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# Single-iron, cobalt, nickel, and copper-atom catalysts for the selective reduction of oxygen to H<sub>2</sub>O<sub>2</sub>†

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The pursuit of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) production *via* two-electron electrochemical oxygen reduction reaction (ORR) is hampered by the lack of high-performance electrocatalysts. In this work, a series of single metal (*i.e.*, Fe, Co, Ni, and Cu) atom catalysts anchored into N-doped carbon nanosheets (NCNSs) are evaluated for H<sub>2</sub>O<sub>2</sub> production at pH-universal electrolytes. The catalytic performance of the samples, including current density, H<sub>2</sub>O<sub>2</sub> selectivity, turnover of frequency (TOF), and faradaic efficiency, are characterized by electrochemical measurements. The generation of H<sub>2</sub>O<sub>2</sub> is monitored by a UV-vis spectrophotometer. Among the samples, Cu/NCNSs exhibits the best catalytic performance with a ring current density of 2.15 mA cm<sup>-2</sup>, TOF of 15.8 s<sup>-1</sup> at 0.1 V vs. reversible hydrogen electrode, Tafel slope of 88 mV dec<sup>-1</sup>, and H<sub>2</sub>O<sub>2</sub> selectivity of 100% at 0.57 V in alkaline media. Importantly, the Cu/NCNSs yields H<sub>2</sub>O<sub>2</sub> selectivity of 81% at 0.05 V in acidic electrolytes. In contrast, Cu nanoparticles possess an inferior current density and much lower H<sub>2</sub>O<sub>2</sub> selectivity *via* the 4e<sup>-</sup> ORR pathway. Further quantitative analysis of H<sub>2</sub>O<sub>2</sub> demonstrates that the Cu/NCNSs catalyst has an H<sub>2</sub>O<sub>2</sub> production rate of 5.1 mol g<sub>catalyst</sub><sup>-1</sup> L<sup>-1</sup> h<sup>-1</sup> in alkaline media at 0.4 V, which is larger than those in acidic media (3.2 mol g<sub>catalyst</sub><sup>-1</sup> L<sup>-1</sup> h<sup>-1</sup>) and neutral media (2.2 mol g<sub>catalyst</sub><sup>-1</sup> L<sup>-1</sup> h<sup>-1</sup>) at -0.2 V. Such performance of Cu/NCNSs renders it as one of the best catalysts for H<sub>2</sub>O<sub>2</sub> production.

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## Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), a valuable and green oxidant, is extensively employed in chemical synthesis, wastewater treatment, paper/pulp bleaching, medical disinfection, and environmental remediation.<sup>1-5</sup> Traditionally, the industrial synthesis of H<sub>2</sub>O<sub>2</sub> relies on the energy-intensive and waste-demanding anthraquinone oxidation/reduction process.<sup>6-8</sup> In addition, the resulting high concentration of H<sub>2</sub>O<sub>2</sub> (*ca.* 70 wt%) poses safety concerns during transportation and storage.<sup>1,9</sup> Alternatively, electrochemical oxygen reduction reaction (ORR) *via* the two-electron (2e<sup>-</sup>) route (O<sub>2</sub> + \* + (H<sup>+</sup> + e<sup>-</sup>) → \*OOH; \*OOH + (H<sup>+</sup> + e<sup>-</sup>) → \* + H<sub>2</sub>O<sub>2</sub>) provides an attractive strategy to achieve on-site and small-scale H<sub>2</sub>O<sub>2</sub> production.<sup>10-12</sup> In this perspective, the selectivity of ORR

toward H<sub>2</sub>O<sub>2</sub> relies on the proper binding energy between \*OOH intermediate and the active sites of the electrocatalysts.<sup>13</sup> Additionally, preserving the O–O bond from cleavage is also a crucial step for H<sub>2</sub>O<sub>2</sub> formation.<sup>14,15</sup> However, since the 4e<sup>-</sup> counterpart toward H<sub>2</sub>O generation is a powerful competitor to the 2e<sup>-</sup> route, it is crucial to design efficient catalysts with high intrinsic selectivity and activity for H<sub>2</sub>O<sub>2</sub> formation.<sup>16,17</sup>

Thus far, state-of-the-art noble-metal-based electrocatalysts such as Pt–Hg, Pd–Hg, and Pd–Au display good catalytic activity for the 2e<sup>-</sup> process.<sup>1,6,17-20</sup> Unfortunately, the scarcity and high price of noble metals seriously limit large-scale applications.<sup>12,15</sup> The earth-abundant carbon-based materials hold great promise for H<sub>2</sub>O<sub>2</sub> electrochemical synthesis due to the high surface areas and tunable porosities, showing comparable activity to the commercial Pt catalysts in alkaline media.<sup>19</sup> Unfortunately, the carbon-based electrocatalysts always show limited activity in acidic media.<sup>21</sup>

Transition-metal (Fe, Co, Ni, *etc.*) single atom catalysts (SACs) have gained remarkable attention in the heterogeneous catalysis field due to their 100% atom efficiency, tunable electronic structure, and unsaturated coordination environments.<sup>17,22-25</sup> In principle, benefiting from the atomically dispersed metal sites of SACs, the adsorption of O<sub>2</sub> on SACs usually takes an end-on type rather than a side-on type,

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thus preventing O–O bond cleavage.<sup>13,26</sup> In particular, SACs with M–N–C moieties have attracted significant attention due to the excellent catalytic activity and selectivity for the ORR.<sup>27,28</sup> Recently, substantial efforts have been devoted to tuning the cost-effective SACs toward the  $2e^-$  ORR pathway, aiming for  $H_2O_2$  formation.<sup>6,15</sup> In detail, SACs containing M–N–C moieties have been synthesized by top-down strategies, including pyrolysis of metal–organic frameworks (MOF),<sup>29–31</sup> covalent organic frameworks (COF),<sup>32</sup> and metal–porphyrin molecules,<sup>33</sup> as well as bottom-up strategies, such as high-energy ball milling and wet-chemistry.<sup>23</sup> However, most catalysts exhibit good ORR activity in alkaline media. Unfortunately, since  $H_2O_2$  is less stable in alkaline media, electrochemical synthesis of  $H_2O_2$  in acidic and neutral media is more suitable in practical applications.<sup>13</sup> Therefore, there is a great challenge to improve the catalytic activity for  $H_2O_2$  formation in acidic or neutral media.<sup>14,34</sup>

Our group developed a universal method to fabricate SACs *via* a simple condensation–carbonization process.<sup>35,36</sup> Efforts have been devoted to evaluating the resultant SACs as electrocatalysts for the electro-oxidation of small molecules. The resulting SACs displayed excellent catalytic performance for the oxidation of water, glycerol, and 5-hydroxymethylfurfural.<sup>35</sup> Motivated by these results, we prepared a series of SACs consisting of isolated Fe, Co, Ni, and Cu atoms anchored into N-doped carbon nanosheets (NCNSs) for the selective reduction of  $O_2$  into  $H_2O_2$  in this work. The catalytic performance of the catalysts was comparatively investigated in alkaline, neutral, and acidic electrolytes. It is demonstrated that the as-prepared Cu/NCNSs displays excellent performance with nearly 100%  $H_2O_2$  selectivity, turnover of frequency (TOF) of  $15.8\text{ s}^{-1}$  at 0.1 V, and  $H_2O_2$  yield rate of  $5.1\text{ mol g}_{\text{catalyst}}^{-1}\text{ L}^{-1}\text{ h}^{-1}$  at 0.4 V in alkaline media.

## Experimental

### Synthesis of single metal (Fe, Co, Ni, and Cu) atom catalysts

SACs were synthesized *via* the authors' previous work with slight modifications.<sup>35</sup> In a typical synthesis, 0.4 g of polystyrene (PS) nanospheres and 0.2 g of SDBS were scattered in 2 mL anhydrous ethanol and 7.6 mL ultrapure water. 2 mL cyanamide and 1 mL furfural were introduced into the emulsion and reacted at 60 °C for 24 h under magnetic stirring. Then, a specific volume of metal solutions ( $10\text{ g L}^{-1}$  of  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Cu(NO_3)_2 \cdot 3H_2O$ , and  $Ni(NO_3)_2 \cdot 6H_2O$ ) were added, mixed, and stirred for at least 2 days. Subsequently, the resulting suspension was evaporated to remove water and ethanol. Finally, the resulting paste was pyrolyzed at 900 °C for 3 h under a flowing nitrogen atmosphere in a tube furnace. The resulting powder was ground with an agate mortar and washed with a solution of 0.5 M  $FeCl_3 + 2\text{ M HCl}$  at 50 °C to remove any metal particles. For comparison, nitrogen-doped carbon, free of any metal, was also prepared. The resultant catalysts were denoted as Fe/NCNSs, Co/NCNSs, Ni/NCNSs, Cu/NCNSs, and NCNSs.

### Electrochemical measurements

Electrochemical measurements were performed on a Solartron Analytical electrochemical station (1470 E, England) with a typical three-electrode configuration consisting of a rotating-ring-disk working electrode (SEN-RRDE, China), a carbon-rod counter electrode, and a Hg/HgO reference electrode in alkaline electrolytes or a saturated calomel electrode (SCE) as a reference electrode in acidic/neutral electrolytes. The rotating-ring-disk electrode (RRDE) assembly was comprised of a glassy carbon disk electrode ( $disk_{OD} = 5\text{ mm}$ ) and a Pt ring ( $ring_{OD} = 7.5\text{ mm}$ ,  $ring_{ID} = 5.5\text{ mm}$ ), with a theoretical collection efficiency of 0.37. Experimentally, the collection efficiency ( $N$ ) was determined by the ferrocyanide/ferricyanide redox couple.<sup>13,28</sup> The potentiodynamic curve was recorded between 0.1–1.2 V on the glassy carbon disk electrode, and the potentiostatic curve was recorded at 0.95 V on the platinum ring electrode in 10 mM  $K_3[Fe(CN)_6] + 1\text{ M KCl}$  solution at a scan rate of  $10\text{ mV s}^{-1}$  and a rotation rate between 400 and 2500 rpm. The collection efficiency refers to the ratio of the ring current to the absolute value of the disk current.

To prepare a working electrode, typically, 2.0 mg of the as-prepared M/NCNS catalysts were dispersed in 249  $\mu\text{L}$  of ethanol, 249  $\mu\text{L}$  of deionized water, 497  $\mu\text{L}$  of isopropyl alcohol, and 5  $\mu\text{L}$  of Nafion solution (5 wt%), and ultrasonicated for 2 h to form a homogeneous catalyst ink. 10  $\mu\text{L}$  of catalyst ink (catalyst loading: *ca.*  $102\text{ }\mu\text{g cm}^{-2}$ ) was pipetted onto the freshly polished disk electrode and dried at room temperature.  $N_2$ - or  $O_2$ -saturated 0.1 M KOH, 0.1 M  $HClO_4$ , and 0.1 M PBS served as alkaline, acidic, and neutral electrolytes, respectively. 0.1 M KOH (pH = 13.0) was prepared by dissolving 5.61 g electron-grade potassium hydroxide in 1 L of deionized water. 0.1 M  $HClO_4$  (pH = 1.0) was prepared by diluting 70% perchloric acid with deionized water. 0.1 M PBS (pH = 7.0) was prepared by dissolving 80 g sodium chloride, 2 g potassium chloride, 14.4 g disodium hydrogen phosphate, and 2.4 g potassium dihydrogen phosphate with deionized water. All the electrode potentials reported in this work are referenced to the reversible hydrogen electrode (RHE) as follows:  $E_{RHE} = E_{Hg/HgO} + 0.0592 \times \text{pH} + 0.098$ ,  $E_{RHE} = E_{SCE} + 0.0592 \times \text{pH} + 0.241$ .

Cyclic voltammetry (CV) curves were recorded in the potential range of 0–1.6 V at  $50\text{ mV s}^{-1}$  under static conditions. The polarization curves of RRDE were recorded in  $O_2$ -saturated electrolyte solutions at a scan rate of  $10\text{ mV s}^{-1}$  under 1600 rpm, and the potentiostatic curves of the Pt ring were recorded at 1.20 V for the oxidation of  $H_2O_2$ . The onset potentials are defined as the potentials required to reach a geometric current density of  $-0.05\text{ mA cm}^{-2}$  and  $0.02\text{ mA cm}^{-2}$  for the disk and ring electrodes, respectively.<sup>32</sup> The selectivity of  $H_2O_2$  and electron transfer number ( $n$ ) were calculated according to eqn (1)<sup>13,29</sup> and (2).<sup>13,18</sup>

$$H_2O_2 (\%) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \quad (1)$$

$$n = \frac{4 \times I_d}{I_d + I_r/N} \quad (2)$$

where  $I_r$  is the ring current,  $I_d$  is the disk current, and  $N$  is the calibrated collection efficiency of RRDE (0.35). The  $\text{H}_2\text{O}_2$  current density ( $J_{\text{H}_2\text{O}_2}$ ) and  $\text{H}_2\text{O}_2$  faradaic efficiency (FE) were calculated using eqn (3)<sup>32</sup> and (4).<sup>37</sup>

$$J_{\text{H}_2\text{O}_2} = I_r / (N \times A_{\text{geom}}) \quad (3)$$

$$\text{FE} (\%) = \frac{\% \text{H}_2\text{O}_2 / 100}{2 - \% \text{H}_2\text{O}_2 / 100} \quad (4)$$

where  $A_{\text{geom}}$  is the surface area of the Pt ring and  $\% (\text{H}_2\text{O}_2)$  is  $\text{H}_2\text{O}_2$  selectivity. The kinetic current density ( $J_k$ ) was calculated using Koutecky–Levich eqn (5)–(8).<sup>29,31</sup>

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_L} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}} \quad (5)$$

$$\omega = 2\pi N \quad (6)$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6} \quad (7)$$

$$J_k = \frac{J_L \times J}{J_L - J} \quad (8)$$

where  $J$  is the apparent current density,  $J_k$  and  $J_L$  are the kinetic and diffusion-limited current densities,  $\omega$  is the angular velocity,  $N$  is the rotation rate,  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $C_0$  is the saturation concentration of  $\text{O}_2$ ,  $D_0$  is the diffusion coefficient of  $\text{O}_2$ , and  $\nu$  is the kinematic viscosity of the electrolyte. The TOF was calculated by eqn (9)<sup>32</sup>

$$\text{TOF} = \frac{J_k \times \text{H}_2\text{O}_2\% \times A_{\text{disk}}}{n \times m \times w \times F/M_w} \quad (9)$$

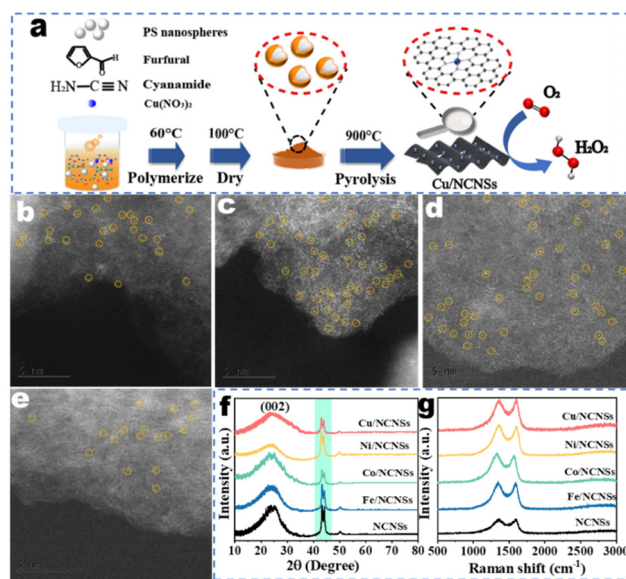
where  $A_{\text{disk}}$  is the geometric surface area of the disk electrode,  $n$  is the electron transfer number of ORR,  $m$  is the mass of the catalyst loading on the disk electrode,  $w$  is the metal content, and  $M_w$  is the molecular weight of the metal.

For the long-term stability test, the potentiostatic curves were recorded at 0.4 V (in alkaline media) and  $-0.2$  V (in acidic and neutral media) for 10 h. The ORR activity was tested after the stability test.  $\text{H}_2\text{O}_2$  production was conducted using a customized H-cell electrolyzer separated by Nafion membranes. A carbon paper ( $1 \times 1 \text{ cm}$ ) loaded with  $100 \mu\text{g cm}^{-2}$  of the catalyst was employed as the ORR cathode, and a carbon rod was employed as the anode. The concentration of  $\text{H}_2\text{O}_2$  was quantified by UV-vis spectrophotometer<sup>38</sup> (Shimadzu UV-1900, Japan).

## Results and discussion

### Structural characterization

The synthetic process of the M/NCNSs catalysts is shown in Fig. 1a. Furfural and cyanamide were polymerized in the presence of PS nanospheres. PS nanospheres served as templates to provide a large surface area. The metal contents in the samples were determined by ICP-AES, as shown in Table S1.† The TEM micrograph of the Co/NCNSs catalyst appears as aggregates of nanosheets without obvious metal nanoparticles



**Fig. 1** The synthetic process of M/NCNSs (a), high-resolution HAADF-STEM images of Fe/NCNSs (b), Co/NCNSs (c), Ni/NCNSs (d), and Cu/NCNSs (e), XRD patterns (f) and Raman spectra (g) of the as-synthesized samples.

(Fig. S1a†). The high-resolution TEM image in Fig. S1b† also confirms the layered structure of the as-prepared Co/NCNSs catalyst. The energy dispersive X-ray (EDX) mapping images indicate that C, N, and Co atoms are uniformly distributed on the NCNSs support (Fig. S1c†). The isolated single Fe (Fig. 1b), Co (Fig. 1c), Ni (Fig. 1d), and Cu (Fig. 1e) sites on the NCNSs are shown as bright dots and highlighted by yellow circles in the aberration-corrected HAADF-STEM images. To determine the crystal structure of the M/NCNSs catalysts, XRD patterns were performed. As shown in Fig. 1f, the five catalysts exhibit similar characteristic diffraction peaks at  $25^\circ$ ,  $43.4^\circ$ , and  $44.2^\circ$ , corresponding to the carbon (002), (103), and (111) planes. No diffraction peaks of metals, metal oxides, and metal nitrides were detected. The Raman spectra exhibited the characteristic D-band and G-band peaks of carbon materials at  $1350 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  for the M/NCNSs catalysts, demonstrating the formation of NCNSs (Fig. 1g). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution of samples were determined as shown in Fig. S2–S6.† The BET surface areas of Fe/NCNSs, Co/NCNSs, Ni/NCNSs, Cu/NCNSs, and NCNSs are calculated to be 389.6, 498.8, 636.0, 436.8, and  $465.0 \text{ m}^2 \text{ g}^{-1}$ , respectively, based on the corresponding  $\text{N}_2$  adsorption–desorption isotherms. The large BET values are attributed to the presence of a number of mesopores and the sheet-like structure of N-doped carbon. Besides, the average pore sizes of the samples are between 3.3 and 4.1 nm. The abundant mesoporous pores are conducive to the dispersion of metal atoms. The presence of single copper atoms in the samples was further verified by X-ray absorption near edge structure analyses, and the average coordination number is 4.8 for the  $\text{Cu-N}_x$  species.<sup>36</sup>

### CV characterization

To verify the ORR activity of the as-prepared M-NCNSs catalysts, CV curves were tested in O<sub>2</sub>-saturated and N<sub>2</sub>-saturated 0.1 M KOH, as shown in Fig. S7†. Under the O<sub>2</sub> atmosphere, similar broad reduction peaks of O<sub>2</sub> are noted at about 0.60 V, 0.60 V, 0.58 V, and 0.48 V for Co/NCNSs, Ni/NCNSs, Cu/NCNSs, and NCNSs, respectively. Notably, there are no obvious peaks associated with the redox of the metal particles, which is consistent with the XRD patterns and further indicative of samples free of metal nanoparticles. In addition, CV curves were also recorded in O<sub>2</sub>/N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> and 0.1 M PBS solutions (see Fig. S8 and S9†). Compared with Fe/NCNSs and NCNSs, the Co/NCNSs, Ni/NCNSs, and Cu/NCNSs catalysts have more pronounced currents of O<sub>2</sub> reduction in acidic and neutral media, indicating the excellent ORR electrocatalytic activities. It should be noted that the currents of glassy carbon disk electrode are close to 0 in 0.1 M KOH, HClO<sub>4</sub>, and PBS solutions, which is consistent with its negligible double layer capacitances (see Fig. S10†). In contrast, Cu nanoparticles (Cu NPs) have distinctive redox peaks of metallic copper and show limited currents of oxygen reduction under alkaline, acidic, and neutral conditions, which indicates that Cu NPs have poor ORR catalytic activity in a broad pH range (see Fig. S11†).

### RRDE characterization

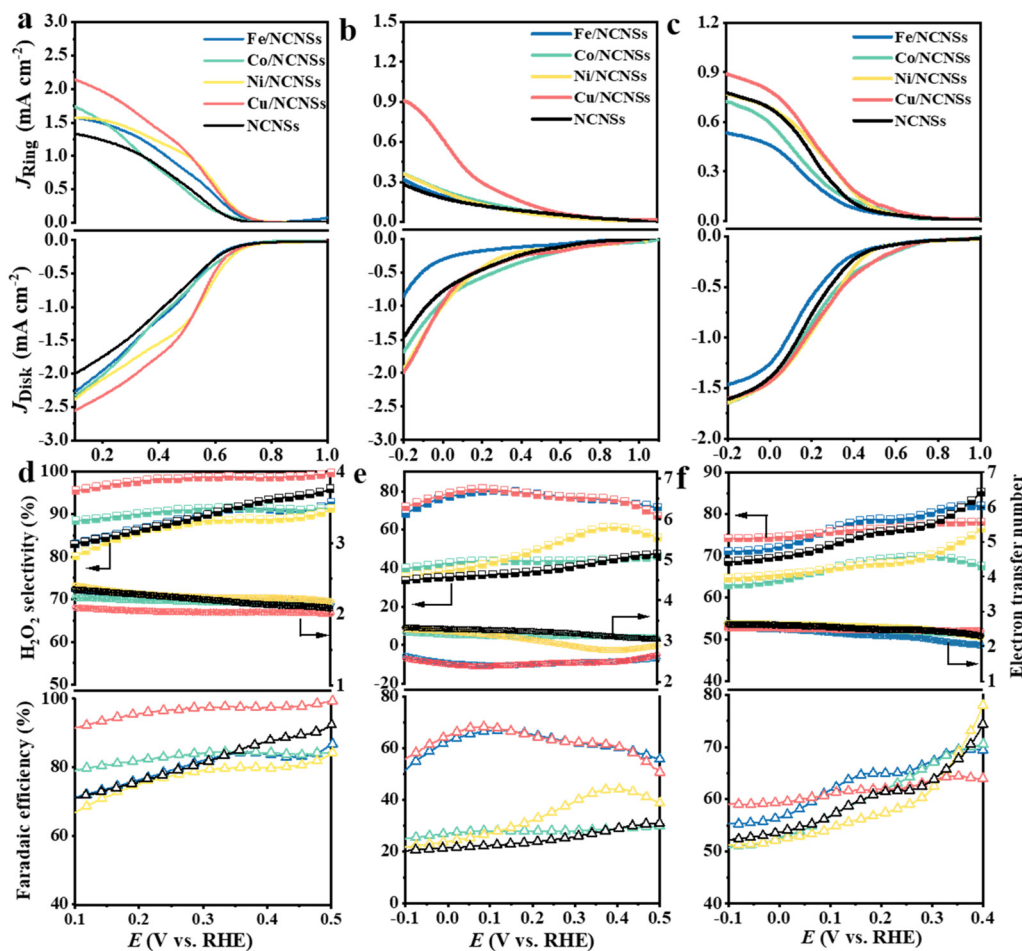
The collection efficiency of RRDE was first calibrated. Fig. S12a† shows the polarization curves of Fe<sup>2+</sup>/Fe<sup>3+</sup> on the RRDE recorded in potassium ferricyanide solutions at rotation rates of 400–2500 rpm. The reduction of Fe<sup>3+</sup> occurs on the disk electrode, while the oxidation of Fe<sup>2+</sup> occurs on the Pt ring electrode. The ratio between ring and disk currents is estimated as 0.35 (see Fig. S12b†). The ORR performances of the M/NCNSs catalysts were evaluated by polarization curves in O<sub>2</sub>-saturated 0.1 M electrolyte on RRDE at 1600 rpm. Since the ORR on the disk electrode occurs simultaneously with the H<sub>2</sub>O<sub>2</sub> oxidation reaction (H<sub>2</sub>O<sub>2</sub>OR) on the ring electrode, the current densities on the ring and disk electrode are generated synchronously. Table S2† summarizes the onset potentials of the M/NCNSs catalysts in 0.1 M KOH, HClO<sub>4</sub>, and PBS solutions. As displayed in Fig. 2a, the Ni/NCNSs catalyst shows the most positive onset potential of 0.77 V on both disk and ring electrodes, indicating its excellent ORR catalytic activity. The Cu/NCNSs catalyst exhibits the highest ORR current density of 2.6 mA cm<sup>-2</sup> at 0.1 V with an onset potential of 0.75 V and the highest H<sub>2</sub>O<sub>2</sub>OR current density of 2.2 mA cm<sup>-2</sup> at 0.1 V with an onset potential of 0.76 V. In contrast, the NCNSs catalyst exhibits limited ORR current density (1.9 mA cm<sup>-2</sup> at 0.1 V) and H<sub>2</sub>O<sub>2</sub>OR current density (1.3 mA cm<sup>-2</sup> at 0.1 V) compared to the M/NCNSs catalysts, implying a critical role of single metal atoms for the ORR catalytic activity in alkaline media.

The corresponding H<sub>2</sub>O<sub>2</sub> selectivity, electron transfer number, and FE were plotted as a function of potential (see Fig. 2d). As expected, the Cu/NCNSs catalyst possesses the highest H<sub>2</sub>O<sub>2</sub> selectivity of over 96% in the potential range of 0.1–0.6 V. Especially, H<sub>2</sub>O<sub>2</sub> selectivity reaches 100% over the

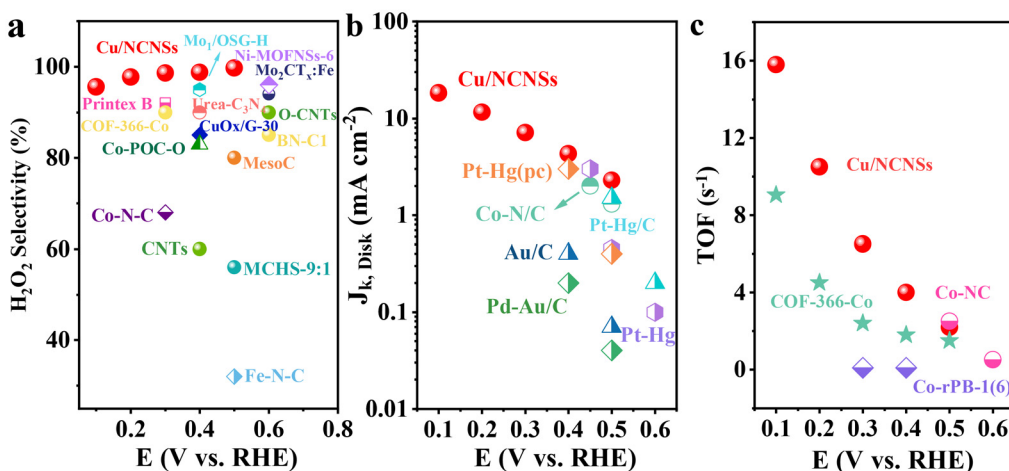
Cu/NCNSs catalyst at 0.57 V, which is superior to most of the electrocatalysts reported in previous studies, such as Mo<sub>1</sub>/OSG-H (*ca.* 95%),<sup>39</sup> O-CNTs (*ca.* 90%),<sup>40</sup> Co-POC-O (*ca.* 85.6%),<sup>41</sup> Mo<sub>2</sub>CT<sub>x</sub>:Fe (*ca.* 67–100%),<sup>42</sup> CuO<sub>x</sub>/G-30 (*ca.* 76–84%),<sup>43</sup> COF-366-Co (*ca.* 90%),<sup>32</sup> and Co-N-C (*ca.* 60–70%)<sup>30</sup> (see Fig. 3a and Table S3†). In detail, the selectivity for H<sub>2</sub>O<sub>2</sub> generation follows the order of Cu/NCNSs (96%) > Co/NCNSs (88%) > Fe/NCNSs (83%) > NCNSs (82%) > Ni/NCNSs (80%) at 0.1 V. Although the NCNSs catalyst is highly selective (>82%) for H<sub>2</sub>O<sub>2</sub>, its ORR catalytic activity is much poorer than the M/NCNSs catalysts. In addition, the electron transfer number of Cu/NCNSs is close to 2, agreeing well with its H<sub>2</sub>O<sub>2</sub> selectivity to nearly 100%. The FE of Cu/NCNSs is higher than 92% in a potential range of 0.1–0.6 V. Overall, all of the M/NCNSs catalysts exhibit excellent H<sub>2</sub>O<sub>2</sub> selectivity, and the Cu/NCNSs catalyst is the most superior candidate due to its excellent ORR activity and high H<sub>2</sub>O<sub>2</sub> selectivity.

To further explore the unique ORR catalytic activity of the M-NCNSs catalysts, the polarization curves were also tested in acidic and neutral media. In Fig. 2b, both Cu/NCNSs and Ni/NCNSs show the highest disk current density of 1.9 mA cm<sup>-2</sup> at -0.2 V. In contrast, Cu/NCNSs has a more positive onset potential of 0.76 V, indicating the Cu/NCNSs catalyst possesses better ORR catalytic activity. For comparison, the ring current density at -0.2 V follows the order of NCNSs (0.28 mA cm<sup>-2</sup>) < Fe/NCNSs (0.31 mA cm<sup>-2</sup>) < Ni/NCNSs (0.36 mA cm<sup>-2</sup>) ≈ Co/NCNSs (0.36 mA cm<sup>-2</sup>) < Cu/NCNSs (0.9 mA cm<sup>-2</sup>), implying that introduction of Fe, Co, Cu, and Ni single atom facilitates the production of H<sub>2</sub>O<sub>2</sub> in acidic media. As shown in Fig. 2e, although Fe/NCNSs and Cu/NCNSs show similar H<sub>2</sub>O<sub>2</sub> selectivity (>70%) in the potential range of -0.1 to 0.5 V, the ORR and H<sub>2</sub>O<sub>2</sub>RR activities of Fe/NCNSs are much poorer than Cu/NCNSs. Especially, the selectivity of the Cu/NCNSs can reach 81% at 0.05 V, and the corresponding electron transfer number is calculated to be 2.3, confirming the dominant 2e<sup>-</sup> ORR pathway over Cu/NCNSs in acidic media. Such selectivity is superior to most catalysts in acidic media<sup>20,30,40,44–47</sup> (Table S4†). In contrast, the NCNSs, Co/NCNSs, and Ni/NCNSs catalysts show an inferior selectivity of about 40% and a large electron transfer number of around 3.0, indicative of the ORR through both 4e<sup>-</sup> and 2e<sup>-</sup> pathways. Besides, the FE of H<sub>2</sub>O<sub>2</sub> production has a similar trend with selectivity. The Cu/NCNSs possesses the highest FE of 68% between 0.06 V and 0.09 V. Generally, Cu/NCNSs catalyst displays the advantages of a promising candidate in acidic media with the highest ring current density, the most positive onset potential (0.82 V) on ring electrode, and the highest selectivity (81%) for the 2e<sup>-</sup> ORR route.

Under neutral conditions, Co/NCNSs, Ni/NCNSs, Cu/NCNSs, and NCNSs exhibit the same ORR current density of 1.6 mA cm<sup>-2</sup> at -0.2 V, whereas Fe/NCNSs exhibit apparently poor ORR activity with the lowest ORR current density of 1.4 mA cm<sup>-2</sup> at -0.2 V and the most negative onset potential of 0.7 V (Fig. 2c). In addition, the ring current density corresponding to the oxidation of H<sub>2</sub>O<sub>2</sub> at -0.2 V follows the order of Fe/NCNSs (0.53 mA cm<sup>-2</sup>) < Co/NCNSs (0.71 mA cm<sup>-2</sup>) <



**Fig. 2** Electrochemical activity of catalysts collected from RRDE system in  $O_2$ -saturated alkaline, acidic, and neutral media. Potentiostatic curves on the Pt ring electrode and potentiodynamic curves on the glassy carbon disk electrode at 1600 rpm in  $O_2$ -saturated 0.1 M KOH (a), 0.1 M HClO<sub>4</sub> (b), and 0.1 M PBS (c); selectivity, electron transfer number, and faradaic efficiency of  $H_2O_2$  production in  $O_2$ -saturated 0.1 M KOH (d), 0.1 M HClO<sub>4</sub> (e), and 0.1 M PBS (f).



**Fig. 3**  $H_2O_2$  selectivity (a),  $J_k$  (b) and TOF (c) of Cu/NCNSs and other electrocatalysts reported in recent studies in alkaline media. Data adapted from: Au/C and Pd-Au/C ref. 52, Pt-Hg, Pt-Hg (pc) and Pt-Hg/C ref. 20, Co-N/C (heat-treated cobalt-porphyrin supported on vapor grown) ref. 53, Co-NC ref. 13, COF-366-Co ref. 32, Co-rPB-1(6) ref. 50 and ref. in Table S3 (see ESI†) for the comparison of  $H_2O_2$  selectivity in alkaline media.

NCNSs  $\approx$  Ni/NCNSs ( $0.77 \text{ mA cm}^{-2}$ ) < Cu/NCNSs ( $0.89 \text{ mA cm}^{-2}$ ), implying Fe/NCNSs and Co/NCNSs are less effective for the  $2e^-$  ORR route in neutral media compared to the Ni/NCNSs and Cu/NCNSs. The  $\text{H}_2\text{O}_2$  selectivity, together with the FE, follows the order of Fe/NCNSs > Cu/NCNSs > NCNSs > Co/NCNSs > Ni/NCNSs at 0.2 V (see Fig. 2f), while the electron transfer number follows the opposite trend. Among the samples, the Cu/NCNSs catalyst is the most favorable catalyst for the  $2e^-$  ORR pathway in neutral media with a ring current density of  $0.89 \text{ mA cm}^{-2}$ , a positive onset potential of 0.77 V, and an  $\text{H}_2\text{O}_2$  selectivity of 76%, which outperformed most of the ORR electrocatalysts reported in the literature<sup>30,39,44,48–51</sup> (Table S5<sup>†</sup>).

To investigate the intrinsic ORR activity of the samples, the electrochemical active surface area (ECSA) was estimated by electrochemical double-layer capacitance ( $C_{\text{dl}}$ ). Fig. S13–S15<sup>†</sup> show CV curves of the M/NCNSs catalysts recorded at varying scan rates in alkaline, acidic, and neutral media, respectively. As shown in Fig. S16<sup>†</sup>, the Cu/NCNSs catalyst has the largest  $C_{\text{dl}}$  values of 2.61, 8.13, and  $5.35 \text{ mF cm}^{-2}$  in alkaline, acidic, and neutral media, respectively, contributing to its superior  $2e^-$  ORR catalytic activity at pH-universal electrolytes.

Additionally, the ORR performance of the bare glassy carbon disk electrode, Cu NPs, and Cu/NCNSs was also evalu-

ated for comparison in alkaline, acidic, and neutral media. The polarization curves are displayed in Fig. S17.<sup>†</sup> Cu NPs exhibit inferior ORR and  $\text{H}_2\text{O}_2\text{OR}$  activity and the most negative onset potential in 0.1 M KOH,  $\text{HClO}_4$ , and PBS compared with Cu/NCNSs (Table S2<sup>†</sup>), indicating the predominant  $4e^-$  ORR route of Cu NPs. The corresponding  $\text{H}_2\text{O}_2$  selectivity and electron transfer number were also calculated in Fig. S18.<sup>†</sup> Cu NPs show a much lower  $\text{H}_2\text{O}_2$  selectivity of 60–77% in alkaline solutions, 20–55% in acidic solutions, and >40% in neutral solutions and a much larger electron transfer number in the range of 3–4 compared with the Cu/NCNSs catalyst.

### ORR kinetics analysis

To investigate the ORR kinetics of the M/NCNSs catalysts, Koutecky–Levich (K–L) analysis was carried out on the RRDE. The Cu/NCNSs catalyst is evaluated by polarization curves at different rotation rates between 400 and 2500 rpm in alkaline, acidic, and neutral media (see Fig. 4a–c). With increasing rotating rate, the current density increases gradually, indicating the high dependence of ORR on oxygen diffusion.<sup>37</sup> As shown in Fig. 4d–f, the K–L plots are obtained by fitting  $J_{\text{k}}^{-1}$  and  $\omega^{-1/2}$  according to eqn (5)–(7), where the slopes correspond to  $1/B$ . It can be seen that these fitted K–L plots (the yellow part) are nearly parallel (*i.e.*, the electron transfer numbers are almost

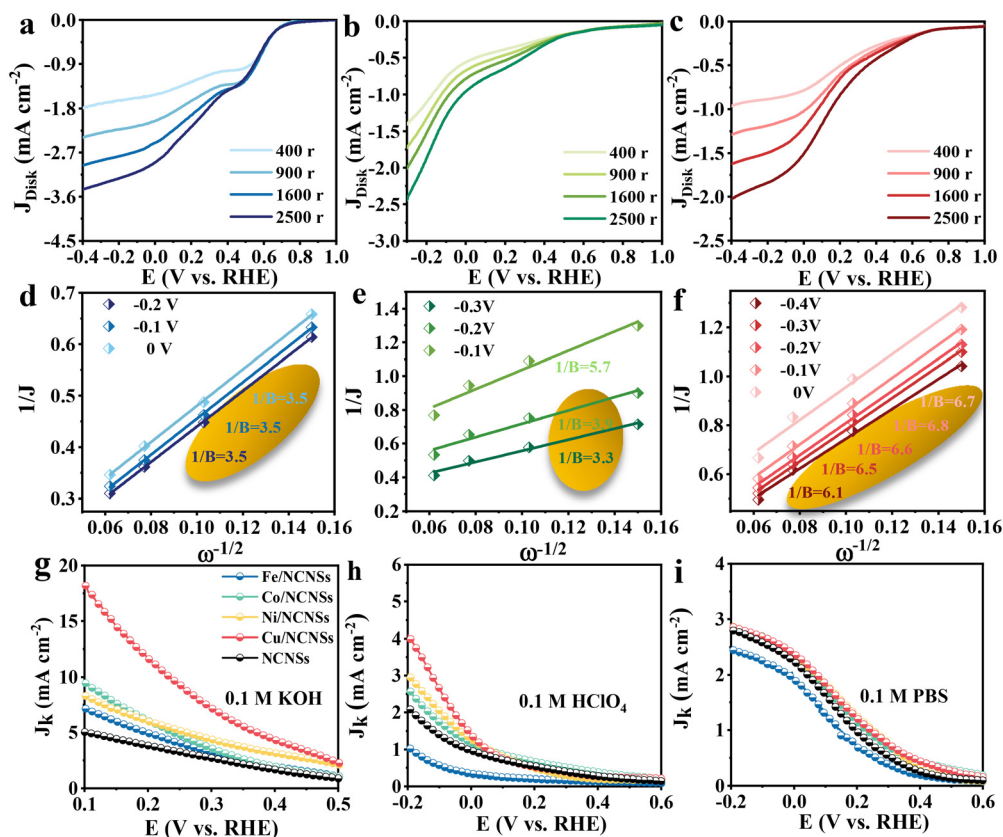


Fig. 4 Disk polarization curves of the Cu/NCNSs recorded in  $\text{O}_2$ -saturated 0.1 M KOH (a), 0.1 M  $\text{HClO}_4$  solution (b) and 0.1 M PBS (c) at rotation rates between 400–2500 rpm, the corresponding K–L plots at different potentials in  $\text{O}_2$ -saturated 0.1 M KOH (d), 0.1 M  $\text{HClO}_4$  (e) and 0.1 M PBS (f), and  $J_{\text{k}}$  values of the catalysts at 1600 rpm in 0.1 M KOH (g), 0.1 M  $\text{HClO}_4$  (h) and 0.1 M PBS (i).

the same under these potentials), which indicates that ORR has reached the limited current density at the potentials and that the reaction process is controlled by the diffusion effect. Besides, the polarization curves and the corresponding K-L plots of Fe/NCNSs, Co/NCNSs, Ni/NCNSs, and NCNSs also show the same ORR phenomenon (Fig. S19–S22†).  $J_k$  values

over the catalysts at 1600 rpm were calculated according to eqn (8), as shown in Fig. 4g–i and Table S6.† It can be found that the  $J_k$  trend toward ORR is consistent with the disk current density. The  $J_k$  values of the M-NCNSs catalysts at 0.1 V were compared. As displayed in Fig. 5a, the Cu/NCNSs catalyst has the highest  $J_k$  of 18.2 mA cm<sup>-2</sup> in alkaline media, which is far superior to its competitors in this study as well as state-of-the-art catalysts (Fig. 3b). Moreover, the Cu/NCNSs catalyst also exhibits a larger  $J_k$  of 1.8 mA cm<sup>-2</sup> at 0.1 V in neutral media. In addition, the  $J_k$  values of the M/NCNSs catalysts in acidic media are smaller than that in alkaline and neutral solutions. These results show that the ORR catalytic activity over the M/NCNSs catalysts is constrained in acidic media.

To further elucidate the ORR kinetics of M/NCNSs, the TOF values were calculated according to eqn (9), as shown in Tables S7 and S8.† The Cu/NCNSs catalyst has the highest TOF of 15.8 s<sup>-1</sup> at 0.1 V in KOH media among the M/NCNSs catalysts (Fig. 5b), which is comparable to state-of-the-art catalysts (Fig. 3c). In addition, the activity of Co/NCNSs and Cu/NCNSs catalysts are also prominent, with TOF values of 1.1 and 1.0 s<sup>-1</sup> at 0.1 V in neutral media, respectively. Moreover, the Tafel slope also reflects the kinetic characteristics of the electrochemical reaction. As shown in Fig. 5c and d, the Tafel slopes of the ring electrode are generally smaller than that of the disk electrode. The superior kinetic of H<sub>2</sub>O<sub>2</sub> production over the Cu/NCNSs catalyst is revealed by the smallest Tafel slope of 88 mV dec<sup>-1</sup> on the ring electrode. The ORR kinetic in alkaline media is faster than in acidic and neutral media (Fig. S23†). It is worth noting that the Cu/NCNSs catalyst possesses superior  $J_k$ , TOF, and Tafel slope values that contribute to its superior 2e<sup>-</sup> ORR catalytic activity.

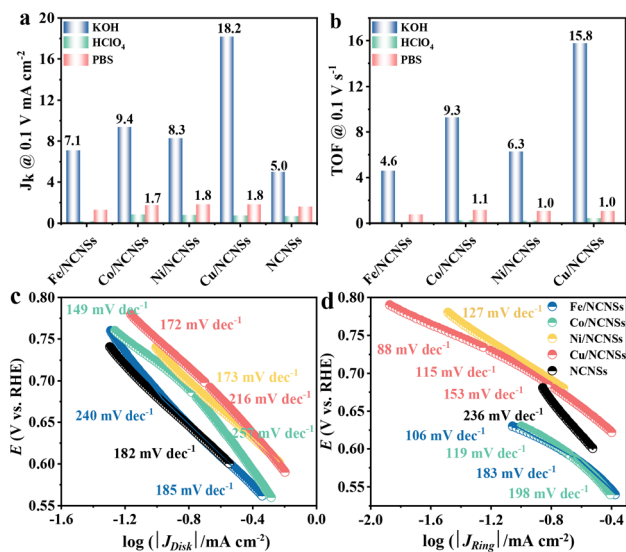


Fig. 5 Comparison of the  $J_k$  (a) and TOF (b) values of the catalysts at 0.1 V in 0.1 M KOH, HClO<sub>4</sub>, and PBS media. Tafel plots of the disk current density (c) and ring current density (d) at a rotating rate of 1600 rpm in the O<sub>2</sub>-saturated 0.1 M KOH media.

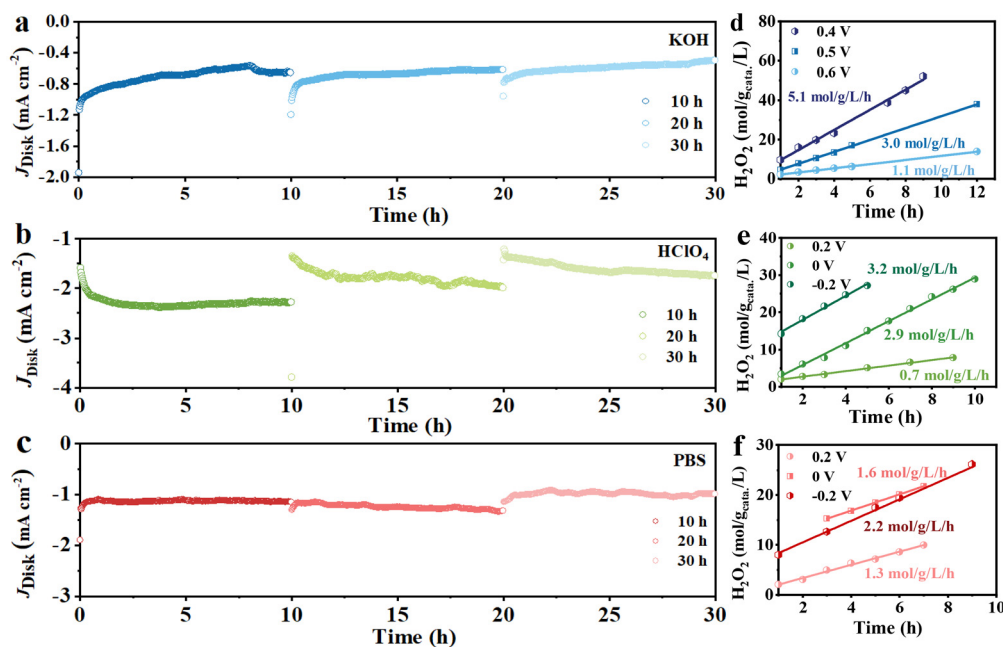


Fig. 6 Potentiostatic stability tests in 0.1 M KOH (a), 0.1 M HClO<sub>4</sub> (b) and 0.1 M PBS (c), H<sub>2</sub>O<sub>2</sub> yield rates of Cu/NCNSs obtained from different potentials in 0.1 M KOH (d), HClO<sub>4</sub> (e) and PBS (f).

## Stability and H<sub>2</sub>O<sub>2</sub> yield rates

The long-term stability of the Cu/NCNSs catalyst was investigated on the RRDE at 1600 rpm in O<sub>2</sub>-saturated 0.1 M KOH (0 V), HClO<sub>4</sub> (−0.2 V), and PBS (−0.2 V) solutions. As shown in Fig. 6a–c, the disk currents gradually level off and remain steady for 10 h in alkaline, acidic, and neutral media. After the test was suspended, the polarization curves were recorded, and the corresponding H<sub>2</sub>O<sub>2</sub> selectivity was calculated (Fig. S24†). When the test is resumed, the disk currents in the alkaline and neutral solutions return to the initial values, while the disk currents in the acidic solution decrease. Moreover, the H<sub>2</sub>O<sub>2</sub> selectivity remains ≥90%, ≥40%, and 70% for 20 h without obvious decay in alkaline, acidic, and neutral media, respectively. H<sub>2</sub>O<sub>2</sub> formation was performed in an H-cell electrolyzer, where the Cu/NCNSs catalyst was cast onto a carbon paper (100 μg cm<sup>−2</sup> catalyst loading), with potentiostatic curves conducted at different potentials. The UV spectrum of H<sub>2</sub>O<sub>2</sub> reveals a characteristic absorption peak at 400 nm (see Fig. S25a†), and the standard curve of H<sub>2</sub>O<sub>2</sub> concentration vs. absorbance is established (see Fig. S25b†). As shown in Fig. 6d–f, the slopes correspond to H<sub>2</sub>O<sub>2</sub> yield rates. The highest H<sub>2</sub>O<sub>2</sub> yield rate of 5.1 mol g<sub>catalyst</sub><sup>−1</sup> L<sup>−1</sup> h<sup>−1</sup> is obtained in 0.1 M KOH at 0.4 V, which is larger than those in 0.1 M HClO<sub>4</sub> (3.2 mol g<sub>catalyst</sub><sup>−1</sup> L<sup>−1</sup> h<sup>−1</sup>) and 0.1 M PBS (2.2 mol g<sub>catalyst</sub><sup>−1</sup> L<sup>−1</sup> h<sup>−1</sup>) at −0.2 V, suggesting that the pH of the electrolyte has a significant effect on the production of H<sub>2</sub>O<sub>2</sub>. In addition, the H<sub>2</sub>O<sub>2</sub> yield rates in 0.1 M KOH at 0, 0.2, and 0.3 V were calculated to be 3.5, 4.5, and 4.1 mol g<sub>catalyst</sub><sup>−1</sup> L<sup>−1</sup> h<sup>−1</sup>, respectively (see Table S9†).

## Conclusions

In summary, a series of SACs consisting of isolated Fe, Co, Ni, and Cu atoms supported by NCNSs were synthesized for the electro-reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. Electrochemical measurements reveal that the M/NCNSs catalysts generally have larger ORR and H<sub>2</sub>O<sub>2</sub>OR current densities compared with the pure NCNSs. Among them, the Cu/NCNSs catalyst displays the highest catalytic activity with a ring current density of 2.2 mA cm<sup>−2</sup>, J<sub>k</sub> value of 18.2 mA cm<sup>−2</sup>, TOF value of 15.8 s<sup>−1</sup> at 0.1 V, Tafel slope of 88 mV dec<sup>−1</sup>, and H<sub>2</sub>O<sub>2</sub> selectivity of nearly 100%. Especially, remarkable H<sub>2</sub>O<sub>2</sub> selectivity of 81% and 76% were obtained under acidic (pH 1.0) and neutral conditions (pH 7.0), respectively. However, the 4e<sup>−</sup> ORR mechanism plays a more prominent role in Cu NPs. Under pH-universal electrolytes, Cu NPs have inferior ORR activity, H<sub>2</sub>O<sub>2</sub> selectivity, and the most negative onset potential compared with Cu/NCNSs, indicating the unique ORR catalytic activity of SACs. The Cu/NCNSs shows excellent long-term stability for H<sub>2</sub>O<sub>2</sub> production. In addition, the Cu/NCNSs possesses an H<sub>2</sub>O<sub>2</sub> yield rate of 5.1 mol g<sub>catalyst</sub><sup>−1</sup> L<sup>−1</sup> h<sup>−1</sup> at 0.4 V in alkaline media, followed by that in acidic media (3.2 mol g<sub>catalyst</sub><sup>−1</sup> L<sup>−1</sup> h<sup>−1</sup>) and neutral media (2.2 mol g<sub>catalyst</sub><sup>−1</sup> L<sup>−1</sup> h<sup>−1</sup>) at −0.2 V. By virtue of the low-cost and outstanding performance, the Cu/NCNSs catalyst holds excellent promise for on-site and high-efficiency H<sub>2</sub>O<sub>2</sub> production.

## Author contributions

Cuizhu Ye: conceptualization, data curation, writing, original draft preparation. Yongfang Zhou and Hongying Li: methodology. Yi Shen: methodology, conceptualization, supervision, funding acquisition, and reviewing.

## Conflicts of interest

There are no conflicts to declare.

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