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偕胺肟基COF材料对拜耳母液中钒镓的提取与分离

王樱璇[1,2]，张伟光[1,2]，张艺龄[1,2]，洪祖畅[1,2]，李义兵[1,2]，曹雪娇[1,2]，韦乾坤[3]，王岩[4]

(1. 桂林理工大学 材料科学与工程学院，广西 桂林 541004；
2. 桂林理工大学 有色金属及材料加工新技术教育部重点实验室，广西 桂林 541004；
3. 河池市科学技术情报研究所，广西 河池 547000；
4. 广西现代职业技术学院，广西 河池 547000)

摘要：针对拜耳母液强碱性、高铝干扰、钒镓浓度低导致传统回收技术低效的难题，本研究制备了耐强碱、高选择性的偕胺肟功能化聚芳醚型共价有机框架吸附材料(COF-HT-AO)，探究其吸附性能、稳定性、实际应用潜力及作用机理。以六羟基三亚苯和四氟对苯二甲腈为单体，经溶剂热法合成COF-HT基体，后修饰转化氰基为偕胺肟活性位点得到目标材料。结构表征显示，其结晶度高、孔道有序，热稳定性及强碱环境下结构稳定性优异，活性位点分布均匀。批量吸附试验表明，材料对镓、钒吸附符合Langmuir等温模型与准二级动力学模型，饱和吸附量分别达到244.20与127.87 mg/g，高铝干扰下选择性优良，5次循环后吸附容量保留率分别为89.3%与84.1%。机理研究表明，偕胺肟基团通过配位键、氢键及静电作用吸附钒镓阴离子，孔道尺寸筛分抑制铝干扰，DFT计算证实吸附强度$Ga(OH)_4^-$>VO_4^{3-}>$Al(OH)_4^-$。该材料为钒镓高效回收提供可行方案，具有重要理论与应用价值。

关键词：共价有机框架；偕胺肟基；拜耳母液；钒；镓；吸附

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钒(V)和镓(Ga)是战略性稀散金属，极少形成独立矿床，主要伴生于铝土矿、钒钛磁铁矿等大宗矿产，已被列入我国战略性关键矿产资源目录[1-2]。镓属于ⅢA族，是砷化镓(GaAs)、氮化镓(GaN)等第三代半导体的核心原料，广泛应用于5G芯片、光电子器件、新能源及国防军工领域，市场需求持续增长[3-5]。钒为VB族过渡元素，约85%用于钢铁强化，同时在钒氧化还原液流电池等大规模储能方向快速增长，战略地位突出[6-10]。两者资源供给的安全直接关系到高端制造与新能源产业链的可持续发展[11]。

工业上，超过90%的原生镓来源于氧化铝拜耳法种分母液，钒同样在该体系中大量富集，使拜耳母液成为钒和镓协同回收的理想原料[12-14]。我国氧化铝产量居全球首位，拜耳母液中钒和镓随生产流程不断

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作者简介：王樱璇(2001—)，女，硕士研究生

通信作者：张伟光(1984—)，男，博士，副教授

韦乾坤(1996—)，男，本科，工程师

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累积,其浓度可分别达到0.1~0.6 g/L与0.1~0.4 g/L,具备大规模低成本回收的潜力[15-18]。从强碱性母液中协同提取钒、镓,不仅可实现稀散金属的高值化利用,还可消除其不断累积对氧化铝生产效率及产品质量造成的不利影响,实现资源、环境与经济效益的统一[19]。

现有钒、镓提取技术主要有碳酸化沉淀、汞齐电解、溶剂萃取与离子交换等,普遍面临选择性差、回收率低、酸碱药剂消耗大、环境风险高以及与氧化铝主流程兼容性不足等问题[20-25]。吸附法可直接在强碱体系中操作,无需酸化预处理,不破坏母液原有组成,符合绿色低碳原则,且工艺简洁、成本较低,被认为是最具工业化前景的技术路线[26]。然而,传统吸附材料普遍存在耐碱性不足、吸附容量低、抗铝干扰能力弱等缺陷,难以适应强碱、高铝的极端工况,亟需发展兼具高稳定性与高选择性的新型吸附材料。

共价有机框架(COFs)是一类结晶性多孔有机聚合物,具有长程有序孔道、高比表面积、可设计的结构及可调的化学稳定性[27-29]。以芳基醚键连接的聚芳醚型COFs,在强碱和高温条件下骨架保持稳定,尤其适用于拜耳母液苛刻环境[30-32]。偕胺肟基团含有N、O双配位原子,对钒、镓含氧阴离子表现出特异性配位能力,其选择性与吸附性能显著优于常规功能基团[33-35]。尽管功能化COFs已初步展现金属离子吸附优势,但在强碱体系中实现钒、镓协同吸附的研究仍十分有限[36]。

本研究以六羟基三亚苯与四氟对苯二甲腈为单体,通过溶剂热法制备聚芳醚型COF前驱体,后修饰引入偕胺肟基团,获得COF-HT-AO。系统考察其吸附性能、循环稳定性及实际应用潜力,结合密度泛函理论(DFT)揭示选择性吸附机理,为拜耳母液中钒、镓的高效绿色回收提供新材料与技术途径。

1 试验部分

1.1 试验材料

本试验所采用的所有试剂均为分析纯,去离子水由水净化系统制备。研究所用的真实拜耳种分母液来自中国铝业广西分公司,各元素浓度为(g/L):V 0.125、Ga 0.212、Al 0.221、Na 0.134、Si 0.560、Ca 0.098。本研究在配置模拟体系时,将铝、钠的浓度下调至与目标金属组分同一数量级,以实现对吸附剂选择性吸附性能的准确评价。

1.2 试验设计

本研究围绕COF-HT与COF-HT-AO的吸附性能、动力学规律、循环稳定性及选择性展开系统测试,所有试验均在298 K恒温条件下进行,平行样与空白对照同步设置,以保证数据可靠性。

等温吸附试验用于探究金属离子初始浓度对吸附性能的影响,获取饱和吸附容量并解析热力学行为。试验在pH>14的强碱性模拟体系中进行,分别配制不同初始浓度的Ga(Ⅲ)与V(Ⅴ)单组分溶液。准确称取2 mg吸附剂加入10 mL模拟液,恒温振荡12 h至吸附平衡。经0.22 μm滤膜固液分离后,采用ICP-OES测定上清液中金属离子平衡浓度,依据浓度变化计算平衡吸附容量。采用Langmuir与Freundlich模型对数据进行非线性拟合,以决定系数R^2评价模型适配性,揭示吸附热力学特征。

吸附动力学试验分别在模拟拜耳母液与真实工业拜耳母液中开展,用于分析吸附速率与控速机制。配制固定浓度的Ga(Ⅲ)、V(Ⅴ)混合模拟液,调节至强碱性;称取100 mg吸附剂,加入50 mL溶液,恒温振荡,并在设定时间点取样,经滤膜过滤与硝酸稀释后,用ICP-OES测定离子浓度,计算不同时刻吸附容量。采用准一级、准二级动力学模型拟合数据,对比模拟体系与真实母液中的吸附行为差异。

解吸与循环稳定性试验以1.5 mol/L盐酸为解吸剂,评估材料再生能力。吸附平衡后抽滤回收吸附剂,经超纯水超声洗涤,在盐酸溶液中解吸,再洗涤至中性并真空干燥。连续开展5次吸附—解吸循环,通过ICP-OES测定浓度并计算吸附容量,以容量保留率评价再生性能与结构稳定性。

多离子竞争吸附试验用于评价材料在复杂体系中的选择性。配制含V、Ga、Al、Na、Si、Ca等组分的模拟液,在恒温条件下吸附至平衡,测定各离子平衡浓度并计算吸附容量、分配系数与选择性系数,系统分析材料对目标离子的识别能力与抗干扰性能。

1.3 测量与表征

本研究围绕偕胺肟功能化COF材料的合成、改性,以及强碱性体系中钒、镓的吸附性能展开系统研究,选取X射线粉末衍射(XRD)、傅里叶变换红外光谱(FT-IR)、场发射扫描电镜-能谱联用仪(FE-SEM-EDS)、热重-微分热重分析(TG/DTG)、电感耦合等离子体发射光谱(ICP-OES)为核心表征测试手段。上述方法可以从晶型结构、官能团组成、微观形貌、热稳定性、离子浓度定量分析等维度对材料进行全面表征,为验证材料合成有效性、评价结构稳定性及解析吸附性能提供直接试验依据。

2　结果与讨论

2.1　材料制备与结构表征

2.1.1　偕胺肟功能化COF-HT-AO的制备

COF-HT和COF-HT-AO的合成路径示意图如图1所示。以2,3,6,7,10,11-六羟基三亚苯(HHTP)与2,4,6-三(4-氟苯甲腈)-1,3,5-三嗪(TFTPN)为单体,经溶剂热法合成含氰基的COF-HT基体,再通过盐酸羟胺原位偕胺肟化反应制备COF-HT-AO,改性过程温和且不破坏骨架结构。

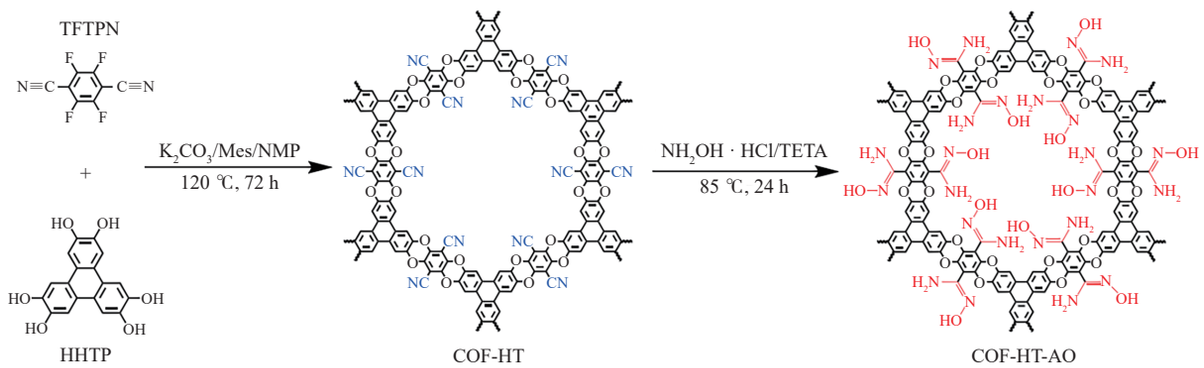


图1　COF-HT和COF-HT-AO的合成路径示意图

Fig. 1　Schematic synthesis route of COF-HT and COF-HT-AO

2.1.2　COF-HT与COF-HT-AO的合成与表征

FT-IR结果(图2)显示,COF-HT在2 239 cm^{-1}处出现氰基特征峰,改性后该峰完全消失,同时,在1 648 cm^{-1}与1 421 cm^{-1}处出现偕胺肟基C═N与N—H特征峰,C—O—C骨架峰基本保留,证实偕胺肟基团成功接枝且共价骨架完整。

COF-HT的衍射图谱(图3(a))显示尖锐且高强度的特征峰,表明其具有优异的晶体有序度和骨架完整性。经偕胺肟化改性得到的COF-HT-AO(图3(b))衍射峰位置基本不变,但峰强有所降低、峰形明显宽化,说明偕胺肟化仅引入局部结构扰动,导致结晶度略微下降,而未破坏材料的基本晶型与长程有序性。

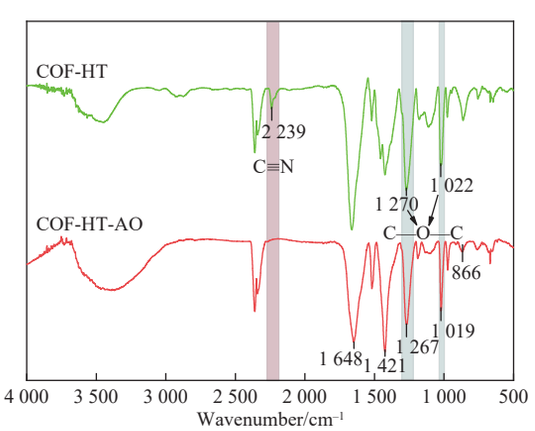


图2　COF-HT和COF-HT-AO的FT-IR光谱

Fig. 2　FT-IR spectra of COF-HT and COF-HT-AO

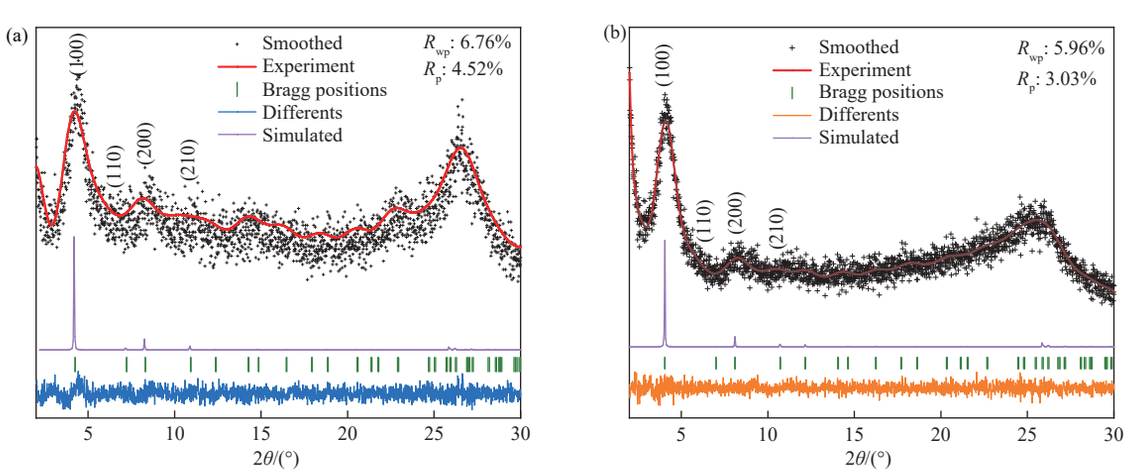


图3　COF-HT (a)和COF-HT-AO (b)的XRD谱图

Fig. 3　XRD patterns of COF-HT (a) and COF-HT-AO (b)

Different曲线表示试验衍射图谱与模拟衍射图谱之间的差异曲线(difference curve),该曲线通过逐点减去模拟图谱与试验图谱的强度值得到,用于直观评估模拟结构模型与试验数据之间的匹配程度。分析发现,模拟结构较好地拟合了试验数据,精修结果进一步证实,两种材料均保持规整的六方晶系结构,COF-HT-AO未发生晶相转变或骨架坍塌,精修因子处于合理范围,表现出良好的结构稳定性。

前驱体COF-HT(图4(a))呈现形貌规整、尺寸均一的微米级棒状形态,表面光滑,缺陷及团聚现象较少。偕胺肟化后,所得COF-HT-AO(图4(b))完全保留了原有棒状骨架、尺寸及三维堆积结构,未出现骨架坍塌、断裂或不可逆团聚等破坏,验证了该改性方法的可行性。与COF-HT相比,COF-HT-AO棒体表面粗糙度显著增大,且均匀覆盖纳米级凸起结构,表明偕胺肟官能团实现了均匀接枝。这种表面重构可提供大量高密度活性位点,有利于钒、镓离子的高效、特异性吸附。

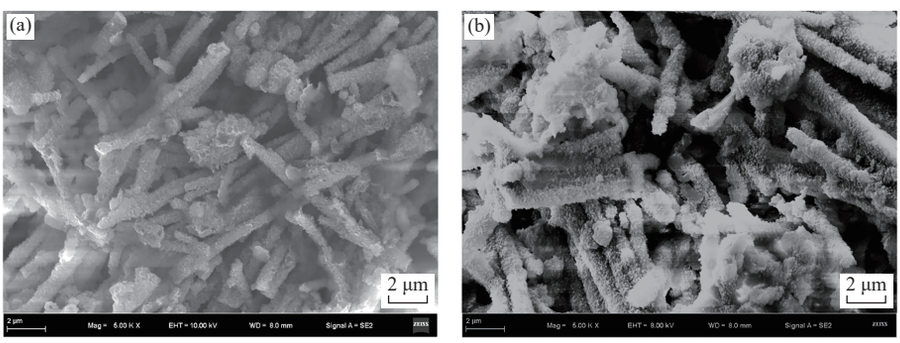


图4 COF-HT (a)和COF-HT-AO (b)的SEM形貌

Fig. 4 SEM morphologies of COF-HT (a) and COF-HT-AO (b)

两种材料的热失重曲线均呈现三个降解阶段。前驱体COF-HT在200 ℃前骨架保持稳定,满足常规吸附操作对耐热性的要求(图5(a))。经偕胺肟修饰后,COF-HT-AO各降解阶段整体向高温方向移动,热稳定性显著增强(图5(b))。低温段吸附水失重减少,中温段侧链基团起始分解温度明显升高,表明偕胺肟与骨架键合牢固;高温骨架热解区间同样移至更高温区,说明修饰增强了骨架交联程度。同时,高温下杂原子官能团释放气态产物的增加使残炭率轻微下降,进一步印证偕胺肟基团已成功接枝。热重分析确认了化学修饰的成功,COF-HT-AO在吸附操作温度窗口内结构稳定,可满足拜耳母液中钒和镓吸附回收的工程需求。

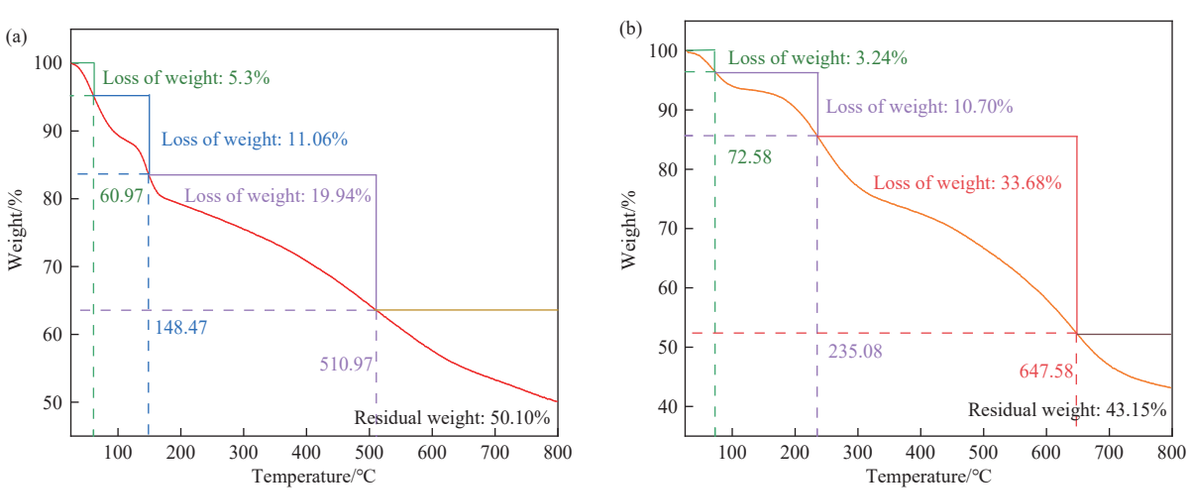


图5 COF-HT (a)和COF-HT-AO (b)的热重曲线

Fig. 5 Thermogravimetric curves of COF-HT (a) and COF-HT-AO (b)

2.2　吸附性能

2.2.1　COF材料对钒和镓的吸附研究

等温吸附结果表明，COF-HT与COF-HT-AO对Ga(Ⅲ)与V(Ⅴ)的吸附均符合Langmuir模型(R^2>0.98)，以单分子层化学吸附为主。COF-HT-AO对Ga、V的理论饱和吸附量分别达到244.20、127.87 mg/g，远高于COF-HT(45.56、22.58 mg/g)(表1)，说明偕胺肟官能团改性可显著提升吸附容量，且对镓离子选择性结合能力更强。为探究初始离子浓度对吸附的影响，在298 K下进行COF-HT与COF-HT-AO对镓、钒的单组分等温吸附试验，采用Langmuir、Freundlich模型拟合数据，结果如图6(a)和图6(b)所示。结果表明，两种材料对Ga、V的吸附数据更符合Langmuir模型，R^2均高于0.98，拟合效果优于Freundlich模型，证明吸附以单分子层吸附为主，作用位点集中在材料表面活性位点，离子间相互作用可忽略。由表1文献对比结果可知，COF-HT-AO对钒、镓的吸附性能优于多数同类材料，在碱性复杂体系中镓回收领域具备良好应用潜力。

表1　已报道的吸附材料对钒或镓的吸附容量

Table 1　The adsorption capacities of the reported adsorption materials for vanadium or gallium

吸附剂	吸附体系	T/℃	吸附时间/min	V吸附容量/(mg·g^{-1})	Ga吸附容量/(mg·g^{-1})	参考文献
偕胺肟聚丙烯腈-苯乙烯-二乙烯苯(A-PSD)吸附剂	拜耳母液	25	60	0.07	0.70	[37]
LSC-600型螯合树脂	低浓度含镓碱性溶液	30	4 320	—	8.64	[38]
HAOPAN NFs	拜耳母液	30	180	—	12.00	[37]
HAOPAN树脂	拜耳母液	25	60	8.09	25.97	[37]
大孔偕胺肟螯合树脂	氧化铝循环母液	25	120	20.16	27.59	[39]
PAO-rGO复合材料	碱性镓溶液	25	960	—	46.16	[40]
沸石-树脂磁性纳米复合材料	拜耳母液	45	100	13.1	—	[41]
纳米多孔聚甲基丙烯酸甲酯(PMMA)吸附剂	拜耳母液	25	596	13.7	—	[42]
LSC-600偕胺肟树脂	拜耳母液	25	300	20.1	—	[43]
LSC-700偕胺肟树脂	拜耳母液	25	180	22.6	—	[44]
Amberlite® IRA-400	钢渣浸出液	20	30	27.4	—	[45]
This work	拜耳母液	25	1 440	127.87	244.20	—

在298 K、混合离子体系下开展时间梯度吸附试验，并准一级、准二级动力学模型进行拟合分析，结果分别如图6(c)~(d)和图6(e)~(f)所示。拟合结果显示，准二级动力学模型相关系数R^2均大于0.99，拟合精度优于准一级模型，说明Ga、V在两种材料表面的吸附以化学吸附为主，受化学作用控速。动力学数据表明，改性后COF-HT-AO对Ga、V平衡吸附量显著提升，分别为前驱体的2.07、1.54倍，偕胺肟官能团不仅有效提高吸附容量，还明显增强对镓的选择性吸附。

2.2.2　COF-HT与COF-HT-AO的循环脱附性能

循环性能测试结果如图7显示，以1.5 mol/L盐酸为解吸液，COF-HT-AO经5次循环后Ga、V吸附容量保留率分别为89.3%、84.1%，循环稳定性优异；而COF-HT因物理吸附主导，解吸不彻底，导致孔道堵塞，第5次循环保留率仅分别为55.9%、48.6%。

2.2.3　多离子竞争吸附与选择性机制的研究

如图8所示，未经偕胺肟功能化修饰的COF-HT，对体系内所有离子的吸附容量均处于极低水平，吸附容量Q_e均低于3 mg/g，几乎不具备选择性吸附富集能力。相比之下，COF-HT-AO的吸附性能显著提升，其对所有被测离子的吸附容量均实现增长，在Ga(Ⅲ)、V(Ⅴ)的吸附表现上提升效果尤为明显。

多离子竞争吸附(图9)表明，COF-HT对各离子无选择性吸附，COF-HT-AO对Ga(Ⅲ)、V(Ⅴ)的分配系数(K)与相对选择性系数(α)远高于Si(Ⅳ)、Ca(Ⅱ)、Al(Ⅲ)、Na(Ⅰ)，在高浓度Al(Ⅲ)干扰下仍可高效分离Ga(Ⅲ)，偕胺肟基团为核心选择性位点。真实拜耳母液动力学验证，COF-HT-AO对Ga、V的吸附仍符合准二级动力学，以特异性化学配位为主，工业适配性良好。

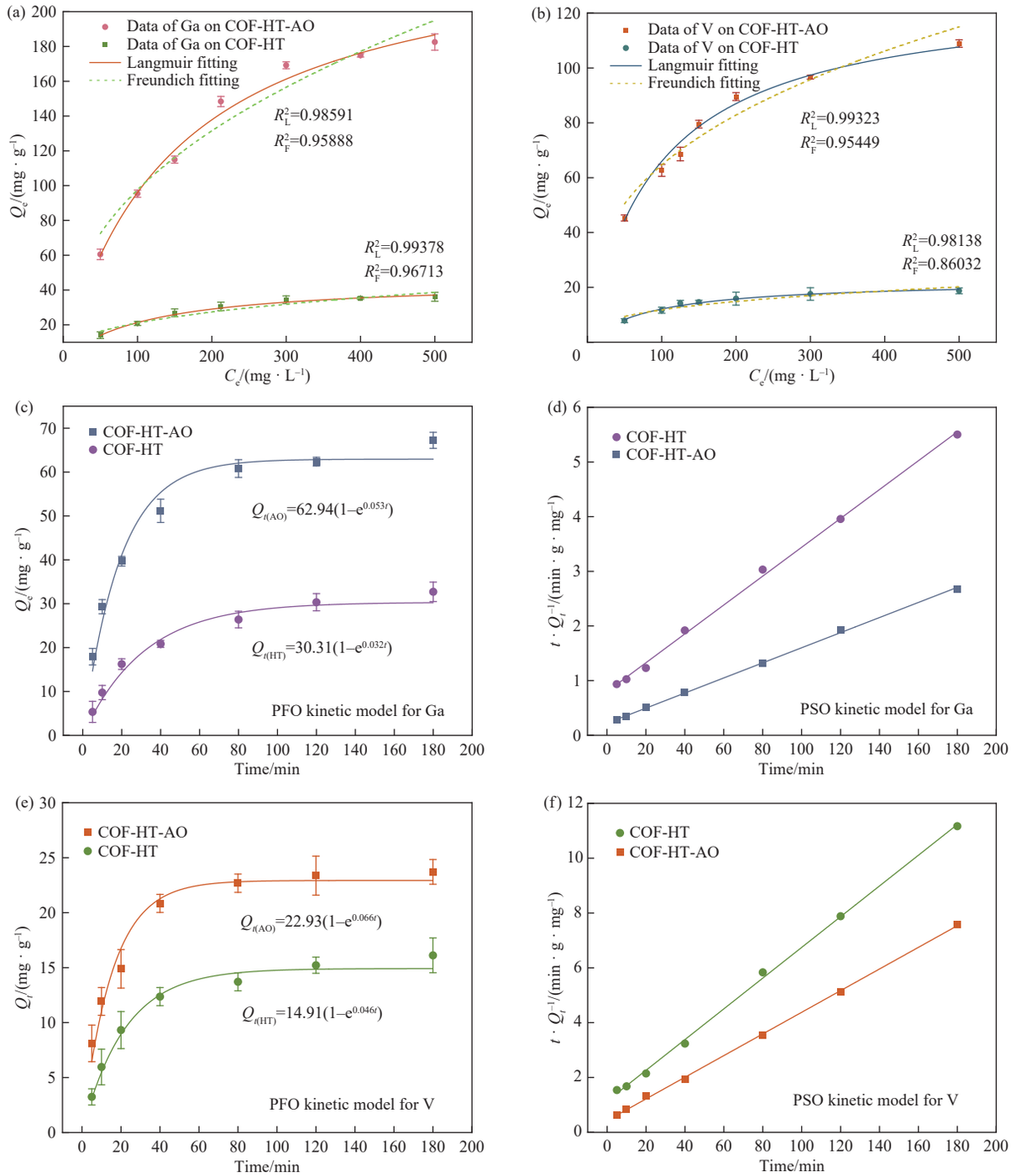


图 6　COF-HT 和 COF-HT-AO 在 298 K 条件下：对 (a) 镓和 (b) 钒的吸附等温线；COF-HT 和 COF-HT-AO 对 (c) Ga 吸附的准一级动力学拟合；(d) Ga 吸附的准二级动力学拟合；(e) V 吸附的准一级动力学拟合；(f) V 吸附的准二级动力学拟合

(试验条件：298 K，C_0(Ga)=212.1 mg/L，C_0(V)=125.2 mg/L，V=50 mL，m=100 mg)

Fig. 6　Adsorption isotherms of gallium (a) and vanadium (b) on COF-HT and COF-HT-AO at 298 K; Pseudo-first-order kinetic fittings for Ga (c) and V (e); Pseudo-second-order kinetic fittings for Ga (d) and V (f) on COF-HT and COF-HT-AO

(Experimental conditions: 298 K, C_0(Ga)=212.1 mg/L, C_0(V)=125.2 mg/L, V=50 mL, m=100 mg)

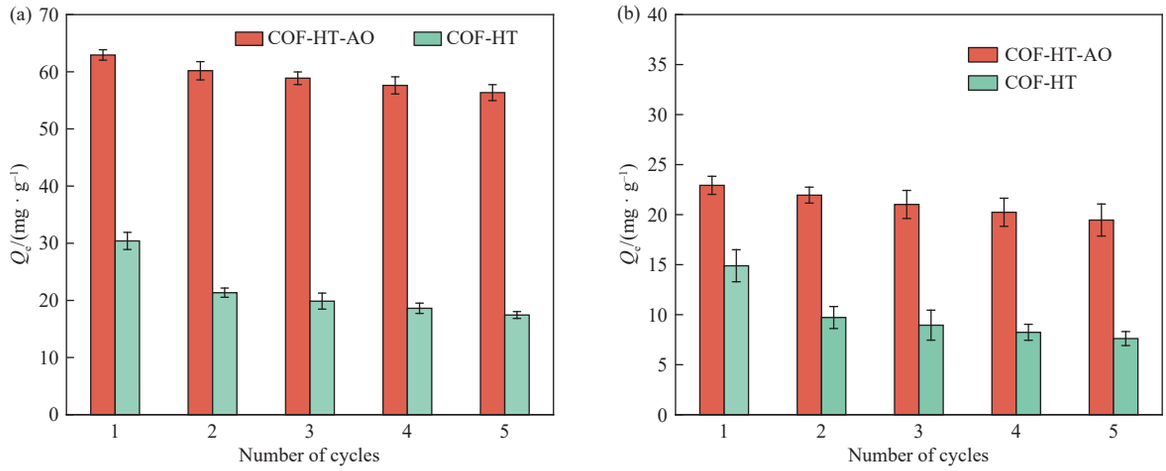


图 7　COF-HT 与 COF-HT-AO 对 Ga (a) 和 V (b) 的循环使用性能

Fig. 7　Cycling performances of COF-HT and COF-HT-AO on Ga (a) and V (b)

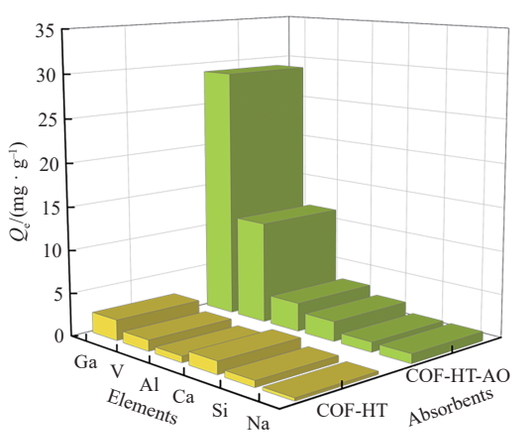


图 8　COF-HT 与 COF-HT-AO 对不同离子的平衡吸附容量对比

Fig. 8　Comparison of equilibrium adsorption capacities of COF-HT and COF-HT-AO for different ions

2.3　吸附机理与 DFT 理论计算

在 V-Ga-Al-H_2O 体系中，当 pH>13.5 时，钒以 VO_4^-、镓以 $Ga(OH)_4^{3-}$、铝以 $Al(OH)_4^-$ 为唯一优势物种，三者均为阴离子，为静电与配位驱动的吸附过程奠定了热力学基础。图 10 为 COF-HT 与 COF-HT-AO 负载钒、镓离子后的红外光谱图，将其与吸附前样品的红外谱图(图 2)对比分析可得：1 678 cm^{-1} 处的偕胺肟 C═N 伸缩振动峰发生显著高波数偏移，源于偕胺肟 N 原子与 V 离子发生双齿配位，C═N 键键级升高，证实 N 位点在吸附过程中参与配位结合；偕胺肟 N—OH 伸缩振动峰从 866 cm^{-1} 处向 879 cm^{-1} 处发生高波数偏移，证实镓离子与偕胺肟的氧活性位点形成单齿配位结构；1 429 cm^{-1} 处的 N—H 弯曲振动峰无明显变化，说明吸附仅发生在偕胺肟端基活性位点，

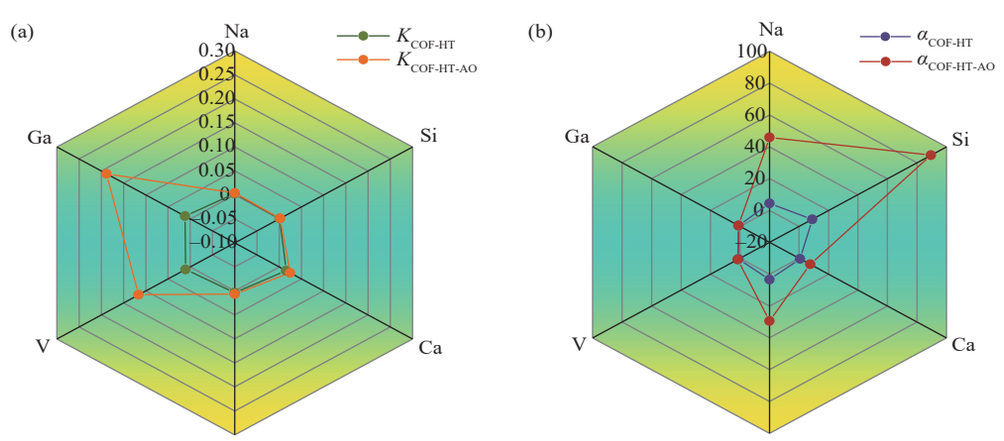


图 9　COF-HT 与 COF-HT-AO 对各离子的分配系数 (K) (a) 和对镓离子的相对选择性系数 (α) (b)

Fig. 9　Distribution coefficient (K) (a) of COF-HT and COF-HT-AO for each ion, and relative selectivity coefficient (α) for gallium ions (b)

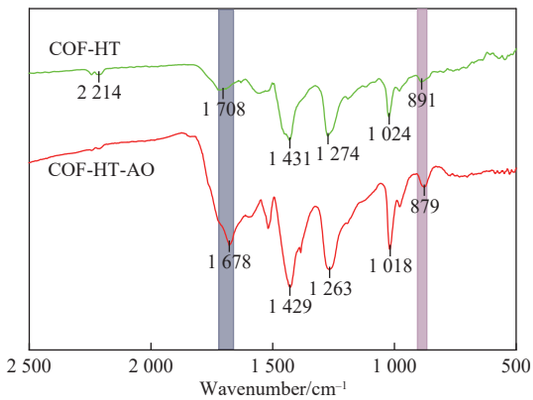


图10 吸附镓钒后的COF-HT与COF-HT-AO的FTIR光谱图

Fig. 10 FTIR spectra of COF-HT and COF-HT-AO after adsorption of Ga(Ⅲ) and V(Ⅴ)

未影响与骨架相连的官能团。红外光谱在分子水平上确认了COF-HT-AO在吸附过程中的结构稳定性，并阐明了钒和镓离子的化学配位吸附路径，为其优异吸附性能提供了直接光谱学依据。

对3种金属含氧酸根离子与COF-HT-AO复合物开展全结构优化，得到能量最低的稳定吸附构型。偕胺肟为该材料核心活性位点，其氮、氧原子带有孤对电子，可通过配位作用与氢键作用结合金属含氧酸根离子。

如图11(a)所示，$Ga(OH)_4^-$稳定结合于孔道内偕胺肟位点，Ga与肟氧作用距离为0.298 7 nm，形成稳定化学吸附。离子自身构型与COF骨架结构均无明显畸变，同时羟基与活性位点形成强氢键，加之空间匹配度高、接触充分，共同构筑强吸附结构。由图11(b)可知，VO_4^{3-}可形成稳定吸附构型，V与偕胺肟位点产生相互作用，作用距离0.326 1 nm，吸附强度居中。离子结构保持完整，但因负电荷较高存在静电排斥，吸附位置偏向孔道中心。材料骨架刚性稳定，离子与孔道尺寸适配，依靠配位作用实现中等强度吸附。如图11(c)所示，$Al(OH)_4^-$与偕胺肟位点作用距离达到0.373 3 nm，作用距离显著增大，相互作用以弱作用力为主。该离子远离活性中心，空间接触与重叠程度低，氢键作用极其微弱，结构结合松散，难以形成强化学吸附，整体吸附性能最弱。

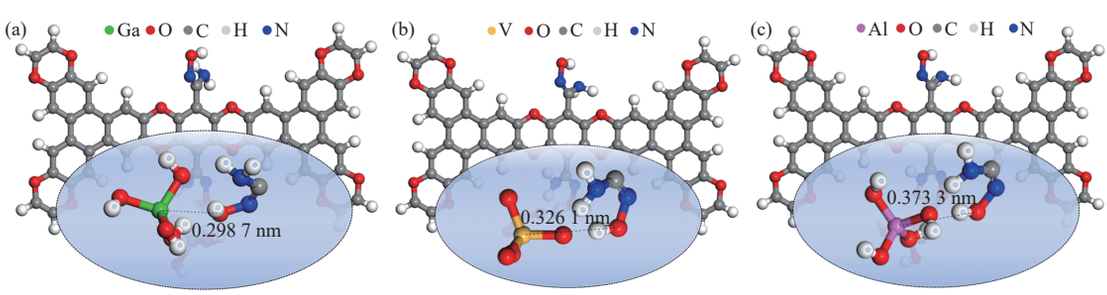


图11 最稳定吸附构型示意图：(a) $Ga(OH)_4^-$；(b) VO_4^{3-}；(c) $Al(OH)_4^-$

Fig. 11 Schematic diagrams of the most stable adsorption configuration of: (a) $Ga(OH)_4^-$; (b) VO_4^{3-}; (c) $Al(OH)_4^-$

差分电荷密度分析可从电子结构层面直观揭示离子与材料间的电子转移、轨道相互作用及成键特征，进而阐明吸附作用本质，并可横向对比不同体系间的电荷重分布程度与键合强度。如图12(a)所示，在$Ga(OH)_4^-$吸附体系中，偕胺肟基团原子周围呈现显著的电子耗尽区，而键合区域电子富集效应明显、电子云重叠程度高，表明存在大量电荷转移与强配位作用，辅以羟基间的弱相互作用，使该体系具有最强的电子效应与吸附稳定性。图12(b)显示，VO_4^{3-}体系表现出中等程度的电荷重分布，电子耗尽与富集区的强度和范围均弱于镓体系；尽管存在有效的电子转移与配位作用，但受静电排斥影响，其配位作用强度有所削弱，表现为中等吸附能力。由图12(c)可见，$Al(OH)_4^-$体系的差分电荷密度响应最弱，仅存在局域、微弱的电子富集区，电子转移量极小，未形成明显的配位键，仅依赖弱静电与微弱氢键作用相结合，因此整体吸附作用最弱。上述电子结构差异与吸附试验所得的亲和顺序高度一致。

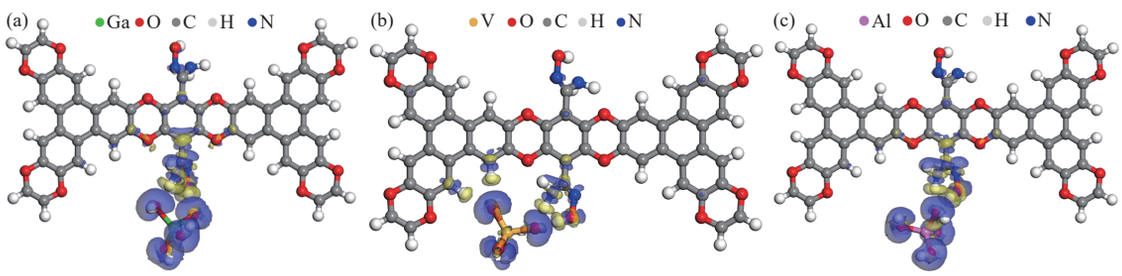


图 12　电子密度差分图：(a) $Ga(OH)_4^-$ 吸附体系；(b) VO_4^{3-} 吸附体系；(c) $Al(OH)_4^-$ 吸附体系

Fig. 12　Electron density difference maps of: (a) $Ga(OH)_4^-$ adsorption system; (b) VO_4^{3-} adsorption system; (c) $Al(OH)_4^-$ adsorption system

3　结论

本研究制备的COF-HT-AO解决了传统偕胺肟功能化COFs骨架易破坏、活性位点分布不均、强碱性稳定性差等问题。材料兼具高结晶度、高比表面积、高密度偕胺肟位点与优异结构稳定性，在强碱性拜耳母液中对Ga和V实现高容量、高选择性、高稳定性吸附。

DFT计算表明，对钒镓吸附能力的强弱为 $[Ga(OH)_4]^{-1}$(–482.66 kJ/mol)>VO_4^{3-}(–428.66 kJ/mol)>$[Al(OH)_4]^-$(–370.52 kJ/mol)。吸附机理研究说明，$[Ga(OH)_4]^-$ 以强配位键与多重氢键稳定结合；VO_4^{3-} 以静电与氢键作用为主；$[Al(OH)_4]^-$ 仅存在弱静电与极弱氢键，难以形成有效吸附。$[Ga(OH)_4]^-$ 与COF-HT-AO在粒径空间上最匹配且成键稳定，而 $[Al(OH)_4]^-$ 几乎无有效成键。偕胺肟基团以特异性配位为核心，协同静电吸引、氢键作用与空间匹配效应将钒镓协同吸附，从微观揭示了选择性差异的根本来源。

该材料在工业镓钒资源回收领域具备显著应用潜力，为强碱性复杂体系高效吸附剂的理性设计提供试验与理论支撑。后续研究可聚焦开发适配强碱性拜耳母液的成型方法，实现材料易分离与连续操作。研究成型后材料的吸附容量、位点活性及长周期碱稳定性，设计固定床或流化床动态吸附工艺，优化钒、镓分离与解吸条件。

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Extraction and Separation of Vanadium and Gallium from Bayer Mother Liquor by Amidoxime-based COF Materials

Wang Yingxuan[1,2], Zhang Weiguang[1,2], Zhang Yiling[1,2], Hong Zuchang[1,2],
Li Yibing[1,2], Cao Xuejiao[1,2], Wei Qiankun[3], Wang Yan[4]

(1. School of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, Guangxi, China;
2. Key Laboratory of Nonferrous Metals and Materials Processing New Technology, Guilin University of Technology, Guilin 541004, Guangxi, China;
3. Hechi Institute of Scientific and Technical Information, Hechi 547000, Guangxi, China;
4. Guangxi Modern Vocational and Technical College, Hechi 547000 Guangxi, China)

Abstract: Gallium and vanadium are strategic metals essential for advanced electronics, aerospace alloys, and energy technologies, yet their sustainable supply remains constrained. Bayer mother liquor, an extremely alkaline waste stream (NaOH>100 g/L) from alumina refining, contains low concentrations of gallium (Ga) and vanadium (V) but a high concentration of aluminum (up to 80 g/L), making their efficient recovery highly challenging. Conventional

methods such as solvent extraction and ion-exchange resins suffer from limited alkali stability, poor selectivity over aluminum, and insufficient enrichment capacity. Covalent organic frameworks (COFs), featuring tunable pore architectures and chemically robust backbones, offer an ideal platform for addressing these demands. Herein, we synthesize a durable amidoxime-functionalized polyarylether COF (COF-HT-AO) for the selective recovery of gallium and vanadium from highly alkaline Bayer mother liquor. The COF-HT precursor was constructed via a solvothermal condensation of 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene with tetrafluoroterephthalonitrile in a mesitylene/dioxane mixture at 120 ℃, forming a crystalline polyarylether network bearing pendent cyano groups. Subsequent amidoximation with hydroxylamine hydrochloride converted ~85% of the cyano groups into chelating amidoxime moieties, yielding COF-HT-AO. Comprehensive structural characterizations confirm high crystallinity and uniform pores with a diameter of ~1.8 nm. Thermogravimetric analysis demonstrates exceptional thermal stability up to 400 ℃. Crucially, after prolonged immersion in 3 mol/L NaOH solution, the material retains its PXRD pattern, porosity, and morphology, evidencing outstanding alkali resistance originating from the robust ether-linked framework. Elemental mapping further verifies the uniform distribution of amidoxime active sites. Batch adsorption experiments reveal that both gallium and vanadium uptake followed pseudo-second-order kinetics, indicative of chemisorption. The equilibrium data conforms well to the Langmuir isotherm model, giving maximum adsorption capacities of 244.20 mg/g for Ga and 127.87 mg/g for V. In highly competitive media containing excess aluminum (Al/Ga molar ratio up to 200), COF-HT-AO retains over 85% of its gallium adsorption capacity, demonstrating outstanding selectivity against aluminum interference. The adsorbent can be effectively regenerated with dilute hydrochloric acid, maintaining capacity retention rates of 89.3% for gallium and 84.1% for vanadium after five consecutive adsorption-desorption cycles. When applied to authentic Bayer mother liquor from an alumina refinery, removal efficiencies of 92% for Ga and 88% for V are achieved with negligible aluminum co-adsorption, validating its practical viability. Mechanistic insights were gained by integrating spectroscopic analyses and density functional theory (DFT) calculations. It is revealed that the amidoxime groups capture anionic $Ga(OH)_4$ and VO_4 through a synergistic combination of coordination bonds, hydrogen bonding, and electrostatic interactions. The uniformly sized pore channels play a critical size-sieving role: while monomeric aluminates similar in size to gallate may enter, kinetically prevalent larger polynuclear aluminum hydroxide species are physically excluded from the pores, thus significantly suppressing Al competition. DFT calculations further corroborate the experimental findings, yielding a binding energy order of $Ga(OH)_4^-$ (−3.82 eV)>VO_4^{3-} (−3.15 eV)>$Al(OH)_4^-$ (−2.47 eV). Electron density difference maps visualize marked charge accumulation between the adsorbent and Ga/V species, but considerably weaker interaction with aluminum. This work demonstrates that the rationally engineered COF-HT-AO, combining robust alkali-stable architecture, high uptake performance, excellent selectivity, and satisfactory reusability, provides an efficient and sustainable strategy for recovering critical gallium and vanadium from complex alkaline industrial streams, offering both fundamental insights and practical guidance for the design of ion-sieving COF adsorbents.

Key words: covalent organic framework; amidoxime; Bayer mother liquor; vanadium; gallium; adsorption

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First author: Wang Yingxuan; Tel: +86-15942262293; E-mail: 15942262293@163.com

Corresponding author: Zhang Weiguang; Tel: +86-0773-5896672; E-mail: zhangwg@glut.edu.cn

Wei Qiankun; Tel: +86-15717782832; E-mail: 756215185@qq.com