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Facile preparation of urchin-like NiCo₂O₄ microspheres for efficient hydrogen peroxide detection†

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In this work, urchin-like NiCo₂O₄ microspheres were prepared *via* a facile ionic liquid-assisted hydrothermal synthesis and used as non-enzymatic H₂O₂ sensors for the first time. The porous structure and high surface area of the NiCo₂O₄ microspheres provide plentiful active sites for electrocatalytic H₂O₂ oxidation. When adapted into an electrochemical sensor for H₂O₂, the microsensors showed fast response of 4 s, a high sensitivity of 392.5 μA·mM⁻¹ cm⁻², and a wide linear range towards H₂O₂ (0–14 mM). The detection limit was as low as 0.05 μM, significantly lower than other published high performance NiCo₂O₄-based H₂O₂ sensors. Furthermore, this non-enzymatic sensor exhibits good selectivity for H₂O₂. These results suggest that NiCo₂O₄ microspheres could be a promising material for trace H₂O₂ detection.

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Introduction

H₂O₂ as a strong oxidant, has been widely used in the chemical industry, medical diagnosis, food safety and environmental analysis fields.^{1–3} H₂O₂ also plays an important role in living organisms as a reactive oxygen species by driving oxidative biochemical processes and maintaining physiological redox homeostasis.⁴ Excessive accumulation of H₂O₂ can cause many diseases, such as Alzheimer's disease, cardiovascular disorders, cancer, and Parkinson's.^{5–8} Therefore, the development of H₂O₂ detection technologies is critical for disease-related diagnostics.

At present, H₂O₂ is typically detected using techniques such as fluorescence assays, chemiluminescence, and electrochemical method.^{9–11} Among them, electrochemical method is considered one of the most promising method due to its low cost, fast response time, and high sensitivity.¹² Electrochemical sensors generally utilize enzymatic or non-enzymatic electrochemical materials for H₂O₂ detection.^{13,14} Despite their high sensitivity and selectivity, enzymatic sensors can be expensive, sensitive to the surrounding environment (pH or temperature), and may have short lifespans, thus limiting their widespread practical applications.¹⁴ Consequently, non-enzymatic sensors have received more attention as potential alternative methods.

In recent years, transition metal oxides have been widely used as electrochemical sensor nanomaterials for H₂O₂ detection. NiCo₂O₄ is a typical binary metal oxide, in which the coupling of Ni and Co ions provides the NiCo₂O₄ with greater

electronic conductivity than either single-component Co₃O₄ and NiO materials, thereby enhancing the overall electrochemical performance of the nanomaterials.^{15–17} Moreover, NiCo₂O₄ has high natural abundance, low cost and relatively low toxicity. Recently, research into NiCo₂O₄-based materials has mainly focused on the synthesis of various morphologies, such as nanoneedles, nanowalls, nanowires, nanorods, nanosheets, hollow structures and multilevel structures.^{18–23} Among them, urchin-like structures have attracted extensive attention due to their high surface area, open structure and abundant active sites, all of which enhance the electrochemical performances of the nanomaterial.²³ However, reports on the preparation of urchin-like NiCo₂O₄ microspheres by an ionic liquid-assisted hydrothermal synthesis pathway has not been published.

Ionic liquids are often composed of hydrophobic organic cations and hydrophilic inorganic anions and can be an environmentally friendly green solvent, they are widely used as solvents and templates in the synthesis of nanomaterials.^{24,25} In this work, urchin-like NiCo₂O₄ microspheres prepared *via* a facile ionic liquid-assisted hydrothermal synthesis are used as non-enzymatic H₂O₂ sensors for the first time. These NiCo₂O₄ microspheres exhibited excellent electrochemical properties and sensitivity towards H₂O₂ detection, demonstrating that the as-prepared hierarchical urchin-like NiCo₂O₄ microspheres could have potential applications as a non-enzymatic H₂O₂ sensor.

Experimental

Materials and reagents

NiCl₂·6H₂O, CoCl₂·6H₂O, urea (CO(NH₂)₂) and NaOH were provided by Tianjin Kemiou Chemical Reagent Co. Ltd. 1-Ethyl-

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3-methylimidazolium nitrate ([EMIm]NO₃) was provided by Lanzhou Institute of Chemical Physics, CAS. H₂O₂ (30%, w/w) was supplied by Chongqing Wansheng Chuandong Chemical Co. Ltd. Nafion (5 wt% in ethanol) was provided by Aldrich. KCl, uric acid (UA), ascorbic acid (AA) and glucose were supplied by Aladdin Co. Ltd. All reagents were of analytical grade.

Preparation of NiCo₂O₄

The NiCo₂O₄ microspheres were prepared using an ionic liquid-assisted hydrothermal method. First, 0.1 mol L⁻¹ CoCl₂·6H₂O and 0.05 mol L⁻¹ NiCl₂·6H₂O were dissolved in 20 mL deionized water. Second, 0.05 mol L⁻¹ 1-ethyl-3-methylimidazole nitrate and 1.25 mol L⁻¹ urea was added and stirred for 0.5 h. Next, the mixture was transferred into a stainless steel autoclave and reacted at 100 °C for 10 h. Finally, the precipitates were collected by centrifugation, dried under overnight, and calcined in air at 400 °C for 2 h.

Characterization

The morphology of products was observed using a Hitachi S-4800 Scanning electron microscopy (SEM) and ZEISS SUPRA 55 transmission electron microscopy (TEM). The annealing temperature was obtained in air by a thermogravimetric analyzer (PerkinElmer 6300). The phase structure of product was obtained using a Panalytical Empyrean X-ray diffraction spectrometer (XRD). X-ray photoelectron spectroscopy (XPS) was performed using a KRATOS AXIS ULTRA. The porosity and surface area were studied by N₂ adsorption (ASAP2460).

Electrochemical measurements

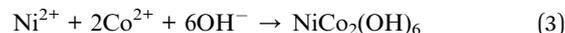
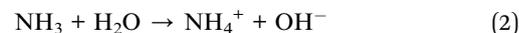
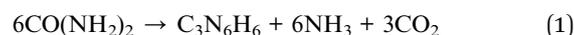
Electrochemical experiments using a three-electrode system on CHI760E electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) in 0.1 mol L⁻¹ NaOH solution. Pt mesh and Hg/HgO (1 mol L⁻¹ KCl) electrode were used as the counter electrode and reference electrode, for the fabrication of working electrode, a rotating-disk electrode (RDE, 5 mm) was polished with 0.03 μm Al₂O₃ slurry, followed by washing in sequence with aqueous nitric acid solution (1:3), water and ethanol. 2.0 mg of NiCo₂O₄ microspheres mixed with 50 μL Nafion was dispersed in 450 μL isopropanol aqueous solution (1:3 vol/vol isopropanol/water) and sonicated for 1 h. Finally, the well-dispersed ink (10 μL) was drop-casted onto the well-polished RDE surface, and then naturally dried to obtain working electrode (NiCo₂O₄/RDE). RDE rotation speed was 1600 rpm.

Results and discussion

Characterization of materials

To investigate the initial growth and formation mechanisms of the NiCo₂O₄ urchin-like microspheres, a detailed time course study was carried out. The synthetic reaction was monitored for up to 10 h, and scans of the related products at various time intervals (Fig. S1a–e†). After reacting for 2 h, a small number of nanowires clustered within the crystal nucleus into a broom shape (Fig. S1a†). Loose sea urchin-like structures gradually to

form between 4–8 h (Fig. S1b–d†). When the reaction time was increased to 10 h, the urchin-like microspheres could eventually be obtained (Fig. S1e†). From this sequence, a possible formation mechanism is proposed as follows: first, the ionic liquids can exhibit easily aggregate and form micelles in solution.²⁵ After further adding urea into the Ni²⁺ and Co²⁺ containing water solution, the OH⁻ anion slowly released during urea hydrolysis, then the metal cations (Co²⁺ and Ni²⁺) reacted with the OH⁻ anion to form the NiCo₂(OH)₆ nucleus.²⁶ The large number of NiCo₂(OH)₆ nuclei were easily adsorbed on micellar surfaces of ionic liquid due to the low surface energy of ionic liquids. These nascent crystal nuclei further grow and self-assemble into nanorods, and eventually form the precursor of urchin-like NiCo₂O₄ microspheres. After calcination in air away the ionic liquid, the NiCo₂(OH)₆ are eventually decomposed into NiCo₂O₄ oxides, causing development of urchin-like NiCo₂O₄ hollow microspheres (Fig. 2e). Notably, in the absence of the ionic liquid [EMIm]NO₃, only NiCo₂O₄ solid microspheres were obtained by hydrothermal synthesis (Fig. S1f and g†). Therefore, the ionic liquid [EMIm]NO₃ is essential for the formation of the urchin-like microspheres. The relevant reactions are as follows:^{26,27}



The optimal calcination temperature of the precursor was determined by thermogravimetric analysis (TG). According to the TG analysis (Fig. 1a), the 3.5 wt% loss below 200 °C due to dehydration. There was a significant reduction in wt% between 200 °C to 400 °C (22.2 wt%), indicating the decomposition of the precursor. Beyond 400 °C, the weight remains constant, indicating that the formation of a stable product. Therefore, the calcination temperature chosen for this study was 400 °C for 2 h.

The phase structures of the calcined product were obtained by XRD measurements (Fig. 1b). The XRD pattern exhibited six characteristic diffraction peaks at 18.9°, 31.1°, 36.7°, 44.6°, 59.1° and 64.9°. All these peaks can be attributed to the (111), (220), (311), (222), (511) and (440) crystal planes of NiCo₂O₄

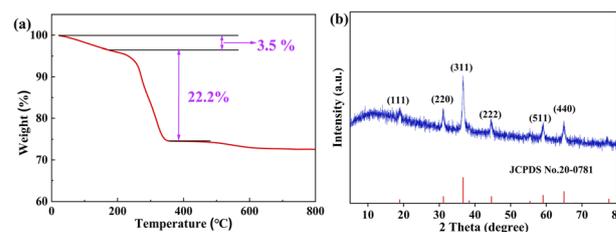


Fig. 1 (a) Thermogravimetric analysis of precursor. (b) XRD diagram of NiCo₂O₄.



(JCPDS No. 20-0781), indicating successful synthesis of NiCo_2O_4 .

The morphologies of the products were obtained by SEM (Fig. 2). The precursor displays an urchin-like microsphere with a morphology of about 5 μm and consists of smooth nanowires (Fig. 2b). After calcination, the resulting NiCo_2O_4 maintains the same morphology as that of the precursor (Fig. 2c and e), but the NiCo_2O_4 microspheres are hollow structures and the nanowires of NiCo_2O_4 microspheres are composed of NiCo_2O_4 nanoparticles 25 nm in diameter (Fig. 2d and f). Meanwhile, the lattice images of HRTEM (Fig. 2g) showed d -spacing of 0.424, 0.208, 0.144 and 0.160 nm, corresponding to (111), (400), (440) and (422) crystal planes of NiCo_2O_4 , respectively.

The porosity and surface area of NiCo_2O_4 microspheres were studied by N_2 adsorption and shown in Fig. 2h. A type IV isotherm was observed, confirming the a mesoporous structure of NiCo_2O_4 microspheres.²⁸ From this isotherm, the BET specific surface area was calculated as 52.15 $\text{m}^2 \text{g}^{-1}$, and the average pore diameter and accumulative pore volume were calculated to be 17 nm and 0.21 $\text{cm}^3 \text{g}^{-1}$, respectively. The high surface area and porous structure of NiCo_2O_4 should provide sufficient space for mass transfer, and also increase the available more active sites, both of which improve the electrocatalytic activity for H_2O_2 oxidation.

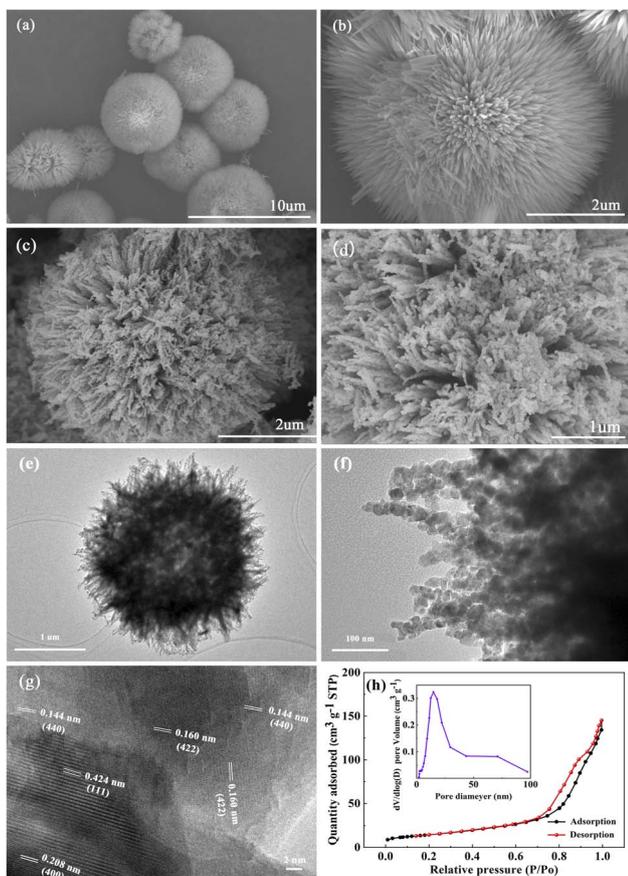


Fig. 2 SEM results of precursor (a and b) and NiCo_2O_4 (c and d). TEM (e and f) and HRTEM (g) image of NiCo_2O_4 . (h) N_2 adsorption isotherm and the corresponding pore diameter distribution (inset) of NiCo_2O_4 .

In order to confirm the surface chemical compositions of NiCo_2O_4 microspheres, we performed the XPS analysis (Fig. 3). The XPS full spectrum analysis (Fig. 3a) indicated only Ni, Co, O, and C in the NiCo_2O_4 microspheres. The Ni 2p spectra (Fig. 3b) shows two major peaks and two shakeup satellites (designated as “Sat.”). The binding energies at 871.8 eV and 853.4 eV correspond to the Ni 2p_{1/2} and Ni 2p_{3/2}, respectively. The Ni 2p_{1/2} and Ni 2p_{3/2} levels were best fitted with double peaks (Ni^{2+} and Ni^{3+}) at high resolution. Similarly, the Co 2p spectra (Fig. 3c) shows the binding energy of Co 2p_{3/2} and Co 2p_{1/2} states at 779.1 eV and 794.2 eV, where the Co^{3+} and Co^{2+} valences are also clearly shown in the Co 2p_{3/2} and Co 2p_{1/2} levels. The presence of redox couples of $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ can significantly improve the electrocatalytic activity.²⁹ In addition, the O1s fine spectrum consists of three components (Fig. 3d). The binding energies of 529.1 eV, 530.6 eV and 532.3 eV were attributed to the lattice oxygen (designated as O1), oxygen within crystalline defects (designated as O2) and physicochemically adsorbed oxygen (designated as O3), respectively.^{30–32}

Electrochemical properties of $\text{NiCo}_2\text{O}_4/\text{RDE}$

Oxidation of H_2O_2 at the $\text{NiCo}_2\text{O}_4/\text{RDE}$. The electrochemical properties of NiCo_2O_4 towards H_2O_2 oxidation were investigated by cyclic voltammetry (CV) and shown in Fig. 4a. The CV plot of $\text{NiCo}_2\text{O}_4/\text{RDE}$ shows two pairs of redox peaks in the absence of H_2O_2 , which correspond to the redox processes of $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox couples in the alkaline electrolyte.³³ Interestingly, upon addition of H_2O_2 into the NaOH electrolyte, the peak current of $\text{NiCo}_2\text{O}_4/\text{RDE}$ increased significantly. This increased current correlated with increases in the H_2O_2 concentration (Fig. 4b). As a control, the CV obtained from a bare RDE is also shown in Fig. 4a.

The bare RDE only exhibited a weaker double-layer charging current, and does not show any redox peaks. These results suggested that the as-prepared NiCo_2O_4 microspheres are redox active and show electrocatalytic activity towards H_2O_2 oxidation. Furthermore, the CVs of $\text{NiCo}_2\text{O}_4/\text{RDE}$ were studied at different scan rates (Fig. 4c). The anodic and cathodic peak currents

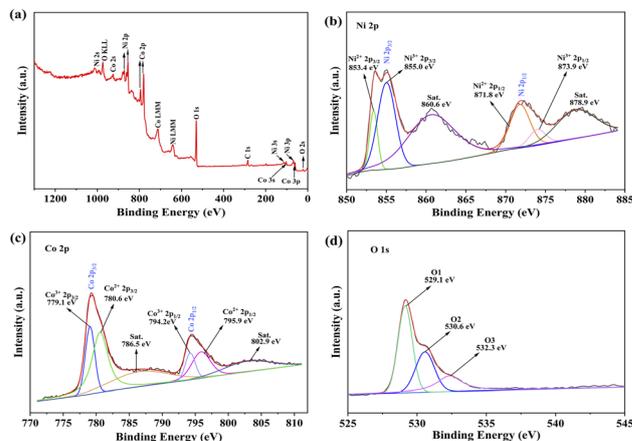


Fig. 3 XPS full spectrum (a), Ni 2p (b), Co 2p (c), and O 1s (d) for NiCo_2O_4 .



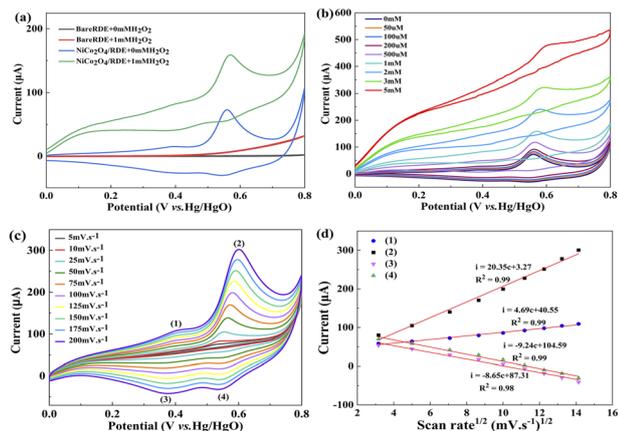


Fig. 4 (a) CVs of NiCo₂O₄/RDE with the absence and presence of 1 mM H₂O₂ in 0.1 M NaOH solution (scan rate 50 mV s⁻¹). (b) CVs of NiCo₂O₄/RDE with the addition of different amounts of H₂O₂ (scan rate 50 mV s⁻¹). (c) CVs of NiCo₂O₄/RDE at different scan rates with the presence of 1 mM H₂O₂. (d) The plot of cathodic and anodic peak currents vs. scan rates.

increase with an increasing scanning rates, and the peak currents were directly proportional to the square root of scan rates (Fig. 4d). The above results suggested that the electrocatalytic/RDE was controlled by diffusion.³³ A possible catalytic mechanism involving NiCo₂O₄ is proposed as follows:³³



Amperometric response of the NiCo₂O₄/RDE towards H₂O₂.

We investigated the effect of the applied potential and catalyst loading on the amperometric response of NiCo₂O₄/RDE towards H₂O₂ oxidation as shown in Fig. S2.† A potential of 0.58 V was selected as the optimal applied potential by comparing the noise current and sensitivity (Fig. S2a and b†). The sensitivity and linear range reached a maximum value when 200 μg cm⁻² NiCo₂O₄ was loaded onto the RDE (Fig. S2c and Table S1†). Therefore, this amount was used in the following studies.

The steady state amperometric response of NiCo₂O₄/RDE to successive additions of H₂O₂ at 0.58 V are shown in Fig. 5a. The NiCo₂O₄/RDE responded immediately following H₂O₂ addition, and the current stabilized within 4 s after adding H₂O₂ into the NaOH solution, suggesting that the NiCo₂O₄/RDE has a rapid and sensitive response behavior to H₂O₂. The response current was measured as a function of H₂O₂ concentration, which exhibited a linear response between 0 μM to 14 mM (Fig. 5b). The calculated sensitivity and detection limit of H₂O₂ from these measurements were 392.50 μA mM⁻¹ cm⁻² and 0.05 μM (S/N = 3), respectively. This marks a significant decreased in detection limit in comparison to previously reported NiCo₂O₄-based H₂O₂ nonenzymatic biosensors (Table 1). The rapid and sensitive response of the NiCo₂O₄ urchin-like microspheres was

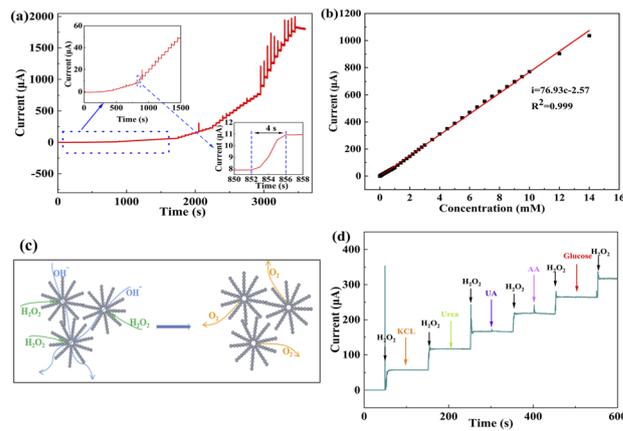


Fig. 5 (a) Amperometric response of NiCo₂O₄/RDE at 0.58 V and its corresponding calibration plot (b). (c) Schematic illustration of the oxidation process of H₂O₂ on the NiCo₂O₄. (d) Amperometric response of NiCo₂O₄/RDE in 0.1 M NaOH buffer following sequential addition of 1 mM H₂O₂, 0.1 mM KCl, 1 mM H₂O₂, 0.1 mM urea, 1 mM H₂O₂, 0.1 mM UA, 1 mM H₂O₂, 0.1 mM AA, 1 mM H₂O₂, 0.1 mM glucose.

attributed to their unique hierarchical architecture, as shown in Fig. 5c. The NiCo₂O₄ urchin-like microsphere consists of nanowires and abundant pores, which not only are beneficial to the transport of H₂O₂ and electrolyte, but also allow the oxygen to rapidly escape from the surface of the catalyst, and the H₂O₂ and electrolyte to effectively infiltrate into the catalyst for continuing catalysis processes.

Assessing the selectivity and stability of the NiCo₂O₄/RDE sensor for H₂O₂ detection. To investigate the selectivity of the NiCo₂O₄/RDE sensor for H₂O₂ detection, the amperometric responses of NiCo₂O₄/RDE to H₂O₂ were studied in the presence of common biological interfering compounds, including KCl, urea, AA, UA and glucose (Fig. 5d). These results demonstrate that there is almost a negligible amperometric response towards all reagents except for H₂O₂, which shows a significant amperometric response. Therefore, the NiCo₂O₄ microspheres appear to be excellent selective for H₂O₂ detection. In order to assess the reproducibility of NiCo₂O₄/RDE as the H₂O₂ sensor, five different NiCo₂O₄/RDE were independently fabricated by the same method. The amperometric responses of these electrodes to addition of 1 mM H₂O₂ were recorded. As a result, the relative standard deviation (RSD) of the response current was 5.4% (*n* = 5). The NiCo₂O₄/RDE sensor maintains 98.1% of its initial amperometric response upon addition of 1 mM H₂O₂ after storage in air for 15 days. For each individual sensor, the RSD in measured current response from fifteen successive measurements 0.43% (*n* = 15). Moreover, the stability of urchin-like morphology after the fifteen successive test was further checked by TEM and HRTEM analysis. The TEM image clearly show the urchin-like morphology, even after the fifteen successive test (Fig. S1h†). The lattice images of HRTEM (inset of Fig. S1h†) showed *d*-spacing of 0.246, 0.234 and 0.208 nm, corresponding to (311), (222) and (400) crystal planes of NiCo₂O₄, respectively. All these results suggest that the sensor



Table 1 The performance comparison of our proposed with other published for H₂O₂ sensors

Material	Linear ranges (mM)	Detection limit (μM)	Ref.
NiCo ₂ O ₄	0–14	0.05	This work
NHGH/NiCo ₂ O ₄	0.001–0.51	0.136	33
ZnO/Co ₃ O ₄ /NiCo ₂ O ₄ /Ni foam	0.0002–2.4	0.163	16
Co ₃ O ₄ /NCNTs	0.005–11	1	34
Co ₃ O ₄ /NiCo ₂ O ₄	0.05–41.7	0.2578	35
NiO/Ti ₃ C ₂ T _x	0.01–4.54	0.348	36
PbS/Co ₃ O ₄	0.005–0.25	1.2	37
Ni _x Co _y -DO	0–0.4	0.28	38
NiCo ₂ O ₄ /CoNiO ₂ @pRGO ₆₀₀	0.005–3, 3–12	0.41	39
NiO-MNS	0.01–0.8	0.62	40
Ni/NiO@C	0.05–6.7, 8.7–80.7	0.9	41

had good reproducibility, repeatability and stability for the H₂O₂ detection.

Conclusion

In conclusion, urchin-like NiCo₂O₄ microspheres were successfully fabricated *via* a relatively simple ionic liquid-assisted hydrothermal method and were used as an effective electrochemical sensor for H₂O₂. The results demonstrate that the urchin-like NiCo₂O₄ microspheres had structural properties that were ideal for its use as a non-enzymatic H₂O₂ sensor. The H₂O₂ sensor based on NiCo₂O₄ microspheres exhibited a fast detection response, a wide linear range, and high sensitivity towards H₂O₂. The high H₂O₂ detection performance achieved by NiCo₂O₄ in this study suggests these microspheres could have promising potential applications as H₂O₂ sensors in the medical diagnostics and biotechnology sectors.

Author contributions

Jiaojiao Jiang: data curation, writing – original draft. Zhixuan Zhang: validation. Chong Yang: conceptualization, data curation. Rui Wang: methodology, data curation. Zhouling Wu: project administration, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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