

Research Article

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Cathodic dehalogenation polymerization of 2',3',5',6'-tetrafluoro-4,4''-diiodo-1,1':4',1''-terphenyl on zinc metal surface for anode protection

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Abstract

Fluorine-containing poly(p-phenylene) (CityU-42) films on zinc surfaces were directly synthesized using a cathodic dehalogenation C-C coupling strategy. The as-prepared polymers can effectively protect the zinc substrate in aqueous zinc-ion batteries. Because CityU-42 is rich in the electronegative fluorine group, it can attract the uniform deposition and rapid diffusion of Zn^{2+} on the surface of the anode. Moreover, a large number of benzene rings provide certain mechanical strength, enabling the protective layer to inhibit the growth of dendrites. As a result, the symmetric Zn|Zn cell used CityU-42@Zn can stably cycle for over 1,900 h under 5 mA cm^{-2} and 1 mAh cm^{-2} , while the CityU-42@Zn| V_2O_5 full cells maintain high capacity retention after 800 cycles at 5 A g^{-1} . The results highlight the potential of synthesizing conjugated polymers using cathodic dehalogenation technology, paving the way for further advancement in the field of energy storage technology.

Keywords: Fluorine-containing poly(p-phenylene) (CityU-42), cathodic dehalogenation polymerization, anode protection, aqueous zinc-ion batteries (AZIBs)



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INTRODUCTION

Conjugated polymers have attracted significant attention in materials science and engineering in recent years, owing to their distinctive electronic and optical properties^[1,2]. These polymers exhibit considerable potential in various applications, including transistors, energy storage devices, thermoelectric materials, sensors and catalysts, primarily due to their tunable physical and chemical characteristics^[3-10]. Notably, the construction of C-C bonds between aryl repeating units is crucial in the synthesis of polymers, as this process not only influences the structure and properties of polymers, but also directly influences their performance in various applications. To achieve C-C bond construction, researchers have developed various synthetic methodologies, including the Ullmann reaction, Grignard reaction, Suzuki reaction, and the Stille and Negishi coupling^[11-14]. Although these methods have made some progress in synthesizing conjugated polymers, they often necessitate a stringent anhydrous and anaerobic environment and the use of heavy metal catalysts^[15]. Such requirements not only complicate the synthesis process and increase costs but also pose potential environmental risks. Furthermore, conjugated polymers produced via these conventional methods frequently exhibit poor solubility, which limits their ability to form uniform and dense films, thereby compromising their performance in practical applications^[16]. Therefore, the development of novel methods for clean C-C bond construction under mild conditions is of particular importance.

Electrochemical techniques are recognized as a promising method for polymer synthesis, owing to their precise and controllable nature. Many organic reactions involve the transfer and coordination of electrons, making electrochemical polymerization - where electrons act as catalysts - an efficient and environmentally sustainable method^[17-19]. Furthermore, electrochemical deposition (ECD) and electrophoretic deposition (EPD) are regarded as versatile and reliable methods for thin film preparation^[20-22]. Thus, employing electrochemical techniques for the growth of polymer films represents an ideal solution to effectively address some limitations of conventional methods while facilitating the formation of C-C bond-coupled polymers. Despite the significant potential of electrochemical methods in organic polymer synthesis, traditional coupling through electrochemical oxidation on anodic surfaces encounters challenges when preparing thin films on metal electrodes^[23,24]. Conversely, utilizing the negative potential of the cathodic metal electrodes can effectively protect the electrode surface, enabling the successful preparation of conjugated polymer films on various metal substrates. Our research group's prior works have demonstrated that this approach offers the advantage of achieving C-C coupling via cathodic dehalogenation reactions, eliminating the need for heavy metal catalysts and resulting in the construction of stable polymer structures^[18,19]. This advancement opens a new pathway for the synthesis of conjugated polymers with substantial application potential.

Aqueous zinc-ion batteries (AZIBs) have garnered significant attention for their high safety, affordability, and environmental friendliness, positioning them as a highly promising option for energy storage devices^[25-27]. However, the performance of zinc metal anodes is hindered by challenges such as poor cycling stability, zinc dendrite formation, hydrogen evolution reactions (HER), corrosion, and surface passivation^[28]. Addressing these issues is critical for the commercial viability of AZIBs, necessitating the design and modification of zinc metal anodes. To overcome these obstacles, various strategies have been developed, among which interface modification stands out as one of the most straightforward and effective approaches^[29-31]. This method involves applying a protective or functional layer on the surface of the zinc anode to suppress dendrite growth and mitigate hydrogen evolution, ensuring more uniform Zn²⁺ deposition and enhancing the anode's reversibility^[32]. Organic polymers, favored for their excellent flexibility, high mechanical strength, and chemical stability, are widely employed in the interface modification of zinc anodes^[33]. Moreover, *in-situ* chemically formed protective layers offer superior

mechanical stability and adhesion compared to *ex-situ* coatings^[34–41]. As a result, the direct fabrication of polymer films on zinc metal surfaces through electrochemical methods presents a highly advantageous solution.

Herein, we synthesized fluorine-containing poly(*p*-phenylene) (named CityU-42) using a cathodic dehalogenation C-C coupling strategy with 2',3',5',6'-tetrafluoro-4,4''-diiodo-1,1':4',1''-terphenyl (TFDITP). Since the cathodic dehalogenation method is effective in protecting metal substrates, we directly synthesized this polymer film on a zinc metal surface with the aim of using it for electrode protection in AZIBs [Scheme 1]. The film is composed of a large number of benzene rings and F atoms altering with each other. The introduction of rigid aromatic rings in the polymer chain improves the overall rigidity and stability of the polymer network, which can enhance the surface strength of the electrode sheet after coating. This can inhibit the growth of sharp dendrites and prevent the rupture of the protective layer^[42,43]. In addition, F atoms exhibit electronegativity, which can attract Zn^{2+} to deposit uniformly and diffuse rapidly on the anode. Owing to these significant functions of the CityU-42 film, the Zn/Zn symmetric cell achieves a long cycle life of 1,900 h at 5 mA cm^{-2} and 1 mAh cm^{-2} . Furthermore, the CityU-42@Zn NVO full cell exhibits high-capacity retention at 5 A g^{-1} . The experimental results show that CityU-42 on the zinc anode surface can effectively inhibit the growth of zinc dendrites, which significantly extends the service life of the battery. This result provides a new material choice and strategy for improving the performance of AZIBs.

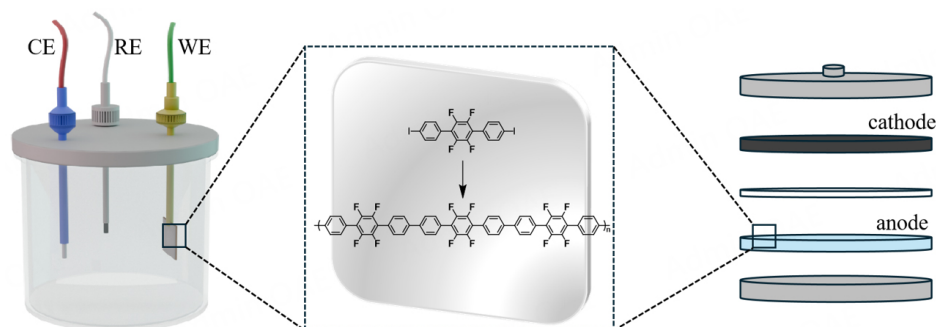
MATERIALS AND METHODS

Synthesis of CityU-42@Zn

The dehalogenated C-C coupling synthesis of CityU-42 films was carried out in a three-electrode electrochemical cell (zinc foil as working electrode, platinum wire as counter electrode, Ag/Ag^+ as reference electrode) containing dimethylsulfoxide (DMSO) as the electrolyte solution and 0.05 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. TFDITP was first synthesized prior to this according to the synthetic route shown in Supplementary Figure 1. The electrochemical synthesis was conducted by multicycle cyclic voltammetry (CV) in the potential range from -1.8 to -3 V (scanning rate: 50 mV/s) on CH Instruments 760E [Supplementary Figure 2]. A uniform and dense CityU-42 film was deposited on the surface of zinc metal foil (working electrode) (CityU-42@Zn).

RESULTS AND DISCUSSION

Successful coupling of CityU-42 was demonstrated by Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy. As shown in Figure 1A, the characteristic peak located at 814 cm^{-1} is the “out-of-plane” C-H stretching of para-disubstituted phenylenes in CityU-42. A characteristic peak of hybridized C-H vibrations on the aromatic ring also appears at $2,924 \text{ cm}^{-1}$ ^[16]. The original vibration peak of the C-I bond located at 498 cm^{-1} disappeared compared with that of the TFDITP monomer, proving the breakage of the C-I bond^[18]. Meanwhile, the C-F vibration peak at 971 cm^{-1} still existed^[44,45]. The Raman spectra further proved the successful preparation of CityU-42 [Figure 1B]. The three peaks located at 1,194, 1,320, and $1,612 \text{ cm}^{-1}$ are characteristic peaks of poly(*p*-phenylene)^[16,18]. In addition, the peaks located at 406, and $1,430 \text{ cm}^{-1}$ can be attributed to the bending and stretching vibration of the C-F bond, respectively^[45]. These characteristic peaks indicate the successful synthesis of CityU-42. Elemental analysis of CityU-42 was performed using X-ray photoelectron spectroscopy (XPS). The XPS survey spectra showed that CityU-42 consists of C and F [Figure 1C]. In detail, the peaks at 284.8, 287.2, and 293 eV in the C 1s spectra can be assigned to C-C/C=C, C-F, and π - π^* stacking, respectively [Figure 1D]^[46,47]. The peak at 688.9 eV in the F 1s spectra belongs to the fluorine of C-F [Figure 1E]^[46,48].



Scheme 1. Schematic of the synthesis of CityU-42@Zn and assembled cell.

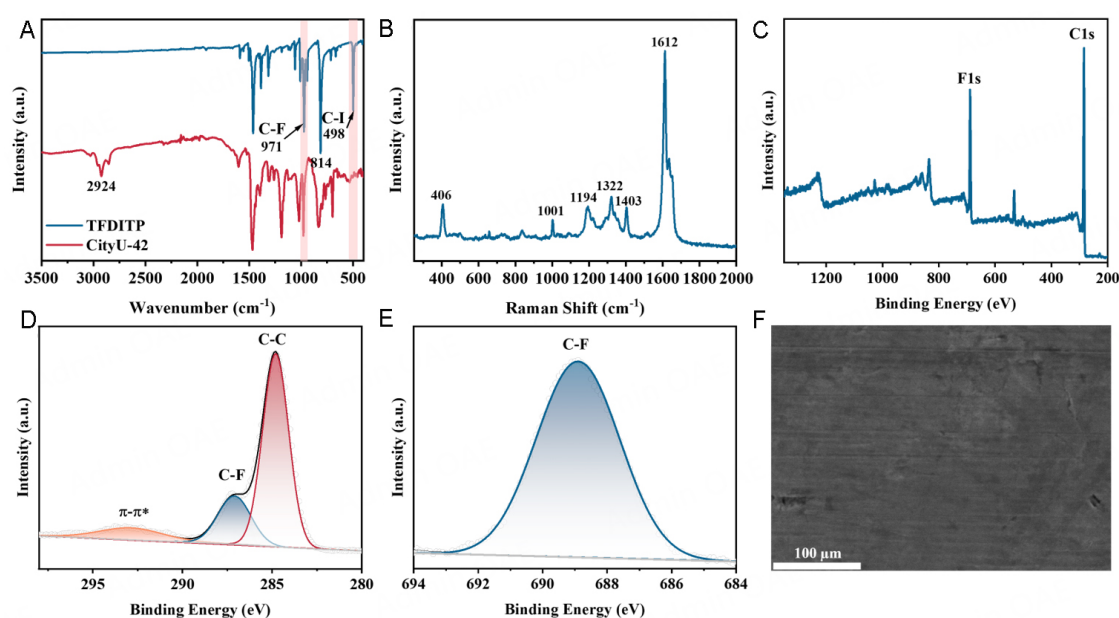


Figure 1. (A) FTIR spectra of the precursor TFDITP and the as-prepared CityU-42 film. (B) Raman spectra of CityU-42. (C) XPS survey of CityU-42. High-resolution XPS spectra of (D) C 1s and (E) F 1s for CityU-42. (F) SEM image of CityU-42@Zn.

A scanning electron microscopy (SEM) image showed that CityU-42 formed a smooth and dense film on the Zn surface [Figure 1F]. The thickness of the CityU-42 film deposited on the Zn surface was about 200 nm [Supplementary Figure 3]. In addition, contact angle measurements were performed by dropping the electrolyte vertically onto the bare Zn and CityU-42@Zn electrodes. The contact angle of CityU-42@Zn was 64.2°, which was significantly lower than that of bare Zn at 85.2° [Supplementary Figure 4]. This is attributed to the great polarity of F atoms in the polymer, which tend to form hydrogen bonds with water molecules, resulting in a lower contact angle. The excellent electrolyte wettability of the CityU-42@Zn surface promotes a uniform distribution of the Zn^{2+} flux on Zn anode surface, reducing the ion transport resistance and promoting uniform Zn^{2+} deposition^[49]. To verify the corrosion resistance, two types of anodes were immersed in the electrolyte for five days. As the SEM images show, the bare Zn is covered with many by-products, while there are almost no by-products on the surface of CityU-42@Zn after immersion [Supplementary Figures 5 and 6]. Besides, according to the XRD pattern, the peak intensity corresponding to the $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ phase on the surface of CityU-42@Zn is significantly reduced compared with that of the bare Zn [Supplementary Figure 7]. This further proves that CityU-42@Zn has good corrosion resistance compared with bare Zn.

The superiority of CityU-42@Zn was further elucidated through comprehensive electrochemical characterization. As depicted in Figure 2A, the symmetric cell based on CityU-42@Zn exhibits a smaller and more stable polarization voltage compared to bare Zn, maintaining stable cycling for nearly 2,000 h. In contrast, the bare Zn cell has a significantly shorter lifespan of only 311 h due to dendrite-induced short circuits (Figure 2A insert). The rate performance of Zn/Zn symmetric cells, measured at progressively increasing current densities from 0.5 to 10 mA cm⁻² while maintaining a fixed area capacity of 1 mAh cm⁻², is illustrated in Figure 2B. Notably, cells using bare Zn experienced short-circuiting due to abrupt changes in current density at the onset of the cycle. Conversely, the symmetric cell with CityU-42@Zn demonstrated enhanced stability, particularly at high current densities, as CityU-42@Zn effectively inhibited Zn dendrite formation. Additionally, when the current density returned to 0.5 mA cm⁻², the cells with CityU-42@Zn maintained continuous stable operation. Throughout the cycling process, cells with CityU-42@Zn exhibited small and stable polarization voltages, especially at high current densities, corroborating the long-cycling performance results mentioned earlier. These findings underscore the excellent stability and reversibility of zinc ion battery (ZIB) cycling, attributed to the protection of the zinc anode by CityU-42 films. Subsequent SEM image observations revealed that after 50 cycles, the bare zinc surface developed numerous disordered dendrites and large corrosion pits [Figure 2C]. In stark contrast, CityU-42@Zn maintained a uniform, dendrite-free surface devoid of corrosion pits, thanks to the protective CityU-42 interfacial layer, indicating superior deposition/stripping reversibility [Figure 2D]. These results demonstrate that CityU-42 is a remarkably promising material to stabilize Zn metal electrodes.

To further evaluate the electrochemical performance, a series of tests were conducted. The linear scanning voltammetry (LSV) curves, spanning a voltage range from -0.5 to 3.0 V, demonstrated changes in decomposition potential and current response [Figure 3A]. The oxygen evolution reaction (OER) and HER at the CityU-42@Zn electrode were significantly suppressed compared to bare Zn, confirming that CityU-42 films improve the electrochemical stability of the electrolyte at the anode surface [Figure 3B and C]. Notably, the response current on the CityU-42@Zn working electrode was consistently lower than that on the bare Zn electrode across the entire voltage range. The electrochemical performance of Zn deposition and stripping was evaluated using Zn/Ti half cells. The voltage profiles during the Zn nucleation stage are shown in Figure 3D. The CityU-42@Ti electrodes exhibit a significantly lower nucleation overpotential compared to bare Ti. This reduction is primarily attributed to the enhanced interfacial smoothness, which facilitates zinc ion deposition and mitigates energy fluctuations. Furthermore, the CityU-42 film, characterized by its strong zincophilicity and linear structure, enhances ion diffusion and improves ionic conductivity. This improvement ensures a more uniform delivery of zinc ions to the electrode surface, promoting stable zinc deposition and minimizing the risk of localized oversaturation at specific sites. Consequently, the nucleation energy is reduced, and uniform deposition is achieved. Additionally, electrochemical impedance spectroscopy (EIS) measurements [Supplementary Figure 8] reveal that the CityU-42@Zn symmetric cell exhibits significantly lower charge-transfer resistance than bare Zn, suggesting improved Zn²⁺ transfer kinetics. Supplementary Figure 9 illustrates the enhanced rate capability of the CityU-42@Zn cell. At a low current density of 0.5 A g⁻¹, it delivers an average capacity similar to that of initial cycles. However, at higher current densities of 1, 2, 3, and 5 A g⁻¹, the CityU-42@Zn cell exhibits superior capacities compared to the bare Zn. Upon returning to the 0.5 A g⁻¹ current density, the cell maintains a capacity of 240 mAh g⁻¹, consistent with the first several cycles. In contrast, the bare Zn cell demonstrates a lower capacity of 230 mAh g⁻¹ under the same conditions. Finally, full cells were assembled to assess the practicality of using commercial V₂O₅ as the cathode for the CityU-42@Zn anode. The Zn/V₂O₅ full cells underwent constant-current cycling at 5 A g⁻¹. The CityU-42@Zn anode exhibited a high reversible capacity of 150 mAh g⁻¹ with significant capacity retention after 1,000 cycles at 5 A g⁻¹, whereas the bare Zn anode failed after approximately 200 cycles due to uncontrolled Zn dendrite growth and by-product formation [Figure 3E]. Notably, this work demonstrates superior performance compared to previously

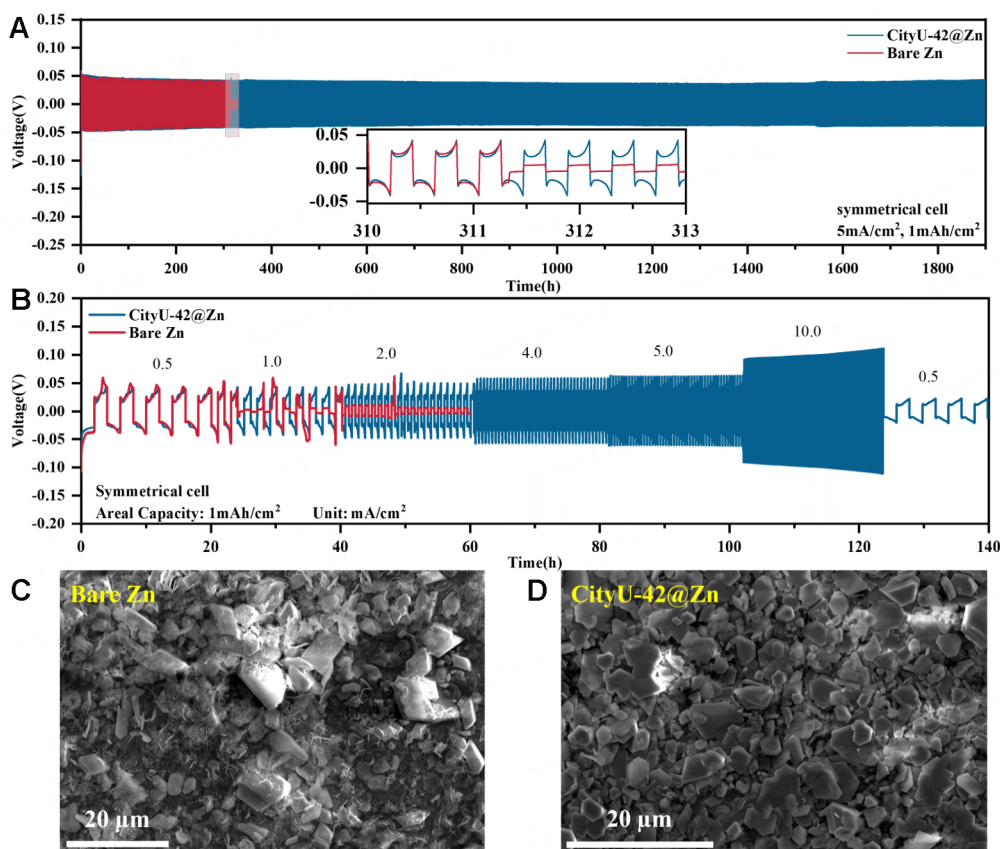


Figure 2. (A) Cycling performance and (B) Rate performance of bare Zn and CityU-42@Zn symmetric batteries. SEM plots of (C) Bare Zn and (D) CityU-42@Zn after cycling.

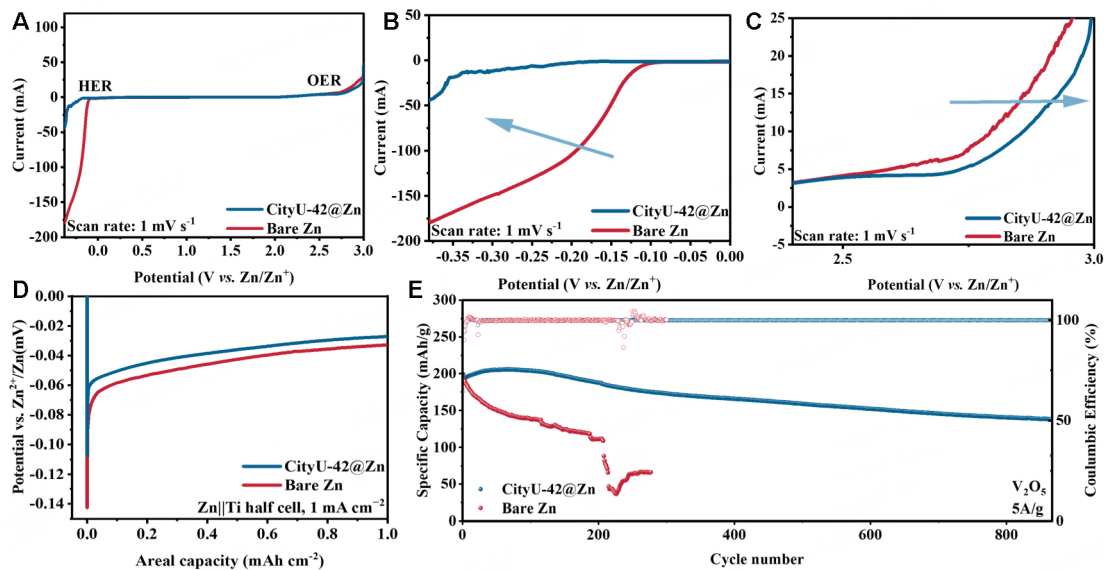


Figure 3. (A) Electrochemical stability window of Zn Zn symmetric cells assembled with bare Zn and CityU-42@Zn. The corresponding zoomed-in curves: (B) Low potential area and (C) High potential area. (D) Voltage profiles during initial Zn plating on the Ti foil and CityU-42@Ti at 1 mA cm^{-2} . (E) Long-term cycling stability tests of Zn V_2O_5 full cells assembled with bare Zn and CityU-42@Zn.

reported results using interfacial modification strategies, particularly *ex-situ* methods [Supplementary Table 1], highlighting the competitive advantage of *in-situ* strategies in enhancing the stability of the Zn anode.

CONCLUSIONS

Employing the cathodic dehalogenation strategy, we directly prepared a polymer film (CityU-42) on the surface of zinc metal for electrode protection in AZIBs. As a result, the symmetric Zn Zn cell used CityU-42@Zn can cycle stably for 1,900 h under the condition of 5 mA cm⁻² and 1 mAh cm⁻². Impressively, the CityU-42@Zn V₂O₅ full cell also exhibits a reversible capacity and high capacity retention. These results confirm that CityU-42@Zn can effectively inhibit the growth of Zn dendrites, significantly extending the service life of the battery. This achievement provides new material selection and strategies for improving the performance of AZIBs and other energy storage devices.

DECLARATIONS

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Authors' contributions

The conception and design of the work: Wu, J.; Naren, T.; Chen, L.; Zhang, Q.

Materials synthesis: Wu, J.; Zhang, S.

Data acquisition: analysis and interpretation: Wu, J.; Naren, T.; Zhang, S.; Jiang, R.; Wang, X.; Gu, Q.; Yan, Y.

Availability of data and materials

The data supporting the findings of this study are available within this Article and its [Supplementary Materials](#). According to reasonable requirements, all the data examined in this research can be obtained from the correspondents.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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