ADVANCED ENERGY MATERIALS
www.advenergymat.de

Controllable Construction of Active Sites for Catalytic Conversion and Spatial Constraints Applied to High-Performance Lithium–Sulfur Batteries

Jiawen Huangfu, Pingxian Feng, Xianfei Di, Yihui Tian, Mengqi Shi, Wei Hu, Xin Zhao, Shoujuan Wang, Yuebin Xi, Fangong Kong,* and Huan Wang**

The structural control of the positive sulfur carrier is very important to inhibit the shuttle effect of polysulfide and improve the overall performance of lithium–sulfur batteries. However, the microstructure of the carbon material carrier is uncontrollable, and it is difficult to coordinate and unify the pores and active sites. Here, Nitrogen and phosphorus co-doped porous carbon (N/P-LPC-900) is obtained through the simple activation method of potassium phosphate to achieve the structural regulation of porous and heteroatoms in one step. N/P-LPC-900 shows a graphene-like porous thin structure, which will provide the particular domain to adsorb polysulfide. The DFT results indicate that N-6-P has the strongest catalytic sulfur conversion ability. Further, in situ Raman characterization proves that the signals of Li_2S_6 and Li_2S_4 on the anode side of the N/P-LPC-900 battery are significantly weakened after the end of the first stage of discharge. Theory combined with experiment to verify that the co-doping of N and P for LPC can efficiently catalyze the conversion of polysulfide into Li_2S to inhibit the shuttle effect. This work provides a feasible way for the study of sulfur carriers, and lays a theoretical foundation for the construction of high-performance heteroatom doped porous carbon.

1. Introduction

Doping with heteroatoms can significantly increase the adsorption and catalytic active sites of carbon materials for polysulfides, thereby effectively improving the utilization rate of active substance sulfur and enhancing the electrochemical performance testing of batteries.[1] However, due to the influence of porous carbon structure, most active sites cannot be effectively or efficiently utilized, resulting in many active sites not being able to fully exert their functions and causing waste of active.[2] In porous carbon, micropores, due to their small size characteristics (0–2 nm), can act as active sites in the process of sulfur redox conversion. By physically confining polysulfides within the microporous structure, the shuttle effect of polysulfides can be suppressed to a certain extent.[2b,3] The combination of polar carbon surfaces doped with heteroatoms and microporous structures with Physical limitations can fully utilize the advantages of each active site and effectively enhance the synergistic effect.[1d,4] That is, sulfur species are confined through micropores, and the heteroatoms doped in the micropores strongly adsorb sulfur species on the carbon surface and efficiently catalyze their conversion, so that the entire sulfur redox conversion process is confined in the micropores, significantly reducing the diffusion of polysulfides toward the anode direction. Therefore, reasonable regulation of the structure and doping of heteroatoms in porous carbon is the key to achieving porous carbon as the sulfur host for high-performance lithium–sulfur batteries (LSBs).

In addition to one kinds of atom doping, the concept of co-doping has also been proposed and widely applied in recent years, and the co-doping of multiple elements exhibits a synergistic effect on the properties of carbon materials.[5] The concept of nitrogen doping has been widely known and applied in the research of heteroatom-doped carbon materials. P and N are located in the same main group and have the same number of outermost electrons. After doping into the carbon skeleton, the surface polarity of carbon materials can be significantly changed, enhancing the adsorption strength between carbon materials and polysulfides. At the same time, recent studies have found that the introduction of P plays a key role in catalyzing the conversion of polysulfides to promote chemical reaction kinetics.[6] However, compared with N, due to the larger atomic radius of P, it has a stronger electron-donating ability, and the defects caused by doping on

---

J. Huangfu, X. Di, Y. Tian, M. Shi, W. Hu, X. Zhao, S. Wang, Y. Xi, F. Kong, H. Wang
Department of Light Industry
State Key Laboratory of Green Papermaking and Resource Recycling
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250353, China
E-mail: qlgdxyb@qlu.edu.cn; kfg@qlu.edu.cn; cewanghuan@gzhu.edu.cn

P. Feng, H. Wang
Guangdong Engineering Technology Research Center for Sensing Materials Devices
Guangzhou Key Laboratory of Sensing Materials Devices
School of Chemistry and Chemical Engineering
Guangzhou University
Guangzhou 510006, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.202502210

DOI: 10.1002/aenm.202502210

Advanced Composites and Hybrid Materials (2025) 8:232
https://doi.org/10.1007/s42114-025-01305-1

RESEARCH

The synergistic effect of hybridization-micro/nano-structural design on the Ti_3C_2Tx MXene@CoFe-MOF@chitosan heterojunction enhances the absorption of electromagnetic waves

Qinggang Peng[1] · **Wenliang Yu**[1] · **Chao Gao**[1,2] · **Linlin Geng**[1] · **Pedram Fatehi**[1,3] · **Shoujuan Wang**[1] · **Fangong Kong**[1]

Received: 9 January 2025 / Revised: 3 April 2025 / Accepted: 8 April 2025

Abstract

The development of wave-absorbing materials is of particular crucialness in dealing with electromagnetic wave (EMWs) pollution. Especially in the fields of aerospace and highly integrated electronic devices, where the demand for lightweight, high-efficiency, broadband and multi-functional EMWs absorbing materials is increasing gradually. In this study, through the synergistic regulation of hybrid fillers and micro-nano structures, an EMWs absorbing material with abundant heterogeneous interfaces and micro-nano pore structures has been successfully formed. The prepared $Ti_3C_2T_x$ MXene@CoFe-MOF@chitosan carbon aerogel significantly enhances the absorption performance of EMWs by stimulating heterogeneous interface polarization relaxation and electromagnetic synergy effects. Under the condition of low density (35.09 mg/cm^3), TMC_{900} exhibits a minimum reflection loss of -50.95 dB and an effective absorption bandwidth (EAB) of 6.1 GHz. In addition, TMC_{900} also possesses excellent heat insulation and flame-retardant characteristics, enabling it to be applied in extreme environments. This research clarifies the synergistic regulation mechanism of hybrid fillers and micro-nano structures, opening a new pathway for the design of heterogeneous structures in EMWs absorbing materials.

Keywords Electromagnetic wave absorption · Hybridization · Micro-nano structure regulation · Heterogeneous interface

1 Introduction

The widespread use of electromagnetic waves (EMWs) in national defense [1], communications [2], household appliances, medical devices [3], and other aspects has led to an increasingly serious EMWs pollution. Meanwhile, with the rapid development of integrated and miniaturized electronic devices [4] as well as the aerospace field [5], EMWs absorbing materials are all developing towards being lighter and thinner. Therefore, the preparation of lightweight [6, 7], efficient [8], broadband [9], and multifunctional absorbing materials has important application value [10, 11]. How to balance the superior impedance matching and strong EMWs attenuation ability remains a critical challenge [12, 13]

In recent years, the development of EMWs absorbing materials has been significantly advanced by the synergistic effects of material hybridization and micro/nanostructure engineering [14]. Hybridization strategies, such as combining magnetic and dielectric components or integrating 2D materials, enable precise tuning of electromagnetic parameters (e.g., permittivity, permeability) through interface polarization, charge transfer, and bandgap modification, thereby introducing multiple loss mechanisms [15]. Meanwhile, micro/nanostructure, including hierarchical porous architectures, core–shell configurations, and metasurface designs, enhances EMWs absorption via multi-scale scattering, impedance matching optimization, and localized field enhancement [16, 17]. The integration of these two approaches allows overcoming the trade-off between impedance matching and EMWs attenuation ability, while also enabling dynamic responses and lightweight design.

✉ Shoujuan Wang
nancy5921@163.com

✉ Fangong Kong
kfgwsj1566@163.com

[1] State Key Laboratory of Green Papermaking and Resource Recyling, Key Laboratory of Pulp & Paper Science and Technology of Shandong Province/Ministry of Education, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China

[2] Shandong Open University, Jinan 250101, China

[3] Department of Chemical Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, ON P7B 5E1, Canada

Advanced Composites and Hybrid Materials (2024) 7:77
https://doi.org/10.1007/s42114-024-00871-0

RESEARCH

Effect of ultrasound-assisted xylanase pretreatment on the soluble substances of *poplar* wood and its model construction

Jiaxin Qu[1] · **Zhongjian Tian**[1] · **Fangfang Zhang**[1] · **Chuanling Si**[2] · **Xingxiang Ji**[1]

Received: 29 December 2023 / Revised: 27 February 2024 / Accepted: 2 March 2024 / Published online: 23 April 2024

Abstract

Cellulose, hemicellulose, and lignin molecules in *poplar* wood are interwoven to form a dense network-like structure, which prevents their degradation into oligomers for the preparation of biomass-based materials and chemicals. Therefore, it is necessary to use a pretreatment process to decompose the complex matrix. In this study, ultrasound-assisted xylanase treatment was used for *poplar* wood pretreatment. The effects of different parameters, such as enzyme treatment time, enzyme dosage, and ultrasound time on soluble substances and the surface of the cell wall were systematically investigated. The optimal conditions for the degradation of hemicellulose and lignin in *poplar* wood were a treatment time of 60 min and a xylanase dosage of 25 U/g. Ultrasound-assisted xylanase treatment improved the efficiency of removing hemicellulose. The contents of glucose, xylose, and lignin were increased by 34.73%, 32.01%, and 59.65%, respectively, with the ultrasound-assisted xylanase treatment. In addition, a least-squares model was constructed to describe the dissolution behavior of component, which is helpful to guide the subsequent conversion and utilization of *poplar* wood biomass.

Keywords *Poplar* wood · Xylanase · Ultrasonication · Least squares method · Ultrasound-assisted xylanase treatment

1 Introduction

Poplar is a fast-growing tree species with strong adaptability and short growth cycle. The main components of *poplar* wood are cellulose, hemicellulose, and lignin. Cellulose is the most highly abundant of the three main components of *poplar* wood and is the most important component required in the pulp and paper process [1–8]. The content of hemicellulose in *poplar* wood is second only to cellulose, and the highest content of hemicellulose is xylan, which is dominated by 4-O-methylglucuronide xylan. Lignin fills the space between cellulose and hemicellulose, playing a role in protection and support [9]. The minor components of *poplar* wood include extractives, starch, inorganic substances, and plant gums. Cellulose, hemicellulose, and lignin are linked through ether bonds, phenyl glycosidic bonds, and other chemical bonds, intertwined with each other to form a complex matrix [10–13]. This structure is highly recalcitrant to enzyme and microbial degradation and is the main obstacle to the conversion of lignocellulosic biomass into biomass-based materials and chemicals. Thus, it is necessary to develop efficient pretreatment processes to decompose the complex structures.

Currently, the main pretreatment methods for lignocellulosic biomass are physical, chemical, physic-chemical, and biological approaches, etc. [14]. Among them, physical methods such as mechanical grinding, ultrasonic, microwave, and high-energy radiation are energy-intensive [15]. Chemical methods that usually involve acid [16], alkali, organic solvents, and ionic liquid are facing the challenges, such as corrosion and solvent recycling [17]. Physic-chemical methods, such as ammonia steam explosion and hydrothermal pretreatment, usually require high reaction temperatures and pressures [18]. Biological methods refer to employing microorganisms or enzymes to degrade biomass feedstocks to improve the efficiency of component utilization [19]. It is a green pretreatment technology with low energy consumption, high catalytic specificity, and low environmental pollution [20].

For the pulp and paper industry, enzyme pretreatment can not only reduce the amount of chemicals but also improved

---

✉ Xingxiang Ji
xxjt78@163.com

[1] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China

[2] Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, China

RESEARCH ARTICLE

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Lignin-Alkali Metal Ion Self-Catalytic System Initiated Rapid Polymerization of Hydrogel Electrolyte with High Strength and Anti-Freezing Ability

*Huawei Su, Qingqing Guo, Congde Qiao, Xingxiang Ji, Ligang Gai, and Libin Liu**

Hydrogel electrolyte is not resistant to freezing and has weak mechanical properties, and its fabrication is time-consuming and energy-consuming, limiting its application. Here, a simple, universal, and fast gelation based on dealkaline lignin (DL) -alkali metal ions is developed. The complex formed by catechol and alkali metal ions promotes the equilibrium of redox reactions. The produced $SO_4^{-}\cdot$, $OH\cdot$ and singlet oxygen ($^1O_2$) radicals are responsible for the rapid polymerization of vinyl monomers. Alkali metal ions play a dual role in the rapid polymerization and frost resistance of hydrogel electrolytes. By modulating the mass ratio of DL and metal ion concentration, the preferred hydrogel electrolyte can be fabricated in an alkaline aqueous solution for 4 min at room temperature and possesses excellent anti-freezing performance (0.51 mS cm^{-1} at −40 °C) and strong mechanical properties (tensile stress: 0.4 MPa, strain: 1125%). The hydrogel electrolyte-assembled supercapacitor exhibits high stability at low temperatures. The specific capacitance retention is 89.7 % and 88.7 % after 5000 charge/discharge cycles at 25 and −20 °C, respectively. The lignin-alkali metal ions self-catalytic system completely different from the reported lignin-oxidizing metal ion system will open up a new way for the fabrication of anti-freezing ionic conductors and energy storage devices.

1. Introduction

The shortage of fossil energy and the increasingly severe environmental issues have stimulated the demand for green manufacturing electronic devices.[1,2,3] Hydrogel electrolyte has been widely used in various electronic devices such as supercapacitors,[4,5] soft robots,[6,7] and new energy batteries,[8,9] due to its adjustable mechanical properties, environmental friendliness, and high conductivity. The fabrication of hydrogel electrolytes mostly requires heating or ultraviolet irradiation to activate the initiator to generate free radicals, then initiate monomer polymerization to form polymer networks. These preparation processes not only take a long time (more than 2 h) and are tedious,[10,11] but also require additional external energy,[12,13] which largely limit the further development of green preparation of hydrogel electrolytes in electronic devices. In addition, the hydrogel electrolyte contains plenty of water, and it will inevitably freeze < 0 °C, resulting in a decline in conductivity, which will seriously affect the normal use of electronic devices. Therefore, it is a great challenge in the rapid polymerization of hydrogel electrolytes with anti-freezing ability at ambient temperature without introducing external energy.

The rational design of polymerization reaction and anti-freezing agent is capable of achieving simultaneously rapid room temperature polymerization and anti-freezing performance of hydrogel electrolyte. For free radical polymerization reactions, the initiators (e.g., ammonium persulfate (APS); potassium persulfate) in the reaction system are highly oxidizing. Thus, the introduction of reducing materials in the reaction system can react with persulfate at ambient temperature to produce free radicals and lead to rapid polymerization. Currently, the commonly used reducing materials are MXene,[14] polyoxometalates,[15] vitamin C,[16] catechol group containing compounds,[17,18] etc. Among these reducing materials, lignin, as a natural biomass material, contains a large number of methoxy (-OCH_3) and phenolic hydroxyl (-OH) groups which can interact with the oxidizing metal ions in situ to convert to the corresponding quinones/semiquinone structures,[19,20] generating free radical to accelerate polymerization of the monomers.[21] For example, Peng et al.[22] reported an organic hydrogel fabricated by taking advantage of a lignin-Cu^{2+} self-catalytic system to achieve rapid polymerization. In these lignin-metal ion-based system, strong oxidizing and high valent metal ions[22,23,24] (such as Cu^{2+}, Ag^{+}, Fe^{3+}) are used to form an oxidation-reduction system with lignin, which can be reduced during the process of phenolic hydroxyl groups being oxidized to quinone.[25,26] In contrast, alkali metal ions (e.g., Li^{+}, Na^{+}, K^{+}) have weak oxidizing properties and have been reported to be unable to promote free radical polymerization reactions.[27,28] However, in our work, it is found that alkali metal ions (Li^{+}, Na^{+}, K^{+}) can form complexes with catechol

---

H. Su, Q. Guo, C. Qiao, X. Ji, L. Gai, L. Liu
School of Chemistry and Chemical Engineering
State Key Laboratory of Biobased Material and Green Papermaking
Qilu University of Technology (Shandong Academy of Sciences)
Jinan 250353, China
E-mail: lbliu@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.202316274

DOI: 10.1002/adfm.202316274

Composites Part B 281 (2024) 111537

Contents lists available at ScienceDirect

Composites Part B

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

Utilizing methacrylated lignin as a sustainable macro-crosslinker for synthesizing innovative PVA/AMPS composites crosslinked hydrogel nanofibers: A potential application for lithium-ion battery separators

Yun Dou, Shen Li, Shoujuan Wang [**], Magdi E. Gibril [*], Fangong Kong [***]

State Key Laboratory of Biobased Material and Green Papermaking, Key Laboratory of Pulp & Paper Science and Technology of Shandong Province/Ministry of Education, Faculty of Light Industry, Qilu University of Technology, Shandong Academy of Sciences, Jinan, 250353, China

ARTICLE INFO

Handling Editor: Prof. Joong Lee

Keywords:
Methacrylated lignin
Electrospinning
Crosslinked hydrogel nanofiber
Separators
Lithium-ion batteries

ABSTRACT

There are significant issues with commercial separators that must be resolved before they can be used in high-energy-density batteries. These problems include low porosity, poor electrolyte wetting, and low mechanical properties. This study presents a facile method for preparing composite crosslinked hydrogel nanofibers of polyvinyl alcohol (PVA) with 2-acrylamide-2-methylpropanesulfonic acid (AMPS) for lithium-ion battery separators by utilizing methacrylated lignin (LMA) as a bio-based crosslinker. Initially, LMA was synthesized by grafting glycidyl methacrylate (GMA) onto lignin via esterification. Subsequently, a crosslinked hydrogel nanofiber membrane (PVA/AMPS-LMA) was electrospun with varying LMA fractions, which were polymerized by combining free radical copolymerization and esterification reactions. The effectiveness of LMA as a crosslinker was assessed against the N, N′-methylene bisacrylamide (MBA). The study showed that using LMA as a crosslinker significantly improved the membrane's properties. The PVA/AMPS-LMA separator displayed superior features such as mechanical strength, thermal stability, porosity, electrolyte uptake, ionic conductivity, and lithium-ion transference number, when compared with PVA/AMPS, PVA, and Celgard separators. Specifically, the PVA/AMPS-LMA separator demonstrated a high mechanical strength of 24.9 MPa, strong thermal stability at 170 °C with no shrinkage, high porosity (84.3 %), and electrolyte uptake (661.4 %). It also exhibited exceptional ionic conductivity (2.75 mS/cm) and a notable lithium-ion transference number ($tLi^{+} = 0.717$). In coin batteries, the PVA/AMPS-LMA separator retained over 96 % capacity (142.4 mAh/g) after 200 cycles at 1C. This performance exceeded that of PVA/AMPS, PVA, and Celgard separators, suggesting that PVA/AMPS-LMA separators have the potential to replace their commercial counterparts.

1. Introduction

Lithium-ion batteries (LIBs) stand out as the foremost energy storage solution among rechargeable batteries, showcasing exceptional features such as high energy/power density, long cycle life, low self-discharge, and unparalleled safety [1]. Their versatile applications span across a broad spectrum, ranging from powering electric vehicles to powering critical medical equipment and satellites [2]. A lithium-ion battery comprises four components: a positive electrode, a negative electrode, an electrolyte, and a separator. The separator plays a crucial role in regulating lithium-ion transport and preventing short circuits [3]. Conventional separators utilized in lithium-ion batteries (LIBs) are typically composed of non-biodegradable materials such as polypropylene (PP) [4] and polyethylene (PE) [5], which exhibit thermal instability, poor wettability, and low ion conductivity [6]. These drawbacks contribute to the diminished performance of lithium-ion batteries, resulting from the incongruity between polar organic solvents and non-polar polyolefin separators, leading to reduced electrolyte absorption capacity [7]. One solution to tackle these challenges is to develop novel separators that possess improved mechanical properties and a nanostructure. In response, researchers have harnessed nanofiber technology to develop innovative types of lithium-ion battery

---

[*] Corresponding author.
[**] Corresponding author.
[***] Corresponding author.

E-mail addresses: nancy5921@163.com (S. Wang), magdi.gibril@gmail.com (M.E. Gibril), kfgwsj1566@163.com (F. Kong).

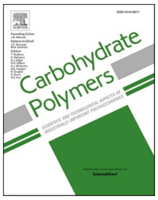
https://doi.org/10.1016/j.compositesb.2024.111537
Received 29 February 2024; Received in revised form 21 April 2024; Accepted 6 May 2024

Carbohydrate Polymers 358 (2025) 123518

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Fabrication of controllable structure of nanocellulose composite aerogel for targeted drug delivery

Yang Li [a,1], Xiaoyan Liu [b,1], Zhongming Liu [a,*], Shoujuan Wang [a], Fangong Kong [a,*]

[a] *State Key Laboratory of Green Papermaking and Resource Recycling, Key Laboratory of Pulp & Paper Science and Technology of Shandong Province/Ministry of Education, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China*
[b] *College of Health Sciences, Shandong University of Traditional Chinese Medicine, Jinan 250353, China*

A R T I C L E I N F O

Keywords:
Nanocellulose composite aerogels
Imatinib
Drug carrier
Sustained release
Kinetic model

A B S T R A C T

The problems of low drug loading capacity and short release time in traditional drug delivery systems would lead to repeated administration and an increase in the burden of treatment. To solve this problem, nanocellulose composite aerogels were designed and prepared as the drug carrier with an adjustable structure, good biocompatibility, high drug loading capacity, and long release time. In this study, polyethylene glycol (PEG) and β-cyclodextrin (β-CD) were introduced into nanocellulose through blending and physicochemical crosslinking to regulate and improve the network structure, drug loading capacity, and sustained release performance of nanocellulose composite aerogels. The pore structure and physicochemical structure of aerogel were explored to reveal the structure and effect between the structure of aerogel and drug release through advanced technologies such as X-ray photoelectron spectroscopy (XPS), micro-CT, scanning electron microscopy (SEM), and specific surface area (BET). The drug loading and release curves of aerogels were simulated to reveal the relevant mechanism through mathematical models, providing a theoretical basis for clinical application.

1. Introduction

With the rapid advancement of biomedicine, various renewable green materials, such as gelatin, silk protein, chitosan, and cellulose, are increasingly used in the treatment and diagnosis of biomedical diseases. These materials help reduce drug toxicity and enhance drug efficacy (Xiao et al., 2023). However, the application of bio-based material in biomedical applications is still in its early stages, as the mechanisms of their structural regulation and drug loading are not fully understood.

Cellulose is a non-toxic, renewable, and biocompatible natural polymer known for its excellent hydrophilicity and structural stability. These properties make it an attractive material for biomedical research (Wang et al., 2024). Nanocellulose is an advanced material obtained by the physical and chemical decomposition of natural cellulose into nano-sized fibers or crystals, which is widely used in drug delivery systems, wound dressings, and tissue engineering (Du et al., 2019). Nanocellulose aerogels are an ultra-light and well-developed three-dimensional porous solid material with a large specific surface area and excellent adsorption properties, which make them ideal for sustained and controlled release of drugs (Yu & Budtova, 2024).

In recent years, many researchers have developed nanocellulose aerogels as candidate materials for drug delivery due to their biocompatibility, ease of processing, and other advantages (García-González et al., 2021). Valo et al. reported that different types of nanocellulose aerogels could continuously release drugs with a drug-loading capacity ranging from 3.5 % to 12 % and a drug-release time of 150 min (Valo et al., 2013). Li et al. (2019) successfully improved the pore structure of nanocellulose composite aerogels by adjusting the amounts and proportions of nanocellulose, gelatin, and dialdehyde starch. The study showed that increasing the content of cellulose nanofibers (CNF) and the degree of crosslinking improved the drug loading efficiencies from 10 % to 35 % and enabled the controllable release of 5-fluorouracil (Li et al., 2019). Yue et al. (2024) used cellulose nanofiber derivatives to prepare nanocellulose composite aerogels through a simple self-assembly pretreatment and directional freeze-drying technique. These aerogels demonstrated excellent pH-responsive drug release performance with a drug release time of 8 h (Yue et al., 2024b). Liu et al. (2024) prepared carboxycellulose composite aerogels as drug carriers of 5-fluorouracil by blending and in-situ synthesis method, the results showed that the loading capacity of aerogels was 180 mg/g and the drug release was

---

* Corresponding authors.
E-mail addresses: liuzhongming126@126.com (Z. Liu), kfgwsj1566@163.com (F. Kong).
[1] These authors contributed equally to this work.

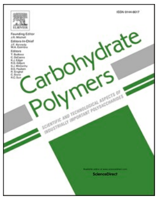
https://doi.org/10.1016/j.carbpol.2025.123518
Received 16 January 2025; Received in revised form 17 March 2025; Accepted 17 March 2025

Carbohydrate Polymers 342 (2024) 122385

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Review

Advances in the preparation and application of cellulose-based antimicrobial materials: A review

Xugang Dang [a,b,*], Nan Li [b], Zhenfu Yu [b], Xingxiang Ji [a,**], Mao Yang [a], Xuechuan Wang [b]

[a] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China
[b] Institute for Biomass and Function Materials & College of Bioresources Chemistry and Materials Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

ARTICLE INFO

Keywords:
Cellulose based antimicrobial materials
Metal nanoparticle-cellulose antimicrobial materials
Natural polymeric-cellulose antimicrobial materials
Cellulose-based antibacterial materials in fabrics
Green antimicrobial functional materials

ABSTRACT

The rise of polymer materials in modern life has drawn attention to renewable, easily biodegradable, environmentally-friendly bio-based polymers. Notably, significant research has been dedicated to creating green antimicrobial functional materials for the biomedical field using natural polymer materials. Cellulose is a rich natural biomass organic polymer material. Given its favorable attributes like film-forming capability, biodegradability, and biocompatibility, it is extensively employed to tackle a wide range of challenges confronting humanity today. However, its inherent drawbacks, such as insolubility in water and most organic solvents, hygroscopic nature, difficulty in melting, and limited antimicrobial properties, continue to pose challenges for realizing the high-value applications of cellulose. Achieving multifunctionality and more efficient application of cellulose still poses major challenges. In this regard, the current development status of cellulose materials was reviewed, covering the classification, preparation methods, and application status of cellulose-based antimicrobial materials. The application value of cellulose-based antimicrobial materials in biomedicine, textiles, food packaging, cosmetics and wastewater treatment was summarised. Finally, insights were provided into the developing prospects of cellulose-based antimicrobial materials were provided.

1. Introduction

With the changing environment, there is a rising prevalence of bacteria and viruses in nature, significantly impacting human life and health. Therefore, it is imperative to take appropriate measures to address these challenges (Wang et al., 2022; Wu et al., 2023). Currently, the management of microorganisms such as bacteria is mainly based on the development of new functional antimicrobial materials to achieve specific inhibition of different bacteria (Hou et al., 2023). Natural polymer materials have garnered significant attention for their functional properties. Concurrently, substantial academic efforts have been directed towards the preparation of green and biodegradable advanced functional materials for the biomedical field (Kumar, Ranwa, & Kumar, 2020; Lin, Wong, Su, Chen, & Chueh, 2018; Rai, Mehrotra, Priya, Gnansounou, & Sharma, 2021). Moreover, cellulose, as a natural biomass organic polymer material, is abundantly available in the natural environment, inexpensive, and easy to obtain. Therefore, it has been employed to address many of the challenges currently faced by humanity (Gao, Zhang, Wang, & Sun, 2023; Tanpichai, Biswas, Witayakran, & Yano, 2019). In addition, cellulose is a biodegradable, biocompatible, environmentally friendly and versatile organic biomaterials (Amarasekara, Nwankwo, & Fernando, 2023). It is considered an almost inexhaustible raw material for the production of environmentally-friendly and biocompatible products, with wide-ranging applications in medicine, fabrics, food packaging, cosmetics, and wastewater treatment (Scheme 1) (Sperandeo et al., 2020; Wang et al., 2020). Meanwhile, there are the large amount of hydroxy groups at C-2, C-3, and C-6 in the glucopyranosyl units of cellulose molecules, enabling the material to be modified and applied with antimicrobial agent molecules. This allows for the preparation of cellulose-based antimicrobial materials, offering a wide range of application value (Liao et al., 2023). Herein, the review provided an overview of the preparation methods of cellulose-based antimicrobial materials and their recent applications. This included cellulose blended with other

---

* Correspondence to: X. Dang, Institute for Biomass and Function Materials & College of Bioresources Chemistry and Materials Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China.

** Corresponding author.

E-mail addresses: xg.dang@sust.edu.cn (X. Dang), xxjt78@163.com (X. Ji).

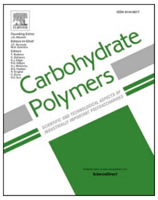
https://doi.org/10.1016/j.carbpol.2024.122385
Received 11 January 2024; Received in revised form 6 June 2024; Accepted 7 June 2024

Carbohydrate Polymers 321 (2023) 121310

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Super-stretching and high-performance ionic thermoelectric hydrogels based on carboxylated bacterial cellulose coordination for self-powered sensors

Luzheng Chen, Jiang Lou [*], Xuhui Rong, Zhuqing Liu, Qijun Ding, Xia Li, Yifei Jiang, Xingxiang Ji [*], Wenjia Han [*]

State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China

ARTICLE INFO

Keywords:
Ionic thermoelectric
TEMPO-oxidized bacterial cellulose
Self-powered
Wearable sensors
Dual-network hydrogel

ABSTRACT

Self-powered sensors that do not require external power sources are crucial for next-generation wearable electronics. As environment-friendly ionic thermoelectric hydrogels can continuously convert the low-grade heat of human skin into electricity, they can be used in intelligent human-computer interaction applications. However, their low thermoelectric output power, cycling stability, and sensitivity limit their practical applications. This paper reports a 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-oxidized carboxylated bacterial cellulose (TOBC) coordination double-network ionic thermoelectric hydrogel with lithium bis(trifluoromethane) sulfonimide (LiTFSI) as an ion provider for thermodiffusion, as LiTFSI exhibits excellent thermoelectric properties with a maximum power output of up to 538 nW at a temperature difference of 20 K. The interactions between the ions and the hydrogel matrix promote the selective transport of conducting ionic ions, producing a high Seebeck coefficient of 11.53 mV K^{-1}. Hydrogen bonding within the polyacrylamide (PAAm) network and interactions within the borate ester bond within the TOBC confer excellent mechanical properties to the hydrogel such that the stress value at a tensile deformation of 3100 % is reaches 0.85 MPa. The combination of the high ionic thermovoltage and excellent mechanical properties ionic thermoelectric hydrogels provides an effective solution for the design and application of self-powered sensors based on hydrogels.

1. Introduction

Flexible wearable electronic devices, which have significant potential in the fields of intelligent robotics (Zheng et al., 2020), electronic skin (Chen, Qian, Cai, Zhou, & Lu, 2022), and biomedicine (Peng et al., 2020), have attracted considerable attention owing to their portability, stretchability, and biocompatibility (Ma, Jiang, Han, & Li, 2023; Xia et al., 2022; Yao et al., 2022). Conventional sensors made of rigid materials have the disadvantages of unstable electrical output signals during cyclic strain and in the presence of environmental hazards (Gao et al., 2022; Li, Tang, et al., 2023; Su et al., 2021). Although strain sensors powered by external batteries have received considerable research attention, frequent charging and discharging cycles have severely limited their practical applications (Xu et al., 2017). Therefore, high sensitivity, environmental stability, excellent mechanical properties, and self-powering capabilities have become the basic requirements for wearable devices (Li, Li, et al., 2023; Ma et al., 2022; Wu et al., 2023; Zhang et al., 2023). However, preparing multifunctional electronic devices with these characteristics is challenging.

Current research on self-powered flexible sensors has mainly focused on piezoelectric nanogenerators (PENGs) (Huang et al., 2017; Zhang et al., 2018), frictional electrostatic nanogenerators (TENGs) (Wu, Li, et al., 2022), and thermoelectric generators (TEGs) (He et al., 2022; Liang et al., 2021). Among these, TEGs based on the Seebeck effect can continuously convert the heat generated by the human body into renewable electrical energy, thereby solving the problem of self-powering multifunctional sensors (Liu et al., 2021). However, TEGs made of inorganic thermoelectric materials have poor tensile properties, which limit the collection of signals for monitoring human activities (Gao et al., 2021). In recent years, ionic hydrogels prepared by combining organic polymers and ionic liquids, polyelectrolytes, and inorganic salts have gained significant attention (Fang et al., 2020; Kim, Kwon, Kim, Choi, & Moon, 2022; Liu, Cheng, et al., 2022; Zhao et al., 2022), and their Seebeck coefficients are of the order of mV K^{-1} (He,

---

[*] Corresponding authors.
E-mail addresses: jlou@qlu.edu.cn (J. Lou), xxjt78@163.com (X. Ji), hwj200506@163.com (W. Han).

https://doi.org/10.1016/j.carbpol.2023.121310
Received 10 July 2023; Received in revised form 4 August 2023; Accepted 15 August 2023

Biosensors and Bioelectronics 259 (2024) 116405

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

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

Strategies for measuring concentrations and forms of amyloid-β peptides

Hangyu Shen [a], Keyin Liu [a], Fangong Kong [a], Mingguang Ren [a], Xiaoying Wang [a,b,*], Shoujuan Wang [a,**]

[a] State Key Laboratory of Biobased Materials and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Jinan, Shandong, 250353, PR China
[b] Shandong Haizhibao Ocean Technology Co., Ltd, Weihai, Shandong, 264333, PR China

ARTICLE INFO

Keywords:
Alzheimer's disease
Amyloid-β
Concentration
Aggregation form

ABSTRACT

Alzheimer's disease (AD) is affecting more and more people worldwide without the effective treatment, while the existed pathological mechanism has been confirmed barely useful in the treatment. Amyloid-β peptide (Aβ), a main component of senile plaque, is regarded as the most promising target in AD treatment. Aβ clearance from AD brain seems to be a reliably therapeutic strategy, as the two exited drugs, GV-971 and aducanumab, are both developed based on it. However, doubt still exists. To exhaustive expound on the pathological mechanism of Aβ, rigorous analyses on the concentrations and aggregation forms are essential. Thus, it is attracting broad attention these years. However, most of the sensors have not been used in pathological studies, as the lack of the bridge between analytical chemist and pathologists. In this review, we made a brief introduce on Aβ-related pathological mechanism included in β-amyloid hypothesis to elucidate the detection conditions of sensor methods. Furthermore, a summary of the sensor methods was made, which were based on Aβ concentrations and form detections that have been developed in the past 10 years. As the greatest number of the sensors were built on fluorescent spectroscopy, electrochemistry, and Roman spectroscopy, detailed elucidation on them was made. Notably, the aggregation process is another important factor in revealing the progress of AD and developing the treatment methods, so the sensors on monitoring Aβ aggregation processes were also summarized.

1. Introduction

Alzheimer's disease (AD), the most common form of dementia, is affecting tens of millions of people worldwide, and this number has been increasing year by year (Lane et al., 2018). In China's 2015 – 2018 research survey on dementia, about 9.83 million people over 60 had AD. (Jia et al., 2020) As estimated in the U.S. 2021 study report (Alzheimer's disease facts and figures, 2021), 6.2 million people aged 65 and older are living with Alzheimer's dementia. In worldwide, about 74.7 million people will suffer from dementia by 2030. In the absence of effective treatments, this number will reach 131.5 million by 2050 (Cummings et al., 2016; Scheltens et al., 2021). This disease seriously affects people's physical health and life quality. As Alzheimer's patients need professional care, this disease also gives heavy human and financial burden to the families of patients. Moreover, the global annual treatment cost is about 1 trillion US dollars, and it is estimated that this fee will increase significantly by 2030, which is heavy burden to the society (Long and Holtzman, 2019).

Due to the complexity of human brain and the lack of research tools for reasonable experimental models, the exact pathogenesis of AD is still unclear. Numerous hypotheses have emerged for the pathogenesis of AD. Among them, amyloid-β (Aβ) seems to be a key factor driving the advance of AD. (Bhatt et al., 2021; Brier et al., 2016; Chen et al., 2017; Haass et al., 2012; Hardy and Higgins, 1992; Mamun et al., 2020; Marucci et al., 2021; Teich and Arancio, 2012) Aβ is generated by two subsequent proteolytic cleavages of amyloid precursor protein (APP), β-secretase at the ectodomain and γ-secretase at the intra-membranous sites (Fig. 1). (Hampel et al., 2021) Aβ possesses a hydrophilic N terminal and a hydrophobic C terminal. Thus, it can spontaneously assemble into micelles, and the resulting products, Aβ aggregates, are toxic. Aβ aggregates can synergize hyperphosphorylation and aggregation of Tau, resulting in senile plaque formation and neurofibrillary

---

* Corresponding author. State Key Laboratory of Biobased Materials and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Jinan, Shandong, 250353, PR China.

** Corresponding author.

E-mail addresses: xywang2019@qlu.edu.cn (X. Wang), wshj@qlu.edu.cn (S. Wang).

https://doi.org/10.1016/j.bios.2024.116405
Received 31 January 2024; Received in revised form 1 May 2024; Accepted 17 May 2024

International Journal of Biological Macromolecules 256 (2024) 128424

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

In situ facile synthesis and antibacterial activity of Ag-MOFs/cellulose filter paper composites for fruit fresh-keeping

Ning Chen, Chao Wang [*], Fangong Kong, Shoujuan Wang [*]

State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China

ARTICLE INFO

Keywords:
MOFs/CMFP
Antibacterial activity
Fruit preservation

ABSTRACT

A large number of fresh fruits are wasted in the supply chain due to spoilage, so it is crucial to develop fruit preservation materials. Herein, two novel Ag-MOFs/carboxymethyl filter paper (Ag-MOFs/CMFP) composites were successfully synthesized by in situ facile synthesis, which can be used as packaging materials to delay fruit spoilage. The synthesis process is simple and environmentally friendly, and the reaction conditions are mild. The mechanical property, water stability, and antibacterial activity of the as-synthesized Ag-MOFs/CMFP composites were investigated. Specifically, the composites exhibited high mechanical performance and the tensile strength was >10.00 MPa. Moreover, the composites displayed good water stability and can remain stable in water environment for >7 days, which can be attributed to the strong interaction between Ag-MOFs and CMFP. Significantly, Ag-MOF particles endow the composite papers with excellent antibacterial activity, which can inactivate 99.9 % of the bacteria. Attributed to these characteristics, these composite papers were used as fruit fresh-keeping materials and can prolong the shelf-life of cherry tomatoes and peaches for >10 days. This research not only provides a facile synthesis strategy for the flexible MOFs paper, but also provides instructive guidance for related research on fruit preservation materials.

1. Introduction

A large number of fresh fruits are severely wasted during transportation and storage, and the principal cause of waste is fruit spoilage [1–3]. The spoiled fruit contain lots of spoilage bacteria that may cause physical discomfort and even serious illness when ingested [4–6]. As is well known, the microbial infection is the major cause of fruit spoilage [7–9]. To prolong quality guarantee period of fruits, it is crucial to develop efficient fruit preservation materials that can inhibit microbial growth.

Metal-organic frameworks (MOFs), as a continuously developing crystalline material, have brought widespread attention in recent decades, especially in antibacterial field [10–12]. MOFs materials have the characteristics of stable dispersion and low toxicity [13–15]. Among them, silver-based MOFs (Ag-MOFs) are considered as one of the most promising antibacterial materials owing to their good antibacterial performance and broad spectrum [16–19]. The synthesis of Ag-MOFs and their related antibacterial properties have been explored in recent years [20–22]. Lu et al. reported the synthesis of two novel Ag-MOFs and their antimicrobial properties [23]. Rauf et al. synthesized an Ag-MOF with good thermal stability and antibacterial activity [24]. However, the intrinsic fragility [25], poor machinability [26,27], and poor water stability of Ag-MOFs are still a major obstacle to their practical application.

To solve the above problems, a feasible strategy is to fix Ag-MOFs onto flexible substrate materials. Cellulose filter paper (FP) is a promising flexible substrate [28] due to its low cost [29], biodegradability, and non-toxicity [30,31]. The combination of Ag-MOFs and flexible cellulose FP is a promising technology, which can make up for the above deficiencies of Ag-MOFs. The flexible cellulose FP substrate endows MOFs with flexibility and processability, which is conducive to fully tapping the potential of MOFs. Moreover, cellulose FP can anchor MOFs on cellulose paper fibers and improve the stability of MOFs. At present, some MOFs/cellulose paper-based composites and their related applications have been reported [32–37]. Li et al. synthesized a Tb^{3+}@Ag-MOFs/detection paper by impregnation method and used it for formaldehyde sensing [38]. Ma et al. prepared Ag-MOF/cellulose fiber composite filter using in-situ deposition method, which showed good filtration performance for PM2.5 [39]. Nevertheless, there are still some challenges for the synthesis of MOFs/cellulose FP composites, including

---

* Corresponding authors.
E-mail addresses: wangchao@qlu.edu.cn (C. Wang), nancy5921@163.com (S. Wang).

https://doi.org/10.1016/j.ijbiomac.2023.128424
Received 3 September 2023; Received in revised form 19 November 2023; Accepted 23 November 2023

International Journal of Biological Macromolecules 257 (2024) 128760

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

A biocompatible chitosan-based fluorescent polymer for efficient H_2O_2 detection in living cells and water samples

Hui Sun [1], Qingyu Xu [1], Mingguang Ren [*], Fangong Kong [*]

State Key Laboratory of Biobased Material and Green Papermaking, Key Laboratory of Pulp & Paper Science and Technology of Shandong Province/Ministry of Education, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, PR China

A R T I C L E I N F O

Keywords:
Fluorescence
Chitosan
Polymeric probe
Hydrogen peroxide
Bio-imaging

A B S T R A C T

As a biomarker of oxidative stress, hydrogen peroxide (H_2O_2) plays a complex role in organisms, including regulating cell signaling, respiration, the immune system, and other life processes. Therefore, it is important to develop a tool that can simply and effectively monitor H_2O_2 levels in organisms and the environment. In this work, naphthalene fluorophores with a borate structure were introduced into chitosan (CTS) azide, and a CTS-based fluorescence sensor (**CTS-HP**) was designed for sensitive H_2O_2 detection. The biocompatibility and degradability of CTS endowed **CTS-HP** with reduced biotoxicity compared with organic fluorescent dyes, and the substitution degree of fluorophores on the CTS chains was 0.703. The randomly coiled chain structure of the **CTS-HP** probe enabled the boronic acid recognition sites on the fluorophores to achieve the enrichment of analyte H_2O_2 through a synergistic effect. Therefore, the probe **CTS-HP** (10 μg mL^{-1}) exhibited a 21-fold fluorescence enhancement and good detection limit (LOD = 8.98 nM) in H_2O_2 solution, reaching the maximum fluorescence response faster (within 16 min). The probe also successfully achieved the fluorescence imaging of endogenous and exogenous H_2O_2 in zebrafish and living cells and labeled the recovery experiment of H_2O_2 in real water samples (recoveries rates of 90.93–102.9 % and RSD < 3.09 %).

1. Introduction

Hydrogen peroxide (H_2O_2) is extensively used in biomedicine, food, and industrial applications due to its excellent sterilization, antiseptic, and bleaching effects [1,2]. The U.S. Food and Drug Administration set the maximum residual amount of H_2O_2 in food to 15 μM [3], as high concentration of H_2O_2 in the body will lead to apoptosis, causing damage to tissues and organs and eventually leading to human aging, cancer, and other disease [4,5]. H_2O_2, as a biomarker of cell metabolism, also serves as an important component of typical reactive oxygen species for biomedical diagnosis [6]. Abnormal H_2O_2 concentrations in living organisms can affect the balance of normal physiological conditions, leading to oxidative stress in different fatal diseases, including cardiovascular, Alzheimer's, and neurodegenerative diseases [7–9]. Therefore, the development of a highly sensitive, rapid, and simple real-time detection tool for H_2O_2 is critical for H_2O_2 and biological science research.

Currently, H_2O_2 detection technologies have been developed through colorimetric sensing, chromatography, electrochemical, and chemiluminescence methods [10,11]. However, these methods generally have issues such as large detection errors, the need for professional personnel and equipment, and an inability to achieve instant detection [12,13]. In addition, most of these detection methods harm organisms and cannot achieve the visual detection of H_2O_2 in organisms [14]. Compared with the above detection methods, fluorescence probes have the advantages of a fast response time, high selectivity, and a simple sample preparation process [15]. After the recognition groups combine with the analyte, optical properties such as the luminous lifespan, color, and intensity of the fluorophores will change. The analyte can be recognized and detected by the change in light signal. In addition, fluorescence imaging has become a key technique for studying the localization and behavior of biomolecules at the cellular level due to its high specificity, sensitivity, and non-invasive advantages [16–18]. Li et al. [19] reported an NIR fluorescence probe using quinolinoxanthracene dye as a fluorophore based on an intramolecular charge transfer mechanism. The probe exhibited better optical properties than semi-cyanine dye and was successfully applied to the fluorescence imaging of H_2O_2 in living cells, zebrafish, and diabetic mice. Koide et al.

---

[*] Corresponding authors.
E-mail addresses: rmg888@qlu.edu.cn (M. Ren), kfg@qlu.edu.cn (F. Kong).

[1] These authors contributed equally to this work.

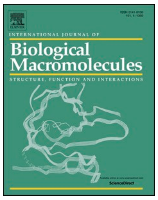
https://doi.org/10.1016/j.ijbiomac.2023.128760
Received 18 September 2023; Received in revised form 29 November 2023; Accepted 10 December 2023

International Journal of Biological Macromolecules 250 (2023) 126157

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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



A water-soluble and biocompatible chitosan-based fluorescent probe for real-time monitoring formaldehyde in living cells and zebrafish

Hui Sun [1], Qingyu Xu [1], Mingguang Ren *, Fangong Kong *

State Key Laboratory of Biobased Material and Green Papermaking, Key Laboratory of Pulp & Paper Science and Technology of Shandong Province, Ministry of Education, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, PR China

ARTICLE INFO

Keywords:
Formaldehyde
Chitosan-based probe
Ultrafast detection

ABSTRACT

Formaldehyde (HCHO) is a common environmental toxicant that can harm the human respiratory tract and nervous system when exposed for long period of time. As a carcinogen, HCHO also increases the risk of cancer in humans. HCHO can be produced endogenously in living systems and plays an essential role in physiological and biochemical reactions and pathogenesis. Therefore, monitoring the level of HCHO in vivo and in vitro has become the focus of attention. The designed naphthalene fluorophore was introduced onto modified chitosan to prepare a chitosan-based fluorescent probe (CS-FA) for HCHO detection. Compared to other small-molecule probe analogs for the detection of HCHO, the randomly coiled polymer chain of chitosan enabled CS-FA to "enrich" HCHO using the synergistic binding of hydrazino-naphthalimide recognition sites. Thus, the reaction of the analyte with the recognition site was accelerated, resulting in a faster equilibrium fluorescence response (2–3 min) and high sensitivity. In addition, the introduction of biomass material chitosan also improved the biocompatibility of the probe. Then a series of composite materials (test strips and hydrogel) were prepared based on the probe to expand the application form of the probe.

1. Introduction

Formaldehyde (HCHO), as the third largest indoor chemical pollutant, also plays a very critical role in the physiological and pathological processes of organisms. At present, clinical tests such as blood routine, liver function, kidney function, and chest X-ray are usually used to determine whether the human body is overdosed with HCHO [1,2]. HCHO is a byproduct of an important intracellular process known as the "one-carbon metabolism (cycle)". This cycle uses folic acid to produce DNA and essential amino acids, which cells need to function and proliferate properly [3,4]. Physiological concentrations of endogenous HCHO range from 100 to 400 μM in living cells and 50–100 μM in blood, and stable levels of endogenous HCHO plays a critical role in human health [5]. On the one hand, HCHO as a toxic molecule causes DNA damage [6]. On the other hand, high levels of HCHO in living organisms increase the likelihood of major diseases such as leukemia, Alzheimer's disease, atherosclerosis, and embryonic malformations [7,8]. Long-term exposure to HCHO may also lead to symptoms such as memory impairment. To research the complexities of HCHO homeostasis and its levels under pathological conditions, it is necessary to obtain efficient and sensitive methods to monitor HCHO levels in and outside living systems [9].

Traditional HCHO detection methods are all in vitro techniques such as polarimetric sensors, high performance liquid chromatography and electrochemical detection [10,11]. These methods have facilitated the biological study of HCHO to some extent, but the damage to the sample and the fact that HCHO detection in biological in vivo systems is not possible have limited their development [12,13]. Fluorescence imaging, a noninvasive technique, uses luminescent probes to achieve monitoring of biomolecules in living organism with minimal interference [14,15]. In recent years, several small molecule fluorescent sensors have been reported for HCHO at the level of cells, organisms, environment and food, which are important for revealing the role of HCHO in living systems. Current research on fluorescent probes for HCHO detection in organisms is mainly focused on cell imaging and visualization of HCHO in mouse tissues and bodies. However, most of the previously reported probes are based on hydrophobic conjugated organic small molecule dyes and are highly cytotoxic [16]. Therefore, the need to perform in toxic and volatile organic solutions during monitoring HCHO greatly limits the practical application of the probes. In addition, the slow

---

* Corresponding authors.
E-mail addresses: rmg888@qlu.edu.cn (M. Ren), kfg@qlu.edu.cn (F. Kong).

[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.ijbiomac.2023.126157
Received 10 April 2023; Received in revised form 24 July 2023; Accepted 4 August 2023

International Journal of Biological Macromolecules 240 (2023) 124368

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Influence of structure and functional group of modified kraft lignin on adsorption behavior of dye

Changyong Song [a], Chao Gao [a], Pedram Fatehi [a,b], Shoujuan Wang [a,*], Chunbo Jiang [c,*], Fangong Kong [a,*]

[a] State Key Laboratory of Biobased Material and Green Papermaking, Key Laboratory of Pulp & Paper Science and Technology of Shandong Province/Ministry of Education, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China

[b] Department of Chemical Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, ON P7B 5E1, Canada

[c] The Fisrt Affiliated Hospital of Shandong First Medical University & Shandong Provincial Qianfoshan Hospital, Jinan 250014, Shandong, China

A R T I C L E I N F O

Keywords:
Lignin
Mannich reaction
Amination of modified
Adsorption

A B S T R A C T

Utilization of kraft lignin to produce bio-based adsorptive material for effective dye adsorption from industrial wastewater is essential to fulfilling the significant environmental protection needs. Lignin is the most abundant byproduct material with a chemical structure containing various functional groups. However, the complicated chemical structure makes it somewhat hydrophobic and incompatible, which limits its direct application as an adsorption material. Chemical modification is a common way to enhance lignin properties. In this work, the kraft lignin was modified through direct amination using Mannich reaction and oxidization followed by amination as new route of lignin modification. The prepared lignins, including aminated lignin (AL), oxidized lignin (OL), and aminated-oxidized lignin (AOL), as well as unmodified kraft lignin, were analyzed by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), elemental analysis and ^{1}H-nuclear magnetic resonance measurements (^{1}HNMR). The adsorption behaviors of modified lignins for the malachite green in aqueous solution were investigated well and discussed, as well as the adsorption kinetics and thermodynamic equations. Compared with other aminated lignin (AL), the AOL displayed a high adsorption capacity of 99.1 % dye removal, due to its more effective functional groups. The change in structure and functional groups on the lignin molecules during oxidation and amination had no effect on its adsorption mechanisms. The adsorption process of malachite green on different kinds of lignin belongs to endothermic chemical adsorption, which mainly consists of monolayer adsorption. The modification of lignin through oxidation followed by amination process, afforded kraft lignin a broad potential application in the field of wastewater treatment.

1. Introduction

Recently, the problem of water pollution damaging the environment has become particularly serious. Industrial wastewater usually includes printing and dyeing wastewater, black liquor from the paper industry, medical wastewater, and domestic sewage. The large-scale discharge of industrial wastewater leads to the decline of surface water quality, which not only affects the environment but also causes many potential hazards. Among them, printing and dyeing wastewater accounted for a high proportion of industrial wastewater. And printing and dyeing wastewater generally have some characteristics such as poor biodegradability, high content of organic pollutants, relatively complex fractions, high turbidity, deep chroma, etc. Wastewater treatment methods mainly include physical treatment, chemical treatment, and biological treatment. At present, the commonly used dye wastewater treatment methods include adsorption [1,2], flocculation [3,4], electrolytic process [5], and oxidation [6], etc. Among the know methods of wastewater treatment, adsorption is considered to be the simplest and fastest method [7]. However, the high cost hinders its application in wastewater treatment, so it is urgent to find a high-efficiency and economical biomass adsorption material [8–10] (Scheme 1).

Lignin is the by-product of paper industry, which is abundant, reasonably priced, and rarely used, and the majority of it is burned after concentration [11,12]. Lignin is a kind of aromatic polymer with

---

* Corresponding authors.
E-mail addresses: wshj@qlu.edu.cn (S. Wang), 1325@sdhospital.com.cn (C. Jiang), kfg@qlu.edu.cn (F. Kong).

https://doi.org/10.1016/j.ijbiomac.2023.124368
Received 15 December 2022; Received in revised form 14 March 2023; Accepted 4 April 2023

International Journal of Biological Macromolecules 266 (2024) 131129

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Transparent, super stretchable, freezing−tolerant, self−healing ionic conductive cellulose based eutectogel for multi−functional sensors

Wei Chen [a,b], Jing Ma [a], Dehai Yu [b], Nan Li [a,b,*], Xingxiang Ji [b,**]

[a] College of Engineering, Qufu Normal University, Rizhao 276826, China
[b] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China

ARTICLE INFO

Keywords:
Cellulose
Eutectogel
Multifunctional sensor

ABSTRACT

In this study, we propose a non − toxic and low−cost fabrication of cellulose−based eutectogel through the $ZnCl_2/H_2O/H_3PO_4$ deep eutectic solvent (DES) to dissolve cellulose followed by free−radical polymerization of acrylamide. Particularly, the introduction of cellulose enhances the mechanical properties of eutectogels while eliminating the environmental concerns of the traditional nanocellulose fabrication process. Owing to the dynamic transfer of ions in the eutectogel network, the prepared eutectogels exhibit adjustable conductivity (0.9– 1.37 $\mathrm{S\,m^{-1}}$, 15 °C) and stretching sensitivity (Gauge factor = 5.4). The resulting DES − cellulose−based eutectogels (DCEs) exhibited ultra stretchability (4086 %), high toughness (261.3 $\mathrm{MJ/m^3}$), excellent ionic conductivity (1.64 $\mathrm{S\,m^{-1}}$, 20 °C), high transparency (>85 %), outstanding antifreezing performance (<−80 °C), and other comprehensive characteristics. The DCEs had been proven to have multiple sensitivities to external stimuli, like temperature, strain, and pressure. As a result, the DCEs can be assembled into multifunctional sensors. Moreover, this work also demonstrated the satisfactory performance of DCEs in flexible electroluminescent devices. The low cost and high efficiency made the preparation method of this experiment an efficient strategy for developing high−performance cellulose−based eutectogels, which would greatly promote the application of such materials in areas such as artificial skin for soft robots and other wearable devices.

1. Introduction

Flexible sensors have attracted tremendous attention on account of their substantial applications in bioelectrodes [1], human motion monitoring, artificial skins [2,3], wearable devices [4–6], and smart electronics [7,8]. The development of flexible sensors depends heavily on soft materials [9]. Conductive hydrogels have attracted extensive attention in the field of flexible and wearable sensors because they combine the soft properties of hydrogels and the electronic characteristics of conductors. Unfortunately, when the ambient temperature is lower than the freezing point, the water molecules in hydrogel networks tend to be inevitably frozen. It not only restricts their ion transport capacity but also makes them rigid and fragile, which thereby limit severely their applications in the low temperature range. Furthermore, achieving high tensile strength, toughness, and self−recoverability simultaneously in conductive hydrogels remains a challenge.

To solve these problems, researchers developed ionogels. Ionogels are polymer networks infused by ionic liquids [10]. Ionic liquids are different from water, and their evaporation can be ignored even at high temperatures [11]. However, the high toxicity and cost of ionic liquids hinder the idealization of ionogels [12]. Besides, the mass transfer resistance and low diffusion coefficient of the ions dissociated from the ILs generally lead to relatively low ionic conductivity [13,14]. Deep eutectic solvents (DESs), composed of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs), have similar properties to ILs but overcome the shortcomings of ILs and are considered a new generation of economic and environmentally friendly green solvents [15–17]. Eutectogels, consisting of a polymeric network structure or low−molecular−weight gelators aggregated supramolecular network structure with over 90 % of deep eutectic solvents (DESs) [18]. Thanks to the inherent properties of deep eutectic solvents (DESs), such as low cost, low vapor pressure, high thermostability, and high conductivity, eutectogels are an alternative option to temperature intolerant hydrogels and expensive ionic liquid gels. They have the potential to be used in various fields, such as environmental sciences and (bio)electronics [19].

---

[*] Correspondence to: N. Li, College of Engineering, Qufu Normal University, Rizhao 276826, China.
[**] Corresponding author.
E-mail addresses: lilylinan@foxmail.com (N. Li), xxjt78@163.com (X. Ji).

https://doi.org/10.1016/j.ijbiomac.2024.131129
Received 16 December 2023; Received in revised form 29 February 2024; Accepted 22 March 2024

International Journal of Biological Macromolecules 320 (2025) 145929

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Tough sustainable bio-based soybean protein adhesive with salt-bridge hydrogen bonds

Lulu Chen [a,b], Jin Qian [a,b], Chunmei Xu [a,b], Zhuqing Liu [a,b,*], Wenjia Han [a,b,*], Xingxiang Ji [a,b,*]

[a] Key Lab of Paper Science and Technology of Ministry of Education, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China
[b] State Key Laboratory of Green Papermaking and Resource Recycling, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China

ARTICLE INFO

Keywords:
Soy protein-based adhesive
Salt-bridge hydrogen bonds
Sustainability

ABSTRACT

Soy protein adhesives have great potential in replacing traditional petrochemical adhesives to produce eco-friendly and formaldehyde-free plywood. However, weak toughness, poor water resistance and low mold resistance during their usage have severely limited their application in practical production. In this study, we introduced bio-based sodium carboxymethyl cellulose (CMCNa) and lauroyl arginine ethyl ester hydrochloride (LAE) into the soybean meal (SM) system to increase the network interweaving density through the electrostatic interactions and multiple hydrogen bonds between CMCNa, LAE and SM. Both SM and CMCNa can form highly specific guanidinium-carboxylate salt-bridge hydrogen bonds with LAE, leading to the formation of a non-homogeneous phase structure in the system, which can improve the internal energy dissipation and further enhance the toughness and water resistance of adhesive. The results show that the modified adhesive has good toughness, and the wet shear strength is significantly increased by 128 % to 1.07 MPa, and can be stored for >8 days. The tough, waterproofing and mildew resistant bio-adhesive offers a eco-friendly alternative to the traditional chemical adhesive.

1. Introduction

Adhesives play a crucial role in wood processing, as they are essential in the production of wooden furniture, floors, doors, and windows [1,2]. Traditional adhesives are predominantly made from non-biodegradable petrochemical materials with a series of problems such as toxic gas emissions, non-renewability, and difficulty in degradation during processing and usage, which fail to meet the requirements of sustainable development [3–5]. As a by-product of soybean processing, soybean meal has the advantages of wide source of raw material, biodegradable, abundant functional groups, low price and easy processing [6,7]. It is considered as one of the most potential substitutes for petroleum-based adhesives, and has received extensive attention. However, soybean meal based adhesives have some disadvantages such as brittleness, insufficient water resistance and poor anti-corrosion properties, which restrict their further development in the field of adhesives to a certain extent [8–10]. Recently, Chemical modification is considered to be effective methods to improve the bonding performance of soy protein adhesives. Studies mainly focus on the introduction of polyamide-epichlorohydrin (PAE), polyurethane (PU), acrylates (AA) and other petrochemicals to modify soybean meal based adhesives, to enhance the adhesion and water resistance, and which to a certain extent, avoid the release of formaldehyde gas [11–13]. But the formulations often include synthetic and harmful components, such as epoxides, isocyanates or acrylates, that cannot be considered “green”. To improve the anti mold performance of soy protein adhesives, anti mold agents always should be added [14]. Chemical preservatives were commonly used, such as alkaline copper quaternary ammonium salts, borides, chlorinated phenols, chromated copper arsenate (CCA), etc. Although they have good anti-corrosion effect, they might cause damage to human organs such as liver and kidney, and increase the risk of cancer [15,16]. In recent studies, the antimicrobial properties of soy protein adhesives are mainly achieved by the addition of natural polyphenols (tannins, lignin), metal ions, borax, and some natural antimicrobials (chitosan) [17,18]. Till now, there is no research on the preparation of green bio-based adhesive systems that are environmentally friendly and harmful components-free

---

* Corresponding authors at: Key Lab of Paper Science and Technology of Ministry of Education, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China.

E-mail addresses: liuzhuqing@qlu.edu.cn (Z. Liu), hwj200506@163.com (W. Han), xxjt78@163.com (X. Ji).

https://doi.org/10.1016/j.ijbiomac.2025.145929
Received 30 April 2025; Received in revised form 22 June 2025; Accepted 10 July 2025

International Journal of Biological Macromolecules 265 (2024) 130532

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Characterization of microcrystalline cellulose prepared from long and short fibers and its application in ibuprofen tablets

Xiao Hao [a], Zhongjian Tian [a], Yingchao Wang [a,b], Zhaoyong Xie [a,b], Xingxiang Ji [a,*]

[a] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Jinan, Shandong 250353, China
[b] State Key Laboratory of Biobased Fiber Manufacturing Technology, Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, China

ARTICLE INFO

Keywords:
Microcrystalline cellulose
Hydrochloric acid hydrolysis
Ibuprofen tablets

ABSTRACT

As a bio-based material, microcrystalline cellulose (MCC) has been applied in many fields including pharmaceuticals, foods, and cosmetics in recent years. However, traditional preparation methods of MCC are facing many challenges due to economic and eco-environmental issues. In this study, softwood dissolved pulp was sieved to long fiber (LF) and short fiber (SF), and subsequently to prepare LF-MCC and SF-MCC by hydrochloric acid hydrolysis at different acid dosages (3–7 wt%), reaction times (30–90 min), and temperatures (75–95 °C). The as-obtained MCC products were compared in terms of morphology, size, crystallinity, and chemical structure. The results indicated that the crystallinity and yield of LF-MCC were high, with maximum values of 78.41 % and 98.68 %, respectively. The particle size distribution of SF-MCC was more uniform in the range of 20–80 μm, with a maximum of 59.44 % at 20–80 μm occupancy proportion. Moreover, SF-MCC had a typical rod-like shape and larger surface area as well as better thermal behavior than LF-MCC. When LF-MCC and SF-MCC were used as fillers in the production of ibuprofen tablets, the tablets added with LF-MCC exhibited higher hardness, friability, dissolution rate, and shorter disintegration time. Therefore, this work is very beneficial for the preparation and application of MCC.

1. Introduction

Microcrystalline cellulose (MCC) is a white, odorless, and insoluble cellulose derivative obtained from natural cellulose [1]. Compared with raw cellulose, MCC has unique advantages, such as high crystallinity of over 60 % and small particle size of 20–80 μm, uniform polymerization degree of approximately 350 on average, and superior liquidity [2]. In the past few years, it has become an important bio-based material and has been used in many fields including pharmaceuticals, foods, cosmetics, and constructions due to its non-toxicity, environmental friendliness, biodegradability, good biocompatibility, and excellent physicochemical characteristics (e.g., low density, large specific surface area, and high mechanical strength) [3,4]. Recently, some pharmaceutical enterprises have applied MCC as a new type of pharmaceutical excipient in solid drug formulations. Many researchers proposed new preparation methods and applications in tablet production. For example, Viera-Herrera et al. extracted MCC from borojó and used it as an excipient in the production of acetaminophen tablets [5]. The produced MCCs exhibited similar characteristics when using commercially available MCCs as controls. In addition, Krivokapi et al. investigated the loading efficiency of ibuprofen and the release kinetics of MCC powder and tablet dosage forms using supercritical impregnation [6]. Getachew et al. extracted MCC from teff straw and investigated its performance as a direct compressible tablet filler. Their results indicated that the prepared tablets using MCC powder met the requirements of the pharmacopoeia [7].

Currently, MCC can be extracted from a wide variety of raw materials, such as cotton [8], wood [9], sugarcane bagasse [10], soybean hulls [11], pomelo peel [12], tea waste [3], oil palm fronds [13], brown algae [14], giant reed [15], corncob [16], chrysanthemum stems [17], and so on. Among them, cotton pulp and dissolved pulp are the main raw materials. Particularly, dissolving pulp, a fine chemical pulp with α-cellulose content of up to 90 %, high fiber whiteness, uniform molecular weight, low content of pentosan and ash, and good reactivity, is an ideal raw material for preparing MCC [18].

There are many methods that can yield MCC, including chemical acid hydrolysis [19,20], biological enzyme hydrolysis [21,22], mechanical treatment [23,24], or a combination of the methods above

---

* Corresponding author.
E-mail address: xxjt78@163.com (X. Ji).

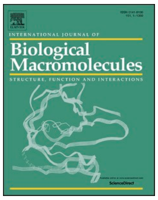
https://doi.org/10.1016/j.ijbiomac.2024.130532
Received 28 October 2023; Received in revised form 19 February 2024; Accepted 27 February 2024
Available online 29 February 2024

International Journal of Biological Macromolecules 260 (2024) 129587

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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



Enhancing photocatalytic destruction of lignin via cellulose derived carbon quantum dots/g-C_3N_4 heterojunctions

Wei Liu [a,b,*], Chuang Jiang [b,1], Jinlong Feng [b,1], Liguo Zhang [b], Qingxi Hou [b], Xingxiang Ji [a,*]

[a] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China
[b] Tianjin Key Laboratory of Pulp & Paper, Tianjin University of Science & Technology, Tianjin 300457, China

ARTICLE INFO

Keywords:
Cellulose
Carbon quantum dots
Photocatalysis
Lignin

ABSTRACT

Lignocellulosic biomass exhibits a promising potential for production of carbon materials. Nitrogen and phosphorus co-doped carbon quantum dots (N,P-CQDs) were fabricated via $(NH_4)_2HPO_4$ assisted hydrothermal treatment of cellulose pulp fibers. The as-prepared N,P-CQDs were characterized by HRTEM, FTIR, fluorescence and UV–vis, and then incorporated into g-C_3N_4 (CN) through sonication and liquid deposition, forming N,P-CQDs/sonication treated g-C_3N_4 (C-SCN) composites, which were then explored as photocatalysts. The photocatalytic ability of C-SCN towards model lignin was further analyzed. The results showed that, the fluorescence intensity and photoluminescence performance of N,P-CQDs were much higher than that of CQDs; the heterojunction was successfully constructed between the composites of N,P-CQDs and SCN; the incorporation of N,P-CQDs enhanced the visible light absorption, but reduced the band gap of the composite heterojunction; the resultant photocatalysts exhibited a good photocatalytic ability of model lignin via catalyze the fracture of β–O–4′ ether bond and C—C bond, i.e., the photocatalytic degradation ratio reached up to 95.5 %; and the photocatalytic reaction generated some valuable organics such as phenyl formate, benzaldehyde, and benzoic acid. This study would promote the high value-added utilization of lignocellulosic resources especially in the transformation of lignin, conforming the concept of sustainable development.

1. Introduction

Lignocellulosic biomass has already been regarded as an ideal candidate to replace non-renewable mineral carbon materials including coal, petroleum and natural gas [1,2]. As one of renewable aromatic compounds, lignin ranks the second largest natural polymers after cellulose [3,4]. The complex structure of lignin makes it difficult to be transformed especially in terms of efficiency and selectively, leading to a low utilization even a huge waste [5]. The complex structure of lignin generates a large spatial hindrance for the adsorption of traditional catalysts. It is reported that a high energy barrier between the rigid surface of traditional catalysts and benzene ring of lignin severely limits its catalytic degradation [6]. By far, some traditional methods have been applying on lignin degradation including physical, chemical and biological methods, but they are severely limited due to existing problems (e.g., low selectivity and efficiency, high environmental pollution, and complex process). Thus, it is very necessary to develop novel method and catalysts to satisfy the requirements in terms of simple operation, low environmental pollution, high efficiency, and relatively mild conditions.

Vacancies g-C_3N_4 has become one of the most promising visible light redox catalysts [7,8], because of the unique properties, e.g., large surface area, low cost, visible light adsorption, and large number of nitrogen atoms. It is reported that the flexible 2D material g-C_3N_4 may provide an ideal surface for catalytic degradation of lignin [9,10]. However, g-C_3N_4 can only absorb sunlight with a wavelength below 450 nm, leading to a low utilization of sunlight. In addition, the electron recombination rate of g-C_3N_4 is fast, thus only a small amount of electrons and holes can participate in the redox reaction during the catalytic process [11–13]. Interestingly, the combination of carbon quantum dots (CQDs) with g-C_3N_4 can significantly improve photocatalytic degradation efficiency. As a new type of zero-dimensional carbon nanomaterial, CQDs are mainly composed of C, H and O elements, and distribute in the range of ≤10 nm [14]. The advantages, such as abundant raw materials,

---

* Corresponding authors at: State Key Laboratory of Biobased Material and Green Paper- making, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China.

E-mail addresses: weiliu@tust.edu.cn (W. Liu), xxjt78@163.com (X. Ji).

[1] Chuang Jiang and Jinlong Feng contributed equally.

https://doi.org/10.1016/j.ijbiomac.2024.129587
Received 7 September 2023; Received in revised form 29 December 2023; Accepted 16 January 2024

International Journal of Biological Macromolecules 257 (2024) 128434

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Schiff base and coordinate bonds cross-linked chitosan-based eutectogels with ultrafast self-healing, self-adhesive, and anti-freezing capabilities for motion detection

Wei Chen [a,b], Jincan Li [b], Wenqing Sun [b], Liyuan Qiu [b], Dehai Yu [a], Nan Li [a,b,**], Xingxiang Ji [a,*]

[a] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, 250353, China
[b] College of Engineering, Qufu Normal University, Rizhao, 276826, China

ARTICLE INFO

Keywords:
Chitosan−protocatechualdehyde−Fe^{3+}
Dual−dynamic−bond cross−linked eutectogels
AmimCl/urea eutectic−based ionic liquid

ABSTRACT

Ion conductors offer great potential for diverse electric applications. However, most of the ion conductors were fabricated from non − degradable petroleum−based polymers with non or low biodegradability, which inevitably leads to resource depletion and waste accumulation. Fabricating ion conductors based on renewable, and sustainable materials is highly desirable and valuable. Herein, a series of eutectogels were designed through dual−dynamic−bond cross−linking among ferric iron (Fe^{3+}), protocatechualdehyde (PA), and chitosan (CS) in 1 − allyl−3 − methylimidazole chloride ionic liquid/urea (AmimCl/urea) eutectic−based ionic liquid. Due to the presence of AmimCl/urea eutectic−based ionic liquid, the obtained CS − PA@Fe eutectogels showed excellent ionic conductivity, superior anti−freezing properties that could maintain flexibility and high electrical properties at −20 °C. Dual−dynamic−bond cross−linking of catechol−Fe coordinate and dynamic Schiff base bonds equip CS − PA@Fe eutectogels with excellent injectable, and self−healing abilities. Additionally, due to the presence of phenolic hydroxyl groups of PA, the obtained CS − PA@Fe eutectogels present good adhesiveness. Based on the CS − PA@Fe eutectogels, multifunctional flexible strain sensors with high sensitivity, stability, as well as rapid response speed at wide operating temperature ranges were successfully fabricated. Thus, this study offers a promising strategy for fabricating naturally occurring biopolymers based eutectogels, which show great potential as high−performance flexible strain sensors for next−generation wearable electronic devices.

1. Introduction

Ion conductors (ICs) have broad application prospects in artificial skins [1–5], supercapacitors [6–9], strain sensors [10–12], and have gained extensive research interest. With the pollution of petroleum−based materials and the depletion of petroleum resources, biosourced polymers have been used to develop green ICs with reduced environmental impact. As recent emerging and promising ionic conductive materials based on ionic liquids (ILs), naturally occurring biopolymers−based ionogels are more suitable as green ICs since they don't confront the risk of function deterioration resulting from water evaporation or freeze, which often occurs in hydrogels [13–16]. The uniformly distributed ILs in polymer matrix endow the biopolymers−based ionogels with low volatility, thermal stability, chemical stability, nonflammability, and sufficient conductivity [17].

Nowadays, various biopolymers−based ionogels can be simply generated by immobilizing free ILs in different kinds of biopolymer gelators [18–20]. For example, Malliaras George G. and Mecerreyes D. et al. fabricated a kind of novel conducting ionogel formed by a natural polysaccharide guar gum, a conductive polymer poly(3,4 − ethylenedioxythiophene) (PEDOT), and an ionic liquid (IL) 1 − butyl−3 − methylimidazolium chloride (BmimCl) [21]. Song et al. reported a series of chemically cross−linked chitosan−cellulose ionogels and gelatin−cellulose ionogels in 1 − ethyl−3 − methylimidazolium acetate (EmimAc) [22,23]. Hu et al. used a hydrogen−bond topological network as the design principle to construct topology tunable cellulose/BmimCl ionogels [24]. Li and Cao et al. reported a series of eutectogels in hydrophobic DES. [25,26]. Unfortunately, despite significant progress

---

* Corresponding author.

** Correspondence to: N. Li, State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, 250353, China.

E-mail addresses: lilylinan@foxmail.com (N. Li), xxjt78@163.com (X. Ji).

https://doi.org/10.1016/j.ijbiomac.2023.128434
Received 8 October 2023; Received in revised form 21 November 2023; Accepted 23 November 2023
Available online 1 December 2023

Journal of CO2 Utilization 79 (2024) 102656

Contents lists available at ScienceDirect

Journal of CO2 Utilization

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

Chromatography-free synthesis of carbamates from CO_2 catalyzed by a green and recyclable biobased ionic liquid/Cu_2O system

Yanyan Gong [a], Yuankun Wang [b], Peng Li [a], Ye Yuan [a,b,*], Fangong Kong [a,**]

[a] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China

ARTICLE INFO

Keywords:
CO_2 utilization
Chromatography-free synthesis
Ionic liquids
Biobased materials

ABSTRACT

Carbamates and related derivatives are crucial skeletons for pesticide design and pharmaceutical chemistry. Recently, a synthetic route for the production of carbamates has drawn great attention, which assembles the economical, renewable and non-toxic CO_2 with propargyl alcohols and amines. This route is 100% atom-economical and free of traditional carbon sources (CO, phosgene, *etc.*), thus attracting scientists to develop numerous catalytic methods for its effective applications. However, the carbamates produced in these methods generally contained residual catalysts, solvents or byproducts. Consequently, column chromatography purification is inevitably required for all the reports up to now. This limitation has fundamentally hindered the practical application of this route. Herein, a chromatography-free method was proposed for the first time. With the catalysis of a green and economical Cu_2O/biobased ionic liquid system, the carbamates could be obtained in good to excellent yields and purity. Additionally, the catalytic metal loading reached the lowest level reported by far under 1 bar of CO_2. Furthermore, this catalytic system could be recycled and reused for at least 5 times.

1. Introduction

Nowadays, anthropogenic climate change has been a global environmental problem, mainly due to the imbalance in the carbon cycle caused by the excess industrial emission of greenhouse gases, especially carbon dioxide (CO_2) [1–3]. As a result, the effective control and management of CO_2 has become a significant challenge for scientists and engineers [4–6]. In this area, carbon capture and storage (CCS) is an effective strategy to achieve this goal. However, this strategy is a unidirectional input process of energy and resource, because CO_2 is treated as a waste and deeply buried underground. In response to this issue, the strategy of integrated CO_2 capture and conversion (ICCC) has emerged, aiming to capture and directly utilize CO_2 as a carbon source for the production of valuable chemicals. By inserting the previously wasted CO_2 into useful organic structures, ICCC creates value and effectively offsets the energy and resource input. Consequently, ICCC is regarded as a potential alternative to CCS and has attracted significant attention. However, due to the thermodynamic stability and kinetic inertness of CO_2, the transformation of CO_2 is a great challenge for both academic research and industrial production. Nonetheless, impressive progress on chemical conversion of CO_2 has been achieved in recent years, particularly with the emergence of novel functional materials such as ionic liquids (ILs) [7–12], which have provided new protocols for the activation and transformation of CO_2 [13–15]. Furthermore, a wide range of reaction routes have been designed to achieve the thermodynamic feasibility of CO_2 conversion. In particular, the reaction of CO_2, propargyl alcohols and amines to produce carbamate compounds has increasingly gained attention.

Carbamates are a series of versatile compounds that have been utilized in numerous areas. They are especially known for their use as pesticides, due to their merits of less environmental pollution, rapid degradation and low toxicity to non-target organisms [16,17]. Carbamates are also important building blocks or skeletons for the construction of various fine chemicals or polymers [18]. In traditional methods, carbamates could be obtained by employing the toxic CO or phosgene [19,20]. However, a more efficient and environmentally friendly approach to produce these carbamates is the newly-emerged three-component reactions of CO_2, propargyl alcohols and amines. This is a

---

* Corresponding author at: State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353, China.
** Correspondence to: State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, 250353.
E-mail addresses: fyyuanye@whut.edu.cn (Y. Yuan), kfg@qlu.edu.cn (F. Kong).

https://doi.org/10.1016/j.jcou.2023.102656
Received 25 September 2023; Received in revised form 22 November 2023; Accepted 18 December 2023