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**Utilization of a Zirconium-Based Porous Metal-Organic Framework
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Suppression of Aggregation-Caused Quenching**

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ABSTRACT

To achieve highly precise measurement of alpha-fetoprotein (AFP) —a key biomarker for hepatocellular carcinoma—a novel electrochemiluminescence (ECL) immunosensor was developed. This sensor is constructed based on a synergistic "donor-acceptor" system, where Au@PCN-224 serves as the ECL signal donor and CeO₂@PDA acts as the ECL signal quenching receptor. The superior performance of this immunosensor stems from its following design advantages: (1) PCN-224 has a well-defined structure that stops TCPP ligands from clumping together through steric hindrance. This improves charge transfer efficiency, which in turn makes the electrochemiluminescence (ECL) signal stronger. (2) The porosity of PCN - 224 offers high - efficiency diffusion pathways for the co - reactant, which leads to the diminishment of mass transfer resistance and the augmentation of the ECL signal generation efficiency during electrochemical excitation. (3) The partial spectral overlap between Au@PCN-224 (donor) and CeO₂@PDA (acceptor) enables efficient electrochemiluminescence resonance energy transfer (ECL-RET), which in turn significantly enhances the detection sensitivity for AFP. This immunosensor exhibited excellent stability, selectivity, and reproducibility across a wide detection range of 0.0001 to 200 ng·mL⁻¹ for AFP. These results indicate its substantial potential for clinical AFP detection and early-stage liver cancer screening.

Keywords: Alpha-fetoprotein (AFP); PCN-224; Electrochemiluminescence (ECL); ECL Resonance Energy Transfer (ECL-RET)

INTRODUCTION

Global cancer mortality statistics position primary liver cancer (PLC) as the fourth leading cause[1]. AFP, a widely utilized serum tumor biomarker, plays a critical diagnostic role in identifying tumor origin[2]. Early detection and diagnosis of AFP, coupled with guided treatment strategies, can significantly reduce PLC incidence and mortality while lowering therapeutic costs. Therefore, developing highly specific and sensitive AFP immunoassays is of critically importance for early clinical diagnosis and pathological research on tumor markers[3]. Over the past decades, a variety of optical biosensing technologies have emerged and matured for AFP detection[4], including fluorescence[5], colorimetry[6], ECL[7], localized surface plasmon resonance (LSPR)[8], photoelectrochemistry(PEC)[9] and surface-enhanced Raman spectroscopy (SERS)[10]. Among them, ECL technology ingeniously integrates the advantages of both electrochemistry and chemiluminescence[11,12], enabling effective minimization of background interference, high detection sensitivity, and rapid analysis. Owing to these distinctive technical strengths, ECL has established a prominent position in analytical detection and has been widely applied.[13–16].

Currently, various organic luminophores have been widely employed in the construction of electrochemiluminescence sensors. Among them, porphyrins and their derivatives, as an important class of organic emitters, are recognized as typical ECL-active materials due to their unique photochemical and photophysical properties, demonstrating significant potential for application in ECL sensing[17,18]. As early as 2015, a breakthrough discovery was reported by Lu's team, which observed that TCPP

could generate a cathodic ECL emission in a phosphate-buffered saline (PBS) solution containing potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$)[19]. From a structural perspective, porphyrins are structurally stable conjugated macrocycles characterized not only by a rigid geometric framework but also by outstanding optoelectronic properties and easily modifiable functional groups. These combined advantages render them excellent organic ECL reagents[11,20]. In reported porphyrin-based ECL systems, porphyrin molecules are prone to form aggregates through π - π stacking. This aggregation triggers an aggregation-caused quenching (ACQ) effect, which significantly diminishes the ECL emission efficiency and consequently constrains the improvement of their sensing performance[21].

To address the prevalent ACQ issue in porphyrins, Han et al. synthesized a coordination polymer (Eu-PCP) constructed from Eu^{3+} and TCPP. This strategy resulted in a 7.7-fold enhancement in ECL intensity and a 4.6-fold improvement in ECL efficiency for Eu-PCP compared to pure TCPP[22]. In a separate strategy, Wu et al. utilized the coordination-driven self-assembly between La^{3+} ions and TCPP to form a three-dimensional lanthanide-porphyrin hybrid (LPH). This LPH exhibited a strong ECL response signal with $\text{K}_2\text{S}_2\text{O}_8$ as a coreactant, demonstrating superior optical properties and stability relative to pure La^{3+} or pristine TCPP, while successfully circumventing the ACQ effect. Studies have revealed that the coordination between metal ions and porphyrins induces the formation of a rigid metal-porphyrin coordination structure[23]. This structure introduces steric hindrance that impedes the close packing of porphyrin molecules, thereby reducing aggregate formation, and

consequently suppresses the ACQ effect[24].

Electrochemiluminescence resonance energy transfer (ECL-RET) is a technique that enables signal modulation through energy transfer between a donor and an acceptor at the nanoscale. A critical requirement for efficient ECL-RET is a strong spectral overlap between the ultraviolet-visible (UV-vis) absorption spectrum of the acceptor and the ECL emission spectrum of the donor[25]. Consequently, the rational design of high-performance ECL donor-acceptor combinations is central to enhancing the detection capabilities of ECL-RET immunosensors. In the screening of acceptor materials, polydopamine (PDA) has garnered significant attention due to its excellent biocompatibility and multifunctionality —properties that also make it well-suited for ECL sensing applications, leading to its broad application across fields such as biology and energy[20,26]. Previous studies have confirmed that PDA can function as an efficient ECL quencher for constructing sensing strategies. For instance, Shi et al. developed a composite material based on ZnO NFs@PDA, which effectively quenched the ECL emission of g-C₃N₄ via a RET mechanism, leading to the development of an immunosensor for sensitive procalcitonin (PCT) detection.[27].

Based on the foregoing, this study successfully constructed a quenching-type ECL sensor utilizing PCN-224 as the energy donor and CeO₂@PDA as the energy acceptor. PCN-224 was first synthesized via a straightforward hydrothermal method and demonstrated strong and stable ECL emission. Its well-ordered framework effectively suppresses the ACQ effect of the TCPP ligands, while its inherent porous structure provides efficient diffusion channels for the coreactant, reducing mass transfer

resistance and thereby enhancing the ECL efficiency during the electrochemical
excitation process. To further improve electrical conductivity and biocompatibility of
the sensing interface[7], gold nanoparticles (Au NPs) were deposited onto the surface
of PCN-224. Meanwhile, CeO₂@PDA was fabricated and utilized as the detection
antibody signal probe. CeO₂@PDA exhibits a broad UV-vis to near-infrared (NIR)
absorption spectrum, which effectively overlaps with the ECL emission spectrum of
PCN-224. This substantial spectral overlap efficiently triggers the ECL-RET process
between the donor (PCN-224) and acceptor (CeO₂@PDA), thereby inducing specific
quenching of the PCN-224-derived ECL signal. Based on the aforementioned ECL-
RET mechanism, a signal-off ECL immunosensor was fabricated (Scheme 1). This
sensor exhibited a wide linear response toward AFP over the concentration range of
0.0001-200 ng·mL⁻¹, along with excellent operational stability, high specificity, and
outstanding reproducibility. This work thus offers a novel technological platform for
the detection of tumor markers relevant to the early diagnosis of hepatocellular
carcinoma.

obtained through centrifugation (10,000 rpm, 15 min). Finally, the collected precipitate was dried in an vacuum oven at 60°C for 10 h to obtain the final powder, which was used for subsequent characterization and analysis.

RESULTS AND DISCUSSION

Characterization of PCN-224 and Au@PCN-224. The morphological features of the synthesized materials were investigated by scanning electron microscopy (SEM). It can be observed from the low-magnification SEM micrograph (Fig. 1A) that the PCN-224 particles exhibited a high degree of aggregation with a dense overall distribution. The high-magnification SEM image (Fig. 1B) more clearly reveals their spherical morphology and relatively uniform particle size, with an average diameter of approximately 200 nm. Elemental mapping (Fig. 1C) confirmed the distribution of C, N, O, Zr (constituent elements of PCN-224) and Au (from Au NPs), indicating the successful and relatively uniform dispersion of Au nanoparticles onto the PCN-224 surface. The energy-dispersive X-ray spectroscopy (EDS) spectrum (Fig. 1D) detected characteristic peaks for C, N, O, Zr, and Au, further verifying the presence of Au in the composite alongside the constituent elements of PCN-224. High-resolution transmission electron microscopy (HRTEM) images (Figs. 1E, F) revealed distinct lattice fringes corresponding to Au NPs. The measured interplanar spacing of 0.235 nm is consistent with the (111) crystal plane of Au, which not only confirms the presence and crystallographic characteristics of Au but also indicates that Au maintained its well-defined crystal structure after compositing with PCN-224[29].

To investigate the interactions within the Au@PCN-224 composite, the surface

charge properties were analyzed by Zeta potential measurements (Fig. 1G). The average ζ -potential values for PCN-224, Au NPs, and Au@PCN-224 were measured at +6.38 mV, -29.77 mV, and -21.55 mV, respectively. The ζ -potential shifted from +6.38 mV (PCN-224, positively charged) to -21.55 mV for the composite, reflecting the incorporation of negatively charged Au NPs (-29.77 mV). This suggests that the significant electrostatic attraction between the negatively charged Au NPs and the positively charged PCN-224 surface drives the formation of a highly stable composite.

The coordination between Zr^{4+} and the TCPP ligand in PCN-224 was further investigated by comparing their Fourier transform infrared (FT-IR) spectra (Fig. 1H). In the spectrum of PCN-224, the asymmetric stretching vibrations of the C=O bond at 1681 cm^{-1} and the C-O bond at 1266 cm^{-1} , associated with the carboxyl (-COOH) groups, were significantly reduced compared to free TCPP, indicating deprotonation of -COOH groups and their coordination with Zr^{4+} (forming Zr-O bonds)[30]. This observation indicates that the -COOH groups of the TCPP ligand participated in coordination with Zr^{4+} ions. Absorption peaks corresponding to the N-H bond were detected at 3433 cm^{-1} in both PCN-224 and TCPP, confirming the presence of uncoordinated nitrogen sites within the PCN-224 framework[31]. The stretching vibration of the C=C bonds from the benzene and pyrrole rings was observed at 1559 cm^{-1} . Furthermore, the characteristic peak at 660 cm^{-1} is assigned to the Zr-O stretching vibration (consistent with Zr-OH species)[32]. Collectively, these spectral features confirm the successful assembly of all TCPP units within the PCN-224 structure.

The X-ray photoelectron spectroscopy (XPS) survey spectrum (Fig. 1I) confirmed

the presence of Zr 3d, C 1s, N 1s, and O 1s core-level peaks. In the high-resolution Zr 3d spectrum (Fig. 1J), the peaks centered at binding energies of 184.52 eV and 182.11 eV were assigned to Zr 3d_{3/2} and Zr 3d_{5/2} of the Zr-O bond, respectively—consistent with previously reported values for Zr⁴⁺ in Zr-based MOFs[33], providing strong evidence for the coordination interaction between Zr⁴⁺ and TCPP ligands. These collective confirm the successful preparation of PCN-224 with well-defined Zr⁴⁺-TCPP coordination.

The N₂ adsorption-desorption isotherm of PCN-224 (Fig. 1K) exhibited a reversible Type IV isotherm with a distinct H1 hysteresis loop. The corresponding pore size distribution (calculated using the BJH method) showed a narrow peak centered at approximately 3.36 nm, indicating uniform mesopore size. This well-defined porous architecture facilitates efficient mass transport pathways for coreactants within the ECL system, effectively reducing mass transfer resistance and thereby enhancing the ECL signal generation efficiency during electrochemical excitation.

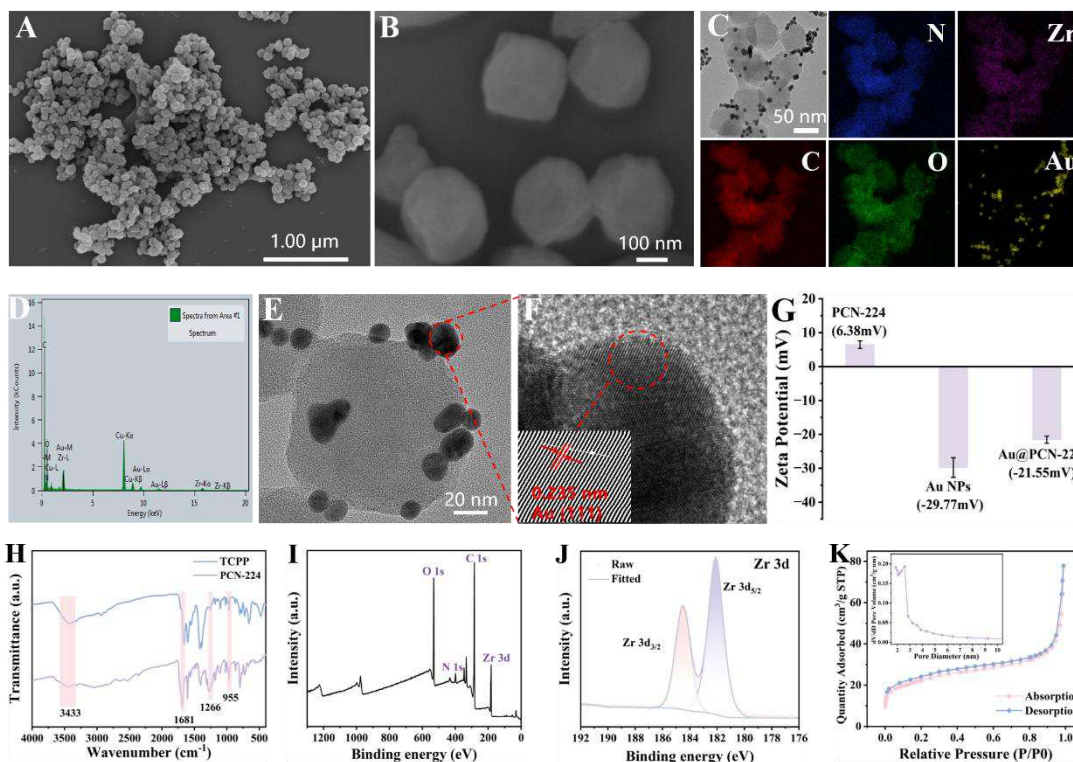


Fig. 1. (A),(B)SEM images of PCN-224, (C)TEM images and EDS mapping of Au@PCN-224, (D)EDS energy spectrum of Au@PCN-224, (E) Local magnification of Au nanoparticles, (F) lattice fringe of Au nanoparticles, (G) Zeta potential of PCN-224, Au NPs and Au@PCN-224, (H) FT-IR spectra of TCPP and PCN-224, (I) XPS energy spectra of PCN-224, (J)XPS fine spectra of Zr 3d, and (K) N₂ adsorption-desorption isotherm of PCN-224 measured at 77 K, with the pore size distribution presented in the inset.

Characterization of CeO₂@PDA Nanocomposites. SEM imaging (Fig. 2A) showed that the CeO₂@PDA composite exhibits a spherical morphology with relatively uniform particle size. TEM observations (Fig. 2B) further revealed a well-defined core-shell structure within individual spherical particles. Elemental mapping (Fig. 2C) demonstrated homogeneous distribution of C, N, and O elements, while Ce was

213 primarily concentrated in the core region of the particles. This elemental distribution
214 corresponds to the darker core areas attributable to CeO_2 in the TEM images,
215 confirming the successful encapsulation of CeO_2 cores by a polydopamine (PDA) shell.

216 The structures of CeO_2 and $\text{CeO}_2@\text{PDA}$ were characterized by FT-IR
217 spectroscopy (Fig. 2D). In the spectrum of pristine CeO_2 (curve a), weak peaks were
218 observed at 688, 1325, and 1628 cm^{-1} —attributed to adsorbed water and surface
219 hydroxyl groups ($-\text{OH}$) on CeO_2 —along with a strong absorption band around 500 cm^{-1}
220 assigned to the Ce-O stretching vibration. In contrast, the spectrum of $\text{CeO}_2@\text{PDA}$
221 (curve b) retained these CeO_2 -related characteristic peaks while exhibiting a broad and
222 intense absorption band in the $3100\text{--}3600\text{ cm}^{-1}$ range, which arises from the overlapping
223 O-H and N-H stretching vibrations of PDA. Additionally, weak peaks at 1510 cm^{-1} and
224 1610 cm^{-1} (aromatic C=C stretching vibrations of PDA) were observed in curve b[34],
225 further confirming the presence of the PDA shell.

226 The XPS survey spectrum (Fig. 2E) of $\text{CeO}_2@\text{PDA}$ confirms the presence of
227 characteristic peaks for C 1s, O 1s, N 1s, and Ce 3d. The O 1s peak originates from both
228 CeO_2 (Ce-O bonds) and PDA (hydroxyl), consistent with the composite composition.
229 The existence of C and N elements provides further evidence for the presence of PDA,
230 which contains both carbon and nitrogen. The appearance of Ce 3d peaks indicates that
231 the presence of Ce 3d peaks confirms that CeO_2 is stably retained as the core component
232 in the composite. The high-resolution Ce 3d spectrum (Fig. 2F) was deconvoluted to
233 analyze the chemical states of cerium. The Ce 3d spectrum can be resolved into two
234 sets of spin-orbit doublets, corresponding to $\text{Ce } 3d_{3/2}$ and $\text{Ce } 3d_{5/2}$. According to the

literature, the characteristic peak at a binding energy of 898.8 eV is assigned to the Ce^{3+} $3d^{10}4f^1$ electronic configuration, while the peaks located at 882.8 eV, 888.8 eV, 901.6 eV, and 917.1 eV are attributed to the Ce^{4+} $3d^{10}4f^0$ configuration. These results indicate the coexistence of both Ce^{3+} and Ce^{4+} valence states in the CeO_2 nanocomposite[35]. These XPS results, combined with the preceding SEM, TEM, and FT-IR characterizations, collectively confirm the successful preparation of the $\text{CeO}_2@\text{PDA}$ core-shell composite.

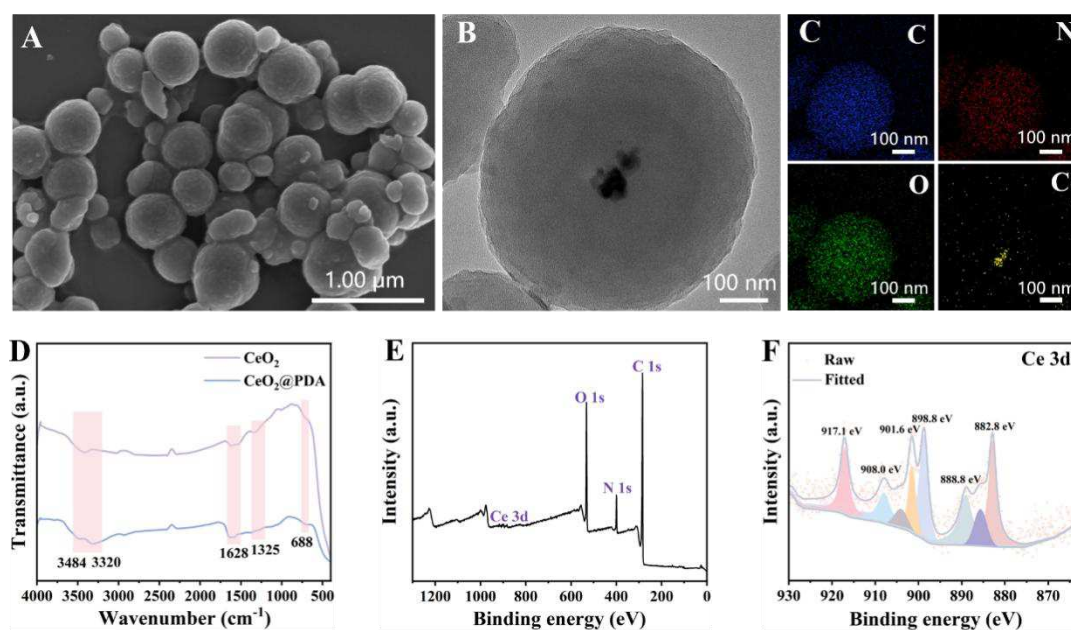


Fig. 2. (A) SEM images of $\text{CeO}_2@\text{PDA}$, (B) TEM of $\text{CeO}_2@\text{PDA}$, (C) EDS mapping of $\text{CeO}_2@\text{PDA}$, (D) FT-IR spectra of CeO_2 and $\text{CeO}_2@\text{PDA}$, (E) XPS energy spectra of $\text{CeO}_2@\text{PDA}$, and (F) XPS fine spectra of Ce 3d.

Electrochemical Characterization of the ECL Biosensor.

At different scan rates, both TCPP and PCN-224 exhibited a pair of reversible redox peaks (Fig. 3A–3D), with the anodic and cathodic peak currents showing a good

linear relationship with the square root of scan rate ($v^{1/2}$) ($R^2= 0.999$), consistent with the Randles–Sevcik equation, indicating that the electrode reactions of both materials are diffusion-controlled[36]. The electrochemically active surface areas of the TCPP- and PCN-224-modified glassy carbon electrodes were calculated to be 0.161 cm^2 and 0.202 cm^2 , respectively, which are approximately 1.6 times that of the bare electrode (0.126 cm^2). Furthermore, the assembly of TCPP into the PCN-224 porous framework results in an increased electrochemically active surface area and enhanced electron transfer efficiency, which can be attributed to the abundant porous channels and more exposed active sites provided by the MOF structure.

The stepwise assembly process of the biosensor and the interfacial electron transfer properties were systematically investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) with the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox pair. The CV curve of the bare glassy carbon electrode (GCE, curve a in Fig. 3A) exhibited the highest redox peak currents, indicating extremely low interfacial electron transfer resistance (R_{ct}) and highly efficient electron transfer of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at the bare GCE surface. The sequential assembly process of the biosensor was monitored by tracking the changes in the CV response of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe (Fig. 3E). Upon modification of the bare GCE with Au@PCN-224 (curve b), a significant decrease in the redox peak currents was observed. This can be attributed to the inherently low electrical conductivity of the PCN-224 framework, which impedes electron transfer of the redox probe at the electrode interface. Subsequent immobilization of the capture antibody (Ab_1 , curve c), followed by blocking with

bovine serum albumin (BSA, curve d), and specific binding of the AFP antigen (curve e), resulted in a stepwise decrease in the redox peak currents of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe. This progressive attenuation arises because Ab₁, BSA, and AFP—all insulating biomolecules—form successive layers on the electrode surface, each further increasing interfacial resistance and retarding electron transfer, leading to successively lower peak currents. This confirms the successful sequential assembly of Ab₁, BSA, and AFP on the electrode surface. Finally, after the introduction of the Ab₂-CeO₂@PDA complex (curve f), the redox peak currents of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe decreased to their lowest level. This final reduction stems from the intrinsically low electrical conductivity of the CeO₂@PDA nanocomposite combined with the insulating properties of the Ab₂ antibody, which synergistically increase the electron transfer resistance at the electrode interface. The sequential and continuous decline in peak current throughout the modification process—with each step introducing a new barrier to electron transfer—collectively provides direct and compelling evidence for the successful layer-by-layer assembly of the ECL immunosensor.

EIS, known for its high sensitivity to interfacial changes, was employed as a complementary technique to characterize the stepwise modification of the biosensor. The EIS data were fitted using the Randles equivalent circuit model, where the charge transfer resistance (R_{ct}) is represented by the diameter of the semicircle in the Nyquist plot. A larger semicircle diameter corresponds to a higher R_{ct} value, indicating more hindered electron transfer at the electrode interface. The EIS curve of the bare GCE (curve a in Fig. 3F) exhibited a very small semicircular diameter, indicating a minimal

293 R_{ct} and highly efficient electron transfer, which is consistent with the CV results. After
294 modification with Au@PCN-224 (curve b), the semicircle diameter increased
295 significantly, confirming that the poor conductivity of PCN-224 elevates the R_{ct} and
296 impedes electron transfer. Subsequent immobilization of non-conductive biomolecules
297 — including Ab₁, BSA, AFP, and finally Ab₂-CeO₂@PDA — resulted in a stepwise
298 increase in the semicircle diameter. These substances form an insulating layer on the
299 electrode surface, which substantially hinders the electron transfer of the [Fe(CN)₆]^{3-/4-}
300 redox probe, leading to a continuous rise in R_{ct} . Both CV and EIS results are in
301 excellent agreement, consistently reflecting the progressive change in electron transfer
302 capability throughout the stepwise assembly process: "bare GCE → Au@PCN-224 →
303 Ab₁ → BSA → AFP → Ab₂-CeO₂@PDA". This systematic impedance increase
304 provides strong evidence for the successful fabrication and assembly of the
305 immunosensor.

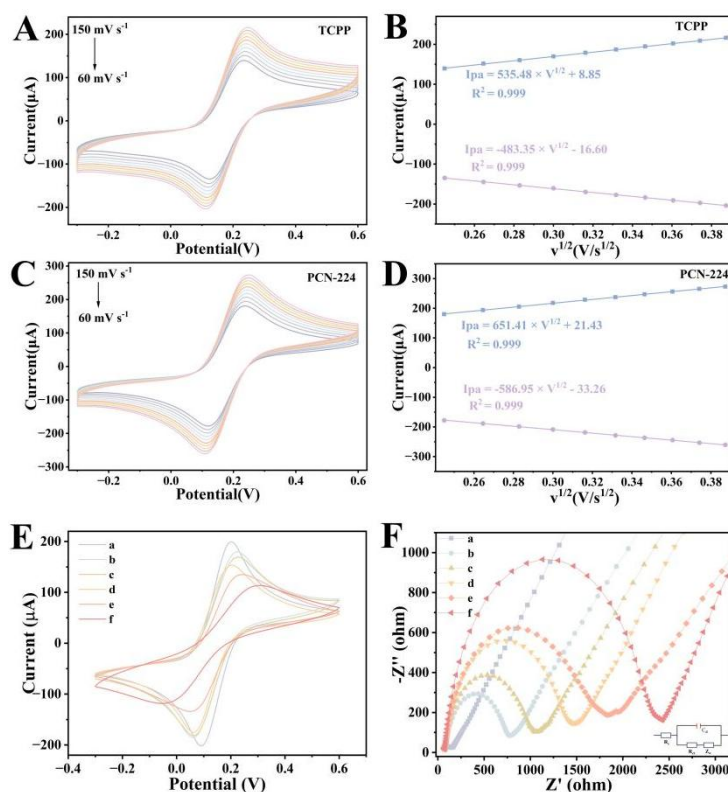


Fig. 3. (A) and (B) Electroactive surfzce areas of TCPP/GCE were investigated;(C) and (D) Electroactive surfzce areas of PCN-224/GCE were investigated;(E) CV curves and (F) EIS curves of electrode assembly process: (a)bare GCE, (b) Au@PCN-224/GCE, (c)Ab₁/Au@PCN-224 /GCE, (d)BSA/Ab₁/Au@PCN-224 /GCE, (e) AFP/BSA/Ab₁/Au@PCN-224 /GCE, (f)CeO₂@PDA-Ab₂/ AFP/BSA/Ab₁/Au@ PCN-224 /GCE.

Optimization of Experimental Conditions. To achieve the optimal ECL response, key parameters including the concentration of PCN-224, the concentration of the coreactant K₂S₂O₈, and the pH of the testing solution were systematically optimized.

As the core luminophore in the ECL system, the concentration of PCN-224 directly governs the signal intensity. Experimental results demonstrated a gradual enhancement in the ECL signal with increasing PCN-224 concentration (Fig. 4A). This trend can be attributed to the increased loading of PCN-224 molecules on the electrode

surface, which provides more active sites for the ECL reaction. The signal reached its maximum intensity at a PCN-224 concentration of $0.15 \text{ mg}\cdot\text{mL}^{-1}$. However, a further increase in concentration beyond $0.15 \text{ mg}\cdot\text{mL}^{-1}$ led to a decline in the ECL signal. This decrease is likely due to the formation of an excessively thick layer of luminophores on the electrode surface, which compromises electrical conductivity, hinders electron transfer, and blocks the diffusion of the coreactant ($\text{K}_2\text{S}_2\text{O}_8$) to the PCN-224 active sites—ultimately quenching the ECL emission.

The concentration of $\text{K}_2\text{S}_2\text{O}_8$, a crucial coreactant in the ECL system, plays a vital role in determining the signal generation efficiency. The maximum ECL intensity was achieved at a $\text{K}_2\text{S}_2\text{O}_8$ concentration of 80 mM (Fig. 4B). As the concentration increased up to this optimal value, the enhanced signal can be attributed to a greater number of strongly oxidizing $\text{SO}_4^{\cdot-}$ radicals generated via electrochemical reduction of $\text{S}_2\text{O}_8^{2-}$ at the electrode surface. The increased population of $\text{SO}_4^{\cdot-}$ radicals promotes more frequent electron transfer reactions with PCN-224, leading to the formation of a larger number of excited-state PCN-224^{*} species and consequently a stronger ECL emission. However, when the $\text{K}_2\text{S}_2\text{O}_8$ concentration exceeded 80 mM, a continuous decrease in the ECL signal was observed. This attenuation may result from two potential factors: firstly, the highly oxidizing environment could cause damage to the biological components immobilized on the sensor; secondly, an excess of $\text{S}_2\text{O}_8^{2-}$ ions might inhibit the formation of PCN-224^{*}, possibly by competing for reduction pathways or engaging in quenching side reactions, thereby reducing the overall ECL efficiency.

The pH of the testing solution plays a dual role: it influences the biological activity

of biomolecules (such as antigens and antibodies used in subsequent detection) and modulates the generation and stability of radicals involved in the ECL process. The effect of pH on the luminescence performance of PCN-224 was investigated over a range of 5.5 to 8.0. The ECL intensity exhibited a characteristic "increase-then-decrease" trend with rising pH, reaching its maximum at pH 7.0 (Fig. 4C).

In summary, the optimal experimental conditions identified in this study are as follows: PCN-224 concentration of $0.15 \text{ mg} \cdot \text{mL}^{-1}$, $\text{K}_2\text{S}_2\text{O}_8$ concentration of 80 mM, and a testing solution pH of 7.0. Under these optimized parameters, the ECL system achieves an optimal balance between signal intensity and operational stability.

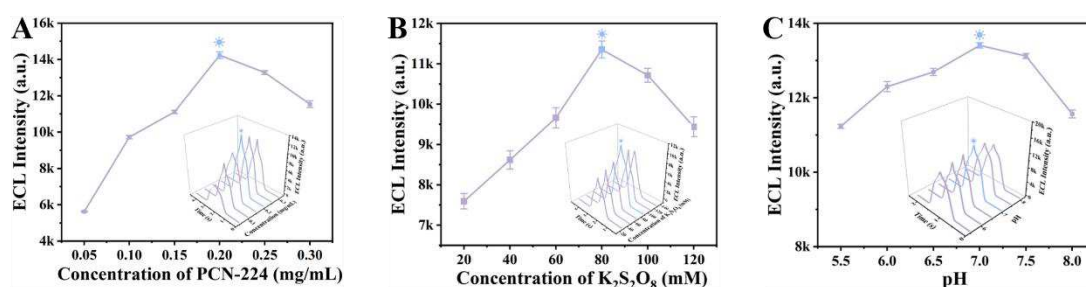


Fig. 4. Experimental condition optimization: (A) concentration of PCN-224, (B) $\text{K}_2\text{S}_2\text{O}_8$, (C) pH.

Investigation of the PCN-224 ECL Mechanism. An efficient coreactant can significantly enhance the ECL signal. This study investigated the PCN-224/ $\text{K}_2\text{S}_2\text{O}_8$ coreaction system (Fig. 5A). ECL-time curves were recorded under a cyclic potential from -1.5 to 0 V for the following three configurations: a bare GCE in PBS containing 100 mM $\text{K}_2\text{S}_2\text{O}_8$, a PCN-224/GCE in pure PBS, and a PCN-224/GCE in PBS containing 80 mM $\text{K}_2\text{S}_2\text{O}_8$.

Bare GCE in PBS containing 100 mM $K_2S_2O_8$ (yellow curve): No detectable ECL signal was observed. This is because the bare GCE lacks a luminophore (PCN-224) to form excited states, even with excess $K_2S_2O_8$. PCN-224/GCE (modified with 0.15 mg·mL⁻¹ PCN-224) in pure PBS (without $K_2S_2O_8$, blue curve): No ECL signal was generated either. Without $K_2S_2O_8$, no $SO_4^{\cdot-}$ radicals are produced to trigger electron transfer with PCN-224, so excited-state PCN-224* cannot form. PCN-224/GCE in PBS containing 80 mM $K_2S_2O_8$ (pink curve): A strong and stable ECL emission was obtained, with a relative intensity of 16800 a.u. These results collectively confirm that $K_2S_2O_8$ serves as an efficient coreactant for PCN-224—providing $SO_4^{\cdot-}$ radicals to drive ECL reactions—and that the ECL emission originates specifically from the synergistic interaction between PCN-224 (luminophore) and $K_2S_2O_8$ (coreactant).

Furthermore, to validate the superiority of $K_2S_2O_8$, the ECL responses of PCN-224 with different coreactants—hydrogen peroxide (H_2O_2), tripropylamine (TPA), and triethylamine (TEA)—were investigated under identical conditions (Fig. 5B). No ECL signal was detected in the presence of H_2O_2 , while only very weak emission was observed with TPA and TEA. These results indicate that $K_2S_2O_8$ exhibits higher relative energy level compatibility with PCN-224 compared to the other coreactants tested, enabling it to function as an effective coreactant that significantly enhances the ECL emission of PCN-224.

The charge transfer capabilities of the luminophores were evaluated by EIS (Fig. 5C). In the Nyquist plots, the diameter of the semicircle directly corresponds to the charge transfer resistance—a larger diameter indicates a higher R_{ct} . The R_{ct} values

extracted from the plots are as follows: Au@PCN-224 (776 Ω), PCN-224 (1008 Ω), and TCPP (1406 Ω). TCPP exhibited the largest R_{ct} , indicating the most hindered electron transfer at its interface. This result demonstrates that the PCN-224 framework effectively enhances the electron transfer capability at the electrode surface compared to the free TCPP ligand. Furthermore, the modification with Au nanoparticles on the PCN-224 surface further improved the charge transport efficiency of the sensing interface, as evidenced by the lowest R_{ct} value of the Au@PCN-224 composite.

The fluorescence spectra (Fig. 5E) — recorded under identical conditions (excitation wavelength = 420 nm)—show that both PCN-224 (blue curve) and TCPP (pink curve) exhibit emission peaks at 678 nm within the range of 650-700 nm. Notably, the fluorescence intensity of PCN-224 is significantly higher than that of TCPP. This enhancement can be attributed to the coordination of TCPP with Zr^{4+} ions during framework formation: Zr^{4+} coordination restricts the rotational and vibrational motion of TCPP's benzene rings, significantly increasing structural rigidity and optimizing the conjugation degree of the porphyrin system. These changes effectively suppress non-radiative transitions and thus improve the fluorescence quantum yield[37]. Furthermore, the three-dimensional fluorescence contour map of PCN-224 (Fig. 5F) reveals a distinct fluorescence signal region around 678 nm, confirming the fluorescent characteristics of the material and corroborating the results obtained from the fluorescence spectra.

The ECL emission mechanism of the PCN-224/ $K_2S_2O_8$ system was investigated by comparing the ECL emission spectrum of PCN-224 with its photoluminescence (PL) spectrum (Fig. 5F). The ECL signal of PCN-224 originates from surface-state-

dominated electronic transitions involving a diversity of surface states. The PL spectrum displays an emission peak at 675 nm, a feature corresponding to electron-hole recombination at specific surface energy levels upon photoexcitation. In contrast, the ECL spectrum exhibits an intense and broad emission band centered at 683 nm. Notably, the minimal Stokes shift of only 8 nm between the PL and ECL maxima suggests that the energy levels involved in the ECL transition are highly correlated with those governing the PL emission.

Validation of the ECL-RET Mechanism. The potential ECL-RET mechanism was first investigated by analyzing the UV-vis absorption and ECL emission spectra (Fig. 5G). A significant spectral overlap was observed between the ECL emission spectrum of PCN-224 and the UV-vis absorption spectrum of $\text{CeO}_2\text{@PDA}$. This overlap indicates that the energy of ECL photons generated by PCN-224 under electrical excitation can be efficiently absorbed by $\text{CeO}_2\text{@PDA}$. This finding suggests the existence of an ECL-RET process, wherein PCN-224 acts as the energy donor, transferring energy to $\text{CeO}_2\text{@PDA}$ (the acceptor) upon electrical excitation, leading to energy absorption by the latter. This relationship satisfies a core requirement for ECL-RET: the overlap between the emission spectrum donor and the absorption spectrum of acceptor.

The feasibility of this ECL-RET mechanism was further verified from an energy level perspective (Fig. 5G). The energy levels of the HOMO and LUMO for PCN-224 were measured at -5.17 eV and -2.62 eV, respectively. For $\text{CeO}_2\text{@PDA}$, the corresponding HOMO and LUMO levels were -5.52 eV and -3.20 eV, respectively[38]. The energy level difference between the donor and acceptor satisfies the

thermodynamic threshold required for energy transfer in an ECL-RET process. This alignment enables the transfer of energy from the excited donor (PCN-224) to the acceptor (CeO₂@PDA) during the donor's return to the ground state, providing further confirmation for the rationality of this energy transfer pathway.

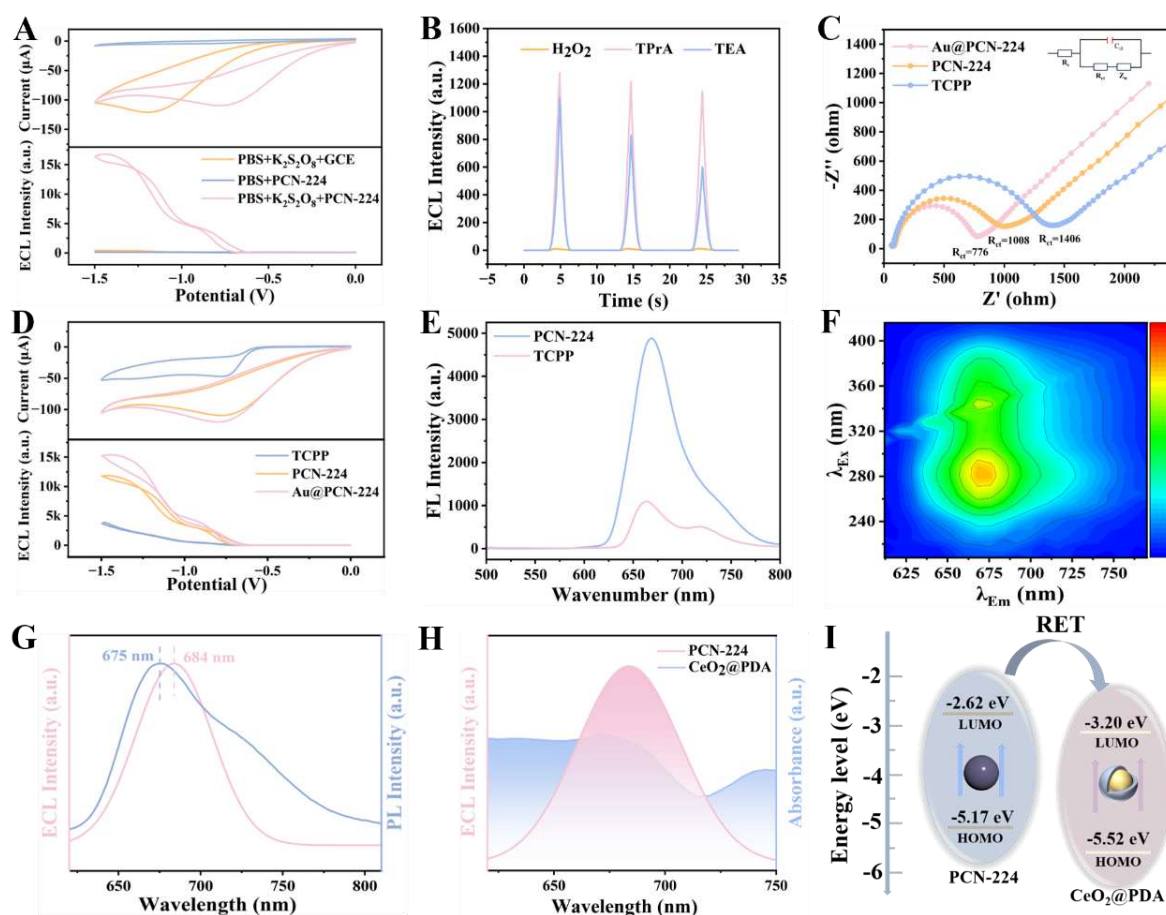
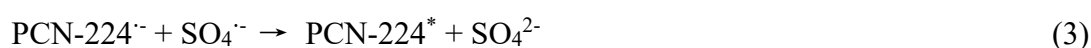


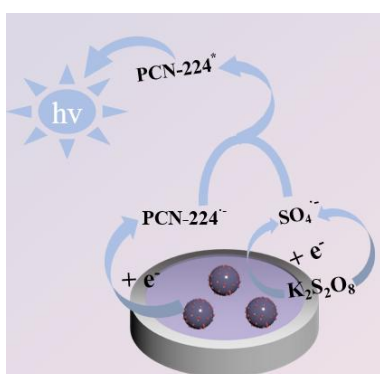
Fig. 5. (A) CV curves and ECL intensity of PCN-224/GCE in PBS solution with 80mM K₂S₂O₈ and PCN-224 in PBS solution without 80mM K₂S₂O₈, (B) ECL signals corresponding to the coreactants H₂O₂, TPrA, and TEA, (C) EIS curves of TCPP, PCN-224 and Au@PCN-224, (D) CV and ECL-potential curves of TCPP, PCN-224, Au@PCN-224, (E) Fluorescence emission spectra of TCPP and PCN-224, (F) 3D fluorescence contour plot of PCN-224, (G) ECL emission spectrum (pink line) and PL

spectrum of (blue line) PCN-224, (H) UV-vis spectrum of Ce₂O@PDA and ECL spectrum of PCN-224, and (I) Energy level structure diagrams of PCN-224 and Ce₂O@PDA.

Based on the aforementioned findings, we propose a plausible ECL mechanism for PCN-224 as follows (Scheme 2). When a potential ranging from -1.5 to 0 V is applied, PCN-224 undergoes reduction to form the radical anion PCN-224^{•-} (Equation 1). Concurrently, the coreactant K₂S₂O₈ is also reduced, forming the strongly oxidizing intermediate SO₄^{•-} (Equation 2). Subsequently, an electron transfer reaction occurs between SO₄^{•-} and PCN-224^{•-}, drives the formation of the excited state PCN-224* (Equation 3). The radiative transition of this excited state back to the ground state then produces the observed ECL emission (Equation 4).



Scheme 2. Signal Enhancement Mechanism.



Analytical Performance of the ECL Immunosensor for AFP Detection. Under the experimental conditions after optimization, the ECL signal intensity showed a gradual decrease with increasing AFP concentration (Fig. 6A). Analysis of the sensor's quantitative detection capability revealed an excellent linear correlation between the ECL intensity and the logarithm of AFP concentration ($\log C_{\text{AFP}}$) (Fig. 6B). The linear regression equation was determined as $y = -1047.1 \log C_{\text{AFP}} + 6326.3$, with a coefficient of determination (R^2) of 0.998, indicating high fitting precision. The sensor achieved an ultra-low detection limit (LOD) of $27.22 \text{ fg} \cdot \text{mL}^{-1}$, demonstrating its high sensitivity. To define the applicable detection range, repeated assays were conducted across an AFP concentration range from 1×10^{-4} to $200 \text{ ng} \cdot \text{mL}^{-1}$. The results further confirmed the signal stability of the sensor over this wide concentration gradient (Fig. 6C), which enables it to meet the requirements for detecting both low- and high-abundance AFP levels.

The practical applicability of a biosensor hinges on its stability, selectivity, and reproducibility, which were systematically verified through targeted experiments. Specifically, to evaluate detection repeatability, the sensor underwent 16 consecutive scanning cycles at three representative AFP concentrations (0.01 , 1 , and $100 \text{ ng} \cdot \text{mL}^{-1}$). The corresponding ECL signals exhibited relative standard deviations (RSD) all below 5% (Fig. 6D), confirming excellent operational stability. Selectivity, a key indicator reflecting the sensor's anti-interference capability in complex serum matrices, was evaluated by testing against typical interfering substances. These included endogenous compounds (human serum albumin (HSA), immunoglobulin G (IgG), triglycerides

(TG), glucose, urea, and inorganic ions) and exogenous substances (ethylenediaminetetraacetic acid (EDTA) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$)). Benefiting from the high antigen-antibody specificity between AFP and its corresponding antibody, none of these interferents induced a significant reduction in the ECL signal, demonstrating superior anti-interference performance. Reproducibility is crucial for ensuring the reliability of detection results. When ECL signals were measured in parallel at AFP concentrations of 0.01, 1, and 100 $\text{ng}\cdot\text{mL}^{-1}$. Statistical analysis revealed no significant differences among the signal values within each concentration group, which further verifies the excellent reproducibility of the sensor. In summary, the constructed ECL immunosensor integrates high sensitivity, a broad linear detection range, and excellent performance in stability, selectivity, and reproducibility. This combination of advantages enables it to provide a reliable technological solution for the accurate clinical detection of AFP.

Furthermore, a comprehensive survey of various technologies recently developed for AFP detection was conducted, detailing the detection ranges and limits of different methods (Table 1). Comparative analysis results highlight that the proposed ECL immunosensor not only exhibits a wider detection range but also achieves a lower LOD compared with most reported approaches, further confirming its competitive edge in clinical AFP detection.

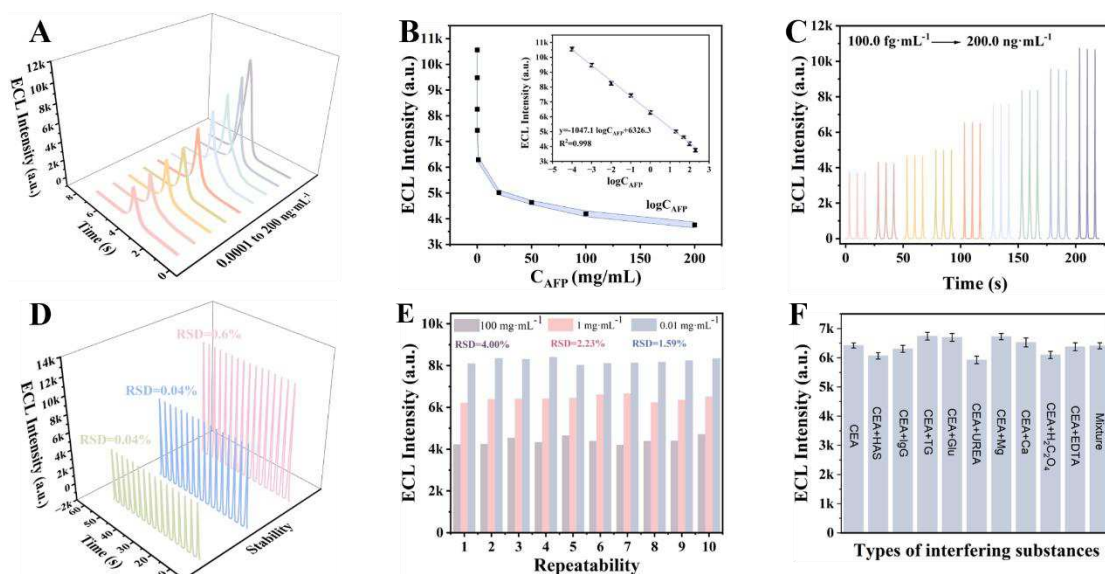


Fig. 6. (A) ECL signals at different AFP concentration , (B) Linear relationship between ECL response and log C_{AFP}, (C) AFP-dependent ECL response of the biosensor, (D) Stability of ECL immunosensors, (E) Selectivity of ECL immunosensors, and (F) Repeatability of ECL immunosensors.

Table 1. Comparison of different methods for detection of AFP.

Detecting Method	Linear (ng • mL ⁻¹)	LOD (fg • mL ⁻¹)	Reference
Fluorescence	0.5-45	400	[39]
Fluorescence	0.01-10	3000	[40]
SERS	0.0038-100	400	[41]
Colormetry	5-200	1900	[42]
EC	0.0001-0.105	33	[43]
EC	0.01-100	4270	[44]
ECL	0.001-100	30	[45]
ECL	0.0005-10	40	[46]
ECL	0.0001-200	27.22	This work

CONCLUSIONS

In the present study, PCN-224 was synthesized via a facile hydrothermal method. The results demonstrate that its framework significantly enhances the charge transfer capability of TCPP, leading to markedly improved ECL performance. Furthermore, the porous structure of PCN-224 provides efficient diffusion channels for the coreactant, thereby increasing the ECL efficiency during the electrochemical excitation process. Due to the broad absorption of CeO₂@PDA in the visible to near-infrared region, which effectively overlaps with the ECL emission spectrum of PCN-224, an efficient ECL-

515 RET process between the donor and acceptor was triggered. Based on this mechanism,
516 a signal-off ECL immunosensor was developed for the sensitive determination of AFP.
517 The fabricated sensor exhibited excellent stability, high specificity, and outstanding
518 reproducibility, demonstrating its potential for reliable bioanalysis.

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