总项目	2
3. 校企横向合作项目	3
4. 河南省博士服务团项目	5
5. 河南农业大学教改项目（重点项目）	7
6. 河南农业大学教改项目 1	8
7. 河南农业大学本科课程项目	9
8. 河南农业大学本科课程考核改革项目	10
9. 河南农业大学教改项目 2	11
10. 河南农业大学在线开放课程项目	12
二、获奖情况	13
1. 河南农业大学本科课堂教学质量奖特等奖	13
2. 河南省人力资源和社会保障厅嘉奖	14
3. 河南农业大学本科高等教育教学成果奖二等奖	15
4. 河南省优秀科技论文一等奖	16
5. 河南省高等教育教学成果奖二等奖	17
6. 河南农业大学本科高等教育教学成果奖一等奖	18
7. 河南省教育系统教学技能竞赛一等奖	19
8. 河南省教育系统教学技能竞赛一等奖	20
三、代表性论文	21

1. Dual-Stimulus Chiroptical Switch of Tetrastable [3]Rotaxanes, Org. Lett. 2026, 28, 7821–7826. (SCI, 中科院一区, TOP 期刊)	21
2. Visible-light-induced dynamic luminescence of cascaded assembly by in situ directional photoisomerization for time-resolved information encryption. Dyes and Pigments, 2026, 255, 114067. (SCI)	27
3. 二维介孔材料在微型超级电容器中的应用进展. 储能科学与技术, 2026, 15(2), 458-478. (中文核心, CSCD)	35
4. 以农为导, “有机化学”课程助力强农人才培养的教学探索与实践. 科技风, 2026, 34-37.	56
5. 农业院校有机化学教学设计与实践——以醚为例. 科教导刊(电子版), 2025, 19, 50-53.	59
6. 乙二胺修饰的吸附树脂合成及其对水中苯酚的吸附性能研究. 湖北大学学报(自然科学版), 2023, 45(3), 460-466.	63
四、代表性著作	70
1. 普通高等教育十四五规划教材《普通化学》, 副主编	70
2. 大国三农系列规划教材《有机化学实验》, 副主编	72
3. 新形态一体化教材《有机化学实验》, 副主编	74

一、教学科研项目

1. 河南省自然科学基金项目

	
河南省自然科学基金项目 结题证书	项目名称: 葫芦脲介导的光控超分子发光体系的构筑及光反应研究
(证书编号: 20240184)	资助类别: 面上项目
该项目提交的研究资料完整, 结题报告系统详实, 经审查符合结 题要求, 准予结题。	项目编号: 232300420132
	依托单位: 河南农业大学
2024 年 7 月 26 日	项目负责人: 刘国星
	项目参与人 (共 5 名) : 姜松, 党玉丽, 李瑞歌, 田长明, 范新慧

2. 河南省科技副总项目



3. 校企横向合作项目

合同编号：

技术开发（委托）合同

项目名称：新型异噁唑类杀虫剂 D156 及其关键中间体的工艺路线研究及产业化开发

委托方（甲方）：河南玄和医药科技有限公司

受托方（乙方）：河南农业大学

签订时间：2025 年 12 月

签订地点：河南郑州

有效期限：2025 年 12 月至 2028 年 12 月

中华人民共和国科学技术部印制

第二十七条 本合同一式四份，具有同等法律效力。

第二十八条 本合同经双方签字盖章后生效。

甲方： 河南玄和医药科技有限公司 (盖章)

法定代表人/委托代理人： 梅佳艳 (签名)



年 月 日



乙方： 河南农业大学 (盖章)

法定代表人/委托代理人： 姜林 (签名)



2025年12月12日

4. 河南省博士服务团项目

中共河南省委人才工作领导小组办公室文件

豫人才办〔2025〕3号

关于做好 2025年省派博士服务团 到岗安置工作的通知

各省辖市党委组织部、济源示范区党工委组织部、航空港区党工委组织部人事处，省直机关各单位组织人事部门，省管各企业、高等院校、科研院所党委组织部：

为全面贯彻落实习近平总书记在豫考察时重要讲话精神和关于河南工作的重要论述，聚焦落实省委十一届九次全会部署和“1+2+4+N”目标任务体系，着力服务推动现代化产业体系和农业强省建设，根据按需选派、条件过硬、人岗相适的原则，经岗位征集、推荐报名、择优比选等程序，研究确定何婷等240名同志为我省2025年省派博士服务团成员。现就到岗工作有关事宜通知如下：

1

张婷婷 郑州大学生态与环境学院讲师

安 超 郑州大学第二附属医院检验科主管技师

李 阳 河南农业大学园艺学院设施农业科学与工程系副主任

周琼琼 河南农业大学园艺学院副教授

姜 松 河南农业大学理学院副教授

武晓霞 河南农业大学理学院副教授

慕文龙 河南农业大学机电工程学院副教授

张 曼 河南师范大学水产学院重点学科秘书

王仁杰 河南工业大学材料科学与工程学院副教授

郭 辉 河南工业大学数学与统计学院副教授

田 园 河南工业大学小麦和玉米深加工国家工程研究中心
讲师

王 冠 河南财经政法大学法学部副教授

顾 波 华北水利水电大学电气工程学院教授

蒋正权 华北水利水电大学特种摩擦与润滑材料研究所所长

韩 澎 华北水利水电大学材料学院科研与学科办公室主任

程龄贺 华北水利水电大学材料学院讲师

戴 力 华北水利水电大学生态环境学院讲师

张 贺 河南中医药大学第二附属医院皮肤科主治医师

熊加斌 中原工学院应用化学系副主任

高广帅 中原工学院电子信息工程系副主任

马绍朔 商丘师范学院电子电气工程学院讲师

- 5 -

5. 河南农业大学教改项目（重点项目）

河南农业大学文件

农大教〔2025〕10号

河南农业大学关于公布2025年本科
教育教学改革研究与实践项目立项的通知

各学院，校直各单位：

为进一步深化学校本科教育教学改革，提升人才培养质量，根据《关于申报2025年校级本科教育教学改革研究与实践项目的通知》，学校组织了2025年校级本科教育教学改革研究与实践项目的申报与评审工作。经个人申报、学院推荐、专家评审、公示，共确定立项207项本科教育教学改革研究与实践项目，其中揭榜项目5项，重点项目42项，青年教师项目160项。

学校对立项的揭榜项目和重点项目给予经费支持，其中揭榜项目4万元，重点项目1.8万元。同时，鼓励各单位给予校级立项的青年教师项目经费支持，鼓励各学院、许昌校区对未获校级立项申报项目予以院级立项。

— 1 —

项目编号	项目名称	主持人	主要成员	项目类别
2025XJGLX041	生成式人工智能赋能“汽车理论”课程教学改革探索	慕文龙	王振伟、郭文翠、高献坤、王艳红、冯珀楠、朱才华、时雪	重点项目
2025XJGLX042	基于“AI（人工智能）+HI（人类智能）”的探究式教学模式实践与应用	云菲	任天宝、时向东、孙亚楠、赵园园、唐飞虎	重点项目
2025XJGLX043	基于知识图谱的《数据库系统原理》课程智慧教学研究	刘倩	刘盼、乔红波、孙昌霞、李杨	重点项目
2025XJGLX044	基于知识图谱的AI赋能《有机化学》智慧教学模式的研究与实践	姜松	刘国星、潘振良、吴璐璐、秦洁琼、魏民	重点项目
2025XJGLX045	基于Gen、AI的大学英语教学改革研究与实践	周亚楠	刘佳、张科、宋荣超、李敬浩、刘甜、刘冰	重点项目
2025XJGLX046	面向新农科的数智化教学资源库建设与共享机制研究	丁松爽	刘冰洋、时向东、黄五星、闫筱筱、王静	重点项目
2025XJGLX047	虚拟仿真教学在食品质量与安全专业工程认证中的应用探索	王小鹏	王银平、张剑、赵改名、索标、贾若萌、闫爽	重点项目
2025XJGLX048	高等院校智慧农业产教融合模式与专业人才培养路径研究	束美艳	乔红波、郭伟、岳继博	青年教师项目
2025XJGLX049	AI驱动下智慧农业创新人才培养机制研究	葛士里	刘合兵、郑光、曹妍、车银超	青年教师项目
2025XJGLX050	中原农耕文明融入涉农高校大学英语课程研究	张科	张帅梁、刘艳君、张海红、周亚楠、李楠	青年教师项目
2025XJGLX051	古今中西之争视域下中国式现代化融入“纲要课”教学的叙事逻辑与关键路径研究	王俏蕊	郭武莉、王榆芳、曹倩倩、于净懿	青年教师项目

— 7 —

6. 河南农业大学教改项目 1

河南农业大学本科教学改革研究与实践项目

结项证书

证书编号: 2022073

项目名称: 新农科背景下基于 MOOC 的线上线下混合式教学模式探索与研究

主持人: 姜 松

主要成员: 徐翠莲 潘振良 苏同福 郑 昕 曹占奇

本项目经审核准予结项, 特发此证。



7. 河南农业大学本科课程项目

河南农业大学文件

农大教〔2024〕7号

关于公布 2024 年度河南农业大学
教学工程项目立项名单的通知

各学院，校直各单位：

为进一步提高本科教学质量，学校开展了本科新专业建设提质增效项目、课程类项目及实践教学基地项目等教学工程项目的立项建设工作。经学院申报、学校组织评审、网上公示，决定立项建设 108 项教学工程项目（名单见附件）。

各项目负责人及学院要高度重视项目实施，优化教学资源配
置，注重建设成效，促进本科教育教学质量再上新台阶。

特此通知。

— 1 —

序号	项目编号	课程名称	课程类别	支持经费 (万元)	课程负责人	学院
33	2024KC33	普通生物学II	课程思政示范课	1	邵毅贞	生命科学学院
34	2024KC34	现代汉语	课程思政示范课	1	吴 亮	文法学院
35	2024KC35	习近平法治思想概论	课程思政示范课	1	赵菊敏	文法学院
36	2024KC36	党的民族宗教政策	课程思政示范课	1	陈书章	党委统战部
37	2024KC37	动物解剖学	课程思政示范课	1	金 鑫	动物医学院
38	2024KC38	统计学	课程思政示范课	1	刘俊娟	信息与管理科学学院
39	2024KC39	动物遗传学	课程思政示范课	1	李春丽	动物科技学院
40	2024KC40	节能技术与工程	课程思政示范课	1	赵淑薇	机电工程学院
41	2024KC41	大气污染控制工程	课程思政示范课	1	袁 远	林学院
42	2024KC42	有机化学	课程思政示范课	1	姜 松	理学院
43	2024KC43	食品安全学	课程思政示范课	1	黄现育	食品科学技术学院
44	2024KC44	食品工艺学	课程思政示范课	1	李 真	食品科学技术学院
45	2024KC45	英语演讲	课程思政示范课	1	宋 扬	外国语学院
46	2024KC46	概率论与数理统计	课程思政示范课	1	王建平	信息与管理科学学院
47	2024KC47	烟草化学	课程思政示范课	1	武志勇	烟草学院
48	2024KC48	卷烟产品设计	“专创融合”特色示范课	1	王欢欢	烟草学院
49	2024KC49	测树学	“专创融合”特色示范课	1	郭 芳	林学院

— 6 —

8. 河南农业大学本科课程考核改革项目

首页

机构设置

规章制度

培养方案

本科教学质量工程

质量文化

师德师风

服务指南

下载中心

联系我们

通知公告

当前位置：首页 > 通知公告 > 教务科 >

关于2025-2026学年本科课程考核改革项目结项评审结果的公示

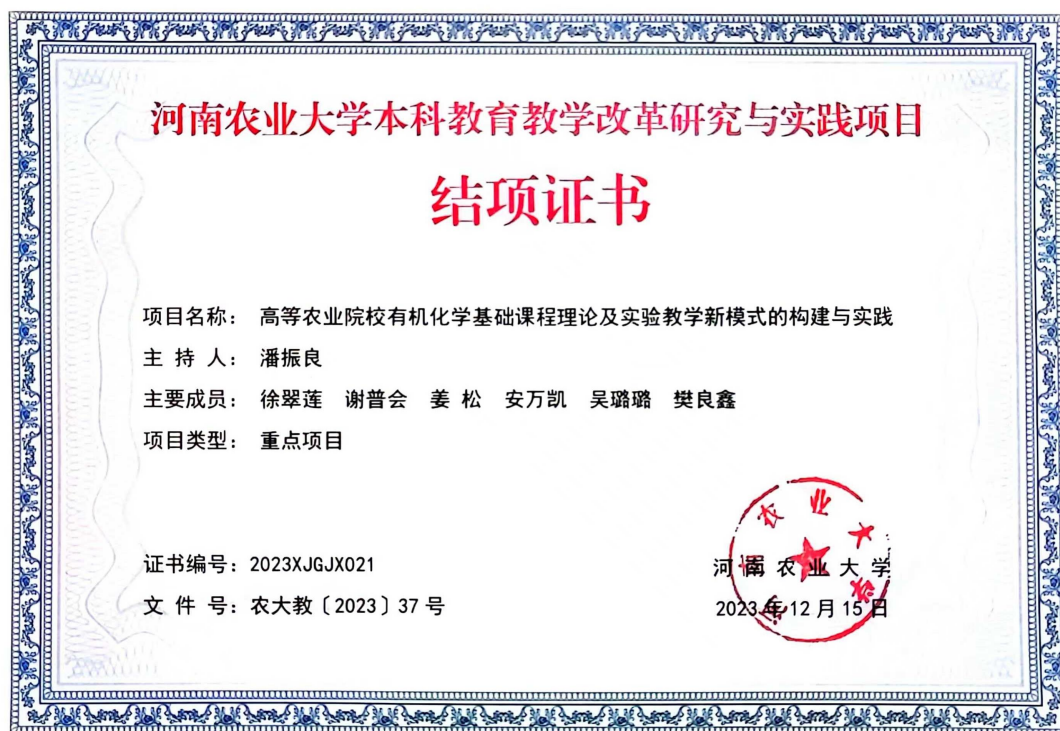
发布时间：2026-07-27 16:14 浏览次数：979

各学院及相关教学单位：
根据《河南农业大学关于开展2025-2026学年本科课程考核改革项目申报的通知》，学校组织了2025-2026学年本科课程考核改革项目的结项评审工作。经个人填报、学院推荐和学校评审，125个课程考核改革项目通过了项目鉴定，其中一等奖13个，二等奖25个，三等奖38个（详见附件），现予以公示。
公示期：2026年7月27日—2026年7月31日。公示期间如有异议，请以书面形式实名向教务处反映。
联系邮箱：jwcjwk@henau.edu.cn
附件：2025-2026学年本科课程考核改革项目结项评审结果

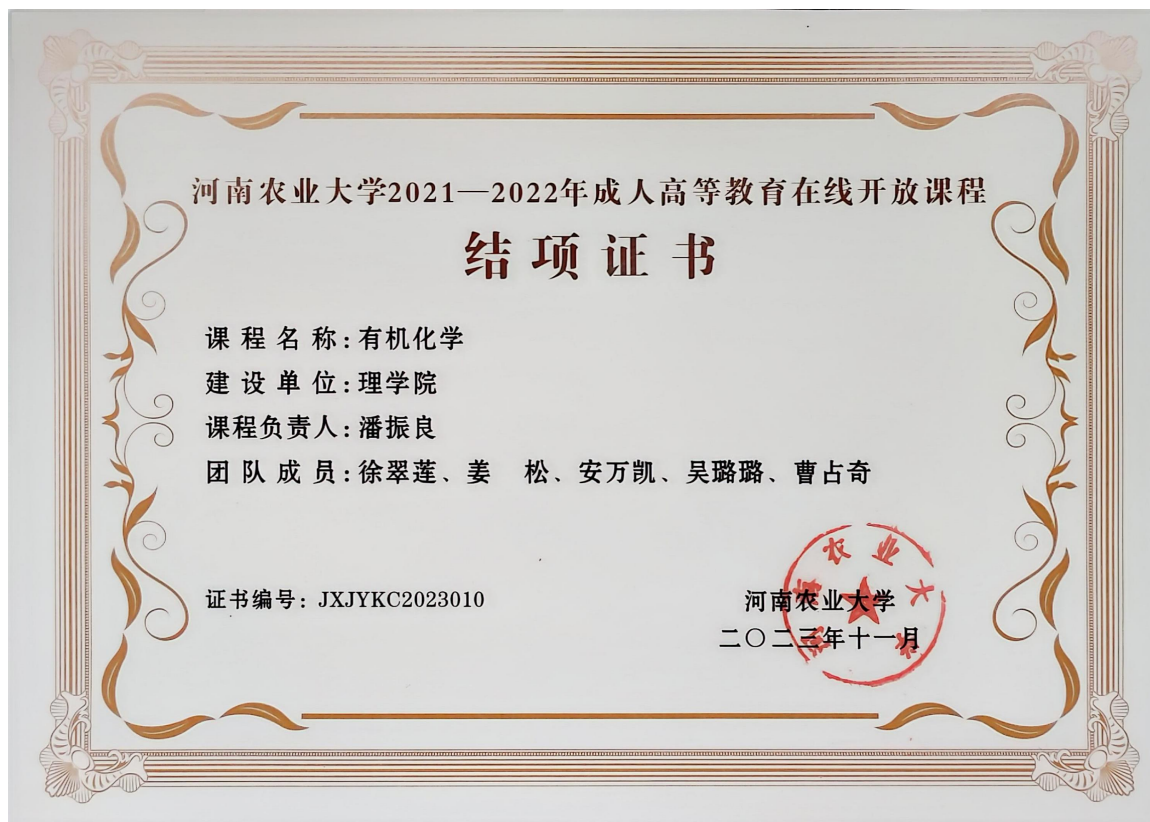
教务处
2026年7月27日

27	软件学院	数据结构	惠向晖 王晓磊 唐 琪 王 燕 李婷婷 张国英	优秀	二等奖
28	烟草学院	香原料学	张明月 邵志晖 李媛媛	优秀	二等奖
29	化学与材料学院	有机化学	姜 松 安万凯 潘振良 刘国星 赵士举 史力军 吴璐璐 曹占奇 田欣哲 秦洁琼 魏 民 武晚霞 樊良鑫 刘立杰	优秀	二等奖
30	机电工程学院	农业机械学	丁 力 李 赫 祝英豪 崔功佩 陈新昌	优秀	二等奖
31	动物医学院	兽医内科学	杨 旭 张君涛 贺秀媛	优秀	二等奖
32	食品科学技术学院	仪器分析	原晓喻 张西亚	优秀	二等奖

9. 河南农业大学教改项目 2

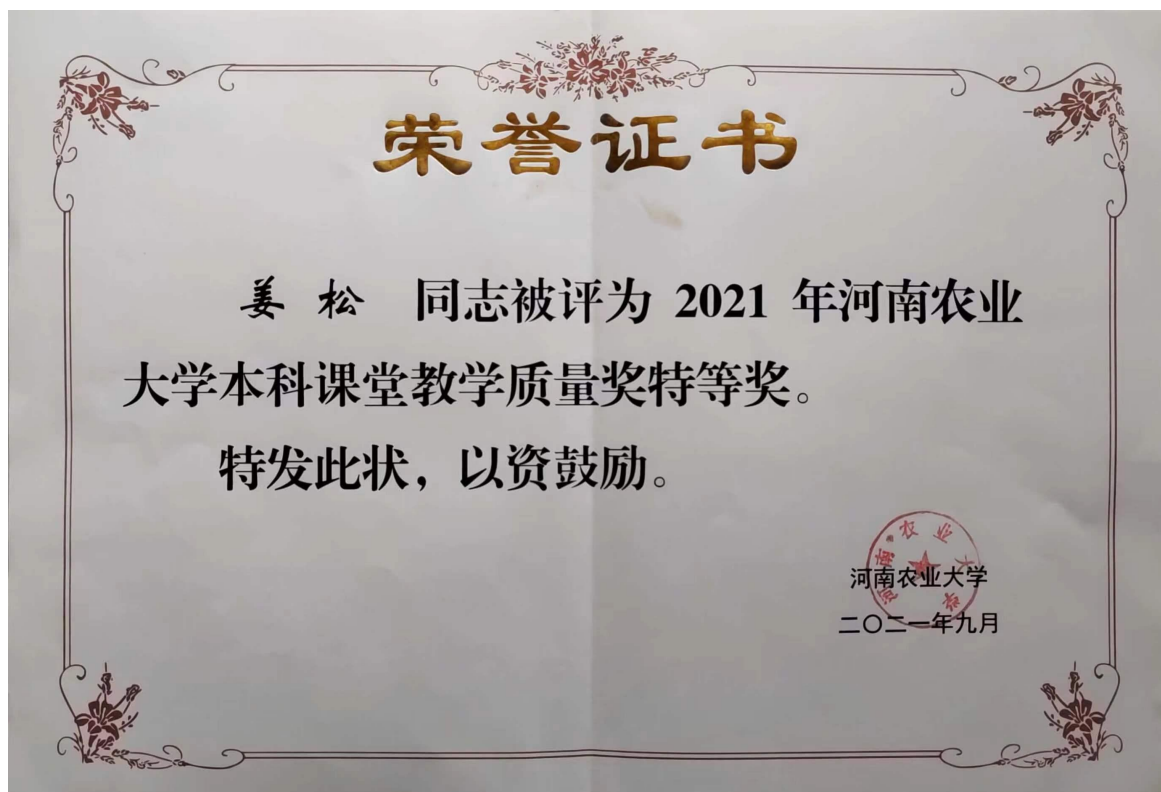


10. 河南农业大学在线开放课程项目



二、获奖情况

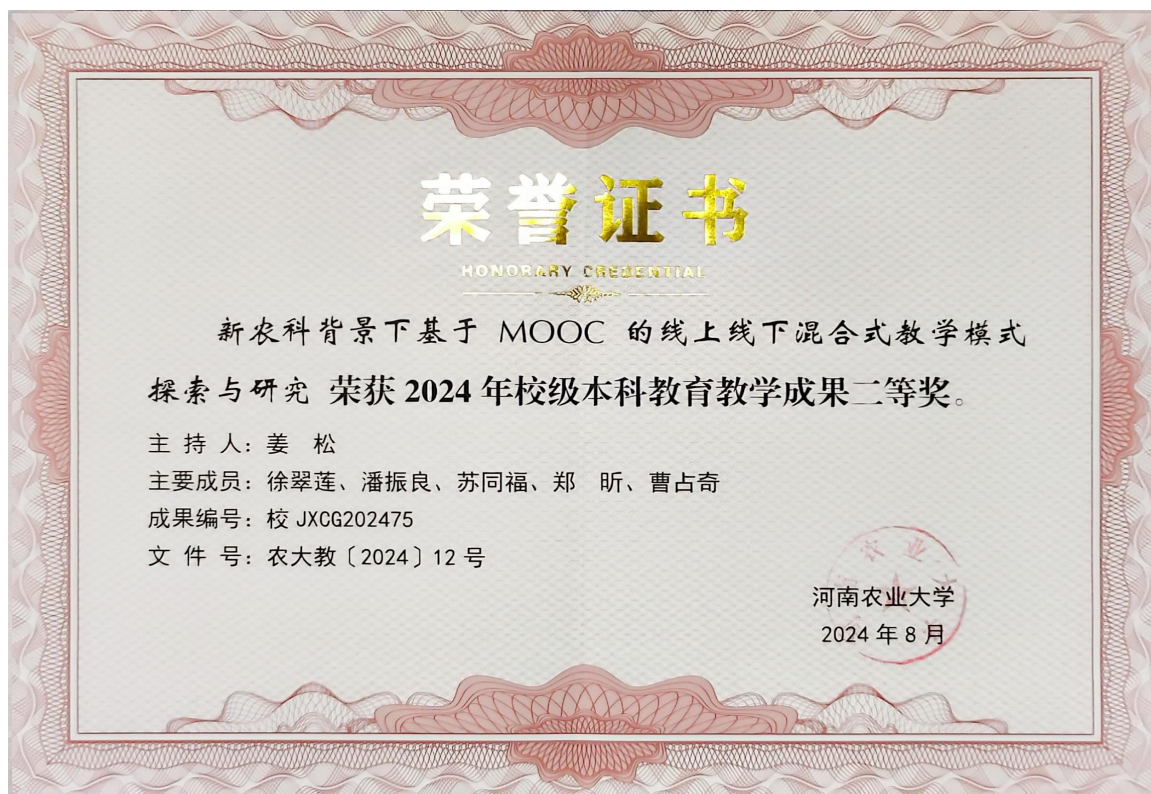
1. 河南农业大学本科课堂教学质量奖特等奖



2. 河南省人力资源和社会保障厅嘉奖



3. 河南农业大学本科高等教育教学成果奖二等奖



4. 河南省优秀科技论文一等奖

河南省教育厅

教科技〔2025〕134号

河南省教育厅
关于公布 2025 年度科技成果评定结果的通知

各高等学校：|

按照《河南省教育厅办公室关于开展 2025 年度科技成果评定暨河南省科学技术奖提名工作的通知》（教办科技〔2025〕59 号）要求，省教育厅组织开展了 2025 年度科技成果评定工作。经高校推荐、专家评审、结果公示，省教育厅决定认定“农作物低空监测与生物质资源潜力评估关键技术及应用”等 158 项成果为科技进步类一等，“选择性芳环 C-H 键官能化及其应用”等 179 项成果为科技进步类二等；认定“Fully sp² carbon-conjugated covalent organic frameworks with multiple active sites for advanced lithium-ion battery cathodes”等 376 篇论文为科

认定编号	项目名称	主要完成单位	主要完成人	认定等级
豫教〔2025〕09660	河南省产业扶贫减贫效应研究	河南牧业经济学院	苗 欣	壹等
豫教〔2025〕09661	The impact of information technology capabilities on agri-food supply chain performance: the mediating effects of interorganizational relationships	河南牧业经济学院, 中国农业大学	曾梦杰, 吕建军	壹等
豫教〔2025〕09662	Boosting excitons dissociation in defective-rich graphitic carbon nitride for efficient hydrogen peroxide photosynthesis and on-site environmental governance	河南农业大学	郑龙辉	壹等
豫教〔2025〕09663	Biodegradation and bioaugmentation of tetracycline by Providencia stuartii TX2: Performance, degradation pathway, genetic background, key enzymes, and application risk assessment	河南农业大学	裴亚欣, 雷澳杰, 杨 森, 陈红歌, 刘新育, 刘亮伟	壹等
豫教〔2025〕09664	Extraordinary p-d Hybridization Interaction in Heterostructural Pd-PdSe Nanosheets Boosts C-C Bond Cleavage of Ethylene Glycol Electrooxidation	河南农业大学	秦毓辰	壹等
豫教〔2025〕09665	Conformational Restriction-Induced Dual Visible Light-Switched Diarylethene Fluorochrome by Composite Films	河南农业大学	刘国星, 姜 松	壹等
豫教〔2025〕09666	The role of selenium vacancies functionalized mediator of bimetal (Co, Fe) selenide for high-energy-density lithium-sulfur batteries	河南农业大学	董玉涛, 靳紫倩, 彭怀启, 刘立杰, 李 鑫, 谢黎霞	壹等
豫教〔2025〕09667	Rational design of a rapidly responsive and highly selective fluorescent probe for SO ₂ derivatives detection and imaging	河南农业大学	杨晓朋, 王海洋, 来 苗, 姬小明	壹等
豫教〔2025〕09668	Dynamic N6-methyladenosine RNA modification regulate peanut resistance to bacterial wilt	河南农业大学	赵 凯, 李忠峰, 任 锐, 邱 鼎, 巩方平, 马兴立, 张幸果	壹等

5. 河南省高等教育教学成果奖二等奖



6. 河南农业大学本科高等教育教学成果奖一等奖



7. 河南省教育系统教学技能竞赛一等奖



8. 河南省教育系统教学技能竞赛一等奖



三、代表性论文

1. Dual-Stimulus Chiroptical Switch of Tetrastable [3]Rotaxanes, *Org. Lett.* 2026, 28, 7821–7826. (SCI, 中科院一区, TOP 期刊)

OL

Organic Letters

pubs.acs.org/OrgLett

Letter

Dual-Stimulus Chiroptical Switch of Tetrastable [3]Rotaxanes

Xinhui Fan,[▽] Yubing Gong,[▽] Zhicheng Guan, Song Jiang,* Yuli Dang, Dongdong Sun, Zhanqi Cao, Xiufang Xu,* Ziyong Li,* and Guoxing Liu*

Cite This: *Org. Lett.* 2026, 28, 7821–7826

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: A pair of dual-stimulus-induced movable enantiomeric chiral tetrastable [3]rotaxanes are readily constructed via a threading–stopping–methylating strategy, displaying tunable photochromic properties ascribed to acid–base-driven reversible mechanical motions that govern the controlled confinement and release of the two macrocycles on the dithienylethene (DTE) moiety. Interestingly, when two chiral rings approach the photoactive site, the inherently achiral DTE segment can be induced to acquire chirality through the conformational confinement of macrocycles. Crucially, the induced chirality can be effectively modulated by acid–base and distinct light through the dynamic interplay between reversible photoisomerization and confinement/release processes.

Chirality, a fundamental and inherently biological property of nature, plays a critical role in governing and modulating essential phenomena in living systems.^{1,2} Although chirality has been extensively studied since Pasteur's resolution of tartaric acid, many aspects remain active areas of ongoing research.³ Chiral molecules exhibit distinct interactions with circularly polarized light and electrons in different spin states, bringing about valuable and exploitable properties and functions.⁴ Enantioselective asymmetric synthesis plays a pivotal role in developing biologically relevant enantiopure drugs due to the chiral selectivity observed in interactions between drug molecules and biomacromolecules.⁵ Consequently, chiral induction is critically important and has garnered more research interest.^{6,7} An array of sophisticated strategies have been employed for chiral induction, including hydrogen bonding, metal coordination, and host–guest complexation, among others.^{8–10} Recently, the dynamic control of chirality has emerged as a rapidly growing research frontier, with diverse physical and chemical stimuli, including pH,¹¹ solvents,¹² additives,¹³ light,¹⁴ redox,¹⁵ and thermal effects¹⁶ now being systematically harnessed for precise chiral regulation. Previously reported studies on chiral induction and regulation have primarily employed single stimuli, whereas achieving reversible chirality changes under the combined action of two or more stimuli remains a significant challenge. Mechanically interlocked molecules, particularly rotaxanes, are characterized by simple structures and facile constructability,^{17–19} making them frequently utilized for the fabrication of molecular machines such as molecular shuttles,²⁰ molecular muscles,²¹ molecular pumps,²² etc. Introducing chiral groups into stimulus-responsive rotaxanes holds an inherent advantage for controlling molecular chirality; i.e., intramolecular mechan-

ical motion can regulate molecular chirality by controlling regularly the spatial conformation between chiral groups and achiral moieties. Therefore, a series of stimulus-driven dynamically stable artificial rotaxanes with adjustable chirality have emerged.^{23–25} To mimic plant-inspired light- and acid–base-responsive motions,^{26,27} acid–base and light are employed as two key physical/chemical drivers to induce controlled motions in dynamically stable rotaxanes that exhibit controllable chiral modulation.^{28,29} For instance, Leigh et al. designed an acid–base-responsive [2]rotaxane as a switchable asymmetric organocatalyst, wherein positional changes of the macrocycle expose or shield an acyclic yet highly effective chiral organocatalytic moiety.³⁰ Tian et al. developed a photoresponsive self-locked [1]rotaxane based on azobenzene that expressed chiroptical switching behaviors.³¹ Nevertheless, both of these studies employ a single external stimulus to construct single-stimulus bistable rotaxanes with chiroptical switches. It is greatly challenging to construct dynamically tetrastable rotaxanes driven by two stimuli, exhibiting reversible chiral regulation.

In this work, we rationally designed two dual-stimulus-controlled tetrastable chiral [3]rotaxanes (Scheme 1), wherein the binaphthyl group was employed to construct a chiral macrocycle and the dithienylethene (DTE)-derived photoactive group constitutes part of the axle. Rational designs are

Received: May 9, 2026
Revised: May 30, 2026
Accepted: June 8, 2026
Published: June 9, 2026

© 2026 American Chemical Society

7821

<https://doi.org/10.1021/acs.orglett.6c02026>
Org. Lett. 2026, 28, 7821–7826

Downloaded from pubs.acs.org on 07/11/2026 10:53:37 AM. For personal use only. All rights reserved. No part of this publication may be reproduced without prior written permission from the American Chemical Society.

21

Scheme 1. Chemical Structures of Axles, Chiral Macrocycles, and [3]Rotaxanes and Photochromic Mechanism of DTE

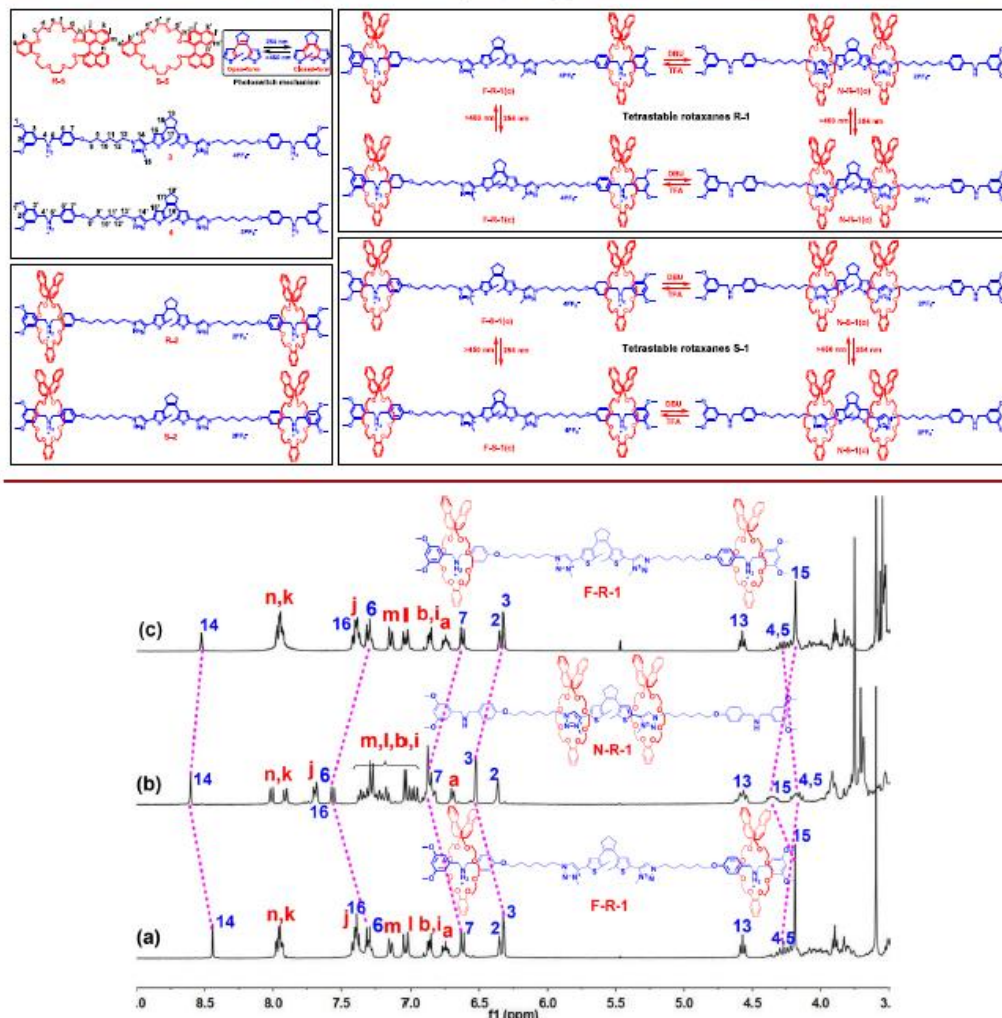


Figure 1. Partial ^1H NMR spectra (400 MHz, 298 K, CD_3CN) of (a) [3]rotaxane F-R-1, (b) after deprotonation with addition of 2.5 equiv of DBU to sample a, and (c) after reprotonation with addition of 3.0 equiv of TFA to sample b.

outlined as follows. (1) Under acid–base stimulation, the two chiral host macrocycles undergo reversible shuttling along the DTE-containing axle, enabling their dynamic positioning either proximal to or distal from the photoactive center, thereby contributing to the tunable photochromic behaviors. (2) Mutually noninterfering dual-mode motions under acid–base stimulation or distinct light irradiation comprise the linear sliding of macrocycles along the axle and the local photoisomerization of the photoactive moiety, respectively. (3) Chiral induction and switching of the DTE by chiral macrocycles are driven by dual-mode motions.

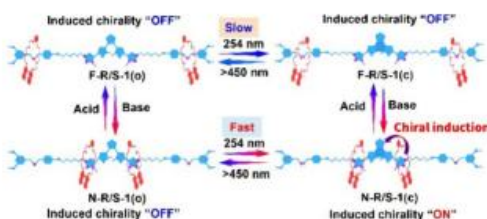
[3]Rotaxanes F-R-1 and F-S-1 were synthesized via several simple steps (Scheme S1). Chiral macrocycles R-5 and S-5 were separately mixed with DTE-bridged diyne 6 and axis 7 featuring a dibenzylammonium (DBA) recognition site to obtain chiral [3]rotaxanes R-2 and S-2 in 66% and 63% yields, respectively, through a “click” reaction by a threading–stopping strategy. The two [3]rotaxanes did not possess the ability to respond to acid–base stimuli. Subsequently, methylation of triazole groups in R-2 and S-2 and counterion exchange with saturated NH_4PF_6 solution afforded acid–base-driven chiral [3]rotaxanes F-R-1 and F-S-1 in 92% and 91% yields, respectively. These detailed synthetic procedures and

structural characteristics are presented in the Supporting Information and Figures S1–S12.

Furthermore, comparative ^1H NMR spectral analysis of [3]rotaxanes F-R-1, F-S-1, R-2, and S-2 with their corresponding macrocycles and axes further supplied reliable proof for the formation of interlocking structures. As shown in Figures S13 and S14, the methylene protons (H_f and H_g) on [3]rotaxanes R-2 and S-2 displayed an obvious downfield shift, and their benzene ring protons (H_2 , H_3 , H_6 , and H_7) showed a remarkable upfield shift, compared to axle 4. Meanwhile, benzene ring protons such as H_4 (H_4'), H_6 (H_6'), H_1 (H_1'), and H_1 (H_1') of R-5 and S-5 showed an apparent upfield shift. These manifestations jointly indicated that the ammonium parts were encircled by the two chiral crown ether rings. Moreover, these specific protons on [3]rotaxane F-R-1 and F-S-1 also revealed similar chemical shifts in comparison to their axle 3 and chiral macrocycles (Figures S15 and S16), manifesting the formation of the two interlocked structures.

As is well-known, dibenzo-24-crown-8 (DB24C8) has weaker affinity for *N*-methyltriazolium (MTA) than dibenzylammonium (DBA).^{32,33} Because the chemical structures of R-5 and S-5 are similar to that of DB24C8, the two rings on F-R-1 and F-S-1 were initially located at the site of DBA, as both binding sites were present simultaneously (Figures S15 and S16). Then, [3]rotaxane F-R-1 was taken as an example to study their acid–base-driven mechanical motion process. When 2.5 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to the solution of [3]rotaxane F-R-1, dialkylammonium ($-\text{NH}_2^+$) was promptly deprotonated, leading to the movement of two macrocycles from DBA to MTA and the structural transformation from F-R-1 into N-R-1. The phenomenon was verified by an analysis of the ^1H NMR spectra that revealed an obvious upfield shift for methylene protons (H_f and H_g) on DBA and an apparent downfield shift for protons (H_{14} and H_{15}) on MTA and benzene ring protons (H_3 , H_7 , and H_6) on DBA (Figure 1a,b). Subsequently, the $-\text{NH}_2$ center was reprotonated with addition of 3.0 equiv of trifluoroacetic acid (TFA), bringing about the return of the two macrocycles from MTA to the DBA location and reconversion from N-R-1 to F-R-1, which was affirmed by regeneration of the original ^1H NMR spectrum (Figure 1c). Besides, identical phenomena were observed for [3]rotaxane F-S-1, as well (Figure S17). These phenomena were confirmed by their 2D ROSEY spectra (Figure S18). As a consequence, the reciprocating motion of two macrocycles between the two recognition sites on the axle of [3]rotaxanes F-R-1 and F-S-1 suffering from acid–base stimuli showed that the two rings could reversibly approach and move away from the DTE photoactive site (Scheme 2).

Scheme 2. Schematic Diagram of Dual-Stimulus-Driven Reciprocating Motions and Chiral Regulation



Considering that R-1 and S-1 both possessed a photoactive moiety, their photochromic properties were investigated. First, we studied photochromic behaviors of [3]rotaxane F-R-1. Its open form, F-R-1(o), gave a maximum absorption peak at 275 nm ($\epsilon = 4.95 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), but a new absorption at 330 nm ($\epsilon = 1.10 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) emerged and increased upon irradiation with 254 nm ultraviolet (UV) light for 80 s, accompanied by the production of an isosbestic point (331 nm) and a change in color from colorless to fuchsia (Figure S19a,d), suggesting that F-R-1(o) was converted into its closed form, F-R-1(c). Its photocyclization conversion yield in the photostationary state (PSS) was measured to be 75% by examining the NMR spectrum of the irradiated sample (Figure S20). Subsequent irradiation of the resultant sample with >450 nm light resulted in a complete restoration of the initial UV–vis and NMR spectra of F-R-1(o) (Figures S19a and S20a,c), implying reversible photoisomerization between the open and closed forms (Scheme 2). The photocyclization quantum yield (Φ_{on}) and photocycloreversion quantum yield (Φ_{off}) of F-R-1 were determined to be 0.17 and 0.0043, respectively (Table S1). When F-R-1 was transformed into N-R-1 with addition of DBU, superior photochromic properties were observed relative to those of F-R-1 (Figure S19b). It is of interest that the photoswitching properties of F-R-1 were improved when it encountered DBU. First, the photocyclization reaction speed of N-R-1 was determined to be $9.3 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$, which was much faster than the value of $5.0 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ for F-R-1 (Figure 2a), indicating the photocyclization was

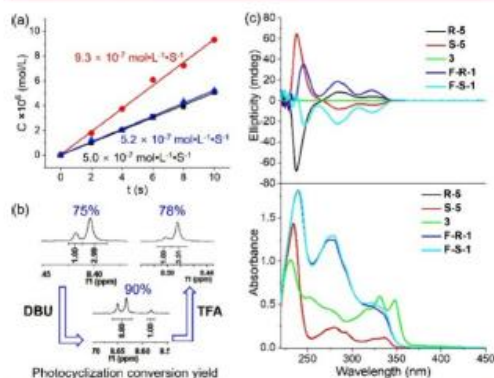


Figure 2. (a) Photocyclization conversion speeds of F-R-1 (black), F-R-1 with DBU (red), and F-R-1 with DBU and TFA (blue). (b) Photocyclization conversion yields of F-R-1, F-R-1 with DBU, and F-R-1 with DBU and TFA. (c) Circular dichroism and UV–vis absorption spectra of R-5, S-5, 3, F-R-1, and F-S-1 in acetonitrile.

accelerated upon stimulation by DBU. Second, the photocyclization conversion yield was apparently enhanced from 75% to 90% after DBU stimulation (Figure S21 and Figure 2b). Third, the photocyclization quantum yield increased from 0.17 to 0.26 for F-R-1 with the involvement of DBU (Table S1). Crucially, with the addition of TFA, the three aforementioned performance parameters were all almost completely returned to the initial levels (Figure 2a, Figures S19c and S22, and Table S1), attributed to the reconversion of N-R-1 to F-R-1. Therefore, originating from reversible interconversion between F-R-1 and N-R-1 with alternating

addition of DBU and TFA, the photochromic performance of [3]rotaxane R-1 was reversibly modulated by acid and base. Meanwhile, its enantiomeric isomer S-1 also expressed tunable photochromic properties triggered by acid and base similar to that of R-1, which further confirmed our assertions (Figures S23–S27 and Table S1). In control experiments, free R-5 and S-5 showed no photoactivity, and photochromic properties of the individual 3 were not affected by acid–base stimulation (Figures S28–S30). The reason for the adjustable photoisomerization capabilities was probably that two macrocycles, R-5 and S-5, confined the conformation of the DTE photoactive center and increased the proportion of its antiparallel conformation and the electron cloud density of the thiophene rings in DTE for N-R-1 and N-S-1 but almost no restrictions of the two rings on DTE for F-R-1 and F-S-1 from ^1H NMR spectral comparison, 2D ROSEY, and optimized structures of N-R-1, N-S-1, F-R-1, and F-S-1 (Figure S31b,d).

Benefiting from the introduction of chiral binaphthalene (BN) macrocycles, macrocycles R-5 and S-5 and tetrastable [3]rotaxanes R-1 and S-1 were investigated via circular dichroism (CD) spectroscopy. As depicted in Figure 2c, the two rings, R-5 and S-5, exhibited three completely opposite CD signals around 238, 284, and 323 nm, assigned to their corresponding R-BN and S-BN moieties. It is noteworthy that F-R-1 manifested an inverse CD band between 225 and 262 nm and enhanced positive CD signals at 284 and 323 nm relative to those of R-5, implying that the conformation of R-BN on R-5 was changed during the formation of F-R-1. Similar phenomena for F-S-1 and S-5 were observed, which further supported our proposed viewpoints. As a control experiment, axle 3 did not show CD signals (Figure 2c). Hence, the chirality of rotaxanes F-R-1 and F-S-1 was derived from their chiral macrocycles R-5 and S-5, respectively.

The acid–base and light dual-stimulus responsiveness and prominent chirality of [3]rotaxanes F-R-1 and F-S-1 inspired us to examine thoroughly their controllable chirality functions. The CD signal peaks at 246, 283, and 323 nm markedly increased for F-R-1(o) and F-S-1(o) with addition of 2.5 equiv of DBU, and subsequent intervention of 3.0 equiv of TFA resulted in the complete recovery of the original CD spectrum (Figure S32). More notably, for F-R-1(c), apart from the changes in the signal peaks mentioned above, a negative CD signal band between 344 and 413 nm and a positive CD band between 413 and 644 nm (that belonged to the closed form of the DTE core) were apparently observed under the influence of DBU (Figure 3a), implying the chirality of the achiral DTE segment on the [3]rotaxane had been induced by chiral macrocycle R-5. As expected, when the resultant sample encountered TFA, the initial CD spectrum of F-R-1(c) was entirely restored (Figure 3a). Meanwhile, S-1(c) also revealed a similar appearance in that its chirality was also reversibly regulated by acid and base (Figure 3a). On the contrary, F-S-1(c) and N-S-1(c) exhibited symmetrical and opposite CD signals with respect to those of F-R-1(c) and N-R-1(c), respectively, indicating that F-S-1(c) and F-R-1(c) (N-S-1(c) and N-R-1(c)) were pairs of enantiomers. In a word, the chirality of the open and closed forms of R-1 and S-1 was modulated by acid and base, attributed to the interconversion between F-R-1 (F-S-1) and N-R-1 (N-S-1) stimulated by acid and base. Afterward, we also studied light-induced chiral modulation of N-R-1 and N-S-1. As displayed in Figure 3b, the open form of N-R-1 gave three CD signal peaks at 246, 283,

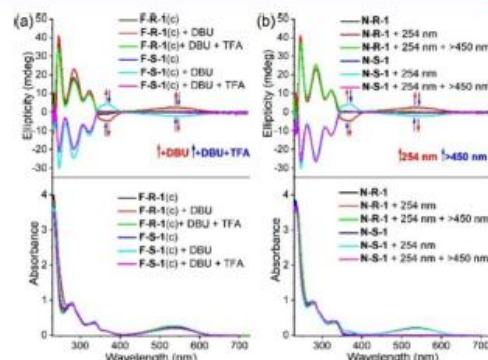


Figure 3. Alteration of the circular dichroism and UV–vis absorption spectra of (a) F-R-1(c) and F-S-1(c) in acetonitrile with sequential addition of 2.5 equiv of DBU and 3.0 equiv of TFA and (b) N-R-1 and N-S-1 in acetonitrile upon alternating 254 and >450 nm light. [R-1] = 2×10^{-5} mol/L; path length of 10 mm.

and 323 nm. To our delight, the other two CD signal bands that were a negative CD signal band between 344 and 413 nm and a positive CD band between 413 and 644 nm (assigned to the closed form of the DTE moiety) appeared upon irradiation with 254 nm UV light (Figure 3b), manifesting chiral induction of the DTE segment from the corresponding chiral macrocycle (R-5) took place so that the chirality of the DTE section took shape. In control experiments, mixtures of 3(c) and R-5 or S-5 exhibited no CD signals between 344 and 644 nm even after the addition of 2.5 equiv of DBU, demonstrating that mechanical confinement is indispensable (Figure S33). Subsequently, the two formed CD bands disappeared and the original CD spectrum was absolutely recovered as the resultant sample was exposed to >450 nm visible light. Simultaneously, the semilabile phenomena of N-S-1 are displayed in Figure 3b, further affirming that the induced chirality could be reversibly switched by UV and visible light. In control experiments, individual axle 3 showed no CD signals, and CD spectra of isolated R-5 and S-5 did not exhibit apparent alteration upon acid–base or different light stimulation, indicating the chirality of the DTE moiety in R-1 and S-1 was not solely induced by these stimuli (Figures S34 and S35). Therefore, in these [3]rotaxanes, the induced chirality could be effectually regulated and controlled by acid and base and distinct lights.

To elucidate the mechanism of its dual-stimulus-induced chiroptical switching, we performed systematic theoretical calculations. Taking the R-type crown ether ring and rotaxane as examples, we optimized the geometries of R-5, F-R-1(o), F-R-1(c), N-R-1(o), and N-R-1(c) and presented the conformational changes of the binaphthyl, dithienylethene (DTE), and DTE-bridged triazole units under dual stimuli (Figure S31). As one can see, the dihedral angle (C5–C6–C7–C8) of the binaphthyl unit of R-5 changes substantially in all four rotaxanes: increasing from -71.6° in the free state of R-5 (Figure S31a) to -78.7° in F-R-1(o) and -97.9° in F-R-1(c) of the R-5-distal-positioned rotaxanes (Figure S31b,c) and further to -112.2° in N-R-1(o) and -110.9° in N-R-1(c) of the R-5-proximal-positioned rotaxanes (Figure S31d,e). Significantly, this result also indicates that the dihedral angle (C5–C6–C7–C8) differs greatly between the distal- and

proximal-mode rotaxanes. For example, this dihedral angle is -78.7° in F-R-1(o) and -112.2° in N-R-1(o), the difference being 33.5° . Moreover, both dihedral angle (C1–C2–C3–C4) of the dithienylethene unit and the dihedral angle (N1–C2–C3–C4) of the DTE-bridged triazole unit differ greatly between the distal-mode and proximal-mode rotaxanes. Taking F-R-1(o) and N-R-1(o) as examples, the dihedral angle (C1–C2–C3–C4) changes from 41.2° in F-R-1(o) to 57.6° in N-R-1(o), the difference being 16.4° (Figure S31b,d). Similarly, the dihedral angle (N1–C2–C3–C4) changes from 28.5° in F-R-1(c) to -11.8° in N-R-1(c), the difference being 40.3° (Figure S31c,e). Based on the above analysis of the significant conformational differences between the distal-mode and proximal-mode rotaxanes, we infer that the significant CD signal variations observed in the aforementioned circular dichroism studies, caused by the threading process and subsequent macrocycle translocation, should originate from pronounced conformational changes in the binaphthyl and DTE backbones, upon acid–base and light stimulation.

In summary, we successfully synthesized two movable enantiomeric chiral tetrastable [3]rotaxanes, R-1 and S-1, through a threading–stopping–methylating strategy, possessing acid–base and light dual-stimulus responsiveness. Interestingly, their photochromic properties such as photocyclization speed, conversion yield, and quantum yield were dramatically boosted with intervention of DBU, and subsequent introduction of TFA led to the recovery of the initial photoisomerization capabilities, ultimately realizing reversibly adjustable photochromic performance induced by acid and base. The tunable photoactive ability was attributed to reversible conformational confinement and release of two rings on the DTE by an acid–base-driven repetitive mechanical movement. Noticeably, the import of chiral macrocycles R-5 and S-5 could effectively induce the chirality of the DTE core in [3]rotaxanes N-R-1 and N-S-1, because the two macrocycles were in a position close to the DTE center and the conformations of the DTE were changed under interference of the two chiral macrocycles. Crucially, the induced CD signals were switched by acid–base and distinct light stimulation, indicating that the induced chirality of the two [3]rotaxanes could be controlled by the dual stimuli. All of these controllable chiral inductions and modulations were attributed to the conformational change of the diarylethene backbone under two stimuli, which was further confirmed by the theoretically optimized molecular structures. This study establishes an instructive methodology for both the design of controllable chiral mechanically interlocked molecular machines and the induction and regulation of molecular chirality.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.6c02026>.

Experimental procedures, characterization data, and supplementary figures (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Song Jiang – College of Science, Henan Agricultural University, Zhengzhou 450002, China; Email: jiangsong@henau.edu.cn

Xiufang Xu – College of Chemistry, Nankai University, Tianjin 300071, China; orcid.org/0000-0002-3510-3267; Email: xxfang@nankai.edu.cn

Ziyong Li – College of Food and Drug, Luoyang Normal University, Luoyang 471934, China; orcid.org/0000-0002-2658-2286; Email: liziyoung@mails.cnu.edu.cn

Guoxing Liu – College of Science, Henan Agricultural University, Zhengzhou 450002, China; orcid.org/0000-0003-1609-3865; Email: gdiu@henau.edu.cn

Authors

Xinhui Fan – College of Science, Henan Agricultural University, Zhengzhou 450002, China

Yubing Gong – College of Science, Henan Agricultural University, Zhengzhou 450002, China

Zhicheng Guan – College of Chemistry, Nankai University, Tianjin 300071, China; orcid.org/0009-0003-5296-6712

Yuli Dang – College of Science, Henan Agricultural University, Zhengzhou 450002, China

Dongdong Sun – College of Science, Henan Agricultural University, Zhengzhou 450002, China

Zhanqi Cao – College of Science, Henan Agricultural University, Zhengzhou 450002, China; orcid.org/0000-0001-8108-5891

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.orglett.6c02026>

Author Contributions

[†]X.F. and Y.G. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the National Natural Science Foundation of China (21801063 and 22578193), the Top-Notch Talents Program of Henan Agricultural University (30501049), the Natural Science Foundation of Henan Province (252300421450), the Key Scientific Research Project of Higher Education Institutions in Henan Province (26A150020), the Scientific and Technological Project of Henan Province (252102311211), and the Backbone Teacher in Henan Province (2021GGJS029) for financial support.

■ REFERENCES

- (1) Cintas, P. Chirality of Living Systems: A Helping Hand from Crystals and Oligopeptides. *Angew. Chem., Int. Ed.* **2002**, *41*, 1139–1145.
- (2) Davankov, V. Chirality as an Inherent General Property of Matter. *Chirality* **2006**, *18*, 459–461.
- (3) De Cat, I.; Guo, Z.; George, S. J.; Meijer, E. W.; Schenning, A. P. H. J.; De Feyter, S. Induction of Chirality in an Achiral Monolayer at the Liquid/Solid Interface by a Supramolecular Chiral Auxiliary. *J. Am. Chem. Soc.* **2012**, *134*, 3171–3177.
- (4) Greenfield, J. L.; Evans, E. W.; Di Nuzzo, D.; Di Antonio, M.; Friend, R. H.; Nitschke, J. R. Unraveling Mechanisms of Chiral

Induction in Double-Helical Metallopolymers. *J. Am. Chem. Soc.* **2018**, *140*, 10344–10353.

(5) Wang, Y.; Xu, J.; Wang, Y.; Chen, H. Emerging chirality in nanoscience. *Chem. Soc. Rev.* **2013**, *42*, 2930–2962.

(6) Goubert, G.; Dong, Y.; Groves, M. N.; Lemay, J.-C.; Hammer, B.; McBrean, P. H. Monitoring interconversion between stereochemical states in single chirality-transfer complexes on a platinum surface. *Nat. Chem.* **2017**, *9*, 531–536.

(7) Masini, F.; Kalashnyk, N.; Knudsen, M. M.; Cramer, J. R.; Lægsgaard, E.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. Chiral Induction by Seeding Surface Assemblies of Chiral Switches. *J. Am. Chem. Soc.* **2011**, *133*, 13910–13913.

(8) Zhang, Q.; Crespi, S.; Toyoda, R.; Costil, R.; Browne, W. R.; Qu, D.-H.; Tian, H.; Feringa, B. L. Stereodivergent Chirality Transfer by Noncovalent Control of Disulfide Bonds. *J. Am. Chem. Soc.* **2022**, *144*, 4376–4382.

(9) Greenfield, J. L.; Evans, E. W.; Di Nuzzo, D.; Di Antonio, M.; Friend, R. H.; Nitschke, J. R. Unraveling Mechanisms of Chiral Induction in Double-Helical Metallopolymers. *J. Am. Chem. Soc.* **2018**, *140*, 10344–10353.

(10) Yang, C.; Inoue, Y. Supramolecular photochirogenesis. *Chem. Soc. Rev.* **2014**, *43*, 4123–4143.

(11) Lin, R.; Zhang, H.; Li, S.; Chen, L.; Zhang, W.; Wen, T. B.; Zhang, H.; Xia, H. pH-Switchable Inversion of the Metal-Centered Chirality of Metallabenzene: Opposite Stereodynamics in Reactions of Ruthenabenzene with L- and D-Cysteine. *Chem. - Eur. J.* **2011**, *17*, 2420–2427.

(12) Martinez, A.; Guy, L.; Dutasta, J.-P. Reversible, Solvent-Induced Chirality Switch in Atrane Structure: Control of the Unidirectional Motion of the Molecular Propeller. *J. Am. Chem. Soc.* **2010**, *132*, 16733–16734.

(13) Qu, Y.; Chen, P.; Guo, P.; Li, Y.; Liu, M. Supramolecular Chiroptical Switches Based on Achiral Molecules. *Adv. Mater.* **2008**, *20*, 2908–2913.

(14) Zheng, Z.; Li, Y.; Bisoyi, H. K.; Wang, L.; Bunning, T. J.; Li, Q. Three-dimensional control of the helical axis of a chiral nematic liquid crystal by light. *Nature* **2016**, *531*, 352–356.

(15) Xiao, C.; Wu, W.; Liang, W.; Zhou, D.; Kanagaraj, K.; Cheng, G.; Su, D.; Zhong, Z.; Chruma, J. J.; Yang, C. Redox-Triggered Chirality Switching and Guest-Capture/Release with a Pillar[6]arene-Based Molecular Universal Joint. *Angew. Chem., Int. Ed.* **2020**, *59*, 8094–8098.

(16) Ooi, T. Heat and Light Switch a Chiral Catalyst and Its Products. *Science* **2011**, *331*, 1395–1396.

(17) Xue, M.; Yang, Y.; Chi, X.; Yan, X.; Huang, F. Development of Pseudorotaxanes and Rotaxanes: From Synthesis to Stimuli-Responsive Motions to Applications. *Chem. Rev.* **2015**, *115*, 7398–7501.

(18) Ebas-Cakmak, S.; Leigh, D. A.; McTernan, C. T.; Nussbaumer, A. L. Artificial Molecular Machines. *Chem. Rev.* **2015**, *115*, 10081–10206.

(19) Ma, X.; Tian, H. Bright functional rotaxanes. *Chem. Soc. Rev.* **2010**, *39*, 70–80.

(20) Gauthier, M.; Fournel-Marotte, K.; Clavel, C.; Waelès, P.; Laurent, P.; Coutrot, F. An Interlocked Figure-of-Eight Molecular Shuttle. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202310643.

(21) Bruns, C. J.; Stoddart, J. F. Rotaxane-Based Molecular Muscles. *Acc. Chem. Res.* **2014**, *47*, 2186–2199.

(22) Binks, L.; Tian, C.; Fielden, S. D. P.; Vitorica-Yrezabal, I. J.; Leigh, D. A. Transamidation-Driven Molecular Pumps. *J. Am. Chem. Soc.* **2022**, *144*, 15838–15844.

(23) Jameson, E. M. G.; Modicom, F.; Goldup, S. M. Chirality in rotaxanes and catenanes. *Chem. Soc. Rev.* **2018**, *47*, 5266–5311.

(24) Mochizuki, Y.; Ikegatsu, K.; Mutoh, Y.; Hosoya, S.; Saito, S. Synthesis of Mechanically Planar Chiral rac-[2]Rotaxanes by Partitioning of an Achiral [2]Rotaxane: Stereoconversion Induced by Shuttling. *Org. Lett.* **2017**, *19*, 4347–4350.

(25) Xu, W.-T.; Li, X.; Wu, P.; Li, W.-J.; Wang, Y.; Xu, X.-Q.; Wang, X.-Q.; Chen, J.; Yang, H.-B.; Wang, W. Dual Stimuli-Responsive

[2]Rotaxanes with Tunable Vibration-Induced Emission and Switchable Circularly Polarized Luminescence. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202319502.

(26) Miao, W.; Qin, L.; Yang, D.; Jin, X.; Liu, M. Multiple-stimulus-responsive supramolecular gels of two components and dual chiroptical switches. *Chemistry* **2015**, *21*, 1064–1072.

(27) Jiang, Q.; Liu, Q.; Shi, Y.; Wang, Z.-G.; Zhan, P.; Lu, J.; Li, C.; Wang, H.; Shi, X.; Zhang, L.; Sun, J.; Ding, B.; Liu, M. Stimulus-Responsive Plasmonic Chiral Signals of Gold Nanorods Organized on DNA Origami. *Nano Lett.* **2017**, *17*, 7125–7130.

(28) David, A. H. G.; Casares, R.; Cuerva, J. M.; Campaña, A. G.; Blanco, V. A [2]Rotaxane-Based Circularly Polarized Luminescence Switch. *J. Am. Chem. Soc.* **2019**, *141*, 18064–18074.

(29) Xu, W.-T.; Li, X.; Xu, X.-Q.; Wang, X.-Q.; Yang, H.-B.; Wang, W. Multistate circularly polarized luminescence switches based on dual stimuli-responsive chiral [2]rotaxanes. *Sci. China Chem.* **2024**, *67*, 4202–4211.

(30) Blanco, V.; Leigh, D. A.; Marcos, V.; Morales-Serna, J. A.; Nussbaumer, A. L. A Switchable [2]Rotaxane Asymmetric Organo-catalyst That Utilizes an Acyclic Chiral Secondary Amine. *J. Am. Chem. Soc.* **2014**, *136*, 4905–4908.

(31) Song, X.; Zhu, X.; Wu, S.; Chen, W.; Tian, W.; Liu, M. Chiroptical switching in the azobenzene-based self-flocked [1]rotaxane by solvent and photoirradiation. *Chirality* **2023**, *35*, 692–699.

(32) Liu, G.; Tian, C.; Fan, X.; Dang, Y.; Qin, J.; Liu, L.; Cao, Z.; Jiang, S. Dual-Stimulus-Driven Dynamically Controllable [3]Rotaxane with Tunable Organic Room-Temperature Phosphorescence. *Org. Lett.* **2023**, *25*, 8761–8765.

(33) Liu, G.; Zhu, J.; Zhou, Y.; Dong, Z.; Xu, X.; Mao, P. Adjustable Photochromic Behavior of a Diarylethene-Based Bistable [3]-Rotaxane. *Org. Lett.* **2018**, *20*, 5626–5630.

2. Visible-light-induced dynamic luminescence of cascaded assembly by in situ directional photoisomerization for time-resolved information encryption. *Dyes and Pigments*, 2026, 255, 114067.(SCI)



Visible-light-induced dynamic luminescence of cascaded assembly by in situ directional photoisomerization for time-resolved information encryption

Zizheng Li^{a,b,1}, Fenghua Yin^{a,1}, Yongmei Xiao^{b,*}, Wenhao Yang^b, Song Jiang^a, Yuli Dang^a, Xinzhe Tian^a, Ziyong Li^{c,**}, Guoxing Liu^{a,***}

^a College of Chemistry and Materials, Henan Agricultural University, Zhengzhou, 450002, China

^b College of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou, 450001, China

^c Luoyang Key Laboratory of Organic Functional Molecules, College of Food and Drug, Luoyang Normal University, Luoyang, 471934, China

ABSTRACT

Photoinduced dynamic luminescence nanosystems are currently witnessing a surge of interest for their cutting-edge applications across the life and materials sciences. Herein, a hydrosoakable polymer-supramolecular nanoaggregate DCS-BQCCB[7]₂-PSS has been fabricated by dicyanostyrylbenzene-modified with bromoisoinoline salt (DCS-BQ), cucurbit[7]uril (CB[7]) and polystyrene sulfonate (PSS) through two-steps assembling process, manifesting photoluminescence enhancement and photo-responsiveness due to the introduction of photoactive DCS and assembly-induced conformational confinement. Interestingly, utilization of in situ directional photoisomerization of DCS-BQ from Z-to E-configuration of DCS by visible light enables DCS-BQCCB[7]₂-PSS with dramatic photoluminescence enhancement and color change from weak yellowish-brown to strong blue. The nanoparticles formed by DCS-BQCCB[7]₂-PSS in photostationary state accommodates energy-matched Nile red to build a FRET-based light-harvesting system accompanied by emitting color from blue to pink. The time-resolved dynamic photoluminescence intensity and color driven by light and fluorochrome-doping demonstrates the application in high-security-level information encryption.

1. Introduction

Stimuli-responsive nanosystems constructed through multicomponent self-assembly are of significant interest, owing to their simple composition, effortless tunability, and good reproducibility. The supramolecular self-assembling method is recognized as one of the most effective and straightforward approaches for incorporating stimuli-responsive scaffolds into functional systems [1–3]. Among various external stimuli, light stands out due to its superior controllability and non-invasiveness, offering significant benefits over acid-base, thermal, host-guest, magnetic, or redox triggers [4–7]. Photoactive molecules have been extensively utilized as fundamental building blocks for constructing stimuli-responsive intelligent supramolecular systems. Photochromic molecules undergo reversible structural changes upon light irradiation, leading to distinct alterations in their optical properties, which makes them promising candidates for applications in molecular switches, optical devices, and data storage systems. Dicyanostyrylbenzene (DCS) derivatives, characterized by their unique

carbon-carbon double bond structures, can typically undergo Z/E isomerization when stimulated by ultraviolet (UV) light [8–11]. Functional DCS derivatives have been used to fabricate stimuli-responsive luminescent materials [12–16]. In recent years, artificial light-harvesting based on Förster resonance energy transfer (FRET), is highly sought-after for developing stimuli-responsive nanosystems, which exhibit controllable changes in emission colour and intensity. For instance, Wang and Hu et al. fabricated a supramolecular artificial light-harvesting nanosystem with two-step sequential FRET via self-assembling strategy, which realized bright white light emission and high-efficiently photocatalyzed dehalogenation of α -bromoacetophenone in aqueous medium [17]. Xiao et al. reported an artificial thermosensitive sequential light-harvesting system based on an amphiphilic molecule TPEO, exhibiting thermosensitive colorimetric fluorescence in both aqueous solution and hydrogel by taking advantage of a combination of lower critical solution temperature and sequential FRET [18]. Our group also developed several light-harvesting nanoassemblies based on FRET by host-guest complexation, exhibiting high-security-level

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: ymxiao@hau.edu.cn (Y. Xiao), liziyong@mails.ccma.edu.cn (Z. Li), gxliu@henau.edu.cn (G. Liu).

¹ Z.L. and F.Y. contributed equally to this work

<https://doi.org/10.1016/j.dyepig.2026.114067>

Received 18 June 2026; Received in revised form 25 July 2026; Accepted 29 July 2026

Available online 1 August 2026

0143-7208/© 2026 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

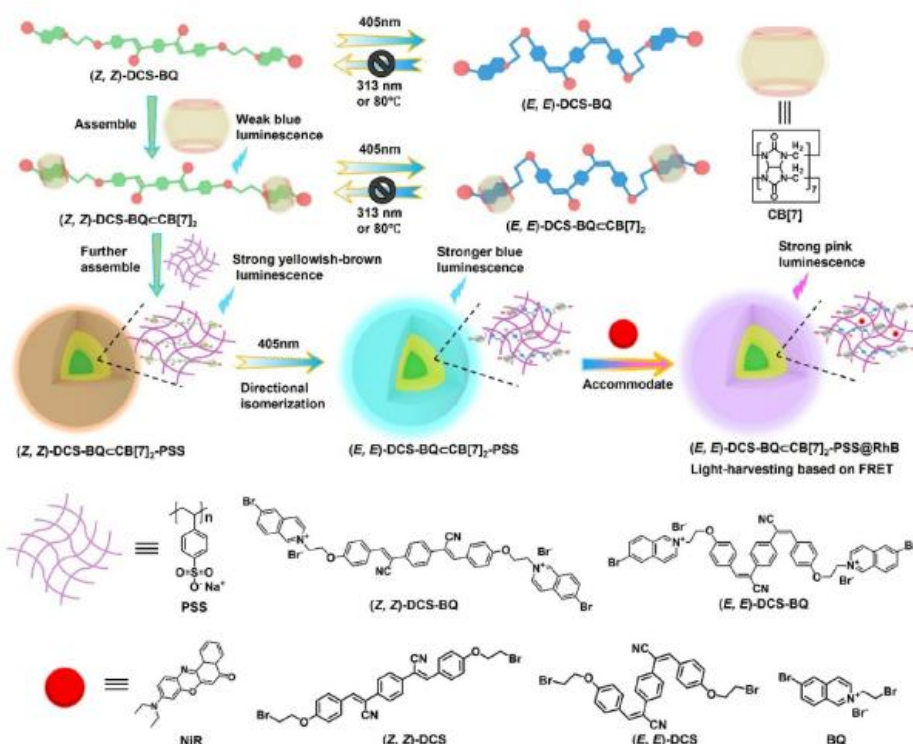
information encryption, anti-counterfeiting, photorecording and information conversion, etc. [19–21] However, it is rarely reported that facile utilization of in situ directional photoisomerization of DCS triggered by visible light and supramolecular cascaded assembly fabricates stimuli-responsive light-harvesting photoluminescence systems with adjustable emission intensity and colour.

In this work, we rationally design a water-soluble photoactive guest molecule i.e. dicyanostyrylbenzene modified with two bromoisquinoline salts (DCS-BQ), as shown in Scheme 1. The guest bearing with two positive charges can assemble with cucurbit[7]uril (CB[7]) to form [1 + 2] supramolecular complex via host-guest interaction. The formed electropositive assembly can further co-assemble with electronegative polymer through electrostatic interaction to polymeric-supramolecular complex. The aforementioned two-step conformational confinement is expected to achieve photoluminescence enhancement. Moreover, the existence of photoactive group DCS enables the resultant polymeric-supramolecular complex to possess photoisomerization ability, and will definitely bring about the changes in the luminescence properties. The polymeric-supramolecular complex has the ability to form nano-aggregates, and can provide accommodation for energy-matching receptor dyes to further build a photo-harvesting photoluminescent nanosystem with color-adjustable emission.

2. Results and discussion

DCS-BQ was prepared through several simple steps (Scheme S1), and all new compounds were characterized by ^1H NMR, ^{13}C NMR and HR-

MS spectra (Fig. S1–S8). It is well-known that size-adaptive guests with positive charge located at right position could be included by CB[7] into its rigid hole [22]. DCS-BQ with this structural feature might assemble with CB[7] to form a supramolecular complex. First of all, their host-guest affinity stoichiometry was determined to be 2:1 through a Job plot of their complexing with each other that showed a peak at molar fraction 0.33 (Fig. 1a). Secondly, assembling behaviors and pattern of DCS-BQ and CB[7] were studied. As displayed in Fig. 1b, the maximum UV-vis absorption peak of DCS-BQ manifested an apparent increase and bathochromic-shift from 370 nm to 374 nm, implying the occurrence of their assembling process. Furthermore, the reference compound BQ instead of DCS-BQ was selected to inspect the assembling pattern of the guest with CB[7]. As shown in Fig. 1c, the resonance for all the aromatic rings protons (H_a – H_f) on the reference compound BQ manifested an obvious upfield shift after addition of CB[7] and the protons (H_g) of the methylene group adjacent to bromoisquinoline showed clear downfield shift compared to that of the detached BQ, indicating that the bromoisquinoline section of BQ were located in the cavity of CB[7] (Fig. 1c, Inset), which was in accordance with the results reported before [23, 24]. Therefore, a feasible assembling mode of DCS-BQ with CB[7] was proposed (Scheme 1). Besides, the maximum emission intensity of DCS-BQ at 465 nm was greatly enhanced by 2.6-fold with sequential addition of CB[7] (Fig. 2a) and meanwhile, the fluorescence quantum yield was enhanced from 0.6% to 0.8% (Table S1), which further implied that their assembling behaviors took place. The appearance should be attributed to the restriction of intramolecular rotation (RIR) induced by macrocycle-based self-assembly. The affinity ability was



Scheme 1. Schematic diagram of visible-light-triggered in situ directional photoisomerization and construction of the light-harvesting cascade assembly.

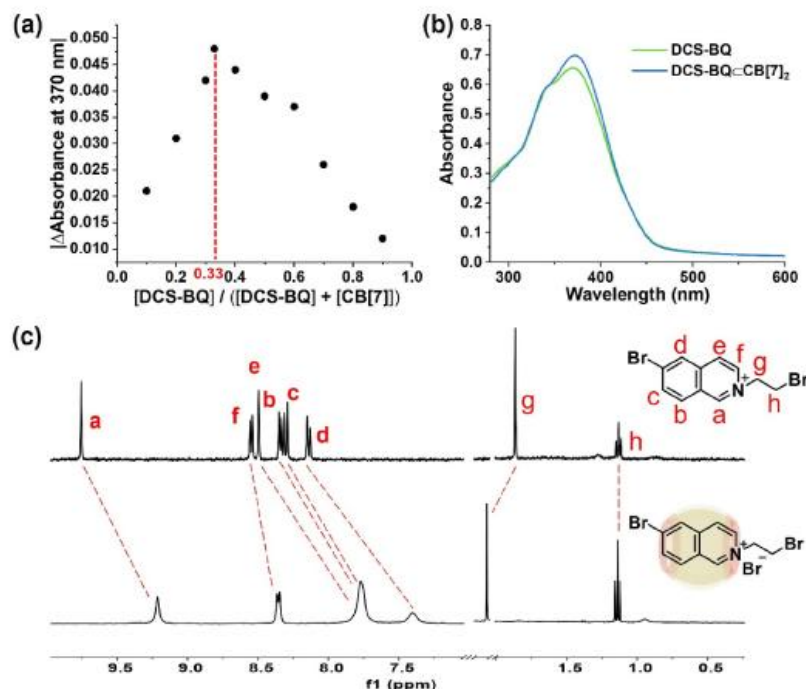


Fig. 1. (a) Job plot of DCS-BQ and CB[7] in 2% DMSO aqueous solution (absorbance changes were recorded at 370 nm for DCS-BQ ([CB[7] + [DCS-BQ] = 2.0×10^{-5} mol/L); (b) The UV-vis absorption spectra of DCS-BQ and DCS-BQ@CB[7]₂, [CB[7]] = 2[DCS-BQ] = 4.0×10^{-5} mol/L; (c) ¹H NMR spectra (D₂O, 400 MHz, 298K) of BQ and BQ with addition of 1.0 equiv of CB[7].

assessed and the binding stability constants (K_s) were determined to be 1.7×10^7 L/mol (K_{s1}) and 4.8×10^5 L/mol (K_{s2}) by analyzing the fluorescence intensity evolution at 470 nm upon sequential addition of CB[7] to the DCS-BQ aqueous solution using the nonlinear least-squares fitting method (Fig. 2a, Inset), and the adopted fitting formula was displayed in Supporting Information.

Despite emission enhancement of DCS-BQ with encapsulation of CB[7], its photoluminescence was still unsatisfactory. Afterwards, electronegative polymers PSS was selected to promote further aggregation of DCS-BQ@CB[7]₂ by a co-assembling way. As was expected, when 0.05 g/L PSS was continuously added in the aqueous solution containing DCS-BQ@CB[7]₂ to construct a polymer-supramolecular complex (DCS-BQ@CB[7]₂-PSS) using electrostatic interaction, its fluorescence intensity gradually increased and ultimately reached the maximum that was equivalent to 2 times that of DCS-BQ@CB[7]₂ and meanwhile, the fluorescence quantum yield was enhanced from 0.8% to 1.1% (Table S1), revealing the optimal mixing ratio (Fig. 2b). Simultaneously, the emission maximum was shifted bathochromically by 12 nm from 465 nm to 477 nm. The reason was probably that the DCS-BQ@CB[7]₂ complex further aggregated under the influence of mutual interaction with PSS, realizing efficient conformational confinement of DCS in the assembly and ultimate inhibition of non-radiative transitions. In above two-step assembling procedures, nonradiative decay constant (k_{nr}) decreased from 2.07×10^9 s⁻¹ to 7.75×10^8 s⁻¹ to 3.73×10^8 s⁻¹, implying non-radiative transitions were suppressed (Table S1).

However, its photoluminescence performance of DCS-BQ@CB[7]₂-PSS still failed to meet the application requirements. Considering the photoactive group (DCS) possessed by the polymer-supramolecular

complex, we further investigated the influence of its photoisomerization on the fluorescence intensity. To our surprise and delight, when its aqueous solution was irradiated by 405 nm visible light in succession for 860 s, the fluorescence intensity at 443 nm was dramatically boosted by up to 7.5-fold (Fig. 2c), which was accompanied by apparent hypsochromic shift of the maximum emission peak from 477 nm to 441 nm. Simultaneously, the fluorescence quantum yield was enhanced from 1.1% to 2.0%, and fluorescence lifetime was prolonged from 2.65 ns to 3.90 ns (Table S1). Furthermore, radiative decay constant (k_r) increased from 4.15×10^6 s⁻¹ to 5.13×10^6 s⁻¹ (Table S1). Intuitively, the weak yellowish-brown fluorescence was gradually changed to be strong blue emission (Fig. 2c, Inset). Hence, 405 nm light irradiation achieved both emission intensity enhancement and color alteration.

To clarify the cause of the change in the fluorescence intensity and color above induced by visible light, we then studied the photoisomerization behaviors of the photoactive guest DCS-BQ. As shown in Fig. 2d, when it was irradiated by 405 nm light, the maximum absorption peak of DCS-BQ at 371 nm declined and meanwhile, the absorption band between 270 nm and 326 nm increased, accompanied by the emergence of an isoabsorptive point at 326 nm. The process took 110 s to reach photostationary state (PS). These UV-vis absorption spectral alterations revealed that a new substance i.e. its (*E*, *E*)-isomer came into being, and the spectral variation and photoisomerization process were both consistent with the results in the reported literatures [15]. In addition, the photoisomerization conversion yield of DCS-BQ from (*Z*, *Z*)-isomer to (*E*, *E*)-form was determined to be 50.5% by examining its ¹H NMR spectral evolution of the irradiated sample containing DCS-BQ

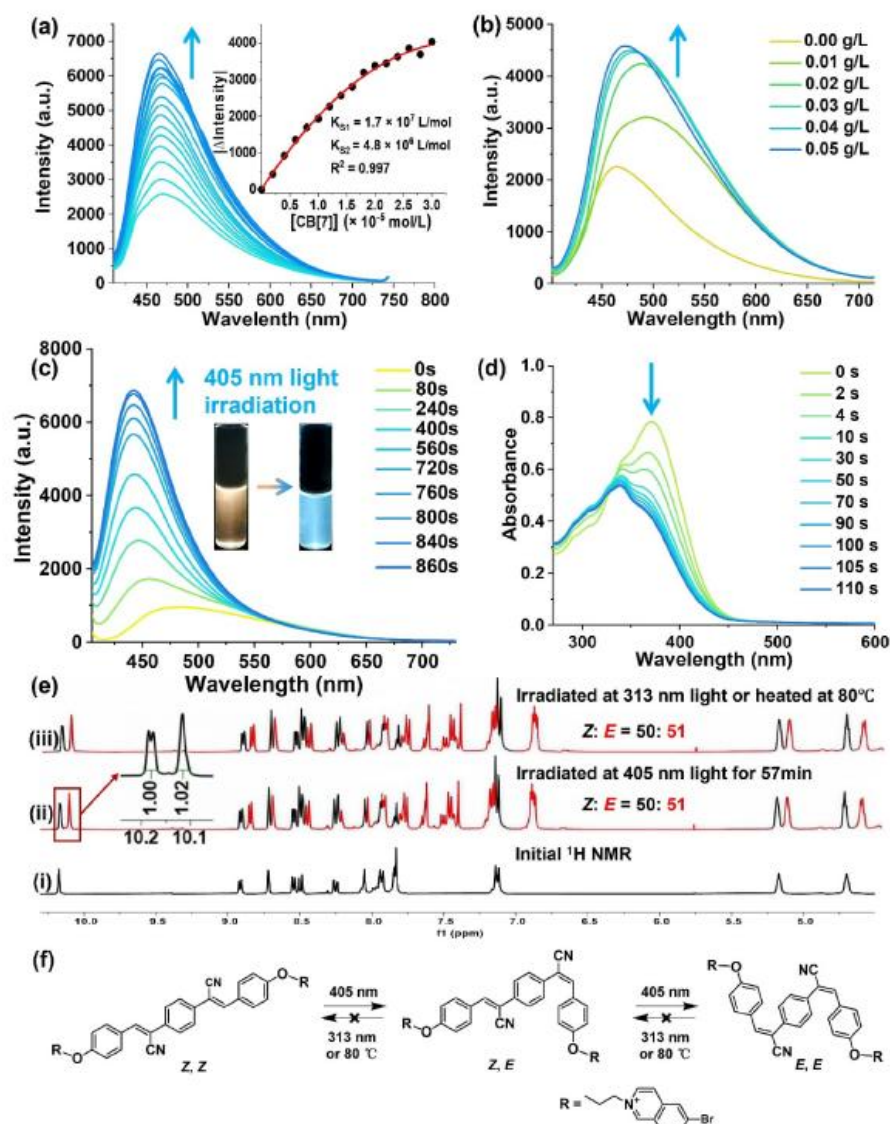


Fig. 2. (a) Fluorescence spectral evolution of DCS-BQ (2.0×10^{-5} mol/L) with sequential addition of 0–2 equiv of CB[7] in 2% DMSO aqueous solution, Inset: Nonlinear least-squares analysis of the fluorescence intensity changes of (Z, Z)-DCS-BQ at 470 nm upon addition of CB[7] to calculate the K_s value between DCS-BQ and CB[7] ([DCS-BQ] = 2.0×10^{-5} mol/L, [CB[7]] = 0.00 – 6.0×10^{-5} mol/L); (b) Fluorescence spectral evolution of DCS-BQ with sequential addition of PSS in 2% DMSO aqueous solution ([CB[7]] = 2[DCS-BQ] = 1.0×10^{-4} mol/L, [PSS] = 0.00 – 0.05 g/L); (c) Fluorescence spectral evolution of DCS-BQ with 405 nm visible light ([CB[7]] = 2[DCS-BQ] = 1.0×10^{-4} mol/L, [PSS] = 0.04 g/L; $\lambda_{\text{exc}} = 380$ nm; Inset: Fluorescent photograph changes of (Z, Z)-DCS-BQ with 405 nm UV light before and after irradiation with 405 nm visible light. (d) UV-vis absorption spectral evolution of the DCS-BQ (2.0×10^{-5} mol/L) in 2% DMSO aqueous solution upon sequential irradiation at 405 nm visible light. (e) ^1H NMR spectra (400 MHz, 298K, DMSO- d_6) of DCS-BQ exposed to 405 nm visible light for 0 min (i) and 57 min (ii) and the sample (ii) after being heated at 80°C for 20 min or irradiated at 313 nm light (iii) (black parts represent Z, Z isomers, red parts assigned to new peaks i.e. its configurational isomers); (f) Schematic diagram of three isomers of dicyanodistyrylbenzene-modified monomer.

in PSS upon irradiation at 405 nm visible light for 57 min (Fig. 2e-i and 2e-ii). Subsequently, the resultant sample was stimulated by the other wavelength light (313 nm) or heating at 80 °C, and no apparent alteration was observed for UV-vis absorption spectrum (Fig. S9 and S10) and ^1H NMR spectrum (Fig. 2e-iii), jointly confirming that the photoisomerization reaction was irreversible. The irreversible behaviors were consistent with the reported literatures [14,15]. This inertness was likely attributable to a prohibitively high isomerization barrier. The structural transformation of DCS-BQ in the aforementioned directional photoisomerization process was presented in Fig. 2f. While Fig. 2f displayed all three theoretical isomers ((Z, Z), (Z, E), (E, E)) to delineate the full reaction coordinate, it should be noted that simultaneous enrichment of all three species did not occur at PSS. One plausible rationale was that the (Z, E) intermediate, formed during 405 nm irradiation, rapidly converted to (E, E) and eludes NMR detection. This transient nature was corroborated by the single isosbestic point in the UV-vis spectra (Fig. 2d) and the strictly maintained 1:1 (Z, Z): (E, E) molar ratio derived from NMR. Meanwhile, the assembly DCS-BQ $\text{C}_{60}\text{B}[7]_2$ formed by DCS-BQ also expressed similar phenomena (Fig. S11–S13), further verifying the occurrence of unidirectional photoisomerization reaction. In addition, the midbody DCS without BQ exhibited almost exactly the same changes in UV-vis absorption (Fig. S14–S16) and ^1H NMR spectra (Fig. S17) and relatively dose conversion yield obtained by examining ^1H NMR of the irradiated sample. In order to eliminate the interference of bromoquinoline salt, it did not manifest any variation in UV-vis absorption and ^1H NMR spectra when stimulated by 405 nm light (Fig. S18 and S19). In a word, the aforementioned proofs, without any doubt, enabled us to conclusively determine that the photoreaction occurred on the DCS group but not bromoquinoline segment, which

might be responsible for the visible-light-induced photoluminescence enhancement above. Therefore, the above remarkable fluorescence enhancement induced by the Z $\rightarrow$ E directional photoisomerization of merely half of DCS-BQ should be primarily attributed to the synergistic effect between the intrinsic molecular configurational change and the consequent alteration in molecular packing modes.

Next, the nanostructural information was acquired for the DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS) assembly from transmission electron microscopy (TEM), scanning electron microscopy (SEM) and dynamic light scattering (DLS) experiments. As discerned from the TEM image (Fig. 3a), many quasi-spherical nanoparticles were presented with an average diameter of 118 nm, which was further verified by scanning electron microscopy (SEM) image (Fig. 3b). Furthermore, the diameter ($D_h = 166.1$ nm) determined by DLS was appreciably greater than the average diameter given by TEM and SEM because of the shrinking of nanoparticles upon air-drying in the sample preparation for TEM and SEM (Fig. 3c), revealing that DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS) formed nanoaggregates in 2% DMSO aqueous solution [25]. On account of these spectroscopic and morphological analyses, a plausible self-assembling pattern of DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS) was illustrated in Scheme 1, which was consistent with the previous report [26].

Possessing typical nanostructure, strong luminescence intensity and good photostability and thermostability, the polymeric-supramolecular complex DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS) after illumination of 405 nm light was anticipated to act as energy donor and accommodate appropriate energy receptor fluorophores to construct FRET-based light-harvesting systems. Considering photoluminescent spectrum of DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS), Nile red (NIR) was chosen as an energy-matching receptor to build a light-harvesting system, originating from good spectral overlap

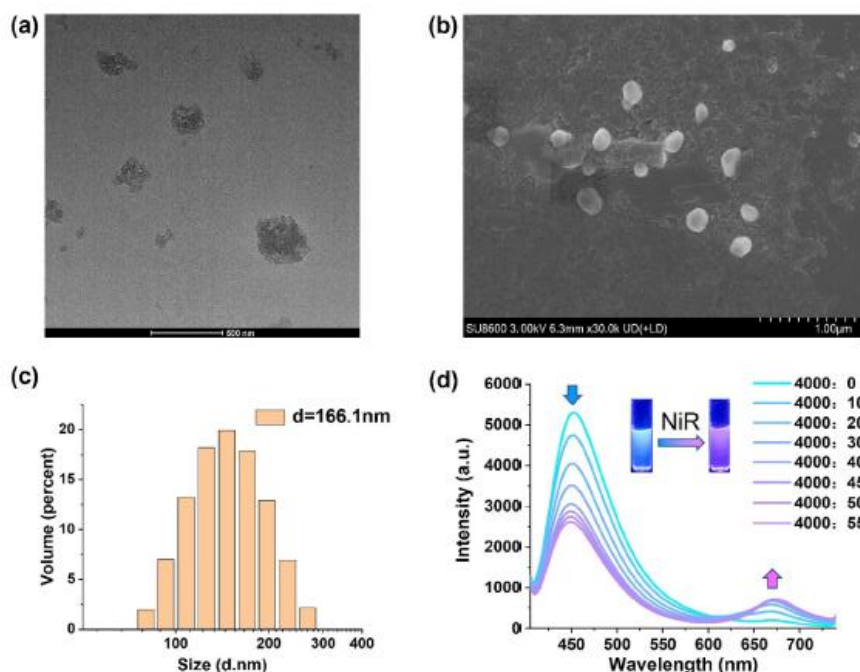


Fig. 3. (a) TEM image of DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS); (b) SEM image of DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS); (c) DLS data of DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS; (d) Fluorescence emission spectral evolution of (E, E)-DCS-BQ $\text{C}_{60}\text{B}[7]_2$ -PSS(PS) with sequential addition of NIR ([CB[7]] = 2[DCS-BQ] = 1.0×10^{-4} mol/L, [PSS] = 0.04 g/L, [NIR] = 0– 4.0×10^{-7} mol/L, $\lambda_{\text{ex}} = 380$ nm).

of the absorption of NiR and the emission of DCS-BQCCB[7]₂-PSS(PS) (Fig. S20). Interestingly, fluorescence intensity of the complex at 452 nm declined, while the emission peak at 674 nm (assigned to NiR, Fig. S21) increased, with sequential addition of NiR in the solution containing DCS-BQCCB[7]₂-PSS(PS), manifesting that light-harvesting process based on FRET took place (Fig. 3d). Noteworthy, the photoluminescent intensity at 674 nm increased no longer with addition of a small amount of NiR in above process until the energy donor/acceptor (D/A) ratio was 800:11 (Fig. 3d). Visually, the fluorescence color of the sample solution was changed from blue to pink (under 365 nm UV light) as NiR was added (Fig. 3d, Inset). In control experiment, the photoluminescent intensity of the individual NiR at 674 nm excited by excitation wavelengths of itself or the assembly was both distinctly less than that of DCS-BQCCB[7]₂-PSS(PS)@NiR (Fig. S22 and S23), implying that photo-harvesting process based on FRET took place. Furthermore, fluorescence lifetime was shortened from 3.90 ns to 1.65 ns (Table S1), also implying that the occurrence of FRET process. The energy transfer efficiency was measured to be 49.5% (452 nm) and simultaneously, the antenna effect value was determined to be 3.0 in the light-harvesting system (seeing Supporting Information), which fell within the conventional range reported for this class of materials [27–29]. In control experiment, Fluorescence emission spectra of DCS-BQ(PS), DCS-BQ(PS)-NiR, DCS-BQCCB[7]₂-PSS(PS), DCS-BQCCB[7]₂-PSS(PS)-NiR, and NiR were acquired under identical conditions (Fig. S24), and the results revealed that both the luminescence intensity and energy transfer efficiency are negligible in the absence of CB[7] and PSS and further demonstrated that the encapsulation by CB[7] and the co-assembly with PSS were indispensable for the efficient performance of this light-harvesting system.

The photophysical and photochemical properties of the system above inspired us to explore their applications in high-security-level information encryption. Interestingly, when the patterns fabricated by DCS-BQCCB[7]₂-PSS(PS) was irradiated by 405 nm light, the fluorescent patterns gradually turned from weak yellowish-brown to strong blue (Fig. 4a), attributed to the alteration of fluorescent intensity and color of the sample (Figs. 4b and 2c). The color and intensity of the patterns

exhibited concurrently variation along with the irradiation time, revealing time-resolved anti-counterfeiting application potentiality. As displayed in Fig. 4c-i, a special information was formed by three diverse models prepared by (Z, Z)-DCS-BQCCB[7]₂-PSS, showing weak yellowish-brown photoluminescence. Subsequently, when it was irradiated at 405 nm visible light, the information was lightened for a strong blue fluorescence pattern (Fig. 4c-ii). Then, parts of the generated pattern were interfered by a small amount of NiR, the interfering parts turned to strong pink luminescence, displaying the change of the pure blue pattern to a blue-pink color information (Fig. 4c-iii).

3. Conclusion

In conclusion, we designed and synthesized a water-soluble dicyanostyrylbenzene derivative DCS-BQ, showing certain light-responsiveness and weak luminescence. The photoactive luminophore as guest assembled with CB[7] to form a [1 + 2] supramolecular complex DCS-BQCCB[7]₂ through host-guest interaction, along with apparent fluorescence enhancement. Afterwards, the complex was further doping with electronegative PSS to prepare polymeric-supramolecular complex DCS-BQCCB[7]₂-PSS by electrostatic interaction, accompanied by further photoluminescence increment. The two-step improvement in the luminous performance was both attributed to the restriction of intramolecular free rotation. However, the photoluminescence capacity of the aforementioned complex was unsatisfactory. Subsequently, visible-light-powered in situ unidirectional photoreaction took place upon irradiation at 405 nm light with structural transformation from Z-to-E-configuration, exhibiting dramatical enhancement of the photoluminescence intensity and color change from yellowish-brown to blue. Excellent photoluminescence properties and typical nanostructure formed by (E, E)-DCS-BQCCB[7]₂-PSS in PS enabled the fabrication of light-harvesting system based on FRET through introduction of energy-matching receptor NiR in accompany with fluorescence color from blue to pink. The dynamic variation of luminescence intensity and color stimulated by light and fluorochrome-doping enabled the application in time-resolved information encryption

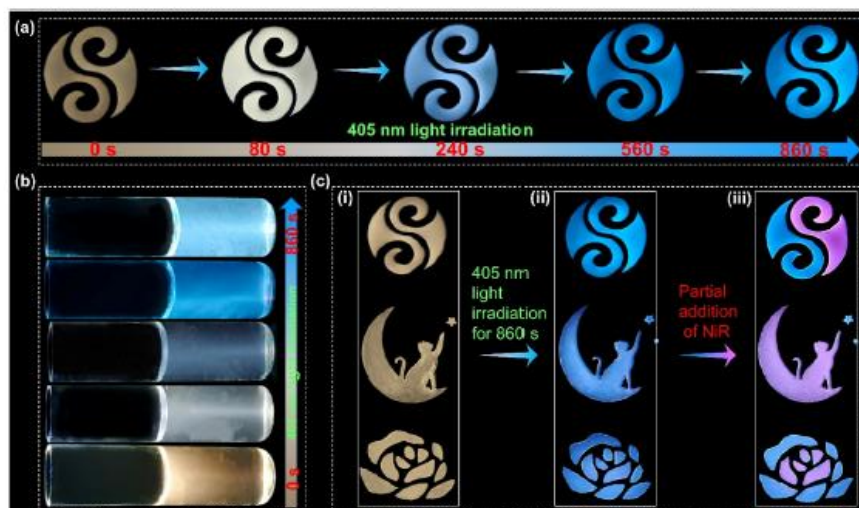


Fig. 4. (a) Image changes of the model fabricated by (Z, Z)-DCS-BQCCB[7]₂-PSS (under 365 nm UV light) along with irradiation time at 405 nm light; (b) Fluorescent photograph changes of (Z, Z)-DCS-BQCCB[7]₂-PSS (under 365 nm UV light) along with irradiation time at 405 nm light; (c) (i) Photographs of the model fabricated by (Z, Z)-DCS-BQCCB[7]₂-PSS under 365 nm UV light; (ii) Photographs of the sample i after the 405 nm UV lamp; (iii) Photographs of the sample ii with addition of NiR.

and anti-counterfeiting with high level of security. The study presented an innovative approach to construct high-performance dynamic photoluminescent materials using in situ directional photoreaction.

4. Experimental section

4.1. Materials and methods

All other starting materials were purchased from the market in analytical purity form and used directly at 25 °C without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 mass spectrometer with TMS as the internal standard at 25 °C. High-resolution mass spectrometry was measured in electrospray mode. Ultraviolet-visible absorption spectra were measured using quartz cells (optical path 10 mm) under a HITACHI U-3900 spectrophotometer. Photoluminescence spectra were measured using conventional quartz cells (optical path 10 mm) under a HITACHI F-4700 FL spectrophotometer. Irradiation experiments ($\lambda = 405\text{ nm}$) were carried out using a CEL-HXF300 20V 300W xenon lamp (Beijing China Education Au-light Co. Ltd., China) with a 25% attenuating filter and a band-pass optical filter for 405 nm light. The exact optical power densities of 405 nm light in irradiation experiments were determined to be 12.72 mW/cm^2 , using an optical power meter (CEL-NP2000-2A). TEM was were acquired using FEI Tecnai G2 F20 under 200 KV. The sample for TEM measurement was prepared by dropping a sample solution onto a copper grid. The grid was then air dried. SEM image was recorded on a ZEISS MERLIN Compact scanning electronic microscope operating at an accelerating voltage of 5 keV. The sample solutions for dynamic light scattering measurements (DLS) were examined on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (Turbo Corr.) at a scattering angle of 90°.

4.2. Synthesis of 2

P-hydroxybenzaldehyde (0.50 g, 4.20 mmol), K_2CO_3 (7.36 g, 53.30 mmol), acetonitrile (50 mL) and 1,2-dibromoethane (1.07 mL, 12.6 mmol) were added into a 100 mL two-necked round-bottom flask equipped with a magnetic stirrer, and the mixture was refluxed at 90 °C for 5 h. After the reaction was completed, the resulting mixture was allowed to cool to room temperature and was filtered. After that, the solvents were removed under vacuum, and the residue was extracted by ethyl acetate and then dried over anhydrous Na_2SO_4 , removed of solvent under reduced pressure, and purified on a silica gel column using ethyl acetate/petroleum ether (1:5) as the eluent to obtain 2 as a white solid [30]. Yield: 0.58 g, 62%. ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 9.90 (s, 1H), 7.85 (d, $J = 8.8\text{ Hz}$, 2H), 7.02 (d, $J = 8.7\text{ Hz}$, 2H), 4.38 (t, $J = 6.2\text{ Hz}$, 2H), 3.67 (t, $J = 6.2\text{ Hz}$, 2H).

4.3. Synthesis of DCS

Compound 2 (0.29 g, 1.28 mmol), 2,2'-(1,4-phenylene)diacetonitrile (0.10 g, 0.64 mmol), tetra-*n*-butyl ammonium hydroxide (TBAH) and 50 mL anhydrous ethanol were added in a 100 mL two-necked flask. The resulting mixture was refluxed at 85 °C for 10 h. After completion of the reaction, a yellow precipitate was produced, and the obtained solid was further washed with *n*-hexane, and then dried to obtain compound DCS as a yellow solid [21]. Yield: 0.08 g, 86%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm) = 8.09 (s, 2H), 7.99 (d, $J = 8.9\text{ Hz}$, 4H), 7.87 (s, 4H), 7.16 (d, $J = 8.9\text{ Hz}$, 4H), 4.44 (t, $J = 5.1\text{ Hz}$, 4H), 3.86 (t, $J = 5.4\text{ Hz}$, 4H).

4.4. Synthesis of DCS-BQ

DCS (0.06 g, 0.10 mmol), 6-bromoisquinoline (0.04 g, 0.21 mmol) and 2 mL DMF were added in the reaction tube. The resulting mixture was refluxed at 90 °C for 5 days under argon atmosphere. After the reaction was complete, 20 mL ethyl ether was added and a yellow

precipitate was produced. The suspension liquid was filtered, and the filter cake was washed with dichloromethane and dried to obtain DCS-BQ as a yellow solid. Yield: 0.05 g, 57%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm) = 10.17 (s, 2H), 8.92 (d, $J = 6.8\text{ Hz}$, 2H), 8.72 (d, $J = 0.6\text{ Hz}$, 2H), 8.54 (d, $J = 6.9\text{ Hz}$, 2H), 8.50 (d, $J = 8.8\text{ Hz}$, 2H), 8.25 (dd, $J = 1.5\text{ Hz}$, 1.6 Hz, 2H), 8.05 (s, 2H), 7.93 (d, $J = 9.0\text{ Hz}$, 4H), 7.84 (d, $J = 5.7\text{ Hz}$, 4H), 7.13 (d, $J = 8.8\text{ Hz}$, 4H), 5.17 (t, $J = 3.9\text{ Hz}$, 4H), 4.70 (t, $J = 4.7\text{ Hz}$, 4H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ (ppm) = 159.5, 151.2, 142.7, 138.1, 136.6, 134.6, 134.3, 132.4, 132.0, 131.4, 131.3, 129.7, 127.0, 126.2, 125.8, 124.7, 118.1, 115.2, 115.1, 106.9, 106.9, 66.2, 60.1. HRMS (ESI) for $\text{C}_{23}\text{H}_{17}\text{BrN}_2\text{O}^+$ ($[\text{M} - 2\text{Br}]^+$): calcd. 416.0519, found 416.0526.

4.5. Synthesis of BQ

1,2-dibromoethane (0.94 g, 5.00 mmol), 6-bromoisquinoline (0.42 g, 2.00 mmol) and 30 mL acetonitrile were added into a 100 mL reaction flask, and the mixture was refluxed at 90 °C for 12 h under argon atmosphere. Then, the resulting mixture was cooled to room temperature, a precipitate was produced and washed with diethyl ether and acetone to obtain BQ as a white solid. Yield: 0.53 g, 68%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm) = 10.14 (s, 1H), 8.87 (dd, $J = 0.7, 0.7\text{ Hz}$, 1H), 8.73 (d, $J = 1.2\text{ Hz}$, 1H), 8.57 (d, $J = 6.8\text{ Hz}$, 1H), 8.46 (d, $J = 8.8\text{ Hz}$, 1H), 8.27 (dd, $J = 1.72, 1.48\text{ Hz}$, 1H), 5.14 (t, $J = 6.0\text{ Hz}$, 2H), 4.18 (t, $J = 6.0\text{ Hz}$, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ (ppm) = 151.0, 138.1, 136.1, 134.8, 132.4, 132.3, 129.8, 125.7, 124.8, 61.3, 31.6. HRMS (ESI) for $\text{C}_{11}\text{H}_9\text{Br}_2\text{N}^+$ ($[\text{M} - \text{Br}]^+$): calcd. 313.9175, found 313.9182.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Zizheng Li: Investigation, Methodology. Fenghua Yin: Investigation, Methodology. Yongmei Xiao: Supervision. Wenhao Yang: Data curation. Song Jiang: Validation. Yuli Dang: Visualization. Xinzhe Tian: Visualization. Ziyong Li: Supervision. Guoxing Liu: Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank National Natural Science Foundation of China (21801063 and 22578193), Top-Notch Talents Program of Henan Agricultural University (30501049), Natural Science Foundation of Henan Province (252300421450), Key Scientific Research Project of Higher Education Institutions in Henan Province (26A150020), Scientific and Technological Project of Henan Province (252102320367 and 252102311211), and Backbone Teacher in Henan Province (2021GGJS029) for financial support.

Appendix. ASupplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.dyepig.2026.114067>.

Data availability

Data will be made available on request.

References

- [1] Song Y, Bian Q, Wang F, Liu J, Yang Y, Zhang Y, et al. *Coord Chem Rev* 2025;524: 216299.
- [2] Song S, Zhang H, Liu Y. *Acc Mater Res* 2024;5:1109–20.
- [3] Nie H, Wei Z, Ni XL, Liu Y. *Chem Rev* 2022;122:9032–77.
- [4] Chen M, Zhong M, Johnson JA. *Chem Rev* 2016;116:10167–211.
- [5] Liu G, Li Y, Tian C, Xiao Y, Liu L, Cao Z, et al. *Chin Chem Lett* 2024;35:109403.
- [6] Cao Q, Xiao Y, Liu G. *Chin. J Org Chem* 2024;44:2124–35.
- [7] Yang L, Li Y, Zhang H, Tian C, Cao Q, Xiao Y, et al. *Chin Chem Lett* 2023;34: 108108.
- [8] Yokoyama S, Nishioka N. *J Org Chem* 2019;84:1192–200.
- [9] An BK, Kwon SK, Jung SD, Park SY. *J Am Chem Soc* 2002;124:14410–5.
- [10] Gierschner J, Park SY. *J Mater Chem C* 2013;1:5818–32.
- [11] Abadía M, Varghese S, Giménez R, Ros MB. *J Mater Chem C* 2016;4:2886–90.
- [12] Wei P, Zhang J, Zhao Z, Chen Y, He X, Chen M, et al. *J Am Chem Soc* 2018;140: 1966–75.
- [13] Li JJ, Chen Y, Yu J, Cheng N, Liu Y. *Adv Mater* 2017;29:1701905.
- [14] Sun X, Liu Z, Wang Z, Huo M, Zhang H, Liu Y. *J Org Chem* 2022;87:7658–64.
- [15] Zhang Z, Li J, Wei W, Wei J, Guo J. *Chin J Polym Sci* 2018;36:776–82.
- [16] Kim DY, Koo J, Lim SI, Jeong KU. *Adv Funct Mater* 2018;28:1707075.
- [17] Hao M, Sun G, Zuo M, Xu Z, Chen Y, Hu X, et al. *Angew Chem Int Ed* 2020;59: 10095–100.
- [18] Tang L, Wu Z, Zhang Q, Hu Q, Dang X, Cui F, et al. *Chem Commun* 2024;60: 4719–22.
- [19] Liu G, Zhang H, Xu X, Zhou Q, Dai X, Fan L, et al. *Mater Today Chem* 2021;22: 100628.
- [20] Fan X, Fan Y, Dang Y, Xie P, Li X, Cao Z, et al. *Chin Chem Lett* 2025;36:110648.
- [21] Gong Y, Xiao Y, Fan X, Li Z, Yang W, Dang Y, et al. *Chem Eng J* 2025;523:168862.
- [22] Barrow SJ, Kaser S, Rowland MJ, delBarrio J, Scherman OA. *Chem Rev* 2015;115: 12320–406.
- [23] Dai XY, Huo M, Dong X, Hu YY, Liu Y. *Adv Mater* 2022;34:2203534.
- [24] Dai XY, Hu YY, Sun Y, Huo M, Dong X, Liu Y. *Adv Sci* 2022;9:2200524.
- [25] Huang P, Wang D, Su Y, Huang W, Zhou Y, Cui D, et al. *J Am Chem Soc* 2014;136: 11748.
- [26] Dai XY, Song Q, Zhou WL, Liu Y. *JACS Au* 2024;4:216–27.
- [27] Lei Z, Li S, Sun P, Chen Y, Zhang X, Liu Y. *Adv Sci* 2026;13:e22017.
- [28] Zhang R, Lei Z, Yu Z, Chen Y, Liu Y. *Adv Sci* 2025;12:e07090.
- [29] Yu J, Liao J, Zhao Y, Liu Y. *Chin Chem Lett* 2026;37:111964.
- [30] Sava A, Buron F, Routier S, Panainte A, Ribire N, Constantin SM, et al. *Int J Mol Sci* 2021;22:7079.

3. 二维介孔材料在微型超级电容器中的应用进展. 储能科学与技术, 2026, 15(2), 458-478. (中文核心, CSCD)

第15卷 第2期
2026年2月

储 能 科 学 与 技 术
Energy Storage Science and Technology

Vol.15 No.2
Feb. 2026

储能材料与器件



二维介孔材料在微型超级电容器中的应用进展

白天娥, 张鸿涛, 陶向阳, 彭域静, 姜 松, 秦洁琼
(河南农业大学理学院, 河南 郑州 450002)

摘 要: 微型超级电容器是一种小尺寸电源, 凭借功率密度高、充放电速率快、使用寿命长、机械柔性好和安全性高等优点, 逐渐成为智能化电子领域的研究热点。为了提升微型超级电容器的能量密度, 开发高导电、高活性和高稳定的电极材料是主要策略之一。近年来, 二维介孔材料由于高的比表面积、丰富的活性位点, 以及发达的介孔结构等特点, 克服了二维材料易堆叠和块体介孔材料离子输运路径长的缺点, 被认为是最具优势的微型超级电容器电极材料之一。基于此, 本文回顾了近年来二维介孔材料在微型超级电容器中的应用进展。首先, 阐述了微型超级电容器的储能机理, 以及二维介孔材料应用于微型超级电容器的结构优势。随后, 总结了二维介孔碳、二维介孔金属化合物、二维介孔导电聚合物, 以及二维介孔石墨烯基、MXene基和金属硫化物基复合材料等在微型超级电容器中的应用, 验证二维介孔结构对其电化学性能的增强机制。最后, 展望了二维介孔材料及其微型超级电容器的发展方向和前景, 以期新型二维能源材料和高性能微型电源的开发提供思路。

关键词: 二维材料; 介孔结构; 微型超级电容器; 高性能

doi: 10.19799/j.cnki.2095-4239.2025.0908

中图分类号: TM 53

文献标志码: A

文章编号: 2095-4239 (2026) 02-458-21

Recent advances of 2D mesoporous materials in micro-supercapacitors

BAI Tiane, ZHANG Hongtao, TAO Xiangyang, PENG Yujing, JIANG Song, QIN Jieqiong
(College of Science, Henan Agricultural University, Zhengzhou 450002, Henan, China)

Abstract: Micro-supercapacitors (MSCs) are microscale power supply systems that exhibit high power density, rapid charge-discharge capability, long cycle life, good flexibility, and excellent safety, making them a research hotspot in intelligent electronics. The development of electrode materials with high electrochemical activity, good conductivity, and outstanding stability is the key to enhancing the energy density of MSCs. Recently, two-dimensional (2D) mesoporous materials have been regarded as a promising electrode candidate for MSCs due to their large specific surface area, abundant active sites, and well-developed mesoporous structures, which can effectively overcome the limitations of restacking of 2D materials and the long ion transport pathways in bulk mesoporous materials. This review focuses on the recent advances of 2D mesoporous materials in MSCs. First, the energy storage mechanisms

收稿日期: 2025-10-13; 修改稿日期: 2025-11-16。

基金项目: 国家自然科学基金面上项目 (22579047), 河南省自然科学基金面上项目 (252300423115), 河南省本科高校青年骨干教师培养计划项目 (2021GGJS029)。

第一作者: 白天娥 (2000—), 女, 硕士研究生, 研究方向为介孔导电聚合物基微型超级电容器。E-mail: 19913780711@163.com; 通信作者: 姜松, 副教授, 研究方向为超分子化学与传感器。E-mail: jiangsong@henau.edu.cn; 秦洁琼, 教授, 研究方向为二维介孔材料与微型储能器件。E-mail: qinjieqiong@henau.edu.cn。

引用本文: 白天娥, 张鸿涛, 陶向阳, 等. 二维介孔材料在微型超级电容器中的应用进展[J]. 储能科学与技术, 2026, 15(2): 458-478.

Citation: BAI Tiane, ZHANG Hongtao, TAO Xiangyang, et al. Recent advances of 2D mesoporous materials in micro-supercapacitors[J]. Energy Storage Science and Technology, 2026, 15(2): 458-478.

of MSCs and the structural advantages of 2D mesoporous materials are highlighted. Second, various 2D mesoporous materials for MSC applications are comprehensively summarized, including 2D mesoporous carbons, metal compounds, conductive polymers, and 2D mesoporous composite materials based on graphene, MXene, metal sulfides, etc. Notably, the mechanisms of electrochemical performance enhancement enabled by the 2D mesoporous structure are elucidated. Finally, an outlook on the development directions and application prospects of 2D mesoporous materials in MSCs is provided, contributing to the conceptualization of novel 2D energy materials and high-performance miniature power supplies.

Keywords: 2D materials; mesoporous structure; micro-supercapacitors; high-performance

随着科学技术的不断发展,人们对智能化、微型化与柔性化电子设备的需求日益增加,例如:可折叠手机、运动手环、物联网感知芯片、可穿戴健康监测装置、可植入医疗器械等,因此,亟须开发与与之相匹配的小尺度电源(微型电池或微型超级电容器)^[1-3]。与微型电池相比,微型超级电容器具有形状可定制、功率密度高、充放电速度快、循环寿命长、机械柔性好和安全性能高的优点,可直接与耗能终端(如传感器等)有效集成,实现在智能电子、物联网、医疗健康、无线环境监测以及食品安全等领域的应用(图1)^[4]。根据构型的不同,微型超级电容器可以分为一维型(纤维)、二维型(平面)和三维型三种^[5-6]。其中,平面型微型超级电容器是指构筑在二维平面基底上的小尺度超级电容器,它能够适应片上微加工工艺,可直接与其他微电子在一个平面上耦合。其平面结构正负极间无须隔膜,显著缩短了两电极之间的距离,减小了电解质离子的传输电阻,具有更高的功率密度和更好的倍率性能^[7]。但是,目前微型超级电容器仍面临能量密度低的问题,严重制约了其发展和应用,而开发高导电、高活性和高稳定的电极材料是解决这一关键问题的主要策略之一。

近年来,二维材料作为微型超级电容器的电极材料受到了广泛关注^[8-9]。二维材料是指在二维平面内可以无限延伸,厚度为单层或少层原子厚度的纳米材料。常见的二维材料有石墨烯^[10-11]、过渡金属碳氮化物(MXenes)^[12-13]、金属氧化物/氢氧化物^[14-16]、金属硫化物^[17-18]、氮化硼(BN)^[19-20]、金属有机框架和共价有机框架纳米片等^[21-23],它们超薄的厚度可以为离子和电子的传输提供二维通道,使其沿平面快速、无障碍迁移;大的比表面积和丰富的

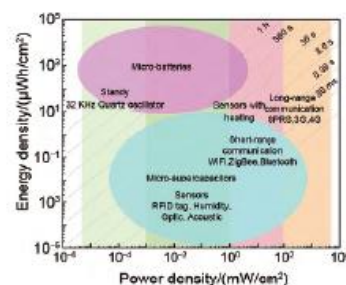


图1 微型超级电容器和微型电池的能量密度与功率密度关系图^[4]

Fig. 1 Ragone plot of the state-of-the-art micro-batteries and MSCs^[4]

活性位点有利于电解质离子与材料的有效接触;优异的力学性能和多样的组成赋予微型超级电容器良好的柔韧性和功能性。但是,由于二维材料片层间 π - π 堆积和范德华力等,使其在使用过程中容易发生不可逆的团聚,从而导致材料的比表面积降低,电化学性能下降。考虑到介孔材料具有大的比表面积、可调的孔径和孔体积等,其适中的孔径可以容纳溶剂化的电解质离子,加快电化学反应动力学,提高电极材料的性能。因此,将二维材料与介孔结构相结合来构筑新型二维介孔材料,有望克服单一材料的缺陷,协同实现高性能的微型超级电容器。

基于此,本文对近年来二维介孔材料在微型超级电容器中的应用进展进行系统回顾。首先,介绍微型超级电容器的储能机理以及二维介孔材料的结构和优势。进一步,聚焦不同结构和组成的二维介孔材料,综述其结构特点、制备方法和微型超级电容器性能。最后,对二维介孔材料和微型超级电容器领域目前存在的挑战和未来的发展前景进行总结和展望。

1 微型超级电容器的储能机理

微型超级电容器一般定义为：占用面积或体积在微米到厘米范围内($\mu\text{m}^2 \sim \text{cm}^2/\mu\text{m}^3 \sim \text{cm}^3$)，且至

少有一个维度(如电极厚度)是微米级的小尺度超级电容器^[5,23]。根据储能机理的不同，可以将微型超级电容器分为双电层型、赝电容型和混合型三种(图2)^[24-26]。

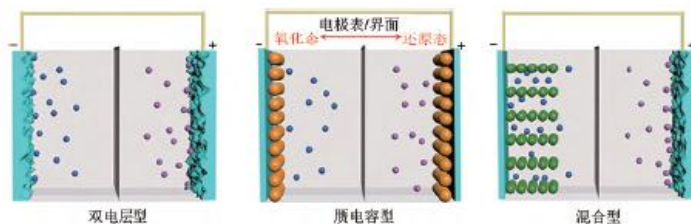


图2 双电层型、赝电容型和混合型微型超级电容器的储能机理示意图

Fig. 2 Schematic diagrams of the energy storage mechanisms of electric double-layer type, pseudocapacitive type, and hybrid type MSCs

双电层型是基于界面双电层理论，通过电极和电解质界面的静电吸附/解吸进行电荷/能量的存储。其储能过程不涉及化学氧化还原反应，无电荷转移，因此表现出优异的充放电速率、倍率性能、功率密度和循环稳定性。活性炭、多孔碳、碳纳米管和石墨烯等碳基材料是双电层型电极材料的典型代表，具有导电性高、比表面积大、稳定性好，以及经济环保等优点，目前已得到了广泛研究和商业化应用^[27-29]。

赝电容型主要基于法拉第反应，通过电极表/界面发生的快速、可逆的氧化还原反应进行电荷/能量存储。其储能机制分为欠电位沉积、氧化还原赝电容和插层赝电容三种^[30]，其中氧化还原赝电容最为常见。赝电容型的储能过程涉及一定的电荷转移，因此具有更高的比容量和能量密度，可达双电层型的10~100倍；但是其倍率性能、循环寿命和功率密度低于双电层型。目前，常用的赝电容型材料包括：杂原子掺杂/带有官能团的碳材料、过渡金属氧化物、导电聚合物、MXenes等^[31-33]。

混合型通常包含一个电容型(双电层/赝电容)电极和一个电池型(体相法拉第反应)电极，两种机理协同进行电荷/能量存储。其储能过程结合了电容型电极的高功率密度和电池型电极的高能量密度，能够填补超级电容器和电池之间的空白，实现可调的功率和能量输出，因此近年来得到了广泛关注。常见的混合型微型超级电容器包括锂离子、钠离子、钾离子、铵离子、锌离子、镁离子等微型电容

器^[34-35]。在活性电极材料的选择上，主要采用高比表面积的碳、杂原子掺杂碳、MXenes及其复合材料等电容器型电极，和具有丰富氧化还原活性位点的金属氧化物、金属氢氧化物、金属盐及其复合材料的电池型电极，最终实现器件能量密度、功率密度和循环寿命的兼顾。

2 二维介孔材料的结构和优势

二维介孔材料的定义为：在面内或面上拥有大量2~50 nm孔径的二维材料^[36-37]。二维介孔材料结合了二维材料和介孔材料的优势，克服了二维材料易自堆叠、块状介孔材料离子输运路径长等缺点，展现出独特的二维形貌、发达的介孔结构、高的比表面积和丰富的活性位点，能够高度匹配微型超级电容器的小尺寸、平面柔性结构，显著提高微型超级电容器的能量密度、功率密度和循环寿命。具体来说，其独特的二维形貌和介孔网络可以为电解质离子的传输提供连续的通道，缩短电解质离子的传输距离，加快其传输速率，并缓解电极在充放电过程的体积变化，提高电极和器件的电化学反应动力学、倍率性能和循环稳定性；大的比表面积和丰富的活性位点增加了电解质离子与电极之间的有效接触面积，有利于离子与电极的充分作用/反应，以及电子的传输，提升电极和器件的比容量和能量密度。

根据形貌结构，可以将二维介孔材料分为面内介孔材料和三明治状介孔复合材料(图3)。二维面

内介孔材料是指在平面上有纵向介孔的二维纳米片, 比如: 介孔碳纳米片^[38-39]、介孔石墨烯^[28, 40-41]、介孔金属氧化物纳米片^[42-43]、介孔金属硫化物纳米片^[44]、介孔MXenes等^[45-48]。其上下贯穿的面内孔道, 使载流子能够同时在水平和垂直方向上快速传输, 显著增强材料的传质速率。而且, 二维面内介孔结构能够提供大量的边缘和缺陷, 提高材料的可接触比表面积和反应活性位点。另一方面, 三明治状二维介孔复合材料主要是指在二维基底两侧各叠加一层介孔功能组分而形成的三明治状复合结构, 例如: 介孔碳-石墨烯-介孔碳纳米片^[47-48]、介孔聚合物-石墨烯-介孔聚合物纳米片^[50-52]、介孔碳-MXene-介孔碳纳米片等^[53-55]。与单一组分的二维面内介孔材料不同, 三明治状二维介孔复合材料能够耦合功能组分和二维基底两者的优势, 增加二维材料的层间距, 抑制其堆叠; 介孔层可以在一定程度上保护一些不稳定的二维材料(MXenes、黑磷烯等)^[56-57], 而基本不影响其活性发挥; 功能组分还可以赋予材料新的物理化学性质, 满足微型超级电容器的多功能需求。

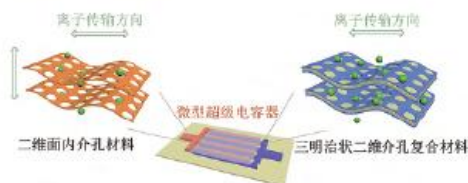


图3 不同结构的二维介孔材料及其离子传输路径示意图
Fig. 3 Schematic diagrams of different 2D mesoporous materials and their ion migration paths

根据化学组成, 二维介孔材料主要分为二维介孔碳材料、二维介孔过渡金属化合物、二维介孔导电聚合物及其二维介孔复合材料等, 其中二维介孔碳、过渡金属化合物、导电聚合物属于二维面内介孔材料, 而二维介孔复合材料属于三明治状二维介孔材料。不同形貌结构和化学组成的二维介孔材料各具特点和优势, 本文主要根据化学组成的分类, 讨论不同二维介孔材料在微型超级电容器中的应用。

3 二维介孔材料在微型超级电容器中的应用

3.1 二维介孔碳

二维介孔碳是一种新型的碳材料, 主要以二维碳

骨架为主体, 内部具有丰富的介孔结构。此类材料具有大的比表面积、丰富的孔隙结构、优异的导电性和耐酸碱能力, 在微型超级电容器中展现出巨大的应用潜力。常见的二维介孔碳主要有介孔碳纳米片^[58-61]、介孔杂原子掺杂碳纳米片^[62-65]、介孔石墨烯^[40, 66-67]等。

3.1.1 介孔碳纳米片

介孔碳纳米片是典型的电化学双电层型材料, 作为微型超级电容器的活性电极时, 其优异的导电性和二维介孔结构, 赋予器件显著提高的比容量、倍率性能和循环稳定性^[38-39]。例如, Yadav等^[68]以生物质(蘑菇)为原料, 通过水处理和KOH活化合成了多孔碳(MDC)纳米片。如图4(a)和(b)所示, MDC纳米片的孔径分布为1~4 nm, 比表面积约为2604 m²/g。将其作为活性电极材料, 通过激光刻蚀技术制备出平面叉指型微电极, 并结合聚乙烯醇(PVA)/H₂SO₄凝胶电解质, 得到了准固态微型超级电容器[图4(c)]。该微型超级电容器的体积比容量为12.92 mF/cm³, 经过15000次充放电和1000次弯曲循环, 均展现出高的稳定性。但是, MDC纳米片的二维形貌不均匀, 孔结构随机分布, 不利于微纳结构与电化学性能之间构效关系的研究。进一步, Xi等^[69]报道了一种软-硬模板辅助策略, 可控制备出具有均匀六边形的有序介孔碳纳米片(OMCS), 并应用于准固态微型超级电容器。如图4(d)所示, 以层状双氢氧化物(MgAl-LDH)为二维硬模板, 聚氧乙烯-聚氧丙烯-聚氧乙烯三嵌段共聚物(F127)为介孔软模板, 酚醛树脂为碳源, 通过调节MgAl-LDH和酚醛树脂-F127胶束的比例, 制备出了垂直孔(OMCS-1)和平行孔(OMCS-2)的OMCSs。这两种OMCS的厚度约为9 nm, 孔径大小约10 nm, 比表面积分别为650 m²/g和640 m²/g[图4(e), (f)]。将它们作为活性电极材料, 结合PVA/H₂SO₄电解质, 成功制备出平面微型超级电容器。如图4(g)~(j)所示, OMCS-1基微型超级电容器呈现出最高的体积比容量与能量密度(3.9 mWh/cm³), OMCS-2基器件展现出更好的倍率性能和体积功率密度(242 W/cm³)。该工作证明了介孔结构和取向对微型超级电容器电化学性能的影响规律, 其中垂直介孔有利于电解质离子的渗透, 缩短离子迁移路径, 因此展现出更高的比容量和能量密度; 平行介孔有利于离子沿孔道无障碍迁移, 加快了离子的传输速率, 因此具有更好的倍率性能和功率密度。

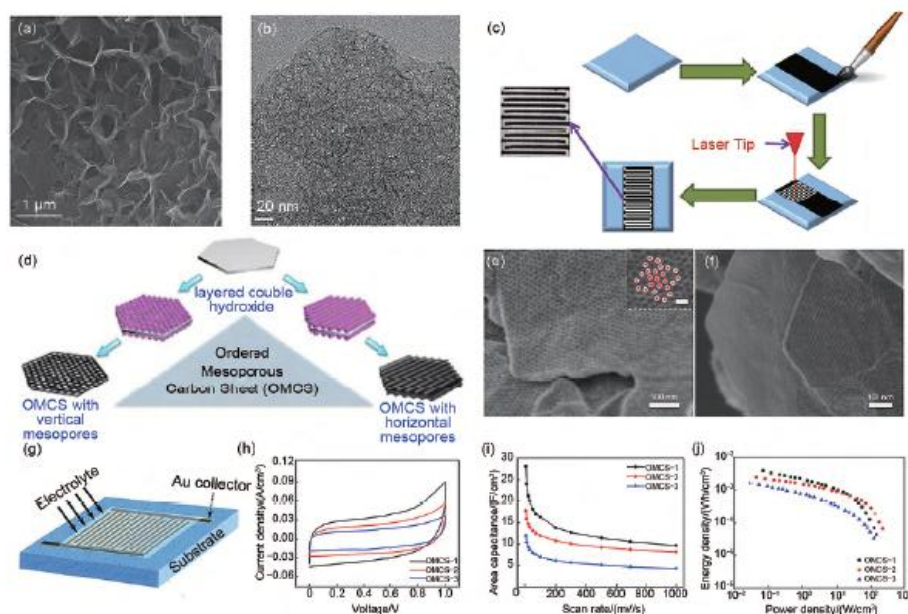


图4 (a) MDC的扫描电镜(SEM)图; (b) MDC的透射电镜(TEM)图, (c) MDC基微型超级电容器的制备示意图^[88]; (d) OMCSs的制备示意图, (e) OMCS-1的TEM图, (f) OMCS-2的TEM图, (g) OMCS基微型超级电容器的结构示意图, 不同OMCS基微型超级电容器的: (h) 循环伏安曲线(CV)对比图, (i) 倍率性能对比图, (j) Ragone图^[89]

Fig. 4 (a) SEM image of MDC, (b) TEM image of MDC, (c) Schematic diagram for MSCs based on MDC^[88]; (d) Schematic diagram of preparation of OMCS, (e) TEM image of OMCS-1, (f) TEM images of OMCS-2, (g) structure diagram, (h) cyclic voltammetry (CV) curves, (i) rate performances, (j) Ragone plot of different OMCS-based MSCs^[89]

3.1.2 介孔杂原子掺杂碳纳米片

在介孔碳纳米片中引入杂原子(N、P、S、F、B等)掺杂已被证明是提升其电化学性能的有效策略^[65-69]。杂原子掺杂可以改变材料的原子、电子和能带结构,引入额外的官能团和赝电容,因此能够显著提高材料的电解质润湿性和电化学反应活性。例如, Zhang等^[70]以奶粉和硼酸为原料,通过溶胶-凝胶和高温碳化过程,成功制备出一种二维硼氮碳纳米片[BCNN, 图5(a)]。得益于其多孔缺陷结构(孔径: 1~10 nm)、高比表面积(415 m²/g)和硼氮共掺杂效应(B: 6.58%, N: 2.17%), BCNN基微型超级电容器展现出80.1 mF/cm²的高面积比容量,优异的倍率能力和循环稳定性(10000次循环后保留率约92%)。当使用离子液体凝胶电解质[1-乙基-3-甲基咪唑四氟硼酸盐(EMIMBF₄)/聚偏氟乙烯六氟丙烯(PVDF-HFP)]时, BCNN基微型超级

电容器的体积能量密度高达67.6 mWh/cm³[图5(b)]。并借助理论计算,揭示了缺陷调控的作用机理,验证了孔结构与硼、氮原子掺杂在提升BCNN量子电容方面的协同效应。近期, Qin团队^[63]提出了一种二维-介孔双模板界面自组装策略,可制备出一系列面内介孔结构的氮掺杂碳(imNC)纳米片,将其作为双功能材料,构筑出微型超级电容器-压力传感器共平面集成系统。如图5(c)和(d)所示,以全氟十八酸为二维模板, SiO₂纳米球为介孔模板,制备出介孔孔径(7.3~23.2 nm)、比表面积(222~413 m²/g)和氮含量(3.8%~5.9%)可调的imNC纳米片,并揭示了材料结构组成(介孔孔径和吡咯氮含量)与电化学性能(比容量、倍率性能和循环稳定性)之间的构效关系。进一步,以imNC为活性电极材料,结合不同的凝胶电解质(PVA-H₂SO₄和EMIMBF₄/SiO₂),实现了微型超级电容器电压从

0.9 V 到 3.8 V, 面积能量密度从 $3.27 \mu\text{Wh}/\text{cm}^2$ 到 $41.90 \mu\text{Wh}/\text{cm}^2$ 的调控。同时, imNC 纳米片可以作为压力传感器的传感材料, 实现同一柔性基底上

imNC 基微型超级电容器-压力传感器集成系统的有效构筑, 用于弯曲、扭转力和声音振动的无线监测[图5(e)], 极大地提升器件的兼容性和可穿戴应用潜力。

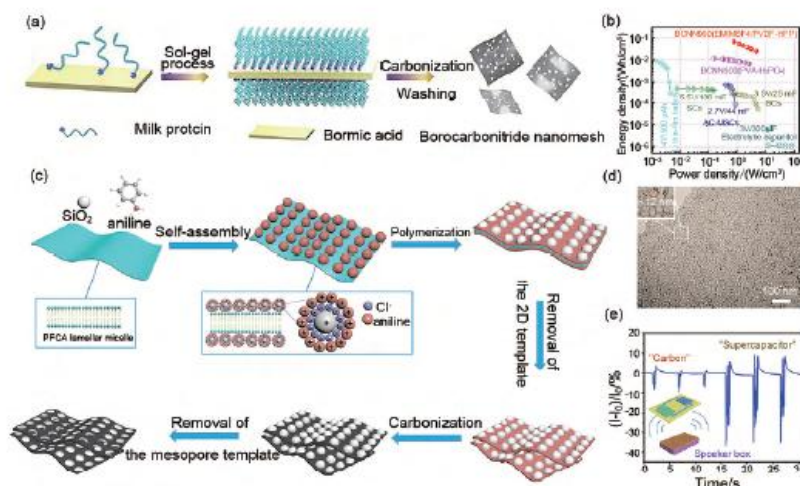


图5 (a) BCNN的制备示意图, (b) BCNN基微型超级电容器的Ragone图^[76]; (c) imNC纳米片的制备示意图, (d) imNC纳米片的TEM图片, (e) imNC基微型超级电容器-压力传感器集成系统对不同声音振动的响应曲线^[83]

Fig. 5 (a) Schematic diagram of the preparation of BCNN, (b) Ragone plot of BCNN-based MSCs^[76]; (c) Preparation schematic of imNC nanosheets, (d) TEM image of imNC nanosheets, (e) response curves of acoustic vibrations of imNC-based MSC-pressure sensor integrated system^[83]

3.1.3 多孔石墨烯

自2004年被发现以来, 石墨烯凭借高导电性($>10^4 \text{ S/m}$)、大比表面积($2620 \text{ m}^2/\text{g}$)、优异的电化学稳定性和机械柔性, 已被广泛报道应用于微型超级电容器^[28,78]。为了抑制石墨烯纳米片层堆叠所带来的比表面积和活性位点降低, 研究者提出在其表面或内部构筑多孔结构, 来增大其可接触表面, 提高电化学性能^[41,72]。近年来, 物理(激光/等离子体)刻蚀和化学刻蚀(如KOH、 H_2O_2 、金属氧化物等)法已被广泛用来制备多孔石墨烯^[73-74], 其中化学刻蚀技术更为简单和常用。例如, Xu等^[65]通过一种温和的 H_2O_2 刻蚀方法制备出具有分级多孔结构的三维石墨烯(HGF), 将其作为一种无黏结剂电极材料应用于高性能的超级电容器[图6(a)]。该HGF具有丰富的微孔、介孔和大孔, 大的离子可及比表面积($1560 \text{ m}^2/\text{g}$), 以及高的电导率(1000 S/m), 相比无孔石墨烯(GF)展现出更高的比容量, 其质量比容量为 298 F/g , 体积比容量为 $212 \text{ F}/\text{cm}^3$ [图6(b)(c)]。

进一步, 构筑的超级电容器具有 35 Wh/kg 和 49 Wh/L 的高能量密度, 与铅酸蓄电池相当, 然而其微型超级电容器应用未进行研究。近年来, 吴忠帅课题组^[75-76]采用多孔的活性炭石墨烯(AG)为正极, 纳米钛酸锂(LTO)或钛酸钠(NTO)为负极, 通过掩模板辅助沉积技术, 在柔性基底上成功构筑出平面锂离子[LTO//AG-LIMCs, 图6(d)]和钠离子微型电容器[NTO//AG-NIMCs, 图6(f)]微电极。结合离子凝胶电解质LiTFSI- P_{14} TFSI-PVDF-HFP和NaTFSI- P_{14} TFSI-PVDF-HFP, 得到的LTO//AG-LIMCs工作电压为 3.0 V , 体积比容量为 $42.8 \text{ F}/\text{cm}^3$, 能量密度为 $53.5 \text{ mWh}/\text{cm}^3$ [图6(e)]; NTO//AG-NIMCs的电压窗口达 3.5 V , 体积比容量为 $19.5 \text{ F}/\text{cm}^3$, 能量密度为 $37.1 \text{ mWh}/\text{cm}^3$ [图6(g)(h)]。而且, 这两种器件均能在 80°C 的高温下稳定工作, 且表现出优异的机械柔性和规模化集成能力。但是, 目前有序介孔石墨烯纳米片及其微型超级电容器的相关报道仍较少且极具挑战。

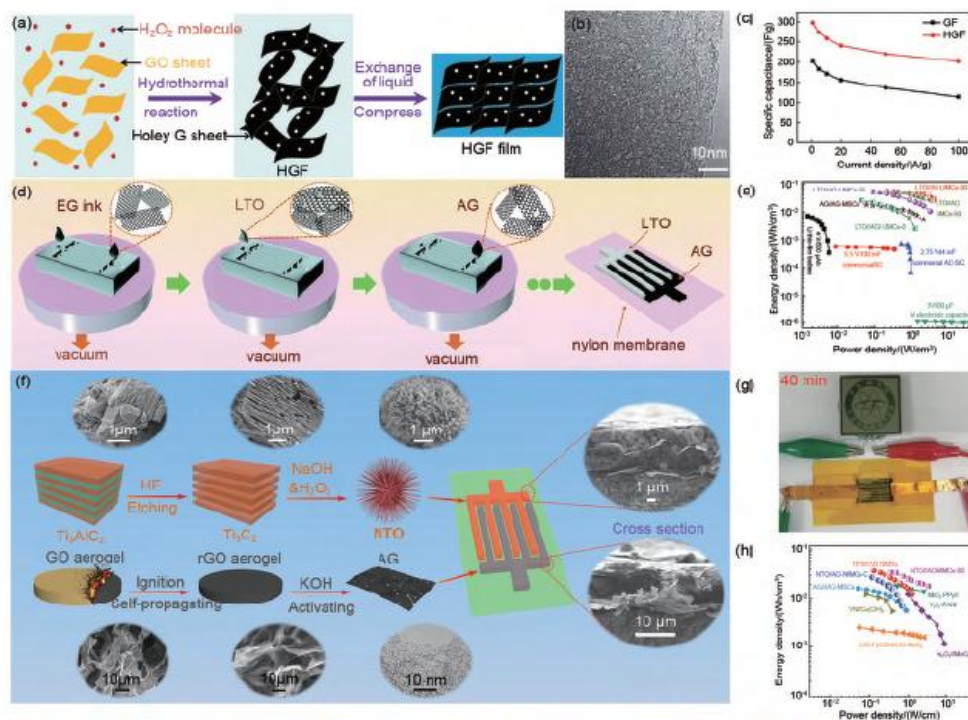


图6 (a) HGF的制备示意图, (b) HGF的TEM图, (c) HGF的比容量^[88]; (d) LTO//AG-LIMCs的制备示意图, (e) LTO//AG-LIMCs的Ragone图^[73]; (f) NTO//AG-NIMCs的制备示意图, (g) NTO//AG-NIMCs点亮显示屏的照片, (h) NTO//AG-NIMCs的Ragone图^[78]

Fig. 6 (a) Schematic diagram of the preparation, (b) TEM image, and (c) specific capacitance of HGF^[88]; (d) Schematic of the preparation, and (e) Ragone plot of LTO//AG-LIMCs^[73]; (f) Schematic of the preparation of NTO//AG-NIMCs, (g) the liquid crystal display powered by one NTO//AG-NIMC, (h) Ragone plot of NTO//AG-NIMCs^[78]

3.2 二维介孔过渡金属化合物

过渡金属化合物中的金属原子通常具有多种价态, 在外加电压的作用下, 容易发生可逆的氧化还原反应, 进而存储大量电荷。另有一些过渡金属化合物, 其体相孔隙或层间可以作为离子扩散通道进行电解质离子的快速、可逆插层来存储电荷。相比于传统的块状过渡金属化合物, 二维介孔过渡金属化合物可以结合二维形貌、介孔结构和过渡金属化合物组分的优点, 应用于微型超级电容器实现高的膜电容、快速的反应动力学、长的循环寿命和优异的结构稳定性。目前, 报道的二维介孔过渡金属化合物主要包括二维介孔过渡金属氧化物^[42, 77]、过渡金属硫化物^[44]、过渡金属碳氮化合物等^[46, 78]。

3.2.1 二维介孔过渡金属氧化物

二氧化锰(MnO_2)纳米片是一种典型的二维过渡金属氧化物, 具有来源丰富、制备简单、理论比容量高(1370 F/g)和环境友好等优点, 是一种理想的微型超级电容器电极材料^[79-80]。介孔的引入可以增加 MnO_2 纳米片的活性比表面积, 有效缓解电极在充放电过程中的体积变化, 从而提升整个电极和器件的比容量、结构稳定性和循环寿命。例如, Qin等^[42]报道了一种超分子自组装策略, 以十八胺的层状胶束为二维模板, 自下而上地合成出面内介孔 $\text{MnO}_2(\text{m-MnO}_2)$ 纳米片[图7(a)], 并应用于高性能的非对称微型膜电容器。该介孔纳米片的厚度约为10 nm, 孔径范围为5~15 nm[图7(b)], 比表面积

为 $128 \text{ m}^2/\text{g}$, 相比于无孔 MnO_2 纳米片, 展现出更高的比容量和循环性能。以 m-MnO_2 纳米片为正极, 多孔 VN 纳米片为负极, 高浓 $\text{LiTFSI}/\text{SiO}_2$ 为凝胶电解质, 制备得到非对称微型电容器 ($\text{VN}/\text{MnO}_2\text{-MSCs}$) 工作电压达 2.0 V , 体积能量密度为 $21.6 \text{ mWh}/\text{cm}^3$, 5000 圈循环后的容量保持率约为 90% [图 7(c)]。此外, 该 m-MnO_2 纳米片结合 $\text{MXene}(\text{Ti}_3\text{C}_2\text{T}_x)$ 负极和 $20 \text{ mol}/\text{kg}$ 的 LiCl 凝胶电解质, 构筑的准固态微型超级电容器 ($\text{MXene}/\text{MnO}_2\text{-MSCs}$) 展现出高达 2.4 V 的工作电压, $53 \text{ mWh}/\text{cm}^3$ 的高体积能量密度, 以及出色的机械柔性和串/并联自集成性能^[81]。该微型超级电容器还能够与太阳能电池和消费电子产品一起构建自供电微系统, 同时实现能量收集、存储和转换[图 7(d)]。这些工作证明了二维介孔 MnO_2 作为电极材料的结构和性能优势, 能够有效提高微型超级电容器的电化性能。另一方面, 五氧化二铌(Nb_2O_5)是一种常见的、典型的插层电容材料, 可以提升电极和器件的电

化学反应动力学^[82]。例如, Ma 等^[83]制备了一种碳包覆的二维介孔 Nb_2O_5 分级微米花 (NF@C-650), 其中丰富的孔结构(约 3.9 nm)有利于电解质离子的渗透和传输, 超薄的导电碳层(约 5 nm)能够提高材料的界面稳定性和电子传输动力学。以 NF@C-650 为负极, 活性炭为正极, 构筑的钠离子微型电容器展现出 3.5 V 的高电压窗口和 $60.7 \text{ } \mu\text{Wh}/\text{cm}^2$ 高能量密度, 在可穿戴和便携式微电子器件领域展现出大的应用前景[图 7(e)]。除了上述报道的二维介孔 MnO_2 和 Nb_2O_5 , 赵东元课题组^[83, 84]还采用模板自组装策略制备出了多种二维介孔金属氧化物, 包括: TiO_2 、 ZrO_2 、 Al_2O_3 和 CeO_2 等, 但是它们在微型超级电容器领域的应用有待进一步探索。

3.2.2 二维介孔过渡金属硫化物

过渡金属硫化物是一种层状材料, 通常由过渡金属元素(钛、钼、钨、铌等)与硫族元素(硫、硒、碲等)组成^[85-89]。二维介孔过渡金属硫化物具有大的比表面积、丰富的孔结构、可调的导电性和多种氧

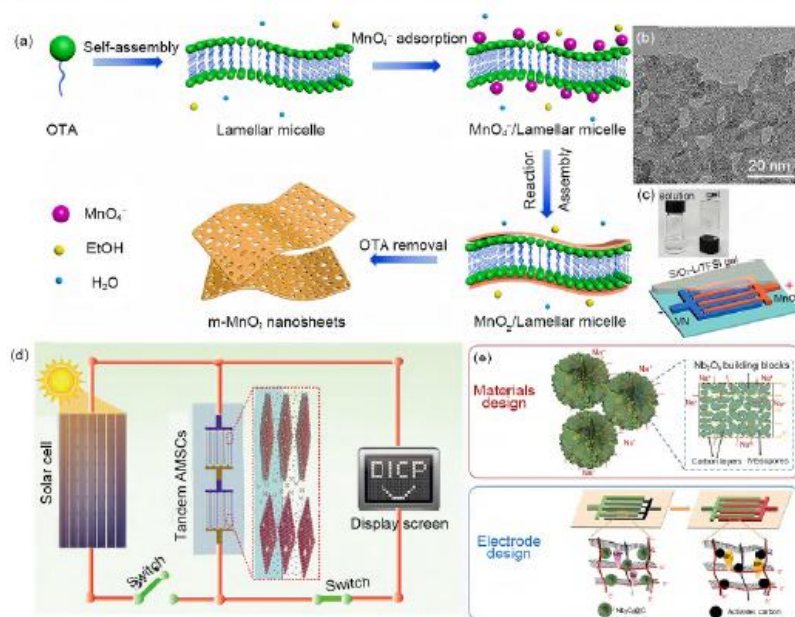


图7 (a) m-MnO_2 纳米片的制备示意图, (b) m-MnO_2 纳米片的 TEM 图, (c) $\text{VN}/\text{MnO}_2\text{-MSCs}$ 示意图^[42]; (d) $\text{MXene}/\text{MnO}_2\text{-MSCs}$ 及其集成系统的示意图^[81]; (e) NF@C-650 及其钠离子微型电容器的示意图^[83]

Fig. 7 (a) Schematic diagram of the preparation, and (b) TEM image of m-MnO_2 , (c) schematic of $\text{VN}/\text{MnO}_2\text{-MSCs}$ ^[42]; (d) Schematic diagram of $\text{MXene}/\text{MnO}_2\text{-MSCs}$ and integrated system^[81]; (e) Schematic diagrams of NF@C-650 and MSCs^[83]

化还原态,具有双电层和赝电容协同储能机制,被认为是一种非常有前景的微型超级电容器电极材料。例如,Wu等^[44]通过酸辅助剥离法制备出了面内多孔的 TaS_2 纳米片,并应用于微型超级电容器,实现了高的体积能量密度。如图8(a)所示,在合成过程中, H^+ 可以同时促进 TaS_2 层间的晶格膨胀和面内的化学蚀刻,快速而温和地获得了具有大尺寸和纳米孔结构的导电 TaS_2 (MSP- TaS_2)纳米片。这种纳米片的大尺寸、单层结构有利于离子-电子的高效传输,面内亚纳米孔(约0.95 nm)能够很好地匹配电解质离子的大小[图8(b)]。将其用作活性电极材料时,所构建的准固态平面微型超级电容器呈现出 508 F/cm^3 的体积比容量和 58.5 Wh/L 的能量密度[图8(c)]。该工作为二维多孔过渡金属硫化物的功能化制备和微型超级电容器应用提供了一种新策略。但是,目前二维介孔过渡金属硫化物仍面临种类少、固有电导率低、充放电时体积变化大和循环寿命有限的问题,未来可以利用半金属或过渡金属硫化物与高导电材料相结合制备二维介孔复合材料,来拓展二维介孔过渡金属硫化物的种类,并有效增强微型超级电容器的电化学性能。

3.2.3 二维介孔过渡金属碳氮化物

MXenes是一类新型的二维材料,通常由二维过渡金属碳化物、氮化物或碳氮化物构成^[87-89]。自2011年被首次报道以来,MXenes凭借金属导电性、高堆积密度、强电荷存储能力、大比表面积、

良好亲水性、出色机械柔性和可调化学组成等优点,已成为一种重要的微型超级电容器电极材料^[92]。为了抑制MXenes片层的重新堆叠,增大材料的比表面积,可以通过构筑二维介孔MXenes,来获得更多的活性位点和离子传输通道,加强电解质离子的无障碍迁移和表面的氧化还原反应。例如,Ren等^[49]利用化学刻蚀的方法成功制备出多孔MXene,并将其应用于锂离子存储。如图9(a)所示,将单层MXene纳米片分散到 CuSO_4 (CoSO_4 或 FeSO_4)水溶液中,在金属离子的催化作用下,溶液中的氧可以将MXene部分氧化,最终经过HF刻蚀 TiO_2 颗粒,就得到了多孔MXene($\text{p-Ti}_3\text{C}_2\text{T}_x$)纳米片。相比于无孔MXene($19.6 \text{ m}^2/\text{g}$), $\text{p-Ti}_3\text{C}_2\text{T}_x$ 纳米片的比表面积提高至 $93.6 \text{ m}^2/\text{g}$,而且具有丰富的孔结构,大小约为几十纳米,因此显著提高了锂离子的可逆存储能力[图9(b)(c)]。近期,Zhang等^[89]采用简单的 H_2O_2 刻蚀技术制备出面内多孔MXene(HMX)和多孔氧化石墨烯(HGO)纳米片,并进一步通过真空抽滤和热还原制备出一种HMX/还原多孔氧化石墨烯(rHGO)自支撑薄膜[图9(d)-(g)]。这种纳米多孔2D/2D异质结构策略,可以充分利用HMX和rHGO纳米片的优点,缓解了纳米片的重新堆叠,优化了离子传输路径,并提高了薄膜的机械柔性和化学稳定性。得益于这种多孔2D/2D异质结构和电化学协同作用,所得的HMX/rHGO自支撑薄膜展现出优异的电容式去离子性能。综上所述

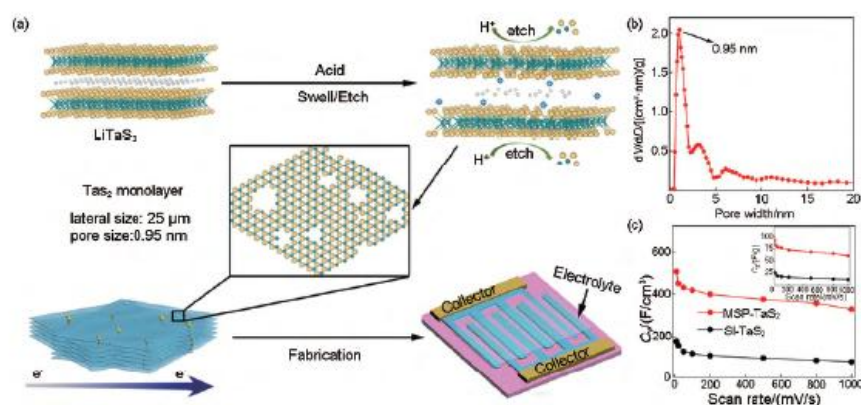


图8 (a) MSP- TaS_2 及其MSCs的制备示意图, (b) MSP- TaS_2 孔径分布图, (c) MSP- TaS_2 基MSCs的体积比容量^[44]
Fig. 8 (a) Schematic diagram of the preparation of MSP- TaS_2 and MSCs, (b) pore size distribution profile of MSP- TaS_2 , (c) volumetric capacitance of TaS_2 -based MSCs^[44]

述, 目前所报道的介孔MXenes纳米片大多通过化学或者物理刻蚀制备得到, 其孔结构随机分布, 孔径大小分布不均, 因此制备有序介孔MXenes纳米片并将其应用于微型超级电容器中将是以后研究的重点。除了二维介孔MXenes, 前面所提到的多孔

VN纳米片由于大的比表面积、良好的导电性、高的膜电容和低的负电位(-1.0 V vs. SCE)等优点^[42], 可作为一种负极材料与 $m\text{-MnO}_2$ 正极进行匹配, 实现高性能的非对称型微型超级电容器, 而其他二维介孔过渡金属碳化物和氮化物有待进一步开发。

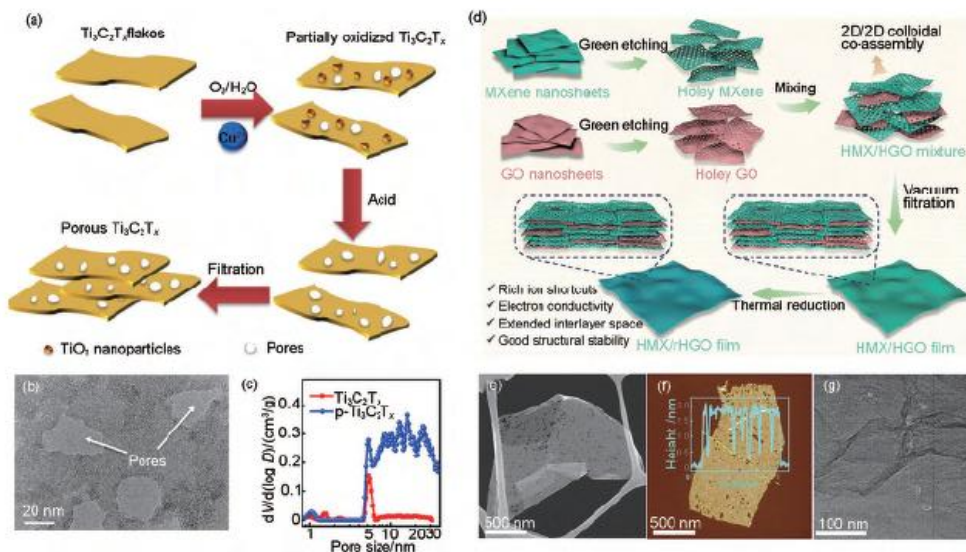


图9 (a) $p\text{-Ti}_3\text{C}_2\text{T}_x$ 的制备示意图, (b) $p\text{-Ti}_3\text{C}_2\text{T}_x$ 的 TEM 图, (c) $p\text{-Ti}_3\text{C}_2\text{T}_x$ 的孔径分布图^[48]; (d) HMX/rHGO 的制备示意图, (e) HMX 的 STEM 图, (f) HMX 的原子力显微镜(AFM)图, (g) HGO 的 TEM 图^[49]

Fig. 9 (a) Schematic diagram of the preparation, (b) HRTEM image, (c) pore size distribution of $p\text{-Ti}_3\text{C}_2\text{T}_x$ ^[48]; (d) Schematic diagram of the preparation of HMX/rHGO film, (e) STEM image of HMX, (f) atomic force microscopy (AFM) image of HMX, (g) TEM image of HGO^[49]

3.3 二维介孔导电聚合物

自1977年发现碘掺杂聚乙炔以来, 导电聚合物(如聚吡咯、聚苯胺和聚噻吩)因其可调的电导率、可逆的氧化还原活性、优异的稳定性和生物相容性, 以及卓越的机械柔性和可加工性而广泛应用于超级电容器领域^[90-91]。相比而言, 二维介孔导电聚合物可以结合二维形态、介孔结构和导电聚合物固有的优势, 克服块状材料的巨大传质阻力和有限比表面积的局限性, 促进电解液的渗透和扩散, 提供更多的电化学活性位点, 并在一定程度上缓解其体积变化, 从而提高其电化学性能, 因此近年来得到了极大关注。例如, 刘少华教授团队^[92-93]通过两亲性脂肪胺(OTA)/全氟羧酸(PFCA)和聚苯乙烯- b -聚环氧乙烷(PS- b -PEO)嵌段共聚物的协同自组装,

实现了具有可控孔径的二维介孔聚吡咯(mPPy)和二维介孔聚苯胺(mPANi)纳米片的自下而上合成。如图10(a)和(d)所示, OTA/PFCA和PS- b -PEO首先分别预组装成二维脂质双分子层和球形胶束, 通过氢键作用, PS- b -PEO球形胶束可以在二维双分子层的两侧进行排列形成二维的三明治状组装体。进一步, 吡咯或苯胺单体在PS- b -PEO球形胶束周围聚合连接, 去除胶束模板后, 得到了具有孔径、厚度和比表面积可调的mPPy和mPANi纳米片, 其中mPPy的孔径在6.8~13.6 nm可调, 厚度在25~30 nm可调, 比表面积在73~96 m^2/g 可调[图10(b), (c)]; mPANi纳米片展现出7~18 nm的可定制孔径和13~45 nm的厚度, 以及约85 m^2/g 的比表面积[图10(e)(f)]。这些研究为二维面内介孔材料

的可控制备提供了新思路,并为低成本、柔性电子和能源设备的设计开发开辟了新道路。目前,单纯的二维介孔导电聚合物已应用钠离子电池,但在微型超级电容器中的应用还未见报道。而二

维介孔的导电聚合物/石墨烯、导电聚合物/MXene和导电聚合物/金属硫化物复合材料已被开发并应用于微型超级电容器,将在下一节中展开具体介绍。

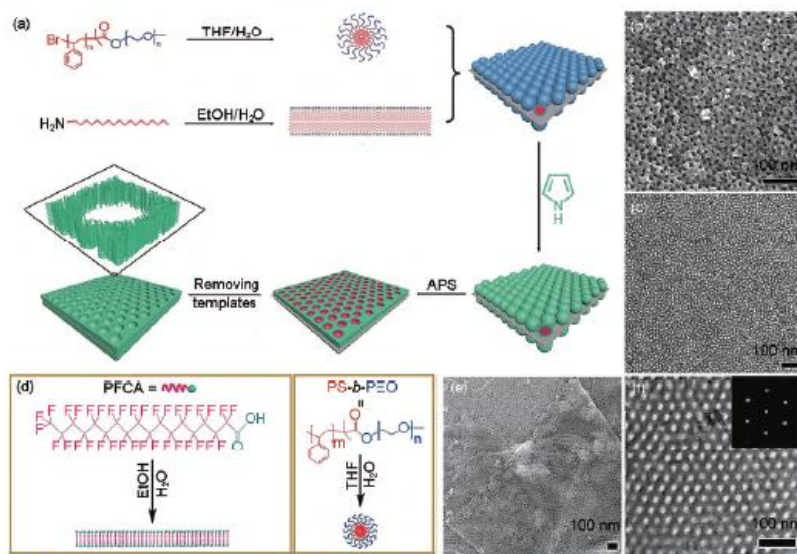


图 10 (a) mPPy 纳米片的制备示意图, (b) mPPy 纳米片的 SEM 图, (c) mPPy 纳米片的 TEM 图^[92]; (d) PFCA 和 PS-b-PEO 胶束的示意图, (e) mPANI 纳米片的 SEM 图, (f) mPANI 纳米片的 TEM 图^[93]

Fig. 10 (a) Schematic of the synthesis, (b) SEM image, and (c) TEM image of mPPy nanosheets^[92]; (d) Schematic diagrams of PFCA and PS-b-PEO micelles, (e) SEM image, and (f) TEM image of mPANI nanosheets^[93]

3.4 二维介孔复合材料

除了上述的二维面内介孔碳、过渡金属化合物和导电聚合物材料外,它们的三明治状介孔复合纳米片也被证明是优异的微型超级电容器电极材料^[93]。这种复合材料可以耦合功能组分、二维基底(石墨烯、MXene、MoS₂等)和介孔结构的优点,协同增加材料、电极和器件的导电性、稳定性、电化学活性和功能性。根据二维基底的差异,可以将三明治状二维介孔复合材料分为二维介孔石墨烯基^[94]、二维介孔MXene基^[46]和二维介孔金属硫化物基复合材料等^[95-96]。

3.4.1 二维介孔石墨烯基复合材料

石墨烯作为高导电的二维基底,可以结合介孔碳、聚合物、金属化合物层来构筑二维介孔石墨烯基复合材料,通过协同作用实现器件良好的导电

性、高的电化学活性和优异的循环稳定性^[11, 47, 50]。例如, Tian 等^[97]开发出一种通用的界面诱导自组装机方法,成功制备出多种二维有序介孔聚合物/石墨烯复合材料,包括介孔聚吡咯/石墨烯(mPPy/rGO)、介孔聚苯胺/石墨烯(mPANI/rGO)和介孔聚多巴胺/石墨烯(mPDA/rGO)纳米片。如图 11(a)所示,以聚环氧乙烷-聚环氧丙烷-聚环氧乙烷(P123)胶束为介孔软模板,氧化石墨烯为二维基底,吡咯/苯胺/多巴胺为聚合物单体,制备得到均匀二维形貌(厚度: 25~27 nm)、指纹状平行介孔(孔径: 约 11 nm)、高比表面积(126~157 m²/g)的 mPPy/rGO、mPANI/rGO 和 mPDA/rGO[图 11(b)(c)]。将 mPPy/rGO 作为电极材料,通过掩模板辅助沉积技术构筑得到平面叉指型微型超级电容器,展现出了良好的电化学活性(面积比容量为 81 mF/cm², 体积

比容量为 102 F/cm^3)和循环稳定性(3500 圈循环以后,容量保持率达 81%)。为了进一步提高二维介孔聚合物/石墨烯的比容量,Qin 等^[98]将磷酸引入到 mPPy/rGO 纳米片上和孔中,制备出具有丰富介孔结构和磷酸均匀负载的 mPPy/rGO 纳米片(mPPy/rGO-POM)。将该材料用作微型超级电容器的活性电极材料,显著提升了器件的体积比容量和体积能量密度。

另一方面,二维介孔聚合物/石墨烯可以作为前驱体制备二维介孔杂原子掺杂碳/石墨烯纳米片。例如,杨志等^[99]以聚苯胺作为碳源,石墨烯作为二维基底,二氧化硅纳米球作为介孔硬模板,成功制备出介孔孔径(7~22 nm)可调的介孔氮掺杂碳/石墨烯(mNC/G)纳米片,并将其应用于准固态的平面微型超级电容器中[图 11(d)]。重要的是,7 nm 孔径的 mNC/G 具有更高的导电性和比容量(267 F/g),构筑的微型超级电容器展现出 1.9 mWh/cm^3 的体积能量密度, 542 mW/cm^3 的体积功率密度,以及优异的循环稳定性[图 11(e)~(g)]。

此外,二维介孔金属化合物/石墨烯复合材料也被报道应用于微型超级电容器。例如,Xia 等^[100]开发了一种简单、高效的脉冲电流沉积(PCD)技术制备平面非对称微型超级电容器。首先,采用喷墨技术在基底上打印石墨烯导电集流体,然后通过 PCD 方法将介孔 MnO_2 纳米片和介孔 Fe_2O_3 纳米片沉积在石墨烯导电层上,分别作为微型超级电容器的正、负极[图 11(h)]。结合 PVA/LiCl 电解质,所构建的非对称型微型超级电容器具有 1.6 V 的电压窗口, 110.6 F/cm^3 的体积比容量, 39 mWh/cm^3 的体积能量密度,以及优异的循环稳定性,在 10000 圈循环后容量保持率达 95.7%。虽然介孔 MnO_2 /石墨烯和介孔 Fe_2O_3 /石墨烯电极中的介孔为纳米片的堆积孔,但是该工作作为其他二维金属氧化物的简单、普适制备以及微型超级电容器的低成本、大规模工业化铺平了道路。

3.4.2 二维介孔 MXene 基复合材料

除了易自堆叠外,MXene 材料在水和氧气存在的环境中还会发生氧化,严重影响其电化学性能与稳定性^[12]。为了解决此问题,可以在其表面原位生长功能组分并构筑介孔结构,制备二维介孔 MXene 基复合材料。该材料能够协同耦合二维 MXene、功能组分和介孔材料各自的优势,防止材

料与水、氧气直接接触,进而显著增强 MXene 基材料的电化学活性和结构稳定性。将其应用于微型超级电容器,能够提供优异的离子和电子传输网络,提升器件的电化学性能。近年来,报道的二维介孔 MXene 基材料包括二维介孔碳/MXene^[84-88]、二维介孔聚合物/MXene^[101-103]和二维介孔硫化物/MXene^[103]等。例如,Qin 等^[104]开发出一种界面限域自组装策略,通过氢键力和冰固化作用,可控制备出一系列具有不同碳源(葡萄糖、蔗糖和壳寡糖)、片厚(15~29 nm)和介孔孔径(7~22 nm)的二维介孔碳/MXene(mC@MXene)异质结构[图 12(a)(b)]。将其作为活性电极材料,结合 EMIMBF₄/SiO₂ 离子凝胶电解质,有效构建出高电压(3.7 V)、高能量密度(181.3 μWh/cm^2)的微型超级电容器(mC@MXene-MSCs),其性能超越了当时所报道的大部分 MXene 基微型超级电容器[图 12(c)~(e)]。重要的是,这种制备方法具有普适性,可以拓展不同的二维基底(石墨烯、BN、MoS₂),得到不同的二维介孔碳异质结构,为新型二维介孔复合材料的制备提供了新思路。

此外,Liu 等^[105]报道了一种膨胀诱导结构转变策略,构建出孔结构可调的二维多孔 PPy/MXene 异质结构,并揭示了材料孔结构与电化学性能之间的构效关系。具体而言,通过调节膨胀剂(1,3,5-三甲基苯)的用量,对多孔 PPy/MXene 的孔结构(圆柱形介孔、球形介孔和球形大孔)、孔径大小(7.8~52.0 nm)及比表面积($129\sim 188 \text{ m}^2/\text{g}$)进行了精确调控[图 12(f)(g)]。其中,具有高比表面积的圆柱形介孔的 PPy/MXene 展现出了最高的比容量(477 F/g),以及优异的倍率性能和循环稳定性[图 12(h)]。这项工作阐明了孔结构对二维多孔聚合物电化学性能的影响,但是未探索其在微型超级电容器的应用。

2024 年,Mei 等^[106]报道了一种具有分级核壳结构的 NiCoMoS-Ti₃C₂T_x 纤维,并将其应用于高性能的纤维形微型超级电容器。基于多孔的金属硫化物阵列和导电网络,NiCoMoS-Ti₃C₂T_x 纤维展现出快速的电荷转移、低扩散势垒、高吸附能,以及稳定的多元金属硫化物多电子反应动力学[图 12(i)~(k)]。因此,NiCoMoS-Ti₃C₂T_x 纤维微型超级电容器展现出高的能量密度(50.6 mWh/cm^3),良好的机械柔性[60°弯曲 2000 次后电容保持率约 85.2%,图 12(l)],可作为微型电源为照明灯、自清洁通风口罩、风扇

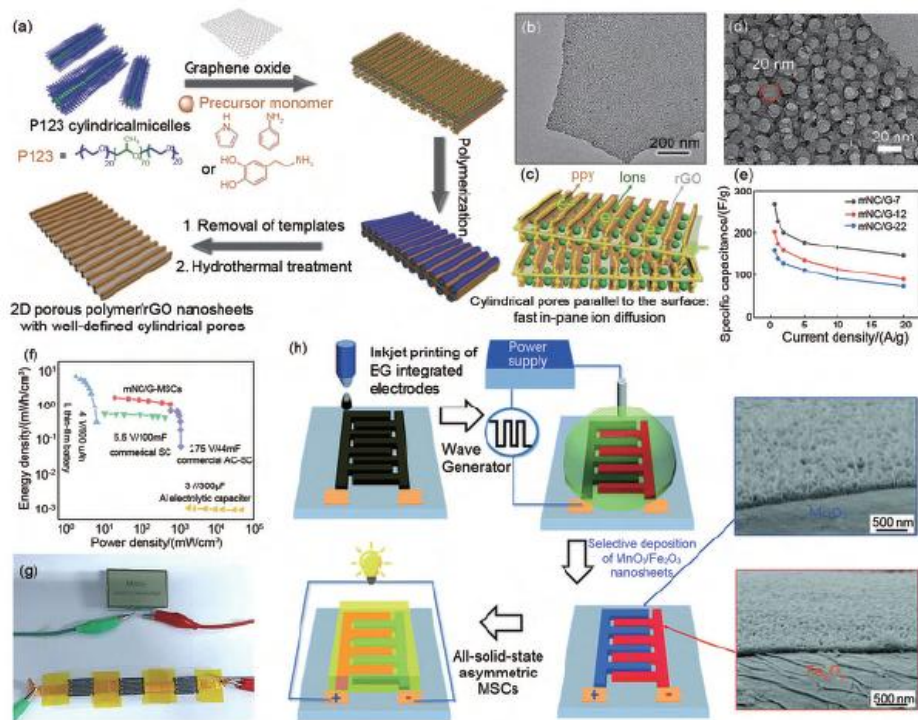


图11 (a) 二维介孔聚合物/石墨烯的制备示意图, (b) mPPy/rGO纳米片的TEM图, (c) mPPy/rGO纳米片中离子-电子传输示意图^[97]; (d) mNC/G的TEM图, (e) 不同孔径mNC/G的比容量对比图, (f) mNC/G基微型超级电容器的Ragone图, (g) mNC/G基微型超级电容器的应用展示图^[98]; (h) PCD技术制备微型超级电容器的流程图以及介孔Fe₂O₃和MnO₂纳米片SEM图^[100]

Fig. 11 (a) Schematic diagram of the synthesis of 2D mesoporous polymer/graphene nanosheets, (b) TEM image of mPPy/rGO, (c) schematic of ion-electron transport in mPPy/rGO^[97]; (d) TEM image of mNC/G, (e) Specific capacitance of mNC/G with different mesopore size, (f) Ragone plot of mNC/G-MSCs, (g) application exhibition of mNC/G-MSCs^[98]; (h) Schematic illustration of the preparation process of MSCs (insets: SEM images of mesoporous Fe₂O₃ and MnO₂ nanosheets)^[100]

进行稳定供电。此外, NiCoMoS-Ti₃C₂T₂纤维还可以作为一种生物电化学传感器,用于多巴胺检测,展现出了良好的灵敏度和低的检测限。该工作为新型纤维电极的设计和在可穿戴电子设备中的应用开辟了道路。

3.4.3 二维介孔金属硫化物基复合材料

大部分二维过渡金属硫化物的导电性较差,且易堆叠,导致在实际应用过程中电容性能显著下降^[88]。因此,通过在其表面生长导电的介孔层来构筑二维介孔金属硫化物基复合材料,能够在不影响金属硫化物和功能层活性发挥的同时,协同增加材

料的比表面积,提升其导电性,改善其电化学性能。例如, Fang等^[96]采用超分子自组装策略,以酚醛树脂为碳源, F127胶束为介孔模板,在MoS₂纳米片表面构筑约1 nm的介孔碳层(平均孔径9 nm),得到三明治结构的有序介孔碳/MoS₂复合纳米片。该纳米片作为活性电极材料,赋予了锂离子电池增强的电化学性能(包括比容量、倍率性能等)。正如上文所述, Qin团队^[104]采用普适的界面自组装策略构筑了二维介孔碳/MXene、二维介孔碳/石墨烯、二维介孔碳/BN、二维介孔碳/MoS₂材料,其中的二维介孔碳/MoS₂基微型超级电容器,展现

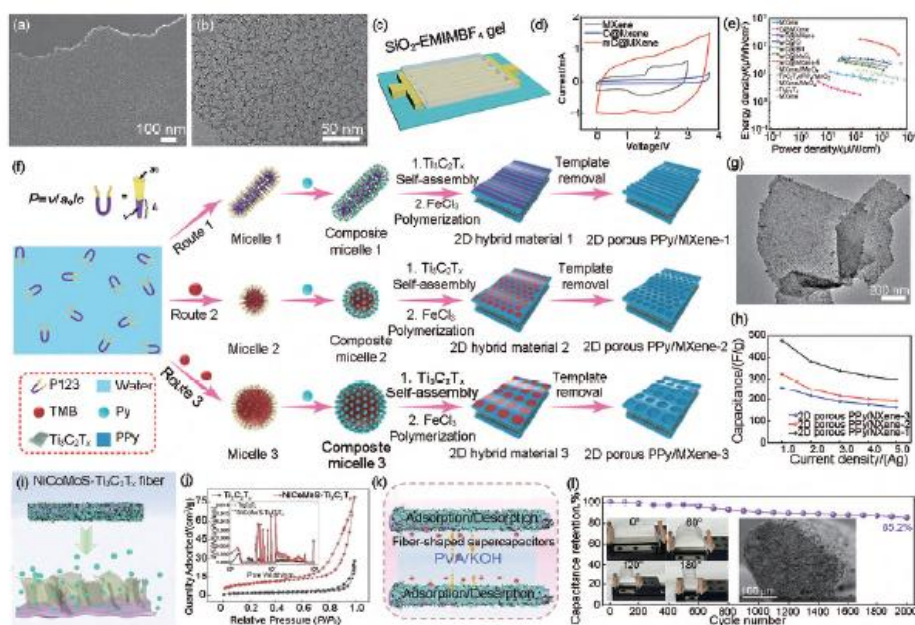


图12 (a) mC@MXene的SEM图, (b) mC@MXene的TEM图, (c) mC@MXene-MSCs的示意图, (d) mC@MXene-MSCs的CV曲线, (e) mC@MXene-MSCs的Ragone图^[104]; (f) 多孔PPY/MXene的制备示意图, (g) 多孔PPY/MXene的SEM图, (h) 多孔PPY/MXene的比容量^[105]; (i) NiCoMoS-Ti₃C₂T_x的结构示意图, (j) NiCoMoS-Ti₃C₂T_x的物理吸附脱附曲线和孔径分布图, (k) NiCoMoS-Ti₃C₂T_x纤维型超级电容器的结构示意图, (l) NiCoMoS-Ti₃C₂T_x纤维型超级电容器在不同弯曲角度下的循环性能^[103]

Fig. 12 (a) SEM image, and (b) TEM image of mC@MXene, (c) schematic diagram, (d) CV curve, and (e) Ragone plot of mC@MXene-MSCs^[104]; (f) Schematic of preparation, (g) SEM image, and (h) specific capacitance of porous PPY/MXene^[105]; (i) Structural schematic, (j) nitrogen adsorption-desorption isotherms (insets: the pore size distribution) of NiCoMoS-Ti₃C₂T_x, (k) schematic diagram, (l) cycling stability at different bending angles of NiCoMoS-Ti₃C₂T_x based fiber-shaped MSCs^[103]

出 30.6 $\mu\text{Wh}/\text{cm}^2$ 的面积能量密度。

此外, 聚苯胺作为一种导电聚合物, 具有成本低、导电性良好和赝电容高的优点, 也可以与二维金属硫化物结合制备二维介孔复合材料。例如, Tian等^[60]以P123的球状和圆柱形胶束为软模板制备出孔结构和孔径可调的二维介孔聚苯胺/MoS₂ (mPANI/MoS₂)材料, 并研究了其电化学性能。其中, 具有较小球形介孔(约12 nm)的mPANI/MoS₂具有更高的比表面积和更大的有效接触界面, 进而展现出优异的导电性、比容量和循环稳定性。该工作揭示了不同孔结构对mPANI/MoS₂电容性能的影响, 有助于理解二维介孔电极材料的孔结构与电化学性能之间的构效关系, 但是其微型超级电容器应用未得到研究。

3.4.4 其他

除了上述介绍的二维介孔石墨烯基、二维介孔MXene基和二维介孔金属硫化物基复合材料, 一些新型的二维介孔聚合物/TiO₂^[50]、介孔碳/TiO₂^[106]、介孔碳/铈酸盐^[54]、介孔碳/BN^[104]、介孔氮掺杂碳/Mo₂C/石墨烯^[107]等也相继被报道。例如, Lan等^[106]通过自下而上的单胶束自组装在介孔TiO₂纳米片表面构筑了有序介孔碳层, 得到二维介孔碳-介孔TiO₂-介孔碳异质结构。这种二维介孔复合材料具有3 nm和15 nm两种介孔, 约20 nm的片厚, 能够提供大的电解液-电极接触面积, 并能有效缓冲电极在充放电过程中的体积变化。因此, 应用于钠离子电池展现出高度可逆的赝电容行为和优异的循环性能。该工作揭示了二维介孔异质结构对材料电化

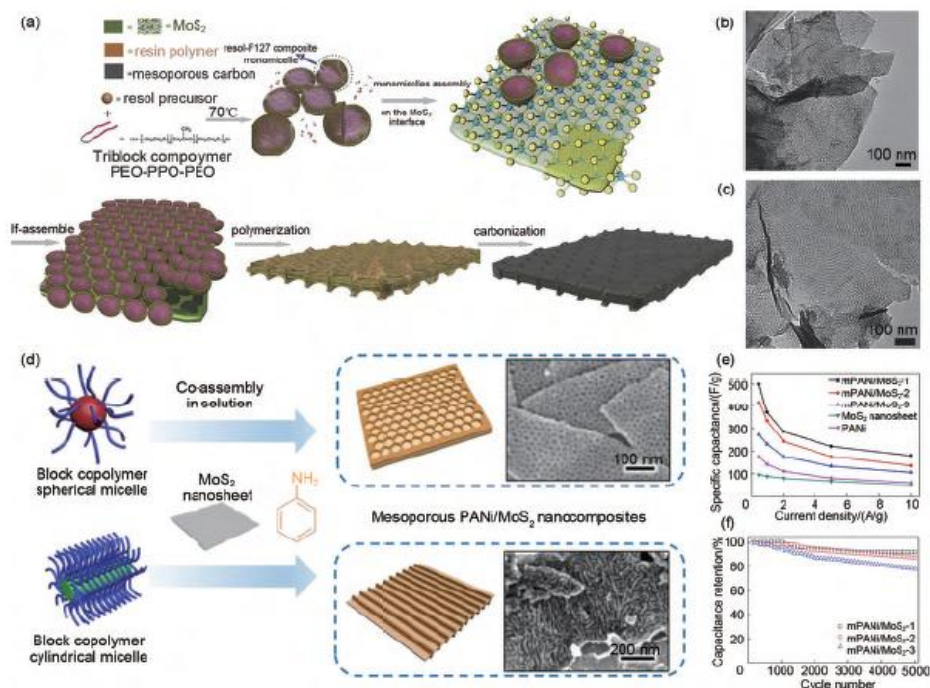


图 13 (a) 有序介孔碳/MoS₂ 纳米片的制备示意图, (b), (c) 有序介孔碳/MoS₂ 纳米片的 TEM 图^[98]; (d) 不同孔结构 mPANI/MoS₂ 的制备示意图及 SEM 图, (e) 比容量曲线, (f) 循环性能^[99]

Fig. 13 (a) Schematic diagram of the preparation, (b), (c) TEM images of ordered-mesoporous-carbon/MoS₂ nanosheets^[98]; (d) Schematic diagram of the synthesis and SEM images, (e) CV curves, and (f) cycling stability of mPANI/MoS₂ nanosheets with different pore structures^[99]

学活性和电荷存储动力学的重要性。尽管近年来一些新型的二维介孔材料被开发,但是主要应用于电池^[106-109]、电催化^[110-111]等领域,它们在微型超级电容器中的应用还需要进一步探索。

4 总结及展望

本文综述了二维介孔材料在微型超级电容器中的应用进展。首先,介绍了微型超级电容器的储能机理,强调了二维介孔材料作为微型超级电容器电极材料的结构优势。进一步,根据化学组成和微纳结构,将二维介孔材料分为二维介孔碳、二维介孔金属化合物、二维介孔导电聚合物,以及二维介孔石墨烯基、MXene 基和金属硫化物基复合材料,并详细讨论了它们在微型超级电容器中的应用,揭示了二维介孔结构对其性能的增强机制和它们之间

的构效关系。不同二维介孔材料在微型超级电容器中的电化学性能见表 1。总之,二维介孔材料具有大的比表面积、丰富的活性位点、发达的介孔结构、快速的离子迁移速率和增强的结构稳定性,将其用作微型超级电容器的活性电极材料,能够明显提升器件的比容量和能量密度。尽管二维介孔材料在微型超级电容器应用方面已经取得了一定进展,但仍面临一些挑战,在未来应重点关注以下方面:

(1) 新型二维介孔材料的设计: 目前报道的二维介孔材料主要集中在常见的碳材料、金属氧化物、金属硫化物、导电聚合物及其复合材料。然而新型的二维金属单质、金属磷化物、硒化物、金属/共价有机框架、高熵材料及其复合物因为其独特的组成和结构,有望产生新的物理化学性能,其在微型超级电容器中的应用也亟待探索。考虑到微

型超级电容器应用, 二维介孔材料应同时具备高的电化学活性和高的导电性, 以加强电极、器件的电子-离子传输和电化学反应动力学。因此, 具有高活性组分和导电网络构筑的三明治型二维介孔异质结构在未来更具应用潜力。特别是对于一些稳定性

较差的材料(如MXenes、黑磷烯等), 这种二维介孔异质结构可以抑制其堆叠, 增加其比表面积, 提高其物理化学稳定性, 而几乎不影响其活性和传质。此外, 需要开发更简单、更普适的合成策略, 实现高质量二维介孔材料的大规模、低成本、可控制备。

表1 不同二维介孔材料基微型超级电容器的电化学性能

Table 1 Electrochemical performances of different two-dimensional mesoporous materials based micro-supercapacitors

电极材料	孔径/nm	比表面积 /(m ² /g)	电解质	面电容 /(mF/cm ²)	体电容 /(mF/cm ³)	面积能量 密度 /(μWh/cm ²)	体积能量 密度 /(mWh/cm ³)	参考文献
MDC	2~4	2604	PVA/H ₂ SO ₄	9	12.92	—	1.8	[58]
OMCS	约10	650	PVA/H ₂ SO ₄	8.44	0.028	—	3.9	[60]
BCNN	1~10	415	EMIMBF ₄ /PVDF-HFP	80.1	—	—	67.6	[70]
imNC	7~22 ^①	222~413 ^①	PVA/H ₂ SO ₄ 和EMIMBF ₄ /SiO ₂	29.1	—	41.90	—	[63]
HGF	—	1560	EMIMBF ₄ /AN ^②	—	0.212	—	49	[65]
AG	—	约2900	LiTFSI-P ₄ TFSI-PVDF-HFP	27.8	0.0428	—	53.5	[75]
AG	—	2380	NaTFSI-P ₄ TFSI-PVD-HFP	—	0.0195	—	37.1	[76]
m-MnO ₂	5~15	128	LiTFSI/SiO ₂	16.1	—	—	21.6	[42]
MnO ₂	3.5~10	41	20 M LiCl	43	66	35	53.3	[81]
NF@C-650	约3.9	—	NaBF ₄ -EMIMBF ₄ -PVDF-HFP	41	—	60.7	—	[83]
MSP-TaS ₂	约0.95	—	PVA/LiCl	—	0.508	—	58.5	[44]
p-Ti ₃ C ₂ T _x	—	93.6	—	—	—	—	—	[45]
mPPy	8~13.6 ^①	73~96 ^①	—	—	—	—	—	[92]
mPANi	7~18 ^①	85	—	—	—	—	—	[93]
mPPy/rGO	约11	126~157	PVA/H ₂ SO ₄	81	—	—	2.3	[97]
mPPy/rGO-POM	—	142	PVA/H ₂ SO ₄	115	—	—	4.8	[98]
mNC/G	7~22 ^①	433	PVA/H ₂ SO ₄	—	0.021	—	1.9	[99]
MnO ₂ /Fe ₂ O ₃	100/50	—	PVA/LiCl	—	0.1106	—	39	[100]
mC@MXene	7~22 ^①	1049	EMIMBF ₄ /SiO ₂	21.9	—	181.3	—	[104]
ppy/MXene	7.8~52.0 ^①	129~188 ^①	—	—	—	—	—	[105]
NiCoMoS-Ti ₃ C ₂ T _x	—	25.1	PVA/KOH	—	1.456	—	50.6	[103]
有序介孔碳/MoS ₂	9	—	—	—	—	—	—	[95]
mPANi/MoS ₂	约12	258	—	—	—	—	—	[96]

注: ①指孔径/比表面积可在该范围进行调控; ②AN: 乙腈。

(2) 微纳结构与电化学性能之间构效关系的揭示: 目前的研究结果表明, 纳米片厚、介孔尺寸、介孔形状和比表面积对其在微型超级电容器中的电化学性能具有显著影响。然而, 不同化学组成和构型的二维介孔材料, 其结构和组成参数对其电容性能的影响规律并不相同, 导致一些文献中的结论是相悖的。所以, 统一标准并进行单变量的结构调控有待进一步探究。在一般情况下, 大的比表面积能够提供更多暴露的活性位点, 增强电子-离子传输, 可以显著提升材料、电极和器件的电容性能。此外, 将大孔作为溶液储库, 介孔作为离子传输通

道, 微孔作为离子限域空间, 将它们结合协同构筑大-介-微孔共存的二维材料有望实现更高性能的微型超级电容器。

(3) 微型超级电容器的储能机理研究: 二维介孔材料在微型超级电容器中的电子-离子传输形式和氧化还原反应理论也至关重要且充满挑战。因此, 应采用先进的理论计算, 如第一性原理和有限元模拟方法, 来研究二维介孔材料的化学键、离子吸附和电子传输作用机制。利用原位表征技术(如: 原位SEM、TEM、AFM、红外光谱、拉曼光谱、X射线光电子能谱、X射线衍射、X射线吸收光谱和

电化学阻抗谱)来实时追踪材料、电极和器件中微观结构演变、化学环境和反应动力学,可视化二维介孔材料在微型超级电容器中的储能机理。将理论计算与原位表征相结合,来验证二维介孔材料的构效关系,建立微型超级电容器电荷存储模型。

(4) 微型超级电容器集成系统的开发: 微型超级电容器设计的终极目标就是构筑自供电集成微系统。其中,微型超级电容器可以作为储能单元与能量收集器(如太阳能电池和纳米发电机)以及能量消耗单元(如传感器和光电探测器等)耦合。对于该集成微系统的制备,3D打印技术展现出了明显的优势,能够以更短的时间、更少的成本实现其大规模制造。但是,由于各单元之间的兼容性差以及复杂的外部电路连接,完全3D打印的自供电微系统仍处于理论实验阶段。为此,下一步应考虑多方面的因素,包括多功能材料设计、微加工技术优化、紧凑结构开发和整体性能提升等。通过这些研究,相信在不久的将来终将实现真正的一体化自供电微系统,极大地推动智能微电子和物联网时代的发展。

(5) 微型超级电容器及其集成系统的柔性化: 微型超级电容器及其自供电集成微系统主要应用于便携式、可穿戴和可植入电子设备,为此对其柔性提出了更高的要求。二维介孔材料基于独特的二维平面结构、丰富的介孔和优异的机械性能,以及与其他材料良好的兼容性,被认为是柔性电子器件最有前途的功能材料之一。因此,构筑二维介孔材料基微型超级电容器、传感器及其集成微系统具有重要意义。目前,对于单个器件的挑战在于多次弯曲、拉伸、压缩等机械形变下,保持电极结构完整和电化学性能的稳定;对于集成微系统需要能量收集器、微型超级电容器与传感单元在同一柔性衬底上实现协同形变。根据相关报道,微型超级电容器及其集成微系统都已基本实现可弯折,且在弯折情况下具有一定的循环性能。但是,与日常生活中的高频次、多维度形变需求仍存在差距,因此,进一步提高微型超级电容器及其集成系统的柔性性能成为目前应用的关键之一。

参考文献

- [1] ZHANG P P, WANG F X, YU M H, et al. Two-dimensional materials for miniaturized energy storage devices: From individual devices to smart integrated systems[J]. *Chemical Society Reviews*, 2018, 47(19): 7426-7451. DOI: 10.1039/C8CS00561C.
- [2] ZHENG S H, SHI X Y, DAS P, et al. The road towards planar microbatteries and micro-supercapacitors: From 2D to 3D device geometries[J]. *Advanced Materials*, 2019, 31(50): 1900583. DOI: 10.1002/adma.201900583.
- [3] ZHANG Y, ZHENG X T, ZHANG X Y, et al. Hybrid integration of wearable devices for physiological monitoring[J]. *Chemical Reviews*, 2024, 124(18): 10396-10434. DOI: 10.1021/acs.chemrev.3c00471.
- [4] MA J X, ZHENG S H, DAS P, et al. Sodium ion microscale electrochemical energy storage device: Present status and future perspective[J]. *Small Structures*, 2020, 1(1): 2000053. DOI: 10.1002/ssstr.202000053.
- [5] WANG J H, LI F, ZHU F, et al. Recent progress in micro-supercapacitor design, integration, and functionalization[J]. *Small Methods*, 2019, 3(8): 1800367. DOI: 10.1002/smt.201800367.
- [6] QIN J Q, ZHANG H T, YANG Z, et al. Recent advances and key opportunities on in-plane micro-supercapacitors: From functional microdevices to smart integrated microsystems[J]. *Journal of Energy Chemistry*, 2023, 81: 410-431. DOI: 10.1016/j.jechem.2023.01.065.
- [7] 王森, 郑双好, 黄海波, 等. 微型超级电容器的器件构型与电极制备最新进展[J]. *新型炭材料*, 2017, 32(6): 501-508. DOI: 10.19869/j.ncm.1007-8827.2017.06.002.
- [8] WANG S, ZHENG S H, HUANG H B, et al. Recent progress in device configuration and electrode fabrication for micro-supercapacitors[J]. *New Carbon Materials*, 2017, 32(6): 501-508. DOI: 10.19869/j.ncm.1007-8827.2017.06.002.
- [9] QIN J Q, DAS P, ZHENG S H, et al. A perspective on two-dimensional materials for planar micro-supercapacitors[J]. *APL Materials*, 2019, 7(9): 090902. DOI: 10.1063/1.5113940.
- [10] POMERANTSEVA E, BONACCORSO F, FENG X L, et al. Energy storage: The future enabled by nanomaterials[J]. *Science*, 2019, 366(6468): eaan8285. DOI: 10.1126/science.aan8285.
- [11] GEIM A K. Graphene: Status and prospects[J]. *Science*, 2009, 324(5934): 1530-1534. DOI: 10.1126/science.1158877.
- [12] WU Z S, FENG X L, CHENG H M. Recent advances in graphene-based planar micro-supercapacitors for on-chip energy storage[Open Access][J]. *National Science Review*, 2014, 1(2): 277-292. DOI: 10.1093/nsr/nwt003.
- [13] SIWACH P, GABA L, DAHIYA S, et al. Advances in MXene-based composites for next-generation flexible supercapacitors: From design and development to applications[J]. *Advances in Colloid and Interface Science*, 2025, 342: 103526. DOI: 10.1016/j.cis.2025.103526.
- [14] ZHU Y Y, WANG S, MA J X, et al. Recent status and future perspectives of 2D MXene for micro-supercapacitors and micro-batteries[J]. *Energy Storage Materials*, 2022, 51: 500-526. DOI: 10.1016/j.ensm.2022.06.044.
- [15] ABDELHAMID A A, YU Y, YANG J H, et al. Generalized synthesis

- of metal oxide nanosheets and their application as Li-ion battery anodes[J]. *Advanced Materials*, 2017, 29(32): 1701427. DOI: 10.1002/adma.201701427.
- [15] HUANG T T, JIANG K, CHEN D, et al. Recent progress and perspectives of metal oxides based on-chip microsupercapacitors[J]. *Chinese Chemical Letters*, 2018, 29(4): 553-563. DOI: 10.1016/j.ccllet.2017.12.007.
- [16] KUMAR J, SOLANGI N H, NEIBER R R, et al. Chemical perspectives on synthesis, functionalization, artificial intelligence, and energy storage applications of layered double hydroxides-based nanomaterials: A comprehensive review[J]. *Coordination Chemistry Reviews*, 2025, 537: 216705. DOI: 10.1016/j.ccr.2025.216705.
- [17] MANZELI S, OVCHINNIKOV D, PASQUIER D, et al. 2D transition metal dichalcogenides[J]. *Nature Reviews Materials*, 2017, 2: 17033. DOI: 10.1038/natrevmats.2017.33.
- [18] ZHANG L Z, YANG Z X, FENG S, et al. Metal telluride nanosheets by scalable solid lithiation and exfoliation[J]. *Nature*, 2024, 628(8007): 313-319. DOI: 10.1038/s41586-024-07209-2.
- [19] ZHANG J, TAN B Y, ZHANG X, et al. Atomically thin hexagonal boron nitride and its heterostructures[J]. *Advanced Materials*, 2021, 33(6): 2000769. DOI: 10.1002/adma.202000769.
- [20] ZHENG S H, LEI W W, QIN J Q, et al. All-solid-state high-energy planar asymmetric supercapacitors based on all-in-one monolithic film using boron nitride nanosheets as separator[J]. *Energy Storage Materials*, 2018, 10: 24-31. DOI: 10.1016/j.ensm.2017.08.002.
- [21] CHETTIANNAN B, DHANDAPANI E, ARUMUGAM G, et al. Metal-organic frameworks: A comprehensive review on common approaches to enhance the energy storage capacity in supercapacitor[J]. *Coordination Chemistry Reviews*, 2024, 518: 216048. DOI: 10.1016/j.ccr.2024.216048.
- [22] ZHANG J, LIU L L, ZHAO Z W, et al. Hydrogen-bonded mesoporous frameworks with tunable pore sizes and architectures from nanocluster assembly units[J]. *Journal of the American Chemical Society*, 2024, 146(26): 17866-17877. DOI: 10.1021/jacs.4c03538.
- [23] 张鸿涛. MXene基二维介孔材料的可控制备及其在微型超级电容器中的应用[D]. 郑州: 河南农业大学, 2024. DOI: 10.27117/d.cnki.ghenu.2024.000136.
- ZHANG H T. Controllable synthesis of MXene-based 2D mesoporous materials for micro-supercapacitors[D]. Zhengzhou: Henan Agricultural University, 2024. DOI: 10.27117/d.cnki.ghenu.2024.000136.
- [24] MATHIS T S, KURRA N, WANG X H, et al. Energy storage data reporting in perspective—Guidelines for interpreting the performance of electrochemical energy storage systems[J]. *Advanced Energy Materials*, 2019, 9(39): 1902007. DOI: 10.1002/aenm.201902007.
- [25] SIMON P, GOGOTSI Y. Perspectives for electrochemical capacitors and related devices[J]. *Nature Materials*, 2020, 19(11): 1151-1163. DOI: 10.1038/s41563-020-0747-z.
- [26] SU F, HOU X C, QIN J Q, et al. Recent advances and challenges of two-dimensional materials for high-energy and high-power lithium-ion capacitors[J]. *Batteries & Supercaps*, 2020, 3(1): 10-29. DOI: 10.1002/batt.201900153.
- [27] ZHAI Y P, DOU Y Q, ZHAO D Y, et al. Carbon materials for chemical capacitive energy storage[J]. *Advanced Materials*, 2011, 23(42): 4828-4850. DOI: 10.1002/adma.201100984.
- [28] HUANG H B, SHI H D, DAS P, et al. The chemistry and promising applications of graphene and porous graphene materials[J]. *Advanced Functional Materials*, 2020, 30(41): 1909035. DOI: 10.1002/adfm.201909035.
- [29] LIU Y, ZHENG S H, MA J X, et al. Aqueous high-voltage all 3D-printed micro-supercapacitors with ultrahigh areal capacitance and energy density[J]. *Journal of Energy Chemistry*, 2021, 63: 514-520. DOI: 10.1016/j.jchem.2021.08.018.
- [30] FLEISCHMANN S, MITCHELL J B, WANG R C, et al. Pseudocapacitance: From fundamental understanding to high power energy storage materials[J]. *Chemical Reviews*, 2020, 120(14): 6738-6782. DOI: 10.1021/acs.chemrev.0c00170.
- [31] AUGUSTYN V, SIMON P, DUNN B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage[J]. *Energy & Environmental Science*, 2014, 7(5): 1597-1614. DOI: 10.1039/C3EE44164D.
- [32] KURRA N, HOTA M K, ALSHAREEF H N. Conducting polymer micro-supercapacitors for flexible energy storage and AC line-filtering[J]. *Nano Energy*, 2015, 13: 500-508. DOI: 10.1016/j.nanoen.2015.03.018.
- [33] JIANG Y Q, LIU J P. Definitions of pseudocapacitive materials: A brief review[J]. *Energy & Environmental Materials*, 2019, 2(1): 30-37. DOI: 10.1002/eeem.12028.
- [34] XING F F, BI Z H, SU F, et al. Unraveling the design principles of battery-supercapacitor hybrid devices: From fundamental mechanisms to microstructure engineering and challenging perspectives[J]. *Advanced Energy Materials*, 2022, 12(26): 2200594. DOI: 10.1002/aenm.202200594.
- [35] LUKATSKAYA M R, DUNN B, GOGOTSI Y. Multidimensional materials and device architectures for future hybrid energy storage[J]. *Nature Communications*, 2016, 7: 12647. DOI: 10.1038/ncomms12647.
- [36] AI Y, LI W, ZHAO D. 2D mesoporous materials[J]. *National Science Review*, 2022(5): 12-14.
- [37] QIN J Q, YANG Z, XING F F, et al. Two-dimensional mesoporous materials for energy storage and conversion: Current status, chemical synthesis and challenging perspectives[J]. *Electrochemical Energy Reviews*, 2023, 6(1): 9. DOI: 10.1007/s41918-022-00177-z.
- [38] ZHENG X Y, LUO J Y, LV W, et al. Two-dimensional porous carbon: Synthesis and ion-transport properties[J]. *Advanced Materials*, 2015, 27(36): 5388-5395. DOI: 10.1002/adma.201501452.
- [39] HE Y F, ZHUANG X D, LEI C J, et al. Porous carbon nanosheets: Synthetic strategies and electrochemical energy related applications[J]. *Nano Today*, 2019, 24: 103-119. DOI: 10.1016/j.

- nantod.2018.12.004.
- [40] BAI J W, ZHONG X, JIANG S, et al. Graphene nanomesh[J]. *Nature Nanotechnology*, 2010, 5(3): 190-194. DOI: 10.1038/nnano.2010.8.
- [41] HAN S, WU D Q, LI S, et al. Porous graphene materials for advanced electrochemical energy storage and conversion devices[J]. *Advanced Materials*, 2014, 26(6): 849-864. DOI: 10.1002/adma.201303115.
- [42] QIN J Q, WANG S, ZHOU F, et al. 2D mesoporous MnO_2 nanosheets for high-energy asymmetric micro-supercapacitors in water-in-salt gel electrolyte[J]. *Energy Storage Materials*, 2019, 18: 397-404. DOI: 10.1016/j.ensm.2018.12.022.
- [43] LAN K, LIU Y, ZHANG W, et al. Uniform ordered two-dimensional mesoporous TiO_2 nanosheets from hydrothermal-induced solvent-confined monomeric assembly[J]. *Journal of the American Chemical Society*, 2018, 140(11): 4135-4143. DOI: 10.1021/jacs.8b00909.
- [44] WU J J, PENG J, YU Z, et al. Acid-assisted exfoliation toward metallic sub-nanopore TaS_2 monolayer with high volumetric capacitance[J]. *Journal of the American Chemical Society*, 2018, 140(1): 493-498. DOI: 10.1021/jacs.7b11915.
- [45] REN C E, ZHAO M Q, MAKARYAN T, et al. Porous two-dimensional transition metal carbide (MXene) flakes for high-performance Li-ion storage[J]. *ChemElectroChem*, 2016, 3(5): 689-693. DOI: 10.1002/celec.201600059.
- [46] BU F X, ZAGHO M M, IBRAHIM Y, et al. Porous MXenes: Synthesis, structures, and applications[J]. *Nano Today*, 2020, 30: 100803. DOI: 10.1016/j.nantod.2019.100803.
- [47] WANG L, DU Z, XIANG L X, et al. The ordered mesoporous carbon coated graphene as a high-performance broadband microwave absorber[J]. *Carbon*, 2021, 179: 435-444. DOI: 10.1016/j.carbon.2021.04.048.
- [48] WEI W, LIANG H W, PARVEZ K, et al. Nitrogen-doped carbon nanosheets with size-defined mesopores as highly efficient metal-free catalyst for the oxygen reduction reaction[J]. *Angewandte Chemie International Edition*, 2014, 53(6): 1570-1574. DOI: 10.1002/anie.201307319.
- [49] XIONG W J, XU Y L, ZHAO F Z, et al. Graphene architecture interpenetrated with mesoporous carbon nanosheets promotes fast and stable potassium storage[J]. *Chinese Chemical Letters*, 2025, 36(4): 109738. DOI: 10.1016/j.ccl.2024.109738.
- [50] LIU S H, GORDIICHUK P, WU Z S, et al. Patterning two-dimensional free-standing surfaces with mesoporous conducting polymers[J]. *Nature Communications*, 2015, 6: 8817. DOI: 10.1038/ncomms9817.
- [51] LIU Z Y, LIU S H, DONG R H, et al. High power in-plane micro-supercapacitors based on mesoporous polyaniline patterned graphene[J]. *Small*, 2017, 13(14): 160338. DOI: 10.1002/sml.201603388.
- [52] QIN J Q, YANG Z, MA J X, et al. Interfacial assembly of 2D polydopamine/graphene heterostructures with well-defined mesopore and tunable thickness for high-energy planar micro-supercapacitors[J]. *Chinese Chemical Letters*, 2024, 35(7): 108845. DOI: 10.1016/j.ccl.2023.108845.
- [53] GOU Z L, QU H Q, LIU H F, et al. Coupling of N-doped mesoporous carbon and $\text{N-Ti}_3\text{C}_2$ in 2D sandwiched heterostructure for enhanced oxygen electroreduction[J]. *Small*, 2022, 18(15): 2106581. DOI: 10.1002/sml.202106581.
- [54] WANG J, CHANG Z, DING B, et al. Universal access to two-dimensional mesoporous heterostructures by micelle-directed interfacial assembly[J]. *Angewandte Chemie International Edition*, 2020, 59(44): 19570-19575. DOI: 10.1002/anie.202007063.
- [55] LIU Z L, XIONG H L, LUO Y X, et al. Interface-induced self-assembly strategy toward 2D ordered mesoporous carbon/MXene heterostructures for high-performance supercapacitors[J]. *ChemSusChem*, 2021, 14(20): 4422-4430. DOI: 10.1002/cssc.202101374.
- [56] GOGOTSI Y, HUANG Q. MXenes: Two-dimensional building blocks for future materials and devices[J]. *ACS Nano*, 2021, 15(4): 5775-5780. DOI: 10.1021/acsnano.1c03161.
- [57] BATMUNKH M, BAT-ERDENE M, SHAPTER J G. Phosphorene and phosphorene-based materials-prospects for future applications [J]. *Advanced Materials*, 2016, 28(39): 8598-8617. DOI: 10.1002/adma.201602254.
- [58] YADAV P, BASU A, SURYAWANSHI A, et al. Highly stable laser-scribed flexible planar microsupercapacitor using mushroom derived carbon electrodes[J]. *Advanced Materials Interfaces*, 2016, 3(11): 1600057. DOI: 10.1002/admi.201600057.
- [59] FUERTES A B, SEVILLA M. Hierarchical microporous/mesoporous carbon nanosheets for high-performance supercapacitors[J]. *ACS Applied Materials & Interfaces*, 2015, 7(7): 4344-4353. DOI: 10.1021/am508794t.
- [60] XI X, WU D Q, HAN L, et al. Highly uniform carbon sheets with orientation-adjustable ordered mesopores[J]. *ACS Nano*, 2018, 12(6): 5436-5444. DOI: 10.1021/acsnano.8b00576.
- [61] FANG Y, LV Y Y, CHE R C, et al. Two-dimensional mesoporous carbon nanosheets and their derived graphene nanosheets: Synthesis and efficient lithium ion storage[J]. *Journal of the American Chemical Society*, 2013, 135(4): 1524-1530. DOI: 10.1021/ja310849c.
- [62] YAO L, WU Q, ZHANG P X, et al. Scalable 2D hierarchical porous carbon nanosheets for flexible supercapacitors with ultrahigh energy density[J]. *Advanced Materials*, 2018, 30(11): 1706054. DOI: 10.1002/adma.201706054.
- [63] QIN J Q, BO W B, DAS P, et al. 2D in-plane mesoporous N-doped carbon for co-planar integrated microsystem of micro-supercapacitor and pressure sensor[J]. *Small Methods*, 2025, 9(10): 2402205. DOI: 10.1002/smt.202402205.
- [64] HAN X G, FUNK M R, SHEN F, et al. Scalable holey graphene synthesis and dense electrode fabrication toward high-performance ultracapacitors[J]. *ACS Nano*, 2014, 8(9): 8255-8265. DOI: 10.1021/nn502635y.
- [65] XU Y X, LIN Z Y, ZHONG X, et al. Holey graphene frameworks for highly efficient capacitive energy storage[J]. *Nature Communications*, 2014, 5: 4554. DOI: 10.1038/ncomms5554.

- [66] XU Y X, CHEN C Y, ZHAO Z P, et al. Solution processable holey graphene oxide and its derived macrostructures for high-performance supercapacitors[J]. *Nano Letters*, 2015, 15(7): 4605-4610. DOI: 10.1021/acs.nanolett.5b01212.
- [67] KIM H K, BAK S M, LEE S W, et al. Scalable fabrication of micron-scale graphene nanomeshes for high-performance supercapacitor applications[J]. *Energy & Environmental Science*, 2016, 9(4): 1270-1281. DOI: 10.1039/C5EE03580E.
- [68] CUI H J, GUO Y B, GUO L M, et al. Heteroatom-doped carbon materials and their composites as electrocatalysts for CO₂ reduction[J]. *Journal of Materials Chemistry A*, 2018, 6(39): 18782-18793. DOI: 10.1039/C8TA07430E.
- [69] WANG H B, CHEN K, LU Z W, et al. Nonmetallic high-entropy-engineered nanocarbons for advanced ORR electrocatalysis[J]. *Angewandte Chemie International Edition*, 2025, 64(19): e202501290. DOI: 10.1002/anie.202501290.
- [70] ZHANG L Z, HUANG K, WEN P C, et al. Tailoring the defects of two-dimensional borocarbonitride nanomesh for high energy density micro-supercapacitor[J]. *Energy Storage Materials*, 2021, 42: 430-437. DOI: 10.1016/j.ensm.2021.07.041.
- [71] ZHU Y W, MURALI S, CAI W W, et al. Graphene and graphene oxide: Synthesis, properties, and applications[J]. *Advanced Materials*, 2010, 22(35): 3906-3924. DOI: 10.1002/adma.201001068.
- [72] ZHU Y W, MURALI S, STOLLER M D, et al. Carbon-based supercapacitors produced by activation of graphene[J]. *Science*, 2011, 332(6037): 1537-1541. DOI: 10.1126/science.1200770.
- [73] TAO Y, SUI Z Y, HAN B H. Advanced porous graphene materials: From in-plane pore generation to energy storage applications[J]. *Journal of Materials Chemistry A*, 2020, 8(13): 6125-6143. DOI: 10.1039/D0TA00154F.
- [74] BO W B, ZHANG H T, YIN G C, et al. Recent advances in graphene-based mesoporous nanosheets for supercapacitors[J]. *C*, 2023, 9(4): DOI: 10.3390/c9040091.
- [75] ZHENG S H, MA J M, WU Z S, et al. All-solid-state flexible planar lithium ion micro-capacitors[J]. *Energy & Environmental Science*, 2018, 11(8): 2001-2009. DOI: 10.1039/C8EE00855H.
- [76] ZHENG S H, WANG S, DONG Y F, et al. All-solid-state planar sodium-ion microcapacitors with multidirectional fast ion diffusion pathways[J]. *Advanced Science*, 2019, 6(23): 1902147. DOI: 10.1002/advs.201902147.
- [77] ZHOU Y G, ZHANG X, DING Y, et al. Redistributing Li-ion flux by parallelly aligned holey nanosheets for dendrite-free Li metal anodes[J]. *Advanced Materials*, 2020, 32(38): e2003920. DOI: 10.1002/adma.202003920.
- [78] WANG S, WU Z S, ZHOU F, et al. All-solid-state high-energy planar hybrid micro-supercapacitors based on 2D VN nanosheets and Co(OH)₂ nanoflowers[J]. *NPJ 2D Materials and Applications*, 2018, 2: 7. DOI: 10.1038/s41699-018-0052-8.
- [79] HU Y T, WU Y, WANG J. Manganese-oxide-based electrode materials for energy storage applications: How close are we to the theoretical capacitance? [J]. *Advanced Materials*, 2018, 30(47): e1802569. DOI: 10.1002/adma.201802569.
- [80] HUANG M, LI F, DONG F, et al. MnO₂-based nanostructures for high-performance supercapacitors[J]. *Journal of Materials Chemistry A*, 2015, 3(43): 21380-21423. DOI: 10.1039/C5TA05523G.
- [81] ZHU Y Y, ZHENG S H, QIN J Q, et al. 2.4 V ultrahigh-voltage aqueous MXene-based asymmetric micro-supercapacitors with high volumetric energy density toward a self-sufficient integrated microsystem[J]. *Fundamental Research*, 2024, 4(2): 307-314. DOI: 10.1016/j.fmre.2022.03.021.
- [82] DENG Q L, FU Y P, ZHU C B, et al. Niobium-based oxides toward advanced electrochemical energy storage: Recent advances and challenges[J]. *Small*, 2019, 15(32): e1804884. DOI: 10.1002/sml.201804884.
- [83] MA J X, QIN J Q, ZHENG S H, et al. Hierarchically structured Nb₂O₅ microflowers with enhanced capacity and fast-charging capability for flexible planar sodium ion micro-supercapacitors[J]. *Nano-Micro Letters*, 2024, 16(1): 67. DOI: 10.1007/s40820-023-01281-5.
- [84] LIU L L, YANG X Y, XIE Y J, et al. A universal lab-on-salt-particle approach to 2D single-layer ordered mesoporous materials[J]. *Advanced Materials*, 2020, 32(10): 1906653. DOI: 10.1002/adma.201906653.
- [85] ÖZTÜRK O, GÜR E. Layered transition metal sulfides for supercapacitor applications[J]. *ChemElectroChem*, 2024, 11(11): e202300575. DOI: 10.1002/celec.202300575.
- [86] HUAN Y H, SHI J P, ZOU X L, et al. Scalable production of two-dimensional metallic transition metal dichalcogenide nanosheet powders using NaCl templates toward electrocatalytic applications[J]. *Journal of the American Chemical Society*, 2019, 141(47): 18694-18703. DOI: 10.1021/jacs.9b06044.
- [87] LUKATSKAYA M R, MASHTALIR O, REN C E, et al. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide[J]. *Science*, 2013, 341(6153): 1502-1505. DOI: 10.1126/science.1241488.
- [88] GHIDIU M, LUKATSKAYA M R, ZHAO M Q, et al. Conductive two-dimensional titanium carbide 'clay' with high volumetric capacitance[J]. *Nature*, 2014, 516(7529): 78-81. DOI: 10.1038/nature13970.
- [89] ZHANG H, PANG B, DI A D, et al. Harnessing holey MXene/graphene oxide heterostructure to maximize ion channels in lamellar film for high-performance capacitive deionization[J]. *Small*, 2024, 20(45): 2403518. DOI: 10.1002/sml.202403518.
- [90] SHI Y, PENG L L, DING Y, et al. Nanostructured conductive polymers for advanced energy storage[J]. *Chemical Society Reviews*, 2015, 44(19): 6684-6696. DOI: 10.1039/C5CS00362H.
- [91] WUSTONI S, OHAYON D, HERMAWAN A, et al. Material design and characterization of conducting polymer-based supercapacitors[J]. *Polymer Reviews*, 2024, 64(1): 192-250. DOI: 10.1080/15583724.2023.2220131.
- [92] LIU S H, WANG F X, DONG R H, et al. Dual-template synthesis of 2D mesoporous polypyrrole nanosheets with controlled pore size[J]. *Advanced Materials*, 2016, 28(38): 8365-8370. DOI:

- 10.1002/adma.201603036.
- [93] LIU S H, ZHANG J, DONG R H, et al. Two-dimensional mesoscale-ordered conducting polymers[J]. *Angewandte Chemie International Edition*, 2016, 55(40): 12516-12521. DOI: 10.1002/anie.201606988.
- [94] WU W M, ZHANG C S, YANG S B. Controllable synthesis of sandwich-like graphene-supported structures for energy storage and conversion[J]. *New Carbon Materials*, 2017, 32(1): 1-14. DOI: 10.1016/S1872-5805(17)60101-X.
- [95] FANG Y, LV Y Y, GONG F, et al. Synthesis of 2D-mesoporous-carbon/MoS₂ heterostructures with well-defined interfaces for high-performance lithium-ion batteries[J]. *Advanced Materials*, 2016, 28(42): 9385-9390. DOI: 10.1002/adma.201602210.
- [96] TIAN H, ZHU S Y, XU F G, et al. Growth of 2D mesoporous polyaniline with controlled pore structures on ultrathin MoS₂ nanosheets by block copolymer self-assembly in solution[J]. *ACS Applied Materials & Interfaces*, 2017, 9(50): 43975-43982. DOI: 10.1021/acsami.7b13666.
- [97] TIAN H, QIN J Q, HOU D, et al. General interfacial self-assembly engineering for patterning two-dimensional polymers with cylindrical mesopores on graphene[J]. *Angewandte Chemie*, 2019, 131(30): 10279-10284. DOI: 10.1002/ange.201903684.
- [98] QIN J Q, ZHOU F, XIAO H, et al. Mesoporous polypyrrole-based graphene nanosheets anchoring redox polyoxometalate for all-solid-state micro-supercapacitors with enhanced volumetric capacitance[J]. *Science China Materials*, 2018, 61(2): 233-242. DOI: 10.1007/s40843-017-9132-8.
- [99] 杨志, 周峰, 张鸿涛, 等. 二维介孔氮掺杂炭/石墨烯纳米片的可控合成及其高性能微型超级电容器[J]. *新型碳材料*, 2022(5): 936-943. DOI: 10.1016/S1872-5805(22)60633-4.
- YANG Z, ZHOU F, ZHANG H T, et al. Controllable synthesis of two-dimensional mesoporous nitrogen-doped carbon/graphene nanosheets and their high-performance micro supercapacitors[J]. *New Carbon Materials*, 2022(5): 936-943. DOI: 10.1016/S1872-5805(22)60633-4.
- [100] XIA Z Y, MISHUKOVA V, SOLLAMI DELEKTA S, et al. Selective deposition of metal oxide nanoflakes on graphene electrodes to obtain high-performance asymmetric micro-supercapacitors[J]. *Nanoscale*, 2021, 13(5): 3285-3294. DOI: 10.1039/D0NR07076A.
- [101] LI Q, XU X T, GUO J R, et al. Two-dimensional MXene-polymer heterostructure with ordered in-plane mesochannels for high-performance capacitive deionization[J]. *Angewandte Chemie International Edition*, 2021, 60(51): 26528-26534. DOI: 10.1002/anie.202111823.
- [102] LI T, DING B, WANG J, et al. Sandwich-structured ordered mesoporous polydopamine/MXene hybrids as high-performance anodes for lithium-ion batteries[J]. *ACS Applied Materials & Interfaces*, 2020, 12(13): 14993-15001. DOI: 10.1021/acsami.9b18883.
- [103] MEI X T, YANG C, CHEN F Y, et al. Interfacially ordered NiCoMoS nanosheets arrays on hierarchical Ti₃C₂T_x MXene for high-energy-density fiber-shaped supercapacitors with accelerated pseudocapacitive kinetics[J]. *Angewandte Chemie International Edition*, 2024, 63(36): e202409281. DOI: 10.1002/anie.202409281.
- [104] QIN J Q, ZHANG H T, BAI T S, et al. Generalized interfacial assembly of 2D mesoporous heterostructures for high-energy solid-state micro-supercapacitors[J]. *Advanced Functional Materials*, 2024, 34(45): 2405224. DOI: 10.1002/adfm.202405224.
- [105] LIU Z L, ZHANG R, XIONG H L, et al. Swelling-induced structural transformation strategy: Controllable synthesis of 2D porous polypyrrole/MXene heterostructures with tunable pore structures[J]. *Advanced Materials Interfaces*, 2023, 10(11): 2202501. DOI: 10.1002/admi.202202501.
- [106] LAN K, WEI Q L, WANG R C, et al. Two-dimensional mesoporous heterostructure delivering superior pseudocapacitive sodium storage via bottom-up monomolecule assembly[J]. *Journal of the American Chemical Society*, 2019, 141(42): 16755-16762. DOI: 10.1021/jacs.9b06962.
- [107] HOU D, ZHU S Y, TIAN H, et al. Two-dimensional sandwich-structured mesoporous Mo₂C/carbon/graphene nanohybrids for efficient hydrogen production electrocatalysts[J]. *ACS Applied Materials & Interfaces*, 2018, 10(47): 40800-40807. DOI: 10.1021/acsami.8b15250.
- [108] ZHOU Z R, LV J L, TAN C, et al. Emerging frontiers of 2D transition metal dichalcogenides in photovoltaics solar cell[J]. *Advanced Functional Materials*, 2024, 34(29): 2316175. DOI: 10.1002/adfm.202316175.
- [109] LAN J J, UNIVERSITY X, ZHANG S, et al. High-power polysulfide redox flow batteries via an interfacial electron field on a 2D mesoporous heterojunction[J]. *ACS Nano*, 2025, 19(35): 31699-31708. DOI: 10.1021/acsnano.5c09873.
- [110] ZHANG Y J, YAM K M, WANG H, et al. Recent progresses in two-dimensional carbon-metal composites for catalysis applications[J]. *WIREs Computational Molecular Science*, 2025, 15(2): e70014. DOI: 10.1002/wcms.70014.
- [111] CHANG Y M, LI P F, ZHAO T, et al. Boosting photocatalytic activity through dual functionalization: Oxygen vacancy-rich 2D mesoporous TiO₂ nanosheets integrated with bimetallic nanoclusters[J]. *Advanced Functional Materials*, 2025, 35(52): e14365. DOI: 10.1002/adfm.202514365.

4. 以农为导,“有机化学”课程助力强农人才培养的教学探索与实践. 科技风, 2026, 34-37.



以农为导,“有机化学”课程 助力强农人才培养的教学探索与实践

姜 松 秦洁琼 魏 民 谢普会 潘振良*

河南农业大学理学院 河南郑州 450002

摘 要:农科“有机化学”课程立足高等农林教育,基于成果导向理念,针对教学过程中存在的课程内容知识点繁多、课程理论与实践联系不紧密、立德树人功能特色不突出等痛点问题,通过实施智慧化教学、交叉融合案例与虚拟仿真并行、融入以“知农爱农”为核心的课程思政等措施创新教学方式,实现知识传授、能力培养与价值引领的同向同行和交相辉映。教学实践表明,该模式能有效激发学生的学习兴趣,拓宽学生视野,助力学生领略研究前沿魅力,充分发挥了课程在农科人才培养中的作用,为农村农业高质量发展提供坚实的人才支撑。

关键词:有机化学;农科;OBE 理念;智慧化教学

作为培养农科专业人才的核心阵地,农业大学要牢牢把握立德树人根本任务,锚定“强农兴农”育人目标,着力培育兼具深厚“三农”情怀、扎实专业功底与较强实践能力的新型农科人才,为农业农村高质量发展筑牢人才根基^[1]。

有机化学作为一门研究有机化合物的结构、性质、合成方法及反应规律的核心基础学科,与农学、园艺、植物保护、动物医学、食品科学与工程等农科各专业存在深度且多元的交叉关联,能为农科各专业的可持续发展夯实理论基础、提供材料支撑与技术保障,在农科人才培养体系中占据不可或缺的关键地位^[2-3]。河南农业大学作为一所具有鲜明农业特色的省属重点大学,其“有机化学”课程经过多年建设与发展,已成功获批国家级一流本科课程,不仅是全校农科各专业的核心基础必修课程,更是培养农学类复合型应用人才的基础,直接支撑全校 14 个国家级一流本科专业和 14 个省级一流本科专业的建设与发展。该课程主要面向大一下学期农科各专学生开设,共计 48 学时(3 学分),年均选课学生达 3000 余人次,覆盖农科所有专业领域,其教学质量直接影响农科学生后续专业课程的学习效果与综合素养的提升。

1 农科“有机化学”课程教学痛点及改革思路

为精准把握新高考改革背景下农科学生的学情特点,团队通过往届和现届授课学生的 402 份问卷调查及 20 余次座谈、授课教师及同行专家的 12 次访谈进行了如下问题总结:(1)“有机化学”课程中不同有机化合物之间性质千差万别,知识点多且复杂,这导致学生学习时存在畏难情绪,学习积极性不高。(2)理论与实践联系不紧密,学生学习的理论知识无法运用于实践,学习目标不明

确。(3)课程思政功能不能突出农业院校特色,达不到培养“知农兴农”新农科创新性人才的育人目标。针对以上问题,本着立德树人、学生中心、产出导向和持续改进的理念,明确提出“以生为本、以农为导”的教学改革思路,着力破解传统教学难题,构建具有农业特色的有机化学教学体系。“以生为本”就是立足学生学情特点与学习需求,借助智慧教学创新模式,实现教学过程的个性化与精准化,破解学生学习畏难问题,激发学生的学习积极性,提升其自主学习能力,夯实农科学生的化学基础。“以农为导”就是紧密结合农业特色与农科专业需求,多途径、多方位地将农科交叉案例、农业前沿技术融入教学全过程,推动理论与实践紧密联系,同时深度融入课程思政元素,塑造学生“学农、兴农、强农”的家国情怀。

2 农科“有机化学”课程教学创新途径与举措

2.1 借助智慧教学创新模式,实现教学过程的个性化和精准化

依托 MOOC 为平台,采用基于人工智能(AI)的智慧教学模式,深度融合学科知识与 AI 技术,通过课前导学、课中探究、课后拓展的教学策略,实现实时学习行为监测与精准反馈。同时,基于大数据分析技术,实现 AI 辅助个性化学习路径规划并生成精准教研报告,促进自主学习能力提升。

课前,基于知识图谱发布课前预习、推送教学案例。知识图谱可将有机化学中官能团、化合物类别、反应类型、物理性质等零散的知识点转化为清晰的节点,通过“包含”“转化”“衍生”等关系链路串联成完整体系。知识点以知识图谱的形式呈现,学生在预习时,借助知识图谱这一可

可视化网络快速把握章节知识框架,明确各知识点的归属与关联,实现从“碎片化记忆”到“系统化认知”的预习转变。教学案例由 AI 精准推送,具体根据学生专业类别,选择与本专业交叉融合具有前瞻性或应用性的案例。比如,将新型绿色农药甲噻磺隆推送给植保等专业学生,二氧化碳全合成淀粉推送给食品类学生等,专业相关的教学案例能有效提升学生的学习兴趣。

课中,教学环节严格秉持“以学生为主体、教师为主导”的理念,全面推行探究式学习模式,实现从“教师讲授”向“学生主动探究”的转变。具体实施过程紧密衔接课前导学及教学案例:首先,各学习小组结合课前推送的教学案例进行汇报,汇报内容需清晰呈现知识预习收获、项目探究思路、初步结论及存在的疑问;其次,开展翻转课堂展示,各小组通过 PPT、实验方案设计等形式分享预习成果,其他小组结合自身预习进行针对性提问、小组间交叉讨论,同时参照预设的评分标准完成互评打分。在学生汇报与讨论的过程中,教师全程把控课堂节奏,针对学生汇报中暴露的问题及小组讨论的争议焦点进行深度解析,帮助学生厘清知识脉络。课中探究不仅有效激发了学生的课堂参与热情,让学生在成果展示、互动讨论与互评过程中获得强烈的学习成就感,更在巩固有机化学基础知识的同时,倒逼学生主动将理论知识与农业生产实际问题相结合,显著提升了其发现问题、分析问题及解决实际农科相关问题的综合能力。

课后,聚焦知识巩固与应用拓展。教师结合课中学生知识掌握情况,设计并布置具有农科交叉融合特性的课后任务。各学习小组延续课堂协作模式,围绕任务主题开展系统性文献调研,梳理相关领域的研究现状、核心有机化学原理及技术应用瓶颈,在深度复盘课堂所学有机化学知识的基础上,结合调研成果撰写课程论文或探究报告。这一过程中,学生不仅能够进一步夯实课堂所学的基础知识,更能主动以有机化学的思维视角审视农科专业领域中的实际问题,学会运用有机化学的原理、方法与技术分析并尝试解决农业生产、农产品加工、农业环境保护等场景中的具体问题,真正实现“学以致用”。

同时,提升教学智慧化水平,对教学全过程进行实时学习行为监测与精准反馈,基于 AI 辅助形成个性化学习路径规划并生成精准教研报告,满足学生多样化学习需求,提高其学习兴趣,促进其自主学习力发展。

2.2 借助虚拟仿真引入典型案例,推动理论与实践融合、学科交叉融合

课程教学体系中专门融入技术赋能与案例驱动模块,借助虚拟仿真技术的沉浸式优势,引入化学与农科深度耦

合的典型应用案例,推动理论知识与实践应用紧密融合、学科知识与农科专业交叉渗透。

首先,深化学科内容与前沿技术的融合创新,依托有机化学虚拟仿真实验平台、智能教学互动系统等技术载体,将抽象的化学反应过程转化为可视化的动态模拟场景,引导学生通过人机交互自主调控反应条件,观察反应进程、分析产物变化,实现化学反应的可视化呈现与学习过程的实时交互,推动理论与实践融合。

其次,精准引入农科导向的交叉融合典型案例,将有机化学核心知识点融入农业生产等实际场景中,让学生深刻领悟有机化学与农科深度交叉融合创新的魅力,激发学生的学习兴趣与专业认同感。教学团队围绕农科各专业特色,筛选整理了一系列具有代表性、接地气的农科交叉案例。例如,在讲解“芳香族化合物的结构与性质”时,引入“植物源农药鱼藤酮的提取与合成”案例,详细介绍鱼藤酮的分子结构、化学性质,以及其在植物保护中的应用原理,讲解鱼藤酮的提取工艺与合成优化方法,让学生在理解知识点的同时,了解农科领域的前沿技术;在讲解“有机合成反应”时,引入“超高效绿色除草剂单噻磺隆的研发”案例,详细介绍单噻磺隆的分子结构设计、有机合成路径,以及其在农药减量增效、农业生态保护中的应用成效,让学生树立“绿色化学、生态优先”的农业发展理念;这些鲜活的农科交叉案例不仅有效拉近了有机化学与农科专业的距离,让抽象的理论知识变得通俗易懂、贴近实际,更让学生直观感受到有机化学技术在农业领域的应用价值,提升了学生学习农科专业的自豪感、成就感和自身价值实现感,同时塑造了学生“学农兴农强农”的家国情怀,增强了学生服务国家、服务人民、服务“三农”的社会责任感。

2.3 立足农大,多途径、多方位融入思政案例

课程立足河南农业大学,挖掘多元特色案例资源,通过多途径、多方位融入思政案例,实现知识传授与价值引领、校情教育的深度融合,让农科“有机化学”教学更具温度与针对性。

在家国情怀与前沿科技认知培养上,引入具有里程碑意义的国家级科研成果案例,将其与有机化学核心知识点深度融合,让学生在学习知识的同时,了解我国科技发展的辉煌成就,增强民族自豪感与科技自信心。在生态环保理念与农科应用能力培养上,聚焦农业绿色发展领域的自主创新成果,强化有机化学与农科实践的紧密关联。在爱校荣校与知农爱农情怀培育上,立足河南农业大学办学特色,挖掘身边接地气的鲜活案例,增强学生爱校荣校的情感认同。

2.4 基于 AI 辅助,打造全过程的多元化评价体系

打造“多元多阶化”评价机制,加强项目式、探究式、论

文式等考核评价方式的应用,将课堂互动、随堂测试、虚拟仿真实验、课程论文与创新项目纳入过程评价体系,注重过程性考核的权重。强化“过程育人”理念,通过阶段性反馈与成长性评价,推动学生从知识获取向综合能力与创新能力全面提升。

在评价内容与形式设计上,构建覆盖“课前预习—课中探究—课后拓展”全教学环节的考核体系,提高项目式、探究式、论文式等质性评价方式的应用比重,将课堂互动表现、随堂知识点检测、虚拟仿真实验操作成效、课程论文质量、创新项目探究成果等核心指标纳入过程评价范畴。具体而言,课前,依托 AI 学习分析平台,追踪学生借助知识图谱梳理知识的完整性与逻辑性,生成个性化预习评价报告;课中,通过 AI 互动教学系统记录小组汇报、翻转课堂讨论、互评打分等过程数据,结合教师精准点评形成综合表现评分;课后,借助 AI 文本分析工具,对学生撰写的农科交叉主题课程论文、调研报告进行查重、逻辑梳理与学术规范性评估,并对虚拟仿真实验中的操作步骤、参数调控、问题解决能力进行量化评分。在此基础上,科学设定过程性考核权重,将其占比提升至总成绩的 60%;终结性考核侧重考查学生有机化学核心原理知识的融会贯通能力及农科场景下的知识迁移应用能力,最终形成“过程性考核为主、终结性考核为辅”的评价结构。

3 教学效果

农科“有机化学”课程改革通过构建“课程设计—技术赋能—特色案例—多元评价”四位一体的改革体系,结合河南农业大学特色与农科专业人才培养需求,有效破解了传统教学中的突出问题,实现了知识传授、能力培养与价值引领的有机统一,课程教学质量与育人成效得到显著提升。学生层面,教学改革有效激发了学生的学习兴趣与主动性,学生的知识掌握与应用能力、综合素养得到显著提升。通过智慧教学模式与农科交叉案例的应用,学生的学习畏难情绪得到有效缓解,学习积极性与主动性显著提高,课堂互动参与率从改革前的 60% 提升至 90% 以上,学生主动参与课前预习、课后探究的比例大幅增加。学生对有机化学知识的掌握更加扎实,知识迁移能力与应用能力显著改善,在后续专业课程的学习中,能够快速运用有机化学知识解决专业相关问题,学习效果明显提升。教师层面,教学改革推动教师的教学能力与科研水平显著提升。在教学改革过程中,教师需要不断学习智慧教学技术、挖掘农科交叉案例、融入课程思政元素,这倒逼教师不断提升自身的专业素养、教学能力与科研水平。

结语

农科“有机化学”课程教学改革以“强农兴农”为根本

指引,立足河南农业大学的办学特色与农科专业人才培养需求,以 OBE 理念为指导,坚持“以生为本、以农为导”,通过智慧教学模式创新、虚拟仿真技术应用、农科交叉案例融入、课程思政渗透与多元化评价体系构建,有效破解了传统教学中的突出问题,构建了具有农业特色的有机化学教学体系,实现了“知识传授、能力培养与价值引领”的三位一体育人目标,为农科人才培养提供了有力支撑,为农业农村高质量发展与乡村振兴战略实施培育了合格人才。

当然,农科“有机化学”课程教学改革仍存在一些不足,如智慧教学技术的融合深度仍需加强、农科交叉案例资源仍需进一步丰富等。未来,课程教学团队将继续深化教学改革,持续提升教学质量与育人成效,为培养更多“知农爱农、强农兴农”的复合型农科人才,为建设农业强国、推进中国式现代化做出更大的贡献。

参考文献:

- [1] 钟登华. 奋力写好“矢志强农报国”的高等教育答卷[J]. 中国高等教育, 2025(21): 1.
 - [2] 万福贤, 李映, 张元红, 等. 农科特色有机化学课程的教学探索与实践[J]. 大学化学, 2024, 39(2): 298-306.
 - [3] 夏旭东, 张红喜, 马小燕. “双向互动、三段齐进、四级融合”用于有机化学教学[J]. 科技视界, 2020(35): 43-45.
 - [4] 何春霞. 中华优秀传统文化融入《有机化学》课程教学的研究[J]. 产业与科技论坛, 2025, 24(2): 183-185.
 - [5] 徐迪, 戴力, 姚文志, 等. 有机化学智慧教学的探索与应用[J]. 大学化学, 2025, 40(9): 189-195.
- 基金项目:** 河南省本科高校青年骨干教师培养计划项目(2021GGJS029); 河南省研究生教育改革与质量提升工程项目(YJS2026XSJC23、YJS2025KC21); 河南农业大学本科教育教学改革研究与实践项目(2025XJGLX044); 河南农业大学本科课程教学工程项目(25KCXM12)
- 作者简介:** 姜松(1985—), 男, 汉族, 河南驻马店人, 博士, 副教授, 主要从事有机功能材料的研究; 秦洁琼(1990—), 女, 汉族, 河南洛阳人, 博士, 教授, 主要从事二维纳米材料和储能器件的研究; 魏氏(1990—), 女, 汉族, 河南新乡人, 博士, 副教授, 主要从事电化学研究和应用; 谢普会(1971—), 女, 汉族, 重庆梁平人, 博士, 教授, 主要从事有机功能材料的研究。

* 通信作者: 潘振良(1972—), 男, 汉族, 河南开封人, 博士, 教授, 主要从事物理有机化学的研究。

5. 农业院校有机化学教学设计与实践——以醚为例. 科教导刊(电子版), 2025, 19, 50-53.

农业院校有机化学教学设计与实践 ——以醚为例

魏 民*, 安万凯, 徐翠莲, 姜 松*

(河南农业大学理学院, 河南 郑州 450002)

摘 要 教学改革是提升课程质量、培养学生综合能力的关键环节。有机化学作为农业院校理、工、农、医等专业的重要基础课程,其教学内容与方法的创新对提高学生学习效果具有重要意义。文章以“醚”一课为例,从学习目标设定、教学内容设计、实践应用拓展、教学反馈与总结四个方面,系统探讨有机化学课程的教学改革与实践,希望通过多元化教学策略提升学生的知识应用能力与科学素养。

关键词 教学改革;有机化学;醚;教学设计;实践应用

中图分类号: G642.1

文献标识码: A

0 引言

有机化学是农业院校理、工、农、医等专业的重要基础课程,涉及专业领域十分广泛。有机化学的内容丰富、知识点众多,涉及反应式多、反应规则多、立体反应复杂,学生在学习时需要记忆和理解的内容繁杂,学生普遍反映学习难度较大。因此,有机化学教学改革与实践尤为重要。为解决这些教学痛点,教学团队坚持以学生为中心、以能力产出为导向、持续改进的教学理念,不断深入进行教学改革探索和实践,通过多元化教学策略提升学生的知识应用能力与科学素养,努力培养高素质应用型农业人才。2020年5月教育部关于印发《高等学校课程思政建设指导纲要》的通知指出“全面推进课程思政建设是落实立德树人根本任务的战略举措”。因此在课程改革过程中需整合课程思政资源,注重价值引领。本文选取《有机化学》^[1]第七章“醇、酚、醚”中“醚”一节作为教学改革和实践案例,从设置学习目标、设计教学内容、教学内容扩展、教学反馈和总结四个方面,深入探讨有机化学课程教学设计与实践。

1 学习目标的设置

根据有机化学“醚”这节课的教学内容和特点,制定以下三个目标层次:知识目标、能力目标以及价值目标。

1.1 知识目标

- (1)理解醚的分类、命名及结构特点。
- (2)掌握醚的物理性质和化学性质。
- (3)了解醚在科学研究及实际生产中的典型应用。

1.2 能力目标

- (1)通过认识醚与醇、酚的结构差异,培养学生辩证思维能力。
- (2)通过学习醚的命名和化学性质,提高学生知识综

合运用能力。

(3)通过了解醚在科研和生产中的应用,培养学生分析和解决问题的能力。

1.3 价值目标

- (1)通过学习醚的物理和化学性质,引导学生独立思考以及对知识的融会贯通。
- (2)通过了解醚的应用过程中出现的安全事故,加强学生对醚的性质的理解,树立学生安全生产意识。
- (3)通过了解冠醚的发现及发展过程,学习科学家孜孜不倦的研究精神,激发学生的学习兴趣,培养学生探索创新的科学素养。

2 教学内容的设计

2.1 课程导入

课程导入是激发学生学习和探索新知识的催化剂。选取与课程内容相关的时事、新闻、图片、科学史料等创设情境,充分调动学生对学习内容的注意力和好奇心,从而顺利开展课程内容教学^[2]。在“醚”的教学中,首先选取一组醚的应用场景(图1, P51)展示给学生,让学生了解醚在日常生活、生产中的重要性,激发学生的学习欲望。从图中可以看出,醚类有机物在日常生产生活的应用非常广泛,引导学生思考醚类物质是一类什么样的有机物?其性质如何?性质与应用之间有着怎样的联系?从而顺利引出本节课的教学内容。

2.2 醚的分类、命名和结构特点

2.2.1 教学设计思路

本节课的先行课程中,学生已经认识了醇和酚,醚类有机物与醇、酚在结构上有相似之处,但性质完全不相同。教师首先向学生阐释醚类的结构特点,让学生对醚的结构特点有清晰的认知。醇酚醚都是含有氧原子的有机物,

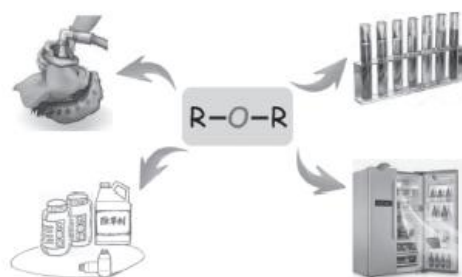


图1 醚类有机物在生产生活中的应用场景

醇和酚是氧原子与一个烃基和一个氢原子相连,而醚则是氧原子与两个烃基相连,即“R-O-R”,其中“-O-”称为醚键。醚与醇、酚的结构异同点是学生区分三类有机物的基础。醚的分类是按照与氧原子所连接的两个烃基类型来决定的。如果两个烃基相同,称为单醚;两个烃基不同,称为混合醚;两个烃基均为脂肪族烃基,称为脂肪醚;两个烃基至少有一个为芳基,称为芳香醚。在认识了醚的结构与分类后,教师向学生讲解如何正确命名醚,主要介绍普通命名法和系统命名法的命名要点。如简单醚和混合醚的命名、复杂醚的命名等。同时设置命名练习题,让学生在练习中理解醚的命名规律和方法,加强对知识的掌握(表1)。

表1 本节课的主要内容及相应的课程思政元素

内容	科学故事	课程思政
醚的引入	日常生活中醚的广泛应用	观察与思考
醚的分类和命名	乙醚麻醉发明人之争	科学精神与社会责任
醚的化学性质	稳定不是永恒的,是相对的;醚类溶剂导致的实验安全事故	辩证思维与发展眼光 安全生产意识
环醚和冠醚	1987年诺贝尔化学奖	多学科交叉与创新
醚的拓展应用	我国科研人员研发高效醚类汽油;聚硫醚在航空航天的应用	民族自豪感 爱国主义与目标树立

2.2.2 教学内容拓展

介绍醚类物质作为麻醉剂的发展历史及其发挥作用,引发学生对醚的学习兴趣,使其以积极的态度学习专业知识,同时拓宽学生的认知范围,树立探索未知、追求真理的科学精神。在麻醉药问世之前,外科手术中的病人通常忍受巨大的疼痛,急需手术麻醉剂。1842年,美国医生克劳福德·朗格首次应用乙醚吸入式麻醉方法,成功为一个颈背部肿瘤患者实施切除手术,这是人类历史上第一次运用乙醚麻醉的手术。手术虽然取得了成功,但是处事严谨的朗格医生考虑到乙醚对人体的副作用尚不了解,他不急于向世人宣布这个发现,因而并没有广泛推广,仅在自己的亲朋好友中小范围试用,直到1848年才将结果发表

在《南方医学与手术杂志》,比美国医生威廉·莫顿的乙醚报道晚了2年,使他与“现代医学全麻第一人”的称号失之交臂。通过这个故事倡导学生学习克劳福德·朗格淡泊名利、追求真理、严谨治学的精神品质,这样的精神品质是每个行业都需要树立和培养的。

2.3 醚的化学性质

2.3.1 教学设计思路

通过对醚的分类和命名的学习,学生对醚有了基本认识。此时教师以课程开头的问题作为过渡,引出醚的化学性质。在本课程的课程导入中已经提到了醚可与多种有机物互溶,可作为良好的有机溶剂,这就说明醚的性质相当稳定。事实上,在常温下除小环醚外,醚与强碱、强氧化剂,以及活泼金属均不反应,其稳定性类似于烷烃。因此教师可提出问题“醚到底在什么条件下发生哪些反应?”引发学生对醚的化学性质的思考。接下来教师通过反应实例(图2)向学生详细讲解醚能够发生的化学反应,如与强酸反应形成盐、醚键断裂反应、醚氧化成过氧化物以及过氧化物的除去方法等。有问有答的教学设计使学生带着问题寻找答案,提高学习的积极性和教学效果。

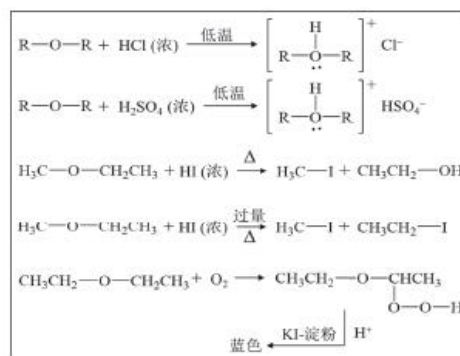


图2 醚的化学反应

2.3.2 教学内容拓展

(1)讲解醚键断裂反应时,引导学生透过现象看本质,培养学生的辩证思维能力。在课程引入中已经讲过,醚性质较为稳定,可以作为溶剂使用,但是稳定不是永恒的,而是相对的、有条件的。醚在氢碘酸作用下发生醚键断裂反应生成碘代烷烃和醇。这里教师须引导学生树立辩证思维,用发展的眼光全面看待问题。

(2)对于混合醚,氧连接了两个不同的烃基,就可以有“哪个烃基与氧原子之间的共价键断裂形成碘代烷”的问题。在解决这个问题时,教师引导学生透过现象看本质,换个角度思考,即“两个C-O共价键的极性越大越易断裂”,让学生学会利用基团的供/吸电子的能力来判断并解

决问题,锻炼思辨能力,实现知识的融会贯通。

(3)讲解醚形成过氧化物的反应时,教师通过生产生活中的事故举例,培养学生的安全生产意识。2006年,加州大学伯克利分校发生一起实验室爆炸事故,一名学生使用旋转蒸发器蒸馏偶氮苯的溶剂二乙醚和四氢呋喃时发生爆炸,导致该学生面部受伤。事后调查发现,引起爆炸的最可能原因就是溶剂中的过氧化物。本次实验中该学生使用的两种溶剂四氢呋喃和二乙醚都是醚类溶剂,长时间放置后会与空气中的氧气反应,生成易燃易爆的过氧化物,从而引起了事故。因此在使用醚类有机物作为溶剂时,一定要先检测过氧化物的含量,用适当的还原剂将过氧化物去除掉后再使用。通过这个事故案例,使学生树立安全无小事的思想意识,培养学生在实际实验、生产生活中利用所学知识解决安全问题的能力。

2.4 环醚和冠醚

2.4.1 教学设计思路

环醚和冠醚均是具有环状结构的醚,因此放在一起讲解较为合适。首先引导学生回顾环烷烃中三元环和四元环的特性:由于存在较大的角张力和扭转张力,这些结构表现出较高的化学活性,容易发生开环反应。随后,基于“结构决定性质”的基本原理,顺势提出以下问题:碳原子数较少的环醚是否存在较大张力而易发生开环反应、环醚的开环反应通常发生在哪个键位、这类反应容易与哪些试剂发生、这些开环反应有哪些实际应用。通过这一系列问题,自然引入环醚化学性质的学习(图3)。冠醚则主要侧重讲解其发现发展过程,列举冠醚在分离、催化、材料等领域的应用,拓宽学生的视野,培养学生的科学素养。1967年美国杜邦公司C. J. Pedersen在偶然中首次合成了形似王冠的大环多醚化合物, Pedersen对这意外发现没有轻易放弃,而是进行了系统研究,合成了60多种全氧大环聚醚,并命名为冠醚,同时他还发现冠醚能与金属离子钾、钠等形成稳定的络合物,这引起了化学家的极大兴趣^[3]。后来,美国化学家C. J. Cram改进了冠醚的合成方法,通过将手性联苯环结构引入冠醚分子,成功合成了具有光学活性的联苯型冠醚,它对苯基甘氨酸甲酯的六氟磷酸盐具有选择性络合作用。Cram夫妇在Science上撰文将冠醚等含有氧、氮、硫等具有一定空腔的分子叫主体分子,将金属离子或有机小分子称为客体分子,主体分子和客体分子之间存在的相互作用称为“主-客体络合作用”,从而开创了“主-客体化学”的新领域。法国化学家J. M. Lehn把氮原子引入到冠醚中,设计了高度稀释法合成了“穴醚”和“球醚”,并由此提出了“超分子”的概念。三人于1987年获得了诺贝尔化学奖,他们为“主-客体化学”

“超分子化学”奠定了基础(图4)^[4]。由于冠醚环的大小可调,氧、氮、硫等原子可与离子、分子等形成配位键,因而冠醚具有选择性叠合离子、分子的能力,在表面活性剂、离子载体、离子选择电极、相转移催化、分离化学等领域具有广泛应用,成为新兴学科的重要载体。

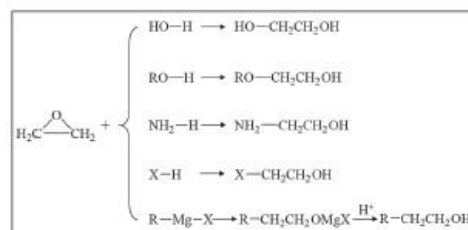


图3 环氧乙烷的化学性质

2.4.2 教学内容拓展

环醚的性质与其环的大小密切相关,在讲解环醚的性质时强调“结构决定性质”的化学思想,引导学生学会联想,利用已经学过的环烷烃进行类比,加强理解和掌握,学会从不同事物中找到自然的共性规律,培养辩证思维能力。冠醚主要结合科学前沿,让学生通过了解冠醚化学的发展历史,学习诺贝尔奖获得者孜孜不倦、勇于探索的精神,调动学生对科学研究的兴趣,培养学生不怕困难、探索创新的科学品质。

The Nobel Prize in Chemistry 1987

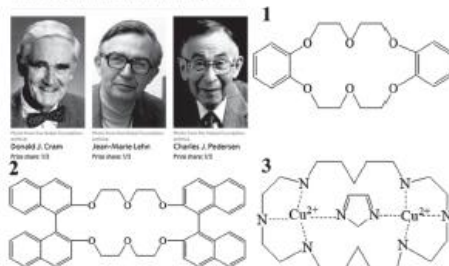


图4 由C. J. Pedersen, D. J. Cram和J. M. Lehn分别合成的大环多元醚(1)、联萘型冠醚(2)和双核络合物(3)

3 教学内容延伸

3.1 高效醚类清洁汽油

近些年来,作为替代能源,人们往往在汽油中掺入甲醇和乙醇。由于汽油对甲醇的含水容忍度为1%,对乙醇的含水容忍度为5%,对甲醇汽油和乙醇汽油的配制使用造成较大困难,阻碍了醇类汽油的发展。经过多年研究,2014年我国科学家将甲醇氧化成醚类物质二甲氧基甲烷(Dimethoxymethane),并将这种液态物质掺入汽油,从而混合出一种高效的醚类清洁汽油——二甲氧基甲烷汽油^[5]。

四川大学刘锦超教授和深圳市二烷能源有限公司的科研人员对掺入二甲氧基甲烷的汽油进行系统研究,并对掺入5%、15%、30%和50%四种比例的二甲氧基甲烷汽油进行了理化指标、发动机台架、行车指标以及耐久性指标测试。测试结果表明,这种新配方的醚类清洁汽油比乙醇汽油点燃速度更快、燃烧效率更高。与标准汽油比,加入二甲氧基甲烷的汽油减少了约70%一氧化碳和碳氢化合物的排放,减少了汽车尾气PM_{2.5}的排放。这是我国在能源领域取得的重要成果,体现了我国科学家勇于开拓、不断创新的精神品质,同时也展现了我国在环境保护和节约能源事业中的担当和作为。在授课过程中,为学生介绍我国在二甲氧基甲烷合成与应用领域的前沿成果(图5)^[6],以此激发学生勇攀科技高峰的勇气和斗志。

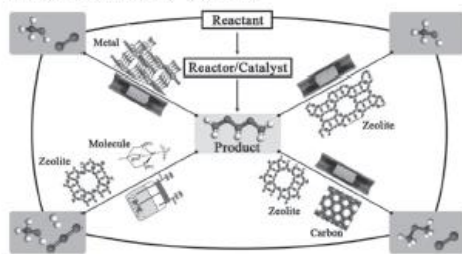


图5 DMF合成路线的反应器及催化剂

3.2 聚苯硫醚在航空航天的重要作用

聚苯硫醚全称聚苯基硫醚(PPS),硫醚是醚键中的氧原子被硫原子替代的醚类有机物,聚苯硫醚是多个由一个苯环与一个硫原子单键相连的基本单元聚合形成的结晶性聚合物,它具有优良的耐高温、耐腐蚀、耐辐射、阻燃、均衡的物理机械性能、极好的尺寸稳定性以及优良的电性能等特点,是一种综合性能优异的特种工程塑料,具有广泛应用价值。众所周知,航空航天材料的工作环境极为苛刻,要面对真空、辐射、温度、压强、电磁波等因素影响,这些因素要求使用材料必须非常可靠且稳定,聚苯硫醚多种多样的优异特性使其在航空航天领域发挥重要作用。PPS优异的耐温、耐辐射、耐电弧径迹以及电绝缘性能使其可以用来保护航空发动机免受太空环境的干扰;PPS优良的阻燃性、耐老化性能使其可用于航空器显示面板中;PPS耐辐射、耐高频电磁波辐照、良好的耐紫外性能可作为战斗机雷达的整流罩材料等。航空航天事业的发展对于一个国家来说至关重要,落后就要挨打,航空航天事业的强大才能保障国家和人民的安全。我国航空航天事业的发展需要大批艰苦奋斗、勇于创新的高素质人才。通过这一案例,可以激励学生树立为中华民族伟大复兴而奋斗的远大理想,并为之不懈努力。

4 教学反馈与总结

教学反馈是教学效果的重要检验,教师根据教学反馈可及时了解学生对知识的掌握情况,从而对教学方法做出调整和改进。完成课程知识讲授后,通过课堂讨论、随堂练习以及创新训练三种形式进行教学反馈。①课堂讨论以分组讨论形式展开,围绕课程知识重点展开。②随堂练习在MOOC上进行,河南农业大学有机化学课程在中国大学MOOC上与线下课程同步开课,学生可以通过MOOC进行巩固学习,加强对知识的掌握。③创新训练设置探究课题,如“结合农业领域需求,探索醚类化合物在农药合成或材料开发中的应用”,让学生自主探索,提交报告。线下讨论、线上练习以及创新作业不仅为教师提供及时教学反馈,使其了解学生的学习情况,还培养学生自主思考能力、创新意识和跨学科整合能力。

课程总结通过知识图谱梳理核心内容,教师组织学生撰写反思报告,总结学习收获并提出课程改进建议。结合教学数据(如成绩分布、项目成果等),形成教学改革效果评估报告,为后续课程优化提供依据。

5 结语

以醚为例的有机化学教学改革,通过整合理论教学、内容拓展、教学反馈,有效提升了学生的科学素养与综合能力。同时专业知识与课程思政资源的有效融合使教学内容更加鲜活生动。未来教学团队将进一步深化校企合作,引入真实产业案例;加强信息化手段应用,开发虚拟仿真实验平台;完善评价机制,形成“教—学—评”良性循环,为农业院校化学课程改革提供可推广的经验。

*通信作者:魏民、姜松

★基金项目:河南省高等学校青年骨干教师培养计划(2021GGJS029);河南农业大学2025年本科教育教学改革研究与实践项目(2025XJGLX089)。

参考文献

- [1] 夏百根,黄乾明,徐翠莲.有机化学[M].3版.北京:中国农业出版社,2013:128-132.
- [2] 段戴平,曾会应.有机化学“课程思政”教学设计案例研究——以生物碱为例[J].大学化学,2021,36(3):169-175.
- [3] Pedersen C J. The discovery of crown ethers[J]. Science, 1988, 241(4865): 536-540.
- [4] 刘刚.冠醚化学的发现及发展[J].怀化师专学报,1990,9(2):115-121.
- [5] 我国研制出高效醚类清洁汽油——二甲氧基甲烷汽油[EB/OL]. (2014-01-15). https://www.gov.cn/jrzq/2014-01/15/content_2567700.htm.
- [6] Ren J, Xin F, Xu Y. A review on direct synthesis of dimethoxymethane[J]. Chinese Journal of Chemical Engineering, 2022, 50(10): 43-55.

6. 乙二胺修饰的吸附树脂合成及其对水中苯酚的吸附性能研究. 湖北大学学报(自然科学版), 2023, 45(3), 460-466.

第 45 卷第 3 期
2023 年 5 月

湖北大学学报(自然科学版)
Journal of Hubei University(Natural Science)

Vol. 45 No. 3
May 2023

文章编号:1000-2375(2023)03-0460-07

乙二胺修饰的吸附树脂合成及其对水中苯酚的 吸附性能研究

金秋,王霄鹏,安万凯,姜松,宋美荣,方佳乐

(河南农业大学理学院,河南 郑州 450002)

摘要:以二乙烯基苯及丙烯酸甲酯悬浮聚合得到弱极性吸附树脂 JL-1;利用树脂上残余的双键及氯甲基进行付-克反应,得到比表面积更大同时含有氯甲基的树脂 JL-2.利用树脂上残留的氯甲基和乙二胺反应,制得乙二胺修饰的碱性吸附树脂 JL-3.树脂 JL-1、JL-2 和 JL-3 树脂内部孔径分布均以中孔为主.以树脂 XAD-4 为参考对象,研究了树脂对水溶液中苯酚的吸附和脱附性能,研究表明,树脂 JL-1($321.85 \text{ m}^2/\text{g}$),树脂 JL-2($397.8 \text{ m}^2/\text{g}$)和 JL-3($313.58 \text{ m}^2/\text{g}$)对水溶液中苯酚的吸附性能均优于 XAD-4($880.0 \text{ m}^2/\text{g}$).树脂对苯酚的静态吸附动力学更符合准二级吸附动力学方程,树脂 JL-1、JL-2 和 JL-3 可以有效吸附水溶液中的苯酚.

关键词:吸附剂;聚合物;吸附;苯酚

中图分类号:0647.3 **文献标志码:**A **DOI:**10.3969/j.issn.1000-2375.2023.00.015

著录信息:金秋,王霄鹏,安万凯,等. 乙二胺修饰的吸附树脂合成及其对水中苯酚的吸附性能研究[J]. 湖北大学学报(自然科学版), 2023, 45(3): 460-466. DOI: 10.3969/j.issn.1000-2375.2023.00.015.

JIN Q, WANG X P, AN W K, et al. Ethylenediamine modified hypercrosslinked resins and their properties on removal of phenol from aqueous solution [J]. Journal of Hubei University(Natural Science), 2023, 45(3): 460-466. DOI: 10.3969/j.issn.1000-2375.2023.00.015.

Ethylenediamine modified hypercrosslinked resins and their properties on removal of phenol from aqueous solution

JIN Qiu, WANG Xiaopeng, AN Wankai, JIANG Song, SONG Meirong, FANG Jiale
(College of Science, Henan Agricultural University, Zhengzhou 450002, China)

Abstract: A weak polar resin JL-1 was synthesized from divinylbenzene (DVB) and methylacrylate (MA) through suspension polymerization. After that, resin JL-2 with larger specific surface area and chloromethyl was synthesized through Friedel-Crafts reaction using chloromethyl ether and the residual chloromethyl on resin JL-1. Then, the ethylenediamine modified hypercrosslinked resin JL-3 was prepared using chloromethyl on resin JL-2 with ethylenediamine. The structure and characterization of resin JL-1, JL-2 and JL-3 indicated that, mesopores was the predominant pore in resin JL-1, JL-2 and JL-3. The adsorptive properties of the resins toward phenol was studied, and resin XAD-4 was employed as reference, the adsorption experiments showed that, resin JL-1 ($321.85 \text{ m}^2/\text{g}$), JL-2 ($397.79 \text{ m}^2/\text{g}$) and JL-3 ($313.58 \text{ m}^2/\text{g}$) had larger adsorption capacity toward phenol than XAD-4 ($880.00 \text{ m}^2/\text{g}$). The results indicate that, the pseudo-second-order rate equation fit the data of the kinetic well, resin JL-1, JL-2 and JL-3 are efficient adsorbent for removal of phenol from aqueous solutions.

Key words: adsorbents; polymers; adsorption; phenol

收稿日期:2022-05-26

基金项目:国家自然科学基金(21702049)资助

作者简介:金秋(1975-),女,博士,副教授,研究方向为反应性及有机功能性高分子,E-mail: jinqiukl@henau.edu.cn

0 引言

超高交联吸附树脂具有较大的比表面积,较好的溶胀性能,内部孔结构以微孔为主,再生效果好等优点。目前,在氢气储存、天然产物提取及污水处理等领域得到广泛应用^[1-4],尤其是从污水中吸附有机芳香小分子污染物应用最为广泛^[3]。超高交联吸附树脂的合成方法很多,最常见的是后交联法,该法先对树脂进行溶胀,然后采用氯甲醚或二氯甲基苯等交联剂对树脂进行后交联,得到比表面更大的超高交联吸附树脂,该法的缺点是得到的树脂亲水性和极性较差^[5]。研究表明,极性吸附树脂对污水中的极性有机小分子具有更好的吸附效果^[6-12]。

本研究以二乙烯基苯、丙烯酸甲酯为原料,过氧化二苯甲酰为引发剂,正庚烷为致孔剂,通过悬浮聚合一步合成出带有弱极性酯基的吸附树脂 JL-1^[13]。然后利用氯甲醚为氯甲基化试剂,无水 FeCl_3 作为催化剂发生付-克烷基化反应,得到超高交联吸附树脂 JL-2。树脂 JL-2 的比表面积较树脂 JL-1 得到提高的同时,在树脂 JL-2 上引入部分氯甲基,氯甲基可以用来对树脂进行后修饰。研究表明,碱性物质修饰的吸附树脂对弱酸性吸附质有更好的吸附效果^[14-17]。利用树脂 JL-2 上残留的氯甲基和乙二胺反应,得到乙二胺修饰的碱性超高交联吸附树脂 JL-3。本研究用的吸附对象为常见的有机污染物苯酚,苯酚为一无色晶体,弱酸,有毒^[18],是一种重要的工业化工原料^[19]。以苯酚作为吸附对象,以大孔吸附树脂 XAD-4 为参照,系统地研究了几种树脂对苯酚的吸附性能。结果表明,在相同的吸附条件下,树脂 JL-1、JL-2 及 JL-3 的吸附性能均优于 XAD-4。因此,本研究所合成的吸附树脂有望在含酚废水治理中得到推广和应用。

1 实验部分

1.1 仪器和试剂 过氧化二苯甲酰、二乙烯基苯、丙烯酸甲酯、无水 FeCl_3 、1,2-二氯乙烷、乙二胺、盐酸及丙酮均为分析纯,氯甲醚为工业品(用前蒸馏)。

红外光谱仪 (FT-IR2000, 美国 Perkin-Elmer), 物理吸附仪 (NOVA2200e, 美国康塔), 紫外分光光度计 (UV-2401PC, 日本 SHIMADZU)。

1.2 结构表征 FT-IR 光谱表征:采用红外光谱仪 (FT-IR2000) 分别对树脂 JL-1、JL-2 及 JL-3 进行结构分析测试。扫描范围为 $3\ 500\sim 500\ \text{cm}^{-1}$ 。BET 分析测试:采用物理吸附仪 (NOVA2200e) 对树脂的比表面积及孔径进行测定。

1.3 吸附树脂 JL-1 的制备^[13] 在 250 mL 的三口烧瓶中加入蒸馏水 160 mL, 白明胶 1.6174 g, 氯化钠 8.0509 g, 甲苯 13 mL, 正庚烷 13 mL, 二乙烯基苯 25 mL, 丙烯酸甲酯 7.4 mL。适当搅拌后, 加入过氧化二苯甲酰 (BPO) 0.2607 g 作为引发剂, 调节搅拌器速度, 80 °C 恒温油浴加热 12 h。滤出树脂蒸馏水洗涤, 抽滤后, 无水乙醇索氏提取 10 h, 80 °C 真空干燥得白色球形树脂 JL-1。

1.4 树脂 JL-2 的合成 准确称取 10.0077 g 树脂 JL-1 于 250 mL 三口烧瓶中, 适量 1,2-二氯乙烷溶胀 12 h, 加入氯甲醚, 并加入 2.0107 g 无水 FeCl_3 作催化剂, 于温度 45 °C 左右恒温油浴反应 5 h, 升高温度至 75 °C 继续反应 5 h。加入质量分数 1% 盐酸溶液 50 mL, 75 °C 加热回流 4 h 后, 冷却, 水洗, 抽滤, 无水乙醇索氏提取 5 h, 80 °C 真空干燥得淡黄色球状树脂 JL-2。

1.5 乙二胺修饰的超高交联树脂 JL-3 的合成 准确称取 5.0006 g 树脂 JL-2 于 100 mL 三口烧瓶中, 加入适量乙二胺, 于 80 °C 温度条件下搅拌反应 20 h。反应结束后冷却至室温, 水洗, 抽滤, 无水乙醇索氏提取 5 h, 真空干燥得乙二胺修饰的超高交联吸附树脂 JL-3。反应示意图 (图 1) 如下:

1.6 几种树脂对苯酚的静态吸附性能研究 取浓度分别为 600、500、400、300、200 和 100 mg/L 的苯酚溶液 25.00 mL 于 100 mL 带塞锥形瓶中, 加入 0.1 g 树脂, 于温度为分别为 298 K, 308 K, 318 K 的恒温振荡箱中振荡 24 h, 等吸附平衡后, 用紫外可见分光光度计于波长 270 nm 处测溶液吸光度, 根据式 (1) 计算平衡吸附量 Q_e 。其中, Q_e 为树脂对苯酚的平衡吸附量, C_0 和 C_e 分别为苯酚的起始和平衡浓度 (mg/L)。

$$Q_e = (C_0 - C_e) V/W \quad (1)$$

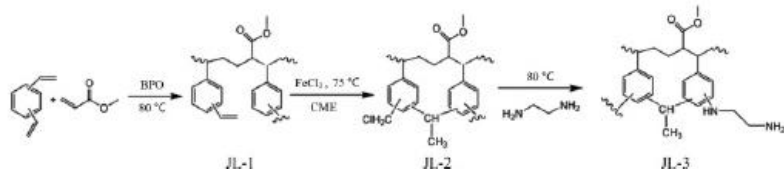


图1 树脂合成示意图

1.7 三种树脂对苯酚的静态吸附动力学研究 分别称取3种树脂0.5 g左右于50 mL锥形瓶中,加入50 mg/L的苯酚溶液,置于气浴恒温振荡器中,调节温度308 K恒温振荡,每过几分钟取样分析苯酚浓度,计算吸附量 Q 。

2 结果与讨论

2.1 树脂的物化特性 表1为几种树脂的比表面积和孔径等物理参数,树脂JL-1、JL-2、JL-3和XAD-4比表面积分别为321.85、397.79、313.55和880.00 $\text{m}^2 \cdot \text{g}^{-1}$,孔径分别为4.80、4.90、4.82及5.80 nm。树脂JL-2的比表面积比JL-1增大的原因是付-克烷基化后交联反应,交联后树脂比表面增大。

表1 树脂的物理参数

树脂	比表面积/($\text{m}^2 \cdot \text{g}^{-1}$)	平均孔径/nm	颜色
JL-1	321.85	4.80	白色
JL-2	397.79	4.90	浅棕
JL-3	313.55	4.82	浅棕
XAD-4	880.00	5.80	白色

2.2 树脂的孔径分布 从图2可以看出,3种树脂内部以中孔为主,孔径主要集中在4~5 nm和19 nm附近,其中树脂JL-1后交联以后,所得树脂JL-2在19 nm附近的中孔数量减少,这一点和后交联后树脂比表面积增大一致。

2.3 树脂的红外表征结果 从图3中可以看到3种树脂的红外光谱中1735 cm^{-1} 左右的振动峰,这是酯基的振动吸收峰^[20];树脂在反应过程中,弱极性的酯基始终存在,没有遭到破坏。而位于989 cm^{-1} 及902 cm^{-1} 处的吸收峰是悬挂双键的吸收峰,树脂JL-1发生交联反应以后所生成的树脂JL-2中这两个吸收峰明显削弱,说明部分悬挂双键在后交联过程中发生了交联反应。树脂JL-2的红外光谱中,位于1264 cm^{-1} 的吸收峰是树脂和氯甲基醚反应后树脂上连接的 $-\text{CH}_2\text{Cl}$ 的吸收峰,这说明,树脂JL-1和氯甲基醚反应后在树脂JL-2上引入了氯甲基。树脂JL-3在3445 cm^{-1} 的吸收峰明显强于树脂JL-1和JL-2,这是接到树脂JL-3上的乙二胺的氮氢键的吸收峰,说明乙二胺被成功地修饰到树脂上。

2.4 几种树脂对水溶液中苯酚的静态吸附研究结果分析 从图4上可以看出,在相同的温度和浓度条件下,树脂对苯酚的吸附能力从强到弱的顺序为JL-3>JL-2>JL-1>XAD-4。并且,吸附量均随着溶液浓度变大而升高。相同浓度条件下,温度为298 K时,JL-1、JL-2及JL-3 3种树脂对苯酚溶液的吸附量都是最大,而温度318 K时,3种树脂对苯酚溶液的吸附量都最小,这说明,树脂对苯酚的吸附过程均是放热的,低温更有利树脂吸附。树脂JL-1对苯酚的吸附性能优于同等条件下树脂XAD-4,树脂JL-1(321.85 $\text{m}^2 \cdot \text{g}^{-1}$)的比表面积却远小于树脂XAD-4(880.00 $\text{m}^2 \cdot \text{g}^{-1}$),树脂JL-1的平均孔径(4.80 nm)

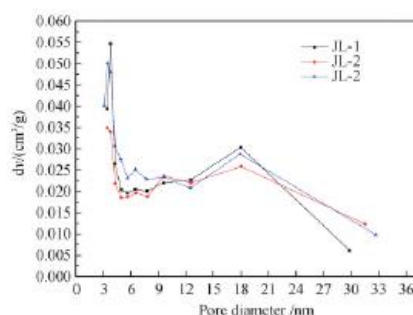


图2 树脂的孔径分布

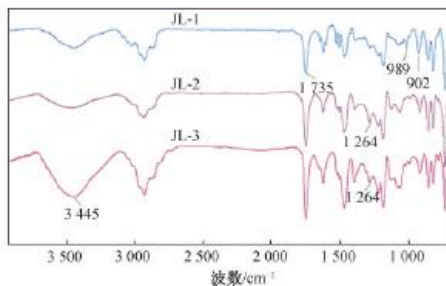


图3 吸附树脂 JL-1、JL-2 和 JL-3 的红外分析光谱图

也小于树脂 XAD-4 (5.80 nm), 在比表面积不占优势的前提下, 吸附性能优于 XAD-4 的主要原因可以归结为树脂 JL-1 的平均孔径较小, 这个在别的文献里也有报道, 微孔对吸附有利. 树脂 JL-2 的吸附性能优于同等条件下树脂 JL-1, 树脂 JL-2 的比表面积为 $397.79 \text{ m}^2 \cdot \text{g}^{-1}$, 大于树脂 JL-1 的比表面积 ($321.85 \text{ m}^2 \cdot \text{g}^{-1}$), 树脂 JL-1 和 JL-2 的平均孔径分别为 4.80 nm 和 4.90 nm, 区别不大. 树脂 JL-3 的吸附性能优于同等条件下树脂 JL-2, 但是, 树脂 JL-3 的比表面积 ($313.55 \text{ m}^2 \cdot \text{g}^{-1}$) 却小于树脂 JL-2 的比表面积 ($397.79 \text{ m}^2 \cdot \text{g}^{-1}$), 这说明, 经过化学修饰后, 树脂 JL-3 的弱碱性增强了树脂 JL-3 对苯酚的吸附性能.

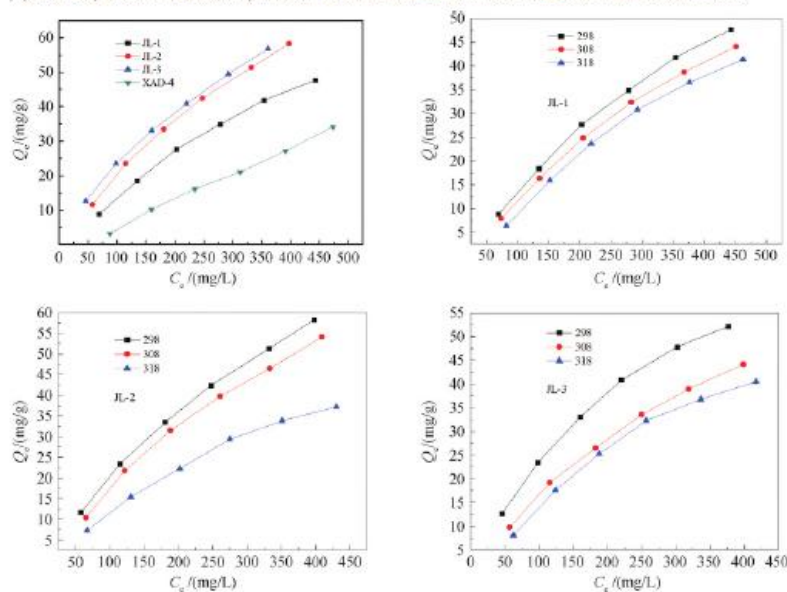


图4 几种树脂对苯酚的吸附等温线及对比图

由表2的相关数据可以看出, 树脂 JL-1、JL-2 和 JL-3 对溶液中苯酚的吸附都比较符合 Freundlich 方程. 且随着温度的升高, K_F 和 n 均变小, 则升高温度不利于树脂对苯酚的吸附. 3 种树脂对苯酚的吸附均属于多分子层吸附, 树脂对苯酚的吸附主要以物理吸附为主.

在吸附过程中, 通常, 树脂的比表面积越大吸附性能越好, 因为比表面积越大物理吸附作用越强. 本研究所合成的 3 种吸附树脂 JL-1、JL-2 和 JL-3 的比表面积分别为 $321.845 \text{ m}^2/\text{g}$ 、 $397.791 \text{ m}^2/\text{g}$ 和 $313.547 \text{ m}^2/\text{g}$. 树脂 XAD-4 的比表面积为 $880.00 \text{ m}^2/\text{g}$, 实验结果表明, 虽然比表面积相差很大, 在相同

表2 Freundlich 等温方程拟合相关参数

	Freundlich	T/K	K_F	n	R
JL-1	$\ln Q_e = 0.922\ 9\ C_e - 1.668\ 4$	298	0.188 6	1.083 5	0.985 7
	$\ln Q_e = 0.958\ 3\ C_e - 1.995\ 9$	308	0.135 9	1.043 5	0.991 0
	$\ln Q_e = 1.079\ 7\ C_e - 2.783\ 0$	318	0.061 9	0.926 2	0.978 2
JL-2	$\ln Q_e = 0.841\ 7\ C_e - 0.905\ 4$	298	0.404 4	1.188 1	0.989 8
	$\ln Q_e = 0.872\ 0\ C_e - 1.190\ 0$	308	0.304 3	1.146 8	0.982 9
	$\ln Q_e = 0.896\ 1\ C_e - 1.703\ 0$	318	0.182 2	1.115 9	0.976 8
JL-3	$\ln Q_e = 0.694\ 0\ C_e - 0.068\ 5$	298	0.933 8	1.440 9	0.986 4
	$\ln Q_e = 0.772\ 0\ C_e - 0.782\ 0$	308	0.457 5	1.295 3	0.988 3
	$\ln Q_e = 0.863\ 0\ C_e - 1.381\ 6$	318	0.251 2	1.158 7	0.962 3

的吸附条件下,本研究所合成的3种吸附树脂对苯酚的吸附能力均优于高比表面积的参照树脂 XAD-4.

原因归结为以下两点,首先,本研究所合成的树脂的平均孔径较小,JL-1、JL-2 和 JL-3 的平均孔径分别为 4.80 nm、4.90 nm 和 4.82 nm,而树脂 XAD-4 的平均孔径为 5.80 nm,树脂内部的微孔对吸附具有明显的促进作用.其次,树脂和吸附质的极性匹配对吸附也有影响.本研究所合成的吸附树脂上含有极性基团,这些极性基团的存在大大提高了树脂对苯酚的吸附性能.树脂 XAD-4 内部孔径较大,树脂表面没有极性基团,是非极性吸附树脂.

2.5 树脂对苯酚的吸附动力学研究结果分析

图5为几种树脂对水溶液中苯酚的静态吸

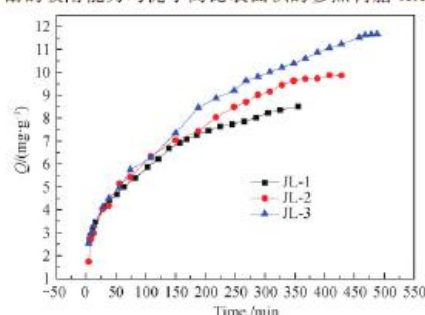


图5 树脂对水溶液中苯酚的静态吸附动力学曲线

附动力学曲线,从图中可以看出,3种树脂对苯酚的吸附均在6 h左右达到吸附平衡.对吸附过程的动力学曲线分别用准一级和准二级吸附动力学方程进行拟合,吸附动力学曲线可以用准一级(2)和准二级(3)吸附动力学方程进行拟合.

$$\ln(1 - F_t) = -K_{ad}t/2.303 \quad (2)$$

$$\ln(1 - F_t^2) = -Kt/2.303 \quad (3)$$

其中, $F_t = Q_t/Q_e$,代表任意时刻 t 的吸附分数, K_{ad} 和 K 分别为准一级和准二级吸附动力学参数.

由表3可知3种吸附树脂对苯酚的准二级吸附动力学方程拟合相关系数较好,这说明,3种吸附树脂对苯酚的吸附更符合准二级吸附动力学方程.苯酚在3种树脂内的扩散过程对苯酚的吸附速率起到很大的控制作用,微孔是树脂对苯酚吸附的主要区域;因此,树脂在合成过程中提高微孔体积可以有效增加树脂对苯酚的吸附力.

表3 树脂对苯酚的吸附动力学相关数据

Adsorbent	Parameters of pseudo-first-order equation			Parameters of pseudo-second-order equation		
	K_{ad}	Intercept	R	K	Intercept	R
JL-1	0.010 82	-0.147 4	0.969 9	0.006 45	-0.032 99	0.982 1
JL-2	0.008 11	-0.131 1	0.954 3	0.004 24	-0.028 45	0.963 7
JL-3	0.007 42	-0.101 3	0.970 7	0.003 41	-0.017 20	0.986 6

2.6 树脂 JL-1、JL-2 和 JL-3 对水溶液中苯酚的吸附热力学研究结果分析

图6中a、b和c分别为树脂 JL-1、JL-2 和 JL-3 对苯酚的吸附等量线.

表4为3种树脂对苯酚的吸附热力学参数,从表中可以看出,3种树脂对苯酚的吸附过程均是放热过程,以物理吸附为主.3种树脂对苯酚的吸附均为自发过程,吸附过程中的自由能变均小于零.3种树脂吸附过程熵变均为负值,这说明,吸附过程是熵减的,物理吸附是吸附的主要驱动力.

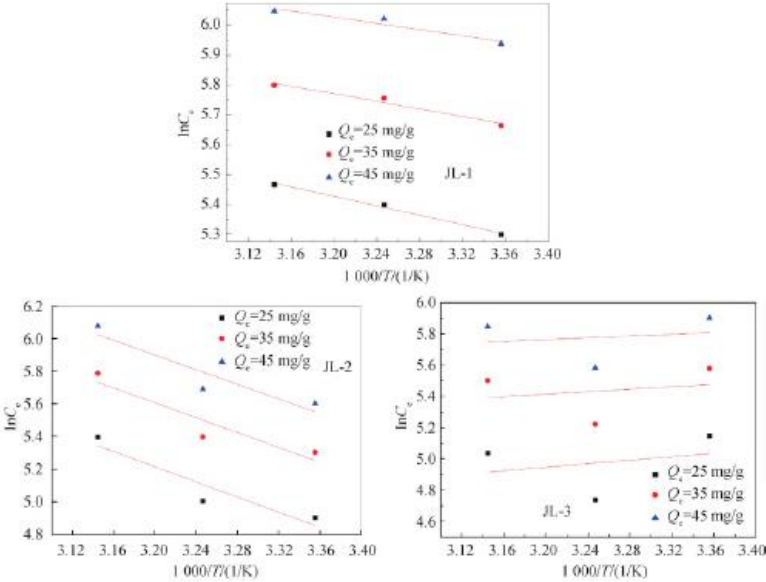


图 6 树脂吸附苯酚的吸附等量线

表 4 树脂对苯酚吸附过程中的热力学参数

树脂	$Q_e/(\text{mg}\cdot\text{g}^{-1})$	$\Delta H/(\text{kJ}/\text{mol})$	$\Delta G/(\text{kJ}/\text{mol})$			$\Delta S/(\text{J}/\text{K}\cdot\text{mol})$		
			298 K	308 K	318 K	298 K	308 K	318 K
JL-1	25	-10.38	-2.69	-2.67	-2.45	-25.83	-25.04	-24.95
	35	-8.32	-2.69	-2.67	-2.45	-18.92	-18.35	-18.47
	45	-6.76	-2.69	-2.67	-2.45	-13.66	-13.26	-13.54
JL-2	25	-23.23	-2.94	-2.94	-2.95	-68.07	-65.88	-82.31
	35	-22.26	-2.94	-2.94	-2.95	-64.84	-62.75	-60.74
	45	-21.55	-2.94	-2.94	-2.95	-62.44	-60.43	-58.49
JL-3	25	-23.52	-3.57	-3.32	-3.06	-66.96	-65.60	-64.34
	35	-19.78	-3.57	-3.32	-3.06	-54.40	-53.45	-52.57
	45	-16.98	-3.57	-3.32	-3.06	-45.02	-44.38	-43.78

3 结论

本研究采用悬浮聚合得到含有少量酯基的弱极性吸附树脂 JL-1;在催化剂作用下进行付-克反应,得到比表面积增大且含有氯甲基的吸附树脂 JL-2;用乙二胺和树脂上残留的氯甲基反应,制得吸附树脂 JL-3.对树脂的结构进行了表征.以 XAD-4 为参照,研究了 3 种树脂对苯酚的各种吸附性能.研究结果表明,3 种吸附树脂对苯酚的吸附性能优于比表面较大的吸附树脂 XAD-4.树脂内部的大量中微孔结构及树脂表面的极性基团是吸附能力强的主要原因.

4 参考文献

[1] CASTALDO R, AMBROGI V, AVOLIO R, et al. Functional hyper-crosslinked resins with tailored adsorption properties for environmental applications[J]. Chem Eng J, 2019, 362: 497-503.

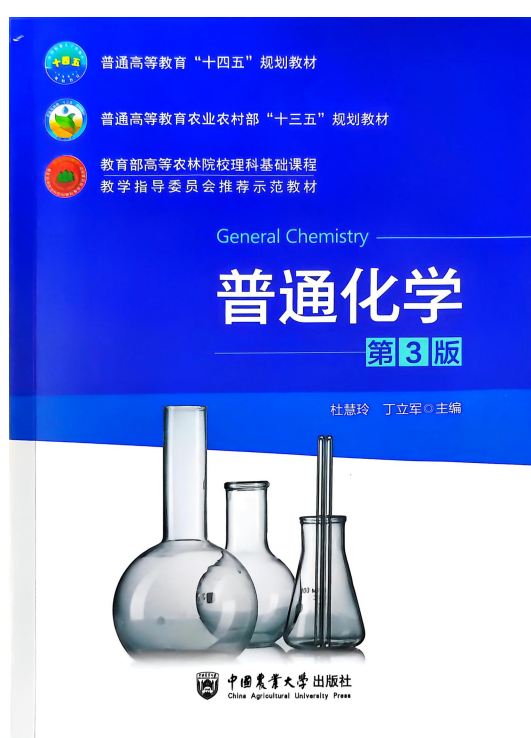
[2] XIAO G Q, WEN R M, WEI D M, et al. A novel hyper-cross-linked polymeric adsorbent with high microporous surface

- area and its adsorption to theophylline from aqueous solution[J]. *Microporous Mesoporous Mater.*, 2016, 228: 168-173.
- [3] KUANG W, LIU Y N, HUANG J H. Phenol-modified hyper-cross-linked resins with almost all micro/mesopores and their adsorption to aniline[J]. *J Colloid Interface Sci.*, 2017, 487: 31-37.
- [4] KUANG W, LI H B, HUANG J H, et al. Tunable porosity and polarity of the polar hyper-cross-linked resins and the enhanced adsorption toward phenol[J]. *Ind Eng Chem Res.*, 2016, 55(47): 12213-12221.
- [5] MA Y, ZHOU Q, LI A M, et al. Preparation of a novel magnetic microporous adsorbent and its adsorption behavior of p-nitrophenol and chlorotetracycline[J]. *J Hazard Mater.*, 2014, 266: 84-93.
- [6] 金秋, 赵林秀, 原思国, 等. 醚键型超高交联吸附树脂对苯胺和苯酚的吸附性能[J]. *高分子材料科学与工程*, 2013, 29(4): 74-78.
- [7] 王津南, 许丽, 李爱民, 等. 氨基修饰超高交联树脂对没食子酸的吸附性能[J]. *高等学校化学学报*, 2010, 31(1): 193-198.
- [8] 金秋, 杨国玉, 谢普会, 等. 超高交联吸附树脂的合成及其对水杨酸的吸附性能[J]. *化工进展*, 2015, 34(6): 1720-1724.
- [9] 金秋, 潘振良, 谢普会. 极性吸附树脂的合成及其对苯酚的吸附[J]. *湖北大学学报(自然科学版)*, 2015, 37(1): 21-24.
- [10] 金秋, 原思国, 安万凯. 含氧超高交联树脂的合成及其对苯酚的吸附性能[J]. *化工进展*, 2012, 31(3): 593-597.
- [11] WANG X M, YUAN X J, HAN S, et al. Aniline modified hypercrosslinked polystyrene resins and their adsorption equilibriums, kinetics and dynamics towards salicylic acid from aqueous solutions[J]. *Chem Eng J.*, 2013, 233: 124-131.
- [12] 周平, 王小梅, 赵晨曦. N-甲基乙酰胺基修饰的超高交联吸附树脂的合成与吸附性能[J]. *精细化工中间体*, 2013, 43(1): 55-58.
- [13] FU Z Y, HUANG J H. Polar hyper-cross-linked resin with abundant micropores/mesopores and its enhanced adsorption toward salicylic acid: equilibrium, kinetics, and dynamic operation[J]. *Fluid Phase Equilibria*, 2017, 438: 1-9.
- [14] HUANG J H, JIN X Y, DENG S G. Phenol adsorption on an N-methylacetamide-modified hypercrosslinked resin from aqueous solutions[J]. *Chem Eng J.*, 2012, 192: 192-200.
- [15] WANG X M, DAI K L, CHEN L M, et al. An ethylenediamine-modified hypercrosslinked polystyrene resin: synthesis, adsorption and separation properties[J]. *Chem Eng J.*, 2014, 242: 19-26.
- [16] 张根成, 费正皓, 刘福强, 等. 新型胺基修饰的超高交联聚合吸附剂吸附水中酚类化合物的研究[J]. *离子交换与吸附*, 2004, 20(3): 214-222.
- [17] 王瑞芳, 史作清, 施荣富, 等. 胺基化超高交联吸附树脂对苯酚和苯胺吸附行为的研究[J]. *高分子学报*, 2005(3): 339-344.
- [18] 王秀芳, 张会平, 肖新颜, 等. 苯酚在竹炭上的吸附平衡和动力学研究[J]. *功能材料*, 2005, 36(5): 746-749.
- [19] 施向荣, 丁洁莲, 赵浩, 等. 改性氧化铝微波诱导催化氧化处理高浓度苯酚废水的研究[J]. *环境工程学报*, 2011, 5(7): 1468-1472.
- [20] ZENG X W, YU T J, WANG P, et al. Preparation and characterization of polar polymeric adsorbents with high surface area for the removal of phenol from water[J]. *J Hazard Mater.*, 2010, 177(1/2/3): 773-780.

(责任编辑 胡小洋)

四、代表性著作

1. 普通高等教育“十四五”规划教材《普通化学》，副主编



第3版编委会

主 编 杜慧玲 丁立军
副 主 编 郭继虎 姜 松 刘青山 陈玉花 宋祖伟 陈媛梅
编写人员 (按姓氏拼音排序)
陈媛梅(北京林业大学)
陈玉花(内蒙古民族大学)
丁立军(内蒙古农业大学)
杜慧玲(山西农业大学)
郭 晨(东北农业大学)
郭继虎(山西农业大学)
海 波(内蒙古农业大学)
姜 松(河南农业大学)
梁爱琴(青岛农业大学)
刘青山(湖州师范学院)
宋祖伟(青岛农业大学)
张天宝(山西农业大学)
郑其格(沈阳农业大学)

内 容 简 介

本书是普通高等教育农业农村部“十三五”规划教材、教育部高等农林院校理科基础课程教学指导委员会示范教材和出版社普通高等教育“十四五”规划教材。全书包括 5 部分内容,物质的状态、物质结构基础、化学反应基本原理、水溶液中的化学反应及其一般规律和化学在我们身边。

本书在保持前两版的特色基础上,增加了学习导引、思政案例、习题答案等数字化资源,学习者通过扫描二维码就能浏览相应的内容。本书主要阅读对象为高等院校农林水、生物、医学等专业的本科生。

图书在版编目(CIP)数据

普通化学/杜慧玲,丁立军主编. —3 版. —北京:中国农业大学出版社,2023. 8
ISBN 978-7-5655-2992-4

I. ①普… II. ①杜…②丁… III. ①普通化学-高等学校-教材 IV. ①O6

中国国家版本馆 CIP 数据核字(2023)第 099461 号

书 名 普通化学 第 3 版

作 者 杜慧玲 丁立军 主编

策划编辑 梁爱荣

责任编辑 梁爱荣

封面设计 李尘工作室

出版发行 中国农业大学出版社

社 址 北京市海淀区圆明园西路 2 号

邮政编码 100193

电 话 发行部 010-62733489,1190

读者服务部 010-62732336

编辑部 010-62732617,2618

出 版 部 010-62733440

网 址 <http://www.caupress.cn>

E-mail cbsszs@cau.edu.cn

经 销 新华书店

印 刷 运河(唐山)印务有限公司

版 次 2023 年 7 月第 3 版 2023 年 7 月第 1 次印刷

规 格 185 mm×260 mm 16 开本 19.25 印张 460 千字

定 价 62.00 元

图书如有质量问题本社发行部负责调换

2. 大国三农系列规划教材《有机化学实验》，副主编



“大国三农”系列规划教材

有机化学实验 (第二版)

主 编 侯士聪 张振华
副主编 董燕红 边庆花 钟江春 姜 松 冯鞠花
参 编 肖玉梅 马晓东 张 威 马永强 刘 宽
万郑凯 李佳奇 黄家兴 林 燕 张云飞
吴燕华 郝向洪 花爱丽

中国出版传媒集团
高等教育出版社·北京

内容提要

本书是在第一版基础上,结合近年来的教学经验修订而成的。全书内容分层次模块化安排,按呈现顺序由基础到综合和设计依次包括:有机化学实验的基础知识、有机化学实验的基本操作、有机化合物的基本制备、综合与提高有机化学实验、设计及研究有机化学实验。本书选取的实验大多与科学研究、生产及生活相关,力图开展具有价值的实验学习实践。本书加强实验文献介绍,为学生检索和利用学科材料提供相关指导。

本书是有机化学实验课程教材,可作为高等农林院校应用化学、生命科学类、生态环境类专业本科生的教学用书,也可供相关专业人员参考使用。

图书在版编目(CIP)数据

有机化学实验 / 侯士聪, 张振华主编. -- 2 版.
北京: 高等教育出版社, 2025. 9. -- ISBN 978-7-04-
-065303-8
I. O62-33
中国国家版本馆 CIP 数据核字第 20258V4M31 号

Youji Huaxue Shiyao

策划编辑 郭新华	责任编辑 沈晓晴	封面设计 张 志	版式设计 杜微言
责任绘图 马天驰	责任校对 吕红颖	责任印制 高 峰	

出版发行 高等教育出版社	网 址 http://www.hep.edu.cn
社 址 北京市西城区德外大街 4 号	http://www.hep.com.cn
邮政编码 100120	网上订购 http://www.hepmall.com.cn
印 刷 廊坊十环印刷有限公司	http://www.hepmall.com
开 本 787mm×1092mm 1/16	http://www.hepmall.cn
印 张 12.25	版 次 2016 年 9 月第 1 版
字 数 310 千字	2025 年 9 月第 2 版
购书热线 010-58581118	印 次 2025 年 9 月第 1 次印刷
咨询电话 400-810-0598	定 价 33.00 元

本书如有缺页、倒页、脱页等质量问题,请到所购图书销售部门联系调换
版权所有 侵权必究
物 料 号 65303-00

3. 新形态一体化教材《有机化学实验》，副主编



有机化学实验

主 编 杨 芬
副主编 姜 松 刘品华 张鸭关

天津出版传媒集团
天津科学技术出版社

图书在版编目(CIP)数据

有机化学实验 / 杨芬主编. — 天津: 天津科学技术出版社, 2023.6

ISBN 978-7-5742-1240-4

I. ①有… II. ①杨… III. ①有机化学-化学实验-高等学校-教材 IV. ①O62-33

中国国家版本馆 CIP 数据核字(2023)第 095437 号

有机化学实验

YOUJI HUAXUE SHIYAN

责任编辑: 王 祯

出版: 天津出版传媒集团
天津科学技术出版社

地址: 天津市西康路 35 号

邮编: 300051

电话: (022) 23332400

网址: www.tjkjcs.com.cn

发行: 新华书店经销

印刷: 天津市蓟县宏图印务有限公司

开本 787×1092 1/16 印张 12 字数 258 000

2023 年 8 月第 1 版第 1 次印刷

定价: 49.80 元