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Organic–inorganic hybrid phosphite-participating S-shaped penta-Ce^{III}-incorporated tellurotungstate as an electrochemical enzymatic hydrogen peroxide sensor for β-D-glucose detection†

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Polyoxometalate chemistry has made rapid advances in innovative structural chemistry. The lower valence state and lone electron pair effect of the subgroup-valence heteroatom Te(IV) can be introduced into tungsten–oxygen systems to construct complicated tellurotungstate (TT) aggregates. Thus, for the first time, we synthesized a phosphite-participating S-shaped penta-Ce^{III}-incorporated tetrameric TT aggregate, Na₄K₃H₆[Ce₅W₄(Hpica)₆H₂P₂O₁₂(H₂O)₄]{[B-β-TeW₇O₂₈]₂[B-β-TeW₈O₃₀]₂·94H₂O (**1**) (Hpica = 2-picolinic acid). The molecular structure of **1** consists of one tetrameric [Ce₅W₄(Hpica)₆H₂P₂O₁₂(H₂O)₄]{[B-β-TeW₇O₂₈]₂[B-β-TeW₈O₃₀]₂}¹³⁻ (**1a**) hybrid polyanion constructed from two symmetrical sandwich-like {[Ce₂W₂(Hpica)₃HP^{III}O₆(H₂O)₂][B-β-TeW₇O₂₈][B-β-TeW₈O₃₀]}⁸⁻ ((Ce₂W₂P^{III}Te₂)) moieties linked by a Ce³⁺ cation. Interestingly, the sandwich-like {Ce₂W₂P^{III}Te₂} moiety can be viewed as a heterometal cluster [Ce₂W₂(Hpica)₃HP^{III}O₆(H₂O)₂]¹⁰⁺ {Ce₂W₂P^{III}} group integrating a tetravacant [B-β-TeW₈O₃₀]⁸⁻ fragment and a pentavacant [B-β-TeW₇O₂₈]¹⁰⁻ fragment. Furthermore, **1** was converted into **nano-1** with the help of ultrasonication in organic solution. **Nano-1** was then complexed with NH₂-graphene (NH₂-G), and a bi-component **nano-1/NH₂-G** nanocomposite was prepared. Without further assembly and modification, the as-prepared **nano-1/NH₂-G** nanocomposite was first used as a sensor to detect hydrogen peroxide. This **nano-1/NH₂-G**-based H₂O₂ sensor shows excellent reproducibility, stability, and anti-interference ability. In quick succession, with the assistance of glucose oxidase, an electrochemical enzymatic method based on the **nano-1/NH₂-G**-based H₂O₂ sensor was developed and further applied for the specific detection of β-D-glucose. This enzymatic sensor also displays good detection performance. The present work provides new insight into electrochemical sensors based on the **nano-1/NH₂-G** nanocomposite and their potential application in enzymatic glucose sensing.

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Introduction

The development of synthetic strategies has promoted important advances in the design of complex cluster architectures such as polyoxometalates (POMs).^{1–8} These metal–oxygen clusters with unmatched physical and chemical properties not only represent a tremendous range of crystalline inorganic clusters but also have been employed as fundamental building

blocks to construct novel gigantic cluster-based functional materials with special electronic characteristics,^{9–12} nano-sized structures,^{13–16} and unique photoelectric or magnetic properties.^{17–21}

In the realm of POMs, heteropolyoxotungstates (HPOTs) are of great importance due to their high structural stability, diverse vacant building blocks and multiple application potentials, and have been extensively used and systematically explored for novel structural design purposes and application considerations.^{22–25} Due to the lower valence state and lone electron pair effect of the subgroup-valence heteroatom Te(IV) with a triangular pyramidal coordination configuration, it has come to be considered an important member to generate lacunary HPOTs, known as tellurotungstates (TTs), which can be further employed to capture lanthanide (Ln) ions to fabricate high-nuclearity Ln-incorporated TTs (HNLITTs). The introduction of the Te(IV) heteroatom can enhance the feasibility of

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†Electronic supplementary information (ESI) available: Experimental details, PXRD, IR, TG curves, related structure and property figures and tables. Crystallographic information for **1**. CCDC 2163291 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2qi00816e>

obtaining excellent HNLITTs with amazing structural features. For instance, an outstanding octameric HNLITT $[(\text{TeO}_3)_8\{\text{Ce}_8(\text{H}_2\text{O})_{20}\}(\text{WO}_2)_4(\text{W}_4\text{O}_{12})]^{48-}$ (Fig. S1a[†]) was obtained through a versatile one-step approach by Su's group,²⁶ which was constructed by eight $\{(\text{TeO}_3)_8\text{W}_9\text{Ce}\}$ segments and other bridging $\{\text{WO}_6\}$ groups. Later, they also reported a larger HNLITT, $[\text{Ce}_{10}\text{Te}_8\text{W}_{88}\text{O}_{298}(\text{OH})_{12}(\text{H}_2\text{O})_{40}]^{18-}$ (Fig. S1b[†]), which is different from the former and consists of two triangle $\{\text{W}_2\text{O}_5\text{Ce}(\text{H}_2\text{O})_7\}$ linking units and two $[\text{Te}_4\text{W}_{42}\text{O}_{144}(\text{OH})_6\text{Ce}_4(\text{H}_2\text{O})_{13}]^{14-}$ fragments.²⁷ Three years later, Hu *et al.* reported a tetrameric HNLITT, $[(\text{Ln}(\text{H}_2\text{O})_5(\text{TeW}_{18}\text{O}_{64}))_4]^{44-}$ (Ln = Eu^{3+} , Gd^{3+}) (Fig. S1c[†]), as the first HNLITT containing four Dawson-type building blocks.²⁸ Importantly, TT segments can also function as good inorganic mono- or polydentate ligands to combine with Ln cations in the participation of N/O-included organic components to construct organic-inorganic hybrid HNLITTs (OIHHNLITTs). At present, OIHHNLITTs, as an important branch of HNLITTs, are gradually becoming a research hotspot due to their diverse components, eye-catching topologies and broad application prospects. For example, in 2017, a series of Hpica-decorated tetrameric OIHHNLITTs, $[\text{Ln}_2(\text{H}_2\text{O})_4(\text{pica})_2\text{W}_2\text{O}_5][(\text{Ln}(\text{H}_2\text{O})\text{W}_2(\text{Hpica})_2\text{O}_4)(\text{B}-\beta\text{-TeW}_8\text{O}_{30}\text{H}_2)_2]^{24-}$ (Ln = La^{3+} , Ce^{3+} , Nd^{3+} , Sm^{3+} , and Eu^{3+}) (Fig. S1d[†]), was isolated by our group,²⁹ which is made up of two Ln-W-heterometal sandwiched $[(\text{Ln}(\text{H}_2\text{O})\text{W}_2(\text{Hpica})_2\text{O}_4)(\text{B}-\beta\text{-TeW}_8\text{O}_{30}\text{H}_2)_2]^{5-}$ moieties linked *via* one $\{\text{Ln}_2(\text{H}_2\text{O})_4(\text{pica})_2\text{W}_2\text{O}_5\}^{6+}$ cluster. Later, the introduction of the flexible ligand gluconic acid into the system led to the formation of a multi-D-gluconic-acid-bridging OIHHNLITT $[\text{Eu}_4(\text{H}_2\text{O})_4\text{W}_6(\text{H}_2\text{glu})_4\text{O}_{12}(\text{B}-\alpha\text{-TeW}_9\text{O}_{33})_4]^{24-}$ (Fig. S1e[†]), which is the first polyhydroxycarboxylic-bridging HNLITT.³⁰ This tetrameric polyanion can be viewed as the aggregation of an innovative $[\text{Eu}_4(\text{H}_2\text{O})_4\text{W}_6(\text{H}_2\text{glu})_4\text{O}_{12}]^{8+}$ core and four $[\text{B}-\alpha\text{-TeW}_9\text{O}_{33}]^{8-}$ fragments. These studies open the door to the design of new-type OIHHNLITTs with amazing structure features. However, all the above-mentioned OIHHNLITTs are almost totally made up of the trivacant $[\text{TeW}_9\text{O}_{33}]^{8-}$ building blocks, limiting structural innovation and breakthrough in the design of novel structures.

To further break the bottleneck in the development of the above-mentioned OIHHNLITTs, another phosphite $[\text{HPO}_3]^{2-}$ anion was chosen to introduce in the reaction system. Because the phosphite anion is composed of one H and three O atoms, it presents an approximate tetrahedral geometry. Although coexisting triangular pyramidal TeO_3^{2-} and tetrahedral HPO_3^{2-} groups in the reaction system may be competitive, they also open up more possibilities for reactions and construction of structures. If the tetrahedral $[\text{HPO}_3]^{2-}$ anion can be incorporated into OIHHNLITTs, it will be conducive to introduce more Ln ions in these structures, which greatly enriches the types of OIHHNLITT structures and promotes the innovation and sustainable development of HPOTs. Based on these ideas, an Hpica-functionalized phosphite-participating S-shaped HNLITT, $\text{Na}_4\text{K}_3\text{H}_6[\text{Ce}_5\text{W}_4(\text{Hpica})_6\text{H}_2\text{P}_2\text{O}_{12}(\text{H}_2\text{O})_4]\{[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]_2[\text{B}-\beta\text{-TeW}_8\text{O}_{30}]_2\}\cdot 94\text{H}_2\text{O}$ (**1**), was synthesized. It is noteworthy that the $[\text{HPO}_3]^{2-}$ anionic units in this structure act as brid-

ging functional groups, connecting two Ce^{3+} cations and two pentavacant $[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]^{10-}$ segments. Furthermore, **1** was further prepared as **nano-1** with the aid of ultrasonication in organic solution. Moreover, **nano-1** was further modified with NH_2 -graphene (**NH₂-G**), resulting in the formation of a bi-component **nano-1/NH₂-G** nano-composite. Subsequently, the as-prepared **nano-1/NH₂-G** nano-composite was used as a sensor for the detection of hydrogen peroxide. Furthermore, with the assistance of glucose oxidase (GOD), an electrochemical enzymatic sensor was created based on the **nano-1/NH₂-G**-based H_2O_2 sensor for the specific detection of β -D-glucose in NaH_2PO_4 - Na_2HPO_4 phosphate buffer (pH = 6.5). The present work provides new insight into electrochemical sensors based on the **nano-1/NH₂-G** nanocomposite and their potential application in enzymatic GOD sensing.

Results and discussion

Synthesis of **1**

$\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (3.402 g, 10.314 mmol), dimethylamine hydrochloride (0.701 g, 8.601 mmol), K_2TeO_3 (0.130 g, 0.512 mmol) and H_3PO_3 (5.000 mL, 0.01 g mL^{-1}) were dissolved in distilled water (20 mL). The pH value was adjusted to 5 using 6 M HCl. The solution was heated to 60 °C for 30 min. $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.402 g, 0.923 mmol) and Hpica (0.201 g, 1.203 mmol) were consecutively added to the solution and the final pH of the solution was kept at 5 using 4.0 M NaOH. The solution was heated at 90 °C for 2 h, cooled and filtered. Slow evaporation led to yellow block crystals after about one week. Yield: 11.8% (based on K_2TeO_3). Elemental analysis (calcd %): C, 3.68 (3.52); H, 1.68 (1.92); N, 0.65 (0.68); P, 0.47 (0.50); Na, 0.66 (0.75); K, 0.86 (0.95); Ce, 6.0 (5.70); Te, 4.26 (4.15); W, 51.20 (50.85). In the synthetic process, the effects of the amount (0.691, 0.923, 1.152, and 1.382 mmol) of $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and pH value (2.00, 3.00, 4.00, 5.00, and 6.00) on the crystal growth were explored. Firstly, with an increase in the $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ dosage from 0.691 mmol to 0.923 mmol, the growth rate of the crystals was accelerated, but an amorphous precipitate was formed when the $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ dosage was greater than 0.923 mmol. The best-quality crystals were obtained when the $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ dosage was 0.923 mmol. Moreover, when the pH was 2 or 6, an amorphous precipitate was produced. **1** was isolated in the pH range of 3–5. However, when the pH was 3 or 4, crystals of **1** were formed, accompanied by some precipitate. When the pH was 5, only crystals of **1** were obtained and no precipitate was observed. Therefore, the optimum pH is 5 for crystal growth of **1**.

Structural description

1 belongs to the monoclinic space group $C2/c$ (Table S1[†]), where the results were also certified by IR spectroscopy (Fig. S2[†]) and PXRD (Fig. S3[†]). Its structure consists of a novel $[\text{Ce}_5\text{W}_4(\text{Hpica})_6\text{H}_2\text{P}_2\text{O}_{12}(\text{H}_2\text{O})_4]\{[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]_2[\text{B}-\beta\text{-TeW}_8\text{O}_{30}]_2\}^{13-}$ (**1a**) hybrid polyanion (Fig. 1a), four Na^+ , three K^+ , six H^+ and eighteen crystal water molecules. The S-shaped **1a** anion can

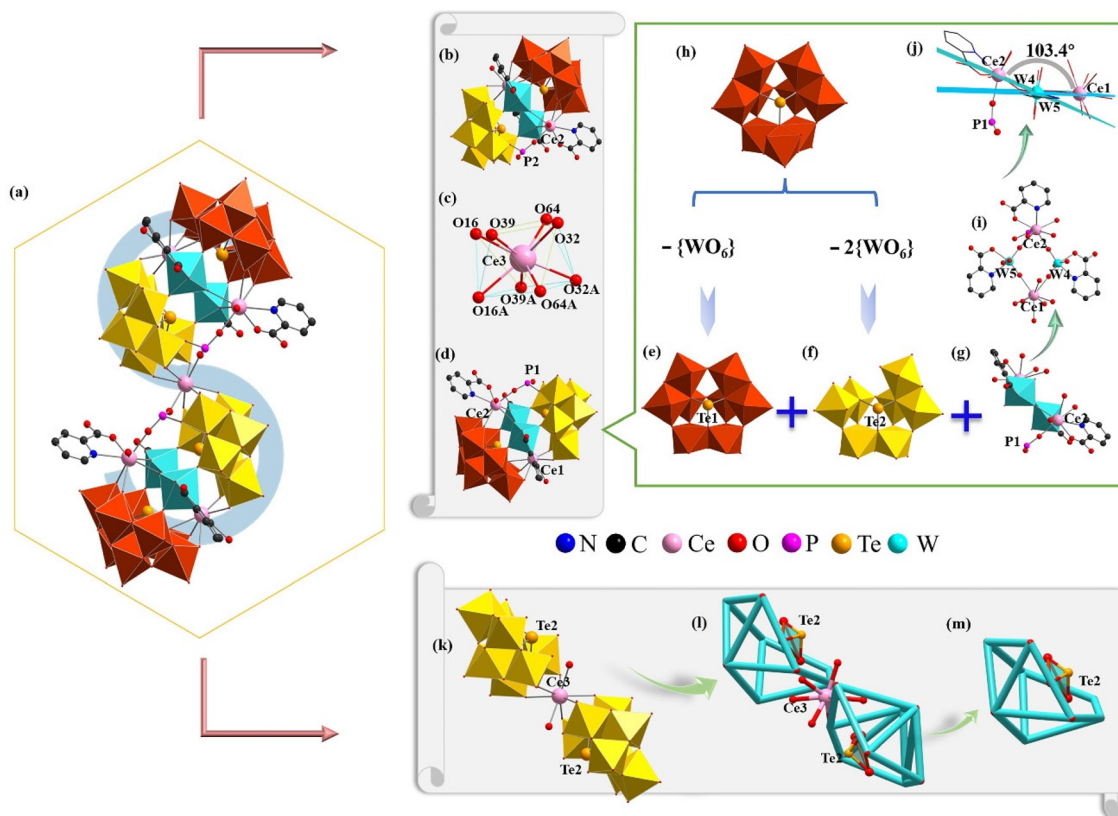


Fig. 1 (a) S-shaped **1a** anion. (b and d) Sandwich-like $\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\text{Te}_2\}$ moiety. (c) Coordination environment of $\text{Ce}3^{3+}$. (e) Tetravalent $[\text{B}-\beta\text{-TeW}_8\text{O}_{30}]^{8-}$ subunit. (f) Pentavalent $[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]^{10-}$ subunit. (g) The $\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\}$ cluster. (h) Trivalent $[\text{B}-\beta\text{-TeW}_9\text{O}_{33}]^{8-}$ fragment. (i) Twisted parallelogram formed by Ce1, Ce2, W4 and W5 atoms. (j) The surface defined by W4, W5, $\text{Ce}1^{3+}$ and $\text{Ce}2^{3+}$ atoms. (k) The 1:2 type $\{\text{Ce}_3[\text{B}-\beta\text{-Te}_2\text{W}_7\text{O}_{28}]_2\}^{17-}$ fragment. (l) Simplified view of the 1:2 type $\{\text{Ce}_3[\text{B}-\beta\text{-Te}_2\text{W}_7\text{O}_{28}]_2\}^{17-}$ fragment. (m) Simplified view of the pentavalent $[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]^{10-}$ subunit. Color code: W, turquoise; Te, light orange; O, red; P, pink; Ce, rose; C, black; N, blue; $\{\text{TeW}_8\}$, brick red; $\{\text{TeW}_7\}$, gold.

be further viewed as two sandwich-like $\{[\text{Ce}_2\text{W}_2(\text{Hpica})_3\text{HP}^{\text{III}}\text{O}_6(\text{H}_2\text{O})_2][\text{B}-\beta\text{-TeW}_7\text{O}_{28}][\text{B}-\beta\text{-TeW}_8\text{O}_{30}]\}^{8-}$ ($\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\text{Te}_2\}$) (Fig. 1b and d) moieties linked by a $\text{Ce}3^{3+}$ cation. The $\text{Ce}3^{3+}$ ion located at the symmetrical center exhibits a twisted square antiprism (Fig. 1c), where four coordination oxygen atoms (O16, O32, O39, and O64) on the same plane come from the $[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]^{10-}$ subunit [Ce3–O16: 2.500 Å, Ce3–O32: 2.447 Å, Ce3–O39: 2.480 Å and Ce3–O64: 2.415 Å]. Furthermore, the sandwich-like $\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\text{Te}_2\}$ moiety could be deemed as one tetralacunary $[\text{B}-\beta\text{-Te}_1\text{W}_8\text{O}_{30}]^{8-}$ (Fig. 1e) subunit and a pentalacunary $[\text{B}-\beta\text{-Te}_2\text{W}_7\text{O}_{28}]^{10-}$ (Fig. 1f) subunit connected by a heterometallic $[\text{Ce}_2\text{W}_2(\text{Hpica})_3\text{HP}^{\text{III}}\text{O}_6(\text{H}_2\text{O})_2]^{10+}$ $\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\}$ (Fig. 1g) cluster. The $[\text{B}-\beta\text{-Te}_1\text{W}_8\text{O}_{30}]^{8-}$ (Fig. 1e) subunit stems from the $[\text{B}-\beta\text{-Te}_1\text{W}_9\text{O}_{33}]^{8-}$ fragment (Fig. 1h) by losing a $\{\text{WO}_6\}$ octahedron in the $\{\text{W}_3\text{O}_{13}\}$ trimetallic cluster. Similarly, the $[\text{B}-\beta\text{-Te}_2\text{W}_7\text{O}_{28}]^{10-}$ (Fig. 1f) subunit can be regarded as being obtained by the trivalent $[\text{B}-\beta\text{-Te}_2\text{W}_9\text{O}_{33}]^{8-}$ (Fig. 1h) fragment, losing two $\{\text{WO}_6\}$ octahedra in two different trimetallic clusters, one of which is the rotated 60° trimetallic cluster, resulting from the α configuration to the β configuration, whereas the other is a trimetallic cluster that links to another trimetallic cluster through a corner-sharing motif. In the $\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\}$

cluster, a twisted quadrilateral is formed by Ce1, Ce2, W4 and W5 atoms through four bridging oxygen atoms (Fig. 1i). The dihedral angle between the surface formed by the Ce1, W4, and W5 atoms and the surface defined by the Ce2, W4, and W5 atoms is 103.4° (Fig. 1j). From another point of view, **1a** can be considered as a combination of two $[\text{B}-\beta\text{-Te}_1\text{W}_8\text{O}_{30}]^{8-}$ (Fig. 1e) subunits, two heterometallic $\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\}$ (Fig. 1g) clusters and a 1:2-type $\{\text{Ce}_3[\text{B}-\beta\text{-Te}_2\text{W}_7\text{O}_{28}]_2\}^{17-}$ fragment (Fig. 1k). This 1:2-type $\{\text{Ce}_3[\text{B}-\beta\text{-Te}_2\text{W}_7\text{O}_{28}]_2\}^{17-}$ fragment can be further simplified to the simple snippets (Fig. 1l), and the half of the simple snippet (Fig. 1l) can be seen as a bowl formed by oxygen atoms on the edge of the pentavalent Keggin $[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]^{10-}$ subunit (Fig. 1m). It is worth mentioning that three 2-Hpica ligands adopt two different coordination environments in the $\{\text{Ce}_2\text{W}_2\text{P}^{\text{III}}\}$ cluster (Fig. 2a). However, there is no 2-Hpica ligand in the $\text{Ce}1^{3+}$ cation. The $\text{Ce}1^{3+}$ cation occupies the eight-coordinate distorted square antiprism established by one water ligand (O1W), three O (O11, O17 and O44) atoms from the tetravalent $[\text{B}-\beta\text{-Te}_1\text{W}_8\text{O}_{30}]^{8-}$ segment and two O atoms (O4 and O14) from the pentavalent $[\text{B}-\beta\text{-Te}_2\text{W}_7\text{O}_{28}]^{10-}$ segment, and one μ_2 -O7 atom and one μ_2 -O21 atom (Fig. 2b). The $\text{Ce}2^{3+}$ cation also adopts a distorted square antiprism geometry (Fig. 2c), in

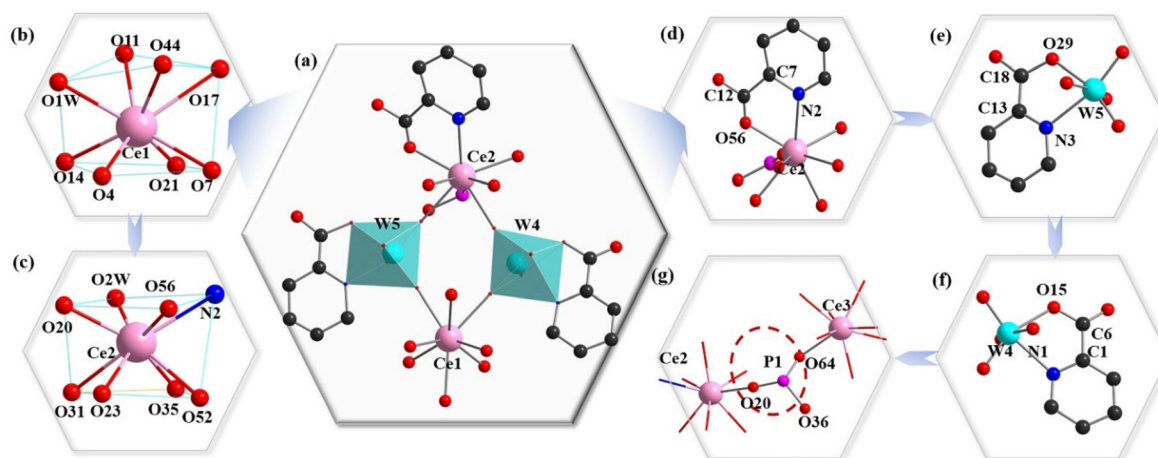


Fig. 2 (a) The $[\text{Ce}_2\text{W}_2(\text{Hpica})_3\text{O}_4(\text{H}_2\text{O})_2]^{10+}$ connectome. (b and c) Square antiprism geometries of Ce^{3+} and Ce^{2+} ions. (d–f) Coordination environments of the Ce^{2+} , W5 and W4 centers, respectively. (g) Connection of the $\{\text{HP}^{\text{III}}\text{O}_3\}$ group and Ce^{2+} and Ce^{3+} ions. Color codes: W, turquoise; Te, light orange; O, red; P, pink; Ce, rose; C, black; N, blue; $\{\text{TeW}_8\}$, brick red; $\{\text{TeW}_7\}$, gold.

which the N2 and O56 atoms are from the same 2-Hpica ligand and μ_2 -O20 is from the $\{\text{HP}^{\text{III}}\text{O}_3\}$ group (Fig. 2d). The remaining coordination atoms are O2 W, μ_2 -O23, μ_2 -O31, O35 and O52, respectively, where the O35 and O52 atoms are from the tetravacant $[\text{B}-\beta\text{-TeW}_8\text{O}_{30}]^{8-}$ subunit. The other two 2-Hpica ligands coordinate with the W4 and W5 atoms *via* a carboxyl oxygen atom and a pyridine nitrogen atom, respectively, producing two five-membered rings, $[\text{W}5\text{-O}29\text{-C}18\text{-C}13\text{-N}3]$ (Fig. 2e) and $[\text{W}4\text{-O}15\text{-C}6\text{-C}1\text{-N}1]$ (Fig. 2f)].

The W4 and W5 atoms display the octahedral configuration (Fig. 2a). This coordination mode and type of 2-Hpica greatly improve the stability of **1a**. It is surprising that the tetrahedral $\{\text{HP}^{\text{III}}\text{O}_3\}$ group (Fig. 2g) (this proton is omitted) links Ce^{2+} , Ce^{3+} and $[\text{B}-\beta\text{-TeW}_7\text{O}_{28}]^{10-}$. The tetrameric **1a** is the first example of a phosphite-participating OIHHNLITT. This type of HNLITT with high-vacancy mixed building TT blocks is very rare in the system of POM structures, which may be related to the higher pH synthetic conditions and offers a new idea for preparing HPOT-based materials in the future.

To maintain charge balance and enhance the structural stability of **1a**, some charge compensation ions (Na^+ and K^+) and lattice water molecules are required, which interact with **1a** through electrostatic and H-bond interactions to give birth to the 3-D supramolecular architecture. To better comprehend the stacking motifs, each **1a** anion is simplified as two diagonally connected triangles along the *a*, *b* and *c* axes (Fig. 3a–h). In the *bc* plane (Fig. 3a–d), the tetrameric **1a** anions present the –ABAB– stacking pattern. To easily observe the stacking pattern of **1a** anions, it was split into layers A (Fig. 3b) and B (Fig. 3c). The simplification of the –ABAB– stacking mode of **1a** anions is further shown in Fig. 4d on the *bc* plane. From the perspective of the *b* axis (Fig. 3e and f), the **1a** anions are distributed in an –AAA– fashion, while the Ce atoms of each **1a** anions are arranged in an Arabic number “8” pattern (Fig. 3f). Additionally, in the *ab* plane (Fig. 3g and h), the **1a** anions present a more complex stacking pattern. Specifically, the **1a**

anions are placed in an –ABAB– pattern along the *a* axis and in the –ABCD– stacking pattern along the *b* axis. However, a special stacking mode is formed among adjacent **1a** anions. Each **1a** anion is surrounded by three polyanions. Through this staggered mode, every six **1a** anions form a lantern-shaped hexagon (Fig. 3h). In addition, it is worth mentioning that **1** shows high stability up to 300 °C in an N_2 atmosphere (Fig. S4[†]), which provides a foundation for its further application and functionalization.

Design strategy and characterization of nano-1 and nano-1/NH₂-G composite

The crystal structure of **nano-1** obtained by ultrasonication is consistent with that of **1**, which can be confirmed by the good agreement of the IR spectra (Fig. S2[†]) and PXRD patterns (Fig. S3[†]) of **1** and **nano-1**. The process for the fabrication of the **nano-1/NH₂-G** composite is schematically represented in Scheme 1a–c. As is known, the introduction of an active substrate possessing a high-specific surface area and electroconductibility is a useful method to promote the electrochemical application of POM-based materials.^{31,32} **NH₂-G** is an ideal conductive substrate due to its low cost, high electrical conductivity, amino-functionalized surface and huge surface area. Also, **NH₂-G** possesses abundant active sites to combine with POMs based on supramolecular interactions and electrostatic attraction. Thus, **NH₂-G** acts as a conductive substrate. Alternatively, nano-POMs can work as functional precursors to produce composite materials owing to the exposure of the abundant active sites of nanosized POMs with stable morphologies.^{33,34} Here, **nano-1** was utilized as a precursor to composite with **NH₂-G** to prepare the **nano-1/NH₂-G** composite. The above-mentioned preparation strategy has the advantages of **NH₂-G** and nano-POMs, compensating for the disadvantage of the single species and adapting to the requirements of electrochemical sensors. Considering the superior properties and prospective potential of nanosized POMs,

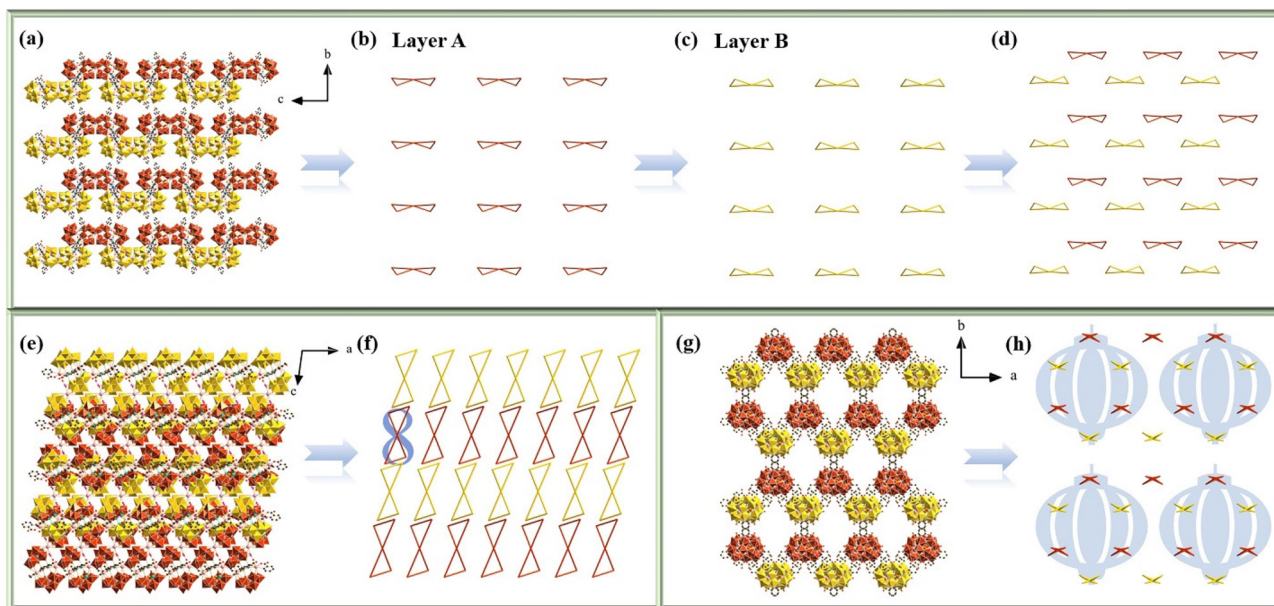


Fig. 3 (a) 3D stacking of **1a** anions in the *bc* plane. (b and c) Simplified layer A and layer B, displaying two spatial orientations of **1a** anions in the *bc* plane. (d) Simplified stacking of **1a** anions in the *bc* plane. (e and f) 3D stacking and simplified stacking of **1a** anions in the *ac* plane. (g and h) 3D stacking and simplified stacking of **1a** anions in the *ab* plane.

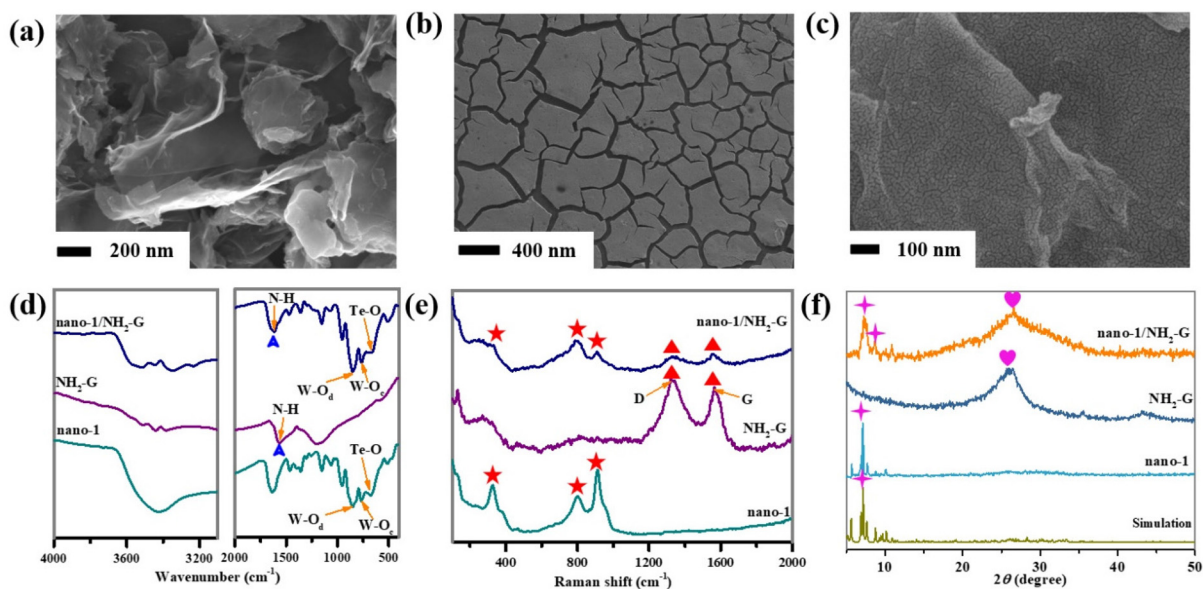
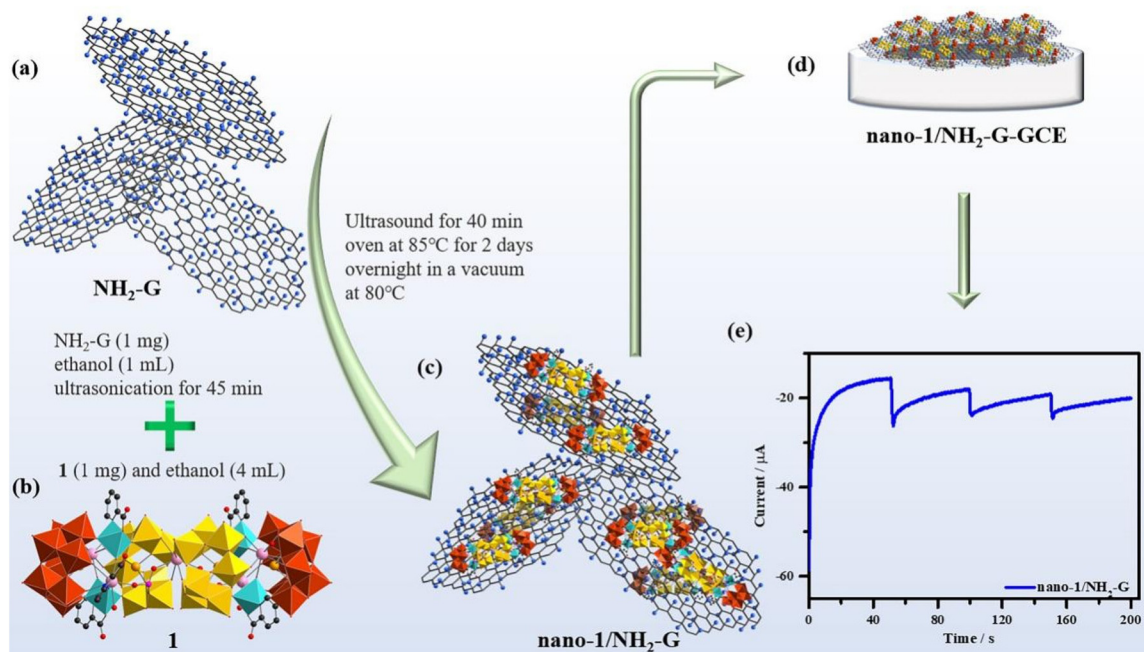


Fig. 4 (a–c) SEM images of **NH₂-G**, **nano-1** and **nano-1/NH₂-G**. (d) IR spectra, (e) Raman spectra and (f) PXRD patterns of simulation of **1**, **nano-1**, **NH₂-G**, and **nano-1/NH₂-G**.

nano-1 was prepared with the help of ultrasonication in EtOH solution. The UV reflection spectrum (Fig. S5†) of **nano-1** was applied to obtain its optical bandgap (2.88 eV) using the Tauc plot method, which proved that it is an optical semiconductor. Specifically, the effective combination of semiconductor **nano-1** and highly electrically conductive **NH₂-G** can facilitate electron transfer and improve the sensing performance of the **nano-1/NH₂-G** composite. To find the optimal proportion of

nano-1/NH₂-G, **nano-1/NH₂-G** composites with proportions of 0.5 : 1, 1 : 1, 1.5 : 1, 2 : 1 and 2.5 : 1 were prepared and their successful preparation was also proved by IR spectra (Fig. S6a†) and PXRD patterns (Fig. S6b†). Through CV measurements (Fig. S7†) of **nano-1/NH₂-G** modified glassy carbon electrodes (GCEs) with different proportions of **nano-1/NH₂-G** in 0.1 M PBS (pH = 6.5) with 6.0 mM H₂O₂, it could be distinctly found that the CV peak current of **nano-1/NH₂-G-GCE** is the strongest



Scheme 1 Schematic preparation process of nano-1/NH₂-G-GCE. (a) Schematic structure of NH₂-G. (b) Crystal structure of 1. (c) Schematic structure of nano-1/NH₂-G. (d) The nano-1/NH₂-G-GCE. (e) Schematic detection curve.

when the proportion of nano-1/NH₂-G is 1 : 1. Therefore, the optimal proportion of nano-1/NH₂-G was determined to be 1 : 1. Furthermore, SEM was used to characterize the morphologies of the as-synthesized materials (NH₂-G : nano-1 = 1 : 1). Fig. 4a illustrates the leaflike nanosheet morphology of NH₂-G with a smooth surface. The morphology of nano-1 shows a cracked film (Fig. 4b), presenting the successful construction of the nano-1 film, which was strongly supported by SEM-EDS elemental mapping analysis (Fig. S8†). The nano-1/NH₂-G nanomorphology is exhibited in Fig. 4c, in which the smooth surface of NH₂-G is fully covered by the cracked film of nano-1, verifying the successfully preparation of the nano-1/NH₂-G composite. It is obvious that the ultrathin nanosheet morphology of NH₂-G was maintained, which acts as the soft highly electrically conducting support of nano-1.

To confirm the structures of all the nanosized samples, the IR spectra, Raman spectra and PXRD patterns of nano-1, NH₂-G and nano-1/NH₂-G were measured. The functional groups of nano-1, NH₂-G and nano-1/NH₂-G were observed in their FT-IR spectra (Fig. 4d). Three groups of characteristic peaks at 852, 759 and 667 cm⁻¹ were observed for nano-1, which correspond to the ν(W-O_d), ν(W-O_c) and ν(Te-O_a) stretching vibrations, respectively. In the spectrum of NH₂-G, the intensity of the signals at 3437 and 1571 cm⁻¹ was greatly reduced. The signal at 1571 cm⁻¹ is attributed to the N-H bond. These observations indicate the successful preparation of nano-1/NH₂-G.³⁵ Furthermore, as revealed in Fig. 4e, the characteristic Raman peaks for nano-1 were observed at 324 (W-O), 793 (Te-O), 920 (W-O) and 966 (P-O) cm⁻¹ (Fig. S9†), whereas the main Raman peaks for NH₂-G were seen at 1328 and 1568 cm⁻¹,

which are consistent with that in the literature.³⁶ For nano-1/NH₂-G, its Raman peaks (330, 791, 915, 1330, and 1563 cm⁻¹) are very similar to that of each of its component. Moreover, the crystalline structures of nano-1, NH₂-G and nano-1/NH₂-G were further characterized by PXRD tests (Fig. 4f). For nano-1, its PXRD peaks match well with its single-crystal XRD mode (Fig. S2†). The PXRD peaks of NH₂-G match that in the literature.³⁶ For nano-1/NH₂-G, its PXRD peaks are made up of that of nano-1 and NH₂-G. In addition, all the samples showed good crystallinity. Meanwhile, the elemental composition of

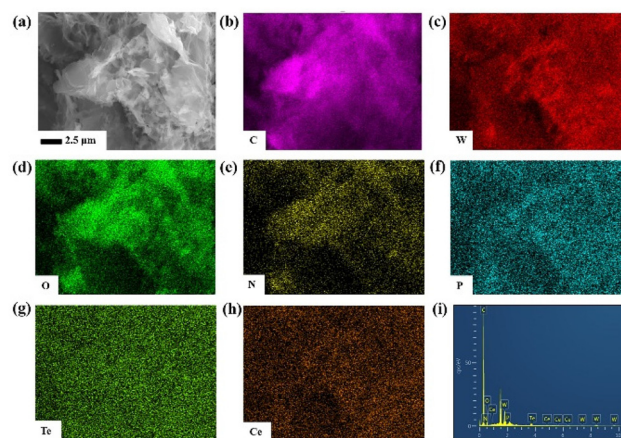


Fig. 5 (a) SEM image of nano-1/NH₂-G at the 2.5 μm scale. (b–h) SEM-EDS C, W, O, N, P, Te and Ce elemental mapping images of nano-1/NH₂-G on a silicon substrate. (i) EDS of nano-1/NH₂-G.

nano-1/NH₂-G was investigated by SEM-EDS mapping measurements. As shown in Fig. 5, the SEM-EDS elemental mapping data of **nano-1/NH₂-G** confirm the existence and a homogeneous distribution of C (Fig. 5b), W (Fig. 5c), O (Fig. 5d), N (Fig. 5e), P (Fig. 5f), Te (Fig. 5g) and Ce (Fig. 5h) elements, further verifying the successful composition of **nano-1** and **NH₂-G**.

Electrochemical properties of the **nano-1/NH₂-G**-based biosensor

H₂O₂ is closely involved in many important physiological and biochemical reactions in organisms.^{37,38} H₂O₂ is produced to mediate a variety of physiological responses, including cell proliferation, differentiation and migration. In addition, H₂O₂ also plays an important role in food processing, disinfection and drug production.^{39,40} In the dairy industry, H₂O₂ is widely used as a preservative to prevent spoilage of dairy products and extend their shelf life.⁴¹ However, excessive H₂O₂ can lead to neurodegenerative diseases, cancer, diabetes and other health problems.^{42,43} Therefore, the accurate measurement of the H₂O₂ concentration is very important. The traditional methods for the determination of H₂O₂ include colorimetry, fluorescence, flow injection and electrochemical luminescence.^{44,45} However, the applications of these methods are limited by their complex and time-consuming procedures and expensive equipment. Hence, the development of economical, efficient and sensitive methods for the detection of H₂O₂ is vital. According to the literature,^{46–48} the electrochemical method has the advantages of quick response, simple operation, high sensitivity and good selectivity.

POMs can be used as an electronic container that can receive or lose one or more electrons.⁴⁹ This, the application of the catalytic activity and biocompatibility of POMs in electrochemical sensing has aroused the interest of researchers. Previously, some investigations on POM-based sensors have been reported for the electrochemical sensing of myricetin,⁵⁰ clenbuterol and ractopamine,⁵¹ cholesterol,⁵² dopamine³⁴ and uric acid.⁵³ At present, in the related research on electrochemical sensors, the introduction of carbon nanomaterials in POM systems endows them with some better electrochemical performances such as improved stability and reproducibility, a wider detection range, lower detection limit and good selectivity.⁵⁴ Among the carbon materials, **NH₂-G** bearing good electroconductibility and biocompatibility can accelerate electron transfer to improve the signal intensity. Also, the positively charged **NH₂-G** can be combined with the negatively charged POMs by electrostatic attractions. Based on these considerations, the **nano-1/NH₂-G** composite was utilized to modify GCE (Scheme 1d and e) for further electrochemically detecting H₂O₂.

Fig. 6a depicts the cyclic voltammetry (CV) curves of GCE (dotted line), **NH₂-G-GCE** (dash line) and **nano-1/NH₂-G-GCE** (solid line) in 0.1 M PBS (pH = 6.5) in the presence (navy blue) or absence (pink) of 6.0 mM H₂O₂ (scan rate 100 mV s⁻¹) in the potential window of -0.5–0.6 V. Apparently, when H₂O₂ was present, only **nano-1/NH₂-G-GCE** showed a dramatic increase in current response at about -0.3 V, which is derived

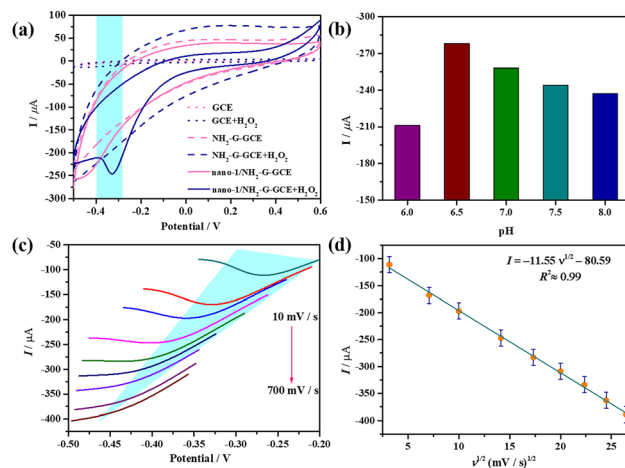


Fig. 6 (a) CV curves of GCE, **NH₂-G-GCE** and **nano-1/NH₂-G-GCE** in 0.1 M PBS (pH = 6.5) with 6.0 mM H₂O₂. (b) Evolution of cathode peak current derived from W centers in **nano-1** with pH for **nano-1/NH₂-G-GCE** in 0.1 M PBS (pH = 6.5) with 6.0 mM H₂O₂. (c) CV curves of **nano-1/NH₂-G-GCE** in 0.1 M PBS (pH = 6.5) with 6.0 mM H₂O₂ at various scan rates. (d) Plot of cathode peak current derived from the W centers in **nano-1** vs. the square root of the scan rate.

from the reduction procedure of tungsten atoms in **nano-1**, indicating the effective electrocatalytic reduction of H₂O₂ by **nano-1/NH₂-G-GCE**. This observation indicates that **nano-1/NH₂-G-GCE** could immensely enhance the electroconductibility and catalytic capability by rapid electron transfer. In contrast, the bare GCE did not display a variation in current intensity in the presence or absence of H₂O₂, demonstrating almost no electrocatalytic reduction activity for H₂O₂.

Afterwards, to explore the optimum H₂O₂ detection conditions, CV measurements of **nano-1/NH₂-G-GCE** under different pH values in 0.1 M PBS with 6.0 mM H₂O₂ (scan rate 100 mV s⁻¹) were performed (Fig. 6b and Fig. S10†). The results indicate that the catalytic activity was affected by pH. The optimal pH was found to be 6.5. In addition, the CV curves of **nano-1/NH₂-G-GCE** under various scan rates were also studied. The influence of scan rate (ν) on the electrocatalytic reduction of H₂O₂ was evaluated in the range of 10–700 mV s⁻¹ (Fig. 6c and Fig. S11†). It is glaringly obvious that the cathode peak current is proportional to the square root of the scan rate, which is fitted using the equation $I = -11.55 (\nu)^{1/2} - 80.59$ ($R^2 = 0.99$) (Fig. 6d). This phenomenon manifests that the electrochemical interface reaction between **nano-1/NH₂-G-GCE** and solution is a diffusion-controlled process.⁵⁵

A suitable working potential is crucial for the electrochemical detection of H₂O₂. This is because a too low working potential will decrease the sensitivity of the sensor to effectively detect H₂O₂. As presented in Fig. 7a, the amperometric response curves (ARCs) were measured under different working potentials in 0.1 M PBS (pH = 6.5) with 6.0 mM H₂O₂, which indicate that the response current gradually decreased when the potential increased in the range of -0.30–0 V. Obviously, the maximum response current appeared at the

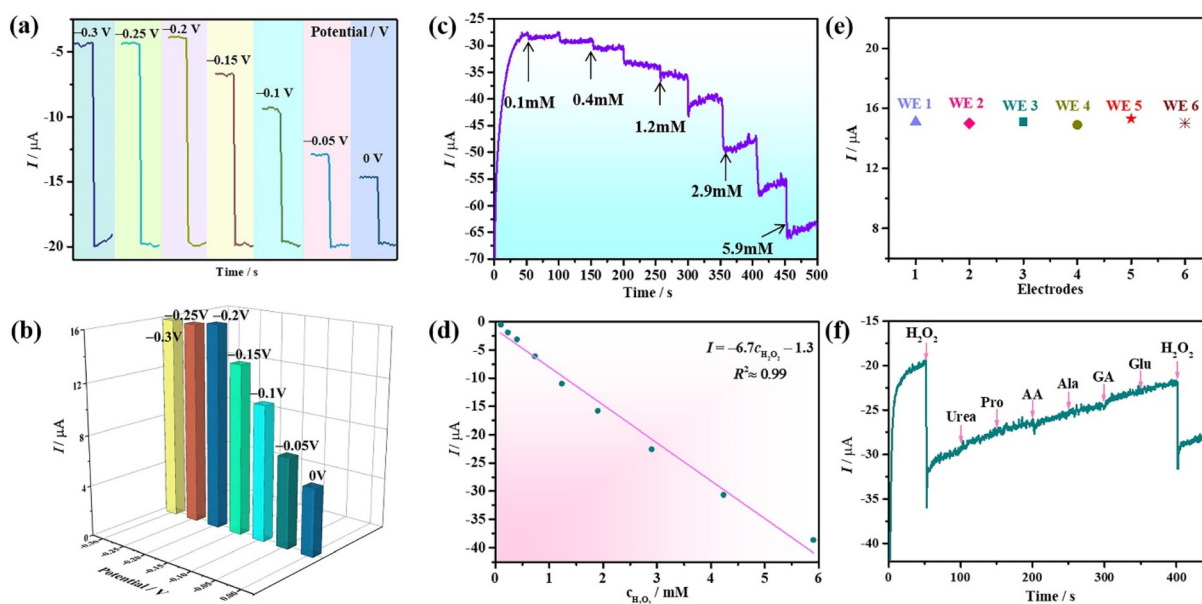


Fig. 7 (a) ARCs of **nano-1/NH₂-G-GCE** under different applied potentials in 0.1 M PBS (pH = 6.5) with 6.0 mM H₂O₂. (b) Comparison of amperometric responses (*I*) at different potentials to obtain the optimal applied potential. (c) ARC of **nano-1/NH₂-G-GCE** with the successive addition of diverse concentrations of H₂O₂ in 0.1 M PBS (pH = 6.5) at -0.20 V. (d) Plot of *I* vs. *c*_{H₂O₂}. (e) Comparison of peak currents of six independent **nano-1/NH₂-G-GCEs** in 0.1 M PBS (pH = 6.5) with 6.0 mM H₂O₂ at -0.20 V. (f) ARC of **nano-1/NH₂-G-GCE** in 0.1 M PBS (pH = 6.5) with the successive addition of 1.0 mM of H₂O₂ and 1.0 mM interferences (urea, Pro, AA, Ala, GA, and glu) in 0.1 M PBS (pH = 6.5) at -0.20 V.

potential of -0.20 V, and consequently -0.20 V was chosen as the best potential for the detection of H₂O₂. Consequently, the potential of -0.20 V was applied for testing the ARCs of **nano-1/NH₂-G-GCE** by successively adding H₂O₂ to 0.1 M PBS (pH = 6.5). To exclude the effect of the baseline current under different applied potentials, the amperometric current response values under different potentials are provided in Fig. 7b, further confirming that the optimal potential is -0.20 V. To quantitatively probe the determination property of **nano-1/NH₂-G-GCE**, the amperometric current response changes were recorded with the continuous addition of different concentrations of H₂O₂ (0.1–5.9 mM) to 0.1 M PBS (pH = 6.5) at -0.2 V (Fig. 7c). A noteworthy variation in the response current was observed after each addition of H₂O₂. When the concentration of H₂O₂ was less than 5.9 mM, **nano-1/NH₂-G-GCE** generated a rapid response signal, revealing that **nano-1/NH₂-G-GCE** has high sensitivity for the detection of H₂O₂ in the range of 0.1–5.9 mM. Fig. 7d reveals the plot of the response current versus H₂O₂ concentration (0.1–5.9 mM), which obeys the function $I = -6.7c_{\text{H}_2\text{O}_2} - 1.3$ with a correlation coefficient of 0.99. The reproducibility of the as-prepared **nano-1/NH₂-G-GCE** as an H₂O₂ sensor was also tested. Herein, six independent **nano-1/NH₂-G-GCEs** were tested in 0.1 M PBS (pH = 6.5) solution with 6.0 mM H₂O₂ at -0.20 V (Fig. 7e). Their relative standard deviation (RSD) was 1.2%, demonstrating the outstanding reproducibility of **nano-1/NH₂-G-GCEs** for the detection of H₂O₂. These results demonstrate that **nano-1/NH₂-G-GCE** is a good electrochemical sensor for the detection of H₂O₂, which may be derived from the synergistic effect of **nano-1** and **NH₂-G**.

Furthermore, antijamming capability, reproducibility and stability are vital parameters affecting the sensing properties. The antijamming capability immediately influences the precision of recognition. Some interferences in the real environment readily generate interference signals in the detection of H₂O₂. Hence, several common interferences such as urea, proline (Pro), ascorbic acid (AA), glucose (Glu), alanine (Ala) and gluconic acid (GA) were selected to evaluate the antijamming capability of **nano-1/NH₂-G-GCE**. Fig. 7f shows ARC of **nano-1/NH₂-G-GCE** after the successive addition of 1.0 mM urea, 1.0 mM Pro, 1.0 mM AA, 1.0 mM Ala, 1.0 mM GA, 1.0 mM Glu, and 1.0 mM H₂O₂ in 0.1 M PBS (pH = 6.5). Obviously, the addition of urea, Pro, AA, Ala, GA, and Glu produced a negligible current response compared to H₂O₂, manifesting the preminent anti-interference ability and selectivity for **nano-1/NH₂-G-GCE** in the detection of H₂O₂. In addition, a time-dependent stability test on **nano-1/NH₂-G-GCE** was also carried out. After one week of storage at 4 °C, the current response of **nano-1/NH₂-G-GCE** still maintained 93% of the initial value (Fig. S12[†]), illustrating its good time-dependent stability.

Electrochemical glucose detection based on **nano-1/NH₂-G-GCE** H₂O₂ biosensor

Although the first enzyme electrode was invented in 1962,⁵⁶ much more endeavours have been dedicated to enhancing blood glucose monitoring techniques in the past five decades. Most commercial glucose monitors utilize the enzyme-based electrochemical method. GOD is a commonly used enzyme, which can specifically catalyze β-D-glucose (β-D-Glu) under

aerobic conditions. The optimum working temperature of GOD is 0–30 °C and the best pH is 5.5–6.5.⁵⁷ The optimum pH of **nano-1/NH₂-G-GCE** in this work is also in this range. Therefore, an enzyme electrochemical glucose sensing system was designed (Fig. 8). 10 mg GOD, 0.1 g β-D-Glu and 10 mg GOD + 0.1 g β-D-Glu were added to 2.0 mL PBS (0.1 M, pH 6.5), respectively, and incubated at 30 °C for 30 min. Then, 100 μL of these solutions were injected into 15.0 mL PBS (0.1 M, pH = 6.5), respectively, and their current response measured. As illustrated in Fig. 8, the **nano-1/NH₂-G-GCE** biosensor showed little or no significant amperometric current response for only the presence of GOD or β-D-Glu in 0.1 M PBS (pH = 6.5) at –0.2 V. In contrast, the GOD + β-D-Glu system for the **nano-1/NH₂-G-GCE** biosensor exhibited a significant amperometric current response. The enzyme-catalysed reaction is as follows:



Thus, with the help of GOD, β-D-Glu can be detected by detecting H₂O₂ using our **nano-1/NH₂-G-GCE** biosensor.⁵⁸ To explore the effect of heating time of β-D-Glu and GOD on the current response, we chose four time points to perform the experiments. As shown in Fig. 9, the heating time was the best at 30 min. After 30 min, the current response decreased slightly with an increase in time. This may be due to the decomposition of trace H₂O₂. Therefore, we chose the current response value to calculate the concentration of H₂O₂ produced by the reaction at a heating time of 30 min. Using the measured current response value in the above-mentioned equation $I = -6.7c_{\text{H}_2\text{O}_2} - 1.3$ led to the concentration of produced H₂O₂ being 250.74 mM in the reaction system consisting of 10 mg GOD and 0.1 g β-D-Glu. This result reveals that 250.74 mM β-D-Glu was detected, while the actual added β-D-Glu concentration was 277.7 mM, and thus the relative error was 9.7%. Therefore, this electrochemical enzymatic method can effectively detect β-D-Glu.

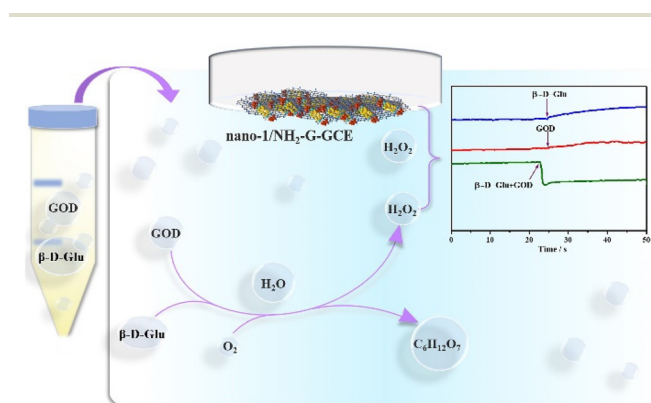


Fig. 8 Schematic enzyme electrochemical glucose sensing system and ARCs of the **nano-1/NH₂-G-GCE** sensor with the addition of β-D-Glu, GOD and β-D-Glu + GOD in 0.1 M PBS (pH = 6.5) at –0.20 V.

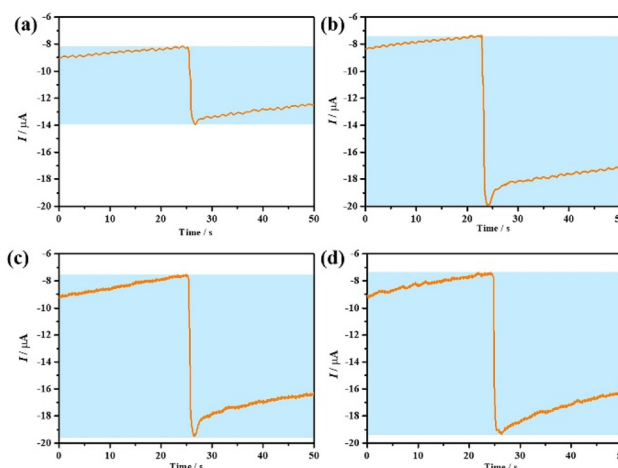


Fig. 9 (a–d) ARCs of **nano-1/NH₂-G-GCE** towards a β-D-Glu + GOD solution at heating times of 0, 30, 60 and 90 min, respectively. The tests were carried out in 0.1 M PBS (pH = 6.5) at –0.20 V.

Conclusions

In conclusion, the introduction of the tetrahedral [HPO₃]²⁻ anion in the OIHHLITT system led to the formation of the fascinating Hpica-functionalized phosphite-participating S-shaped HNLITT **1**. This result indicates that the [HPO₃]²⁻ anion can be used as an anion template to tune the structural assembly of HNLITTs, demonstrating a feasible synthetic route to generate new HPOTs with different types of heteroatoms. In addition, the **nano-1/NH₂-G** composite was successfully prepared using a simple method, which then was used to develop an electrochemical sensor platform for the detection of H₂O₂ and β-D-Glu, respectively. The electrochemical studies showed that this HNLITT may be a good candidate for developing promising electrochemical sensing applications.

Author contributions

Nizi Song and Yanzhou Li performed syntheses, characterization, electrochemical properties and wrote the manuscript. Yanying Wang, Menglu Wang participated in PXRD, IR and TG characterization. Lijuan Chen and Junwei Zhao provided research ideas, determined crystal structures and revised all over the manuscript.

Conflicts of interest

There are no conflicts to declare.

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