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# MOF-derived ZnCo<sub>2</sub>O<sub>4</sub> porous micro-rice with enhanced electro-catalytic activity for the oxygen evolution reaction and glucose oxidation†

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A porous ZnCo<sub>2</sub>O<sub>4</sub> micro-rice like microstructure was synthesized *via* calcination of a Zn–Co MOF precursor at an appropriate temperature. The as-prepared ZnCo<sub>2</sub>O<sub>4</sub> sample presented good electrocatalytic oxygen evolution reaction performance with a small overpotential ( $\eta_{10} = 389$  mV) and high stability in basic electrolyte. Furthermore, in basic medium, the as-synthesized ZnCo<sub>2</sub>O<sub>4</sub> micro-rice also showed good electrocatalytic activity for glucose oxidation. A ZnCo<sub>2</sub>O<sub>4</sub> micro-rice modified glass carbon electrode may be used as a potential non-enzymatic glucose sensor. The excellent electrocatalytic OER and glucose oxidation performances of ZnCo<sub>2</sub>O<sub>4</sub> might be attributed to the unique porous structure formed by the nanoparticles. The porous architecture of the micro-rice can provide a large number of electrocatalytically active sites and high electrochemical surface area (ECSA). The result may offer a new way to prepare low-cost and high performance oxygen evolution reaction and glucose oxidation electrocatalysts.

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## 1 Introduction

Metal–organic frameworks (MOFs), also named metal–organic coordination polymers (MOCs), are a new class of porous materials and have attracted great attention due to their potential applications in the gas storage and separation, catalysis, luminescence, sensing, and energy storage fields.<sup>1–4</sup> In recent years, the micro-nano structured MOFs with special morphologies have been prepared from metal ions and organic ligands in different solvent systems.<sup>5–11</sup> Utilizing MOFs as hard templates or precursors can provide an effective strategy to synthesize novel micro-nano structured materials including metal oxides, metal chalcogenides, metal phosphides, metal carbides, porous carbon materials, and other complex micro-nanostructures.<sup>5–14</sup> The MOF-derived micro-nano materials can exhibit several structure-dependent merits in the electrocatalytic oxygen evolution reaction (OER) and glucose oxidation fields.

In recent years, spinel A<sup>II</sup>B<sub>2</sub><sup>III</sup>O<sub>4</sub> micro-nano structures have aroused great attention because of their potential application in

batteries, supercapacitors, catalytic, and sensing fields.<sup>15</sup> So far, a great of spinel Co<sub>3</sub>O<sub>4</sub> (Co<sup>II</sup>Co<sup>III</sup>O<sub>4</sub>) structures with different sizes and morphologies have been synthesized as electrode materials for electrochemical oxygen evolution reaction.<sup>16,17</sup> Unfortunately, the Co<sub>3</sub>O<sub>4</sub>-based electrodes own poor electrical conductivity and high-cost, thus hampered to extensively practical applications. Therefore, using low-cost metal Zn(II) ions to partially substitute Co(II) ions of Co<sub>3</sub>O<sub>4</sub> to get ZnCo<sub>2</sub>O<sub>4</sub> could improve the electrocatalytic properties.<sup>18–20</sup> Ternary ZnCo<sub>2</sub>O<sub>4</sub> materials reveal higher electrical conductivity and enhanced electrochemical activity ascribed to the co-existence of the Zn and Co species. Therefore, zinc cobalt oxides (ZnCo<sub>2</sub>O<sub>4</sub>) with unique porous structure are anticipated with good performance for electrochemical energy storage and conversion.

Recently, a great of attentions have been paid to the development of electrocatalysts for OER, and OER plays a critical role in water splitting, Zn–air batteries, and regenerative fuel cells fields.<sup>21–27</sup> To date, different Co-based micro-nano structured catalysts, including Co<sub>3</sub>O<sub>4</sub>,<sup>16,17</sup> Co<sub>3</sub>S<sub>4</sub>,<sup>28</sup> CoSe<sub>2</sub>,<sup>29</sup> CoMoO<sub>4</sub>,<sup>30</sup> Ni<sub>x</sub>Co<sub>3–x</sub>(PO<sub>4</sub>)<sub>2</sub>,<sup>31</sup> have been developed as OER catalysts and showed good OER performances. On other hand, in recent ten years, electrochemical non-enzymatic glucose sensors based on metal oxides have caused widespread interest due to their easy preparation, cheap cost, and portable characteristics in the detection of glucose.<sup>32–34</sup> Up to now, many metal oxides micro/nano-structures such as NiO, CuO, Co<sub>3</sub>O<sub>4</sub>, CuCo<sub>2</sub>O<sub>4</sub>, and NiCo<sub>2</sub>O<sub>4</sub>, have been extensively used for glucose sensing.<sup>35–42</sup> Porous hierarchical micro/nano-structures have attracted great interest in electrocatalytic OER and glucose sensing attribute to

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the unique structure with rich active sites, large electrolyte contact area, and quick electron/active species transfer rate. Based on the above considerations, we exhibit the rational design of  $\text{ZnCo}_2\text{O}_4$  hierarchical porous micro-rice like structure based on thermolysis of a Zn-Co MOF precursor, and the as-prepared material shows enhanced electrocatalytic activity for OER and glucose oxidation.

## 2 Experimental

### 2.1 Synthesis of $\text{ZnCo}_2\text{O}_4$ porous micro-rice like structure

In a typical synthesis procedure, zinc nitrate hexahydrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.010 g, 0.03 mmol), cobalt nitrate hexahydrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.0189 g, 0.06 mmol), *p*-phthalic acid (0.012 g, 0.07 mmol), and polyvinylpyrrolidone (PVP, K30, 0.92 g) were added to the mixture of 5.0 mL *N,N*-dimethylformamide (DMF) and 3.0 mL ethanol, the above mixed solution was stirred vigorously for 30 min, sealed and heated to 160 °C for 3 h. After cooling to room temperature, the obtained powder was isolated by centrifugation and washed by ethanol three times, and then dried at 60 °C for 2 h. The porous  $\text{ZnCo}_2\text{O}_4$  micro-rice like structure was obtained by annealing the as-synthesized MOF precursor at 400 °C for 2 h in air (2 °C min<sup>-1</sup>).

### 2.2 Reagents and materials characterization

The chemicals include  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , glucose (GLU), dopamine (DA), uric acid (UA), ascorbic acid (AA), and polyvinyl pyrrolidone (PVP) were purchased from Beijing Chemical Reagent Co., China. *p*-Phthalic acid was purchased from Aladin Ltd. (Shanghai, China). All of these chemical reagents are of analytical grade and used as received without further purification.

The phase of  $\text{ZnCo}_2\text{O}_4$  was characterized by X-ray diffraction (XRD) on a Rigaku-Ultima III diffractometer with  $\text{Cu}_{\text{K}\alpha}$  radiation. Field scanning electron microscopy (FSEM, Hitachi SU8010) and transmission electron microscopy (TEM, FEI Tecnai G2 s-twin D573) equipments were used to characterize the morphology and microstructure for the as-synthesized samples. The data of specific surface areas was collected by  $\text{N}_2$  adsorption on Gemini VII 2390 Analyzer at 77 K. The chemical composition and valence of the obtained materials were analyzed by X-ray photoelectron spectroscopy on XPS Thermo 250Xi. Thermogravimetric analysis (TGA) was carried out in the nitrogen atmosphere on a Netzsch STA-449F3 thermogravimetric analyzer at a heating rate of 10 °C min<sup>-1</sup>.

### 2.3 Preparation and measurement of OER electrocatalytic electrode

The electrochemical test was conducted on an electrochemical workstation (CHI 760E) equipped with high-speed rotators from Pine instrument, using  $\text{O}_2$  pre-saturated 1.0 M KOH solution as the electrolyte (pH = 14.0). For the electrochemical measurement, a three-electrode setup was employed in which a glassy carbon electrode (GCE) with a diameter of 5 mm (0.196 cm<sup>2</sup>), a platinum wire and a Ag/AgCl electrode were employed as the working electrode, counter electrode and reference electrode,

respectively. The catalyst ink was prepared as follow, an amount of 5 mg  $\text{ZnCo}_2\text{O}_4$  sample was added to a mixture of  $\text{H}_2\text{O}$ /isopropanol (v/v = 3 : 1, 1 mL) with 50  $\mu\text{L}$  Nafion solution, and the above solution was strongly ultrasonic to acquire a homogenous ink dispersion. Then, 10  $\mu\text{L}$  of the catalyst ink was casted onto the polished GCE and dried at room temperature. The linear sweep voltammetry (LSV) test was carried out with a scan rate of 1 mV s<sup>-1</sup> at 1600 rpm. Electrochemical impedance spectroscopy (EIS) was recorded at open circuit potential in the frequency scan range from 100 kHz to 0.01 Hz.

### 2.4 Preparation and measurement of electrochemical sensor electrode

The bare GC electrode was carefully polished with different sizes of  $\text{Al}_2\text{O}_3$  slurries (1.0, 0.3, and 0.05  $\mu\text{m}$ ) prior to modification. The as-obtained  $\text{ZnCo}_2\text{O}_4$  catalyst (1.0 mg) was dispersed to 1.0 mL ultrapure water (18.2 M $\Omega$  cm), giving a dispersion with strongly ultrasonic technique. After that, a 5.0  $\mu\text{L}$  of the micro-rice catalysts suspension was dropped on the cleaning GC electrode with a diameter of 3 mm and dried at room temperature before to use.

## 3 Results and discussion

The scanning electron microscopy (SEM) images of the as-prepared Zn-Co-based MOF precursors and porous  $\text{ZnCo}_2\text{O}_4$

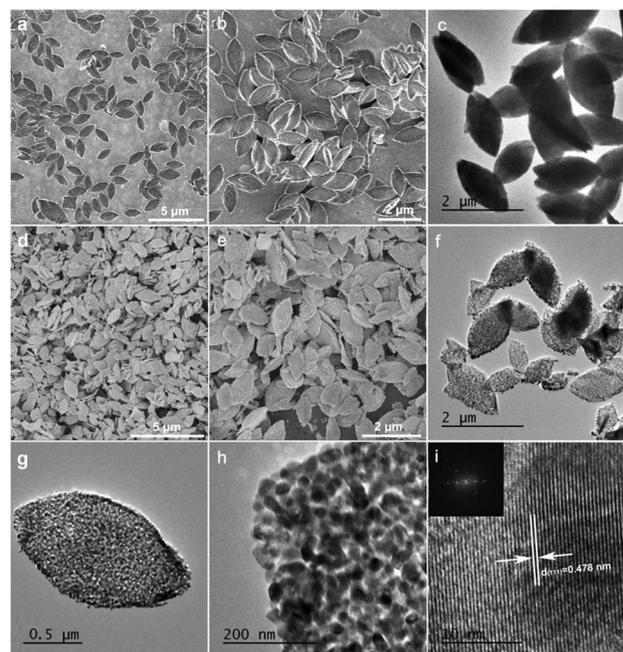


Fig. 1 (a and b) The SEM images of the 3D structure of Zn-Co-based MOF precursors, (c) TEM image of Zn-Co-based MOF precursors, (d and e) the SEM images of the 3D structure of  $\text{ZnCo}_2\text{O}_4$  porous micro-rice like structure obtained after calcination of Zn-Co-based MOF precursors, (f) the TEM image of  $\text{ZnCo}_2\text{O}_4$  porous micro-rice like structure, (g) the TEM image of a single  $\text{ZnCo}_2\text{O}_4$  micro-rice, (h) magnified TEM image of (g), (i) the HRTEM image and FFT of the  $\text{ZnCo}_2\text{O}_4$  porous micro-nano structure (inset).



micro-rice like structure was shown in Fig. 1. The as-prepared MOF precursor displays micro-rice structure roughly 1.71  $\mu\text{m}$  in length and 0.85  $\mu\text{m}$  in width, which assembled by nanosheets (Fig. 1a, b, S1a and b $\dagger$ ).

The formation process of the Zn–Co-based MOF precursors was tuned by a series of control experiment. When 0.09 mmol of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was used as raw material with the absence of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and kept other reaction parameters unchanged, only microspheres can be obtained. The large size of irregular rectangle-like nanosheets can be obtained when the usage of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  increased to 0.27 mmol with the Zn/Co molar ratio of 1 : 9 (Fig. S2 $\dagger$ ). Although most of the micro-rice morphology is remained as decreasing the amount of *p*-phthalic acid to half, however, the dispersibility of nanosheets becomes inferior (Fig. S3 $\dagger$ ). When tuned the solvent volume ratio of DMF and ethanol from 5 : 3 to 4 : 4, the yield of micro-rice morphology of nanosheets became fewer (Fig. S4 $\dagger$ ). As shown in Fig. S5 $\dagger$ , other things being equal, spindle-like microparticles can be synthesized when DMF was substituted by isometric *N,N*-dimethylacetamide (DMA). The TEM image also reveals that a nonporous feature of the precursors and the micro-rice morphology composing of closely stacked lamella with different contrast of the observed layers as shown in Fig. 1c, S6a and b $\dagger$ . Thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability of the Zn–Co MOF sample between 40 and 800  $^\circ\text{C}$ . TG curve of MOF shows sharp weight loss of 46.40% from 328 to 399  $^\circ\text{C}$  corresponds to the decomposition of the *p*-phthalic acid ligand (Fig. S7 $\dagger$ ). Thus, we selected 400  $^\circ\text{C}$  as the calcination temperature. After annealing at 400  $^\circ\text{C}$  for 2 h in atmosphere condition, the MOF precursors can be easily converted to  $\text{ZnCo}_2\text{O}_4$ , which maintains the initial micro-rice precursor morphology well with a slight dimension shrinkage (Fig. 1d, e, S8a and b $\dagger$ ). The high magnified SEM image in Fig. 1e further demonstrated that the distinctly hierarchical structure of  $\text{ZnCo}_2\text{O}_4$ , as shown in the lateral section, which is easy to yield by sintering. The TEM images of  $\text{ZnCo}_2\text{O}_4$  were presented in Fig. 1f and h, clearly certifying porous architecture can be derived from pyrolysis of Zn–Co-based MOF. The porous and hierarchical structure of  $\text{ZnCo}_2\text{O}_4$  with accessible surface facilitated to the fast ions and molecules transfer, suggesting potential good properties. The high resolution TEM image in Fig. 1i indicates the micro-rice presence clear lattice finger with a lattice interplanar space of 0.478 nm, which is corresponded to the (111) crystal plane of spinel  $\text{ZnCo}_2\text{O}_4$ . The FFT inset in Fig. 1i also revealed the high crystallinity of the annealed sample.

The XRD pattern of the as-prepared  $\text{ZnCo}_2\text{O}_4$  is shown in Fig. 2a. All the peaks present in the pattern can well match with the standard cards of  $\text{ZnCo}_2\text{O}_4$  (JCPDS 23-1390). Energy-dispersive X-ray (EDX) analysis reveals the coexistence of Zn, Co, O elements in the  $\text{ZnCo}_2\text{O}_4$  micro-rice (Fig. 2b), and the atomic ratio of Zn and Co is about 1 : 2.15. The Brunauer–Emmett–Teller (BET) specific surface area of  $\text{ZnCo}_2\text{O}_4$  obtained from  $\text{N}_2$  sorption isotherms is 25  $\text{m}^2 \text{g}^{-1}$ . The as-synthesized sample shows a typical mesoporous structure with an average pore diameter of  $\sim 3.6$  nm (inset in Fig. 2c). This unique mesoporous structure is beneficial for molecules/ions diffusion and

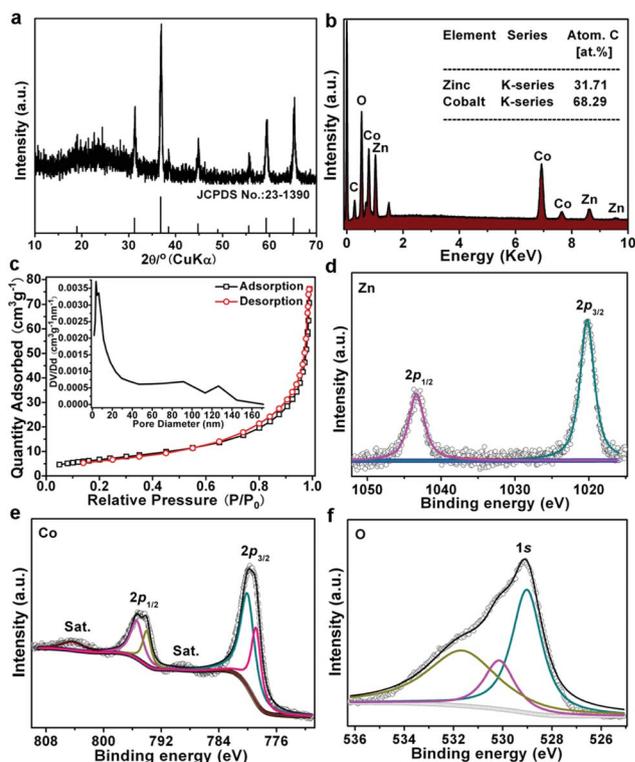


Fig. 2 (a) Powder X-ray diffraction patterns of the simulated and as-synthesized  $\text{ZnCo}_2\text{O}_4$ . (b) EDX of the  $\text{ZnCo}_2\text{O}_4$  micro-rice structure, (c)  $\text{N}_2$  adsorption/desorption isothermal curve and pore size distribution of the  $\text{ZnCo}_2\text{O}_4$  micro-nano structure, high-resolution XPS spectrum of (d) Zn 2p, (e) Co 2p, (f) O 1s.

adsorption. The surface chemical state of  $\text{ZnCo}_2\text{O}_4$  micro-rice was also investigated by XPS, the survey spectrum in Fig. S5 $\dagger$  illustrated the existence of Zn, Co, and O elements. The high-resolution XPS spectrum of Zn 2p in Fig. 2d exhibited two peaks at binding energy of 1020.16 and 1043.40 eV, which is corresponded to Zn  $2p_{3/2}$  and Zn  $2p_{1/2}$  of  $\text{Zn}^{2+}$  ions. Meanwhile, the doublet peaks located at 780.16 and 795.42 eV was assigned to Co  $2p_{3/2}$  and Co  $2p_{1/2}$  of  $\text{Co}^{2+}$  ions, and another pair of peaks at 778.95 and 794.11 eV was ascribed to  $\text{Co}^{3+}$  ions (Fig. 2e), which is benefitting for the electrocatalytic process of OER. The O 1s peaks can be deconvoluted into three separated peaks, the peaks of BEs at 529.02 and 531.71 eV matched well with metal–oxygen bonds and physisorption of oxygen in hydroxyl groups, respectively, while, the peak at 530.18 eV suggested the present of oxygen vacancy (Fig. 2f), which could be attributed to the high conductivity of  $\text{ZnCo}_2\text{O}_4$  electrocatalyst.

### 3.1 OER activity and stability

The OER test of  $\text{ZnCo}_2\text{O}_4$  micro-rice like structure was recorded in an  $\text{O}_2$ -saturated alkaline solution (1.0 M KOH) with a three-electrode setup. Fig. 3a showed the linear sweep voltammogram (LSV) of catalyst with a scan rate of 1  $\text{mV s}^{-1}$ , the overpotential of  $\text{ZnCo}_2\text{O}_4$  micro-rice like structure is 389 mV at current density of 10  $\text{mA cm}^{-2}$ , which can compare to some  $\text{ZnCo}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  based catalysts, such as  $\text{ZnCo}_2\text{O}_4$  micro-



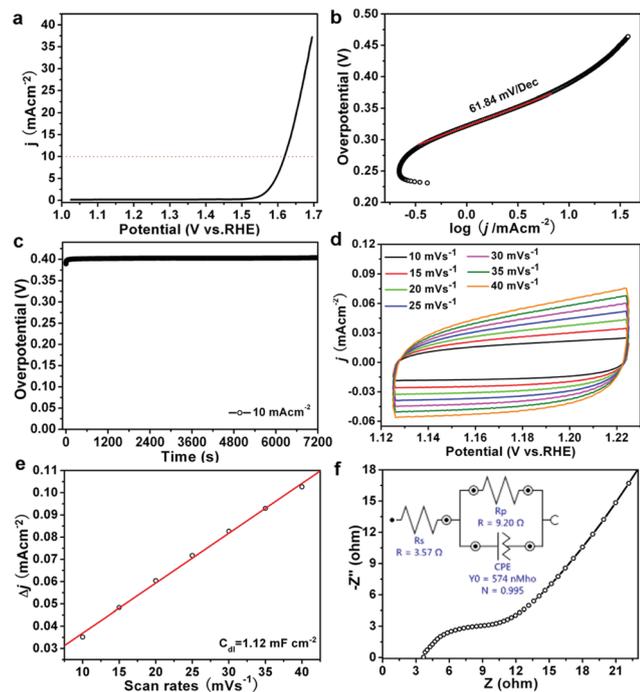


Fig. 3 The catalytic OER process of porous  $\text{ZnCo}_2\text{O}_4$  micro-rice sample: (a) LSV curves obtained at a sweep rate of  $1 \text{ mV s}^{-1}$ , (b) Tafel plots of OER currents in (a). (c) The chronoamperometry curves at the current density of  $10 \text{ mA cm}^{-2}$  (d) CVs at different scan rates in  $1 \text{ M KOH}$ . (e) Plot of current density at  $1.17 \text{ V}$  (vs. RHE) versus the scan speed. (f) Nyquist plots of porous  $\text{ZnCo}_2\text{O}_4$  measured at open circuit potential.

spindle,<sup>18</sup>  $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$  porous willow-leaf like structure,<sup>19</sup> mesoporous  $\text{Co}_3\text{O}_4$ ,<sup>43</sup> and  $\text{CuCo}_2\text{O}_4$  sample.<sup>44</sup> The Tafel plot of  $\text{ZnCo}_2\text{O}_4$  catalyst was investigated to evaluate the OER performance and as shown in Fig. 3b. The  $\text{ZnCo}_2\text{O}_4$  micro-rice like structure exhibits small Tafel slope of  $61.84 \text{ mV dec}^{-1}$ . The small Tafel slope of  $\text{ZnCo}_2\text{O}_4$  sample implied a fast OER reaction kinetics and practical applications. Furthermore, stability of the sample was evaluated by chronoamperometry test, as shown in Fig. 3c, the OER overpotential of  $\text{ZnCo}_2\text{O}_4$  micro-rice exhibits almost unchanged during 2 h at the current density of  $10 \text{ mA cm}^{-2}$ , indicating the good durability of the porous sample in alkaline medium. The ECSA of  $\text{ZnCo}_2\text{O}_4$  was evaluated by double-layer capacitance ( $C_{dl}$ ) and shown in Fig. 3d, the  $C_{dl}$  value ( $1.12 \text{ mF cm}^{-2}$ ) of  $\text{ZnCo}_2\text{O}_4$  micro-rice structure is not very big (Fig. 3e). The electrochemical impedance spectroscopy (EIS) of  $\text{ZnCo}_2\text{O}_4$  exhibits a small charge transfer resistance of  $9.20 \Omega$  (Fig. 3f), revealing that  $\text{ZnCo}_2\text{O}_4$  porous structure own fast charge transfer and small charge transfer resistance for OER process.

### 3.2 Non-enzymatic glucose sensor

To evaluate the  $\text{ZnCo}_2\text{O}_4$  catalytic performance for nonenzymatic glucose sensing, the CVs was conducted at first. The CV curves of  $\text{ZnCo}_2\text{O}_4/\text{GC}$  electrodes were recorded in  $0.1 \text{ M NaOH}$  solution containing  $0\text{--}2 \text{ mM}$  glucose (Fig. 4a), a quick current density response was observed as the increasing of glucose

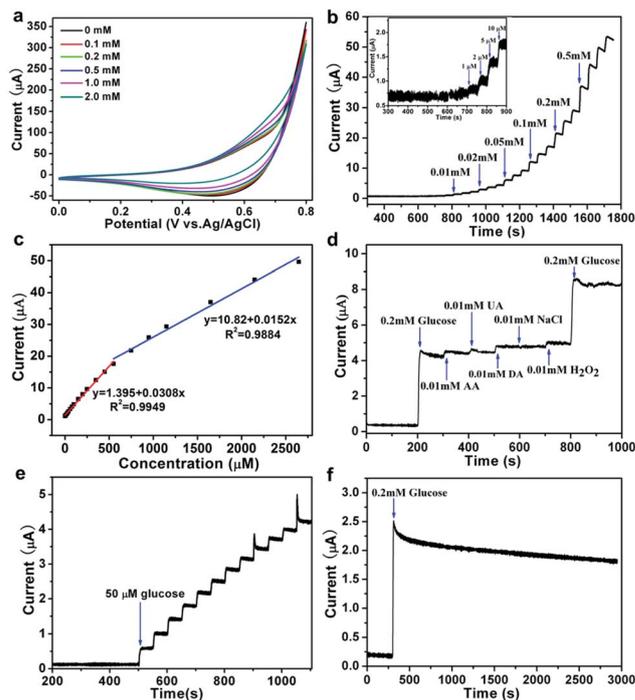


Fig. 4 (a) The CV curves of  $\text{ZnCo}_2\text{O}_4/\text{GC}$  electrode in the absence and presence of  $0.1\text{--}2 \text{ mM}$  glucose. (b) Amperometric responses of the mesoporous  $\text{ZnCo}_2\text{O}_4/\text{GC}$  electrode towards successive addition of glucose at the potential of  $0.55 \text{ V}$  in  $0.1 \text{ M NaOH}$ . (c) The calibration curve of current response and glucose concentration. (d) The selectivity and anti-interference. (e) The reproducibility of  $\text{ZnCo}_2\text{O}_4/\text{GC}$  electrode for detection  $50 \mu\text{M}$  glucose. (f) The stability for 2600 s.

concentration from  $0.1\text{--}2 \text{ mM}$ , which suggested that the porous  $\text{ZnCo}_2\text{O}_4$  modified electrode owns rich active sites for glucose oxidation.  $\text{Co(II)}$  ions occupy the largest part of the  $\text{ZnCo}_2\text{O}_4$  surface are easily converted to  $\text{Co(OH)}_2$  in alkaline solution, and the  $\text{Co(OH)}_2$  can be oxidized to  $\text{CoOOH}$  intermediate, which can electrocatalytic oxidation the glucose to gluconolactone.

In  $0.10 \text{ M NaOH}$  solution, the typical amperometric response of the  $\text{ZnCo}_2\text{O}_4/\text{GC}$  electrode was recorded by the successive addition of glucose at a potential of  $0.55 \text{ V}$  (Fig. 4b), the modified electrode needs less than  $3 \text{ s}$  to equilibrate each additive amount of glucose. As shown in Fig. 4c,  $\text{ZnCo}_2\text{O}_4/\text{GC}$  not only showed excellent responds in low detection limit, but also in high concentration, the corresponding calibration curve for glucose detection displayed two linearity regions of  $0.01\text{--}0.55 \text{ mM}$  ( $R^2 = 0.9949$ ) and  $0.55\text{--}2.65 \text{ mM}$  ( $R^2 = 0.9884$ ), and the matched sensitivity of  $\text{ZnCo}_2\text{O}_4/\text{GC}$  electrode in low and high concentration regions is  $436.1$  and  $215.1 \mu\text{A mM}^{-1} \text{ cm}^{-2}$ , respectively. Fig. 4b exhibits the detection limit of  $\text{ZnCo}_2\text{O}_4/\text{GC}$  electrode is  $5 \mu\text{M}$ , which is lower than  $\text{CoOOH}$  nanosheet arrays sensor ( $30.9 \mu\text{M}$ ),<sup>47</sup>  $\text{Co}_3\text{O}_4$  nanocrystals sensor ( $50 \mu\text{M}$ ),<sup>49</sup>  $\text{Co}$  nanobeads/rGO sensor ( $47.5 \mu\text{M}$ ),<sup>56</sup> octahedral  $\text{Cu}_2\text{O}$  sensor ( $128 \mu\text{M}$ ),<sup>57</sup> and  $\text{FeOOH}$  nanowires sensor ( $15 \mu\text{M}$ ).<sup>59</sup> Both the sensitivity values of the constructed sensor electrode are higher than that of the reported  $\text{Co}_3\text{O}_4$  porous film electrode ( $366.03 \mu\text{A mM}^{-1} \text{ cm}^{-2}$ ),<sup>48</sup>  $\text{Co}_3\text{O}_4$  nanofibers modified electrode ( $36.25 \mu\text{A mM}^{-1} \text{ cm}^{-2}$ ),<sup>52</sup>  $\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$  double-shelled nanocages@G



Table 1 Comparison of the performance of the as-prepared ZnCo<sub>2</sub>O<sub>4</sub> micro-rice sensor with other reported nonenzymatic glucose sensors

Electrode material	Potential (V vs. Ag/AgCl)	Linear range (mM)	Detection limit		Ref.
			( $\mu\text{M}$ )	Sensitivity ( $\mu\text{A mM}^{-1} \text{cm}^{-2}$ )	
Cobalt oxide microspheres	+0.55	0.00083–8.61	0.46	669.78	45
Porous CoOOH nanosheet arrays	+0.52	0.003–1.109	1.37	526.8	46
CoOOH nanosheet arrays	+0.40	0.03–0.7	30.9	341.0	47
Co <sub>3</sub> O <sub>4</sub> porous film	+0.60	Up to 3.0	1	366.03	48
Co <sub>3</sub> O <sub>4</sub> nanocrystals	+0.55	0.1–0.9	50	743.6	49
Co <sub>3</sub> O <sub>4</sub> nanowires	+0.20	0.001–1.2	0.265	45.8	50
Nanoporous Co <sub>3</sub> O <sub>4</sub> nanowires	+0.60	0.005–0.57	5	300.8	51
Co <sub>3</sub> O <sub>4</sub> nanofibers	+0.59	Up to 2.04	0.97	36.25	52
Co <sub>3</sub> O <sub>4</sub> /NiCo <sub>2</sub> O <sub>4</sub> double-shelled nanocages@GO	+0.55	0.01–3.54	0.384	304	53
Cobalt oxide NP/r-GO	+0.45 (vs. SCE)	0.04–4	1.44	1.21	54
CuO <sub>x</sub> -CoO <sub>x</sub> /graphene	+0.50 (vs. SCE)	0.005–0.57	0.5	507	55
Co nanobeads/rGO	+0.55 (vs. SCE)	0.15–6.25	47.5	39.32	56
Octahedral Cu <sub>2</sub> O	+0.60	0.3–4.1	128	241	57
CuO microspheres	+0.45 (vs. SCE)	0.001–4	0.5	349.6	58
FeOOH nanowires	+0.40 (vs. SCE)	0.015–3	15	12.13 ( $\mu\text{A mM}^{-1}$ )	59
NiCo <sub>2</sub> O <sub>4</sub> hollow nanorods	+0.60	0.0003–1	0.16	1685.1	60
ZnCo <sub>2</sub> O <sub>4</sub> microrice	+0.55	0.01–0.55 0.55–2.65	5	436.1 215.1	This work

modified electrode ( $304 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ),<sup>53</sup> CuO microspheres modified electrode ( $349.6 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ),<sup>58</sup> CoOOH nanosheet arrays electrode ( $341 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ),<sup>47</sup> and FeOOH nanowires modified electrode ( $12.13 \mu\text{A mM}^{-1}$ ),<sup>59</sup> but lower than that the NiCo<sub>2</sub>O<sub>4</sub> hollow nanorods modified electrode with a sensitivity of  $1685.1 \mu\text{A mM}^{-1} \text{cm}^{-2}$ .<sup>60</sup> The performance of the as-prepared ZnCo<sub>2</sub>O<sub>4</sub>/GC electrode for glucose sensing is compared with some of recently reported glucose sensors based on Co-based and other transition metal compounds nanomaterials (Table 1).

The selectivity is also a critical factor to assess the performance of an electrochemical sensor. The common existing interferences such as ascorbic acid (AA), uric acid (UA), and dopamine (DA) in human blood serum were researched to evaluate the selectivity of ZnCo<sub>2</sub>O<sub>4</sub>/GC electrode. Fig. 4d shows amperometric response of successive addition of 200  $\mu\text{M}$  glucose, 10  $\mu\text{M}$  AA, UA, DA, 10  $\mu\text{M}$  NaCl, and 200  $\mu\text{M}$  glucose, all the interfering species exhibit negligible responses compared with glucose. The ZnCo<sub>2</sub>O<sub>4</sub>/GC electrode exhibit superior selectivity toward glucose. The reproducibility tested by parallel addition of 50  $\mu\text{M}$  glucose for 12 times, the relative standard deviation is 9.4% (Fig. 4e). The stability of the ZnCo<sub>2</sub>O<sub>4</sub>/GC was tested for 2600 s *via* continuous detection of the amperometric response, and it still retained 72% of the initial value (Fig. 4f). The above results of the ZnCo<sub>2</sub>O<sub>4</sub>/GC electrode demonstrate low detection limit, high sensitivity and good stability for glucose detection, and it may be used as non-enzymatic glucose sensor in the future.

## 4 Conclusion

A porous ZnCo<sub>2</sub>O<sub>4</sub> micro-rice like structure was synthesized from a MOF precursor calcinated at a high temperature. The as-prepared ZnCo<sub>2</sub>O<sub>4</sub> sample presented good electrocatalytic OER activity with a small overpotential ( $\eta_{10}$ ) and high stability. The excellent electrocatalytic performance of ZnCo<sub>2</sub>O<sub>4</sub> may be

attributed to the unique porous structure exposed large active sites and high conductivity of ZnCo<sub>2</sub>O<sub>4</sub>. The micro-rice porous structure assembled by nanoparticles can provide many electrocatalytic sites and high ECSA. The result should offer a new designing way to prepare low-cost and high performance electrocatalysts.

## Conflicts of interest

There are no conflicts to declare.

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