nature nanotechnology

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https://doi.org/10.1038/s41565-020-00782-3

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Proton-driven transformable nanovaccine for cancer immunotherapy

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Cancer vaccines hold great promise for improved cancer treatment. However, endosomal trapping and low immunogenicity of tumour antigens usually limit the efficiency of vaccination strategies. Here, we present a proton-driven nanotransformer-based vaccine, comprising a polymer–peptide conjugate-based nanotransformer and loaded antigenic peptide. The nanotransformer-based vaccine induces a strong immune response without substantial systemic toxicity. In the acidic endosomal environment, the nanotransformer-based vaccine undergoes a dramatic morphological change from nanospheres (about 100 nanometres in diameter) into nanosheets (several micrometres in length or width), which mechanically disrupts the endosomal membrane and directly delivers the antigenic peptide into the cytoplasm. The re-assembled nanosheets also boost tumour immunity via activation of specific inflammation pathways. The nanotransformer-based vaccine effectively inhibits tumour growth in the B16F10-OVA and human papilloma virus-E6/E7 tumour models in mice. Moreover, combining the nanotransformer-based vaccine with anti-PD-L1 antibodies results in over 83 days of survival and in about half of the mice produces complete tumour regression in the B16F10 model. This proton-driven transformable nanovaccine offers a robust and safe strategy for cancer immunotherapy.

Cancer vaccines that aim to stimulate tumour-specific immunity hold promise for tumour treatment[1–4]. Cytosolic delivery of appropriate tumour antigens, stimulation of the innate immune system, and cross-presentation of tumour antigens by antigen-presenting cells are essential for inducing strong tumour-specific immunity[1,5]. Nanocarrier systems are promising non-viral agents with which to facilitate cytosolic delivery of many different cargos. Strategies including the use of 'proton sponge' polymers[6,7], cell-penetrating peptides[8–10], charge-reversible molecules[11–13] and pore-formation molecules[14–17] have been developed to promote the cytosolic delivery of vaccines[18–20]. In addition, co-delivery of a tumour antigen and an adjuvant in a single nanoparticle has been achieved to boost the poor immunogenicity of the tumour antigen[21–23]. Despite these advances in the field, development of highly efficient antitumour vaccines—especially personalized vaccines that can potently induce T cell priming in humans—is still a challenge[24,25].

Here we report on a proton-driven nanotransformer-based vaccine (NTV) (Fig. 1). The NTV is comprised of a polymer–peptide conjugate-based nanotransformer (NT), along with a loaded antigenic peptide (AP). In acidic media, the particles transform into bigger structures, which causes endosomal membrane disruption and thus cytosolic delivery of the AP. Endosomal membrane integrity and dendritic cell (DC) maturation were analysed after NTV treatment in vitro. Lymph-node-trafficking of NTV and the elicitation of tumour-specific $CD8^+$ T-cells were investigated in vivo. OT-I mice were used to evaluate the antigen-specific T-cell proliferation in vivo. An in vivo killing assay was also exploited to assess the antigen-specific killing induced by the vaccine. The antitumour efficiency of NTV was evaluated in three tumour models (B16F10-OVA, the human papillomavirus (HPV)-E6/E7 tumour model and the B16F10 neoantigen model). Finally, we investigated the effect of combined administration of the neoantigen-loaded NT with anti-PD-L1. All these experiments reveal that the proton-driven transformable nanovaccine induces a robust and safe antitumour immunity.

Synthesis and characterization of the NTV

A schematic illustration of the synthesis of a representative NT is shown in Fig. 1a,b and Supplementary Fig. 1. p($DMAEMA_{22}$-$OGEMA_4$)-*b*-p($MAVE)_{30}$ was synthesized using reversible addition-fragmentation chain transfer polymerization[26] (Supplementary Fig. 2). Naphthalene-conjugated D-peptide (NDP) forms nanofibres in cells[27]. We found that when naphthalene was replaced with pyrene to give pyrene-conjugated D-peptide (PDP), we obtained nanosheets in water (Supplementary Fig. 3 and 4). This may be because PDP has a larger aromatic structure than the NDP, which may induce stronger π–π stacking interactions among molecules. We then developed two kinds of NT based on NDP and PDP. Different amounts of hydroxylated NDP

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ARTICLES
https://doi.org/10.1038/s41589-022-01074-8
nature chemical biology

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A modification-centric assessment tool for the performance of chemoproteomic probes

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Chemoproteomics has emerged as a key technology to expand the functional space in complex proteomes for probing fundamental biology and for discovering new small-molecule-based therapies. Here we report a modification-centric computational tool termed pChem to provide a streamlined pipeline for unbiased performance assessment of chemoproteomic probes. The pipeline starts with an experimental setting for isotopically coding probe-derived modifications that can be automatically recognized by pChem, with masses accurately calculated and sites precisely localized. pChem exports on-demand reports by scoring the profiling efficiency, modification homogeneity and proteome-wide residue selectivity of a tested probe. The performance and robustness of pChem were benchmarked by applying it to eighteen bioorthogonal probes. These analyses reveal that the formation of unexpected probe-derived modifications can be driven by endogenous reactive metabolites (for example, bioactive aldehydes and glutathione). pChem is a powerful and user-friendly tool that aims to facilitate the development of probes for the ever-growing field of chemoproteomics.

Chemical probe coupled with mass spectrometry (MS)-based proteomics, herein termed chemoproteomics, offers versatile tools to globally profile protein features and to systematically interrogate the mode of action of small molecules in a native biological system[1]. For instance, bioorthogonal probes surrogating endogenous metabolites (for example, sugars and lipids) enable the proteome-wide mapping of post-translational modifications (PTMs) on specific amino acid residues[2]. In addition, various activity-based protein profiling (ABPP) probes have been developed by targeting amino acid residues including cysteine, lysine, tyrosine, methionine, histidine, aspartate, and glutamate, as well as their PTM forms, which greatly expand the chemical space in complex proteomes for probing fundamental biology and for discovering new small-molecule-based therapies[3].

Nonetheless, the development of an efficient and selective probe for chemoproteomics can still be challenging. It is particularly difficult to unbiasedly assess its chemoselectivity at a proteome-wide scale, since a chemical probe displaying selectivity well-characterized in vitro would possibly generate unexpected modifications owing to potential cross-reactivity in complex biological systems. In addition, unforeseeable probe-derived modifications (PDMs) may yield during sample preparation or in-source MS fragmentation, thereby causing inhomogeneous modifications on the same sites and complicating data analysis.

Notably, the last decade has witnessed tremendous progress in the development of blind search informatic tools[4]. Such tools, in combination with isotope-coding approaches for probes (Supplementary Fig. 1), can provide an unbiased survey of PDMs that can be distinguished from unmodified or endogenously modified ones, considering that only those peptides bearing PDMs would yield an isotopic MS signature (Fig. 1a). For example, we have previously used this pipeline (that is, TagRecon for blind search[5]) to substantiate the performance of several newly developed chemoselective probes for proteomic mapping of cysteine redox forms[6,7]. The pipeline also allowed us to uncover unexpected PTMs being captured by chemoproteomic probes in situ[8,9]. Most recently, Hacker and coworkers have applied a similar pipeline (that is, MSFragger for blind search[10]) to systematically investigate the proteome-wide selectivity of diverse electrophilic probes[11]. These studies underscore the power of blind search tools, which provide an ideal means to unbiasedly assess the proteome-wide residue selectivity of a probe and to uncover new chemotypes in the proteome.

Despite these advances, a set of challenges have emerged. First, most blind search tools cannot automatically unify the localization probability (or residue selectivity) and accurate masses of PDMs, as most of them only offer identification and site localization at the peptide-spectrum match (PSM) level. Second, no available tools can automatically distinguish isotopically coded PDMs from non-probed ones, while manual evaluation of dozens to hundreds of mass shifts can be a daunting task. Last but not the least, for probe developers—even those with substantial bioinformatics expertise—managing the existing tools can be tedious, as all require laborious installation and setup, and output many redundant information rather than on-demand reports.

The challenges discussed above have therefore inspired us to develop an automated, user-friendly, fit-for-purpose computational tool for the ever-growing field of chemoproteomics. Here we present pChem, a modification-centric blind search and summarization tool to provide a pipeline for rapid and unbiased assessment of the performance of ABPP and metabolic labeling probes. This pipeline starts experimentally by isotopic coding of PDMs, which can be automatically recognized, paired, and accurately reported by pChem, further allowing users to score the profiling efficiency,

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nature communications

Article

https://doi.org/10.1038/s41467-024-46287-8

Water-dispersible X-ray scintillators enabling coating and blending with polymer materials for multiple applications

Received: 6 June 2023

Accepted: 21 February 2024

Published online: 06 March 2024

Check for updates

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Developing X-ray scintillators that are water-dispersible, compatible with polymeric matrices, and processable to flexible substrates is an important challenge. Herein, Tb^{3+}-doped $Na_5Lu_9F_{32}$ is introduced as an X-ray scintillating material with steady-state X-ray light yields of 15,800 photons MeV^{-1}, which is generated as nanocrystals on halloysite nanotubes. The obtained product exhibits good water-dispersibility and highly sensitive luminescence to X-rays. It is deposited onto a polyurethane foam to afford a composite foam material with dose-dependent radioluminescence. Moreover, the product is dispersed into polymer matrixes in aqueous solution to prepare rigid or flexible scintillator screen for X-ray imaging. As a third example, it is incorporated multilayer hydrogels for information camouflage and multilevel encryption. Encrypted information can be recognized only by X-ray irradiation, while the false information is read out under UV light. Altogether, we demonstrate that the water-dispersible scintillators are highly promising for aqueous processing of radioluminescent, X-ray imaging, and information encrypting materials.

X-ray scintillators have emerged as excellent light emitting radioluminescent materials, which can convert high energy X-ray radiations into visible or near visible light that may be further captured and converted into visual information or electrical signals by a photomultiplier[1–3]. Such attractive characteristics make X-ray scintillators promising materials for applications in the fields of X-ray detectors[4], space exploration[5], medical imaging[6], light-emitting diodes[7], and radiation exposure monitoring[8]. Straightforward incorporation of X-ray scintillators into polymeric materials would represent a huge breakthrough in organic-inorganic composite materials, which is quite beneficial to mount multi-components[9], satisfy the requirement of flexible screens[10], and extend their application in a wider range of fields[11,12]. Despite many kinds of X-ray scintillators have been reported in past decades[13,14] and the light yield has been improved to a great extent (Supplementary Tables 1 and 2), developing X-ray scintillators as polymer composite materials is still full of difficulties and challenges. Even though some single crystals exhibit high light yields (Supplementary Table 1), the harsh growth conditions, non-flexibility, and high fabrication cost limited their application to conventional hard devices. The poor water-dispersibility of X-ray scintillating crystals and particles also results in limited processability in water. Moreover, aggregation of inorganic particles is commonly observed leading to microphase separation and inhomogeneous composites with compromised performance. The toxicity of lead and unpredicted thermal quenching effects of perovskite-based X-ray scintillators (Supplementary Table 2) are remaining challenges[15–18]. Organic X-ray scintillators have also been developed in recent research[19], but usually suffer from a limited effective atomic number[20]

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nature communications

Article

https://doi.org/10.1038/s41467-024-47559-z

X-ray-activated polymerization expanding the frontiers of deep-tissue hydrogel formation

Received: 2 July 2023

Accepted: 4 April 2024

Published online: 15 April 2024

Check for updates

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Photo-crosslinking polymerization stands as a fundamental pillar in the domains of chemistry, biology, and medicine. Yet, prevailing strategies heavily rely on ultraviolet/visible (UV/Vis) light to elicit in situ crosslinking. The inherent perils associated with UV radiation, namely the potential for DNA damage, coupled with the limited depth of tissue penetration exhibited by UV/Vis light, severely restrict the scope of photo-crosslinking within living organisms. Although near-infrared light has been explored as an external excitation source, enabling partial mitigation of these constraints, its penetration depth remains insufficient, particularly within bone tissues. In this study, we introduce an approach employing X-ray activation for deep-tissue hydrogel formation, surpassing all previous boundaries. Our approach harnesses a low-dose X-ray-activated persistent luminescent phosphor, triggering on demand in situ photo-crosslinking reactions and enabling the formation of hydrogels in male rats. A breakthrough of our method lies in its capability to penetrate deep even within thick bovine bone, demonstrating unmatched potential for bone penetration. By extending the reach of hydrogel formation within such formidable depths, our study represents an advancement in the field. This application of X-ray-activated polymerization enables precise and safe deep-tissue photo-crosslinking hydrogel formation, with profound implications for a multitude of disciplines.

Photo-crosslinking has emerged as a powerful technique for fabricating three-dimensional polymer networks with broad applications across diverse fields, including biomedicine[1–4]. It offers precise spatial and temporal control over hydrogel synthesis, making it invaluable for wound healing[5,6], drug delivery[7], tissue repair[8–10], bioengineering[11], and bioimaging[12]. The hallmark advantage lies in the ability to trigger polymerization on-demand using light, enabling highly controlled synthesis[13,14]. However, the current approach relies on ultraviolet/visible (UV/Vis) light (200 ~ 780 nm) for activation, which poses significant limitations[15–18]. UV/Vis light exhibits restricted tissue penetration, typically reaching only a few millimeters[19], thus severely hampering its utility in biological systems. Moreover, concerns surrounding DNA damage associated with UV light raise critical safety considerations, particularly for patient applications[20]. Recent attempts have explored the use of near-infrared (NIR) light with longer wavelengths to enhance penetration depth to some extent[21–23]. There are

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nature communications

Article

https://doi.org/10.1038/s41467-022-33920-7

Lactose azocalixarene drug delivery system for the treatment of multidrug-resistant pseudomonas aeruginosa infected diabetic ulcer

Received: 8 May 2022

Accepted: 6 October 2022

Published online: 21 October 2022

Check for updates

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Diabetic wound is one of the most intractable chronic wounds that is prone to bacterial infection. Hypoxia is an important feature in its microenvironment. However, it is challenging for antimicrobial therapy to directly apply the existing hypoxia-responsive drug delivery systems due to the active targeting deficiency and the biofilm obstacle. Herein, we customizes a hypoxia-responsive carrier, lactose-modified azocalix[4]arene (LacAC4A) with the ability to actively target and inhibit biofilm. By loading ciprofloxacin (Cip), the resultant supramolecular nanoformulation Cip@LacAC4A demonstrates enhanced antibacterial efficacy resulting from both the increased drug accumulation and the controlled release at the site of infection. When applied on diabetic wounds together with multidrug-resistant *Pseudomonas aeruginosa* infection in vivo, Cip@LacAC4A induces definitely less inflammatory infiltration than free Cip, which translates into high wound healing performance. Importantly, such design principle provides a direction for developing antimicrobial drug delivery systems.

Diabetic wound, which is vulnerable to hyperglycemia[1] and the microenvironment of oxidative wound[2,3], is one of the chronic wounds that are difficult to heal. Moreover, the diabetic wound is susceptible to bacteria, then further aggravates the wound healing[4–6]. Compared with normal tissues, bacterial infections often touch off a series of changes in microenvironments including hypoxia[7,8], lower pH[9,10], reactive oxygen species (ROS)[11,12], toxins[13], enzymes[14], temperature[15], etc. These microenvironment characteristics have been engaged in targeted antibacterial therapy by developing the corresponding drug delivery systems (DDSs) that respond to these stimuli, primarily focused on pH and ROS[16–18]. The DDSs improved the bioavailability of antibiotics and reduced antibiotic resistance pronouncedly[19–22]. Oxygen deficiency at the bacterial infectious site leads to anaerobic glycolysis and an increase in the local acidity[23], overexpression of the reductive enzymes (azoreductase[24–26], nitroreductase[27–29], and so on), increased temperature[30], and elevated ROS level[31]. Moreover, the hypoxic characteristics of bacterial infections and the resulting strongly reductive environment constitute an important alternative target for antibacterial treatment. Therefore, it is highly in demand to develop a hypoxia-responsive DDS for antibacterial treatment as well

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Near-Infrared Light and Acid/Base Dual-Regulated Polymerization Utilizing Imidazole-Anion-Fused Perylene Diimides as Photocatalysts

Qihui Ti, Liping Fang,* Weihe Zhao, Libin Bai, Hongchi Zhao, Xinwu Ba, and Weiping Chen*

Cite This: J. Am. Chem. Soc. 2023, 145, 26160−26168
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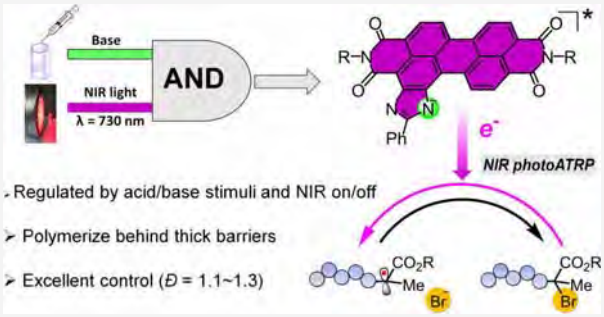
ABSTRACT: This work presents the first example of acid/base-responsive and near-infrared (NIR)-absorbing photocatalysts based on imidazole-anion-fused perylene diimide chromophores. The photocatalysts were in situ generated by deprotonation of imidazole-fused perylene diimide under an alkaline environment. NIR (λ = 730 nm, 128 mW/cm^2) photoinduced atom transfer radical polymerization (ATRP) was implemented, exhibiting high efficiency and excellent livingness under ppm level of photocatalysts (15 ppm relative to monomer) and Cu(II) complex (10 ppm relative to monomer) concentrations. The method showed capabilities to polymerize behind opaque barriers (i.e., paper and pig skin) and under aerobic condition. Notably, this work demonstrated a dual temporal control of polymerization by adding weak base/acid and switching NIR light on/off. The polymerization can even be halted by bubbling CO_2 and was then fully recovered by adding triethylamine. The NIR photoATRP of acrylamide monomers in aqueous solution was also performed, which can be regulated by the change of pH.



1. INTRODUCTION

The growth of macromolecules in organisms is stimulated by specific triggers.[1,2] In an effort to simulate this natural process, researchers have sought to regulate polymerization "on" and "off" on demand by utilizing external stimuli.[3−11] This has opened a new way to exert spatial and temporal control over polymerization and, moreover, increase complexity of the polymer architecture and microstructure.[12−30] The development of physical- or chemical-switchable catalysts has garnered most attention.[3−30] However, current state-of-the-art catalysts rely primarily on single stimulus including temperature,[5,6] pH,[7−10] light,[22−24] applied voltage,[25,26] mechanical force,[26−28] or chemical reagents.[29,30] There is a scarcity of "biolike" polymerization that can be regulated by dual or multiple stimuli.[12−33]

Utilizing light as both regulator and trigger has become a popular method for polymer synthesis due to its ubiquity, noninvasive nature, and adjustable spectra/energy.[34−42] In particular, photoinduced reversible deactivation radical polymerization involving organic photocatalysts (PCs) has been extensively studied, including photoinduced atom transfer radical polymerization (photoATRP) and photoinduced electron/energy transfer-reversible addition−fragmentation chain transfer (PET-RAFT) polymerization.[43−52] The dormant polymer chains are activated by the photoexcited organic photocatalyst via electron/energy transfer, generating propagating radical species.[43−46] The radical species undergo deactivation via back-electron transfer to establish an activation−deactivation equilibrium. This enables the polymerization to be halted by simply switching the light irradiation off. Furthermore, there is significant potential to access the switchable photocatalyst system through rational molecular design, thus realizing dual/multiple-regulated polymerization based on light and other stimuli.[47−50] In pioneering works, Johnson et al. presented the heat/light dual-regulated PET-RAFT polymerization using thermally responsive gels that covalently embed 10-phenylphenothiazine as photocatalysts.[10] Boyer et al. employed zinc(II) tetra (4-sulfonatophenyl) porphyrin as a photocatalyst for PET-RAFT polymerization in aqueous solution, which demonstrated distinct polymerization rates under different pH conditions.[12] Later, they discovered a highly pH-sensitive photocatalyst based on halogenated xanthene, enabling pH/light dual-regulated PET-RAFT polymerization.[13] Martell et al. covalently embedded a photocatalyst and a quencher into DNA aptamers.[49] The DNA changed the secondary structure in response to complementary DNA and a range of chemical stimuli, bringing the photo-

Received: August 5, 2023
Revised: November 14, 2023
Accepted: November 15, 2023
Published: November 24, 2023

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Photothermocatalytic Wet Reforming of Waste Plastics to Syngas

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Cite This: J. Am. Chem. Soc. 2025, 147, 9879−9890
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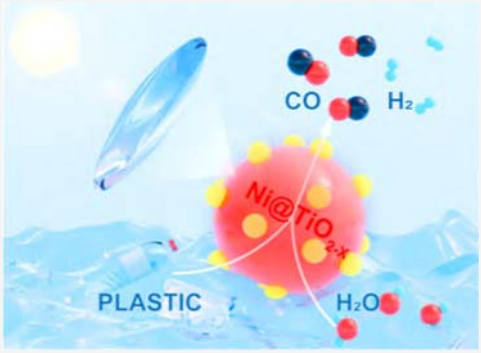
ABSTRACT: The increasing accumulation of plastic waste in the environment poses a serious threat to the ecosystem and health sector, urging us to develop sustainable strategies to tackle this issue. Converting plastic waste into platform chemicals using sustainable energy and primary resources can mitigate environmental pollution and reduce CO_2 emissions. In this study, polyolefins were transformed into syngas through a wet reforming process over a nickel-supported oxygen vacancy-rich titanium dioxide (Ni/TiO_{2-x}) catalyst with water as the reactant under light irradiation. The focused light irradiation can readily increase the temperature in the reactor for the dehydrogenation and degradation of polyethylene (PE) to occur, followed by the wet reforming of PE-derived compounds and gaseous hydrocarbons to syngas. Additionally, the transfer of electrons from TiO_{2-x} to the nickel components under light irradiation facilitates the aforementioned reactions. The current work presents a sustainable strategy for valorization of plastic waste to syngas, serving as a platform feedstock for the subsequent production of various chemicals.



INTRODUCTION

Plastics have become ubiquitous in our daily lives since the 1950s due to their affordability, convenience, durability, and ease of processing.[1,2] However, the inherent ultrastability and low recycling efficiency of plastic waste present significant challenges because of the sluggish natural degradation rate and associated environmental threat.[3] This discrepancy has resulted in a rapid accumulation of plastic waste, leading to environmental crises and posing a threat to human health.[4] Statistics indicate that a total of 10.5 billion tons of plastics has been produced since their inception, with an annual growth rate of approximately 380 million tons.[5] Moreover, it is estimated that the plastic production will exceed 1.1 billion tons per year by 2050.[6] Despite the staggering amount of plastic production, only a small portion of the plastics is effectively recycled. The majority of plastic waste ends up in landfills or incineration, leading to the inevitable environmental pollution.[7,8] Therefore, there is a growing need for recycling and upcycling of plastic waste to promote sustainable development.

Currently, mechanical recycling is widely used for plastic recycling due to its low cost and ease of operation.[9] However, this method often results in the production of lower value plastic products with inferior properties. Considering the abundance of CH_2 or CH units in the polymer backbone, chemical recycling is considered as a promising alternative that can transform plastic wastes into high-value products.[10] Pyrolysis and hydrogenolysis have traditionally been the most commonly adopted chemical recycling technologies.[11−15] Nonetheless, these approaches face challenges such as high energy consumption, the generation of liquid and solid wastes, and unpredictable product distribution, which greatly limit their practical applications. Therefore, it is imperative to explore sustainable and low-carbon-emission strategies for effectively converting plastic waste into high-value products. Recently, photocatalytic degradation has emerged as a novel approach for treating plastic wastes by utilizing sunlight as the renewable energy source.[16] For instance, the Reisner group utilized CdS/CdO_x quantum dots to degrade various plastic wastes into H_2 and valuable organic products.[17] Additionally, Luo et al. developed a photothermal reaction system and successfully converted LDPE into H_2 and jet fuel with the assistance of a Ni−Ti−Al catalyst.[18]

Syngas, which consists primarily of H_2 and CO, can serve as a raw material for the production of versatile fuels and chemical intermediates such as methanol, ethanol, etc.[19,20] However, the production of syngas typically involves the high-temperature and high-pressure dry or wet reforming of fossil feedstock.[21] Alternatively, with solar irradiation as renewable energy, producing syngas from plastic waste instead of a fossil reserve serves as a promising and efficient approach to recycling plastic waste and conserving valuable fossil resources.

Herein, we propose an environmentally friendly approach to achieve the wet reforming of plastics for syngas production using nickel-supported oxygen vacancy-rich titanium dioxide as the catalyst. With the light irradiation as the sole energy input,

Received: January 13, 2025
Revised: February 20, 2025
Accepted: February 21, 2025
Published: February 28, 2025

https://doi.org/10.1021/jacs.5c00620
J. Am. Chem. Soc. 2025, 147, 9879−9890

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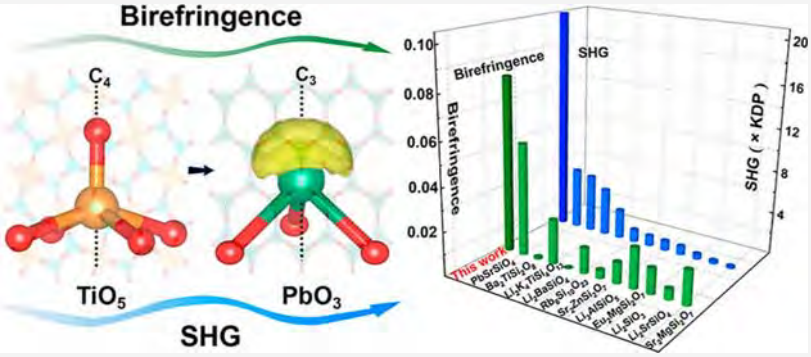
Stereochemically Active Lone-Pair Containing Metal Substitution in Polar Axis toward a Giant Phase-Matchable Optical Nonlinear Silicate Crystal $Li_3(OH)PbSiO_4$

Yuanyu Yang,[⊥] Yan Xiao,[⊥] Bingxuan Li, Yi-Gang Chen,* Penghui Guo, Bingbing Zhang,* and Xian-Ming Zhang*

Cite This: J. Am. Chem. Soc. 2023, 145, 22577−22583



ABSTRACT: Atoms in special lattice sites can play a crucial role in realizing materials properties, which is long pursued but difficult to control. Herein, by adopting a stereochemically active lone-pair-containing metal substitution strategy, a nonlinear-optical (NLO) silicate crystal $Li_3(OH)PbSiO_4$ was successfully synthesized, featuring $[PbSiO_4]_\infty$ layers with the perfect orientation of the stereochemically active lone-pair Pb(II) cation in the polar-axis lattice. $Li_3(OH)PbSiO_4$ overcomes the long-standing problem of silicates, that is, poor nonlinear properties because it exhibits both the largest birefringence of 0.082 and the largest phase-matchable second-harmonic-generation (SHG) efficiency of 21 × KDP among the known silicates. The successful polar-axis lattice substitution could offer a new direction for realizing the rational control of materials structures and properties.

INTRODUCTION

Nonlinear-optical (NLO) crystal materials with the second-harmonic-generation (SHG) effect have high scientific and industrial significance which can offer the key functions of laser frequency conversion, electro-optic effect, generation of entangled photon pairs, etc.[1−9] NLO materials with a high laser conversion efficiency require not only a large SHG effect but also phase-matching properties. The anionic group theory points out that macroscopic SHG coefficients are the geometrical superposition of microscopic second-order susceptibilities. It indicates that uniformly aligned anionic groups with a large microscopic hyperpolarizability can give rise to a large SHG effect.[10−15] Phase-matching of SHG is extremely sensitive to birefringence properties of a crystal. The large birefringence is closely related to the large polarizability anisotropy of anionic groups. However, combining multiple interrelated performances, including a large SHG, a large birefringence, and a wide band gap, in one crystal is a huge challenge because of the difficulty in controlling the microstructure in crystal engineering.

Silicate is an attractive system for ultraviolet (UV) NLO crystal materials. The SiO_4 tetrahedron as a fundamental building group in silicates has high UV transmittance ability because of the strong electron-binding energy of Si−O σ-bonds. However, it is also known that silicates suffer from both the small SHG effect and small birefringence due to nonpolar T_d symmetry of the rigid SiO_4 tetrahedron. In order to improve the optical nonlinear properties, introducing a d^0 transition metal with large polarizability and polarizability anisotropy is currently an effective strategy, and it has been applied in crystals, such as $Li_2K_4TiSi_4O_{13}$ (4.5 × KDP (KH_2PO_4), 0.021@1064 nm),[16] $Li_2Rb_4TiSi_4O_{13}$ (4.5 × KDP, 0.018@1064 nm),[16] and $Ba_2TiSi_2O_8$.[18−20] However, they exhibit a small birefringence. Among them, fresnoite $Ba_2TiSi_2O_8$ is a

Received: July 15, 2023
Published: October 9, 2023

https://doi.org/10.1021/jacs.3c07547
J. Am. Chem. Soc. 2023, 145, 22577−22583

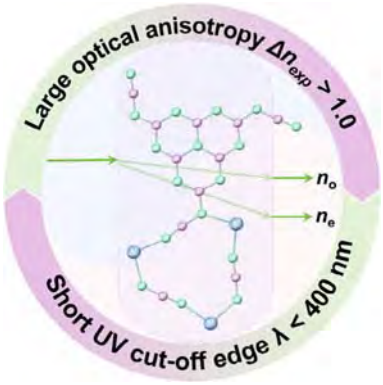
Research Article

NLO Materials

D. Dou, C. Wei, B. Zhang, D. Yang, Y. Wang* —— **e202504761**

Ultra-High Optical Anisotropy with UV Transmission Achieved by Rational Arrangement of Extended π-Conjugated Groups

A UV organic–inorganic hybrid birefringent material with large optical anisotropy has been prepared by employing the strategy of appropriately aligned extended π-conjugated groups.



Zitierweise: *Angew. Chem. Int. Ed.* **2023**, *62*, e202304444
doi.org/10.1002/anie.202304444

Zn Metal Batteries | Hot Paper

In-Situ Integration of a Hydrophobic and Fast-Zn^{2+}-Conductive Inorganic Interphase to Stabilize Zn Metal Anodes

Mengyu Liu[+], Wentao Yuan[+], Guoqiang Ma, Kaiyue Qiu, Xueyu Nie, Yongchang Liu, Shigang Shen, and Ning Zhang**

Abstract: The irreversible issues of Zn anode stemming from dendrite growth and water-induced erosion have severely hindered the commercialization of rechargeable aqueous Zn batteries. Herein, a hydrophobic and fast-Zn^{2+}-conductive zinc hexacyanoferrate (HB-ZnHCF) interphase layer is in situ integrated on Zn by a rapid room-temperature wet-chemistry method to address these dilemmas. Different from currently proposed hydrophilic inorganic cases, the hydrophobic and compact HB-ZnHCF interphase effectively prevents the access of water molecules to Zn surface, thus avoiding H_2 evolution and Zn corrosion. Moreover, the HB-ZnHCF with large internal ion channels, strong zincophilicity, and high Zn^{2+} transference number (0.86) permits fast Zn^{2+} transport and enables smooth Zn deposition. Remarkably, the resultant HB-ZnHCF@Zn electrode delivers unprecedented reversibility with 99.88 % Coulombic efficiency over 3000 cycles, realizes long-term cycling over 5800 h (>8 months, 1 mA cm^{-2}) and 1000 h (10 mA cm^{-2}), and assures the stable operation of full Zn battery with both coin- and pouch-type configurations.

Introduction

Metallic zinc (Zn) features a high theoretical specific capacity (820 mAh g^{-1}; 5855 mAh cm^{-3}), natural abundance, and intrinsic safety in water, making it an ideal anode material for aqueous batteries.[1] Primary alkaline batteries with Zn metal anode (e.g., alkaline Zn-MnO_2 battery) are centuries-old technologies and are still widely used in portable devices. In recent years, rechargeable aqueous Zn batteries (RAZBs) are emerging as promising grid-scale energy storage devices by virtue of their high safety, easy fabrication, and cost efficiency.[2] Although significant advances have been achieved in the exploration of cathode materials, the industrialization of RAZBs is still limited by the poor reversibility facing conventional Zn anodes associated with the notorious dendrite growth and the water-induced erosion (e.g., H_2 evolution reaction (HER) and Zn corrosion).[3] Strategies for tackling the irreversible issues of Zn anodes have been proposed mainly involving regulating electrolyte compositions,[4] designing host structures,[5] and modifying separators.[6]

Constructing an artificial solid electrolyte interphase (ASEI) layer on Zn is also an important approach to modulate Zn^{2+} plating chemistry.[7] The ASEI materials including inorganics (e.g., TiO_2,[8] $CaCO_3$,[9] ZnF_2,[10] $BaTiO_3$,[11] $ZnSiO_3$,[12] Mxene,[13] zeolite molecular sieve,[14] etc.) and organics (e.g., polyamide,[15] sulfonic acid polymer,[16] metal organic frameworks,[17] covalent organic frameworks,[18] etc.) have been developed to suppress Zn dendrite growth. Compared with the apparent dendrite issue, the effect of water-induced erosion plays a quite concealed but very critical role in determining the performance of Zn anodes. The state-of-the-art inorganic-based ASEI layers are hydrophilic and H_2O molecules are prone to transport through their pores and/or gaps between particles/flakes onto Zn. In this regard, the water-induced H_2 evolution inevitably occurs during long-term cycling and it would corrode the Zn surface, loosen the contact between ASEI and Zn, and initiate the formation of hydroxide-based by-products, resulting in the detachment of protective layers from Zn surface and low Coulombic efficiency (CE) of Zn^{2+} plating/stripping.[5b,19] Although some hydrophobic organic films can inhibit the access of water to Zn surface,[19a,20] they generally show poor ionic conductivity and large interfacial resistance. On the other hand, most ASEI layers rely on ex situ physical preparation methods (e.g., doctor blading or spin coating),[8–10,11,14b,21] which suffer from cracking or detaching from Zn surface due to poor adhesion, especially at deep cycling conditions. Moreover, additional binders are required for inorganic materials and the coating thickness is often up to tens of micrometers, which would obstruct the mass transport and increase the non-active weight of Zn electrode.[12] Thus, the reported stable cycling of Zn with ASEI layers was usually achieved at a low current with limited areal capacity (<5 mA cm^{-2} and 3 mAh cm^{-2}), im-

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How to cite: *Angew. Chem. Int. Ed.* **2022**, *61*, e202202654
International Edition: doi.org/10.1002/anie.202202654
German Edition: doi.org/10.1002/ange.202202654

Heterogeneous Catalysis | Hot Paper

Catalytic Synthesis of Formamides by Integrating CO_2 Capture and Morpholine Formylation on Supported Iridium Catalyst

Danyang Cheng, Meng Wang, Lipeng Tang, Zirui Gao, Xuetao Qin, Yongjun Gao,* Dequan Xiao, Wu Zhou, and Ding Ma**

Abstract: Herein we report an efficient and recyclable catalytic system for tandem CO_2 capture and N-formylation to value-added chemicals. CO_2 is apt to be captured by morpholine solution, while a highly efficient heterogeneous catalyst, isolated iridium atoms supported over nanadiamond/graphene, is discovered to be highly reactive for the formylation of morpholine, leading to the formation of N-formylmorpholine with excellent productivity (with a turnover number of 5120000 in a single batch reaction) and selectivity (> 99%). In addition, the CO_2 captured by morpholine under atmospheric conditions can be converted to N-formylmorpholine with decent conversion (51%), which realizes the integration of CO_2 capture and conversion to value-added chemicals.

The rise of atmospheric CO_2 concentration and the associated global warming have prompted researchers to develop strategies for direct CO_2 capturing and fixing from both emission sources and diffuse sources like ambient air.[1] Transformation of CO_2 into value-added chemicals is a sustainable approach that complements the natural carbon cycle.[2] CO_2, a linear molecule without a dipole moment, is inert to most reaction conditions. Amines can coordinate with CO_2 to produce a carbamate intermediate by forming C–N bonds, decreasing the activation energy for the reduction of CO_2. The introduction of amine represents diagonal approaches to CO_2 chemical recycling, which combine both CO_2 conversion and C–N bond formation process.[3]

Formamides are a class of chemicals with widespread applications in industry as raw materials and solvents for synthesis.[4] Industrially, formamides (such as N,N-dimethylformamide) are produced by $NaOCH_3$-catalyzed reaction of amines with toxic and flammable CO in methanol.[5] The hydrogenation of CO_2 into formamides has been investigated as a promising route over the past decade,[6] and significant progresses including enhanced activity, improved overall yield, mild reaction conditions, recyclable catalysts have been made using both homogeneous and heterogeneous catalytic systems. In 2015, Ding et al.[7] demonstrated a Ru/PNP pincer complex homogeneous catalyst for the preparation of N-formylmorpholine with a turnover number (TON) of 1940000. Since a heterogeneous catalytic system could benefit product isolation and catalyst recoverability, Tu developed a series of linear N-heterocyclic carbene iridium coordinated polymers (POMP-NHC-Ir) for synthesizing N,N-dimethylformamide (DMF) with a TON of 1580000.[8] Despite these remarkable achievements, however, high pressure CO_2 is needed, implying that the CO_2 from the industrial exhaust or atmosphere cannot be used as C1 source directly and thus the energy issue in CO_2 capture and separation still remains.[9] Although several process for CO_2 removal from the atmosphere have been well-established, the really technological challenge consists of concentrating and compressing CO_2 with efficient use of non-fossil energy sources.[10]

Integrating CO_2 capture and transformation into one process, wherein the captured CO_2 can be directly converted to value-added chemicals, is an attractive route as it can bypass otherwise intermediary and energy-intensive desorption/compression steps to produce pure CO_2.[11] Morpholine is an amine well known for CO_2 capture, as it shows high CO_2 absorption rate (three times higher than the traditional monoethanolamine[12]) and low maximum estimated stripper temperature.[13]

Herein, we use morpholine as a CO_2 capture and also formylation reagent to participate in CO_2 capture and transformation simultaneously. The captured CO_2 was subsequently converted in situ into N-formylmorpholine over an iridium catalyst supported over nanodiamond/graphene hybrid (Ir/ND@G). The CO_2 consumption rate reached 3.2 $mol_{CO_2}\ mol_{Ir}^{-1}\ s^{-1}$ over atomically dispersed Ir_1

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How to cite: *Angew. Chem. Int. Ed.* **2022,** *61,* e202114817
International Edition: doi.org/10.1002/anie.202114817
German Edition: doi.org/10.1002/ange.202114817

Heterogeneous Catalysis

Highly Efficient Conversion of Propargylic Alcohols and Propargylic Amines with CO_2 Activated by Noble-Metal-Free Catalyst Cu_2O@ZIF-8

Ai-Ling Gu[+], Ya-Xin Zhang[+], Zhi-Lei Wu, Hui-Ya Cui, Tian-Ding Hu,* and Bin Zhao**

Abstract: The cyclization reactions of propargylic alcohols and propargylic amines with CO_2 are important in industrial applications, but it was a great challenge that non-noble-metal catalysts catalyzed both reactions under mild conditions. Herein, the catalyst Cu_2O@ZIF-8 was prepared by encapsulating Cu_2O nanoparticles into robust ZIF-8, and it can effectively catalyze the cyclization of both propargylic alcohols and propargylic amines with CO_2 into valuable α-alkylidene cyclic carbonates and oxazolidinones with turnover numbers (TONs) of 12.1 and 19.6, which can be recycled at least five times. The mechanisms were further uncovered by NMR, FTIR, ^{13}C isotope-labeling experiments and DFT calculations, in which Cu_2O and DBU can synergistically activate the C≡C bond and the hydroxy/amino group of substrates. Importantly, it is the first example of a noble-metal-free catalyst that can catalyze both propargylic alcohols and propargylic amines with CO_2 simultaneously.

Introduction

Carbon dioxide, as the main component of greenhouse gases, has attracted much attention as its rapid accumulation in the atmosphere causes a series of environmental problems.[1] Therefore, the capture and conversion of CO_2 to produce high-value products has become one of the hotspots in green chemistry, which can not only reduce the CO_2 emissions but also provide a green route for efficient utilization of CO_2 as a low cost and renewable C1-building block.[2] To date, various valuable chemicals have been obtained by constructing C–C, C–O and C–N bonds between substrates and CO_2, such as carboxylic acids,[3] carboxylic esters,[4] cyclic carbonates,[5] benzimidazoles,[6] N,N′-disubstituted ureas,[7] etc.[8] Among them, the cyclization of propargylic alcohols and propargylic amines with CO_2 are environmentally friendly and atom-economic reactions,[9] and the resulting products α-alkylidene cyclic carbonates and oxazolidinones with alkene functionality are important building blocks in organic polymer synthesis and the pharmaceutical chemistry. However, due to the high thermodynamic stability and kinetic inertness of CO_2, massive efforts have been devoted to develop effective strategies for CO_2 activation. Accordingly, many homo- and heterogeneous catalytic systems were established for these two reactions. For example, Ag salt,[10] Pd complex,[11] Ag@COF,[12] Ag^I@MOF,[13] $lnCu_4I_4$-MOF,[14] Ag-TCPE[15] are employed for promoting the conversion of CO_2 with propargylic alcohols, and $ZnCl_2(TBD)_2$,[16] CuI,[17] PdSCS,[18] TOS-Ag4,[19] Ag27-MOF[20] Ag@TpPa-1[21] have been utilized in the cyclization reaction of propargylic amines with CO_2. Nevertheless, most of them involve noble metal element and/or suffer from low-efficiency even under harsh reaction conditions (e.g., high temperature and high CO_2 pressure). Moreover, all these catalysts can be only applied in the reaction of propargylic amines or propargylic alcohols with CO_2. Impressively, a Ag^I-decorated sulfonate-MOF synthesized by the Fei group in 2018 exhibited highly efficient conversion of CO_2 with propargylic alcohols and propargylic amines.[22] Up to now, the application of non-noble metal-based heterogeneous catalysts for both reactions has never been reported. Thus, the explorations of noble-metal-free catalysts to simultaneously achieve efficient conversion of CO_2 with propargylic alcohols and propargylic amines are highly desirable, but a great challenge.

Featuring the traits of eco-friendliness, low-cost and high-activity, Cu_2O exhibits attractive application prospects in the field of heterogeneous catalysis.[23] But Cu_2O is easily oxidized and/or chemically etched especially during the catalytic reaction. This stimulates the development of

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How to cite: *Angew. Chem. Int. Ed.* **2023**, *62*, e202310408
doi.org/10.1002/anie.202310408

Fluorescent Probes

A Fluorescent Probe for Investigating the Role of Biothiols in Signaling Pathways Associated with Cerebral Ischemia-Reperfusion Injury

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Abstract: Cerebral ischemia-reperfusion injury (CIRI) is intimately associated with the redox regulation of biothiol, a crucial antioxidant marker that precludes the onset of ROS. We designed a novel fluorescent probe, **DCI-Ac-Py**, showing various physicochemical properties, such as high selectivity, exceptional signal-to-noise ratio, near-infrared (NIR) optical window, and blood–brain barrier (BBB) penetrability, for detecting biothiols in the brain. The picolinate serves as a specific recognition group that is rapidly activated by biothiol and undergoes nucleophilic substitution with the adjacent acrylic ester to yield the desired NIR probe. Additionally, the probe's lipid solubility is improved through the inclusion of halogen atoms, which aids in penetrating the BBB. Using **DCI-Ac-Py**, we investigated changes of biothiols in vivo in the brains of mice during CIRI. We found that biothiol-mediated NF-kB classical (P65-related) and nonclassical (RelB-related) pathways contribute to abundant ROS production induced by CIRI and that biothiols are involved in redox regulation. These findings provide new insights into the study of CIRI and shed light on the physiological and pathological mechanisms of biothiols in the brain.

Introduction

Stroke, an acute cerebrovascular disease, is one of three principal fatal human diseases. It is characterized by high morbidity, mortality, disability, and a high recurrence rate. Ischemic stroke accounts for about 80 % of the total number of stroke cases.[1–3] At present, reperfusion is an important measure for reversing brain injury after ischemic stroke,[4–6] but the treatment may cause secondary cell and tissue damage, called cerebral ischemia-reperfusion injury (CIRI).[7] The pathogenesis is complicated and involves the disorders of energy metabolism, oxidative stress, inflammatory reaction, and excitatory amino acid toxicity.[8–10] Among these disorders, the role of oxidative stress in CIRI has recently attracted great attention. It is related to excessively producing reactive oxygen species (ROS). Meanwhile, it also causes biologically active substance changes in varying degrees in the redox system. As an important antioxidant in organisms, biothiol is essential in studying oxidative stress in the pathogenesis of CIRI and other neurodegenerative diseases.[11–15] Because of the complex physiology and pathology of CIRI and the lack of ideal tools, the molecular mechanism remains incipient. To clarify the exact roles of biothiol in CIRI, a reliable method is needed to accurately track the level of biothiols in the brain.

Recently, fluorescence optical imaging and analysis techniques have greatly progressed in disease observation and fundamental biological studies at (sub−)cellular and small-animal scales due to high sensitivity, non-invasive nature, and convenient operation. Additionally, near-infrared (NIR) fluorescence spectroscopy has been established as a cornerstone in vivo imaging with the advantages of deeper penetration depth and lower background fluorescence. Thus, several NIR fluorescent probes have been applied to monitor biothiols in vitro and in vivo.[16–26] Given the complex structure of the brain, developing small molecules to cross the blood–brain barrier (BBB) is extremely challenging. Thus, fluorescent probes are very rare to real-time monitor biothiol changes in the brain because of the protective BBB.[27–32] This rareness severely limits studying the physiology and pathology of biothiol-mediated CIRI. Therefore, an activated, highly selective NIR fluorescent probe must be developed across the BBB to monitor biothiol in the brain. It is also crucial for further understanding the relationship between oxidative stress and brain diseases for accurately guiding imaging diagnosis and evaluating treatments.

Our previous studies have suggested the development of noticeable fluorescent probes to explore their roles in

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PNAS RESEARCH ARTICLE | ENGINEERING

Low-grade wind-driven directional flow in anchored droplets

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Edited by Alexis Bell, University of California, Berkeley, CA; received March 1, 2023; accepted July 22, 2023

Low-grade wind with airspeed V_{wind} < 5 m/s, while distributed far more abundantly, is still challenging to extract because current turbine-based technologies require particular geography (e.g., wide-open land or off-shore regions) with year-round V_{wind} > 5 m/s to effectively rotate the blades. Here, we report that low-speed airflow can sensitively enable directional flow within nanowire-anchored ionic liquid (IL) drops. Specifically, wind-induced air/liquid friction continuously raises directional leeward fluid transport in the upper portion, whereas three-phase contact line (TCL) pinning blocks further movement of IL. To remove excessive accumulation of IL near TCL, fluid dives, and headwind flow forms in the lower portion, as confirmed by microscope observation. Such stratified circulating flow within single drop can generate voltage output up to ~0.84 V, which we further scale up to ~60 V using drop "wind farms". Our results demonstrate a technology to tap the widespread low-grade wind as a reliable energy resource.

wind energy | contact angle | wettability

Significance

Wind energy, as a renewable power resource, is emerging due to the wide-spreading distribution and has supplied over 6% of the electricity consumption all over the world. However, low-speed wind (<5 m/s) is still challenging to extract using current technologies, which is far more abundant than high-speed wind. Here, we report a well-designed nanostructured surface that allows pinning and rotating of ionic liquid droplets under wind. It converts wind to electricity even when the speed is reduced to 0.2 m/s.

Recent decades have witnessed the explosive growth of global wind power capacity from 24 GW in 2001 to 840 GW in 2021 (over 7% of the world's electricity demand) because of its renewability, nonpollution, bargain price, ecological compatibility, and worldwide distribution, etc. (1–11). Currently, wind energy conversion uses wind turbines to transform airflow into mechanical rotation of specially designed blades, which finally actuates a generator for supplying electricity (2, 4, 12, 13). The power output P_{wind} of turbine under wind velocity V_{wind} (m/s) can be given by (4, 14, 15):

$$P_{wind} = \frac{\rho_{air} A_b C_p V_{wind}^3}{2}, \quad [1]$$

where ρ_{air} is the air density (kg/m^3), A_b is the swept area of the rotor blade (m^2), and C_p denotes the power regulation coefficient. One can see from Eq. **1** that the P_{wind} is proportional to the cube of V_{wind} and a decrease in wind velocity will result in dramatical decline in power output (16). Unfortunately, high-speed wind is typically abundant only in open lands without obstacles, such as offshore platforms and mountain tops (17–20). Land areas with averaged wind speed less than 5 m/s are far richer and more widely distributed (*SI Appendix*, Fig. S1) (21–23), including forests and urban areas, where trees and building structures obstruct wind flow. The above elaborations hint the substantial potential of global low-grade wind as well as the strong needs for strategies capable of effectively harvesting low-speed wind energy.

Droplet movement (sliding, bouncing, falling, etc.) actuated by external factors (gravity, drawing, etc.) have been used to harvest energy from raining or mechanical dragging (24–29). A signature of droplet moving is interfacial charge redistribution, which arises because of dynamic deformation and wetting–dewetting compromised by surface tension (30–38). More recently, droplet impacting on superwetting surfaces is adapted to harvest hydraulic power from falling water drops (24). Inspired from these drop-based generators, here, we report a discovery that ionic liquid (IL) droplets sitting on a nanowire array with capillary-stabilized three-phase contact line (TCL) can sensitively turn wind blowing-induced air/liquid interfacial friction into internal rotation, as confirmed by microscope imaging. Our experimental and simulation results reveal that TCL pinning (*SI Appendix*, Fig. S2 and Movie S1), which we create by nanowire array enlarged solid/liquid adhesion hysteresis and advancing contact angle (39–42), geometrically blocks fluid flow at drop/air interfaces. To sustain the cap-shaped drop profile under surface tension and remove excess IL fluid near TCL perimeter, headwind flow arises along the bottom of the drop surrounding the nanowire array. Electrical tests, microscope images, and theoretical calculations together confirm that such IL flow within nanoconfined space spontaneously induces redistribution of positive and negative ions and persistently generates electricity (43), a clear disparate working mechanism from previous studies (44–49). Specifically,

Author contributions: S.Z. designed research; S.P., B.X., Y.W., M.W., X.C., X.J., N.H., H.H., and S.Z. performed research; S.P., B.X., Y.W., M.W., X.C., C.Z., G.L., H.H., and S.Z. contributed new reagents/analytic tools; S.P., B.X., Y.W., M.W., X.C., D.W., R.H., Z.M.W., N.H., H.H., Y.D., and S.Z. analyzed data; and S.P., B.X., M.W., N.H., Y.D., and S.Z. wrote the paper.

The authors declare no competing interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2303466120/-/DCSupplemental.

Published September 11, 2023.

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Lipid Nanoparticles Optimized for Targeting and Release of Nucleic Acid

Yaru Jia, Xiuguang Wang, Luwei Li, Fangzhou Li, Jinchao Zhang,* and Xing-Jie Liang**

Lipid nanoparticles (LNPs) are currently the most promising clinical nucleic acids drug delivery vehicles. LNPs prevent the degradation of cargo nucleic acids during blood circulation. Upon entry into the cell, specific components of the lipid nanoparticles can promote the endosomal escape of nucleic acids. These are the basic properties of lipid nanoparticles as nucleic acid carriers. As LNPs exhibit hepatic aggregation characteristics, enhancing targeting out of the liver is a crucial way to improve LNPs administrated in vivo. Meanwhile, endosomal escape of nucleic acids loaded in LNPs is often considered inadequate, and therefore, much effort is devoted to enhancing the intracellular release efficiency of nucleic acids. Here, different strategies to efficiently deliver nucleic acid delivery from LNPs are concluded and their mechanisms are investigated. In addition, based on the information on LNPs that are in clinical trials or have completed clinical trials, the issues that are necessary to be approached in the clinical translation of LNPs are discussed, which it is hoped will shed light on the development of LNP nucleic acid drugs.

1. Introduction

Nucleic acid drugs such as siRNA, mRNA, and plasmid DNA offer therapeutic potential for gene therapy.[1] However, naked nucleic acid drugs are unstable in circulation and prone to degradation, the negative charge of RNA, DNA and other biological materials limits their entry across the cell membrane, which is also negatively charged.[2] Therefore, all kinds of materials have been developed in recent years for nucleic acid delivery, such as lipids and lipid-like materials,[3] polymers,[4] and protein derivatives.[5] Most delivery systems cannot deliver these DNA- or RNA-based drugs efficiently and safely, which has been the most significant obstacle in the successful translation of gene therapeutic.[6] With the launch of the first siRNA drug (Onpattro) in 2018, LNPs are attracting increasing attention.[7] Compared to other vectors, LNPs have advantages such as high encapsulation efficiency, structural stability, and simple preparation.[8]

LNPs are the basis for the prosperous development of COVID-19 mRNA vaccines and have superb possibilities for other therapeutic strategies. LNPs have been widely researched and clinically applied for nucleic acid drug delivery, whereby nearly 80 LNP-based gene drugs have entered clinical development.[9] Significant issues remain despite the Food and Drug Administration (FDA) approval, Emergency Use Authorization (EUA), and valuable clinical data. The intra- an extracellular barriers are the main reason for limiting the development of LNPs for broader applications. The extracellular transport barrier for LNPs is mainly hepatic enrichment.[10] It accumulates as high as 30–90% in the liver, making it a severe off-target effect in treating nonhepatic diseases (**Figure 1**).[11] Furthermore, even with FDA-approved LNPs, only 1–4% of nucleic acids can escape from the endosomal and reach the cytoplasm.[12] This is the principal intracellular barrier for the efficient delivery of nucleic acid drugs. These barriers are critical rate-limiting links for in vivo targeted delivery and efficient intracellular expression of nucleic acid drugs.

This review covers the two significant challenges of LNP delivery and the current strategies to overcome them. These include changing administration routes, altering lipid structure and composition to modulate organ targeting, and enhancing the expression efficiency of nucleic acid drugs. In addition, we give examples of current clinical applications of LNPs and discuss the difficulties of industrializing LNPs, such as storage, low drug loading, and difficulties in mass production. Finally, we provide future perspectives for LNPs and hope to inspire new ideas for developing LNP-based nucleic acid drugs efficiently.

2. Development of Lipid Nanoparticles

Nucleic acid drugs can target many human diseases at the gene level and have various functions in medicine, such as protein

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DOI: 10.1002/adma.202305300

RESEARCH ARTICLE

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Reversing Immune Checkpoint Inhibitor–Associated Cardiotoxicity via Bioorthogonal Metabolic Engineering–Driven Extracellular Vesicle Redirecting

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The cardiotoxicity induced by immune checkpoint inhibitors (ICIs) is associated with high mortality rates. T cells play an important role in ICI-induced cardiac injury. The inhibition of local T-cell activity is considered an effective strategy for alleviating ICI-related cardiotoxicity. Tumor-derived extracellular vesicles (EVs) contribute to immunosuppression via PD-L1 overexpression. In this study, a bioorthogonal metabolic engineering–driven EV redirecting (Biomeder) strategy for in situ engineered EVs with myocardial-targeting peptides is developed. Accumulated tumor-derived EV (TuEVs) reverses the immune environment in the heart by increasing PD-L1 levels in cardiomyocytes and/or by directly inhibiting T-cell activity. More importantly, it is found that the redirection of TuEVs further disrupts immunosuppression in tumors, which facilitates anti-tumor activity. Thus, redirecting TuEVs to the heart simultaneously enhances the antitumor efficacy and safety of ICI-based therapy. Furthermore, the Biomeder strategy is successfully expanded to prevent ICI-induced type 1 diabetes. This Biomeder technique is a universal method for the treatment of various ICI-related adverse events.

1. Introduction

Currently, immune checkpoint blockade therapy is the most mature and widely used immunotherapy in clinical practice. Although the use of ICIs has significant advantages in reducing the mortality rate of various kinds of tumors, the continuous activation of T cells leads to a range of immune-related adverse events, such as immune myocarditis, type 1 diabetes (T1D), and immune hepatitis.[1–5] Most immune-related disorders are well-controlled and have low fatality rates, with the exception of immune myocarditis, which has a reported mortality rate of up to 50%.[6–8] ICI-induced severe myocarditis was first brought to the attention of the global medical community after two fatal cases were reported in the *New England Journal of Medicine* in 2016.[9] Furthermore, *Lancet* published a special review article to remind doctors and patients to be highly vigilant against immune myocarditis caused by tumor immune checkpoint blockade therapy.[10] Recently, an expert consensus on the monitoring and management of ICI-associated myocarditis was released.[11] Immune myocarditis caused by immune checkpoint blockade therapy has attracted attention globally.

There are no effective treatments for ICI-induced immune myocarditis and clinical interventions remain the primary approach. For example, corticosteroids and intravenous immunoglobulins have been used as early treatments to provide immune

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.202412340

DOI: 10.1002/adma.202412340

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RESEARCH ARTICLE

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Fine-Tuning the *d*-Band Center Position of Zinc to Increase the Anti-Tumor Activity of Single-Atom Nanozymes

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The exceptional biocompatibility of Zn-based single-atom nanozymes (SAzymes) has led to extensive research in their application for disease diagnosis and treatment. However, the fully occupied $3d^{10}$ electron configuration has seriously hampered the enzymatic-like activity of Zn-based SAzymes. Herein, a B-doped Zn-based SAzymes is fabricated by carbonizing zeolite-like Zn-based boron imidazolate framework at different temperatures (Zn-SAs@BNC_x, x = 800, 900, 1000, and 1100 °C). The formed B—N bond yielded a local electric field, which changes the position of the *d*-band center and improved the oxidation state of Zn by facilitating the electron transfer from Zn to N to B. These changes enhanced the adsorption and activation of H_2O_2 and O_2 by Zn-SAs@BNC_{1000}, increasing the nanozymes' multi-enzyme catalytic activity. B doping led to 24.81-, 32.37-, and 13.98-fold increase in the peroxidase-, oxidase- and catalase-like, respectively, catalytic efficiency (K_{cat}/K_m) of Zn-SAs@BNC_{1000} when compared with no B doping. In addition, Zn-SAs@BNC_{1000} showed excellent ability to kill tumor cells both in vitro and in vivo. This study demonstrates that the modulation of the electron configuration of Zn is an effective strategy to develop efficient anti-tumor approaches by boosting the enzymatic activity of Zn-based SAzymes.

1. Introduction

Single-atom catalysts (SACs) with isolated metal atom sites anchored on supports have been extensively studied in the nanocatalytic therapy of various diseases, including tumors.[1] The anti-tumor therapeutic efficacy of SACs is determined by their catalytic activity. Many studies demonstrated that the electronic structure of the individual metal active sites in transition metal-nitrogen-carbon (M-N-C) based SACs modulates the catalytic efficiency.[2] Tuning the electronic structure of metal active sites can endow SACs with strong catalytic activities.[3] The electronic structure of metal catalytic centers significantly influences the chemisorption of reactants, reaction intermediates, and reaction products on the metal's active site, thereby determining the catalytic activity of SACs.[4] *D*-band center theory revealed that the electronic structure of metal active sites in SACs is related to the position of

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DOI: 10.1002/adma.202412368

RESEARCH ARTICLE

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High-Lactate-Metabolizing Photosynthetic Bacteria Reprogram Tumor Immune Microenvironment

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The elevated levels of lactate in tumor tissue play a pivotal role in fostering an immunosuppressive microenvironment. Therefore, efficiently reducing lactate levels to reprogram tumor immune microenvironment (TIM) is considered a crucial step for boosted immunotherapy. Here, a high-lactate-metabolizing photosynthetic bacteria (LAB-1) is selectively screened for TIM reprogramming, which then improves the efficacy of tumor immunotherapy. The culture medium for LAB-1 screening is initially developed through an orthogonal experiment, simulating the tumor microenvironment (TME) and utilizing lactate as the sole organic carbon source. As demonstrated in a murine 4T1 model, LAB-1 colonizes the TME selectively, resulting in a significant reduction in lactate levels and a subsequent increase in pH values within the tumor tissue. Furthermore, single-cell RNA sequencing analysis reveals that LAB-1 effectively reprograms the TIM, thereby enhancing the effectiveness of antitumor immune therapy. This approach of utilizing lactate-consuming bacteria represents a potent tool for augmenting tumor immunotherapy efficiency.

1. Introduction

Cancer immunotherapy, harnessing the body's immune system to target malignant tumor cells, has demonstrated encouraging therapeutic results.[1] Multiple immune therapies have received clinical approval, broadening the spectrum of cancer treatment modalities.[2,3] However, these therapies have not demonstrated timely effectiveness in a significant number of patients, which is mainly attributed to the immunosuppressive tumor microenvironment (TME).[4,5] Many cell metabolites that contribute to tumor immunosuppression have been identified. Among them, lactate, generated primarily by tumor cells, serves as a key immunosuppressive agent in this context.[6,7] Lactate induces an immunosuppressive phenotype in numerous immune cells, safeguarding the tumor from immune attacks and fostering tumor progression.[8] In addition to its direct impact on immune cells, elevated lactate concentrations play a role in creating an acidic tumor environment. Maintaining a pH range of 6–6.6 is critical for processes such as tumor cell metastasis, angiogenesis, and resistance to therapy.[8] Hence, reducing lactate levels within the TME shows promise as a therapeutic approach to mitigate tumor-induced immunosuppression and enhance the effectiveness of immunotherapy.

Photosynthetic bacteria (PSB) possess inherent lactate metabolism capabilities and are anticipated to serve as "living drugs" for depleting lactate. Nevertheless, the poly-substrate metabolic properties of natural PSB significantly constrain their lactate metabolic capacity, and subsequently impact the efficiency of tumor immune microenvironment (TIM) reprogramming. In

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.202405930

DOI: 10.1002/adma.202405930

RESEARCH ARTICLE

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Organic Cations Texture Zinc Metal Anodes for Deep Cycling Aqueous Zinc Batteries

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Manipulating the crystallographic orientation of zinc (Zn) metal to expose more (002) planes is promising to stabilize Zn anodes in aqueous electrolytes. However, there remain challenges involving the non-epitaxial electrodeposition of highly (002) textured Zn metal and the maintenance of (002) texture under deep cycling conditions. Herein, a novel organic imidazolium cations-assisted non-epitaxial electrodeposition strategy to texture electrodeposited Zn metals is developed. Taking the 1-butyl-3-methylimidazolium cation ($Bmim^+$) as a paradigm additive, the as-prepared Zn film ((002)-Zn) manifests a compact structure and a highly (002) texture without containing (100) signal. Mechanistic studies reveal that $Bmim^+$ featuring oriented adsorption on the Zn-(002) plane can reduce the growth rate of (002) plane to render the final exposure of (002) texture, and homogenize Zn nucleation and suppress H_2 evolution to enable the compact electrodeposition. In addition, the formulated $Bmim^+$-containing $ZnSO_4$ electrolyte effectively sustains the (002) texture even under deep cycling conditions. Consequently, the combination of (002) texture and $Bmim^+$-containing electrolyte endows the (002)-Zn electrode with superior cycling stability over 350 h under 20 mAh cm^{-2} with 72.6% depth-of-discharge, and assures the stable operation of full Zn batteries with both coin-type and pouch-type configurations, significantly outperforming the (002)-Zn and commercial Zn-based batteries in $Bmim^+$-free electrolytes.

1. Introduction

Developing safe, reliable, and cost-effective battery technologies is highly demanded to efficiently integrate renewable energy, such as solar and wind sources. As one of the most attractive post-lithium battery technologies, rechargeable aqueous zinc (Zn) metal batteries (ZMBs) have gained significant attention for large-scale energy storage applications, due to the intrinsic properties of Zn metal, including low cost, facile manufacturing, non-flammability in water, and high theoretical capacity (820 mAh g^{-1}).[1–4] Moreover, the widely used mild aqueous electrolytes (e.g., $ZnSO_4$ electrolyte) feature high safety, excellent ionic conductivity, and environmental benignity.[5–7] However, the practical implementation of ZMBs still faces many issues, including short lifespan, poor reversibility, and low Zn utilization mainly caused by the hydrogen evolution reaction (HER), Zn corrosion, and dendrite growth on Zn metal anodes.[8–11] Specifically, the HER on Zn would render continuous electrolyte consumption, provoke the by-product formation (e.g., Zn-based hydroxides), and influence the Zn electrodeposition process to form porous Zn.[12–14] Dendritic Zn growth would increase the electrode's surface area, deteriorate parasitic reactions on Zn, and raise the potential threat of battery short-circuit.[15–17] Hence, building advanced Zn metal anodes with high reversibility/stability is the prerequisite for commercializing ZMBs.

Various strategies for stabilizing Zn metal anodes have been proposed including interface coating,[18–21] electrolyte optimization,[22–26] Zn hosts design,[27–29] and separator modification.[30,31] Different from the modulation of Zn external environments, regulating the crystallographic orientation of Zn metal substrate promises a straightforward and practical approach to intrinsically enhance Zn reversibility.[32–34] As a hexagonal close-packed (hcp) metal, the closest-packed Zn-(002) plane processes minimum surface energy and weak electrochemical activity with aqueous electrolytes. Accordingly, the Zn metal electrode with a (002) plane-dominated texture has a stronger capability to suppress side reactions and dendrite growth than the common (101) textured Zn (e.g., commercial Zn metal foil, denoted as com-Zn).[35,36] Current methodologies for fabricating Zn metal with high (002) texture (denoted as (002)-Zn) include plastic deformation of com-Zn,[37,38] annealing treatment of com-Zn by controlling the cooling rate,[39,40] and

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DOI: 10.1002/adma.202408287

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Delivery Systems Developed for Treatment Combinations to Improve Adoptive Cell Therapy

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Adoptive cell therapy (ACT) has shown great success in the clinic for treating hematologic malignancies. However, solid tumor treatment with ACT monotherapy is still challenging, owing to insufficient expansion and rapid exhaustion of adoptive cells, tumor antigen downregulation/loss, and dense tumor extracellular matrix. Delivery strategies for combination cell therapy have great potential to overcome these hurdles. The delivery of vaccines, immune checkpoint inhibitors, cytokines, chemotherapeutics, and photothermal reagents in combination with adoptive cells, have been shown to improve the expansion/activation, decrease exhaustion, and promote the penetration of adoptive cells in solid tumors. Moreover, the delivery of nucleic acids to engineer immune cells directly in vivo holds promise to overcome many of the hurdles associated with the complex ex vivo cell engineering strategies. Here, these research advance, as well as the opportunities and challenges for integrating delivery technologies into cell therapy s are discussed, and the outlook for these emerging areas are criticlly analyzed.

1. Introduction

Adoptive cell therapy (ACT) has shown great success in the clinic for the treatment of many cancers.[1] For a typical ACT therapy, the patient's own immune cells are isolated and the cells are engineered ex vivo to express certain constructs before infusion back to patients for tumor cell killing.[2] ACT has shown tremendous advantages in controlling tumor progression over traditional cancer therapy modalities.[3] In 2017, the US Food and Drug Administration (FDA) approved the first chimeric antigen receptor (CAR) T cell therapy Kymriah.[4] Until now, there are six CAR T cell therapy products and a tumor-infiltrating lymphocyte (TIL) therapy products approved by the FDA, and many other T cell therapies,[5] macrophage therapies,[6] and NK cell therapies[7] are undergoing clinical or pre-clinical studies. The approved products are all for hematological malignancies, and many of them have shown up to 80% complete response rate and significantly extended patient survival.[8] The approved CAR T cell therapies, even though effective in the treatment of hematological malignancies, failed to induce solid tumor regression in the clinic. TIL therapy has shown great promise in treating advanced melanoma, but the relatively low response rate limits its application in the treatment of broader solid tumors.[9] However, ≈90% of adult cancers globally are solid tumors.[10] Developing effective cell therapies for solid tumor treatment holds great promise in the clinic.[11] CAR T cells that target solid tumors have been developed and tested in clinical trials. However, these therapies failed to induce sustained cancer remission.

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.202407525

DOI: 10.1002/adma.202407525

Chemical Science

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Cite this: *Chem. Sci.*, 2022, **13**, 11320

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 25th July 2022
Accepted 26th August 2022

DOI: 10.1039/d2sc04143j

rsc.li/chemical-science

Non-flammable, dilute, and hydrous organic electrolytes for reversible Zn batteries†

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Rechargeable Zn batteries hold great practicability for cost-effective sustainable energy storage but suffer from irreversibility of the Zn anode in aqueous electrolytes due to parasitic H_2 evolution, corrosion, and dendrite growth. Herein, we report a non-flammable, dilute, and hydrous organic electrolyte by dissolving low-cost hydrated $Zn(ClO_4)_2 \cdot 6H_2O$ in trimethyl phosphate (TMP), which homogenizes plating/stripping and enables *in situ* formation of a $Zn_3(PO_4)_2$–$ZnCl_2$-rich interphase to stabilize the Zn anode. A dilute 0.5 m $Zn(ClO_4)_2 \cdot 6H_2O$/TMP electrolyte featuring a H_2O-poor Zn^{2+}-solvation sheath and low water activity enables significantly enhanced Zn reversibility and a wider electrochemical window than the concentrated counterpart. In this formulated electrolyte, the Zn anode exhibits a high efficiency of 99.5% over 500 cycles, long-term cycling for 1200 h (5 mA h cm^{-2} at 5 mA cm^{-2}) and stable operation at 50 °C. The results would guide the design of hydrous organic electrolytes for practical rechargeable batteries employing metallic electrode materials.

Introduction

Rechargeable Zn batteries (RZBs) are promising candidates for large-scale energy storage applications, benefiting from the advantages of Zn such as an abundant reservoir, low cost, and high theoretical specific gravimetric/volumetric capacity (820 mA h g^{-1} and 5855 mA h cm^{-3}). Most RZBs employ aqueous electrolytes that feature high safety and good environmental compatibility.[1–4] Nonetheless, in aqueous electrolytes, Zn metal anodes are generally plagued by severe irreversibility caused by water-induced side reactions (*e.g.*, H_2 evolution and Zn corrosion).[5–8] In non-aqueous Li batteries, the formation of a stable solid electrolyte interphase (SEI) derived from the decomposition of an organic solvent and/or salt anion allows ionic transport but blocks the solvents and electrons, which is critical for the reversible cycling of metal anodes.[9–11] Unfortunately, the water decomposition along with H_2 evolution in aqueous electrolytes makes it difficult to form a protective SEI on Zn anodes. Instead, the elevation of local pH near the Zn surface incurs the formation of loose by-products of hydroxides/oxides, causing low Zn plating/stripping efficiency.[12–15] Simultaneously, the rampant dendritic Zn growth in aqueous electrolytes would exacerbate the parasitic reactions and battery failure.[16–18]

Effective strategies to stabilize Zn anodes include designing highly concentrated aqueous electrolytes[19–23] and using aqueous–organic hybrid electrolytes.[24–29] Alternatively, exploring organic electrolytes would offer another opportunity to boost Zn reversibility because of the high thermodynamic stability of Zn in organic solvents.[30–33] However, nonaqueous RZBs often employ solvents of acetonitrile (AN),[34,35] ethylene glycol (EG),[36,37] and carbonates,[38,39] which are highly flammable and pose safety hazards. Very recently, a concentrated hydrous organic electrolyte composed of 4 mol kg^{-1} (m) hydrated $Zn(BF_4)_2$ in EG has been proposed to tackle Zn dendrite growth and water-induced parasitic reactions.[36] Compared with the aqueous counterpart, most anhydrous or hydrous organic electrolytes have lower ionic conductivity and permit limited current density and areal capacity (*e.g.*, 1 mA cm^{-2} and 1 mA h cm^{-2}) of Zn anodes, which remains far from the goal for practical applications of RZBs.[40] Besides, current oxide-based cathode materials suffer from dissolution in aqueous electrolytes, leading to rapid performance degradation.[20,41–43] It is desirable to formulate dilute hydrous organic electrolytes with lower viscosity, higher conductivity and suppressed metal dissolution whilst maintaining the intrinsic safety merits of aqueous materials. Furthermore, the development of hydrous organic electrolytes calls for more efforts to unravel the effect of

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Chemical Science

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Cite this: *Chem. Sci.*, 2022, **13**, 2640

All publication charges for this article have been paid for by the Royal Society of Chemistry

Unprecedented mid-infrared nonlinear optical materials achieved by crystal structure engineering, a case study of $(KX)P_2S_6$ (X = Sb, Bi, Ba)†

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Received 7th December 2021
Accepted 2nd February 2022

DOI: 10.1039/d1sc06849k

rsc.li/chemical-science

Three acentric type-I phase-matchable infrared nonlinear optical materials $KSbP_2S_6$, $KBiP_2S_6$, and $K_2BaP_2S_6$, showing excellent balance between the second harmonic generation coefficient, bandgap, and laser damage threshold, were synthesized *via* a high-temperature solid-state method. $KSbP_2S_6$ is isostructural to $KBiP_2S_6$, which both crystallize in the β-$KSbP_2Se_6$ structure type. $K_2BaP_2S_6$ was discovered for the first time, which crystallizes in a new structure type. $KSbP_2S_6$ and $KBiP_2S_6$ exhibit close structural similarity to the parent compound, centrosymmetric $Ba_2P_2S_6$. The $[P_2S_6]$ motifs, isotypic to ethane, exist in $Ba_2P_2S_6$, $KSbP_2S_6$, $KBiP_2S_6$, and $K_2BaP_2S_6$. The mixed cations, K/Sb pair, K/Bi pair, and K/Ba pair, play a dual-role of aligning the $[P_2S_6]$ structure motifs, contributing to a high SHG coefficient, as well as enlarging the bandgap. $KSbP_2S_6$, $KBiP_2S_6$, and $K_2BaP_2S_6$ are direct bandgap semiconductors with a bandgap of 2.9(1) eV, 2.3(1) eV and 4.1(1) eV, respectively. $KSbP_2S_6$, $KBiP_2S_6$, and $K_2BaP_2S_6$ exhibit a high second harmonic response of 2.2× $AgGaS_2$, 1.8× $AgGaS_2$, and 2.1× $AgGaS_2$, respectively, coupled with a high laser damage threshold of 3× $AgGaS_2$, 3× $AgGaS_2$, and 8× $AgGaS_2$, respectively. The DFT calculations also confirm that the large SHG coefficient mainly originates from $[P_2S_6]$ anionic motifs.

Introduction

Middle infrared lasers have various important applications such as instrumental spectroscopy,[1] optical sensing,[2] optical imaging,[3,4] and long-distance communications.[5] One critical way to obtain middle infrared lasers is *via* the nonlinear harmonic process, where middle infrared nonlinear optical materials (MIR NLO) are the key components. Even after many years of intense research, state-of-the-art MIR NLO materials utilized to cover the spectrum range of 3–25 μm are still underdeveloped. The commercial materials such as $ZnGeP_2$, $AgGaS_2$, and $AgGaSe_2$ are impeded from use in the range of 3–25 μm due to their intrinsic efficiency loss originating from double photon absorption ($ZnGeP_2$), the low laser damage threshold ($AgGaS_2$), and non-phase matchable behavior ($AgGaSe_2$).[6–9] A state-of-the-art MIR NLO should balance a large second harmonic generation coefficient (d_{ij} > $AgGaS_2$), moderate birefringence Δn for phase matchability, a high laser damage threshold (LDT, many times > $AgGaS_2$), and a large bandgap for a good transmission range (>3.5 eV), which is almost impossible for many systems. Many studies, including experimental and theoretical studies, all proved the existence of a "3.5 eV wall" for middle IR NLO.[10–15] Now the major strategy to achieve a large bandgap is through the investigation of oxides, with good examples of $Cs_4V_8O_{22}$,[16] $La_3SnGa_5O_{14}$,[17] $LiCd(IO_3)_3$,[18] Li_2MTeO_6 (M = Ti, Sn),[19] and M_2LiVO_4 (M = Rb, Cs).[20] Compared with oxygen, which has intrinsic vibration modes within the infrared spectrum range, sulfides constituted from heavier sulfur atoms can have better performance.[21–24] For sulfide MIR NLO materials, they currently remain in a vacuum without a promising material to balance d_{ij}, Δn, and LDT with a bandgap breaking through the "3.5 eV wall". A new research strategy is called for to break the "3.5 eV wall" with a good balance of d_{ij}, Δn, and LDT for MIR NLO.

Mixed cations with a combination of two chemically different atoms may increase the structural complexity of the target system, which has a higher chance of forming NCS structures, moderate birefringence for phase-matching behavior, and interactions between cations and anionic groups for better NLO properties.[21,25–30] Our research was firstly inspired by $Ba_2P_2S_6$, which contains $[P_2S_6]$ ethane-like motifs and crystallizes in a centrosymmetric structure.[31] The K^+ cation was selected to replace Ba^{2+} cations due to their comparable ionic sizes: 152 pm and 149 pm, respectively.[32] Trivalent cations containing stereochemically active lone pair electrons (SCALP) such as Sb and Bi were also incorporated into the system. Many previous studies have demonstrated that SCALP play an

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† Electronic supplementary information (ESI) available: The crystallographic data, powder X-ray diffraction results, Tauc plots, DFT calculation, calculated birefringence, and the calculated SHG intensity map. CCDC 2119928. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc06849k

Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2024, **15**, 19496

All publication charges for this article have been paid for by the Royal Society of Chemistry

Large second harmonic generation and birefringence from extended octupolar π-conjugated structures†

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The exploration of crystal materials for optical manipulation by nonlinear optical (NLO) and anisotropic light–matter interaction is of paramount importance in modern science and technology. However, in such crystal materials, finding the right balance between second harmonic generation (SHG), birefringence, and the bandgap presents a significant challenge. In this contribution, we employ extended octupolar π-conjugated groups devoid of intrinsic dipole moments to construct melonate-based inorganic–organic hybrid crystals, thereby achieving simultaneous large optical nonlinearity and anisotropy. In accordance with this strategy, $Rb_3[C_6N_7(NCN)_3]\cdot 3H_2O$ (I) and $Cs_3[C_6N_7(NCN)_3]\cdot 3H_2O$ (II) were obtained and subjected to detailed investigation. Strong SHG responses of ~9× KH_2PO_4 and a large birefringence of at least 0.6@546 nm were observed for I and II crystals, respectively, together with a suitable bandgap for visible-UV application. Theoretical calculations indicated that octupolar $[C_6N_7(NCN)_3]^{3-}$ groups of I and II arranged in a near parallel configuration exhibit a discrete π electron distribution, resulting in enhanced NLO susceptibilities and maximal polarizability difference. This work underscores the potential of octupolar structures with extended π-conjugation as a promising avenue for the discovery of NLO and birefringence crystals.

Received 27th August 2024
Accepted 31st October 2024

DOI: 10.1039/d4sc05756b

rsc.li/chemical-science

Introduction

As an important component of cutting-edge optical materials, nonlinear optical (NLO) and birefringent crystals have plentiful frontier applications in the military, medical, and aerospace fields.[1–5] However, the development of high-performance optical functional crystal materials with strong second-harmonic generation (SHG) and large optical anisotropy continues to face significant challenges.[6–10] High-performance optical materials rely on special functional units with a significant microscopic SHG response and optical anisotropy, and achieve their optimal spatial arrangement within the lattice. The design of non-centrosymmetric (NCS) heteroanionic groups such as $[BO_3F]$,[11] $[SO_3NH_2]$,[12,13] $[PO_3F]$,[14] $[PO_3NH_3]$,[15] $[MoO_2O_4]$,[16] $[SbO_2F_2]$,[17] $[YO_3F_3]$,[18] $[SbO_4F_2]$,[19] and MF_7 (M = Zr, Hf)[20] has been a recent hot topic in the study of NLO and birefringent materials. A common feature of these asymmetric functional units is their large intrinsic dipole moments, which usually lead to strong microscopic NLO polarizability. However, as the dipole functional units usually produce dipole–dipole interactions in the crystal leading to antiparallel arrangements, they eventually form centrosymmetric (CS) materials that are SHG inert. In addition, such antiparallel arrangements also cancel out optical anisotropy, resulting in limited birefringence.[17,21]

Recently, small flat π-conjugated groups have been widely adopted as the basic building units (BBUs) to design optical materials. Borates containing planar π-conjugated $[BO_3]^{3-}$ and $[B_3O_6]^{3-}$ groups have been considered a treasure trove of UV NLO materials,[22] such as the classical NLO materials $KBe_2BO_3F_2$ (KBBF),[23] $Sr_2Be_2B_2O_7$,[24] and β-BaB_2O_4 (BBO).[25] In subsequent studies, a series of cyanurates containing organic planar π-conjugated $[C_3N_3O_3]^{3-}$ groups similar to $[B_3O_6]^{3-}$ have been reported to have excellent linear and nonlinear properties,[26] *e.g.*, $Ca_3(C_3N_3O_3)_2$ (CCY)[27] and β-$Sr_3(C_3N_3O_3)_2$ (β-SCY).[28] Meanwhile, the $Cs_3C_3N_3(NCN)_3\cdot 3H_2O$ crystal containing the triazine $[C_3N_3]$-nuclear derivative $[C_3N_3(NCN)_3]^{3-}$ exhibits a strong SHG response and large birefringence.[29] By extending the π-conjugated system, the derivative of the heptazine $[C_6N_7]$-core, $[C_6N_7O_3]^{3-}$, was also proved to be an excellent high-performance NLO moiety.[30] It is interesting to point out that these π-conjugated anionic groups are octupolar moieties, and are organized into a two-dimensional (2D) layered structure that exhibits a strong SHG and significant birefringence.[17,31,32]

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† Electronic supplementary information (ESI) available: Crystallographic data, PXRD, additional crystal pictures, EDX results, XPS, IR spectra, TG-DSC curves, UV-vis-NIR diffuse reflectance spectra, and theoretical calculations. CCDC 2375217 and 2375218. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4sc05756b

Chemical Science

ROYAL SOCIETY OF CHEMISTRY

PERSPECTIVE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2024, **15**, 19188

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 7th August 2024
Accepted 16th October 2024

DOI: 10.1039/d4sc05309e

rsc.li/chemical-science

Recent advances in porous organic cages for energy applications

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In recent years, the energy and environmental crises have attracted more and more attention. It is very important to develop new materials and technologies for energy storage and conversion. In particular, it is crucial to develop carriers that store energy or promote mass and electron transport. Emerging porous organic cages (POCs) are very suitable for this purpose because they have inherent advantages including structural designability, porosity, multifunction and post-synthetic modification. POC-based materials, such as pristine POCs, POC composites and POC derivatives also exhibit excellent energy-related properties. This latest perspective provides an overview of the progress of POC-based materials in energy storage and conversion applications, including photocatalysis, electrocatalysis (CO_2RR, NO_3RR, ORR, HER and OER), separation (gas separation and liquid separation), batteries (lithium–sulfur, lithium-ion and perovskite solar batteries) and proton conductivity, highlighting the unique advantages of POC-based materials in various forms. Finally, we summarize the current advances, challenges and further perspectives of POC-based materials in energy applications. This perspective will promote the design and synthesis of next-generation POC-based materials for energy applications.

1 Introduction

In order to achieve the goal of sustainable energy development, exploring and innovating renewable energy sources is critical to reducing the current serious dependence on fossil fuels. However, the region limitations of renewable energy such as tidal energy and solar energy are still a serious bottleneck for its large-scale practical application.[1] In addition, some energy-intensive industries have also urgently prompted researchers to develop advanced and sustainable energy-related technologies towards separation, rechargeable batteries, electrocatalysis and photocatalysis.[2] In order to further realize these advanced applications, it is imperative to develop novel materials with appropriate structures and functions. Recently, emerging materials based on porous organic cages (POCs), including pristine POCs, POC composites and POC derivatives, have attracted great attention due to their significant advantages compared to traditional inorganic materials in energy applications.[3–5]

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Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2024, **15**, 7308

All publication charges for this article have been paid for by the Royal Society of Chemistry

Structure-regulated enhanced Raman scattering on a semiconductor to study temperature-influenced enantioselective identification†

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Surface-enhanced Raman scattering (SERS) spectroscopy is an effective technique that can reveal molecular structure and molecular interaction details. Semiconductor-based SERS platforms exhibit multifaceted tunability and unique selectivity to target molecules as well as high spectral reproducibility. However, the detection sensitivity of semiconductors is impeded by inferior SERS enhancement. Herein, a surface and interference co-enhanced Raman scattering (SICERS) platform based on corrugated TiO_2 nanotube arrays (c-TiO_2 NTs) was developed, and the coupling of structural regulation and photo-induced charge transfer (PICT) effectively optimized the SERS performance of the semiconductor substrate. Due to the regularly oscillating optical properties of the c-TiO_2 NTs, well-defined interference patterns were generated and the local electric field was significantly increased, which greatly promoted both the electromagnetic mechanism and PICT processes. The c-TiO_2 NTs were subsequently applied as a highly sensitive SICERS substrate to investigate the mechanism of temperature influence on enantioselective identification. This identification process is related to the existence of temperature-sensitive hydrogen bonds and $\pi-\pi$ interaction. This work demonstrates a simply prepared, low-cost, and sensitive SERS substrate that enables better investigation into molecular identification.

Received 5th February 2024
Accepted 17th April 2024

DOI: 10.1039/d4sc00855c

rsc.li/chemical-science

Introduction

Surface-enhanced Raman scattering (SERS) is a powerful technique for trace analysis. SERS offers insights into the chemical structure and composition of molecules, enabling a wide range of potential applications across various fields ranging from nanostructure characterization to biochemical analysis.[1–3] Conventional SERS substrates are based on the electromagnetic mechanism (EM),[4] which utilizes the localized surface plasmon resonance (LSPR) effect of incident light excitation on a rough-surfaced metal to locally amplify an electromagnetic field.[5,6] Typical EM strategies involve the construction of noble metal nanostructures with small gaps to generate "hotspots" and enhance the Raman scattering of nearby molecules. However, the signals of traditional EM-based SERS substrates significantly fluctuate due to the inherently non-uniform distribution of hotspots in the plasmonic nanostructures, and the poor selectivity of these substrates for target molecules usually results in complicated signal outputs. Another SERS mechanism is the chemical mechanism, which is derived from the efficient photo-induced charge transfer (PICT) that occurs between a substrate and molecules. PICT amplifies both the molecular polarizability tensor and Raman scattering cross-section.[7,8] To date, the cost-effective fabrication, high spectral stability, and repeatability of semiconductors enable them competitive SERS substrates. Unfortunately, owing to their short-range charge transfer (CT) processes, the sensitivity of semiconductor-based SERS substrates is still much lower than that of noble metal-based SERS substrates.

Many strategies have been developed to enhance the performance of semiconductor-based SERS substrates.[9] Among them, defect engineering is a well-established solution that can effectively activate the innate SERS activity of semiconductor-based substrates. Generally, defect engineering alters the band structure, surface properties, and densities of state of semiconductors. This is achieved by using complicated synthesis routes or post-treatment steps to introduce surface defects, which endow semiconductors with enhanced CT efficiency.[10] Moreover, the structure of semiconductors is a crucial

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† Electronic supplementary information (ESI) available: The interferometric reflectance spectra, Raman spectra, and SEM images of TiO_2 NTs; Raman measurement of R6G and MB on TiO_2 membrane, s-TiO_2 NTs, and c-TiO_2 NTs; schematic illustrations of preparation of chiral SICERS substrate; SERS spectra for sensing L/D-DOPA under different chiral recognition time, Fe^{3+} concentration, and Fe^{3+} chelation time; Interferometric reflectance spectra, XPS survey spectra, EDS mapping images, FTIR spectra, zeta potential, and CD spectra of different substrate. See DOI: https://doi.org/10.1039/d4sc00855c

Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
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Cite this: *Chem. Sci.*, 2024, **15**, 6002

All publication charges for this article have been paid for by the Royal Society of Chemistry

Facile preparation of high-efficiency peroxidase mimics: modulation of the catalytic microenvironment of LDH nanozymes through defect engineering induced by amino acid intercalation†

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Received 20th January 2024
Accepted 15th March 2024

DOI: 10.1039/d4sc00469h

rsc.li/chemical-science

Nanozymes have gained much attention as a replacement for natural enzymes duo to their unique advantages. Two-dimensional layered double hydroxide (LDH) nanomaterials with high physicochemical plasticity are emerging as the main forces for the construction of nanozymes. Unfortunately, high-performance LDH nanozymes are still scarce. Recently, defects in nanomaterials have been verified to play a significant role in modulating the catalytic microenvironment, thereby improving catalytic performances of nanozymes. Therefore, the marriage between defect engineering and LDH nanozymes is expected to spark new possibilities. In this work, twenty kinds of natural amino acids were separately inserted into the interlayer of CoFe-LDH to obtain defect-rich CoFe-LDH nanozymes. The peroxidase (POD)-like activity and catalytic mechanism of the as-prepared LDH nanozymes were systematically studied. The results showed that the intercalation of amino acids can effectively enhance the POD-like activity of LDH nanozymes owing to the increasing oxygen/metal vacancies. And L-cysteine intercalated LDH exhibited the highest catalytic activity ascribed to its thiol group. As a proof of concept, LDH nanozymes with superb POD-like activity were used in biosensing and antibacterial applications. This work suggests that modulating the catalytic microenvironment through defect engineering is an effective way to obtain high-efficiency POD mimics.

Introduction

As a new generation of artificial enzymes, nanozymes, which are nanomaterials with enzyme-like activity and which follow enzymatic kinetics, have gained a lot of attention.[1] Two-dimensional layered double hydroxide (LDH) nanomaterials with high physicochemical plasticity are emerging as main forces for the construction of nanozymes.[2,3] LDH is an anionic two-dimensional plate-like nanomaterial consisting of positively charged divalent and trivalent cation layers and anion exchangeable interlayer galleries alternatingly. The flexible composition of LDH enables the metal cations and defect sites in the LDH layer to be tailored to mimic the properties of natural enzymes.[4] Therefore, LDH nanozymes are considered to have excellent potential for biocatalysis and biomedicine.

To meet the high requirements of practical applications, the performances of nanozymes are improved by accurately adjusting their components, sizes and so on.[5] However, the activity of most nanozymes is relatively low in comparison with that of natural enzymes. How the development of effective strategies to achieve the preparation of high-performance nanozyme has always been a key issue in the field of nanozyme research. As for LDH nanozymes, various strategies have been developed to enhance their catalytic activities, such as multi-metal coordination, intercalation of functional molecules, exfoliation of the layer and combination of other materials. Unfortunately, LDH nanozymes with high catalytic activity are still scarce.

The catalytic microenvironment is very important for nanozymes to exert catalytic activity, so it is expected that highly active nanozymes can be obtained by the directional modification of the catalytic microenvironment. For example, Yan's group reported that the introduction of histidine residues onto

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4sc00469h

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Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2024, **15**, 2133

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 25th September 2023
Accepted 30th December 2023

DOI: 10.1039/d3sc05023h

rsc.li/chemical-science

Copper and conjugated carbonyls of metal–organic polymers as dual redox centers for Na storage†

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Metal–organic polymers (MOPs) are fascinating electrode materials for high-performance sodium-ion batteries due to their multiple redox centers and low cost. Herein, a flower-like π–d conjugated MOP (Cu-TABQ) was synthesized using tetramino-benzoquinone (TABQ) as an organic ligand and Cu^{2+} as a transition metal node under the slow release of Cu^{2+} from $[Cu(NH_3)_4]^{2+}$ and subsequent dehydrogenation. It possesses dual redox centers of Cu^{2+}/Cu^{+} and C=O/C–O to render a three-electron transfer reaction for each coordination unit with a high reversible capacity of 322.9 mA h g^{-1} at 50 mA g^{-1} in the voltage range of 1.0 to 3.0 V. The flower-like structure enhances fast Na^{+} diffusion and highly reversible organic/inorganic redox centers. This results in excellent cycling performance with almost no degradation within 700 cycles and great rate performance with 198.8 mA h g^{-1} at 4000 mA g^{-1}. The investigation of the Na-storage mechanism and attractive performance will shed light on the insightful design of MOP cathode materials for further batteries.

Introduction

Sodium-ion batteries (SIBs) have attracted great attention for large-scale energy storage due to the high abundance and uniform distribution of Na resources.[1,2] A wide range of inorganic materials, such as $Na_3V_2(PO_4)_3$, $Na_{0.67}MnO_2$, and $Na_2FeFe(CN)_6$, have been attempted as cathodes for SIBs, to deliver capacities below 200 mA h g^{-1} due to the limited redox of $V^{4+/3+}$, $Mn^{4+/3+}$, and $Fe^{3+/2+}$.[3–6] Polymer-based organic electrode materials have been actively studied as host materials for Na^{+} storage owing to their environmental friendliness and good flexible stability with devisable organic monomers, which could introduce multiple organic/inorganic redox centers to increase theoretical capacity.[7–10] However, the electrochemical performances of these polymers are governed by their electrically insulating nature (except for conductive polymers) and disordered molecular chain entanglement, leading to the limited utilization of redox-active sites with low capacity and inferior rate performance.[11–13] It is rational to design organic cathode materials with more redox sites and great electrical conductivity for Na^{+} storage and robust structures for Na^{+} (de)intercalation for high energy density and reversibility.

Redox-active π–d coordination metal–organic polymers (MOPs) exist as the framework structure or linear structure by adjusting the type of inorganic metal nodes and organic ligands, which is favorable for eliminating the dissolution of the hybrid materials in organic electrolytes and avoiding the organic chain agglomeration.[14–17] Moreover, the abundantly delocalized electrons and strong metal–ligand interaction bonds in MOPs guarantee high electrical conductivity and good structural stability, promoting the electron transfer to activate redox-active sites with higher capacity.[18,19] It is noteworthy that the selection of organic ligands and transition metal centers for MOPs is important to affect the discharge capacity, working potential, and cycling performance. Several typical organic ligands, such as hexaaminobenzene (HAB), 1,2,4,5-tetraaminobenzene (BTA), and 2,3,6,7,10,11-hexaaminotriphenylene (HITP), have been widely used as the anode, while their electrochemical performance is stilled limited by the single active site and low discharge capacity.[20–23] Recently, many studies on conjugated carbonyl-derived linkers have indicated to construct a high-capacity MOP-type cathode material because of its low molecular weight, high potential redox sites (carbonyl group, C=O), and *ortho*-diamine groups ($-NH_2$, coordination form of robust metal–nitrogen bonds), like tetramino-benzoquinone (TABQ)[16,24–32] This is favorable for increasing the discharge

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3sc05023h

Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2021, **12**, 5843

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 9th December 2020
Accepted 15th March 2021

DOI: 10.1039/d0sc06734b

rsc.li/chemical-science

Non-concentrated aqueous electrolytes with organic solvent additives for stable zinc batteries†‡

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Rechargeable aqueous zinc batteries (RAZBs) are promising for large-scale energy storage because of their superiority in addressing cost and safety concerns. However, their practical realization is hampered by issues including dendrite growth, poor reversibility and low coulombic efficiency (CE) of Zn anodes due to parasitic reactions. Here, we report a non-concentrated aqueous electrolyte composed of 2 m zinc trifluoromethanesulfonate ($Zn(OTf)_2$) and the organic dimethyl carbonate (DMC) additive to stabilize the Zn electrochemistry. Unlike the case in conventional aqueous electrolytes featuring typical $Zn[H_2O]_6^{2+}$ solvation, a solvation sheath of Zn^{2+} with the co-participation of the DMC solvent and OTf^- anion is found in the formulated H_2O + DMC electrolyte, which contributes to the formation of a robust ZnF_2 and $ZnCO_3$-rich interphase on Zn. The resultant Zn anode exhibits a high average CE of Zn plating/stripping (99.8% at an areal capacity of 2.5 mA h cm^{-2}) and dendrite-free cycling over 1000 cycles. Furthermore, the H_2O + DMC electrolytes sustain stable operation of RAZBs pairing Zn anodes with diverse cathode materials such as vanadium pentoxide, manganese dioxide, and zinc hexacyanoferrate. Rational electrolyte design with organic solvent additives would promote building better aqueous batteries.

Introduction

Safe, reliable, and cost-effective electrochemical energy storage technologies are demanded for the efficient utilization of renewable energy sources such as solar and wind.[1,2] Among various options, rechargeable aqueous Zn batteries (RAZBs) hold great promise because of the advantages of metallic Zn anodes including abundant resources, environmental benignancy, low cost, and high theoretical specific/volumetric capacity (820 mA h g^{-1} and 5855 mA h cm^{-3}).[3–5] Moreover, compared with flammable organic electrolytes widely adopted in lithium-ion batteries (LIBs), aqueous electrolytes intrinsically provide improved safety, and their higher ionic conductivities favor high rate capability.[6,7] These features promote the recent renaissance of RAZBs with extensive research on a variety of cathode materials, including manganese oxides,[8–10] Prussian blue analogues,[11,12] vanadium oxides,[13–16] and organic compounds.[17–20]

Nonetheless, state-of-the-art RAZBs are plagued by the issues associated with metallic Zn anodes, such as low plating/stripping efficiency, dendrite growth, and unstable Zn–electrolyte interface along with water-induced side reactions (*e.g.*, H_2 evolution and surface passivation).[4,21,22] To address these challenges, an efficient strategy is to construct hierarchical structures[23–26] or modification layers[27–30] on Zn anodes. Besides, electrolyte modulation is considered to be a facile approach to stabilize metal anodes by regulating the interface chemistry.[31–35] Recently, highly concentrated electrolytes (*e.g.*, 1 m $Zn(TFSI)_2$ + 20 m LiTFSI (m: mol kg^{-1})[36]) and deep eutectic electrolytes (*e.g.*, ~4.2 m $Zn(TFSI)_2$ in nonaqueous acetamide[37]) were proposed to form an anion-derived solid electrolyte interphase (SEI) layer on the Zn anode. This SEI allows rapid Zn^{2+} diffusion while blocking solvents and electrons, and thus suppressing water-induced side reactions.[36,37] However, the higher cost, reduced ionic conductivity, and increased viscosity of these salt-concentrated electrolytes raise much concern towards their practical use. In a conventional aqueous electrolyte (concentration generally below 2 mol L^{-1}), the typical solvation structure of $Zn[H_2O]_6^{2+}$ without anion coordination makes it infeasible to form a protective SEI from the reductive decomposition of anions before Zn deposition.[35,36] Instead, competitive water decomposition with H_2 evolution occurred ($H_2O \rightarrow H_2 + OH^-$), which increases the local pH and induces the generation of Zn hydroxides or zincates to passivate the Zn anode.[35,38] Therefore, it is desirable to stabilize the Zn electrochemistry in non-concentrated aqueous electrolytes.

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† Dedicated to the 100th anniversary of Hebei University.

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/d0sc06734b

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