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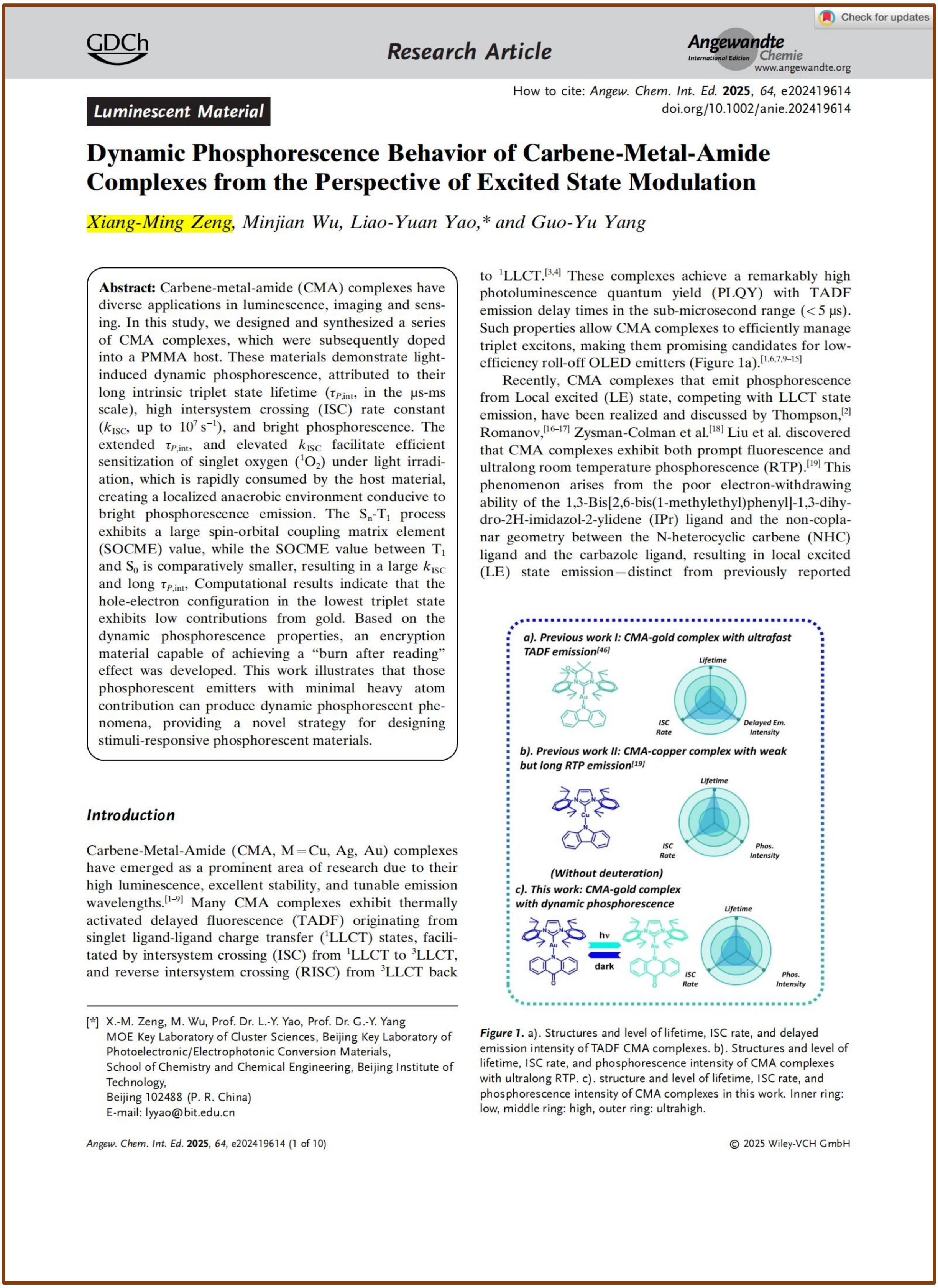

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Luminescent Material

Dynamic Phosphorescence Behavior of Carbene-Metal-Amide Complexes from the Perspective of Excited State Modulation

Xiang-Ming Zeng, Minjian Wu, Liao-Yuan Yao, and Guo-Yu Yang*

Abstract: Carbene-metal-amide (CMA) complexes have diverse applications in luminescence, imaging and sensing. In this study, we designed and synthesized a series of CMA complexes, which were subsequently doped into a PMMA host. These materials demonstrate light-induced dynamic phosphorescence, attributed to their long intrinsic triplet state lifetime ($\tau_{P,\mathrm{int}}$, in the μs-ms scale), high intersystem crossing (ISC) rate constant (k_{ISC}, up to $10^7\,\mathrm{s}^{-1}$), and bright phosphorescence. The extended $\tau_{P,\mathrm{int}}$, and elevated k_{ISC} facilitate efficient sensitization of singlet oxygen ($^1O_2$) under light irradiation, which is rapidly consumed by the host material, creating a localized anaerobic environment conducive to bright phosphorescence emission. The S_n-T_1 process exhibits a large spin-orbital coupling matrix element (SOCME) value, while the SOCME value between T_1 and S_0 is comparatively smaller, resulting in a large k_{ISC} and long $\tau_{P,\mathrm{int}}$, Computational results indicate that the hole-electron configuration in the lowest triplet state exhibits low contributions from gold. Based on the dynamic phosphorescence properties, an encryption material capable of achieving a "burn after reading" effect was developed. This work illustrates that those phosphorescent emitters with minimal heavy atom contribution can produce dynamic phosphorescent phenomena, providing a novel strategy for designing stimuli-responsive phosphorescent materials.

Introduction

Carbene-Metal-Amide (CMA, M = Cu, Ag, Au) complexes have emerged as a prominent area of research due to their high luminescence, excellent stability, and tunable emission wavelengths.[1–9] Many CMA complexes exhibit thermally activated delayed fluorescence (TADF) originating from singlet ligand-ligand charge transfer (^{1}LLCT) states, facilitated by intersystem crossing (ISC) from ^{1}LLCT to ^{3}LLCT, and reverse intersystem crossing (RISC) from ^{3}LLCT back to ^{1}LLCT.[3,4] These complexes achieve a remarkably high photoluminescence quantum yield (PLQY) with TADF emission delay times in the sub-microsecond range (<5 μs). Such properties allow CMA complexes to efficiently manage triplet excitons, making them promising candidates for low-efficiency roll-off OLED emitters (Figure 1a).[1,6,7,9–15]

Recently, CMA complexes that emit phosphorescence from Local excited (LE) state, competing with LLCT state emission, have been realized and discussed by Thompson,[2] Romanov,[16–17] Zysman-Colman et al.[18] Liu et al. discovered that CMA complexes exhibit both prompt fluorescence and ultralong room temperature phosphorescence (RTP).[19] This phenomenon arises from the poor electron-withdrawing ability of the 1,3-Bis[2,6-bis(1-methylethyl)phenyl]-1,3-dihydro-2H-imidazol-2-ylidene (IPr) ligand and the non-coplanar geometry between the N-heterocyclic carbene (NHC) ligand and the carbazole ligand, resulting in local excited (LE) state emission—distinct from previously reported

Figure 1. a). Structures and level of lifetime, ISC rate, and delayed emission intensity of TADF CMA complexes. b). Structures and level of lifetime, ISC rate, and phosphorescence intensity of CMA complexes with ultralong RTP. c). structure and level of lifetime, ISC rate, and phosphorescence intensity of CMA complexes in this work. Inner ring: low, middle ring: high, outer ring: ultrahigh.

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Topochemical synthesis of an atomic Pt modified plasmonic yolk–shell nanostructure for enhanced photocatalytic hydrogen evolution†

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The combination of plasmonic metals with semiconductors, driven by the hot injection effect and enhanced electromagnetic field effects, enables the improved absorption of incident light energy and the separation of photogenerated charge carriers. Among various metal–semiconductor topological structures, yolk–shell (Y–S) architectures are ideal photocatalysts due to their light-scattering capabilities and large surface area, but with unmanageable photocarrier dynamics. Building on this, we introduced single-atom dispersed Pt sites (Pt-SA) to increase surface catalytic sites for directional migration of charge carriers in photocatalytic hydrogen evolution reactions. By employing cation exchange and galvanic replacement, Y–S nanostructures with an Au-core and a Pt-SA modified CdS shell (namely Au@Pt-SA/CdS Y–S) were synthesized. The as-prepared catalyst exhibits an enhanced photocatalytic hydrogen evolution rate of 10.9 mmol g^{-1} h^{-1} under visible light (λ > 420 nm) irradiation, which is twice that of Au@CdS Y–S nanostructures. This work provides new insights into the topochemical synthesis of Y–S structures and the engineering of plasmonic metals and atomic sites for enhanced photocatalysis.

Introduction

The utilization of solar energy is commercially advantageous to maintain the sustainability of human society and alleviate the consumption of fossil fuels.[1,2] Photocatalysis, directly converting solar energy to storable chemical fuels, has been regarded as an ideal strategy for energy production.[3–7] To optimize the energy conversion efficiency of photocatalysis, rationally designed photocatalysts with engineered composition, geometry and carrier dynamics are imperative.[8–11] Compared to pristine semiconductor and metal based photocatalysts, the synthesis of plasmonic metal–semiconductor hybrid nanostructures has gained considerable interest due to the plasmon-mediated electron-transfer (PMET).[12,13] Typically, the integrated metal–semiconductor hybrid nanostructure could facilitate the injection of localized surface plasmon resonance (LSPR) hot carriers with optimized charge dynamics for improved carrier utilization.[14–17] The efficiency of this energy transfer is highly dependent on the proximity between the metal and semiconductor components, underscoring the critical need for precise geometric alignment of these elements within the nanostructures to optimize various photocatalytic performance parameters.[18–22]

The metal/semiconductor core–shell nanostructure has been widely investigated in photocatalysis,[23–25] due to the "antenna effect" facilitated enhanced charge transfer and efficient plasmon enhancement.[26,27] While retaining the benefits of traditional core–shell structures,[28,29] plasmonic yolk–shell nanostructures (Y–S NSs) could provide new opportunities with maintained carrier dynamics and increased specific surface area.[30] In particular, light undergoes multiple instances of reflection and scattering within the void between the yolk and the shell, which serves to amplify the capacity for capturing light.[31] Besides, the Y–S structure offers a substantial specific surface area that supplies ample active sites for surface redox reactions and allows for the introduction of cocatalysts on the surface, thereby improving the photocatalytic performance.[32] However, due to the irregular morphologies and crystallinities of the plasmonic Y–S NSs, it could be a challenge to manipulate the charge dynamics especially considering the complex LSPR under light irradiation for efficient photocatalysis.[33]

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† Electronic supplementary information (ESI) available: Details of the synthesis strategies, photocatalytic procedures and characterization methods; characterization of NSs by TEM, HRTEM, EDS, and XRD; product identification by GC; and EXAFS fitting curves. See DOI: **https://doi.org/10.1039/d5ta00271k**

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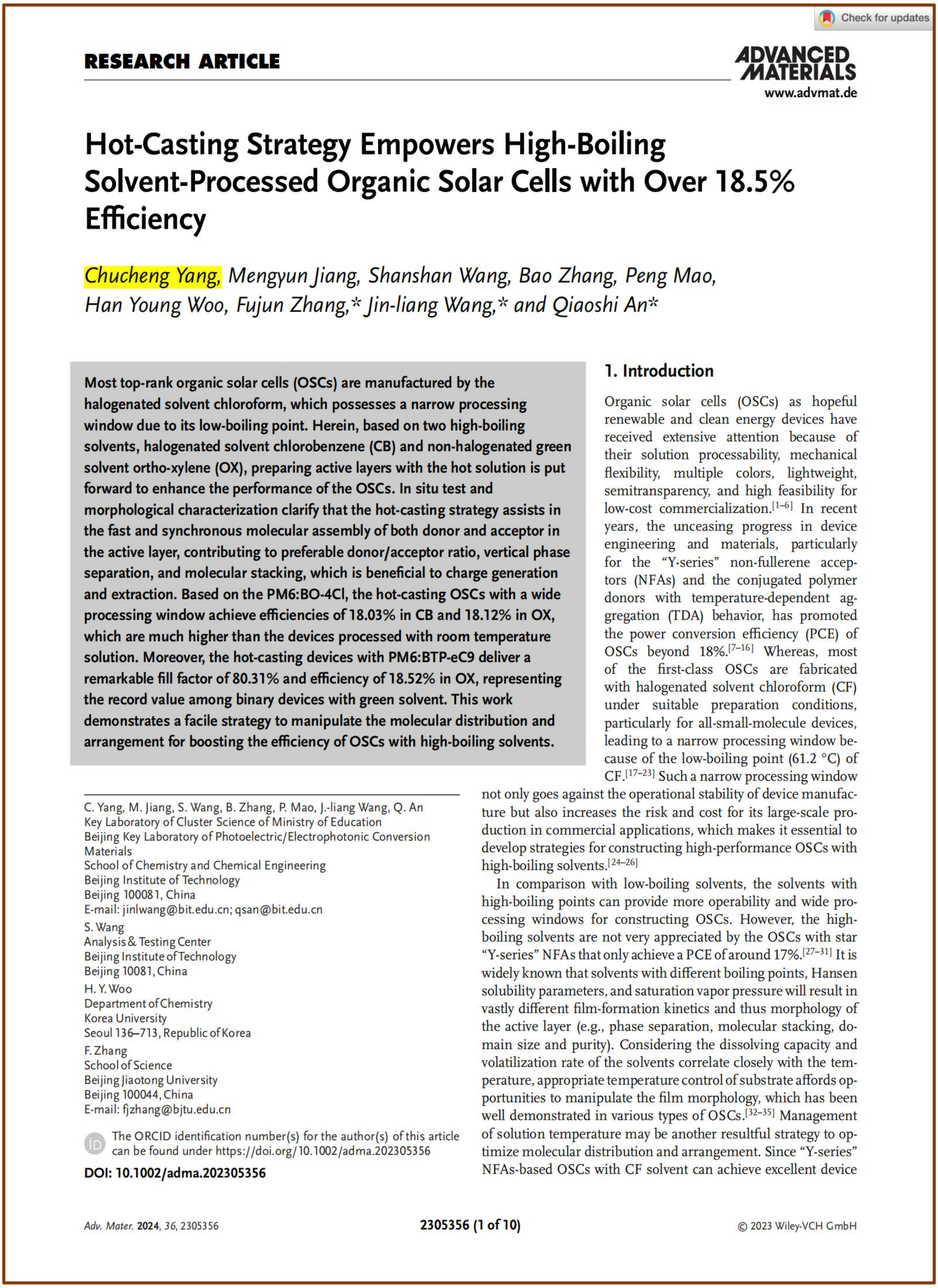

RESEARCH ARTICLE

ADVANCED MATERIALS
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Hot-Casting Strategy Empowers High-Boiling Solvent-Processed Organic Solar Cells with Over 18.5% Efficiency

Chucheng Yang, Mengyun Jiang, Shanshan Wang, Bao Zhang, Peng Mao, Han Young Woo, Fujun Zhang, Jin-liang Wang,* and Qiaoshi An**

Most top-rank organic solar cells (OSCs) are manufactured by the halogenated solvent chloroform, which possesses a narrow processing window due to its low-boiling point. Herein, based on two high-boiling solvents, halogenated solvent chlorobenzene (CB) and non-halogenated green solvent ortho-xylene (OX), preparing active layers with the hot solution is put forward to enhance the performance of the OSCs. In situ test and morphological characterization clarify that the hot-casting strategy assists in the fast and synchronous molecular assembly of both donor and acceptor in the active layer, contributing to preferable donor/acceptor ratio, vertical phase separation, and molecular stacking, which is beneficial to charge generation and extraction. Based on the PM6:BO-4Cl, the hot-casting OSCs with a wide processing window achieve efficiencies of 18.03% in CB and 18.12% in OX, which are much higher than the devices processed with room temperature solution. Moreover, the hot-casting devices with PM6:BTP-eC9 deliver a remarkable fill factor of 80.31% and efficiency of 18.52% in OX, representing the record value among binary devices with green solvent. This work demonstrates a facile strategy to manipulate the molecular distribution and arrangement for boosting the efficiency of OSCs with high-boiling solvents.

1. Introduction

Organic solar cells (OSCs) as hopeful renewable and clean energy devices have received extensive attention because of their solution processability, mechanical flexibility, multiple colors, lightweight, semitransparency, and high feasibility for low-cost commercialization.[1–6] In recent years, the unceasing progress in device engineering and materials, particularly for the "Y-series" non-fullerene acceptors (NFAs) and the conjugated polymer donors with temperature-dependent aggregation (TDA) behavior, has promoted the power conversion efficiency (PCE) of OSCs beyond 18%.[7–16] Whereas, most of the first-class OSCs are fabricated with halogenated solvent chloroform (CF) under suitable preparation conditions, particularly for all-small-molecule devices, leading to a narrow processing window because of the low-boiling point (61.2 °C) of CF.[17–23] Such a narrow processing window not only goes against the operational stability of device manufacture but also increases the risk and cost for its large-scale production in commercial applications, which makes it essential to develop strategies for constructing high-performance OSCs with high-boiling solvents.[24–26]

In comparison with low-boiling solvents, the solvents with high-boiling points can provide more operability and wide processing windows for constructing OSCs. However, the high-boiling solvents are not very appreciated by the OSCs with star "Y-series" NFAs that only achieve a PCE of around 17%.[27–31] It is widely known that solvents with different boiling points, Hansen solubility parameters, and saturation vapor pressure will result in vastly different film-formation kinetics and thus morphology of the active layer (e.g., phase separation, molecular stacking, domain size and purity). Considering the dissolving capacity and volatilization rate of the solvents correlate closely with the temperature, appropriate temperature control of substrate affords opportunities to manipulate the film morphology, which has been well demonstrated in various types of OSCs.[32–35] Management of solution temperature may be another resultful strategy to optimize molecular distribution and arrangement. Since "Y-series" NFAs-based OSCs with CF solvent can achieve excellent device

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Ligand-Enabled, Cysteine-Directed β-C(sp^3)−H Arylation of Alanine in Linear and Cyclic Peptides: Overcoming the Inhibitory Effect of Peptide Bonds

Zhen-Lin Hou,[§] Yinian Tang,[§] Yu Lu,* and Bo Yao*

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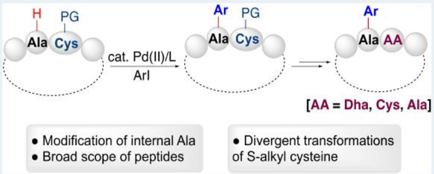

ABSTRACT: Peptide modification by coordination-assisted C(sp^3)−H functionalization on the aliphatic side chains of residues at the internal positions remains underdeveloped because of the inhibitory effect of peptide bonds. Using *S*-alkyl cysteine as the directing group and 2-pyridones as the ligands of Pd catalysts, we developed a Pd-catalyzed β-C(sp^3)−H arylation approach for highly position-selective modification of both linear and cyclic peptides at the internal positions. Control experiments supported that the *S*-alkyl cysteine acted as a *N*,*S*-bidentate directing group, and the choice of protecting groups on the sulfur atom was vital to retaining the coordinating ability and preventing the side reaction of cysteine. The result inspired us to discover a protecting group, 4-methoxy-3-nitrobenzyl (PMNB), which was stable under the reaction conditions to facilitate efficient C−H arylation and easily removed by a sequential four-step reaction. In addition, the facile transformation of *S*-methyl cysteine to dehydroalanine (Dha) and the desulfurization of *S*-(*p*-nitrobenzyl)cysteine to alanine under mild conditions further expanded the synthetic utilities of the established C−H arylation protocol.

KEYWORDS: *peptide modification, cyclic peptide, cysteine, C−H arylation, alanine*

■ INTRODUCTION

The chemical modification of peptides has broad applications in biological study, drug development, and biomaterial design.[1] Compared to the existing methods based on transformations of polar functional groups and activated C−H bonds,[2] direct functionalization of C(sp^3)−H bonds on aliphatic side chains of peptides has been much less explored.[3] Owing to the advances in coordination assisted transition-metal catalyzed C(sp^3)−H functionalization of amino acids and their derivatives,[4] peptide modification by this strategy has been extensively studied in the past decade, although most of the established protocols in this period was restricted to functionalization of residues at the N- or C-terminus (Scheme 1a).[5−7] So far, C(sp^3)−H functionalization of residues at the internal positions of peptides has been rarely reported (Scheme 1a).[8]

Coordinating side-chain assisted C(sp^3)−H functionalization has been developed for peptide modification in recent years (Scheme 1b). Weng et al. first used L-asparagine (Asn) as the directing group to promote β-C(sp^3)−H arylation of *N*-terminal alanine in peptides.[9] Later on, Weng et al. reported L-aspartic acid (Asp) directed β-C(sp^3)−H arylation and alkynylation of peptides at the *N*-terminus.[10] Besides, Chen et al. and our group developed methionine-directed C(sp^3)−H functionalization protocols, respectively reporting the γ- or β-C(sp^3)−H arylation of *N*-terminal residues in linear peptides[11] or internal alanine in head-to-tail cyclic peptides.[12] Despite the progress above, application of all these methods to the functionalization of residues at the internal positions of linear peptides encountered poor yields due to the inhibitory effect of backbone amides.[13]

The inhibitory effect of backbone amides (secondary amides) is a major obstacle in coordination assisted transition-metal catalyzed side-chain C(sp^3)−H functionalization of peptides (Scheme 1c). In general, the catalytic reaction was proposed to begin with the formation of two metal−peptide complexes (**A** and **B**).[12] The concerted metalation−deprotonation of **A** afforded the organometallic intermediate **C**, which proceeded with the subsequent oxidative addition and reductive elimination to deliver the C−H functionalization product. Meanwhile, deprotonation of the backbone N−H bond in **B** furnished the complex **D**, which accounted for the low reactivity in C(sp^3)−H functionalization of internal residues. In this context, several strategies had been proposed to overcome this challenge in recent years. Ackermann et al. used triazole as the peptide bond isostere and realized internal residue modification by β-C(sp^3)−H arylation.[6f] With the *N*-terminal free amino group as the auxiliary, we developed γ-C(sp^3)−H arylation of residues at

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REVIEW

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The separation membranes in artificial organs

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Separation membranes play a crucial role in the functioning of artificial organs, such as hemodialysis machines, membrane oxygenators, and artificial liver models. The current COVID-19 pandemic has highlighted the importance of these technologies in the medical community. However, membrane technology in artificial organs faces significant challenges, such as the clearance of low-middle-molecule and protein-bound toxins and limited blood compatibility. In this review, we will discuss the separation mechanisms, separation performance, and biocompatibility of different types of separation membranes used in artificial organs. We will also highlight the opportunities and challenges for next-generation membrane technology in this field, including the need for improved clearance of toxins and increased blood compatibility, as well as the potential for microfluidic devices.

1. Introduction

Membrane separation is a powerful technology that has gained increasing popularity in various fields such as industrial wastewater treatment, seawater desalination, fuel cells, and gas separation owing to its merits of lower energy consumption, simplicity, high efficiency, and easy operation and control.[1–5] This technology relies on the selective permeability of a membrane to the components of a fluid mixture, allowing for separation, concentration, and purification. The driving force behind this process can be a concentration difference, pressure difference, temperature difference, or potential difference,[6] and the primary membrane separation processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, dialysis, electrodialysis, gas separation, osmotic vaporization, *etc.*

In recent years, membrane separation technology has gained great attention in the biomedical field, particularly in the development of artificial organs. With the median age of the world population increasing, the incidence of human organ failure is also on the rise. Although organ transplantation is the best solution for such patients,[7–9] there is a significant gap between the number of organ donors and the number of patients in need. As a result, artificial organs, such as dialysis, have emerged as a crucial short-term solution for patients with organ failure. Additionally, since the outbreak of the Corona Virus Disease 2019 (COVID-19) pandemic, the use of extracorporeal membrane oxygenators (artificial lungs) has increased greatly in the treatment of patients with acute lung

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Dafei Sheng received her Bachelor's degree from Liaocheng University in 2020. She then joined Prof. Xiao Feng's group and is working towards her PhD degree at the School of Chemistry and Chemical Engineering, Beijing Institute of Technology. Her current research focuses on the design, synthesis, and functional application of covalent organic framework membranes.

Xiao Feng

Xiao Feng received his BS degree in materials chemistry in 2008 and PhD degree in materials science in 2013 from Beijing Institute of Technology. He pursued his study in Japan as a joint PhD student at the Institute for Molecular Science (2009–2012). He is now a professor at Beijing Institute of Technology and is mainly engaged in the research of mass transport and separation in covalent organic frameworks.

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RESEARCH ARTICLE

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Versatile Agar-Zwitterion Hybrid Hydrogels for Temperature Self-Sensing and Electro-Responsive Actuation

Jueying Yang, Weiting Huang, Kelin Peng, Zhekun Cheng, Lizhi Lin, Jingjing Yuan, Yi Sun, Nam-Joon Cho, and Yu Chen**

Although recent years have seen considerable interest in stimuli-responsive hydrogels, their strict preparation conditions and narrow applicability limit their use as diverse sensors and soft robots. Herein, a versatile Agar-Zwirrions hybrid hydrogel actuator (Agar/PSBMA) integrated with simultaneous temperature self-sensing and wide-range electrical response is developed. To prepare the Agar/PSBMA hydrogel, a simple and controllable preforming post-enhancing and mechanical pressing method is used by introducing zwitterions materials into a temperature-sensitive Agar matrix. Owing to the design, the compact multiplex complementary structure generated by this method and the materials can facilitate the improvement of flexibility, stretchability, and toughness while providing mechanical dissipation and adhesion properties. Importantly, the visible detected temperature self-sensing ability during 10–40 °C, and quick and wide-range bending responses of both high-voltage and low-voltage electric fields make it unique over other actuators. Furthermore, the electrical response behavior of the hydrogel is found to be impacted by mechanical characteristics and charge polarization based on the finite element Abaqus simulations analysis. The prepared versatile hydrogels show the potential for applications as soft robotics and controlled transportation of adhered substances while simultaneously monitoring their working temperature, which expands the response range of hydrogel actuators and broadens the scope of application.

1. Introduction

As a class of intelligent polymers, hydrogel actuators can convert external stimuli,[1] such as pH,[2] light,[1] temperature,[3] magnetic,[4] and electric fields[5] into mechanical motion by shrinking, expanding, or bending. Among them, electro-responsive hydrogel actuators have received a lot of interest because of their low energy consumption,[6] quick response,[7] and accurate "on/off" process[8] under external electric field stimuli. Although current studies have demonstrated the large deformation[9] and quick motion modes[10] of electro-response hydrogels, most reports show strict preparation procedures and a narrow response range.

To improve the electro-responsive properties, ionizable groups are required in electro-responsive hydrogels that can provide a large number of fixed charges and respond quickly to electric fields.[11] Among them, zwitterion polymers exhibit a quick response to electric fields due to a large number of fixed charges and strong

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Construction of physically crosslinked chitosan/sodium alginate/calcium ion double-network hydrogel and its application to heavy metal ions removal

Shuxian Tang, Jueying Yang, Lizhi Lin, Kelin Peng, Yu Chen*, Shaohua Jin, Weishang Yao

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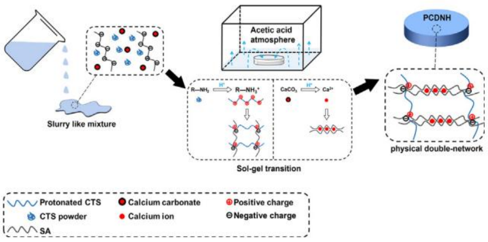
HIGHLIGHTS

- A novel eco-friendly physically-crosslinked double-network hydrogel was prepared.
- Semi-dissolution acidification sol–gel transition and internal gelation methods were combined.
- The mechanical property of the hydrogel was significantly improved.
- The hydrogel showed excellent adsorption capacities for Pb^{2+}, Cu^{2+} and Cd^{2+}.
- The adsorption mechanism, kinetics, isotherms and thermodynamics were studied.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Physical hydrogel
Chitosan
Sodium alginate
Calcium ion
Double-network
Heavy metal ions adsorption

ABSTRACT

Chemical hydrogels have been extensively applied to the removal of heavy metal pollutants. However, most of chemical hydrogels inevitably contain toxic chemical crosslinker residues, which impose serious threats on the environment. Herein, a novel eco-friendly physically-crosslinked double-network hydrogel of chitosan/sodium alginate/calcium ion (CTS/SA/Ca^{2+} PCDNH) was prepared by the combination of the semi-dissolution acidification sol–gel transition method with the internal gelation method. The PCDNH is formed via the physical crosslinking of sustainable biopolymers, which avoids the excessive use of toxic chemical reagents. In addition, the PCDNH exhibits significantly better mechanical properties than the single-network physical hydrogel crosslinked via electrostatic interactions, which overcomes the weak mechanical properties of physical hydrogels. The formation mechanism and structure of the hydrogel were determined by Fourier-transform infrared spectroscopy (FTIR), ^{13}C solid state nuclear magnetic resonance spectroscopy (^{13}C-SSNMR) and scanning electron microscopy (SEM). The heavy metal ions adsorption mechanism was explored by X-ray photoelectron spectroscopy (XPS) analysis. The adsorption kinetics, isotherms and thermodynamics were further studied to understand the adsorption mechanism. Our work has provided a new method for the fabrication of natural polymers-based eco-friendly, low-cost and robust physical hydrogels for the heavy metal ions removal.

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Preparation of a chitosan/carboxymethyl chitosan/AgNPs polyelectrolyte composite physical hydrogel with self-healing ability, antibacterial properties, and good biosafety simultaneously, and its application as a wound dressing

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ARTICLE INFO

Keywords:
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In situ photoreduction
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ABSTRACT

The preparation of hydrogel wound dressing materials with high antibacterial activities and good biosafety simultaneously can be relatively challenging. Aiming at solving this crucial problem, a multi-functional chitosan/carboxymethyl chitosan/silver nanoparticles (CTS/CMCTS/AgNPs) polyelectrolyte composite physical hydrogel is constructed by *in situ* photoreduction of silver ions with α-hydroxy of CMCTS and semi-dissolution acidification sol-gel transition (SD-A-SGT) methods using natural polymers with no chemical reductant involved. The XRD, TEM and IR characterizations reveal a highly uniform structure of the composite hydrogel with good mechanical strength. The composite hydrogel also exhibits good self-healing ability, and the self-healing mechanism of the composite hydrogel prepared by natural polymers with high similarity is put forward on the basis of molecular dynamics simulation. The AgNPs gives the hydrogel excellent antibacterial activities against both *S. aureus* and *P. aeruginosa*., while the preparation method with no chemical reductant and crosslinking agent required endows the hydrogel high biocompatibility. The great application potentials of CTS/CMCTS/AgNPs polyelectrolyte composite hydrogel are demonstrated with its promoting effects on the healing of *P. aeruginosa* infected wounds as the wound dressing. It is a breakthrough in achieving hydrogels with desired biosafety and antibacterial activities simultaneously. The composite hydrogel is found with great application potentials as wound dressing.

1. Introduction

Hydrogel is a functional polymer material with good biocompatibility, high water retention and low cytotoxicity [1–3], and has been applied to wound dressings following the "wet wound healing theory" [4–6]. It can create a wet healing environment similar to the physiological state on wound to facilitate the growth of granulation and the division of skin cells, and thus promote wound healing [7–10]. However, the application of hydrogels as wound dressings is currently limited because it is very challenging to achieve high antibacterial activities and good biosafety simultaneously [11,12].

Bacteria can multiply on wet wounds easily, causing secondary infection [13]. Therefore, hydrogel wound dressings with high antibacterial activities are needed in moist environments [14]. Among all antibacterial agents, silver is the most widely used, efficient and broad-spectrum antibacterial agent [15]. In particular, silver nanoparticles (AgNPs) can show excellent antibacterial performances [3,16]. However, AgNPs are usually prepared by chemical reduction, which can leave residual reductants in the particles, causing high cytotoxicity [17–19]. In addition, the hydrogels containing AgNPs are mainly achieved by physical adsorption [20,21]. The low adsorption capacity and poor dispersion of AgNPs may result in insufficient antibacterial capacities.

Hydrogels based on natural polymers are the first choice for the preparation of wound dressing matrix because of their good biodegradability and biocompatibility [22,23]. Currently available hydrogels are mainly prepared by the chemical cross-linking of natural polymers, which can contaminate the resultant hydrogels with the residues of

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