Review

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Recycling valuable materials from the spent lithium ion batteries to catalysts: methods, applications, and characterization

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Abstract

As the prevailing technology for energy storage, the extensive adoption of lithium-ion batteries (LIBs) inevitably results in the accumulation of numerous spent batteries at the end of their lifecycle. From the standpoints of environmental protection and resource sustainability, recycling emerges as an essential strategy to effectively manage end-of-life LIBs and reclaim valuable elements within them. Hydrometallurgy, closely intertwined with catalysis, stands as a relatively mature strategy for achieving high-value utilization of spent LIBs. In this review, our emphasis is placed on the interconnected themes of catalysis within the realm of hydrometallurgical recycling. Specifically, we delve into the crucial role that catalysis plays in both the recycling process of LIBs and the sustainable utilization of their extracted materials in various catalytic applications. This focused exploration aims to contribute insights into the intricate relationship between catalysis and the broader context of LIB recycling, shedding light on its pivotal role in achieving both environmental sustainability and functional material repurposing. Moreover, we highlight advanced characterization techniques, represented by surface-sensitive enhanced Raman spectroscopy, to fundamentally understand the reaction mechanism of catalysts, which, in turn, would inform more rational catalyst designs.

Keywords: Spent lithium-ion batteries, recycling, catalysis, characterization, *in situ* Raman spectroscopy

INTRODUCTION

Over the past two centuries, fossil energy has been instrumental in propelling the advancement of human civilization while providing essential support for economic and social development. However, as the finite and non-renewable nature of fossil energy becomes increasingly apparent, humanity has proactively pivoted towards exploring and exploiting renewable energy sources[1]. Concurrently, there has been notable progress in energy storage technologies, encompassing mechanical, electrochemical, and thermal storage methods, among others[2]. Electrochemical energy storage, exemplified by lithium-ion batteries (LIBs), stands out as a prominent focal point in the ongoing global energy transition[3]. LIBs have achieved successful industrialization and found widespread applications in diverse fields such as intelligent devices, electric vehicles, aerospace, and more. This popularity stems from their numerous advantages, including high voltage, substantial specific energy, commendable safety performance, rapid charge/discharge capabilities, and a broad operating temperature range.

The fundamental structure of a LIB is characterized by essential components involving the cathode, anode, current collector, separator, and electrolyte, each composed of a diverse array of chemical elements. However, in practical applications, these foundational elements are intricately integrated to create complex battery structures, encompassing various designs such as coin-type, cylindrical-type, prismatic-type, and more. This amalgamation ensures the stable charge/discharge performance of the battery across diverse usage scenarios and applications. Regardless of the configurations, LIBs have a limited lifespan from a practical point of view, necessitating disposal when their capacity diminishes to less than 80%[4]. In the upcoming years, a considerable number of actively used LIBs will face renewal, potentially triggering a crisis of battery resource waste. Importantly, the inadequate recycling of specific materials within LIBs poses a significant risk of water and soil pollution when these batteries are exposed to the natural environment[5]. In fact, LIBs house valuable elements such as Li, Ni, Co, and Mn, which are integral components of effective catalysts[6,7]. Ensuring the proper recycling and utilization of these materials becomes not only a means of mitigating environmental hazards but also a commitment to the principles of resource sustainability and economic benefit. Effectively managing the impending surge of spent LIBs is crucial for charting a course toward a more sustainable and environmentally conscious future[8,9].

The recycling stream of LIBs is typically segmented into three stages: upstream, midstream, and downstream. Batteries scrapped from electronic devices in the upstream stage undergo recycling and processing in the midstream, ultimately reintegrating into use in the downstream. A portion of spent batteries retaining high specific energy and relatively intact structures can be strategically repurposed through gradient utilization[10]. These batteries find applications in areas such as low-speed electric vehicles, large-scale energy storage equipment, communication base stations, and other sectors where stringent battery performance requirements are not critical. Conversely, batteries exhibiting a significant decline in specific energy and extensive structural damage necessitate recycling for their constituent materials. Crucially, the midstream and downstream stages are intricately linked to the "catalysis". The primary methods employed in midstream recycling encompass pyrometallurgy[11-13], hydrometallurgy[14-17], and direct recycling[18-23]. Direct recycling emerges as a non-destructive method that directly collects and rejuvenates active electrode materials for LIBs. This approach encompasses four distinct recovery techniques: solid-state, electrochemical, solution-based, and eutectic salt relithiation[24]. Among these approaches, eutectic salt recrystallization stands out for its effective recovery of spent battery materials, leveraging the self-saturation property. This makes it the more popular direct recovery method currently. By blending various salts to lower the eutectic point, this technique not only replenishes the anode with lithium but also rejuvenates the cathode. Despite its high efficiency and energy-saving attributes, direct recycling is currently confined to laboratory stages and has not yet been industrialized. The pyrometallurgy and hydrometallurgy constitute

comparatively straightforward procedures with high recovery efficiency, making them prevalent in the field of LIB recycling. Pyrometallurgy encompasses three main steps: roasting, smelting, and refining, involving high-temperature processing, which can result in significant energy consumption and potential air pollution[25]. Nevertheless, it continues to play a significant role in today's recycling of used batteries due to its straightforward nature. Furthermore, continuous improvements have been made in pyrometallurgical processes, with researchers prioritizing energy consumption reduction. Techniques such as microwave-assisted carbothermal reduction or salt-assisted reduction roasting in the roasting stage have been developed, enabling the reduction of high-valent metals to low-valent metals at lower reaction temperatures. This reduction not only facilitates easier leaching of metals but also enhances environmental friendliness. In contrast, hydrometallurgical process, employing low-temperature leaching and subsequent separation and purification, effectively extracts valuable metals from spent LIBs. This method has matured over time, and the integration of catalytic methods during the leaching process ensures a high leaching rate while maintaining an environmentally friendly and sustainable approach. On the other hand, the metal-rich leachate obtained through recovery can undergo further regeneration through diverse techniques to yield corresponding metal salts or metal oxides. These materials can act as precursors for synthesizing high-performance catalysts or be directly utilized as catalysts themselves. Their primary applications range from environmental pollution degradation, remediation of harmful substances in water bodies, electrocatalytic oxidation, *etc*. As a result, the hydrometallurgy, closely intertwined with catalysis, is currently a promising strategy for achieving high-value utilization of spent LIBs. Therefore, an in-depth review of existing catalytic methods within hydrometallurgical approaches for recycling spent LIBs, along with the subsequent application of recycled products in catalytic processes, is essential to establish a common knowledge framework in this research area.

In this review, we focus on the interconnected themes of catalysis within the realm of LIB recycling, especially the pivotal role catalysis plays in both the recycling processes of LIBs and the sustainable utilization of their extracted materials across various catalytic applications. First, several catalytic strategies for extracting metals from spent LIBs are presented. Subsequently, the recyclable components derived from cathodes and/or anodes, along with their applications in diverse catalytic fields, are systematically summarized. Moreover, advanced spectroscopic characterization techniques, exemplified by X-ray-based techniques and Raman spectroscopy, are underscored for their capability to enhance the fundamental understanding of catalyst structure and catalytic mechanisms. This focused exploration aims to provide valuable insights into the intricate relationship between catalysis and the broader context of LIB recycling, thereby illuminating its crucial role in achieving both environmental sustainability and the effective repurposing of functional materials. This delimitation distinguishes this review from existing articles that have broader scopes and are more comprehensive. For example, the readers can refer to ref.[26-30] for an overview of the current process for LIB recycling.

CATALYTIC STRATEGIES APPLIED IN RECYCLING OF LI-ION BATTERIES

For the recycling of spent LIBs, hydrometallurgy, primarily relying on leaching, emerges as a well-established technique. The leaching process involves the application of inorganic/organic acids and bases to dissolve metal oxides, followed by obtaining corresponding metal salts through stepwise precipitation. However, this process is often constrained by experimental conditions, such as pH, temperature, and leaching time. By catalyzing this reaction through external means, the energy consumption of the process can be minimized, facilitating a substantial improvement in leaching kinetics, metal leaching rates, and even selective leaching of metals. This catalytic intervention proves particularly effective under mild acidic and alkaline conditions, holding significant implications for promoting environmental sustainability. In this section, we highlight three recently developed catalysis-assisted strategies for enhancing the LIB recycling efficiency.

Photocatalysis-assisted recycling

Photocatalysis is a chemical reaction facilitated by light[31,32]. This photochemical process involves molecules absorbing specific wavelengths of electromagnetic radiation, inducing molecular excited states. Subsequently, a chemical reaction occurs, forming new substances or intermediate chemical products that can initiate thermal reactions. The activation energy for photochemical reactions is derived from the energy of photons. Ultraviolet (UV) light, characterized by its potent photon energy, serves as an effective photocatalyst, enhancing the overall efficiency of the reaction.

Lv *et al.* utilized UV-assisted leaching for recycling cathodes in spent LIBs, employing H_2O_2 widely used in hydrometallurgy as a reductant [Figure 1A][33]. Under UV irradiation, the excitation of unstable O–O and H–O bonds in H_2O_2 accelerates their decomposition into oxygen and hydrogen atoms. The rapid combination of O atoms to form O_2 enhances the reducibility of O in H_2O_2, thereby further facilitating the leaching of metals and increasing the leaching rate. By employing the UV-assisted recovery method with optimized parameters, including citric acid concentration (1.25 M), solid-liquid ratio (45 $g \cdot L^{-1}$), H_2O_2 dosage (3 mL), and a temperature of 50 °C, the recycling efficiency of Li and Co in heavily degraded $LiCoO_2$ cathodes increased by over 35% compared to a non-UV-assisted approach. The photocatalysis-assisted strategy has also proven effective in recycling high-Ni cathodes in spent LIBs, which confirms its universal applicability.

Ultrasound-assisted recycling

Ultrasound-assisted leaching is another popular technique in hydrometallurgy for recycling spent LIBs. Almost all ultrasonication techniques performed in liquids are associated with cavitation[34]. Ultrasonic cavitation occurs when the ultrasonic energy is sufficiently high, causing tiny bubbles (cavitation nuclei) in the liquid to vibrate, grow, and continuously gather sound field energy. When the energy reaches a certain threshold, the cavitation bubbles dramatically collapse and close. Ultrasonic cavitation serves to accelerate chemical reactions and can also control the reaction process, enhancing yield while reducing side reactions. In certain cases, reactions that are difficult to occur under normal circumstances can proceed smoothly under ultrasonic irradiation.

Jiang *et al.* employed an ultrasound-assisted leaching method to recover Li and Co from spent LIBs, using H_2SO_4-H_2O_2 as a leaching agent[35]. Compared to conventional leaching methods, this approach achieved a high leaching rate, with improved Li and Co leaching efficiencies reaching up to 98.62% and 94.63%, respectively, under an ultrasonic power of 360 W with leaching time of 30 min. Similarly, Li *et al.* applied an ultrasound-assisted strategy to leaching Li and Co using citric acid [Figure 1B][36]. Due to the unique ultrasonic cavitation effect, the optimized leaching efficiencies for the two elements reached as high as 100% and 96%, respectively, within 5 h using a lower ultrasonic power of 90 W. Recently, Li *et al.* proposed a mechano-catalytic method, termed contact-electro-catalysis (CEC), for the spent LIB recovery, which utilizes free radicals generated by contact electrification to promote metal leaching in the presence of an ultrasound-assisted scenario[37]. For spent $LiCoO_2$ batteries, the leaching efficiencies of 100% for Li and 92.19% for Co were achieved within 6 h at 90 °C. In contrast, for ternary Li batteries, the leaching efficiencies within 6 h at 70 °C were 94.56% for Li, 96.62% for Ni, 96.54% for Mn, and 98.39% for Co, respectively. The CEC-leaching strategy offers a green, efficient, and economical approach to recovering LIBs, which is expected to meet the growing demand for LIB recycling.
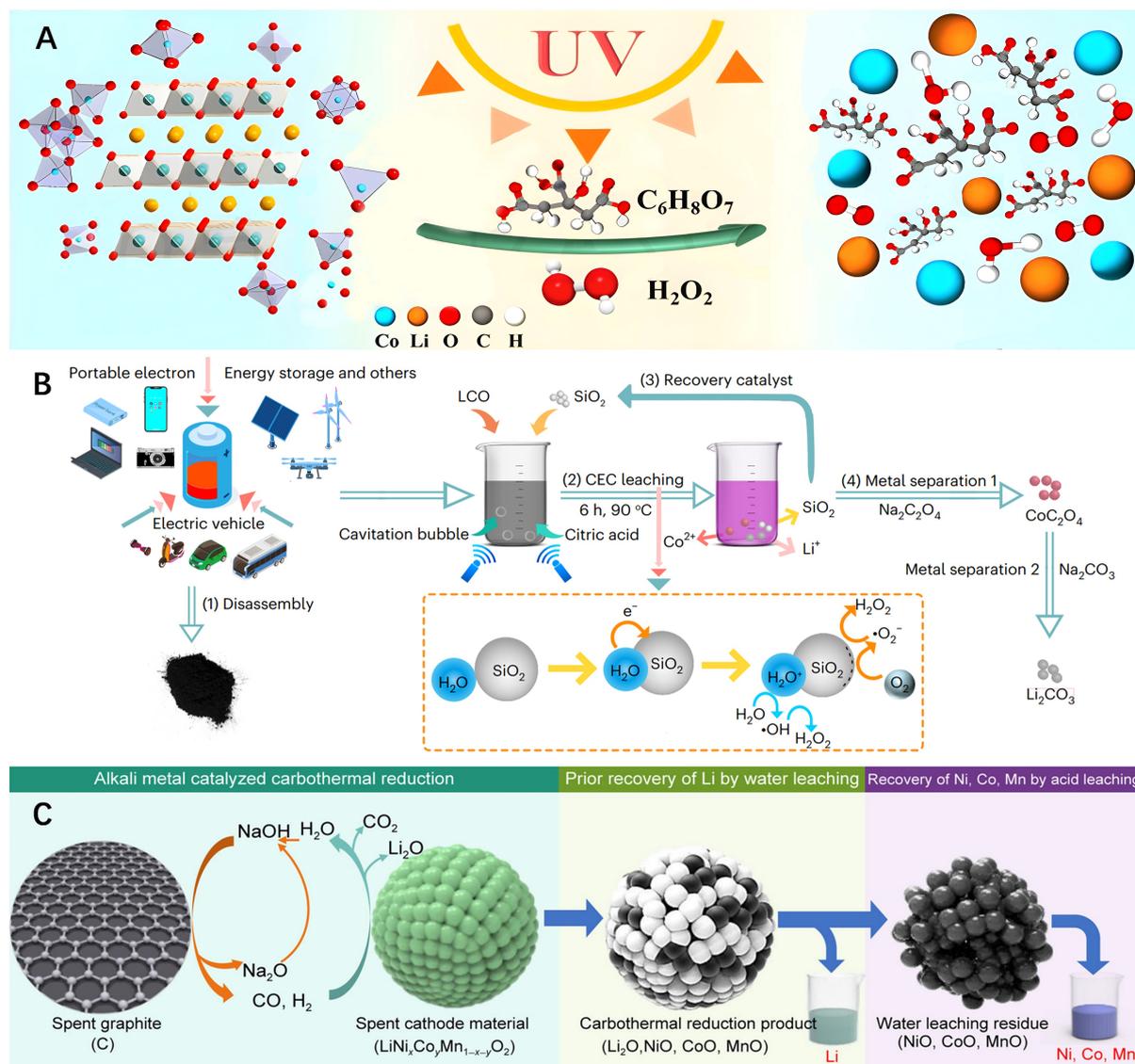
Figure 1. Three catalytic methods applied in hydrometallurgy recovery processes. (A) Schematic diagram of photocatalysis-assisted recycling. Quoted with permission from Lv *et al.*[33]; (B) Illustration outlining the CEC-leaching strategy. Quoted with permission from Li *et al.*[37]; (C) Schematic diagram of alkali metal catalytic carbothermal reduction. Quoted with permission from Zhang *et al.*[38]. CEC: Contact-electro-catalysis. UV: ultraviolet; LCO: lithium cobalt oxide.

Metal catalyst-assisted recycling

Adding metal catalysts to the leaching system, capitalizing on their excellent catalytic activity, can significantly enhance the leaching rate and efficiency. Zhang *et al.* employed alkali metals as catalysts, such as NaOH, significantly reducing the temperature needed for carbothermic reduction of spent $LiNi_xCo_yMn_zO_2$ cathodes [Figure 1C][38]. This approach allowed for targeted control of the reduction product phase. The separation process involved initial water leaching to extract Li, followed by acid leaching to recycle Ni, Co, and Mn. Additionally, high leaching efficiencies of Ni, Co, and Mn were successfully achieved under specific conditions, including a leaching time of 3 h, calcination temperature of 550 °C, and using 15 wt.% NaOH and 15 wt.% graphite. Nshizirungu *et al.* employed subcritical water for metal leaching from spent $LiCoO_2$ cathodes, with the assistance of added Ni catalyst and waste chlorinated polyvinyl chloride (CPVC) in the leaching system[39]. The presence of Ni accelerated the decomposition of CPVC,

generating HCl for the leaching system. This, in turn, expedited the metal leaching of $LiCoO_2$. After optimizing the reaction conditions, including a reaction temperature of 240 °C for 40 min, a Ni^{2+} concentration of 0.04 M, and a 25:1 $(mL·g^{-1})$ liquid-solid ratio, this process effectively improved the leaching efficiency. Porvali *et al.* recovered the spent $LiCoO_2$ cathodes using metallic Cu and dissolved Fe from battery casings as catalysts, with H_2SO_4 as the leaching agent[40]. Their proposal suggests that Cu can donate electrons to Fe^{3+}, and the resulting Fe^{2+} facilitates the electron transfer, enabling the reduction of $LiCoO_2$. In this scenario, the extraction efficiency of Co exceeded 95%.

APPLICATION OF EXTRACTED MATERIALS FROM SPENT LIBS IN CATALYTIC FIELDS

By recovering metals, such as Li, Ni, Co, Mn, Cu, and Fe, from cathodes and anodes in spent LIBs, various highly efficient catalysts can be prepared for applications including the degradation of toxic organics in the environment, electrocatalysis, and air batteries, *etc*. The performance of these obtained catalysts is comparable to or even surpasses that of commercial catalysts, showcasing significant potential and economic benefits. To facilitate discussion, this section delves into the potential extraction of materials and their applications in different catalytic fields, categorized by electrodes.

Cathode

The valuable metals Ni, Co, Mn, and Fe possessing commendable catalytic properties, obtained by recycling around the common cathodes in spent LIBs, can be converted into catalysts. Moreover, the catalyst can undergo modification through multiple metal doping, resulting in an improved catalyst that exhibits excellent catalytic activity [Table 1].

Spent $LiCoO_2$

$Li_{1-x}MO_2$, represented by the $LiCoO_2$ with layered structure, was the primary commercial cathode material (CM) in the early era of LIBs[41]. Its extensive use in portable electronic devices stemmed from its outstanding overall performance and high volumetric energy density. However, with the growth and widespread adoption of these devices, a substantial number of spent LIBs with $LiCoO_2$ cathodes are generated annually. The component of Co possesses physiological toxicity and is a typical heavy metal pollutant. Additionally, Co is a crucial metal resource, and Co-based catalysts exhibit excellent catalytic properties applicable in various catalytic reaction systems. Consequently, the recycling of spent $LiCoO_2$ has garnered significant attention in recent years.

Co-based catalysts are recognized for their robust catalytic oxidation properties, making them highly effective in degrading harmful organic compounds. Zhao *et al.* recovered the $LiCoO_2$ cathode through a meticulous calcination process [Figure 2A][42]. They utilized the resulting CM, composed of 94% $LiCoO_2$ and 6% Co_3O_4 and other constituents, directly as a catalyst for activating peroxymonosulfate (PS) in degrading the levofloxacin hydrochloride (LFX) within wastewater. The catalytic mechanism within the CM catalyst was elucidated, highlighting the pivotal role of the Co^{2+}/Co^{3+} species in PS activation, while the SO_4^- group and non-radioactive singlet oxygen in PS were identified as key contributors to the LFX degradation process. Upon careful optimization of the degradation conditions, a high LFX removal rate of 94% was achieved. Hossain *et al.* developed thermally isolation and controlled recycling methods for selectively regenerating spent $LiCoO_2$ cathodes[43]. Through this process, they transformed the $LiCoO_2$ into porous Co_3O_4 catalysts characterized by nanoscale grains and a substantial specific surface area. These tailored Co_3O_4 catalysts exhibited notable applicability in photodegrading toxic dyes, with particular success observed in effectively decomposing methyl blue dye (MBD) under visible light conditions. The results revealed not only the efficacy of the obtained Co_3O_4 catalyst in the MBD decomposition but also its reusability over multiple cycles.

Table 1. Summary of catalysts made from spent LIBs

Electrode	Materials	Catalyst	Application	Ref.
Cathode	LCO	94% $LiCoO_2$ and 6% Co_3O_4	Decomposition of VOC	[42]
		Porous Co_3O_4	Decomposition of VOC	[43]
		3D layered $LiCoO_2$	OER	[44]
		Gram-scale spinel Co_3O_4 nanoparticles	OER	[45]
	LFP	Fe-N-P-doped catalysts	ORR	[48]
		Defect-rich NiFe catalysts	OER	[49]
	NCM	Mn-based multi-oxide catalysts	Decomposition of VOC	[53]
		Ternary NCM electrocatalyst	OER	[54]
		NiMnCo-based catalysts	OER/ORR	[55]
Anode	C	N-Fe-doped carbon-based catalysts	ORR	[58]
	Cu/C	CuO/C catalyst	Decomposition of VOC	[59]
Mix	LCO/LFP	CoFe/C catalysts	ORR	[60]
	LCO/C	Co@NG catalysts	ORR	[61]

LIBs: Lithium-ion batteries; LCO: lithium cobalt oxide; VOC: volatile organic compound; OER: oxygen evolution reaction; LFP: lithium iron phosphate; ORR: oxygen reduction reaction; NCM: $LiNi_xCo_yMn_{1-x-y}O_2$.

Co-based catalysts are also widely acknowledged for their outstanding electrocatalytic properties in oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Kang *et al.* recovered spent $LiCoO_2$ cathodes into a three-dimensional layered $LiCoO_2$ catalyst through a two-step chemical delithiation and hydrogen thermal treatment process [Figure 2B][44]. This restructuring created additional active sites and oxygen vacancies within the catalyst, enhancing its electrocatalytic performance. The developed catalyst exhibited remarkable capabilities in promoting charge transfer, significantly enhancing OER performance. The results showcased a low overpotential of 365 mV and a minimal Tafel slope of 67 mV·dec^{-1} at a current density of 10 mA·cm^{-2}. Kim *et al.* synthesized gram-scale spinel Co_3O_4 nanoparticles, serving as OER catalysts, by strategically applying the stepwise leaching reaction method on spent $LiCoO_2$ cathodes[45]. This approach resulted in an increased number of electrocatalytically active sites within the catalyst. Consequently, the Co_3O_4 nanoparticles demonstrated superior OER catalytic activity, comparable to the widely acknowledged RuO_2 catalyst.

In addition, several teams recovered Co from spent $LiCoO_2$ for catalytic pyrolysis of biomass for hydrogen production. Yu *et al.* employed carbothermal reduction to recover Co from spent $LiCoO_2$ for biomass pyrolysis and steam reforming for H_2 production, investigating the impact of various carbon sources on the recovery efficiency[46]. They observed that the energy consumption was relatively low when utilizing coconut shell carbon as the carbon source for the reaction. Furthermore, considering the impacts of pore structure of carbon materials on reduction, they prepared activated carbon with a specific surface area of 653.0 m^2·g^{-1} for Co recovery. By optimizing the mass ratio of the CM to the activated carbon, they achieved a H_2 yield of up to 28.3 mmol·g^{-1}.

Spent $Li_{1-x}FePO_4$ (0 < x < 1)
$LiFePO_4$ cathodes, classified as an olivine material, have gained widespread adoption in electric and hybrid vehicles owing to their exceptional thermal stability, extended cycle life, and cost-effectiveness[47]. The rising prevalence of electric vehicles in recent years would lead to a substantial increase in the accumulation of waste $LiFePO_4$ batteries. However, the advantageous characteristic of $LiFePO_4$ is that the Fe element within its composition can be efficiently recovered from these spent batteries. The recovered Fe functions as a valuable resource for producing Fe-based catalysts with commendable physical and chemical stability. These
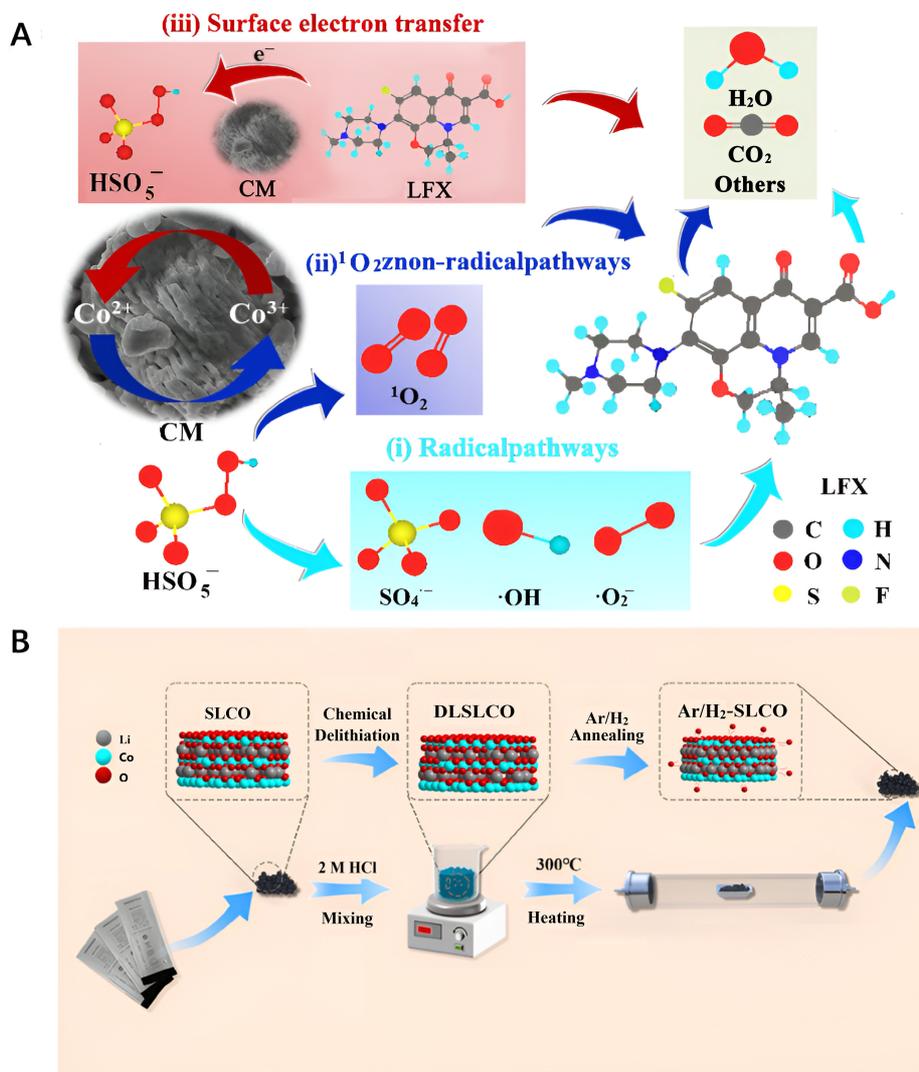
Figure 2. (A) Schematic diagram of reclaimed CM as a catalyst for activating PS in the degradation of the LFX within wastewater. Quoted with permission from Zhao *et al.*[42]; (B) Flow chart for the reconstruction and process of spent $LiCoO_2$. Quoted with permission from Kang *et al.*[44]. CM: Cathode material; PS: peroxymonosulfate; LFX: levofloxacin hydrochloride; SLCO: spent lithium cobalt oxide; DLSLCO: delithiation from spent lithium cobalt oxide.

catalysts exhibit low sensitivity to moisture, further enhancing their practical utility, and showcase high catalytic activity, with Fe^{3+}/Fe^{2+} acting as the primary active component.

Luo *et al.* conducted a recovery of spent $LiFePO_4$ cathodes using a leaching method, employing H_2SO_4-H_2O_2 as the leaching agent [Figure 3A][48]. The resulting $FePO_4$ was subjected to further calcination under a nitrogen atmosphere to generate Fe-N-P-doped carbon-based catalysts tailored for ORR. These Fe-N-P-doped catalysts showcased exceptional ORR performance, particularly in an alkaline medium. Remarkably, the Fe-N-P-doped catalysts demonstrated a high peak power density of up to 80 mW·cm⁻² when applied in zinc (Zn)-air batteries. Cui *et al.* synthesized defect-rich NiFe catalysts by employing a recycling method for spent $LiFePO_4$ cathodes, involving impregnation and combination with Ni [Figure 3B][49]. Theoretical calculations conducted in their study revealed that the incorporated Ni was crucial in optimizing the free energy of the ˙OOH intermediate. This effectively activated the Fe sites within the catalyst. Additionally, the catalyst benefited from a substantial number of oxygen defects, which facilitated the oxygen desorption. The synergistic effect resulting from the presence of Ni and oxygen defects manifested in the impressive OER
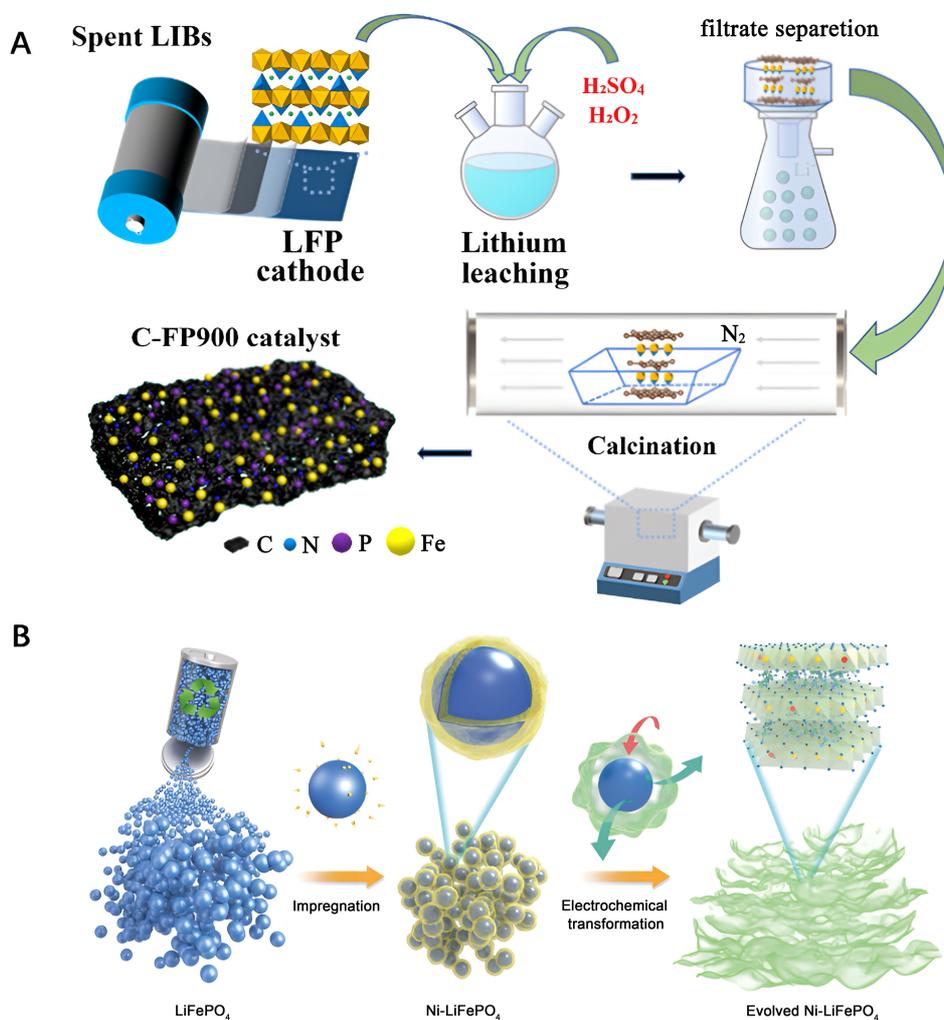
Figure 3. (A) Schematic illustration of the recycling process of spent LiFePO$_4$ batteries to prepare Fe-N-P-doped catalysts. Quoted with permission from Luo *et al.*[48]; (B) Schematic diagram of the recycling process of spent LiFePO$_4$ to regenerate defect-rich NiFe catalysts. Quoted with permission from Cui *et al.*[49]. LIBs: Lithium-ion batteries; LFP: lithium iron phosphate.

catalytic activity of the catalyst. At a current density of 10 mA·cm^{-2}, the obtained catalyst exhibited a low overpotential of 285 mV and a small Tafel slope of 45 mV·dec^{-2}.

Spent LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ (0 < x, y < 1)

The ternary layered transition metal oxide material, LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ (NCM), has garnered widespread attention as a promising CM for LIBs[50-52]. This material offers a range of advantages, including low cost, a high specific discharge capacity, excellent cycling performance at both room and high temperatures, and a structurally stable framework. One feature of NCM is its flexibility in composition, allowing for the adjustment of the Ni, Co, and Mn ratios to meet specific requirements. This adaptability results in various forms of NCM electrode materials, each exhibiting distinct properties based on the variation in transition metal elements. Due to its composition of various transition metals, the spent NCM demonstrates high recycling efficiency, making it a valuable resource for producing diverse catalysts. These catalysts can find applications in a wide range of catalytic reactions, showcasing the material's potential to contribute to various catalytic processes.

Guo *et al.* employed a citric acid leaching method to efficiently recover precious metals from spent NCM cathodes [Figure 4A][53]. Subsequently, they utilized the recovered materials to synthesize Mn-based multi-oxide catalysts designed for the oxidation of volatile organic compounds (VOCs). The resulting catalysts were characterized by several advantageous features, including a large specific surface area, a rich mesoporous structure, excellent low-temperature reducibility, elevated Mn^{4+} and lattice oxygen concentration, and a robust weak acid site strength. These distinctive characteristics collectively contributed to the exceptional performance of the obtained catalysts in the oxidation of toluene, a representative VOC. Li *et al.* demonstrated an electrochemical approach by applying electrochemical delithiation technology to directly repurpose spent NCM cathodes into a ternary NCM electrocatalyst for the OER [Figure 4B][54]. This electrochemical delithiation process induced significant alterations in the electronic and microstructure of the catalyst. As a result, a substantial number of Ni^{3+} and oxygen vacancies were formed. These modifications not only enhanced the electronic conductivity of the catalyst but also provided an increased number of active sites for OER. The optimized NCM electrocatalyst exhibited good performance, characterized by a low overpotential of 270 mV at 10 mA·cm^{-2}. Furthermore, the catalyst demonstrated excellent stability, showcasing durability over a period of 300 h. Jiao *et al.* repurposed waste NCM cathodes, converting them into highly efficient NiMnCo-based catalysts by combining acid leaching and radiant heating techniques [Figure 4C][55]. These catalysts were then applied as cathodes in zinc-air batteries. The synthesized catalyst showcased a core-shell structure featuring face-centered cubic Ni in the core and spinel $NiMnCoO_4$ in the shell. This unique architecture led to a redistribution of the electronic structure of the prepared catalyst, resulting in a lowered energy barrier for the ORR and OER processes, ensuring high electrocatalytic activity. The constructed zinc-air battery exhibited impressive performance metrics, including a high power density of 187.7 mW·cm^{-2} and long cycle stability with a sustained performance over 200 h at a current density of 10 mA·cm^{-2}.

It is noteworthy to mention that, alongside the primary focus on LIB recycling, recycling other types of spent rechargeable batteries, such as nickel-metal hydride (Ni-MH) batteries, can also result in the recovery of valuable materials. For instance, Pham *et al.* demonstrated the recycling of the cathode of spent Ni-MH batteries to produce NiO-based electrodes for use in supercapacitors, showcasing a maximum capacitance of 106 C·g^{-1} at 0.5 A·g^{-1}[56]. Furthermore, they developed the $LiNi_{0.5}Mn_{1.5}O_4$ cathode applied in LIBs with a discharge specific capacity of 137.4 mAh·g^{-1}.

Overall, the recycling strategy for recovering spent LIB cathodes to prepare catalysts offers a dual benefit by preventing the wastage of precious metals such as Ni, Co, and Mn while curbing their environmental pollution. Economically, the catalyst preparation process involves high-temperature calcination, entailing some energy consumption. Nonetheless, when factoring in the catalytic efficiency and energy-saving attributes during catalytic reactions, catalysts derived from recycled cathodes yield higher economic value than the energy expended in their preparation.

Recycling of anodes

Graphite is presently the preferred anode material in LIBs, primarily due to its excellent electrochemical properties[57]. However, recycling graphite from spent LIBs has faced challenges, primarily associated with its relatively low added value and the difficulty in recovery processes. Despite its prevalence in battery technology, graphite recycling has not been as extensively pursued as other components of LIBs. Recently, there has been a growing awareness of the environmental impact and economic potential associated with recycling anode materials, including graphite and Cu current collectors, from spent LIBs [Table 1]. The surge in the number of waste LIBs, coupled with the widespread use of graphite active materials and Cu in various fields, such as catalysis, has underscored the need for developing effective recycling strategies.
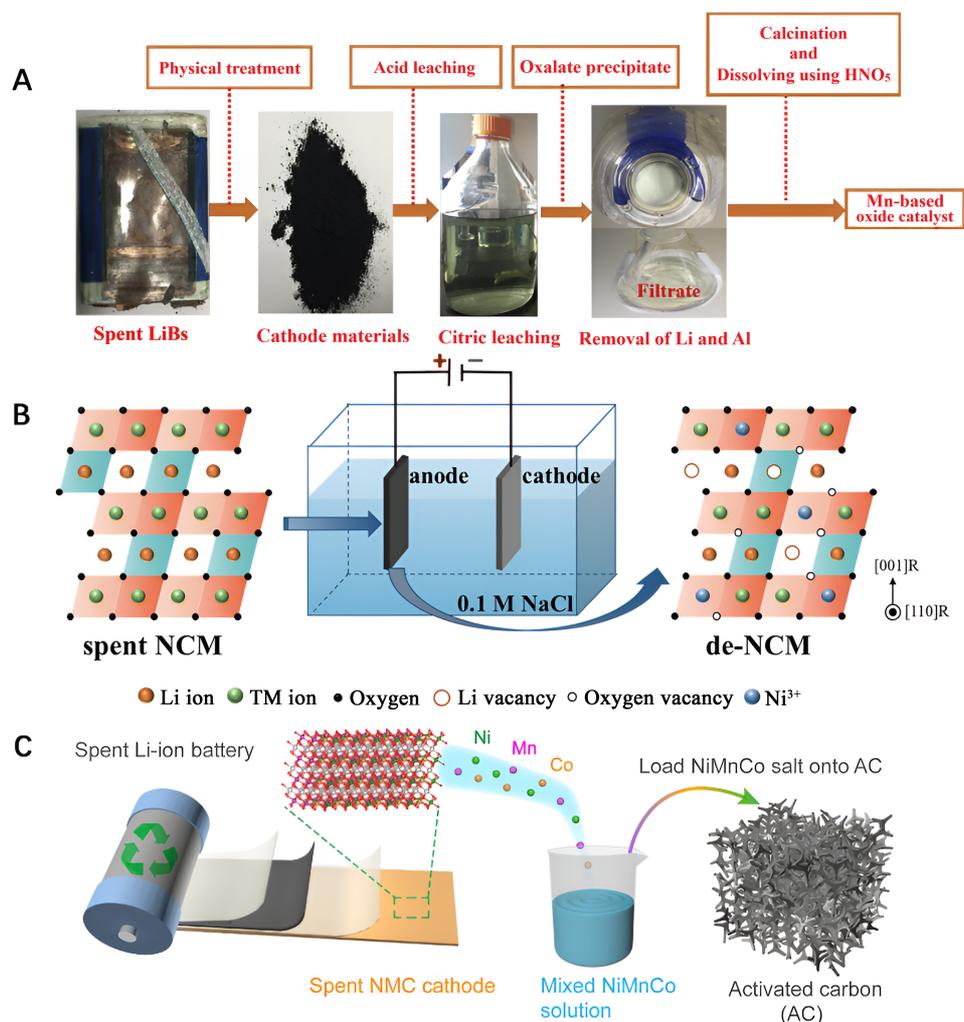
Figure 4. (A) Flow chart of utilizing the recovered materials from spent ternary LIBs to synthesize Mn-based multi-oxide catalysts. Quoted with permission from Guo *et al.*[53]; (B) Schematic diagram of reuse of spent LiNi$_{0.94}$Co$_{0.05}$Mn$_{0.01}$O$_2$ cathodes via electrochemical delithiation technology. Quoted with permission from Li *et al.*[54]; (C) Schematic diagram of preparation for NiMnCo-based catalysts from spent LIBs. Quoted with permission from Jiao *et al.*[55]. LIBs: Lithium-ion batteries; NCM: LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$; de: delithiation; AC: activated carbon.

Ruan *et al.* conducted a study wherein they repurposed graphite anodes extracted from spent LIBs [Figure 5A][58]. These graphite anodes were then utilized as carriers to create N- and Fe-doped carbon-based catalysts through a pyrolysis process involving polyaniline and iron salts. The resulting catalysts were specifically designed for the ORR in fuel cells. The synthesized catalysts demonstrated commendable performance characteristics, including robust ORR catalytic activity and stability. Meanwhile, they exhibited good resistance to methanol toxicity. Remarkably, the performance of these catalysts was found to be comparable to that of commercial Pt/C catalysts in catalyzing the ORR. Zhao *et al.* fabricated a CuO/C catalyst through a one-step calcination method, employing spent anode materials from LIBs as the raw materials [Figure 5B][59]. This catalyst was designed to activate PS to degrade organic pollutants in wastewater. The study demonstrated that the redox transition between Cu(II) and Cu(I) in the catalyst was crucial in promoting the activation of PS and facilitating the generation of oxygenated species, such as SO$_4^-$·, ·O^{2-}, and ^{1}O$_2$. One notable feature of the CuO/C catalyst was its versatility across a wide pH range, making it applicable for wastewater treatment under various environmental conditions. Additionally, the catalyst exhibited effectiveness in degrading a diverse range of organic compounds, including Rhodamine B,
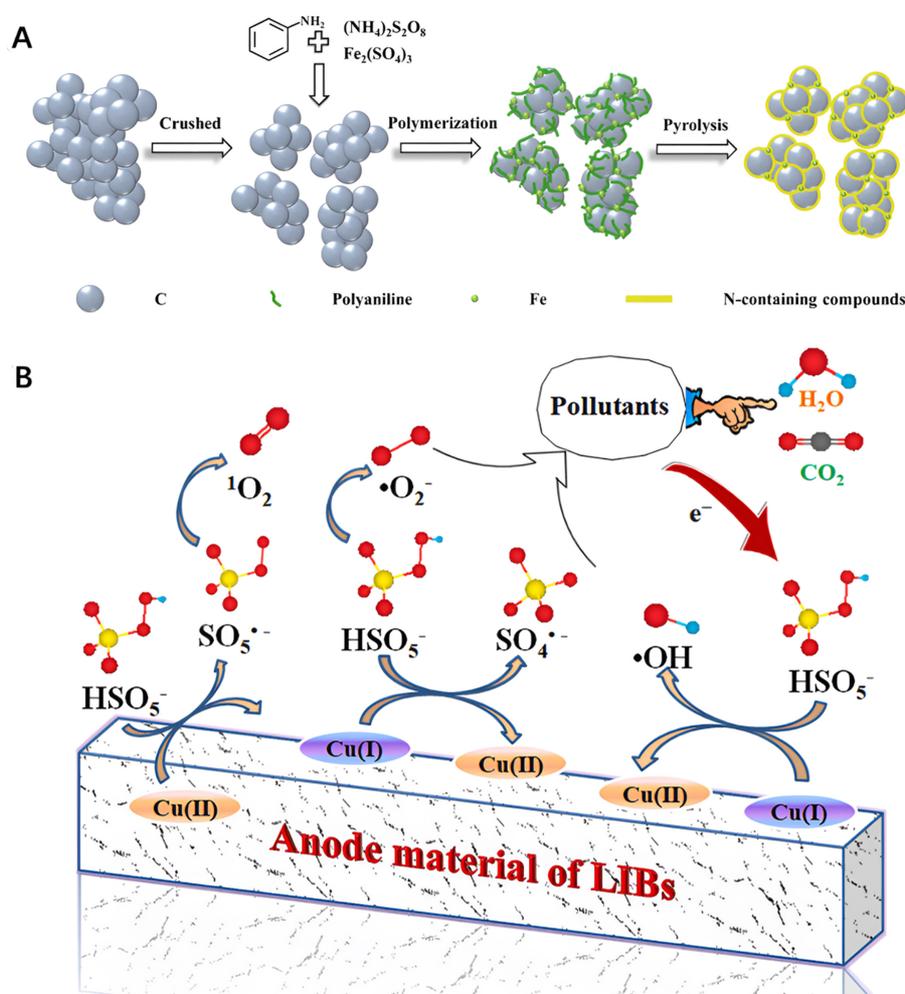
Figure 5. (A) Schematic illustration of the preparation of N- and Fe-doped carbon-based catalysts recovered from spent LIBs. Quoted with permission from Ruan *et al.*[58]; (B) Schematic diagram of reaction mechanism of CuO/C catalyst recovered from spent LIBs to activate PS for RhB degradation. Quoted with permission from Zhao *et al.*[59]. LIBs: Lithium-ion batteries; PS: peroxymonosulfate; RhB: Rhodamine B.

indicating its potential for broad-spectrum pollutant removal.

Compared to cathode recovery, the process of recovering anodes for catalyst preparation does not require high ambient temperatures, leading to reduced energy consumption and frequently yielding catalysts with notable catalytic performance. Nevertheless, since anode materials such as C and Cu are more prevalent compared to cathodes, the economic advantages of utilizing recovered anodes for catalyst production are relatively modest.

Synergistic recycling of cathodes and anodes
Recycling various cathodes and anodes sourced from diverse spent LIBs has the potential to generate a versatile array of catalytic materials. This includes the production of metal-doped catalysts and/or carbon-based transition metal-doped catalysts. The resulting recycled materials hold promise for applications across various catalytic fields. For example, Jiao *et al.* employed a synergistic recycling strategy, utilizing leaching and calcination methods, to selectively extract Co and Fe from spent $LiCoO_2$ and $LiFePO_4$ cathodes,

respectively [Figure 6A][60]. Subsequently, they synthesized CoFe/C catalysts utilizing carbon derived from sawdust as a carrier for zinc-air batteries. The study revealed that CoFe nanoparticles were uniformly dispersed on the carbon carrier, attributed to electrostatic interactions between Co^{3+} and Fe^{3+}. The distinctive electronic structure of the catalyst contributed to its exceptional ORR performance. In practical battery applications, the cathode employing CoFe/C showcased an extended cycle stability of 350 h and a high power density of nearly 200 mW·cm^{-2}. Serbara Bejigo *et al.* employed hydrometallurgy to recover Co metal from spent $LiCoO_2$ batteries, and concurrently, graphite anodes were also reclaimed and transformed into graphene oxide [Figure 6B][61]. These retrieved components were then integrated through a calcination method to synthesize cobalt-integrated nitrogen-doped graphene (Co@NG) catalysts, specifically designed for the ORR. The obtained Co@NG exhibited noteworthy activity in ORR, demonstrating performance comparable to commercial Pt/C catalysts. Moreover, when incorporated into a direct methanol fuel cell setup with Co@NG as the cathode and commercial Pt-Ru/C as the anode, the fuel cell exhibited exceptional performance and sustained stability.

ADVANCED SPECTROSCOPIC CHARACTERIZATIONS FOR FUNDAMENTAL INSIGHT INTO CATALYSTS

Catalyst characterization is pivotal in the entire catalyst lifecycle, from preparation to application. This process allows for the feedback and prediction of catalyst properties, facilitating the targeted design of catalysts and the exploration of catalytic reaction mechanisms. Comprehensive catalyst characterization encompasses both macroscopic and microscopic perspectives. Macroscopic characterization methods in catalysis primarily concentrate on factors such as catalyst density, particle size, pore structure, pore size distribution, specific surface area, and thermal and pressure resistance. These macroscopic attributes provide crucial insights into the physical and mechanical properties of the catalyst, influencing its performance under various conditions. On the microscopic level, catalyst characterization delves into studying the catalyst surface and/or interface. This includes analyzing the component distribution, active center, surface structure, grain size, coordination environment, energy state, and redox properties. These microscopic details are vital for understanding the intricacies of catalyst behavior at the atomic and molecular levels, allowing for a deeper comprehension of catalytic processes. On the other hand, the significance of *in situ* characterization becomes increasingly apparent as a pivotal aspect in capturing dynamic information essential for understanding catalytic reactions. The real-time insights afforded by *in situ* characterization are decisive in evaluating catalyst performance and unraveling the intricate details of catalytic mechanisms. Herein, we highlight X-ray-based techniques and *in situ* surface-sensitive enhanced Raman techniques as powerful tools that address some of the most critical and fundamental questions encountered in exploring catalytic reaction mechanisms.

X-ray-based techniques

X-ray, characterized by short wavelengths and high energy, interacts with the analyte to provide valuable insights into its structure and composition. Numerous X-ray-based analysis methods have been established, including X-ray absorption, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), leveraging the unique characteristics of X-ray. These techniques yield rich chemical information about the sample being analyzed, encompassing elemental composition, content, valence, and chemical bonding. Additionally, they provide insights into the structure, surrounding environment, and depth distribution of the sample. X-ray-based analysis serves as a potent tool for characterizing catalysts derived from recycled lithium-ion cathodes, enabling the exploration of their structure, chemical components, catalytic performance, and catalytic mechanisms.
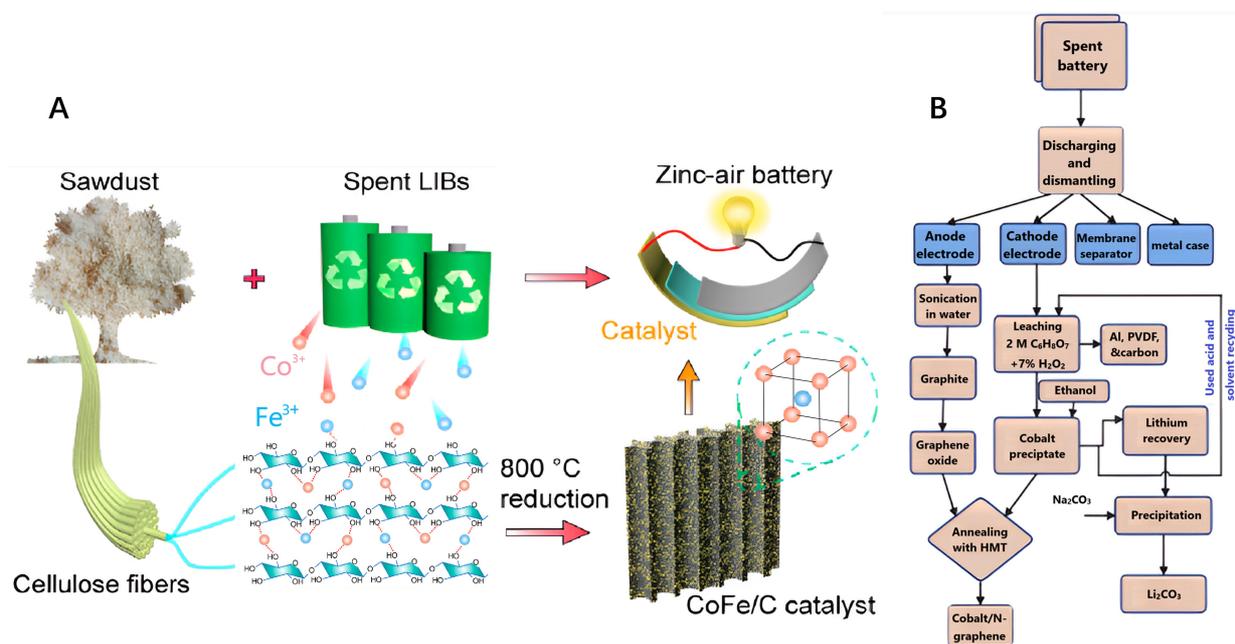
Figure 6. (A) Schematic illustration of the CoFe/C catalyst cathode synthesis from spent LIBs to optimize Zn-air batteries. Quoted with permission from Jiao *et al*.[60]; (B) The route of recycling spent LIBs to prepare Co@NG catalyst. Quoted with permission from Serbara Bejigo *et al*.[61]. LIBs: Lithium-ion batteries.

X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) employs the energy of X-ray photons as a variable to excite photoelectrons on a solid surface. These photoelectrons are then analyzed with an energy analyzer to determine the X-ray absorption coefficient of the material. XAS offers valuable insights into the coordination environment and chemical state of the probed atoms, making it a common technique for characterizing various catalyst types, including single-atom catalysts, surface reactions, nanoscale catalysts, and atomic occupancy.

XAS is typically divided into two regions: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). XANES provides information on chemical valence and electronic structure, while EXAFS yields details about neighboring atomic structures. Jiao *et al*. repurposed spent NCM cathodes to synthesize a NiMnC-activated carbon (NiMnCo-AC) catalyst featuring a core-shell structure, intended for OER and ORR applications[55]. Characterization of the catalyst via XANES analysis revealed that the white line intensity and absorption edge energy of the NiMnCo-AC catalyst were higher than those of the corresponding metal foils. This finding suggests that Ni, Mn, and Co in the NiMnCo-AC catalyst existed in a high valence state, indicative of the formation of metal oxides within the catalyst. In another study, Jiao *et al*. recovered lithium cobalt oxide (LCO) and lithium iron phosphate (LFP) cathodes, synthesizing a CoFe/C catalyst for use as an OER and ORR bifunctional catalyst in zinc-air batteries[60]. XANES analysis revealed that the white line edges of Co and Fe in the CoFe/C catalyst were more pronounced than those of the respective metal foils [Figure 7A and B]. This intensification was attributed to the alloying effect of Co and Fe, resulting in a modification of the electronic structure. Additionally, examination of the EXAFS results showed that the spectrum of the Fe K edge in CoFe/C matched the body-centered cubic (bcc) structure of Fe foil, while that of the Co K edge aligned with the face-centered cubic structure of Co foil [Figure 7C and D]. This disparity indicated that the formation of the CoFe alloy adopted a bcc structure.
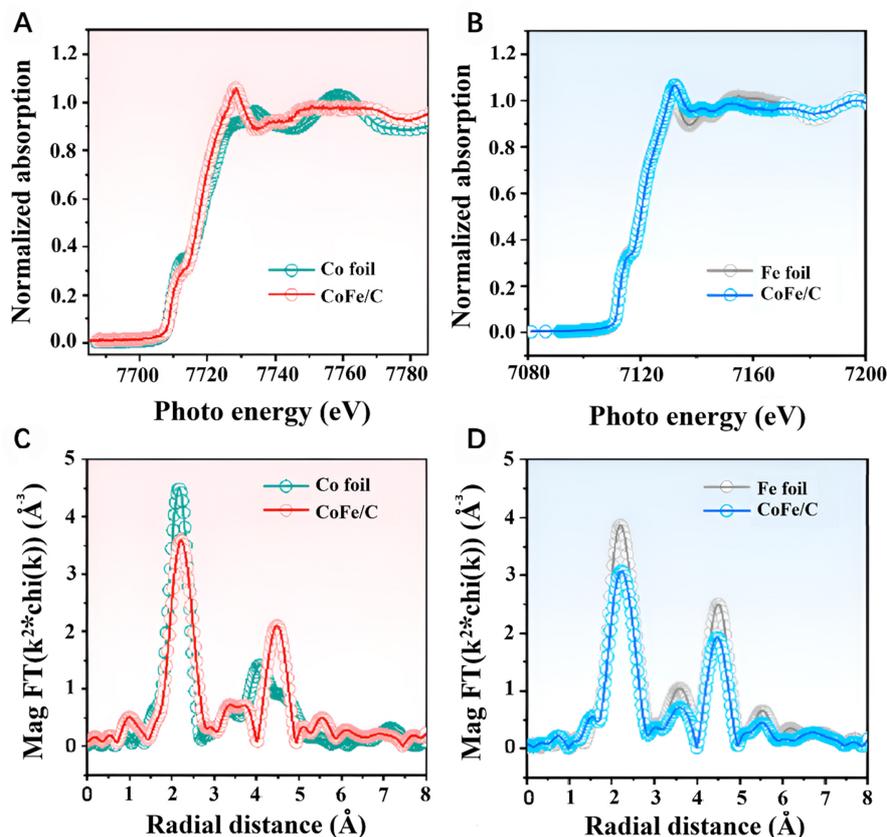
Figure 7. XAS characterization of catalysts prepared from recycled LIBs. (A) and (B) XANES spectra of the CoFe/C catalyst and the respective metal foils; (C) and (D) k^2-weighted R-space EXAFS spectra of the CoFe/C catalyst and the respective metal foils. Quoted with permission from Jiao *et al.*[60]. XAS: X-ray absorption spectroscopy; LIBs: lithium-ion batteries; XANES: X-ray absorption near edge structure; EXAFS: extended X-ray absorption fine structure.

X-ray diffraction and X-ray photoelectron spectroscopy

XRD analysis serves to identify the composition of a material and scrutinize its internal crystal structure. When X-rays are irradiated into a sample from various angles, they undergo diffraction, causing a change in the diffraction pattern corresponding to the crystal structure, leading to deflection. By scrutinizing the direction and intensity of this deflection and applying the Bragg equation to interpret the signal output, insights into the internal crystal structure of the sample can be gleaned. Zhou *et al.* employed a pH gradient method to recycle waste $LiMn_2O_4$ from spent LIBs[62]. The process involved leaching the spent $LiMn_2O_4$ cathodes and subsequently calcining the resulting metal oxides to obtain the desired materials for synthesizing the OER catalyst. Experimental optimization was conducted to enhance the metal leaching rate by adjusting parameters such as leaching current, temperature, and time. These variables were subjected to gradient experiments, and the resulting products were characterized using XRD to determine the optimal experimental conditions. XPS employs X-ray with a specific energy to irradiate a sample, resulting in the release of electrons from the atoms of the sample being measured, thus generating free electrons. By analyzing the energies of the excited photoelectrons, XPS enables investigation into the composition of elements in the catalyst, its chemical state, and other relevant properties. Zhao *et al.* synthesized catalysts by repurposing LCO anodes to activate PS in degrading LFX within wastewater[42]. XPS results revealed the co-existence of Co^{2+} and Co^{3+} species, which played a significant role in activating PS.

Raman spectroscopy

Raman spectroscopy stands out as a straightforward, efficient, and non-destructive analysis method, enabling direct application for testing target samples[63,64]. Its efficacy becomes evident in exploring and identifying intermediates during reactions, offering valuable insights into molecular structures and chemical bonds while preserving the sample integrity. For example, Wang *et al.* repurposed graphite anodes from spent LIBs and synthesized reduced graphene oxide (rGO) used for catalytic ozone oxidation. The catalyst structure was characterized by Raman spectroscopy, revealing that the obtained rGO exhibited a higher I_D/I_G ratio. This observation suggests the presence of more sp^3 carbons, which can provide additional defect sites and enhance the catalytic activity[65]. However, when confronted with trace amounts of surface materials on metal catalysts, conventional Raman spectroscopy encounters limitations in detection sensitivity[64,66]. Overcoming this challenge requires implementing surface enhancement techniques to amplify Raman signal responses, facilitating the detection of even minute quantities of materials.

Surface-enhanced Raman spectroscopic strategy

Surface-enhanced Raman spectroscopy (SERS) is a technique that leverages nanostructures with surface plasmon resonance (SPR) effects to amplify Raman signals by up to 6~10 orders of magnitude[64,67,68]. This enhancement is achieved by concentrating the electromagnetic field into a localized space[69,70]. SERS goes beyond offering chemical fingerprints of samples. It can detect molecules at the single-molecule level and provides high spatial resolution. Over the past two decades, SERS technology has experienced substantial development in both fundamental and applied research directions, including catalytic fields. Nonetheless, the robust SERS effects are primarily associated with nanostructured coinage metals such as Au, Ag, and Cu[64,71]. The practical utility of conventional SERS has been constrained by the choice of substrate material and its structure. Consequently, there have been endeavors in the literature to overcome these limitations by borrowing SPR strategies. These efforts aim to extend the applicability of SERS to non-SERS active substrates, marking a significant advancement in broadening the scope of SERS applications.

For example, Yang *et al.* engineered bifunctional Au@CdS core-shell structured nanoparticles, strategically applied onto an Au substrate [Figure 8A][72]. This combined substrate not only serves as SPR-enhanced photocatalysts for efficiently degrading organic compounds such as methylene blue and p-nitrophenol but also functions as a SERS substrate allowing the real-time monitoring of the reaction process and probing the intricacies of the reaction mechanism. Ze *et al.* conducted an *in situ* electrochemical Raman spectroscopic study of the ORR process catalyzed by PtNi alloy catalysts, employing a borrowing SERS strategy[73]. They synthesized Au@PtNi nanoparticles by coating PtNi catalysts onto the surface of Au nanoparticles [Figure 8B]. The Raman signal amplification was achieved by leveraging the SERS effect of the nanostructured Au. Their findings revealed that increasing the Ni content in PtNi enhanced the binding of *OOH on the Pt surface, facilitating rapid and efficient electron transfer, ultimately leading to an increase in the ORR rate.

Shell-isolated nanoparticle-enhanced Raman spectroscopic strategy

As a derivative of SERS, shell-isolated nanoparticle (SHIN)-enhanced Raman spectroscopy (SHINERS), developed by our group in 2010, has progressively evolved into a fundamental technology in the realm of enhanced Raman spectroscopy[74,75]. This innovative technique involves using SHINs, where the metal nanoparticle cores (typically Au or Ag) with inherent SERS activity are enveloped by an ultra-thin, pinhole-free, and chemically inert oxide shell (such as SiO_2 or Al_2O_3). The presence of this inert shell serves to prevent direct contact between the internal SERS active source and the external chemical environment, ensuring a controlled and isolated environment[76,77]. Importantly, the ultrathin shell does not compromise the Raman signal enhancement. These distinctive features of SHINERS address critical limitations present in traditional SERS and meet the requirements of *in situ* monitoring of electrocatalytic and multiphase
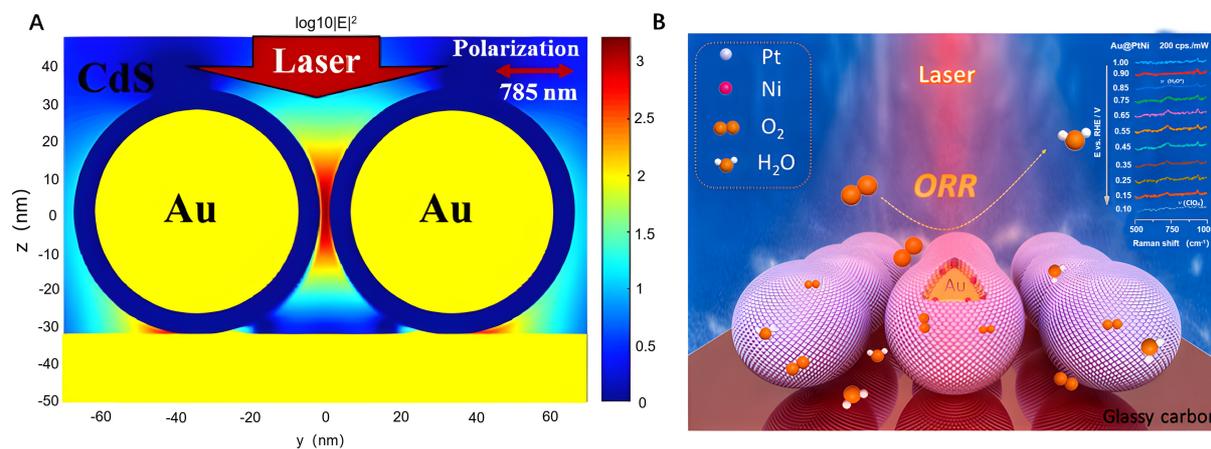
Figure 8. (A) Au@CdS core-shell catalyst used for SPR enhanced photocatalytic degration. Quoted with permission from Yang *et al.*[72]; (B) Schematic illustration of investigation of the crucial role of PtNi alloy catalysts for enhancing ORR by borrowing SERS strategy. Quoted with permission from Ze *et al.*[73]. SPR: Surface plasmon resonance; ORR: oxygen reduction reaction; SERS: surface-enhanced Raman spectroscopy.

catalytic processes in diverse environments, making SHINERS widely used in various catalytic fields.

Dong *et al.* conducted a thorough exploration of the ORR process on the surface of Pt(*hkl*) single crystals using the *in situ* SHINERS technique [Figure 9A][77]. Their study successfully captured direct Raman spectral evidence of crucial reactive intermediate species, including O_2^-, OH^*, and HO_2^*, which was further confirmed by isotopic substitution experiments and theoretical calculations [Figure 9B]. This comprehensive approach enabled the proposal of a mechanistic understanding of the ORR on the surface of Pt(*hkl*) single crystals under acidic conditions. The combination of experimental evidence and theoretical insights provided a nuanced perspective on the intricacies of the catalytic processes at the atomic level. Zhang *et al.* delved into the ORR mechanism within Na-O_2 cells using *in situ* SHINERS techniques[78]. They meticulously investigated the aprotic Na^+-ORR process on the surfaces of Au(*hkl*) single crystals. Their detailed exploration yielded direct spectroscopic evidence of superoxide on Au(110) and peroxide on Au(100) and Au(111) as intermediates or products, unraveling the molecular-level intricacies of the reaction mechanism. The combined findings from experimental results and theoretical simulation analyses led to the conclusion that the surface effects of the Au(*hkl*) electrode on aprotic Na^+-ORR activity are primarily attributed to the distinct adsorption behaviors of Na^+ and O_2.

SHINERS-gap and SHINERS-satellite strategies

Despite the notable success of SHINERS in facilitating *in situ* studies of electrocatalytic processes, particularly on single-crystal model electrodes, challenges arise when probing interfacial processes on real nanocatalysts. The inherent limitations stem from the small size of actual nanocatalyst particles and the associated weak Raman enhancement. In response to these challenges, our group has pioneered the development of SHINERS-gap and SHINRES-satellite strategies, building upon the foundation of the SHINERS technique. These innovative strategies aim to overcome the constraints posed by actual nanocatalysts, thereby extending the applicability of SHINERS to real-world catalytic systems.

Wei *et al.* introduced an innovative SHINER-gap strategy, building upon the SHIN/nanocatalyst/SiO_2/Au structure [Figure 10A][79]. This approach facilitated an *in situ* investigation of structure-activity relationships concerning the selective oxidation of benzyl alcohol over Au@Pd core-shell nanocatalysts [Figure 10B]. The results revealed that the tensile strain effect induced by the Pd shell was pivotal in promoting oxygen
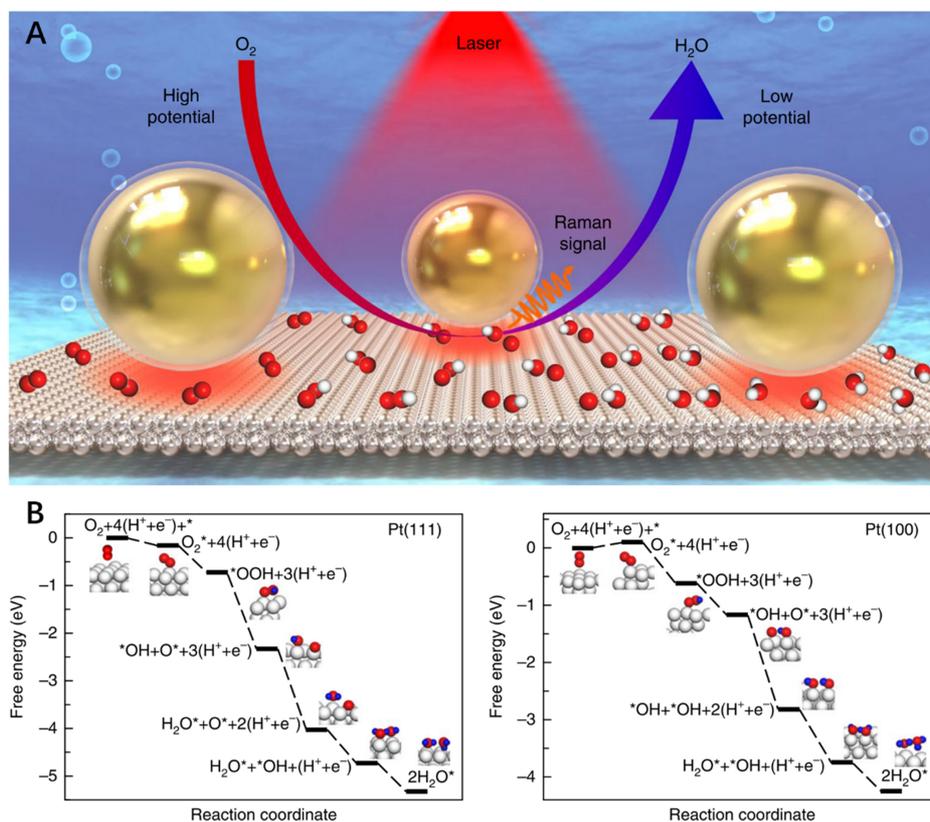
Figure 9. (A) Schematic diagram of the investigation of oxygen reduction reaction process on Pt(*hkl*) using SHINERS; (B) The proposed mechanism of oxygen reduction reaction on Pt(*hkl*) surfaces. Quoted with permission from Dong *et al*.[77]. SHINERS: Shell-isolated nanoparticle-enhanced Raman spectroscopy.

activation. Importantly, the selective oxidation activity of the catalyst for benzyl alcohol exhibited a notable increase at an optimal shell thickness [Figure 10C and D]. Zhang *et al*. established a SHINERS-satellite structure by assembling nanocatalysts, such as PtFe and Pd, onto the surface of Au@SiO$_2$ SHINs [Figure 11A][80]. This approach utilized core Au nanoparticles to enhance Raman signals on the catalyst surface, while a SiO$_2$ shell effectively isolated the influence of Au on the catalyst and the reaction [Figure 11B and C]. This strategy allowed for the direct acquisition of real-time information about the species present on the nanocatalyst surface. Employing such a strategy, they achieved *in situ* monitoring of the CO oxidation reaction and directly observed crucial information, such as adsorbed species on the catalyst surface under reaction conditions. Wang *et al*. created satellite structures by attaching Pt$_3$Co nanoparticles to the surface of Au@SiO$_2$ SHINs, enabling *in situ* SHINERS to investigate the mechanism of the Pt$_3$Co-catalyzed ORR[81]. The results revealed that the ORR on Pt$_3$Co follows an associated reaction mechanism involving *OOH as an intermediate. The enhanced ORR performance on Pt$_3$Co was attributed to the compression of the surface Pt-Pt lattice and the electron transfer from Co to the metal Pt, leading to the weakening of the adsorption of oxygen species.

CONCLUSION AND OUTLOOK

To summarize, we started by providing a brief overview of the recycling processes of spent LIBs and outlining the interconnectedness between battery recycling and catalysis. Notably, the midstream and downstream stages in the recycling stream of spent LIBs exhibit a significant association with catalysis. We then focused on three catalytic strategies within hydrometallurgy techniques for improving the recycling
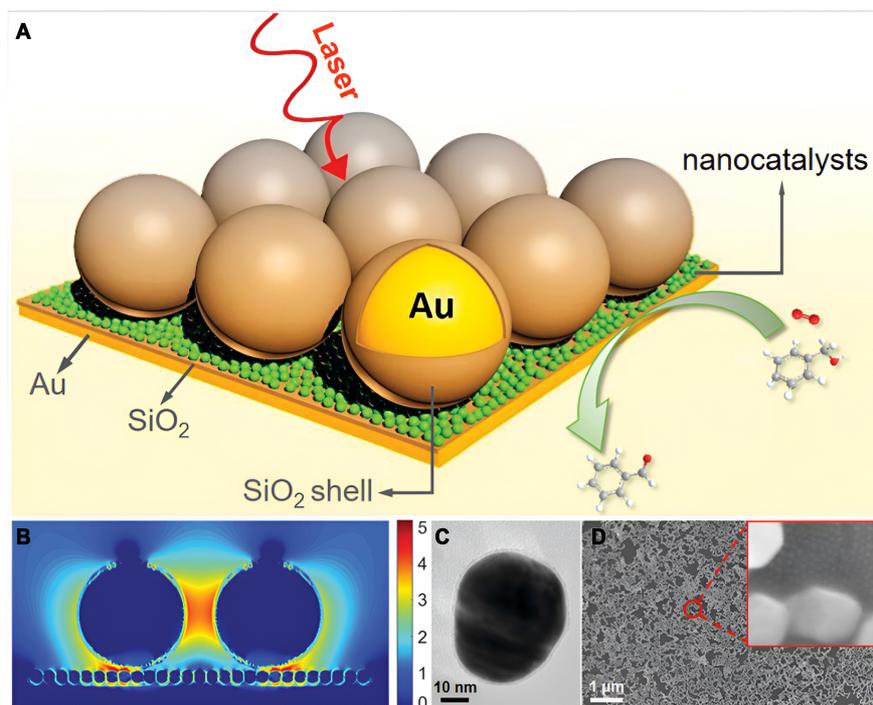
Figure 10. (A) Schematic diagram of the SHINERS-gap strategy; (B) Theoretical simulation of the SHINERS-gap configuration; (C) and (D) Morphologies of SHIN and SHINERS-gap configuration. Quoted with permission from Wei *et al.*[79]. SHINERS: Shell-isolated nanoparticle-enhanced Raman spectroscopy.
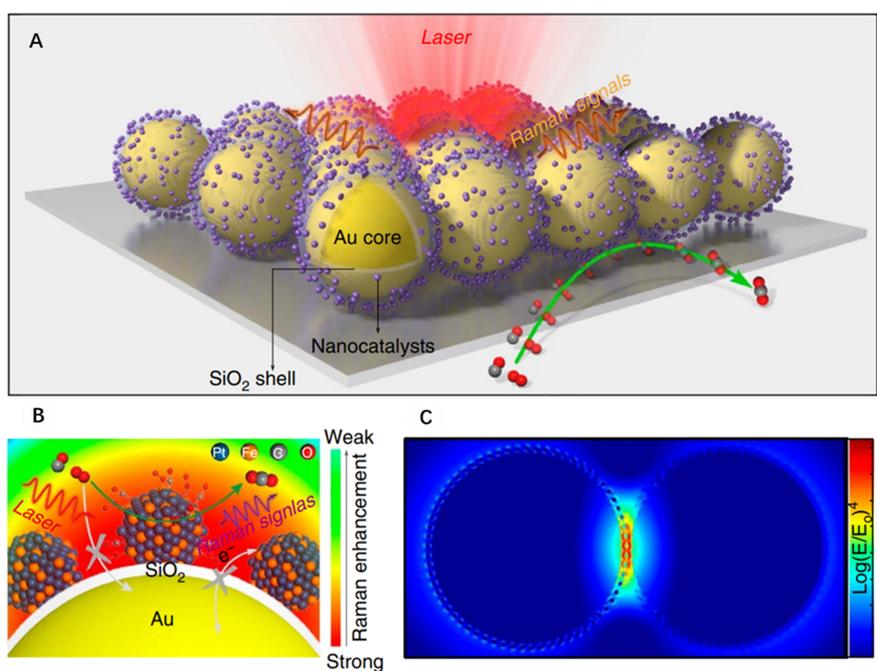

Figure 11. (A) Schematic diagram of the SHINERS-satellite strategy; (B) Schematic diagram of CO oxidation on SHINERS-satellite configuration; (C) Theoretical simulation of the SHINERS-gap configuration. Quoted with permission from Zhang *et al.*[80]. SHINERS: Shell-isolated nanoparticle-enhanced Raman spectroscopy.

rate and efficiency of the spent LIBs and discussed transforming reclaimed valuable materials into catalysts tailored to diverse catalytic applications. Moreover, we underscored the pivotal role of advanced spectroscopic characterizations, particularly surface-sensitive enhanced Raman techniques, in unraveling the intricate reaction mechanisms of both model and practical catalysts at the molecular level.

To explore the full potential of catalysis in recycling spent LIBs and harness the capabilities of advanced characterization techniques in studying catalytic reactions, several practical suggestions for future development are outlined below: (1) Currently, diverse catalytic methods have been developed with broad applicability and demonstrated efficacy in various leaching systems. To further enhance leaching efficiency, future emphasis can be placed on optimizing the pretreatment process for electrode materials. For instance, applying Joule-heat technology would enable the rapid carbothermal reduction of high valence metal compounds in a matter of seconds. This rapid reduction can substantially enhance the solubility of these compounds in the solvent, significantly improving the metal leaching rate. Furthermore, achieving green standards is imperative for the leaching system. Deep eutectic solvents (DES), marked by low cost, non-toxicity, and reusability, deserve heightened consideration. Given the vast diversity within DES systems, they are anticipated to emerge as a significant and versatile option for hydrometallurgical processes; (2) The original metal salts can be obtained through conventional pyrometallurgy and hydrometallurgy, serving as catalyst precursors or resynthesized electrode materials. However, there is a pressing need to enhance the recovery process to achieve greater energy conservation and emission reduction. It is crucial to note that any recycling method that compromises the energy storage structure is not the most energy-efficient. There is growing optimism surrounding the emerging direct recycling method, positioning it as the primary direction for environmentally conscious and energy-efficient recycling practices; (3) The purity of the catalyst precursor significantly influences its performance, with higher purity correlating to more favorable conditions for directed synthesis. For instance, refining recovered catalysts through electrometallurgy offers distinct advantages, including heightened efficiency, reduced costs, and enhanced product purity. Through meticulous control of current potential, considerable purification of precipitates can be achieved. Notably, despite its potential, this purification method remains underutilized, emphasizing its significance as a promising avenue for future endeavors in catalyst recovery from spent LIBs; (4) *In situ* characterization techniques are advancing to offer researchers more robust information on catalytic reactions. However, these techniques may not be ideal for practical catalytic characterization due to the inherent complexities and information-rich nature of the actual working environment. Operando characterization holds the potential to comprehensively reflect the catalytic process in a real-world scenario. The future development of operando characterization techniques can delve into the actual state of catalytic reactions, providing significant insights into catalyst reaction mechanisms, the practical catalytic environment, and failure mechanisms.

DECLARATIONS

Authors' contributions
Prepared and revised the manuscript: Sun HL, Gu Y, Xu YP, Ding L
Designed and revised the manuscript: Gu Y, Li JF

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