

3-12 学生高质量代表性论文

序号	论文题目	期刊名称	时间	分区	页码
1	Nanoarchitectonics and applications of artificial molecular machines in smart polymer materials	Materials Today Chemistry 24 (2022) 100893	2022.06	IF7.6 一区	334
2	Potassium tantalate niobate crystals: Efficient quadratic electro-optic materials and their laser modulation technology	Journal of Materiomics 9 (2023) 838-854	2023.06	IF9.5 一区	335
3	Rb3B5O8F2 and K0.6Rb2.4B5O8F2: two new deepultraviolet transparent nonlinear optical fluorooxoborates designed by cation regulation	Inorg. Chem. Front. 2023, 10, 787-792	2023.11	IF6.4 一区	336
4	Achieving High Piezoelectric Performance Across Multidomains Design in K(Ta,Nb)O3-Based Lead-free Single Crystals	ACS Appl. Mater. Interfaces 2024, 16, 65004–65011	2024.03	IF8.2 一区	337
5	Enhanced piezoelectricity of Cu-doped K(Ta,Nb)O3 single crystals	Journal of Materiomics 10 (2024) 1017-1025	2024.04	IF9.6 一区	338
6	Measurement of space charge density distributions and dielectric resonance enhancement of beam deflection properties of KTN crystal	Journal of Materiomics 11 (2025) 100902	2025.02	IF9.6 一区	339
7	Broadband NIR-II Emission Generated by Tetrahedral Cr ³⁺ /Cr ⁴⁺ in SrLaGa3O7	Laser Photonics Rev. 2025, 19, 2401212	2025.05	IF10.2 一区	340
8	Atomic Layer Deposition Assisted Superassembly of Ultrathin ZnO Layer Decorated Hierarchical Cu Foam for Stable Lithium Metal Anode	Energy Storage Materials 37 (2021) 123-134	2021.02	IF20.2 一区	341
9	The chemical environment and structural ordering in liquid Mg-Y-Zn system: An ab-initio molecular dynamics investigation of melt for the formation mechanism of LPSO structure	Journal of Magnesium and Alloys 12 (2024) 815-824	2024.02	IF13.8 一区	342
10	Stress-Dispersed Superstructure of Sn3(PO4)2@PC Derived from Programmable Assembly of Metal–Organic Framework as Long-Life Potassium/Sodium-Ion Batteries Anodes	Advanced Science 10(17): 2206587	2023.04	IF14.1 一区	343

11	Spatially Resolved Organic Whispering-Gallery-Mode Hetero-Microrings for High-Security Photonic Barcodes	Angewandte Chemie International Edition 2023,	2023.08	IF16.6 ☒	—	344
12	Planetary centrifugal mixing for robust, ultrahighly sensitive sensors with positive piezoresistive effect across an exceptionally broad pressure range based on polyurethane/carbon black composite foam	Chemical Engineering Journal 483:149354	2024.02	IF13.2 ☒	—	345
13	Achieving Bright and Long-Lived Aqueous Room-Temperature Phosphorescence of Carbon Nitrogen Dots Through In Situ Host–Guest	Advanced Materials 2024, 2401493	2024.02	IF26.8 ☒	—	346
14	Towards practical Li-ion full batteries with glass anodes	Nano Energy 128, 109950	2024.06	IF16.8 ☒	—	347
15	Facilitating sulfur species capture and bi-directional redox in Li-S batteries with single-atomic Co-O ₂ N ₂ coordination structure	Journal of Energy Chemistry 99: 604–614	2024.08	IF14	—☒	348
16	Constructing Compact Hybrid Buffer Interface via Ion Agglomeration Zone Electrolyte for Stable Zn Metal Battery	Advanced Energy Materials 2025, 2405738	2025.01	IF26	—☒	349
17	In-situ characterization technologies and theoretical calculations in carbon dioxide reduction: In-depth understanding of reaction mechanisms and rational design of electrocatalysts	Coordination Chemistry Reviews 533, 216541	2025.06	IF23.5 ☒	—	350
18	Recent Advances in Phosphorescent Carbon Dots via Host–Guest Engineering	Advanced Functional Materials 2025, 2409088	2025.07	IF19	—☒	351
19	Na ₂ BaB ₁₂ O ₁₈ F ₄ : A Mixed Alkali/Alkaline-Earth Metal Fluorooxoborate with Two Unprecedented Interpenetrating Three-Dimensional B–O/F Anionic Networks and a Short Ultraviolet Cutoff Edge	Inorg. Chem. 2023, 62	2023.1	IF5.2	—☒	352
20	Inverse Design of Ferroelectric-Order in Perovskite Crystal for Self-Powered Ultraviolet Photodetection	Adv. Mater. 2022, 2105108	2022.1	IF26.8 ☒	—	353



Contents lists available at ScienceDirect

Materials Today Chemistry

journal homepage: www.journals.elsevier.com/materials-today-chemistry/

Nanoarchitectonics and applications of artificial molecular machines in smart polymer materials

P. Qiao^a, Q. Shi^{a,*}, S. Zhang^a, X. Zhang^b, Y. Yang^a, B. Liu^{a,**}, X. Wang^a, Q. Luo^d, L. Wang^{c,a}

^a Key Laboratory of Light Conversion Materials and Technology of Shandong Academy of Sciences, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China

^b Shandong Provincial Key Laboratory of High Strength Light Weight Metallic Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China

^c Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China

^d Shandong Labor Vocational and Technical College, Jinan, 250300, China

ARTICLE INFO

Article history:

Received 15 January 2022

Received in revised form

5 March 2022

Accepted 10 March 2022

Available online xxx

Keywords:

Polymers

Polyrotaxanes

Catenanes

Gel

Daisy Chains

ABSTRACT

Artificial molecular machine is one of the most brilliant areas in the last half a century. They represent people's control abilities to the microscopic molecules in solution. Beside the hard works in the proof-of-concept research on the exploration of fundamental principles, the wide hybrid of them with diverse materials was confirmed. Through the coupling of these movable molecules with various materials, the microscopic motion of molecular machines could be easily translated and amplified to macroscopic world to produce useful work. The integration further improves the ability of us to control the molecules in solid state. Among the various materials, polymers have the widest applications in many areas. The incorporation of artificial molecular machines into the bulk polymer materials would produce more influence on our life in the near future. In this review, we summarized the proofed hybrid strategies of polymers with different molecular machines. We hope that the summarization could provide a research roadmap for the related researchers.

© 2022 Elsevier Ltd. All rights reserved.

1. Introduction

Machines are one of the indispensable equipment with diverse functions in industrial production. Not only in macroscopic world, but also at the bottom of life, machines are playing a vital role in the proper functioning of the systems. Diverse protein machines [1] support the energy, matter and information flow between organelles and cells. One of the classic examples which have been studied in detail is ATPase [2,3]. It is a kind of rotary motor to produce ATP molecules at a high speed fueled by the proton gradient difference between two sides of the biofilm created by respiration. Another well-explored example is sodium–potassium pump. It is an ATP-powered machine [4] that controls the concentration gradients of sodium and potassium ions between membranes. Sodium–potassium pumps could transform the chemical energy of ATP molecules

to chemical potential energy of Na⁺ and K⁺. On a smaller scale, organic molecules could also be artificially weaved into specific devices with fascinating motion features and related functions [5,6]. As one of the potential candidates to mimic sophisticated protein machines, artificial molecular machines [7,8] based on small organic molecules are on its way to be explored and applied in various related fields [9,10]. After J.-P. Sauvage synthesized his [2] catenanes by using metal template strategy [11,12], in 1991, J. F. Stoddart constructed the first [2]rotaxane-based molecular machine [13]. In 1999, B. L. Feringa [14] first reported a light-driven molecular motor that can rotate 360° in one direction. In 2016, these three scientists won the Noble Prize for their pioneering contribution in the area of artificial molecular machines. Following these groundbreaking works, in the past few decades, the proof-of-concept explorations of the artificial molecular machines composed of the main text of this field (see Scheme 1).

Various movement modes and mechanisms of artificial molecular machines were developed and studied [15,16]. At present, there are mainly three types of mechanical movement of artificial molecular machines reported: translational motion, rotate motion,

* Corresponding author.

** Corresponding author.

E-mail addresses: shiqiang@sds.org (Q. Shi), liubing@sds.org (B. Liu).



Contents lists available at ScienceDirect

Journal of Materiomics

journal homepage: www.journals.elsevier.com/journal-of-materiomics/

Potassium tantalate niobate crystals: Efficient quadratic electro-optic materials and their laser modulation technology

Xuping Wang^{a, b, *}, Xinguo Mao^a, Pan Chen^b, Qian Du^a, Yuguo Yang^{a, b}, Panyu Qiao^a, Shadong Zhang^a, Zhijian Li^a, Rui Zhang^a, Bing Liu^{a, **,}, Jiyang Wang^c

^a Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China

^b Qilu University of Technology (Shandong Academy of Sciences), Advanced Materials Institute, Key Laboratory of Light Conversion Materials and Technology of Shandong Academy of Sciences, Jinan, 250014, China

^c State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan, 250100, China

ARTICLE INFO

Article history:

Received 5 January 2023

Received in revised form

13 February 2023

Accepted 14 February 2023

Available online 16 March 2023

Keywords:

Electro-optic effect

Kerr effect

Electro-optic crystal

Crystal growth

Potassium tantalate niobate crystal

Laser modulation

Deflector

ABSTRACT

Electro-optic (EO) crystals are important material for all-solid-state laser technology, which can be used to fabricate various laser modulators, such as EO switches, laser deflectors, and optical waveguide. The improvements in new high-efficiency EO crystal materials have held great significance to the development of laser technology. Potassium tantalate niobate (KTN) is a popular multifunctional crystal because of its remarkable and excellent quadratic EO effect. KTN EO modulation technology offers numerous advantages, such as high efficiency, good stability, a quick response time, and inertia-free characteristics. In this paper, we summarize the research progress of KTN series crystals systemically, including the theoretical exploration on quadratic EO effect, solid-melt crystal growth technique, comprehensive physical characterization, new physical effect and mechanisms exploration, new EO devices development and design. The EO modulation technique based on the Kerr effect of KTN series crystal offers obvious advantages in reducing the drive voltage and device size, which could better meet the developmental needs of future lasers with a wide wavelength, miniaturization, and integration. This may provide theoretical guidance and an experimental basis for the design and development of new EO crystal devices and promote the development of laser technology.

© 2023 The Authors. Published by Elsevier B.V. on behalf of The Chinese Ceramic Society. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

1. Introduction	839
2. Growth and preparation of KTN series crystals	840
3. Characterization of KTN series crystals	841
3.1. Crystallographic properties of KTN series crystal	842
3.2. Basic physical properties of KTN series crystal	842
4. Kerr effect analysis and measurement of KTN series crystals	843
4.1. Theoretical source of the giant Kerr effect of the KTN series crystals	844
4.2. Dielectric properties of the KTN series crystals	845
4.3. Measurements of the Kerr coefficients for the KTN series crystals	845
5. Laser modulation technology based on Kerr effect of the KTN crystals	846
5.1. KTN beam deflector	846
5.2. KTN EO laser modulator	849
6. Applications of KTN EO modulation technology	849

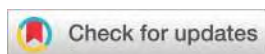
* Corresponding author. Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China.

** Corresponding author.

E-mail addresses: wangxp@sas.org (X. Wang), liubing@sas.org (B. Liu).

Peer review under responsibility of The Chinese Ceramic Society.

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Inorg. Chem. Front.*, 2023, 10, 787

Rb₃B₅O₈F₂ and K_{0.6}Rb_{2.4}B₅O₈F₂: two new deep-ultraviolet transparent nonlinear optical fluoro-oxoborates designed by cation regulation†

Ruonan Zhang,^{‡a,b} Bingliang Cheng,^{‡a,b} Xuping Wang,^{‡a} Rong Yang,^{a,b} Zhihua Yang,^{‡a} Shujuan Han^{‡a*} and Shilie Pan^{‡a*}

Two new fluorooxoborates, Rb₃B₅O₈F₂ and K_{0.6}Rb_{2.4}B₅O₈F₂, were successfully obtained by cation regulation. Both of them crystallize in a non-centrosymmetric space group *P*2₁. The structural evolution from Li₂Na_{0.9}K_{0.1}B₅O₈F₂ to Rb₃B₅O₈F₂, as well as the structural comparison between RbB₅O₈ and Rb₃B₅O₈F₂, is discussed in detail. The linear optical and nonlinear optical properties were measured. Furthermore, the structure–property relationships of the alkali metal fluorooxoborates were determined by theoretical calculations.

Received 8th July 2022,
Accepted 5th December 2022

DOI: 10.1039/d2qj01466a

rsc.li/frontiers-inorganic

Nonlinear optical (NLO) crystals, which can broaden the output wavelength of the laser from the deep-ultraviolet (DUV, $\lambda < 200$ nm) to the far-infrared spectral range, play a significant role in the area of laser medical treatment, material micromachining, laser radar, and infrared countermeasures, *etc.*^{1–9} With the sustained development of science and technology, new requirements are also constantly put forward for the laser light source. There are three rigorous but indispensable performance criteria for practical UV or DUV NLO crystals: relatively large second harmonic generation (SHG) response, wide optical transparency window down to the UV or DUV spectral regions and suitable birefringence. However, the above three properties conflict.^{10,11} According to the anionic group theory,¹² the π -conjugated BO₃ unit with a large optical anisotropy is an excellent gene for designing such crystals,^{13–17} and familiar examples including β -BaB₂O₄,¹⁸ LiB₃O₅,¹⁹ CsB₃O₅,²⁰ and KBe₂BO₃F₂²¹ have been developed as novel NLO crystals to generate UV/UV coherent light *via* the direct SHG method. Since then, borates are the preferred candidates for

exploring new UV/UV NLO crystals due to their rich structures and functionalities.^{22–26}

To improve the SHG response of borates, one of the effective methods is to use structural units with acentric activity, including cations with lone pairs and *d*¹⁰ cations, which tend to sacrifice the large band gap of the crystal.^{27,28} Recently, Pan's group has proposed a 'fluorination strategy' by substituting one oxygen with two fluorine atoms in LiB₃O₅ (Li₂B₆O₁₀) to generate a fluorooxoborate NLO crystal, Li₂B₆O₉F₂²⁹ with a predicted short type-I SHG wavelength of 192 nm. The fluorooxoborates with B–F bonds have more variety in their crystal structures, which play a positive role in regulating the above three key performance criteria of borates, since F atoms with the largest electronegativity can shift the absorption edges to the shorter wavelength region, resulting in a widened transparency area,^{30–35} meanwhile, the [BO_{4–x}F_x] (*x* = 1–4) units exhibit stronger polarizability anisotropy and hyper-polarizability than the [BO₄] units, regulating the balance between the SHG response and birefringence.^{36,37} Therefore, fluorooxoborates are superior candidates for high-performance DUV NLO crystals, and promising candidates such as AB₄O₆F (*A* = NH₄, Na, Rb, and Cs),^{38–41} MB₅O₇F₃ (*M* = Mg, Ca, and Sr),^{42–44} and M₂B₁₀O₁₄F₆ (*M* = Ca and Sr)⁴⁵ have been developed.

How to efficiently prepare the fluorooxoborate NLO crystals? In crystal engineering, cation substitution is an important approach to modify the crystal structure and further optimize its performance.^{46–54} Previously, we obtained a fluorooxoborate, Li₂Na_{0.9}K_{0.1}B₅O₈F₂,⁵⁵ with a DUV cutoff edge; however, it crystallizes in the centrosymmetric space group. Herein, the cation with a larger atomic radius, Rb⁺, was introduced to substitute for the smaller cations in Li₂Na_{0.9}K_{0.1}B₅O₈F₂, so as to obtain new fluorooxoborates with a non-centrosymmetric

^aResearch Center for Crystal Materials; CAS Key Laboratory of Functional Materials and Devices for Special Environments; Xinjiang Technical Institute of Physics and Chemistry, CAS, 40-1 South Beijing Road, Urumqi 830011, China.

E-mail: hansj@ms.xjb.ac.cn, splan@ms.xjb.ac.cn

^bCenter of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

†Electronic supplementary information (ESI) available: Experimental sections, computational methods, crystallographic data tables, powder XRD patterns, optical property measurements for Rb₃B₅O₈F₂ and K_{0.6}Rb_{2.4}B₅O₈F₂. CCDC 2181617 for Rb₃B₅O₈F₂ and 2181618 for K_{0.6}Rb_{2.4}B₅O₈F₂. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2qj01466a>

‡These authors contributed equally to this work.

Achieving High Piezoelectric Performance Across Multidomains Design in K(Ta,Nb)O₃-Based Lead-free Single Crystals

Fulin Zhang, Yingxu Zhu, Songtao Fan, Huajian Yu, Yuguo Yang, Limei Zheng, Yuanyuan Zhang,* Bing Liu,* Xuping Wang, and Jiyang Wang

Cite This: *ACS Appl. Mater. Interfaces* 2024, 16, 65004–65011

Read Online

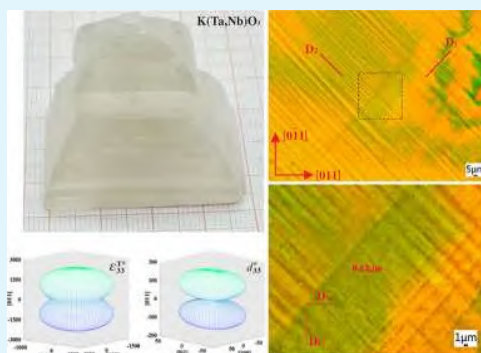
ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: In light of environmental issues, the lead-free ferroelectric single crystal K(Ta_{1-x}Nb_x)O₃ (KTN) has attracted considerable interest due to its excellent piezoelectric properties. This research focus on improving the piezoelectric performance of KTN by engineering domains through polarization in the [011]_c direction. The full-matrix parameters of KTN crystals after polarization along the [011] direction were determined. The finding reveal that KTN polarized in the nonspontaneous polarization direction [011]_c exhibits higher piezoelectric constants ($d_{33} = 156$ pC/N, $d_{15} = 155$ pC/N) and dielectric constants ($\epsilon_{33}^T \sim 2337$). Additionally, tensor matrix transformation techniques were utilized to analyze the directional dependence of the piezoelectric (d_{33}^*), dielectric (ϵ_{33}^*), elastic (s_{33}^E) constants, and electromechanical coupling coefficient (k_{33}). The results indicate that these constants reach their maximum values along the polarized [011]_c direction. A comparison of the experimental polarization values in the [011]_c direction with those calculated for a single-domain state, demonstrates that ferroelectric domains in KTN crystals contribute significantly to the piezoelectric properties. Finally, polarized light microscopy was used to conduct a detailed analysis of the domain structure in KTN single crystals, revealing various orientations and sizes of domain walls. This research offers strategies for optimizing piezoelectric performance.

KEYWORDS: lead-free piezoelectric materials, K(Ta,Nb)O₃, domain, [011]_c-direction polarization, full-matrix parameters



1. INTRODUCTION

Piezoelectric materials are an important category of functional materials known for their outstanding piezoelectric, electro-optical, and electrothermal characteristics. They can effectively transform mechanical energy into electrical energy, which makes them popular in applications such as transducers, thermoelectric sensors, and energy storage devices.^{1–9} Due to concerns about lead toxicity, there has been a growing interest in lead-free piezoelectric materials. One of the leading candidates in this area is potassium tantalate niobate, K(Ta_{1-x}Nb_x)O₃ (KTN), which has a perovskite structure and has been thoroughly researched for its remarkable piezoelectric properties.^{10–20}

The KTN crystal is particularly fascinating due to its designation as a typical perovskite ferroelectric, which experiences a series of phase transitions (cubic → tetragonal → orthorhombic → rhombohedral) when cooled from the paraelectric state. Each ferroelectric phase exhibits unique orientations of the polar vectors (P_s). In the rhombohedral phase, the polar vector aligns with the [111]_c direction, while in the orthorhombic phase, it aligns with the [011]_c direction, and in the tetragonal phase, it aligns with the [001]_c direction. When an electric field is applied to a tetragonal KTN crystal

with 4 mm symmetry along the polar [001]_c direction, a monodomain state is formed.^{21,22} The tetragonal KTN crystal, poled along the [001]_c direction, has demonstrated high electromechanical properties, with k_t around 0.642 and k_{33} approximately 0.679.²³

As reported [001]_c-polarized 0.955 Pb(Zn_{1/3}Nb_{2/3})O₃-0.045 PbTiO₃ multidomain single crystals exhibit higher electro-mechanical coupling coefficients and piezoelectric constants when compared with [111]_c-polarized monodomain crystals.²⁴ As far as we know, the only study that has documented the dielectric and piezoelectric constants of [011]-poled K-(Ta_{0.51}Nb_{0.49})O₃ crystals is by Nava Setter et al., who measured the dielectric constant ϵ_{33} at 3510 and the piezoelectric constant d_{33} at 190 pC/N. There have not been any detailed reports on the complete matrix parameters of [011]_c-poled KTN crystals and their variations in different directions.²⁵ This

Received: August 8, 2024

Revised: October 30, 2024

Accepted: November 6, 2024

Published: November 13, 2024





Contents lists available at ScienceDirect

Journal of Materiomics

journal homepage: www.journals.elsevier.com/journal-of-materiomics/

Research paper

Enhanced piezoelectricity of Cu-doped K(Ta,Nb)O₃ single crystalsFulin Zhang^a, Songtao Fan^a, Yingxu Zhu^a, Wendie Chen^a, Bing Liu^{a,b}, Yuguo Yang^{a,b}, Limei Zheng^c, Yuanyuan Zhang^{a,b,*}, Xianshun Lv^{a,b,**}, Xuping Wang^{a,b,***}^a Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China^b Qilu University of Technology (Shandong Academy of Sciences), Advanced Materials Institute, Key Laboratory of Light Conversion Materials and Technology of Shandong Academy of Sciences, Jinan, 250014, China^c School of Physics, Shandong University, Jinan, 250100, China

ARTICLE INFO

Article history:

Received 27 September 2023

Received in revised form

18 October 2023

Accepted 2 November 2023

Available online 23 November 2023

Keywords:

Solid solution material

Lead-free piezoelectric

Enhanced piezoelectricity

ABSTRACT

As a class of solid solution material, K(Ta,Nb)O₃ (KTN) single crystals have attracted significant interest due to their excellent piezoelectric and electro-optic performance. In this study, the piezoelectric properties of KTN were improved through Cu doping. Utilizing the advantages of composition-regulating phase transition, a large, high-quality Cu:KTN crystal measuring 30 mm × 25 mm × 20 mm in size was grown using the improved top seeded solution growth method. Cu-doped KTN exhibited better piezoelectric properties than pure KTN, and the full matrix parameters were investigated. Excellent dielectric, piezoelectric, and electromechanical coupling responses ($\epsilon_{11}^T \sim 2,136$, $d_{33} \sim 303$ pC/N, $k_t \sim 0.515$, and $k_{33} \sim 0.672$) were successfully obtained. To realize the optimized orientation of the piezoelectric properties, the orientation dependence of the single domain properties was investigated, and the mechanism of Cu doping to improve piezoelectric properties was explored. We found that 0.36% (in mass) Cu doped crystal consisted of A-site substitution, following ferroelectric and domain analysis. The small ferroelectric domain sizes led to a large domain wall mobility rate and high domain wall density, which contributed to high piezoelectric properties. This work revealed the effect of A-position doping on piezoelectric properties and provided a theoretical and experimental foundation for the performance optimization of KTN-based materials.

© 2023 The Authors. Published by Elsevier B.V. on behalf of The Chinese Ceramic Society. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Solid solution piezoelectric crystals with perovskite structures (general formula: ABO₃) such as (1-x)Pb(Zn_{1/3}Nb_{2/3})O₃-xPbTiO₃ (PZN-PT) and (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ (PMN-PT) possess excellent piezoelectric performance, with a variety of applications ranging from transducers to electro-mechanical sensors, as well as communications and medical ultrasound imaging [1,2]. High piezoelectric properties can be attributed to the morphotropic

phase boundary (MPB) corresponding to a flat averaged free energy density. Li *et al.* [3] reported that the Gibbs free energy outlines of piezoelectric materials could be flattened by introducing point defects through A/B-site modification.

The properties of piezoelectric crystals can be tailored by doping lower or higher-valent cations at the A/B site. When higher-valent cations replace the A-site ions, the cation vacancy concentration will increase, promoting domain wall motion, and benefiting piezoelectric and dielectric performance optimization. In this case, the doping cations act as soft doping ions. By contrast, the doping of lower-valent cations at the B site will create oxygen vacancies near the doping cations, thus sustaining electric neutrality. Doping cations and the nearest oxygen vacancies will form defect dipoles, therefore, reducing the mobility of domain walls, leading to high mechanical quality [4].

As a class of solid solution materials, K(Ta,Nb)O₃ (KTN) single crystals have attracted significant interest due to their excellent piezoelectric and electro-optic performance [5]. KTNs have also attracted research interest because they appear as a series of phase

* Corresponding author. Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China.

** Corresponding author. Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China.

*** Corresponding author. Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, China.

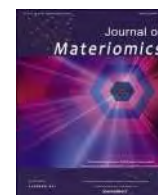
E-mail addresses: zhangyuanyuan@sdas.org (Y. Zhang), xianshunlv@sdas.org (X. Lv), wangxp@sdas.org (X. Wang).

Peer review under responsibility of The Chinese Ceramic Society.



Contents lists available at ScienceDirect

Journal of Materiomics

journal homepage: www.journals.elsevier.com/journal-of-materiomics/

Research paper

Measurement of space charge density distributions and dielectric resonance enhancement of beam deflection properties of KTN crystal

Pan Chen ^{b,*}, Wendie Chen ^{a,1}, Shuo Zhang ^a, Jianwei Zhang ^b, Jianxing Shen ^c, Bing Liu ^{a,**}, Xuping Wang ^{a,***}^a Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250353, China^b Department of Electron and Optics Engineering, Space Engineering University, Beijing, 101416, China^c Key Laboratory of Processing and Testing Technology of Glass & Functional Ceramics of Shandong Province, School of Materials Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250353, China

ARTICLE INFO

Article history:

Received 21 November 2023

Received in revised form

1 April 2024

Accepted 25 April 2024

Available online 27 June 2024

Keywords:

Dielectric constant

DC voltage

Phase delays

Charge density

Deflection angle

ABSTRACT

In recent years, potassium tantalum niobate (KTN) electro-optical deflection devices have gained considerable attention because of their notable advantages, such as large deflection angles, low operational voltage requirements, and compact dimensions. This study uses the phase-shifted interferometric optical path to characterize the influence of direct current (DC) voltage on charge density. An interferogram is acquired using the four-step phase-shifting technique, enabling the calculation of phase delays and deducing the variation in charge density. Experimental results demonstrate that the charge density near the cathode increases with an increase in DC voltage. Subsequently, we utilize the frequency dependence of the dielectric constant of the KTN crystal on the electric field. The dielectric constant can be enhanced when the characteristic frequency of the motion of the polar nanoscale region matches the frequency of the electric field. This field-induced enhancement effect improves the beam deflection performance of the KTN crystal. Application requirements in the field of high-speed random scanning can be realized through the mechanism of the KTN crystal co-acting with DC and alternating current electric fields.

© 2024 Published by Elsevier B.V. on behalf of The Chinese Ceramic Society. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Space laser communication is widely applied in satellite laser communication due to its advantages, including ample capacity, high bandwidth, robust confidentiality, and resistance to electromagnetic interference. In the field of space optical communication, the establishment of an interstellar chain is a prerequisite for realizing stable and efficient space laser communication. At present, the scanning and acquisition of laser terminals predominantly follow a one-to-one traditional beam chaining approach, which is time-consuming and allows only point-to-point communication

with simultaneous multiterminal actions [1,2]. To efficiently network and simultaneously capture multiple optical signals, modifying the pointing of transmitters and receivers has become imperative. However, space targets and spacecraft cannot freely adjust their attitude and position due to constraints associated with orbital dynamics and energy availability. The application of beam deflection technology effectively addresses this challenge [3,4]. Traditional mechanical beam deflectors, including those that utilize electric-coupled, polygonal, and microelectromechanical system mirrors, impose inherent limitations on scanning speed. Among various beam deflection methods, electro-optical deflectors exhibit rapid switching speeds and precise control [5–9]. To improve scanning speed, extensive research has focused on beam deflection based on electro-optic effects. Typical electro-optic materials include KH_2PO_4 , PZT, and LiTaO_3 [10,11]. The current research centers on uniaxial crystals with piezoelectric properties, which use their linear electro-optic effect for beam deflection. By contrast, the utilization of the quadratic electro-optic effect of crystal materials, specifically the Kerr effect, has been relatively limited due to

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: 10431220952@stu.qilu.edu.cn (P. Chen), liubing@sdas.org (B. Liu), wangxp@sdas.org (X. Wang).

Peer review under responsibility of The Chinese Ceramic Society.

¹ P.C., and W.C., contributed equally to this work.

Broadband NIR-II Emission Generated by Tetrahedral $\text{Cr}^{3+}/\text{Cr}^{4+}$ in $\text{SrLaGa}_3\text{O}_7$

Xiao-Na Shen, Zhi-Jian Li, Yu-Guo Yang,* Yuan-Yuan Zhang, Bing Liu, Hua-Jian Yu, Cheng-Cheng Qiu, Xian-Shun Lv, Rui Zhang, Qiang Shi, Hua-Di Zhang, and Xu-Ping Wang*

Broadband near-infrared (NIR) phosphors have garnered significant attention due to their potential applications in phosphor-concerted NIR light-emitting diodes (pc-NIR-LEDs). Cr^{3+} -doped NIR phosphors are particularly intriguing because of their broad NIR emission and high efficiency. However, reports on Cr^{3+} -doped NIR-II (900–1700 nm) phosphors are scarce. In this study, a novel Cr^{3+} -doped $\text{SrLaGa}_3\text{O}_7$ NIR-II phosphor is presented, where the Cr^{3+} ions are located at tetrahedral sites. The full width at half maximum (FWHM), peak wavelength, internal quantum efficiency (IQE), and thermal activation energy (ΔE) for the synthesized $\text{SrLaGa}_3\text{O}_7:0.9\%\text{Cr}^{3+}$ phosphor are 194 nm, 1167 nm, 76.12%, and 0.269 eV, respectively. The substitution of Sc^{3+} for Ga^{3+} enhances the luminescence performance, and the $0.9\%\text{Cr}^{3+}/3\%\text{Sc}^{3+}$ co-doped $\text{SrLaGa}_3\text{O}_7$ phosphor exhibits a peak wavelength of 1208 nm, an IQE of 92.78%, and a ΔE of 0.285 eV. Furthermore, the sintering process in the air induces a transition from Cr^{3+} to Cr^{4+} , resulting in the formation of $\text{SrLaGa}_3\text{O}_7:0.9\%\text{Cr}^{4+}$ phosphor, which has a peak wavelength of 1270 nm and an FWHM of 305 nm. The potential application of the $0.9\%\text{Cr}^{3+}/3\%\text{Sc}^{3+}$ co-doped $\text{SrLaGa}_3\text{O}_7$ phosphor in pc-NIR-LEDs is also evaluated.

sources that combine commercial near-ultraviolet (NUV) or blue LED chips with NIR phosphors, are becoming increasingly popular due to their affordability, durability, and high efficiency. In these pc-NIR-LEDs, phosphors absorb the photon energies from the LED chips and convert them into NIR light. To date, several ions have been reported as luminescent centers for NIR phosphors, including Eu^{2+} ,^[4] $\text{Mn}^{2+}/\text{Mn}^{4+}/\text{Mn}^{5+}$,^[5,6] $\text{Cr}^{3+}/\text{Cr}^{4+}$,^[7] Ni^{2+} ,^[8] and Bi^{3+} .^[9] Since a broader emission band generally facilitates the detection of more components, and there are fewer reports on NIR-II phosphors compared to NIR-I, the exploration of phosphors that possess a large full-width at half-maximum (FWHM), high efficiency, and excellent thermal stability, with emissions located in the NIR-II region, presents a significant challenge for NIR phosphors.^[10,11]

$\text{Cr}^{3+}/\text{Cr}^{4+}$ ions, which possess $3d^3/3d^2$

electronic configurations, are regarded as ideal activators. The investigation of $\text{Cr}^{3+}/\text{Cr}^{4+}$ -doped NIR phosphors began several decades ago.^[7] For Cr^{3+} as an activator, the widely accepted view is that it tends to occupy octahedral sites, exhibiting different emission spectra based on crystal field conditions. To date, numerous NIR phosphors with octahedral Cr^{3+} occupancy have been reported, including $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$, which has an FWHM of 185 nm and external quantum efficiency (EQE) of 20.2%;^[3] $\text{Mg}_4\text{Ta}_2\text{O}_9:\text{Cr}^{3+}$, with an FWHM of 167 nm, an EQE of 61.25%, and thermal stability of 55% at 373 K;^[12] $\text{LaGa}_{0.5}\text{Sb}_{1.5}\text{O}_6:\text{Cr}^{3+}$, exhibiting an FWHM of 200 nm, an EQE of 22%, and thermal stability of 65% at 393 K;^[13] $\text{CaLu}_2\text{Mg}_2\text{Si}_3\text{O}_{12}:\text{Cr}^{3+}$, which has an FWHM of 120 nm, an EQE of 20.7%, and thermal stability of 92.1% at 373 K;^[14] and $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Cr}^{3+}$, with an FWHM of 93 nm, an internal quantum efficiency (IQE) of 92.3%, and thermal stability of 97.4% at 423 K.^[15] To obtain Cr^{3+} -doped NIR phosphors with a wide FWHM, researchers are focusing on inorganic hosts that contain multiple suitable sites for Cr^{3+} substitution. Liu et al. reported the $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$ phosphor, which exhibits an FWHM of 330 nm, where Cr^{3+} ions substitute for both octahedral and tetrahedral sites.^[16] Wang et al. presented the $\text{BaMgGa}_5\text{Al}_7\text{O}_{17}:\text{Cr}^{3+}$ phosphor, with an FWHM of 300 nm, in which Cr^{3+} ions occupy two octahedral Al^{3+} sites

1. Introduction

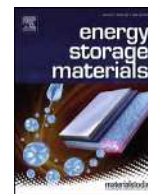
Near-infrared (NIR) radiation, which includes the NIR-I (700–900 nm) and NIR-II (900–1700 nm) regions, provides real-time, non-invasive testing for biological entities, leading to its widespread applications in food science, medical diagnostics, night vision, and more.^[1–3] Phosphor-converted NIR light-emitting diodes (pc-NIR-LEDs), a new generation of NIR light

X.-N. Shen, Y.-G. Yang, Y.-Y. Zhang, B. Liu, H.-J. Yu, C.-C. Qiu, X.-S. Lv, R. Zhang, Q. Shi, H.-D. Zhang, X.-P. Wang
Advanced Materials Institute
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250014, P. R. China
E-mail: yangyuguo@sdas.org; wangxp@sdas.org

Z.-J. Li
Key Laboratory of Luminescence and Optical Information
Ministry of Education
School of Physical Science and Engineering
Beijing Jiaotong University
Beijing 100044, P. R. China

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/lpor.202401212>

DOI: 10.1002/lpor.202401212



Atomic layer deposition assisted superassembly of ultrathin ZnO layer decorated hierarchical Cu foam for stable lithium metal anode

Runhao Zhang^{a,b,1}, Yong Li^{a,1}, Li Qiao^a, Dongwei Li^a, Jianlin Deng^a, Junjie Zhou^a, Lei Xie^b, Yue Hou^c, Tao Wang^a, Wei Tian^a, Jinchao Cao^a, Fengli Cheng^a, Bo Yang^a, Kang Liang^d, Pu Chen^e, Biao Kong^{b,*}

^a National Supercomputer Research Center of Advanced Materials, Advanced Materials Institute, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250014, P. R. China

^b Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Department of Chemistry, Laboratory of Advanced Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China

^c Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong 999077, P. R. China

^d School of Chemical Engineering and Graduate School of Biomedical Engineering, The University of New South Wales, NSW 2052, Australia

^e Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

ARTICLE INFO

Keywords:

Atomic Layer Deposition
Superassembly
Ultrathin ZnO Layer
Hierarchical Cu Foam
Lithium Metal Anode

ABSTRACT

Lithium metal (Li) is regarded as the “holy grail” in the anode material of next-generation high-energy-density batteries. However, the Li dendrites and “dead Li” produced during cycling limit its commercialization process. A properly designed three-dimensional (3D) skeleton plays an important role in determining the performance of Li metal anodes (LMA). Herein, we develop a super-assembled surface-modified lipophilic thin ZnO layer by atomic layer deposition (ALD) and multi-level Cu nanofibers (MCN) on a Cu foam (ZnO-MCNCF) as an advanced Li metal anode host. During the Li plating process, lipophilic ZnO layer can induce uniform nucleation of Li. Meanwhile, the unique hierarchical structure provides a larger specific surface area to distribute the surface charge uniformly, adjust the current density, and ensure more uniform Li deposition. Consequently, the as-designed ZnO-MCNCF host enables dendrite-free deposition of Li, high coulombic efficiency, and remarkable cycling stability at various current densities. Compared with CF and MCNCF host, ZnO-MCNCF has significantly improved Li plating/stripping behavior, with high coulombic efficiency (CE) and excellent Li dendrite growth inhibition ability. The Li@ZnO-MCNCF electrode can be operated for 1400 h at a current density of 10 mA cm⁻² and large area specific capacity of 10 mAh cm⁻² with an ultra-low overpotential (57.1 mV) without significant fluctuations. The LiFePO₄-Li (LFP-Li) and LiCoO₂-Li (LCO-Li) full cells also exhibit superior cycling and rate performance.

1. Introduction

The development of electric vehicles and portable electronic devices has accelerated the demand for high energy density rechargeable batteries [1–3]. The theoretical specific capacity of graphite anodes used in traditional lithium ion batteries (LIBs) is only 372 mAh g⁻¹. Consequently, graphite anodes cannot meet the needs of high-density secondary batteries such as lithium-sulfur (Li-S) and lithium-air (Li-O₂) batteries [4–9]. Li metal is regarded as an ideal anode for energy storage systems owing to its extremely high theoretical specific capacity (3860 mAh g⁻¹), the lowest reduction potential (−3.04 V vs. the standard hydrogen electrode) and a small gravimetric density (0.534 g cm⁻³) [10]. However, uncontrolled growth of Li dendrites and infinite volume expansion are two

intractable problems that hinder the practical utilization of Li metal anodes [11–13]. The formation of Li dendrites and “dead Li” continuously consume electrolyte, leading to low coulombic efficiency, short cycle life, internal short circuits and even catastrophic cell failure [14–16]. Infinite volume expansion during Li plating/stripping process causes the extremely loose and fragile solid electrolyte interface (SEI) and poor reversible capacity [17,18]. Therefore, it is necessary to improve the cycle stability and safety of lithium metal anodes to meet the needs of next-generation energy storage systems.

In recent years, various methods have been developed to inhibit the growth of Li dendrites and to build stable Li metal anodes, such as enhanced SEI layers [19–22], three-dimensional (3D) composite anodes [23–25] and solid-state electrolytes (SSE) [26–28]. Many researchers

* Corresponding author.

E-mail address: bkong@fudan.edu.cn (B. Kong).

¹ These authors contributed equally to this work.



Full Length Article

The chemical environment and structural ordering in liquid Mg-Y-Zn system: An *ab-initio* molecular dynamics investigation of melt for the formation mechanism of LPSO structure

Tangpeng Ma^a, Jin Wang^{a,*}, Kaiming Cheng^a, Chengwei Zhan^a, Jixue Zhou^{a,*}, Jingyu Qin^b, Guochen Zhao^a, Xinfang Zhang^c

^a Shandong Provincial Key Laboratory of High Strength Lightweight Metallic Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250014, China

^b Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, China

^c School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

Received 3 March 2022; received in revised form 23 May 2022; accepted 20 June 2022

Available online 7 July 2022

Abstract

In an effort to clarify the formation mechanism of LPSO structure in Mg-Y-Zn alloy, the chemical environment and structural ordering in liquid Mg-rich Mg-Y-Zn system are investigated with the aid of *ab-initio* molecular dynamics simulation. In liquid Mg-rich Mg-Y alloys, the strong Mg-Y interaction is determined, which promotes the formation of fivefold symmetric local structure. For Mg-Zn alloys, the weak Mg-Zn interaction results in the fivefold symmetry weakening in the liquid structure. Due to the coexistence of Y and Zn, the strong attractive interaction is introduced in liquid Mg-Y-Zn ternary alloy, and contributes to the clustering of Mg, Y, Zn launched from Zn. What is more, the distribution of local structures becomes closer to that in pure Mg compared with that in binary Mg-Y and Mg-Zn alloys. These results should relate to the origins of the Y/Zn segregation zone and close-packed stacking mode in LPSO structure, which provides a new insight into the formation mechanism of LPSO structure at atomic level.

© 2022 Chongqing University. Publishing services provided by Elsevier B.V. on behalf of KeAi Communications Co. Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer review under responsibility of Chongqing University

Keywords: Mg-Y-Zn; Chemical environment; Structural ordering; *ab-initio* molecular dynamics.

1. Introduction

Mg-Y-Zn alloys have attracted widespread attention due to their excellent mechanical properties since Kawamura et al. [1] prepared a Mg₉₇Zn₁Y₂ alloy with yield strength of above 600 MPa by a rapid solidification powder metallurgy process. It was later proved that its excellent performance was due to the long-period stacking-ordered (LPSO) structure containing high-density stacking faults [2,3], which has given impetus to lots of research centering on LPSO structure in the Mg-Y-Zn alloy system [4–8]. The usual configurations in reports

on LPSO so far are 10H [9,10], 14H [11], 18R [11,12], 24R [13], etc., and they have a common feature that Y and Zn atoms tend to be gathered. As Kawano et al. [14] mentioned, hexagonal close-packed (HCP) and local face-centered cubic (FCC) lattice structures coexist in the LPSO structure of Mg-rich Mg-Y-Zn alloy, and Y and Zn atoms are segregated in the stacking fault layer of the local FCC lattice.

The formation mechanism of LPSO structure in Mg-Y-Zn alloy during the solidification process is still unclear due to the confusion over the origin of the Y/Zn segregation zone. It was reported that the segregation is caused by the different chemical potentials of the elements in FCC and HCP [15], which is the so-called Suzuki effect [16]. This follows the formation model earlier suggested by Abe et al. [2], that is, the stacking faults are formed first and then Zn and Y

* Corresponding authors.

E-mail addresses: wangjin@sdas.org (J. Wang), zhoujx@sdas.org (J. Zhou).

Stress-Dispersed Superstructure of $\text{Sn}_3(\text{PO}_4)_2$ @PC Derived from Programmable Assembly of Metal–Organic Framework as Long-Life Potassium/Sodium-Ion Batteries Anodes

Huimin Jiang, Shuo Zhang, Liting Yan,* Yanlong Xing, Zhichao Zhang, Qiuju Zheng, Jianxing Shen, Xuebo Zhao,* and Lianzhou Wang*

The structures of anode materials significantly affect their properties in rechargeable batteries. Material nanosizing and electrode integrity are both beneficial for performance enhancement of batteries, but it is challenging to guarantee optimized nanosizing particles and high structural integrity simultaneously. Herein, a programmable assembly strategy of metal–organic frameworks (MOFs) is used to construct a Sn-based MOF superstructure precursor. After calcination under inert atmosphere, the as-fabricated $\text{Sn}_3(\text{PO}_4)_2$ @phosphorus doped carbon ($\text{Sn}_3(\text{PO}_4)_2$ @PC-48) well inherited the morphology of Sn-MOF superstructure precursor. The resultant new material exhibits appreciable reversible capacity and low capacity degradation for K^+ storage (144.0 mAh g^{-1} at 5 A g^{-1} with 90.1% capacity retained after 10000 cycles) and Na^+ storage (202.5 mAh g^{-1} at 5 A g^{-1} with 96.0% capacity retained after 8000 cycles). Detailed characterizations, density functional theory calculations, and finite element analysis simulations reveal that the optimized electronic structure and the stress-dispersed superstructure morphology of $\text{Sn}_3(\text{PO}_4)_2$ @PC promote the electronic conductivity, enhance K^+ / Na^+ binding ability and improve the structure stabilization efficiently. This strategy to optimize the structure of anode materials by controlling the MOF growth process offer new dimension to regulate the materials precisely in the energy field.

1. Introduction

The rapidly increasing demand for lithium-ion batteries (LIBs) encounter great challenges, such as low abundance and heterogeneous distribution of lithium raw materials. Therefore, batteries based on other abundant alkaline metals, such as potassium-ion batteries (PIBs) and sodium-ion batteries (SIBs) have been considered a promising alternative to LIBs.^[1] At present, conversion-alloying type anode materials exhibit high theoretical capacity for SIBs and PIBs have drawn great attention.^[1d,2] However, poor conductivity, severe volume expansion, and harmful pulverization of the materials during charge/discharge cycles seriously impact the cycle stability.

Prior studies have revealed that downsizing the feature size to the nanoscale allows the material to tolerance larger (de)sodium/ (de)potassium strains without fracture.^[3] Nanostructuring is beneficial to the life cycle of anode materials. However, it could introduce new fundamental challenges, including low Coulombic efficiency (CE), which could hinder ionic diffusion and

H. Jiang, S. Zhang, L. Yan, Q. Zheng, J. Shen, X. Zhao
School of Materials Science and Engineering
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250353, P. R. China
E-mail: yanlt@qlu.edu.cn; zhaoxuebo@upc.edu.cn

H. Jiang, S. Zhang, X. Zhao
State Key Laboratory of Heavy Oil Processing
College of Chemistry and Chemical Engineering
China University of Petroleum (East China)
Qingdao 266580, P. R. China

Y. Xing
Key Laboratory of Emergency and Trauma
Ministry of Education
Hainan Medical University
Haikou 571199, P. R. China

Z. Zhang
Tianmu Lake Institute of Advanced Energy Storage Technologies Co., Ltd
Liyang 213300, P. R. China

L. Wang
School of Chemical Engineering and Australian Institute for
Bioengineering and Nanotechnology
University of Queensland
St Lucia, QLD 4072, Australia
E-mail: l.wang@uq.edu.au

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adv.202206587>

© 2023 The Authors. Advanced Science published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adv.202206587



Spatially Resolved Organic Whispering-Gallery-Mode Hetero-Microrings for High-Security Photonic Barcodes

Xingwei Feng⁺, Ru Lin⁺, Shuo Yang, Yuyu Xu, Tongjin Zhang, Shunwei Chen, Yingke Ji, Zifei Wang, Shiwei Chen, Chaofeng Zhu, Zhenhua Gao,^{*} and Yong Sheng Zhao^{*}

Abstract: Whispering-gallery-mode (WGM) microcavities featuring distinguishable sharp peaks in a broad-band exhibit enormous advantages in the field of miniaturized photonic barcodes. However, such kind of barcodes developed hitherto are primarily based on microcavities wherein multiple gain medias were blended into a single matrix, thus resulting in the limited and indistinguishable coding elements. Here, a surface tension assisted heterogeneous assembly strategy is proposed to construct the spatially resolved WGM hetero-microrings with multiple spatial colors along its circular direction. Through precisely regulating the charge-transfer (CT) strength, full-color microrings covering the entire visible range were effectively acquired, which exhibit a series of sharp and recognizable peaks and allow for the effective construction of high-quality photonic barcodes. Notably, the spatially resolved WGM hetero-microrings with multiple coding elements were finally acquired through heterogeneous nucleation and growth controlled by the directional diffusion between the hetero-emulsion droplets, thus remarkably promoting the security strength and coding capacity of the barcodes. The results would be useful to fabricate new types of organic hierarchical hybrid WGM hetero-structures for optical information recording and security labels.

Introduction

Miniaturized photonic barcodes featuring small footprints have exhibited great potentials in the field of high-throughput bioassays, materials tracking and advanced anti-counterfeiting.^[1] Whispering-gallery-mode (WGM) microcavities with distinguishable sharp peaks arising from the WGM modulation, provide an innovative system for constructing miniaturized photonic barcodes.^[2] The ever-increasing demand for encoding capacity and security performance in highly integrated photonic devices calls for the micro/nanoscale barcodes to be capable of simultaneously achieving multicolor output and spatially resolved characteristics.^[3] Benefiting from the easy processability,^[4] excellent flexibility^[5] and wide spectral tunability of the organic materials,^[6] current multicolor WGM micro-/nanocavities were realized mainly through blending different organic gain medias into a single matrix.^[7] Nevertheless, the short-wavelength emissions are severely suppressed due to the absorption loss resulting from the narrow-gap material in such mixed systems, thus severely restricting their applications in development of high-quality and spatially resolved photonic barcodes.

By contrast, constructing the WGM microcavities with spatially separated luminescent components would minimize the internal absorption loss, thus providing an effective solution to this problem.^[8] Moreover, the domain-controlled emissive colors and recognizable spectra are beneficial to the integration of structure-based graphical encoding with spectrum-based spectroscopic encoding, thereby significantly improving the coding capacity of the barcodes.^[9] Inheriting the linear morphological characteristics from its parental microrods, the ring-shaped geometries allow us to construct the spatially resolved polychromatic WGM microcavities along their circular directions via the successive epitaxial assembly.^[3b,10] Current ring-shaped crystalline microcavities primarily were fabricated from a straight single crystal via the Mechanophotonics technique.^[11] However, the hetero-microrings have not yet been realized and still in their infancy. Firstly, the construction of microrings have been serendipitously discovered case by case, thus seriously restricting the molecular requirements for achieving full-color microrings. Secondly, the effective integration of the multiple spatial colors into a free-standing microring faces a great challenge due to the uncontrollable epitaxial growth in annular directions.

Herein, we propose a surface tension assisted heterogeneous assembly strategy to construct the WGM hetero-

[*] X. Feng, ⁺ R. Lin, ⁺ S. Yang, Y. Xu, S. Chen, Z. Wang, S. Chen, Prof. C. Zhu, Prof. Z. Gao
 School of Materials Science & Engineering,
 Qilu University of Technology (Shandong Academy of Sciences)
 Jinan 250353, Shandong Province (China)
 E-mail: gaozhenhua@qlu.edu.cn

T. Zhang, Prof. Y. S. Zhao
 Key Laboratory of photochemistry, Institute of Chemistry,
 Chinese Academy of Sciences
 Beijing 100190 (China)
 E-mail: yszhao@iccas.ac.cn

Y. Ji
 Key Laboratory of Light Field Manipulation and Information
 Acquisition, Ministry of Industry and Information Technology, and
 Shanxi Key Laboratory of Optical Information Technology,
 School of Physical Science and Technology,
 Northwestern Polytechnical University
 Xi'an 710129 (China)

[†] These authors contributed equally to this work.



Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Planetary centrifugal mixing for robust, ultrahighly sensitive sensors with positive piezoresistive effect across an exceptionally broad pressure range based on polyurethane/carbon black composite foam

Shurong Guo^a, Xiaoxia Cai^{a,*}, Cong Li^{a,*}, Jinshui Yao^a, Zhongjian Tian^a, Qiang Wang^a, Shengyuan Tan^a, Xian Zhang^a, Yanshao Liu^b, Fengshan Zhang^b

^a School of Materials Science & Engineering, State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China

^b Shandong Huatai Paper Co., Ltd. & Shandong Yellow Triangle Biotechnology Industry Research Institute Co. LTD, China

ARTICLE INFO

Keywords:

Polyurethane foam
Positive piezoresistive sensor
Planetary centrifugal mixing
High sensitivity
Broad measurement range

ABSTRACT

The pursuit of high sensitivity across a broad measurement range has been a significant and intriguing subject in developing piezoresistive sensors. However, it is important to acknowledge that high sensitivity often comes at the cost of sacrificing the measurement (pressure or strain) range due to the negative piezoresistive coefficient. In this study, a robust piezoresistive sensor based on aqueous polyurethane (APU)/conductive carbon black (CCB) composite foam was fabricated through a planetary centrifugal mixing (PCM) strategy. Under the dual action of high centrifugal and tangential forces in PCM, nano-scaled dispersion of CCB particles and resulting conductive network were embedded within the foam skeleton, combined with a unique thick-wall pore structure through the high viscosity APU/CCB blending during the foaming process. This robust sensor exhibited a distinctive positive piezoresistive behavior. It demonstrated impressively high sensitivity (gauge factor up to 211 at strain over 35 %) across an exceptionally broad pressure range (0.5 kPa–2.84 MPa), far exceeding previously reported piezoresistive sensors. Good durability and reproducibility were also testified over 2000 compression cycles, even at high pressures of 500 kPa, 1000 kPa and 1500 kPa after an initial stabilization process. The sensor can monitor diverse stimuli and give stable real-time feedback, ranging from low-pressure fingertip bending to extremely high-pressure vehicle rolling. Without the need for complex preparation processes or expensive materials, the developed strategy opens up an attractive pathway for designing advanced piezoresistive sensors with high sensitivity across a broad measurement range.

1. Introduction

In the 21st century, the rapid advancements in artificial intelligence and wireless communication have driven the demand for portable electronic devices. This has led to significant interest in developing and applying of flexible sensors [1–7]. Various pressure sensing mechanisms, including piezoelectric [8–10], capacitive [11,12], and piezoresistive [13–18], have been developed based on their respective working principles. Piezoresistive pressure sensors stand out due to their simple structure, direct readout mechanism and low energy consumption. They are extensively employed in the fields of health monitoring [19,20], wearable electronic devices [21,22] and intelligent robots [23]. Compared to metal-based and semiconductor-based sensors,

piezoresistive conductive polymer sensors are lightweight and flexible, making them a desirable option [24,25] in the sensing field. Recent research has heavily emphasized enhancing sensitivity and broadening the measurement range of piezoresistive devices to meet the diverse demands of different areas [26,27]. Li et al. [28] developed a piezoresistive flexible sensor consisting of polydimethylsiloxane and multi-walled carbon nanotubes, based on the synergistic effect of porous and microstructures in piezoresistive materials. This sensor provides a highly sensitive response over a wide pressure range of 0–100 kPa. Zhang et al. [29] improved the sensitivity of a highly compressible waterborne polyurethane-carbon nanotube composite foam by introducing brittle nanocrystals. However, it is important to note that most existing piezoresistive sensor devices demonstrate negative piezoresistive behavior,

* Corresponding authors.

E-mail addresses: cxx@qlu.edu.cn (X. Cai), congli2016@163.com (C. Li).

<https://doi.org/10.1016/j.cej.2024.149354>

Received 22 October 2023; Received in revised form 31 December 2023; Accepted 2 February 2024

Available online 5 February 2024

1385-8947/© 2024 Elsevier B.V. All rights reserved.

Achieving Bright and Long-Lived Aqueous Room-Temperature Phosphorescence of Carbon Nitrogen Dots Through In Situ Host–Guest Binding

Jie Li, Heng Zhou, Shan Jin, Bin Xu, Qian Teng, Chenhao Li, Jinsui Li, Qijun Li, Zhenhua Gao, Chaofeng Zhu, Zifei Wang,* Wen Su,* and Fanglong Yuan*

The development of bright and long-lived aqueous room-temperature phosphorescent (RTP) materials holds paramount importance in broadening the application scope of RTP material system. However, the conventional RTP materials usually exhibit low efficiency and short lifetime in aqueous solution. Herein, an in situ host–guest strategy is proposed to achieve cyanuric acid (CA)-derived phosphorescent carbon nitrogen dots (CNDs) composite (CNDs@CA) that demonstrates a significant enhancement of both quantum yield (QY) and lifetime mediated by water. Detailed investigations reveal that the robust hydrogen bonding networks between CNDs@CA and water effectively stabilize triplet excitons and suppress nonradiative decays, as well as facilitate efficient energy transfer from CA to CNDs, thereby prolonging the lifetime and enhancing the efficiency of RTP. The phosphorescent QY and lifetime of CNDs@CA can be increased to 26.89% (3.9-fold increase) and 951.25 ms (5.5-fold increase), respectively, with the incorporation of 50 wt% water under ambient conditions. Even in fully aqueous environments (with up to 400 wt% water added), CNDs@CA exhibits persistent water-boosted RTP properties, demonstrating exceptional stability. The robust water-boosted RTP property of CNDs@CA in aqueous solutions presents significant potential for high signal-to-noise ratio afterglow bioimaging as well as advanced information encryption.

between the lowest triplet excited state and the ground state,^[1–4] has sparked considerable attention in recent years due to its potential applications for photonics, organic electronics, and bio-electronics.^[5–7] To date, a plethora of RTP materials have been successfully developed through incorporating hetero-/heavy-atom effect and introducing the rigidity effect into the RTP system,^[8–16] demonstrating tunable phosphorescent colors, high quantum yields (QYs), and prolonged emission lifetimes. Unfortunately, the practical utility of RTP materials in aqueous conditions is limited due to the quenching effect caused by high concentrations of dissolved oxygen and rapid molecular motions occurring in aqueous solutions, which is a common challenge for most solid-state systems exhibiting RTP emission.^[17–21] Consequently, the subsequent formidable task in this field lies in achieving effective RTP emission in solution phase, which is of great significance for exploring the potential applications of RTP materials in the realms of biomedicine and information security.

1. Introduction

Room-temperature phosphorescence (RTP), an intriguing photophysical phenomenon arising from the radiative transition

Despite extensive efforts dedicated to the design of efficient RTP materials in solution or gel phases, only a limited number of reports have achieved the aqueous phase RTP emission by embedding phosphor into encapsulation layer.^[22–25]

J. Li, H. Zhou, S. Jin, B. Xu, Z. Gao, C. Zhu, Z. Wang
School of Materials Science and Engineering
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250353, China
E-mail: zfwang@qlu.edu.cn

Q. Teng, C. Li, J. Li, F. Yuan
Key Laboratory of Theoretical and Computational Photochemistry
of Ministry of Education
College of Chemistry
Beijing Normal University
Beijing 100875, China
E-mail: flyuan@bnu.edu.cn

Q. Li
School of Mechanical Engineering
Yangzhou University
Yangzhou 225009, China
W. Su
CAS Center for Excellence in Nanoscience
National Center for Nanoscience and Technology
Beijing 100190, China
E-mail: suwen@nanoctr.cn

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202401493>

DOI: 10.1002/adma.202401493



Full paper

Towards practical Li-ion full batteries with glass anodes

Kai Zheng^a, Lanxiang Chen^a, Zhitao Shan^a, Jiayan Zhang^a, Chengwei Gao^{b,*},
Yuanzheng Yue^{c,*}, Yanfei Zhang^{a,*}

^a School of Materials Science and Engineering, Qilu University of Technology, Jinan 250353, China

^b Laboratory of Infrared Material and Devices, The Research Institute of Advanced Technologies, Ningbo University, Ningbo 315211, China

^c Department of Chemistry and Bioscience, Aalborg University, Aalborg 9220, Denmark

ARTICLE INFO

Keywords:

V₂O₅-P₂O₅-B₂O₃ glass anode
Lithium-ion half/full batteries
Electronic conductivity
Lithium-ion diffusivity

ABSTRACT

Vanadium (V)-based glasses have recently garnered considerable attention as promising anode materials for lithium-ion batteries (LIBs) due to their abundance of Li⁺ storage sites, neglectable volume expansion upon lithiation/delithiation, and facile preparation. However, the inherently low electronic conductivity and relatively low energy density of V-based glass anodes hinder its application in full LIBs. In this work, we tackled this challenge by optimizing the chemical composition of the V-based glass anode to achieve high-performance half and full cells. We investigated the impact of partially substituting B₂O₃ for P₂O₅ in 50V₂O₅-(50-x)P₂O₅-xB₂O₃ (mol%) (VPB) glass series on its structure and electrochemical performances. The glass with 30 mol% B₂O₃ (VPB30 glass) was found to deliver the highest electronic conductivity, an enhanced reversible capacity of 470 mA h g⁻¹ at 1 A g⁻¹ after 500 cycles, and an excellent rate capability. The optimized performances were ascribed to the boosted lithium-ion diffusivity and the increased lithium storage sites. We assembled a full cell by coupling a VPB30 glass anode with a LiCoO₂ cathode to test its cycling performance. The VPB30//LiCoO₂ cell exhibits the required power density, and hence, high practicality. Our work implied the practical application of glass anodes in high-performance LIBs.

1. Introduction

Lithium-ion batteries (LIBs) have been the mainstream of the growing market for green energy production and storage ever since its first commercial application [1]. Their applications span many different areas ranging from portable electronics and electric vehicles to large-scale smart grids [2–4]. Nevertheless, despite their widespread usage, the current generation of commercial LIBs are approaching its theoretical specific capacity limit and, hence, fails to satisfy the growing demands for more advanced energy storage systems [5,6]. To realize advanced LIBs with the higher energy density, longer lifespan, and faster charge/discharge rates, developing high-performance anode materials is of paramount importance. This is especially true given that the commercial graphite anode used in LIBs has a relatively modest theoretical capacity of 372 mA h g⁻¹ and the energy density of the current commercial LIBs only ranges from 150 to 300 Wh kg⁻¹ [7,8].

Among numerous promising anode materials, the vanadium pentoxide (V₂O₅), a conversion-type anode material, stands out owing to its high theoretical capacity (~1472 mA h g⁻¹ when fully reduced from V⁵⁺

to V⁰), multiple redox states, low cost, and abundant resources [9–11]. Consequently, extensive research has been carried out to develop V₂O₅-based anode materials [12,13]. Despite their potential applications, V₂O₅-based anodes suffer from two critical problems: slow diffusion kinetics and rapid capacity decay [13]. To address these issues, numerous strategies have been proposed, such as morphology optimization, doping with graphene oxide or other metal oxides [12–16]. However, it is still a challenge to realize an facile fabrication of high performance V₂O₅ anode materials for practical applications.

Encouragingly, disorder-order engineering, such as tailoring glassy materials, has been proposed as an effective method to enhance anode performances [17–24]. Unlike their crystalline counterparts, disordered materials lack a periodic arrangement of atoms, conferring unique advantages such as buffering the volume changes upon lithiation/delithiation, facilitating an isotropic transport of Li⁺ ions, and providing more reaction sites for Li⁺ ions [17–22]. The disorder-order engineering concept was employed to enhance the capacity and cycling stability of anode materials in LIBs. Utilizing the solid-state NMR technique, the microstructural evolution in TeO₂-V₂O₅-P₂O₅ (TVP) glass

* Corresponding authors.

E-mail addresses: chengwei-gao@outlook.com (C. Gao), yy@bio.aau.dk (Y. Yue), zhang-yanfei@hotmail.com (Y. Zhang).

<https://doi.org/10.1016/j.nanoen.2024.109950>

Received 14 June 2024; Received in revised form 27 June 2024; Accepted 29 June 2024

Available online 29 June 2024

2211-2855/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).



Facilitating sulfur species capture and bi-directional redox in Li-S batteries with single-atomic Co-O₂N₂ coordination structure

Yunqiang Zhang^{a,1}, Huaming Yuan^{a,1}, Enyan Guo^{a,*}, Shunwei Chen^a, Manman Ren^a, Jingyun Ma^a, Jiayi Cui^b, Mei Li^{a,*}, Laiying Jing^a, Li Li^{c,*}

^a School of Materials Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, Shandong, China

^b Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, Sichuan, China

^c School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, China

ARTICLE INFO

Article history:

Received 10 July 2024

Revised 5 August 2024

Accepted 5 August 2024

Available online 12 August 2024

Keywords:

Asymmetrically coordinated Co-O₂N₂

Zeolitic imidazolate framework-67

Melamine resin

Carbon nanoflakes

Shuttle effect

ABSTRACT

Lithium-sulfur (Li-S) batteries suffer from the shuttle effect of soluble lithium polysulfides (LiPSs) and slow redox kinetics, significantly limiting their practical application. Although single-atom catalysts (SACs) offer a promising strategy to address these challenges, designing materials with optimal adsorption force and high catalytic activity remains a grand challenge. Here, we present a cobalt (Co)-based SAC with unique Co-O₂N₂ coordination structures for Li-S batteries. Both experimental and theoretical studies demonstrate that O, N-coordinated Co single atoms anchored on a porous carbon framework (Co/NOC) effectively capture LiPSs and dramatically catalyze bidirectional polysulfide conversion. The expanded carbon layer spacing facilitates lithium ions diffusion and maximizes the exposure of active sites. As a result, Li-S batteries incorporating Co/NOC as separators exhibit outstanding rate performance (906.6 mAh g⁻¹ at 3 C) and exceptional cycling stability, even at -10 °C. Furthermore, with a high sulfur loading of 12.0 mg cm⁻², the areal specific capacity reaches up to 12.36 mAh cm⁻². This work provides some useful insights for the design of high-performance SACs for Li-S batteries.

© 2024 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by ELSEVIER B.V. and Science Press. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

1. Introduction

Among many battery energy storage technologies, lithium-sulfur (Li-S) batteries have received much attention because of their excellent gravimetric energy density (E_g , ~2600 Wh kg⁻¹), low manufacturing costs, and environmental friendliness [1,2]. However, in addition to the low conductivity of sulfur (S) and discharge products (Li₂S/Li₂S₂) and the apparent volume change of S electrode during the charge and discharge processes, the shuttle effect of high-order lithium polysulfides (LiPSs) between the two electrodes and the slow solid-liquid phase transformation kinetics of S species also hinder the actual use of Li-S batteries to a large extent [3]. Even worse, under harsh operating conditions such as high S loadings, lean electrolyte usage, and low temperatures, the above defects result in lower specific capacity (C_s) and S utilization

of Li-S batteries, as well as poorer coulombic efficiency, rate capability, and cycle life [4–6]. In this connection, it is very necessary to add effective adsorption-catalytic media to fix the lithium polysulfides and promote the transformation dynamics between multi-phase S.

At present, various metal-based catalysts, such as metal (e.g., Pt, Ni, and Co) nanoparticles [7,8], metal compounds [9–12], metal organic frameworks (MOFs) [13–15], and heterojunctions (e.g., FeCoO_xS_y, WO_{3-x}-W₃N₄, and NbP-NbC) [16–18], have been designed to achieve rapid capture-transport-conversion of LiPSs, hoping to fundamentally solve the above problems of Li-S batteries. However, the active sites of these electrocatalysts cannot be completely exposed, and the electrocatalytic activity can only be enhanced through increasing the weight percentage of the catalysts, which is bound to sacrifice the total E_g of the Li-S batteries [19]. Moreover, the surface structure of most catalysts is heterogeneous and complex, which makes it easy to produce different catalytic sites (such as faces/edges/corners), resulting in the difficulties in accurately identifying the active centers [20]. Hence, it is of great significance to design high-exposure exemplary

* Corresponding authors.

E-mail addresses: eyguo1985@qlu.edu.cn (E. Guo), lim@qlu.edu.cn (M. Li), lilicmu@alummi.cmu.edu (L. Li).

¹ These authors contributed equally to this work.

RESEARCH ARTICLE

Constructing Compact Hybrid Buffer Interface via Ion Agglomeration Zone Electrolyte for Stable Zn Metal Battery

Yefei Chen, Weidong He, Kangning Zhao, Xingyun Luo, Jiafeng Zhang, Yongzhong Wu, and Xiaopeng Hao*

The development of aqueous Zn batteries is plagued by longevity limited at practical condition, due to the unstable electrode-electrolyte interface. Here, this work designs an extended-scale ion agglomeration zone (EIAZ) electrolyte to obtain anion combined with cation structures and reduce water activity. The electrolyte nanostructure features nanometer-scale depleted water zones in which ion pairs are densely packed together to form EIAZ, which facilitates compact hybrid buffer interface formed via a collective ion transmission process and ionic co-opetition relationship. The convergence and densification models of buffer interface for Zn surface is the result of cations adaptive adsorption that mitigates the concentration polarization of interfacial Zn^{2+} and prevents water contact with electrodes, constituting an indispensable premise for stabilizing both anode and cathode interface. Moreover, unique electrolyte nanostructure achieves Zn crystallographic optimization and fast interfacial reaction kinetics, generating ultralong cycling stability of 5500 h. Therefore, zinc-organic batteries can exert outstanding stability for over 3000 cycles and 1000 cycles under high current (10 A g^{-1}) and high mass loading (14 mg cm^{-2}). Impressively, pouch cell shows an excellent capacity retention of 99.8% with 26.1 mAh after 250 cycles. This study offers a novel perspective for designing electrolyte nanostructures and electrode interfaces for high-performance Zn batteries.

batteries (AZMBs) are receiving intense research interest because of their high theoretical energy density, low cost, and intrinsic safety.^[5,6] However, AZMBs yield a poor life span, arising from severe H_2 gas evolution, large Zn volume change (Zn pulverization/dendrite) and cathode cracking in weakly acidic electrolytes (e.g., $\text{Zn}(\text{OTf})_2$ and ZnSO_4 electrolytes with $3 \leq \text{pH} \leq 5.5$).^[7–9] The solvent (H_2O)-derived parasitic reactions associated with adverse domino effects at electrode/electrolyte interface regions, such as water decomposition, proton transport and H–bond remodeling.^[10–12] Electrolyte design plays a significant role in improving ZMBs lifespan by tuning electrode/electrolyte interface and solvation structure.^[9,13–15]

Advances in designing solid–electrolyte interphase (SEI) have been made by promoting fluorinated anion reduction or using rich–S/P organic solvents.^[16–19] However, solvent–derived organic and mixed organic–inorganic SEI layers formed on energetic anodes, such as Li metal, Si, Na metal, and Zn

metal, often fail to withstand the stress induced by large anode volume changes during subsequent cycling, resulting in cracked SEI.^[20,21] The cracked SEI allows the electrolyte to penetrate the grain boundary and particle gap of electrodeposition Zn, resulting in the excessive electrolyte depletion and forming redundant SEI, which causes rapid dendrite growth.^[22,23] Notably, SEI composition, growth location and threshold are hardly controlled,

1. Introduction

Lithium metal batteries with high energy density needed ($>500 \text{ Wh kg}^{-1}$) are facing safety issues from carbonate electrolytes and cost challenge from Li metal, limiting its application space especially in grid-scale energy storage systems for intermittent renewable energy resources.^[1–4] Aqueous Zn metal

Y. Chen, Y. Wu, X. Hao
School of Materials Science and Engineering
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250353, P. R. China
E-mail: xphao@sdu.edu.cn

W. He, J. Zhang
Department of Applied Physics
The Hong Kong Polytechnic University
Hong Kong SAR 999077, P. R. China

K. Zhao
School of Physical Sciences
Great Bay University
Dongguan 523000, P. R. China

X. Luo
School of Environmental and Material Engineering
Yantai University
Yantai 264005, P. R. China

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aenm.202405738>

DOI: 10.1002/aenm.202405738



Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

In-situ characterization technologies and theoretical calculations in carbon dioxide reduction: In-depth understanding of reaction mechanisms and rational design of electrocatalysts

Rutao Wang, Xiaokun Yang, Jianpeng Zhang, Shilong Wen, Liting Yan^{*}, Xuebo Zhao^{*}, Enyan Guo^{*}

School of Materials Science and Engineering, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, PR China

ARTICLE INFO

Keywords:

Electrochemical carbon dioxide reduction
In-situ characterization
Reaction mechanisms
Theoretical calculations
Technological integration

ABSTRACT

The electrochemical reduction of carbon dioxide (CO₂RR) enables the transformation of CO₂ into valuable chemicals and fuels using renewable electricity, offering a crucial pathway toward addressing the global energy crisis and achieving carbon neutrality. Traditional theories of catalyst stability and activity can be complicated by the dynamic reorganization of catalysts under operating circumstances, which is a significant issue in this subject. To address this, advanced in-situ technologies and theoretical calculations reveal the dynamic evolution of catalysts and intermediates during CO₂RR. In this review, we systematically analyze the integration of in-situ characterization technologies with theoretical calculations which underscores their critical role in understanding the mechanisms of CO₂RR and facilitating the design of efficient catalysts. Subsequently, we systematically summarize the recent advances in-situ studies and theoretical calculations on probing the reaction mechanisms during the CO₂RR. In this perspective, we can deepen our understanding of reaction mechanisms by combining advanced real-time monitoring and theoretical calculation approaches that relate the dynamic evolution of variable response environments to theoretical evolutionary models. Finally, this review seeks to enhance the understanding of reaction mechanisms and provide guidance for the rational design of efficient catalysts through the integration of in-situ characterization techniques and theoretical calculations.

1. Introduction

The relentless consumption of fossil fuels has driven atmospheric CO₂ concentrations to unprecedented levels, severely disrupting the global carbon cycle. This disruption manifests in alarming phenomena such as accelerated global warming, increasingly severe weather patterns, and rising sea levels [1–3]. In response to escalating climate threats, immediate efforts are needed to advance breakthrough technologies aimed at achieving complete carbon cycle closure, focusing on practical, scalable solutions for carbon management [4,5]. Current CO₂ conversion strategies include thermochemical [6,7], electrochemical [8–10], photochemical [11,12], and biochemical approaches [13,14]. While photochemical and biochemical methods remain largely in the research phase due to limited efficiency, electrochemical methods have emerged as particularly promising, given their milder reaction conditions and potential for direct utilization of renewable electricity.

Compared with the thermochemical method which requires a large heat input, the electrochemical method necessitates reaction conditions of moderate severity and thus contributes to achieving carbon neutrality [15,16]. By utilizing renewable electricity, CO₂RR to value-added chemicals offers a practical solution to offset additional carbon footprints [17,18]. Despite its promise, the inherent symmetry and the strong C=O bonds (CO₂ molecule structure) in its structure pose a great kinetic challenge for CO₂RR [19,20]. Addressing these barriers requires innovative electrocatalyst designs, which have attracted growing attention in recent years. The sluggish kinetics of CO₂ electroreduction underscore the critical role of electrocatalysts [21]. Significant advancements have been achieved over the past decade in the progression of advanced materials for energy storage and conversion, with governments and researchers worldwide dedicating substantial resources to this rapidly evolving field [22,23]. Overcoming these challenges demands innovative electrocatalyst designs, which have received

^{*} Corresponding authors.

E-mail addresses: yanlt@qlu.edu.cn (L. Yan), zhaoxuebo@upc.edu.cn (X. Zhao), eyguo1985@qlu.edu.cn (E. Guo).

<https://doi.org/10.1016/j.ccr.2025.216541>

Received 10 November 2024; Received in revised form 18 January 2025; Accepted 8 February 2025

Available online 28 February 2025

0010-8545/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

Recent Advances in Phosphorescent Carbon Dots via Host–Guest Engineering

Youquan Yan, Hao Qiu, Heng Zhou, Yida Zhang, Xueni Wu, Zhenhua Gao, Chaofeng Zhu, and Zifei Wang*

Room temperature phosphorescence (RTP) materials, featuring large Stokes shifts, high exciton utilization, long lifetime, and multicolor emission, have consequently attracted widespread attention across various fields. Carbon dots (CDs) have rapidly emerged as a burgeoning research hotspot in materials science, owing to their ease of synthesis, low toxicity, excellent biocompatibility, and outstanding optical properties. Recent studies have highlighted the crucial role of host–guest strategies in both enhancing and precisely modulating the RTP performance of CDs, thereby expanding their potential applications across a wide range of fields. Despite significant progress, there remains a lack of comprehensive reviews that systematically elucidate the design strategies of CDs-based host–guest materials and their correlation with RTP property modulation. This review addresses this gap by summarizing the latest advancements in CDs-based host–guest RTP materials, with a particular focus on fundamental design strategies and mechanisms for performance modulation. On this basis, the potential applications of these materials in information security, intelligent optical devices, bioimaging, and optical sensing are discussed. Finally, in light of the current research landscape, the opportunities and future prospects for CDs-based host–guest RTP materials are outlined, aiming to offer new insights for the advancement of this emerging field.

1. Introduction

Room-temperature phosphorescence (RTP), arising from the radiative relaxation of triplet excitons, represents a compelling optical phenomenon with unique characteristics, such as extensive Stokes shifts, high exciton utilization, prolonged emission lifetimes, and the capacity for multicolor output.^[1–5] These attributes have spurred extensive investigations across disciplines including anti-counterfeiting,^[6,7] information encryption,^[8,9] biosensing,^[10] and optoelectronic devices.^[11,12] Traditionally, inorganic and organometallic phosphors, primarily comprising

noble metals or rare-earth elements, have dominated the RTP landscape. While these materials often deliver robust emission performance, their widespread application is curtailed by prohibitive synthesis costs, potential biological toxicity, and the scarcity of essential raw elements.^[13–16] In parallel, pure organic RTP materials have emerged as promising alternatives, celebrated for their abundant and cost-effective starting materials and diverse synthetic methodologies.^[17–20] However, these systems frequently confront issues related to complex synthetic routes, laborious purification protocols, and unpredictable biocompatibility, thereby impeding their translational potential.

Since their serendipitous discovery in 2004, carbon dots (CDs) have evolved into a vibrant research frontier, owing to their facile synthesis, low toxicity, remarkable water solubility, and superior photostability.^[21,22] Early investigations predominantly focused on the fluorescent attributes of CDs, leading to a profound understanding of their photoluminescence mechanisms and a plethora of

applications.^[23–28] However, the RTP properties of CDs are often constrained by two key factors: a relatively weak inter-system crossing (ISC) process and a high nonradiative transition rate, which limit the generation and stabilization of triplet excitons.^[29–31] To address these issues, various strategies such as heteroatom doping,^[32,33] surface functionalization,^[34,35] aggregation-induced emission,^[36] and host–guest strategy,^[37–45] have been developed to enhance spin–orbit coupling (SOC) and suppress nonradiative transitions. In contrast, the host–guest strategy not only circumvents complex synthetic procedures and allows for the flexible selection of host and guest components, thereby enhancing the structural tunability of materials, but also exhibits significant potential for large-scale applications of RTP materials, owing to its broad raw material availability and high cost-effectiveness. Therefore, host–guest engineering has emerged as a particularly effective and versatile approach, offering a tunable and structurally flexible platform for optimizing RTP emission (Figure 1).

The host–guest strategy plays a crucial role in addressing two fundamental aspects of RTP enhancement: triplet exciton stabilization and emission modulation.^[46–49] First, embedding

Y. Yan, H. Qiu, H. Zhou, Y. Zhang, X. Wu, Z. Gao, C. Zhu, Z. Wang
School of Materials Science and Engineering
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250353, China
E-mail: zfwang@qlu.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.202509988>

DOI: 10.1002/adfm.202509988

Na₂BaB₁₂O₁₈F₄: A Mixed Alkali/Alkaline-Earth Metal Fluorooxoborate with Two Unprecedented Interpenetrating Three-Dimensional B–O/F Anionic Networks and a Short Ultraviolet Cutoff Edge

Tuohetijiang Baiheti, Abudukadi Tudi, Minqiang Gai, Xuping Wang,* and Shujuan Han*

Cite This: *Inorg. Chem.* 2023, 62, 5008–5015

Read Online

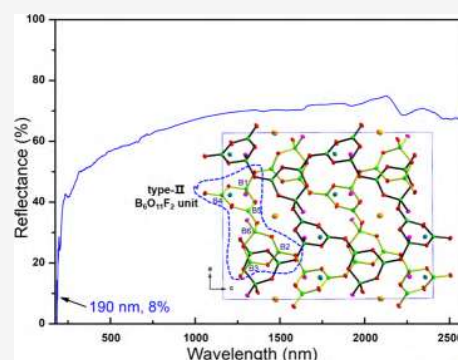
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Fluorooxoborates are promising yet largely untapped crystal materials for linear and nonlinear optical applications. The introduction of a strong electronegative F atom into an oxyboron anionic group offers a virtually unlimited chance for structural engineering and ultimately purposeful tuning of the macroscopic optical properties of the crystal. Herein, a new mixed alkali/alkaline-earth fluorooxoborate, Na₂BaB₁₂O₁₈F₄, was synthesized in a closed system. Na₂BaB₁₂O₁₈F₄ features a [B₆O₁₁F₂][−] fundamental building unit (FBB), which polymerizes into two new (first example) independent interpenetrating three-dimensional (3D) B–O/F anionic networks constructed entirely from BO₃ and BO₃F units. Based on optical characterizations and the first-principles calculations, Na₂BaB₁₂O₁₈F₄ exhibits a moderate birefringence (0.054 @ 1064 nm) and a short ultraviolet (UV) cutoff edge (below 190 nm). The successful synthesis and characterization of Na₂BaB₁₂O₁₈F₄ may speed up the subsequent discovery of other mixed alkali/alkaline-earth metal fluorooxoborates.



1. INTRODUCTION

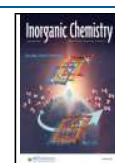
Inorganic borates and their structural derivatives have long appealed to widespread research interest due to their indispensable role in various modern optical devices.^{1–3} The subsequent discovery of outstanding practical crystals like LiB₃O₅, α/β-BaB₂O₄, and KBe₂BO₃F₂ confirmed the potentiality of borates in linear and nonlinear optical fields.^{4–7} However, recently in response to ever-increasing stringent demands for linear and nonlinear optical properties from practical fields, the purposeful hunt for new borate structures and property upgrades from the microscopic structure constituents become increasingly urgent.

The aforementioned necessity promoted the emergence of fluorooxoborates as paradigm-shifting UV materials in nonlinear optics. As structural derivatives of borates, the partial substitution of oxygen by fluorine (or O/F substitution) in BO₄ units in borates leads to fluorooxoboron groups, BO_xF_{4–x} ($x = 1, 2, 3$).^{8–10} This seemingly simple fluorination of BO₄ units creates a manifold of positive impacts on the structure and properties of a crystal. From the structural aspect, the number of possible basic units in borates multiplies from BO₂, BO₃, and BO₄ to BO₂, BO₃, BO₄, and BO_xF_{4–x} ($x = 1, 2, 3$) in fluorooxoborates, and these units can assemble themselves in different combinations with various connection modes (via common corners or edges). Thus, it is evident that fluorooxoborates can provide a virtually unlimited chance for the discovery of new structures with special characteristics. From the property modulation point, with partial O/F

substitution, the inherent vulnerability of the BO₄ unit is recouped, and BO_xF_{4–x} ($x = 1, 2, 3$) units can display enhanced hyperpolarizability and optical anisotropy compared to the BO₄ unit, benefiting both linear and nonlinear optical performance of the crystal.^{8–10} In addition, the F atom can act as a terminal atom. Hence, the number of dangling bonds can be effectively reduced, which is conducive to realizing a shorter cutoff edge in the UV region.¹⁰ Multiple advantages mentioned above led to the design, synthesis, and characterization of more than 69 fluorooxoborates over the past 5 years.^{11–13} Many of the above-mentioned crystals inherit the structural characteristics of famous borate crystals. For instance, AB₄O₆F (A = Na, Rb, Cs, NH₄) (or ABF family)^{14–17} and MB₂O₃F₂ (M = Sr, Pb, Sn),^{18,19} both of which display 2D anionic frameworks, respectively, were developed by adopting of KBBF (KBe₂BO₃F₂) and SBBO (Sr₂Be₂B₂O₇) as a model, whereas, BaB₂O₃F₂ (I–V),²⁰ BaB₈O₁₂F₂,²¹ and BaB₄O₆F₂²² crystals structurally evolved from BaAlBO₃F₂,²³ α-BaB₂O₄, and LnB₄O₆(OH)₂Cl.²⁴ Yet, despite the progress mentioned above, compared to the number of reported borates and

Received: January 17, 2023

Published: March 16, 2023



Inverse Design of Ferroelectric-Order in Perovskite Crystal for Self-Powered Ultraviolet Photodetection

Yabo Wu, Xuping Wang, Gang Tian, Limei Zheng, Fei Liang,* Shujun Zhang,* Haohai Yu,* and Huaijin Zhang

It has always been a hot topic to design an orderly mesoscopic structure in functional materials to tailor the macroscopic properties or realize new functions. The existence of domains in ferroelectric materials has been proven to affect the macroscopic properties, being actively studied in nonlinear optical conversion and piezoelectric effects. However, the high-efficiency photoelectric conversion capability of ferroelectric crystals has not yet been explored. Here, the authors study the orderly arrangement of ferroelectric order in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN) perovskite crystals, and design the “head-to-head” domains by tuning the Curie temperature T_c , thereby generating abundant charged domain walls and robust conductive channels for electrons and holes. An ultrahigh ultraviolet photoresponsivity is achieved in the KTN crystal under zero bias voltage, being about four orders magnitude higher than that of the well-known ferroelectric materials. The substantial improvement can be attributed to the judiciously designed ferroelectric order, as demonstrated by the conductive atomic force microscopy. In addition, KTN detector exhibits high stability and reliability after high-temperature and fatigue treatment. KTN crystal features giant photoresponsivity, high electric–optical coefficient, and large $\chi^{(2)}$ nonlinearity concurrently, indicating its great potential for application of all-optical devices on photonic chips.

microscopic structure and composition,^[1,2] including atoms, molecules, defects, and their spatial arrangement in real space. This traditional “structure–property–relationship” paradigm is followed by most researchers and has been applied in many fields such as photo/electrical catalysis,^[3,4] high-entropy alloys,^[5] and semiconductors,^[6,7] to name a few. A larger functional unit with mesoscopic scale beyond a single atom or molecule, on the other hand, can also be assembled in a certain spatial order;^[8] this leads to exceptional physicochemical properties and unprecedented functions. The coupling of functional units and ordered structure ubiquitously exists in functional materials, which has become a new pursuit in the material research field. Ferroelectric domain with the scale of hundreds of nanometers to tens of microns is one of the functional units, the coupling and interaction between ferroelectric domains and electrons, and photons and phonons

1. Introduction

The macroscopic properties and practical applications of optoelectronic functional materials are closely associated with the

are expected to enable emerging phenomena and applications.^[9–12] For example, Dong et al. fabricated the superelastic and ultraflexible BaTiO_3 single-crystal membrane with quasi-continuous electric dipole rotation.^[13] Qiu et al. reported the transparent $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 piezoelectric crystals with near-perfect transparency by erasing the scattering domain walls,^[14] while Guo et al. reported the self-organized toroidal polar topology in strained ferroelectric polymer with periodic terahertz waves absorption.^[15] All these results demonstrate that the manipulation of ferroelectric order is of great significance for realization of the long-term desired properties.

In the ferroelectric–optical interaction, spontaneous polarization can provide an intrinsic built-in electric field to drive the separation of photogenerated carriers.^[16–18] Therefore, the electrical signal can be detected under zero bias, that is, self-powered photodetectors.^[19] Since there is no external power supply, self-powered detectors have a low dark current, a large on-off ratio, small size, are easy to integrate, and have low energy consumption, which has attracted extensive attention in the field of optoelectronics.^[20] The traditional self-powered photodetectors are made of p–n junction or Schottky junction based on 2D materials, which are usually costly, complicated to fabricate, and have low stability at high temperature. Ferroelectric crystal-based self-powered photodetectors are expected to overcome these challenges, but suffer from the low photocurrent due to low quantum efficiency rate and limit of low

Y. Wu, F. Liang, H. Yu, H. Zhang
State Key Laboratory of Crystal Materials and Institute of Crystal Materials
Shandong University
Jinan 250100, China
E-mail: liangfei@sdu.edu.cn; haohaiyu@sdu.edu.cn

X. Wang
Advanced Materials Institute
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250014, China

G. Tian, L. Zheng
School of Physics
Shandong University
Jinan 250100, China

S. Zhang
Institute for Superconducting and Electronic Materials
AIMM
University of Wollongong
Wollongong, New South Wales 2500, Australia
E-mail: shujun@uow.edu.au

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202105108>.

DOI: 10.1002/adma.202105108