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Carbon-black-coupled bimetallic CoCu-ZIF composites for monohydroxylated polycyclic aromatic hydrocarbon metabolite sensing



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Polycyclic aromatic hydrocarbons are hazardous, carcinogenic pollutants produced by the incomplete combustion of organic materials, and their detection remains a technological challenge. Here, we develop bimetallic cobalt-and-copper-based zeolitic imidazolate framework (CoCu-ZIF) particles coupled with carbon black (CB) for highly sensitive and selective electrochemical sensing of 2-Naphthol, a monohydroxylated polycyclic aromatic hydrocarbon. The CoCu-ZIF with dual redox-active sites of $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Cu}^{2+}/\text{Cu}^{+}$ promotes efficient electron transfer during the oxidation process, thus effectively catalyzing the oxidation of 2-Naphthol. Carbon black provides a conductive network facilitating efficient electron transport between CoCu-ZIF and electrode surface. The fabricated sensors exhibit a sensitivity and limit of detection of $0.98 \mu\text{A} \mu\text{M}^{-1}$ and $0.46 \mu\text{M}$, respectively, during exposure to 2-Naphthol within a detection range of 1–500 μM . Moreover, due to their excellent sensing performance, selectivity, reproducibility, and recovery rate in non-biological urine, the developed composites offer strong potential for real-time polycyclic aromatic hydrocarbon monitoring and future use in environmental sensor technologies.

Polycyclic aromatic hydrocarbons (PAHs) are pollutants produced from the incomplete combustion of carbon-containing organic compounds at both industrial and household levels, consisting of two to six aromatic rings¹. PAHs are classified as priority pollutants because their exposure to the human body through the formation of reactive oxygen species can lead to cellular dysfunction due to oxidative damage to macromolecules (e.g., deoxyribonucleic acid (DNA), proteins, and lipids)². Once entering the body through exhalation or skin contact, PAHs are metabolized by the liver into monohydroxylated compounds (OH-PAHs), which are more harmful than

their parent compounds^{3,4}. Various studies have shown that PAH exposure can be detected by measuring OH-PAH levels in urine or feces^{5,6}. Among OH-PAHs, 2-Naphthol is the most dominant biomarker for PAH exposure, accounting for 60–90% of the total detected OH-PAHs⁷. Therefore, highly sensitive and selective sensors for 2-Naphthol are essential to improve the accuracy and reliability of PAH monitoring in biological samples.

The standard analytical methods for OH-PAHs are gas chromatography, mass spectrometry, and isotope dilution^{8–10}. However, they require expensive instrumentation, complex operation, and extensive sample

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preparation. Electrochemical sensors offer a promising alternative for detecting OH-PAHs, as their hydroxyl groups undergo redox reactions at specific potentials, producing measurable electrochemical signals¹¹. Zhang et al. measured the amperometric response to 2-Naphthol using a meso-NiCo₂O₄ nanosphere-modified electrode¹². Using linear sweep voltammetry, Li et al. detected 2-Naphthol with an electrode based on poly(N,N-dimethylacrylamide) and multi-walled carbon nanotubes¹³. Noble metals and two-dimensional materials have also been used to produce strong electrochemical responses with OH-PAH^{14–16}. Several studies have successfully determined OH-PAH levels in urine with an average recovery rate of over 90%^{11,17}. In electrochemical sensing, high density of active sites and efficient mass transport are required, yet these are often limited in conventional materials such as carbon-based materials, metal oxides, and conductive polymers. Carbon materials often rely on defect/dopant engineering because their pristine surfaces typically exhibit low catalytic activity and limited oxidation resistance¹⁸. In parallel, metal oxides may suffer from limited accessibility of active sites because of their non-porous characteristics¹⁹, while polymeric films can impose additional mass- and charge-transfer resistance when thicker coatings are required²⁰. In contrast, metal organic frameworks (MOFs) can effectively overcome these limitations due to their high specific surface area and intrinsic porosity. The target analytes can rapidly diffuse to the active sites, where they undergo redox reactions catalyzed by abundant active-metal centers^{21,22}. Therefore, MOFs are among the most widely explored materials to enhance the performance of electrochemical devices in various applications^{23–25}.

Various strategies have been reported to improve the electrochemical properties of MOFs, including the introduction of functional groups, metal doping (or bimetallic systems), guest molecule incorporation, or defect engineering²⁶. Among those approaches, having bimetallic structures can transform the MOF properties due to their multi-metal active sites, internal synergistic interactions, and morphological changes^{26,27}. Moreover, modification of the physicochemical properties of MOFs can be done by controlling the proportions of metal precursors. Feng et al. reported that the mixed metal (Zn, Zr)-UiO-66 produced a missing cluster defect, which is tunable by the ratio of Zn and Zr precursors. At specific ratios, (Zn, Zr)-UiO-66 owns two missing linkers that contribute to the formation of cluster defects, resulting in significantly higher surface area and catalytic conversion than pristine UiO-66²⁸. Hou et al. produced a vacancy-rich MOF by partially replacing the Fe³⁺ with Cu²⁺ through a cation-exchange strategy to detect ammonia gas²⁹. Despite all those success stories on metal precursor engineering strategies to either modify the material properties or enhance the electrochemical sensor performance, the potential of such metal-modified MOF structures, especially based on bimetallic zeolitic imidazolate framework (ZIF), for the detection of a low-molecular-weight OH-PAH (i.e., 2-Naphthol) has not been proven.

In this work, we developed bimetallic cobalt-and-copper-based ZIF (CoCu-ZIF) particles coupled with carbon black (CB) for highly sensitive and selective electrochemical sensing of 2-Naphthol, a low-molecular-weight OH-PAH. Here, ZIF-67 was used as the parent material, comprising Co²⁺ cations coordinated with imidazole anions to form a tetrahedral framework. In addition, ZIF-67 was selected as the main sensing material due to its high surface area, abundant porosity, stronger chemical stability, and enhanced redox activity compared to other ZIF variants. ZIF-67 is generally more effective in electron transfer and catalytic processes, compared to ZIF-8 (Zn²⁺) which is more beneficial for adsorption purposes. Its large surface area offers numerous active sites for surface reactions, while the porous structure facilitates analyte diffusion and provides channels for efficient redox interactions^{30,31}. Our previous studies have also demonstrated the successful use of bimetallic ZIF-67 for electrochemical sensors³². The introduction of Cu into ZIF-67 was intended to generate a variation in redox-active sites and modulate the local electronic environment. These properties lead to dynamic Co and Cu redox-couples interconversion, which facilitates electron transfer between the metal centers, thereby enhancing catalytic activity toward an electro-oxidation of 2-Naphthol^{33–35}. Furthermore, the inherently low electrical conductivity of CoCu-ZIF was

addressed by integrating it with carbon-based materials to improve the overall detection response^{36–39}.

To ensure the desired morphology and structure of CoCu-ZIF particles, their metal precursor ratios were carefully controlled in one-pot synthesis via chemical co-precipitation. Various material characterizations (i.e., X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FE-SEM), nitrogen adsorption/desorption analysis, and X-ray photoelectron spectroscopy (XPS)) methods were conducted to investigate the effects of Cu incorporation and Co/Cu ratio on morphology, surface, and electronic states of the bimetallic CoCu-ZIF. Furthermore, to enhance their electrical conductivity, the CoCu-ZIF particles were combined with CB by ultrasonication, resulting in CoCu-ZIF@CB composites. To prove their function as OH-PAH electrochemical sensors, these composites were deposited on a glassy carbon electrode (GCE) and subsequently used to monitor various 2-Naphthol concentrations in an amperometric sensing fashion. In addition to sensitivity measurements for 2-Naphthol, reproducibility tests using multiple electrodes and cross-sensitivity assessments with various interfering agents were conducted to demonstrate the practical applicability of CoCu-ZIF@CB composites as 2-Naphthol sensors.

Results and discussion

Material and structural characteristics of CoCu-ZIF particles

The CoCu-ZIF particles were successfully fabricated through a co-precipitation method involving Co and Cu precursors, and 2-methylimidazole (2-MeIm) in methanol solution (see Fig. 1a). We produced Co_xCu_y-ZIF particles with different Co:Cu precursor molar ratios, where *x* and *y* are the molar fractions of Co and Cu, respectively. Four sample variants of ZIF-67, Co₄Cu_{0.5}-ZIF, Co₄Cu₁-ZIF, and Co₄Cu₂-ZIF particles were initially prepared for investigation in terms of their material and structural characteristics prior to combination with CB and deposition on a GCE for detecting target 2-Naphthol (see Fig. 1b).

After 24 h of aging, the precipitates of all CoCu-ZIF variants were harvested. Figure 2a shows the particles resulting from a synthesis with 60 mL of total precursors, producing masses of 66.5 mg, 43.5 mg, 36.0 mg, and 7.0 mg for ZIF-67, Co₄Cu_{0.5}-ZIF, Co₄Cu₁-ZIF, and Co₄Cu₂-ZIF samples, respectively. The particle amounts decreased as the concentration of Cu precursors increased. Furthermore, a higher Cu fraction (i.e., Co₄Cu₃-ZIF) did not yield harvestable precipitates, as shown in Supplementary Fig. 1. The recipes used to synthesize bimetallic CoCu-ZIF particles could not be directly adopted to produce their single-metal Cu-ZIF counterparts. Since the formation enthalpy of Cu-(2-MeIm) is less exothermic (−14.03 kJ mol^{−1}) compared to their Co-based counterparts (−46.01 kJ mol^{−1}), Cu in ZIF frameworks is more difficult to form and thermodynamically less stable⁴⁰. The synthesis of Cu-ZIF particles needs a higher metal composition compared to the ligand, as opposed to the composition used in this bimetallic study⁴¹. The crystallographic structures of the obtained CoCu-ZIF particles were analyzed by XRD, in which their diffraction peaks match well with those of simulated ZIF-67 in the COD reference card: 7222297 (see Fig. 2b)⁴². The XRD patterns show the major peaks of ZIF-67 located at 2θ (*hkl*) of 12.81° (112), 14.79° (022), 16.53° (013), 18.11° (222), 22.21° (114), 24.57° (233), 25.68° (224), 26.74° (134), 29.71° (334), 30.64° (044), 31.56° (244), and 32.44° (235). Here, θ denotes the angle of X-ray incidence relative to the crystal plane defined by Miller indices (*hkl*). Generally, the incorporation of Cu²⁺ metal ions does not cause a significant change to the crystallographic structure of ZIF, indicating a maintained framework. A slight shifting to lower diffraction angles was observed along with an increasing fraction of Cu, indicating a larger interplanar spacing (*d*-spacing) in bimetallic ZIF. This finding can be explained by the larger ionic radius of Cu²⁺ (0.73 Å), which substitutes the smaller Co²⁺ (0.70 Å) in the crystal lattice, causing *d*-spacing expansion^{43,44}, as reported in a previous CoCu-MOF study^{45–48}. The Bragg equation analysis of the (112) peak was used to calculate the corresponding *d*₍₁₁₂₎-spacing (the distance between the (112) planes) for all samples. The *d*₍₁₁₂₎-spacing values

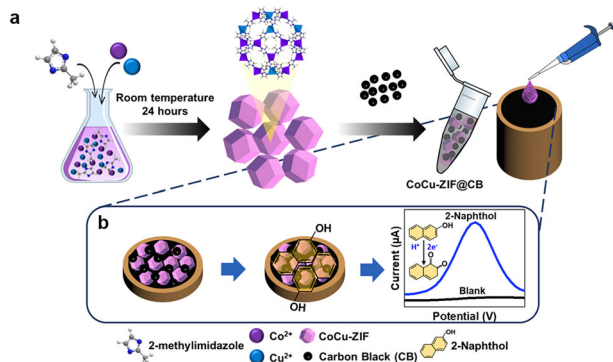


Fig. 1 | Bimetallic cobalt-and-copper-based ZIF (CoCu-ZIF) particles coupled with carbon black (CB) for electrochemical sensing of 2-Naphthol. a Synthesis of CoCu-ZIF particles using co-precipitation followed by a mixing process with CB to result in CoCu-ZIF@CB composites. **b** Illustration of CoCu-ZIF@CB composites deposited on a glassy carbon electrode (GCE) and their expected output sensing signal to 2-Naphthol. The response signal is shown by the appearance of square wave voltammetry (SWV) peaks at the redox potential of 2-Naphthol after undergoing the redox reaction.

of ZIF-67, $\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$, $\text{Co}_4\text{Cu}_1\text{-ZIF}$, and $\text{Co}_4\text{Cu}_2\text{-ZIF}$ are 6.903 Å, 6.932 Å, 6.935 Å, and 6.944 Å, respectively.

Supplementary Fig. 2 shows the FTIR spectra of all four different CoCu-ZIF samples to clarify the presence of the functional groups in those materials. The fingerprint of 2-MeIm is identified by the existence of peaks at 600–1500 cm^{-1} reflecting the in-plane and out-of-plane bending modes of the imidazole ring. A peak at 1583 cm^{-1} and 1689 cm^{-1} results from the C = N stretching and C = C band in the imidazole rings^{49,50}. The presence of these characteristic peaks of the imidazolate linker has confirmed the successful fabrication of ZIF materials. Additional peaks at 2924, 3130, and 3431 cm^{-1} correspond to aliphatic C–H stretching, aromatic C–H stretching, and O–H stretching, respectively. The sharp peak at 422 cm^{-1} comes from the M–N bonds, where M represents the metal (Co or Cu). The only slight shift of the M–N bond vibration indicates that Cu^{2+} coordinates with the deprotonated imidazolate linker in similar energy ranges as the Co^{2+} ^{51–53}.

The materials synthesized by bimetallic precursors inherit the dodecahedron morphology of ZIF-67, which is favored in many ZIF-based electrochemical studies because of its high number of exposed active sites to achieve strong catalytic activity⁵⁴. By defining the ZIF-67 in Fig. 3a as a reference (no Cu incorporation), various alterations were observed for the different precursor ratios. Particle size becomes the first parameter to be noticed, where the higher Cu fraction results in a larger particle size. The ZIF-67, $\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$, $\text{Co}_4\text{Cu}_1\text{-ZIF}$, and $\text{Co}_4\text{Cu}_2\text{-ZIF}$ samples possess average particle sizes of 678.45 nm, 1972.69 nm, 1941.12 nm, and 5237.80 nm, respectively. Referring to LaMer's model, the small and narrow size distribution obtained for ZIF-67 indicates a promoted nucleation over particle growth due to an unhindered coordination of Co^{2+} and 2-MeIm^{55,56}. In contrast, the presence of Cu^{2+} introduces a disturbance to the overall metal–ligand coordination, thereby slowing down nucleation and favoring crystal growth, resulting in larger particle sizes in bimetallic CoCu-ZIF^{27,40}. For $\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$ (see Fig. 3b), the Cu^{2+} content might not be sufficient to accommodate coordination across the solution, leading to non-uniform particle size. At the intermediate fraction of $\text{Co}_4\text{Cu}_1\text{-ZIF}$ (see Fig. 3c), the particle exhibits a more uniform size distribution. Notably, $\text{Co}_4\text{Cu}_2\text{-ZIF}$ (see Fig. 3d) shows markedly increased average particle size and broadened size distribution (~3–6 μm), indicating contributions from both enlarged primary particles and aggregation/coalescence. This suggests that at high Cu fraction, growth and aggregation become more pronounced, while coordination-related defects or lattice distortions may contribute to the increased particle size^{57,58}. Supporting evidence from X-ray photoelectron spectroscopy (XPS) is provided later in this section.

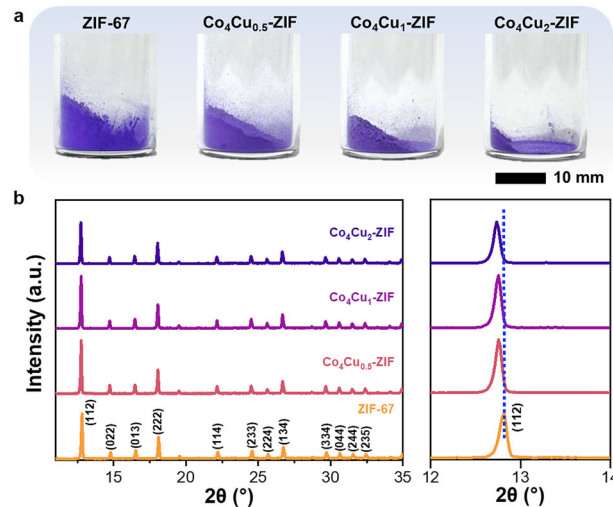


Fig. 2 | Material characteristics of the as-prepared CoCu-ZIF particles with different metal precursor molar ratios. a Photographs of all four CoCu-ZIF particle variants resulting from the same synthesis volume. Increasing Cu precursor concentration results in a lower number of synthesis end-products (particles), as indicated by the yellow arrow in those images. **b** X-ray diffraction (XRD) patterns showing the crystalline phases present in the samples, with characteristic diffraction peaks corresponding to ZIF-67 in the COD ref. card: 7222297. A left-shifted (112) peak is observed with an increase of the Cu fraction (see the middle panel).

Following FE-SEM analysis, energy-dispersive X-ray (EDX) spectroscopy mapping was performed to screen elemental composition, specifically to confirm the incorporation of Cu into the ZIF matrix. Figure 4a–d shows the superimposed maps of elemental distributions consisting of carbon (C), nitrogen (N), oxygen (O), cobalt (Co), and copper (Cu) for single CoCu-ZIF particles. Cu is represented by light blue in the mapping experiments. Cu increased in intensity in the superimposed images, reflecting the higher Cu content as a greater amount of Cu precursor was used in the synthesis. Individual mappings for each element and EDX spectra are included in Supplementary Fig. 3. The EDX spectra provide the atomic percentages for each element in the bulk composition. As shown in Supplementary Table 1, the atomic concentration ratios of N/CoCu for each CoCu-ZIF are close to the theoretical CoN_4 coordination in ZIF-67 of 4^{59,60}. Meanwhile, the high N/Co ratio in ZIF-67 indicates a high portion of unreacted 2-MeIm, which is formed by rapid nucleation due to the abundant availability of the 2-MeIm ligand. This supports the discussion of Fig. 3a.

Furthermore, quantification of the element composition was conducted using XPS, the corresponding low-resolution survey spectra are shown in Supplementary Fig. 4. A near-surface composition in atomic percentage is obtained from the CoCu-ZIF main peaks (i.e., C 1 s, N 1 s, O 1 s, Co 2p, and Cu 2p) as listed in Supplementary Table 1. A similar finding on the N/CoCu ratio has been observed with both EDX and XPS. The incorporation of Cu into the bimetallic ZIFs results in a lower N/CoCu ratio, suggesting partial loss or reduced coordination of 2-MeIm ligands. This condition is commonly reported in carbonized ZIF and is related to more coordinatively unsaturated metal sites, which can improve the material's catalytic reactivity^{61,62}. The metal contents of the CoCu-ZIF samples were quantified using atomic absorption spectroscopy (AAS), as shown in Table 1. According to AAS, the Co:Cu metal fractions obtained in the final products follow the ratios prepared for synthesis. With increasing Cu content in the precursor, the Co concentration in the final product gradually decreases, while the Cu concentration increases correspondingly. This trend confirms the successful incorporation of Cu into the ZIF framework through partial substitution of Co sites. Supplementary Table 2 compares the Co:Cu atomic fractions obtained from EDX and XPS analyses. In general, the incorporated Cu content in the final CoCu-ZIF samples was lower than expected from the initial precursor ratio, likely due to the weaker Cu–N

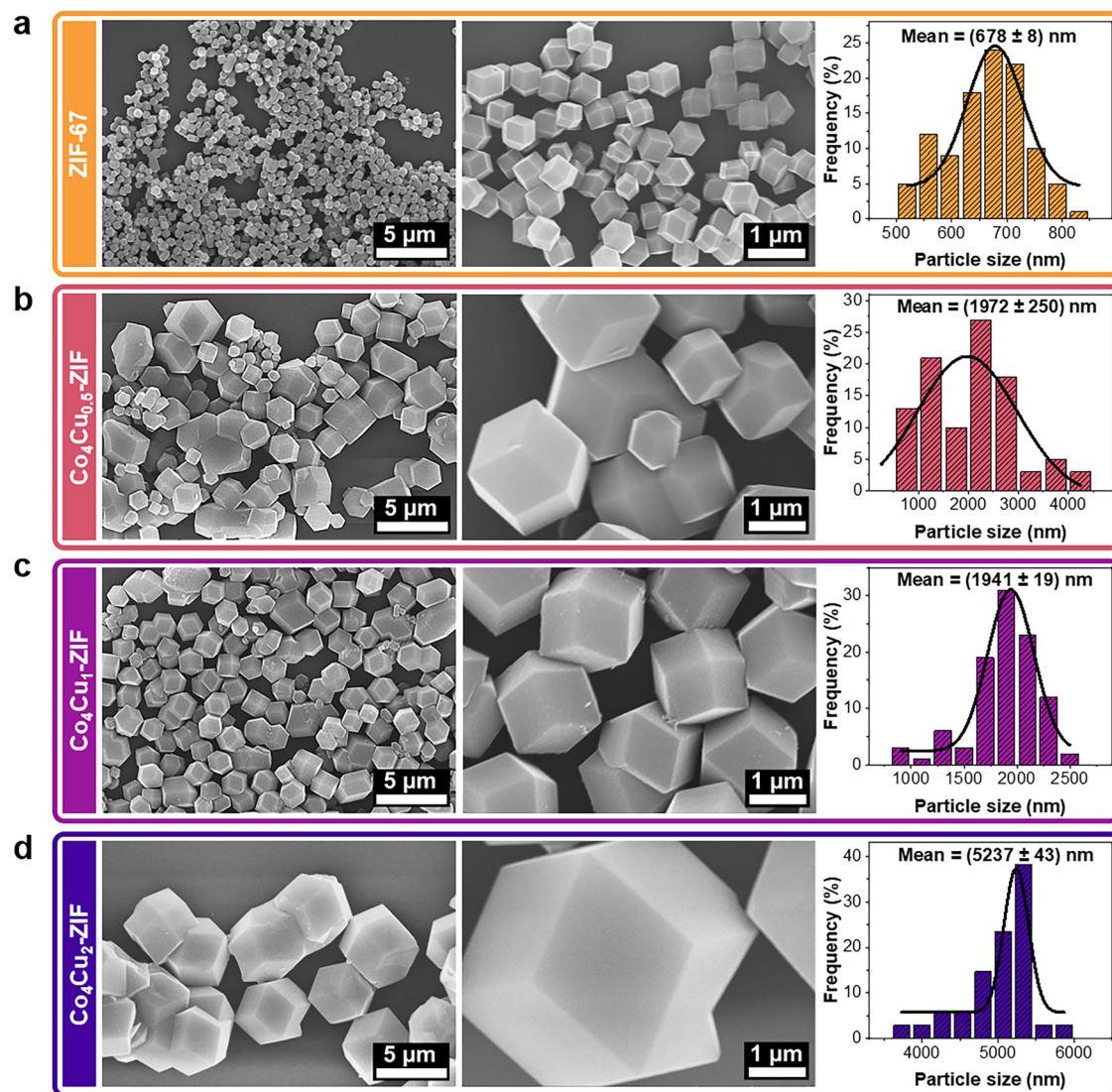


Fig. 3 | Morphologies and size distributions of CoCu-ZIF particles with different metal precursor molar ratios. The field emission scanning electron microscopy (FE-SEM) images in low and high magnification, and size distribution of **a** ZIF-67,

b $\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$, **c** $\text{Co}_4\text{Cu}_1\text{-ZIF}$, and **d** $\text{Co}_4\text{Cu}_2\text{-ZIF}$ particles, respectively. Their respective size distributions were generated from low-magnification FE-SEM images at two different positions.

coordination bonds compared to Co–N bonds. This observation is consistent with a lower exothermic formation enthalpy of Cu–(2-MeIm) relative to Co–(2-MeIm)⁴⁰.

Figure 4e presents the high-resolution XPS spectra of Co 2p for each bimetallic CoCu-ZIF and exhibits the two spin-orbit doublets $2p_{3/2}$ and $2p_{1/2}$ at around 781 eV and 796 eV, respectively. Peak fitting reveals that each spin-orbit doublet possesses three distinct peaks identified as Co^{3+} (~780 eV and ~796 eV) and Co^{2+} (~782 eV and ~797 eV), followed by their respective shake-up satellites at a higher binding energy^{61,62}. In Fig. 4f, the XPS spectra of Cu 2p also reveal $2p_{3/2}$ and $2p_{1/2}$ doublets as a result of spin-orbit coupling, located at around 933 eV and 953 eV, respectively. The $2p_{3/2}$ region comprises Cu^+ and Cu^{2+} , with a different binding energy of Cu^{2+} for each sample. Meanwhile, the $2p_{1/2}$ region exhibits only Cu^+ at a similar binding energy for each sample^{63,64}. Based on the quantitative analysis in Supplementary Table 3, the calculated $\text{Co}^{3+}/\text{Co}^{2+}$ ratios from $2p_{3/2}$ for $\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$, $\text{Co}_4\text{Cu}_1\text{-ZIF}$, and $\text{Co}_4\text{Cu}_2\text{-ZIF}$ are 1.07, 1.98, and 1.82, respectively. Meanwhile, the $\text{Cu}^+/\text{Cu}^{2+}$ ratios from $2p_{3/2}$ are 2.05, 3.05, and 4.31, respectively. The elevated mixed-valence contributions at higher Cu fractions indicate changes in the metal–ligand coordination environment, consistent with the decreasing N/CoCu ratio depicted in Supplementary Table 1^{61,62}. This interpretation is further supported by high-resolution N 1s

spectra (Supplementary Fig. 5a), where the M–N component systematically shifts from 398.63 eV ($\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$) to 398.30 eV ($\text{Co}_4\text{Cu}_2\text{-ZIF}$), indicating a modified electronic environment of coordinated nitrogen upon Cu incorporation. The converging evidence of the perturbed coordination is potentially associated with partial ligand loss, which may disrupt the original ZIF framework and promotes structural defect formation^{62,65}. These defects may contribute to the increased particle size observed in bimetallic CoCu-ZIF (see Fig. 3) by altering nucleation and growth kinetics⁵⁷.

Besides the intensity analysis, the binding energy shifts can provide information regarding the electronic environment of the metal centers. Generally, the Co 2p and Cu 2p binding energies shift as the Cu content in the bimetallic CoCu-ZIF increases. As shown in Fig. 4e, the Co^{3+} binding energy decreases, while the Co^{2+} binding energy increases with higher Cu content. In Fig. 4f, Cu^{2+} peaks also shifts slightly to a lower binding energy, as the Cu^+ peak shifts dramatically to a higher binding energy. The observed shifts in the Co and Cu binding energies correlate with an electron transfer between the metal centers, where Cu^{2+} is reduced to Cu^+ and promotes reduction of Co^{3+} to Co^{2+} . A similar electronic interaction was observed in other bimetallic systems and has been confirmed by density functional theory (DFT) studies^{33–35}. DFT analysis quantified core-level binding energy shifts and electron transport between the two metal centers. Furthermore,

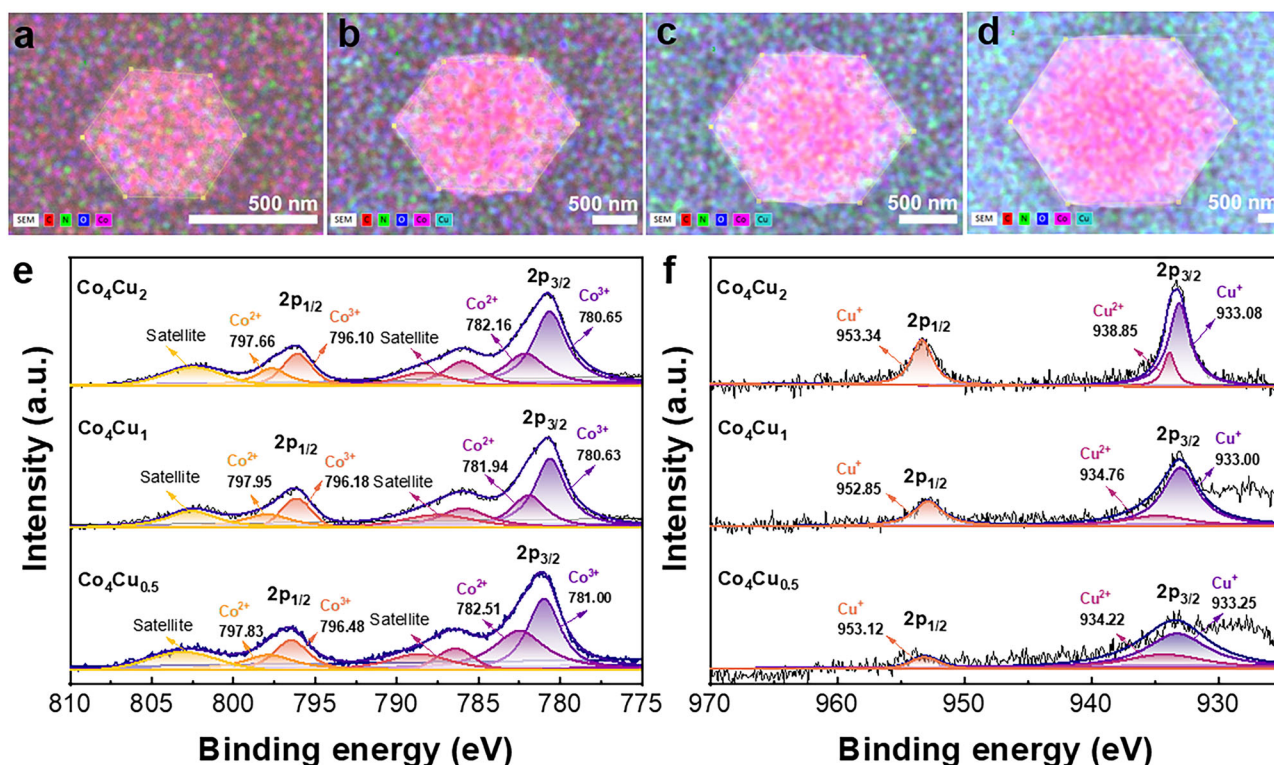


Fig. 4 | Elemental analysis of CoCu-ZIF particles in bulk and surface regions. Energy-dispersive X-ray (EDX) superimposed mappings comprising C, N, O, Co, and Cu elements for **a** ZIF-67, **b** $\text{Co}_4\text{Cu}_{0.5}$ -ZIF, **c** Co_4Cu_1 -ZIF, and **d** Co_4Cu_2 -ZIF.

X-ray photoelectron spectroscopy (XPS) at high resolution provides the oxidation states of Co and Cu that are identified by the respective core level spectra of **e** Co 2p and **f** Cu 2p, respectively.

Table 1 | Metal composition of CoCu-ZIF with different metal precursor molar ratios

Sample	Prepared Co:Cu (at%)	Metal concentration (ppm)		Obtained Co:Cu (at%)
		Co	Cu	
ZIF-67	4:0	5.059	–	4:0
$\text{Co}_4\text{Cu}_{0.5}$ -ZIF	4:0.5	7.326	0.252	4:0.13
Co_4Cu_1 -ZIF	4:1	6.323	0.276	4:0.16
Co_4Cu_2 -ZIF	4:2	5.135	0.295	4:0.21

Atomic absorption spectroscopy (AAS) was used to measure the concentrations of Co and Cu in CoCu-ZIF. These concentrations were used to calculate the obtained Co:Cu fractions in the synthesized product.

these studies also demonstrated that strong electronic coupling between Co and Cu enhances charge transfer and catalytic activity. Moreover, the metal-ligand system reflected by the N 1s and C 1s spectra shifting to lower binding energy (see Supplementary Fig. 5) indicates electron delocalization around the ligand atoms. These synergistic electronic effects enable dynamic redox interconversion and facilitate charge transfer during the electrochemical process⁶³.

The nitrogen adsorption/desorption behavior of all samples shows typical Type-1 nitrogen isotherms, where a rapid adsorption occurs at $p/p_0 \approx 0.05$, followed by a stagnant adsorption at $p/p_0 > 0.05$ (Fig. 5a). The adsorption isotherm indicates a microporous structure characteristic of CoCu-ZIF. Brunauer–Emmett–Teller (BET) analysis reveals that the single metal ZIF (ZIF-67) has a large surface area. Meanwhile, a similar surface area is maintained by each bimetallic ZIF. Furthermore, a density functional theory (DFT) analysis has confirmed the pure microporous structure known for CoCu-ZIF with an average pore size of around 1 nm (see Fig. 5b). From the DFT-based surface area analysis, the ZIF-67, $\text{Co}_4\text{Cu}_{0.5}$ -ZIF, Co_4Cu_1 -ZIF, and Co_4Cu_2 -ZIF samples possess surface areas of 1837.35 m²

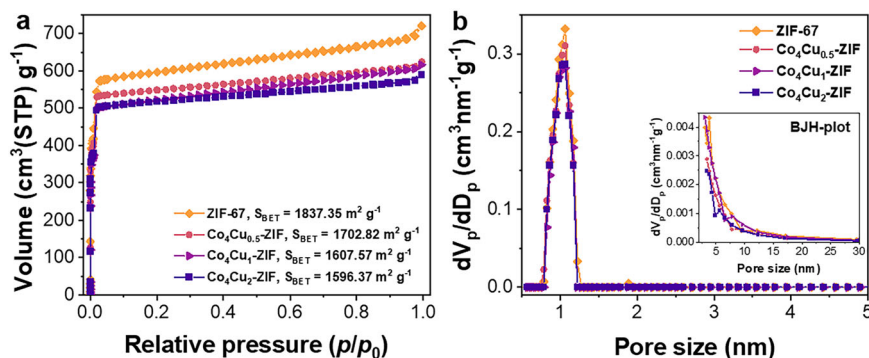
g⁻¹, 1702.82 m² g⁻¹, 1607.57 m² g⁻¹, and 1596.37 m² g⁻¹, respectively. Good agreement has been reached between DFT (full lines) and adsorption/desorption isotherm curves (filled circles, see Fig. 5b), where the bimetallic ZIF variants (i.e., $\text{Co}_4\text{Cu}_{0.5}$ -ZIF, Co_4Cu_1 -ZIF, and Co_4Cu_2 -ZIF) have a slight decrease in the porous volume compared to the single metallic ZIF (i.e., ZIF-67) related to their lower surface area. The Barrett–Joyner–Halenda (BJH) plots, attached as an inset in Fig. 5b, show that the material lacks mesoporosity. Generally, the incorporation of Cu into the ZIF does not lead to a significant reduction of surface area, which otherwise may have resulted in a decrease in electrochemical performance due to a lower number of active sites.

Electrochemical properties of CoCu-ZIF particles

To evaluate the electrochemical properties of the synthesized CoCu-ZIF particles, they were first coated onto a GCE. A three-electrode system was utilized, comprising Ag/AgCl and platinum wire as reference and counter electrodes, respectively. The electrolyte solution of 5 mM potassium ferrocyanide [$\text{K}_3(\text{FeCN})_6$] with 0.1 M of potassium chloride (KCl) in 0.01 M phosphate-buffered saline (PBS, pH 7.4) was used in the entire series of electrochemical measurements of the materials. Cyclic voltammetry (CV) was performed in the potential range of -0.10 to $+0.55$ V with a scan rate of 50 mV s⁻¹, producing cyclic voltammograms with distinct redox peaks, where each CoCu-ZIF variant exhibits different current levels (see Fig. 6a). The pristine ZIF-67 sample yielded the lowest currents at 0.300 V (oxidation) and 0.180 V (reduction) compared to its bimetallic CoCu-ZIF counterparts. The redox reactions in ZIF-67 were mostly attributed to the Faradaic reaction of Co ($\text{Co}^{3+}/\text{Co}^{2+}$ redox couples)⁶⁶. In contrast, two redox pairs of $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Cu}^{2+}/\text{Cu}^+$ existed in CoCu-ZIF as confirmed by their XPS spectra (see Fig. 4e, f). The coexistence of two redox pairs increases the density of redox-active sites, leading to higher peak currents and improved redox reversibility. This interpretation was further supported by comparing the electrochemical behaviors of the monometallic variants (ZIF-67 and Cu-ZIF) to those of the bimetallic Co_4Cu_1 -ZIF and the physically mixed

Fig. 5 | Surface analysis of CoCu-ZIF particles by nitrogen adsorption/desorption measurement.

a Adsorption/desorption isotherm curves of four CoCu-ZIF particles having different precursor molar ratios and their respective Brunauer–Emmett–Teller (BET) surface area (S_{BET}). **b** The differential pore volume (dV_p/dD_p) vs. pore size obtained from density functional theory (DFT) analysis, supported by Barrett–Joyner–Halenda (BJH) plots as inset.



monometallic ZIFs (Cu-ZIF@ZIF-67). The Cu-ZIF was independently characterized by FTIR spectroscopy, confirming the successful formation of an imidazolate framework (Supplementary Fig. 6a). The Cu-ZIF@ZIF-67 mixture was prepared to match the Co:Cu ratio of the synthesized Co₄Cu₁-ZIF, as described in detail in Supplementary Note 1. As shown in Supplementary Fig. 6b, c, Cu-ZIF@ZIF-67 exhibits neither well-defined redox peaks nor a semi-circle in Nyquist plot. It has lower current compared to the Co₄Cu₁-ZIF, indicating that simple coexistence of two monometallic phases does not reproduce the enhanced performance⁶⁷. Furthermore, the weak current responses from ZIF-67 and Cu-ZIF suggest that the improvement in CoCu-ZIF is not driven by standalone properties of either monometallic phase. These findings emphasize that synergistic effects arise when the two metals are integrated within the same framework environment^{67,68}. Consistently, incorporating Cu into a Co-based ZIF framework (CoCu-ZIF) notably enhances redox response and interfacial charge-transfer kinetics relative to the monometallic ZIFs^{33–35}. To further elucidate the electronic interaction between Co and Cu within the bimetallic framework, the composition dependence of the electrochemical properties was analyzed.

The redox peaks of Co₄Cu_{0.5}-ZIF, Co₄Cu₁-ZIF, and Co₄Cu₂-ZIF shifted to 0.310, 0.312, 0.330 V for oxidation and to 0.181, 0.179, 0.167 V for reduction, respectively. These potential shifts are most likely attributed to an internal redox-coupling mechanism between Cu⁺ and Co³⁺ centers. The electron-rich Cu⁺ species act as local electron donors, while the Co³⁺ species serve as electron acceptors, facilitating internal charge redistribution^{69,70}. This internal electron transfer partially oxidizes the active sites prior to external electrochemical oxidation, leading to a more stabilized reduced state⁷¹. Consequently, the oxidation peak shifts positively, while the reduction peak shifts slightly negatively, reflecting the redox coupling equilibrium between Cu²⁺/Cu⁺ and Co³⁺/Co²⁺ pairs. In addition, these electronic behaviors of Co and Cu metal centers also result in higher currents due to the enhanced electron transfer. From electrical impedance spectroscopy (EIS) analysis shown in Fig. 6b, the Nyquist plots of Co₄Cu_{0.5}-ZIF, Co₄Cu₁-ZIF, and Co₄Cu₂-ZIF have smaller semi-circle EIS curves than that of ZIF-67, indicating that the Cu addition can lower the charge-transfer resistance (R_{ct}) in the material system. Nonetheless, in our experiments, the highest current peaks are obtained by Co₄Cu₁-ZIF, followed by Co₄Cu₂-ZIF and Co₄Cu_{0.5}-ZIF. This could be correlated with the lack of uniformity and aggregation provided by the Co₄Cu_{0.5}-ZIF and Co₄Cu₂-ZIF particles in Fig. 3c, d.

Moreover, these electrochemical trends can be rationalized by a balance between the population of surface-exposed metal sites and morphology-dependent accessibility. Supplementary Table 1 shows that the N/CoCu ratio of Co₄Cu_{0.5}-ZIF, Co₄Cu₁-ZIF, and Co₄Cu₂-ZIF decreases according to 2.92, 2.86, and 2.74, respectively. A lower N/CoCu ratio indicates a more metal-rich surface relative to the coordinating nitrogen, indicating a higher population of surface-exposed metal centers as potential electroactive sites^{52,65}. Although Co₄Cu₂-ZIF exhibits the lowest N/CoCu ratio, its markedly enlarged particle size and aggregation can reduce the accessibility of the external surface area and thereby hinder mass transport.

In contrast, the Co₄Cu₁-ZIF exhibits a relatively metal-rich surface along with a uniform particle size distribution, which provides more accessible active sites and more efficient mass transport. Therefore, Co₄Cu₁-ZIF exhibits the most favorable characteristics and accordingly has produced the highest peak current and lowest charge-transfer resistance in CV and EIS, respectively, rationalizing its selection for 2-Naphthol sensing.

Since the Co₄Cu₁-ZIF had demonstrated the optimum characteristics among other samples (i.e., produced the highest peak current and lowest charge-transfer resistance in the first CV and EIS assessments shown in Fig. 6a, b), we decided to further explore and use this bimetallic material variant for the next experiments (i.e., evaluation of scan rate effects, composite creation involving CB, and sensing performance evaluation towards 2-Naphthol). Here, the electrochemical properties of Co₄Cu₁-ZIF were studied in detail by varying the CV scan rate in the range of 10 to 100 mV s^{-1} with a step interval of 10 mV s^{-1} in potential windows of -0.10 to $+0.55$ V (see Fig. 6c). The faster the scan rates, the higher the produced current due to the decrease of diffusion layer thickness. Since a quasi-reversible electron transfer is indicated by the redox couple peaks, the Randles–Sevcik equation can be used to explain the electrochemical reaction through the relationship between the peak current (I_p) and the square root of scan rate ($v^{1/2}$)⁷². Figure 6d shows that the current changes linearly to the square root of the scan rate. This implies that the analyte is freely diffusing in the solution, without any adsorption to the surface of the material, which can alter the reactivity of electrodes⁷².

Carbon-black-coupled CoCu-ZIF composites

After the optimal CoCu-ZIF variant had been found (i.e., Co₄Cu₁-ZIF), this material was then coupled with CB to enhance its electrical transport properties. Here, a simple ultrasonication method was used to form a homogenous Co₄Cu₁-ZIF@CB composite for GCE modification. Prior to electrochemical applications, the electrical properties of the materials were evaluated using a Picotest M3500A multimeter and interdigitated electrodes coated with the corresponding materials ink. The measured resistance listed in Supplementary Table 4 was then used to calculate conductance. The measurements indicated that Co₄Cu₁-ZIF exhibited very low conductance ($< 0.01 \mu\text{S}$), whereas CB showed a high conductance (448.4 μS). After these two materials are combined into Co₄Cu₁-ZIF@CB composite, the electrical transport in Co₄Cu₁-ZIF@CB was significantly improved as a conductance of 71.4 μS was reached. These results confirm that the incorporation of CB successfully enhances the electrical conductivity of Co₄Cu₁-ZIF material. Consequently, compared to its pristine Co₄Cu₁-ZIF and CB counterparts, the Co₄Cu₁-ZIF@CB composite has demonstrated a superior CV response (see Supplementary Fig. 7a). These results are consistent with the Nyquist plots analysis in Supplementary Fig. 7b, that exhibited a relatively low R_{ct} value of Co₄Cu₁-ZIF@CB (57.64 Ω) compared to CB (128.20 Ω) and Co₄Cu₁-ZIF (414.30 Ω). While CB provides excellent electrical transport, the better CV and EIS performance of the composite demonstrates that integrating CB with CoCu-ZIF effectively couples fast charge transfer with the number of metal-centered redox sites.

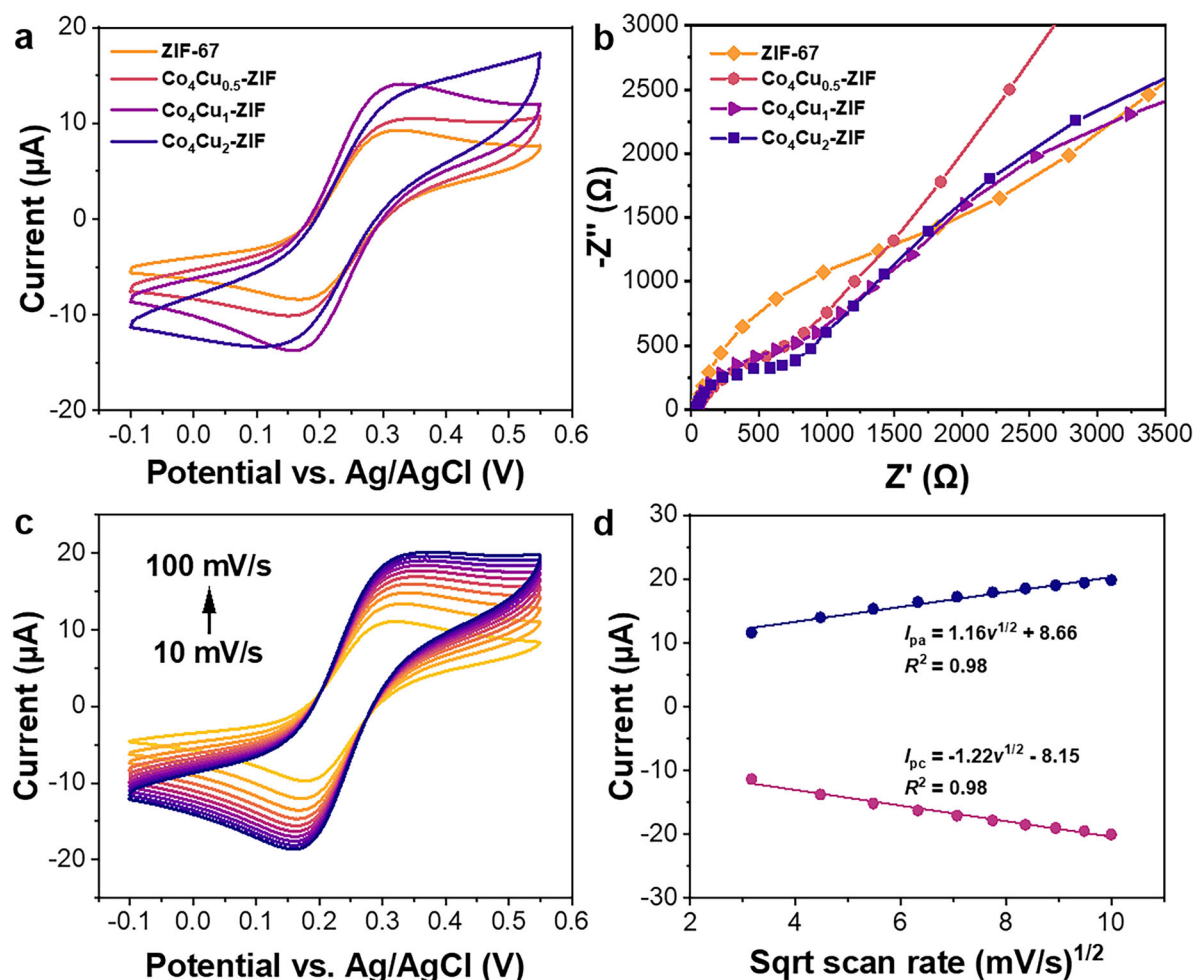


Fig. 6 | Electrochemical properties of CoCu-ZIF particles. **a** Cyclic voltammetry (CV) and **b** electrochemical impedance spectroscopy (EIS) analyses of four different CoCu-ZIF particles (ZIF-67, $\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$, $\text{Co}_4\text{Cu}_1\text{-ZIF}$, and $\text{Co}_4\text{Cu}_2\text{-ZIF}$) coated on glassy carbon electrodes (GCEs) at a scan rate of 50 mV s^{-1} . **c** Cyclic voltammograms of $\text{Co}_4\text{Cu}_1\text{-ZIF}$ -coated GCE at different scan rates ranging from 10 to

100 mV s^{-1} , and **d** their corresponding plots of the square root of scan rate vs. oxidation (blue dots) and reduction (red dots) current peaks with linear fitting (full lines). All these electrochemical properties were measured in a mixture of 5 mM $[\text{K}_3(\text{FeCN})_6]$ and 0.1 M KCl in 0.01 M PBS (pH 7.4).

Figure 7a shows the FE-SEM image of the $\text{Co}_4\text{Cu}_1\text{-ZIF@CB}$ composite constructed by the close-packed reticular structure of CB with distributed $\text{Co}_4\text{Cu}_1\text{-ZIF}$ particles. The EDX mapping clearly identifies the CoCu-ZIF by dense carbon and cobalt mapping dots at the locations of polyhedra-shaped particles. The carbon mapping (red dots) also displays a strong, uniform signal across the entire mapped area, indicating even distribution of the CB. The XRD pattern of the $\text{Co}_4\text{Cu}_1\text{-ZIF@CB}$ composite exhibits diffraction features from both $\text{Co}_4\text{Cu}_1\text{-ZIF}$ and CB (see Supplementary Fig. 7c). The presence of CB is evidenced by broad peak ((002) and (100) marked with black arrows). However, its incorporation does not significantly alter the crystallinity of the ZIF framework⁷³. The high surface area of CoCu-ZIF is a key benefit for electrochemical reactions. Therefore, BET analysis of the composites (CB: $\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratio, 4:2) was performed to assess the effect of CB on their surface accessibility. Supplementary Fig. 7d shows nitrogen adsorption/desorption isotherm curves, with BET surface area of 300.79 and $920.98 \text{ m}^2/\text{g}$ for CB and $\text{Co}_4\text{Cu}_1\text{-ZIF@CB}$, respectively. A notable increment was obtained despite the composite mainly consisting of CB, indicating that the high surface area of $\text{Co}_4\text{Cu}_1\text{-ZIF}$ ($1607.57 \text{ m}^2/\text{g}$, see Fig. 5) significantly contributes to the final surface area. These results confirm that the surface accessibility of CoCu-ZIF is well preserved and not hindered by the presence of surrounding CB.

To find the optimum $\text{Co}_4\text{Cu}_1\text{-ZIF@CB}$ composite composition and to investigate the effect of CB on the material's electrochemical properties, five samples having different CB: $\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratios (i.e., 1:4, 2:4, 4:4, 4:2, and

4:1) were prepared and subsequently electrochemically evaluated in CV measurements using 5 mM $[\text{K}_3(\text{FeCN})_6]$ and 0.1 M KCl in 0.01 M PBS (pH 7.4) (see Supplementary Fig. 8a). The composite sample having a CB: $\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratio of (4:2) demonstrated the highest redox current peaks of 40.50 μA , followed by the other samples possessing CB: $\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratios of (4:1), (4:4), (2:4), and (1:4), respectively. These results demonstrate the effectiveness of CB in addressing the low conductivity issue of pristine ZIF. For the (4:2) and (4:1) variants, their obtained current levels differ only slightly, which indicates a possible electrochemical performance saturation when integrating too high CB concentrations into the composite material system. This saturation can be attributed to a conductivity-active-sites trade-off. Increasing the CB up to 4:2 forms an effective conductive network that connects more ZIF to the electrode, thereby enhancing the electron transfer compared to the lower CB fractions. Further increasing the CB content from 4:2 to 4:1 yields diminishing improvements in conductivity while decreasing the fraction of electroactive ZIF relative to CB in the composite, impairing overall performance. In addition, excess CB may partially cover the ZIF-particle surface, reducing electrolyte access to CoCu-ZIF active sites. A similar behavior has been reported in numerous studies involving carbon-based composites for electrochemical sensing^{74–76}.

After their electrochemical properties had been evaluated, the $\text{Co}_4\text{Cu}_1\text{-ZIF@CB}$ composite samples having different CB: $\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratios were then assessed in the detection scenario towards 500 μM 2-Naphthol (0.01 M PBS, pH 7.4), as displayed in Fig. 7b. Here, two additional samples of the

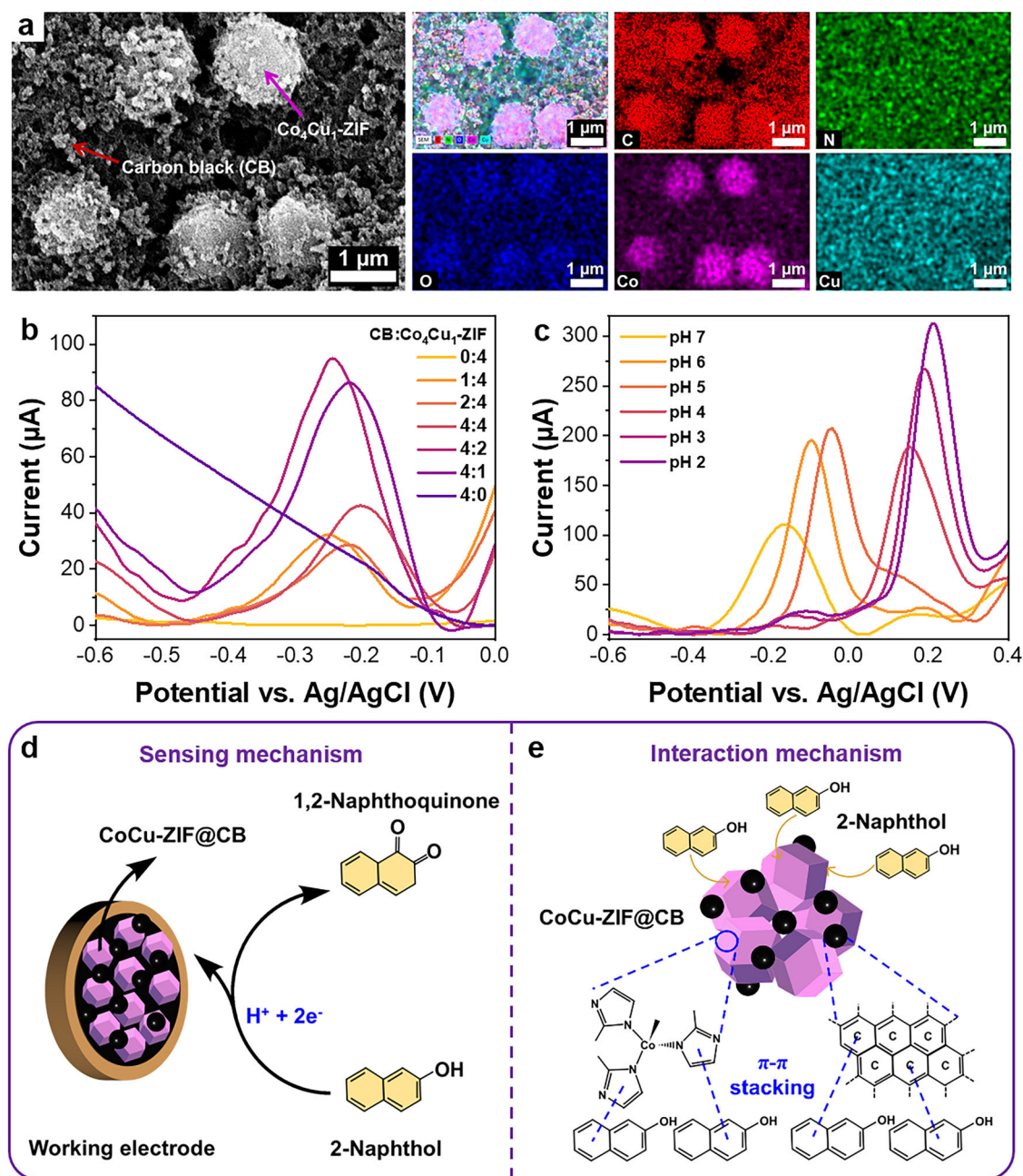


Fig. 7 | Carbon-black-coupled CoCu-ZIF composites for 2-Naphthol detection. **a** Field emission scanning electron microscope (FE-SEM) and energy-dispersive X-ray (EDX) images of carbon-black-coupled CoCu-ZIF ($\text{Co}_4\text{Cu}_1\text{-ZIF@CB}$) composite for glassy carbon electrode (GCE) modification. The EDX images contain superimposed and individual elemental mappings of C, N, O, Co, and Cu. **b** Square wave voltammetry (SWV) responses of $\text{Co}_4\text{Cu}_1\text{-ZIF@CB/GCE}$ having different

ratios of $\text{CB}:\text{Co}_4\text{Cu}_1\text{-ZIF}$ towards $500\ \mu\text{M}$ 2-Naphthol in $0.01\ \text{M}$ PBS (pH 7.4). **c** SWV responses of $\text{Co}_4\text{Cu}_1\text{-ZIF@CB/GCE}$ having $\text{CB}:\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratio of (4:2) towards $500\ \mu\text{M}$ 2-Naphthol in $0.01\ \text{M}$ PBS with different pH levels. **d** Schematic of a possible sensing mechanism of 2-Naphthol catalyzed by Co and Cu metal centers in CoCu-ZIF. **e** Schematic of a possible interaction mechanism between CoCu-ZIF@CB and 2-Naphthol through π - π stacking.

pristine ZIF and CB denoted as (0:4) and (4:0), respectively, were also prepared and tested. A potential windows of -0.60 to $+0.40\ \text{V}$ was selected for the square wave voltammetry (SWV) measurements, as the redox peaks in the CV response to $500\ \mu\text{M}$ 2-Naphthol appeared around $-0.20\ \text{V}$. The absence of redox peak in the SWV signal from pristine CB demonstrates its lack of catalytic redox active-sites. Meanwhile, the presence of $\text{Co}_4\text{Cu}_1\text{-ZIF}$ in the composite provides $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Cu}^{2+}/\text{Cu}^{+}$ redox pairs that can catalyze oxidation of 2-Naphthol. The results indicate that at specific $\text{CB}:\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratios of 4:2, an optimal balance between high conductivity of CB and increased surface area and accessible metal centers provided by the ZIF was achieved. This improvement led to a more efficient redox

reaction of 2-Naphthol, shifting the peaks to more favorable potentials. The trend in SWV responses is consistent with that in CV results shown in Supplementary Fig. 8b, where the $\text{Co}_4\text{Cu}_1\text{-ZIF@CB}$ composite, having a $\text{CB}:\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratio of (4:2) outperformed the other prepared samples.

Since the pH has been considered one of the most important parameters in the test platform because of its strong influence on the protonation state of the target molecules and materials, determining the responsible molecule-material interaction^{77–79}, we investigate the pH effect on the sensing performance of $\text{Co}_4\text{Cu}_1\text{-ZIF@CB/GCE}$. Here, the composite sample having a $\text{CB}:\text{Co}_4\text{Cu}_1\text{-ZIF}$ ratio of (4:2) was tested by SWV using $500\ \mu\text{M}$ 2-Naphthol ($0.01\ \text{M}$ PBS) at different pH levels (pH 2–7), as shown in

Fig. 7c. In 2-Naphthol detection, a more acidic solution could lead to a peak shift to higher potential from -0.16 to $+0.21$ V for pH 7 to 2, respectively, indicating the involvement of protons in the reaction¹². Supplementary Fig. 9a shows a linear relationship between pH and peak potential. At pH levels of 7 to 5, the slope of a linear regression is -60 mV pH⁻¹, which follows the theoretical value from the Nernst equation for the condition of electron-proton balance in the reaction process (-59.1 mV pH⁻¹)^{12,80}. However, at low pH levels of 4 to 2, the peak potential shifted further, changing the slope to -30 mV pH⁻¹, suggesting an additional protonation effect of the 2-Naphthol and the Co₄Cu₁-ZIF. Since the dissociation constant (pK_a) of 2-Naphthol molecules is 9.5, they will be protonated at pH < 9.5 (neutral to acidic conditions), making them more stable in their neutral form. Therefore, the more acidic the conditions, 2-Naphthol is expected to form stronger π - π stacking interactions with the Co₄Cu₁-ZIF@CB, thereby reinforcing the redox reaction. The protonation of Co₄Cu₁-ZIF also occurred at low pH, weakening the coordination between the metal center and the imidazole ligands⁷⁹, thus promoting accessible metal sites for the redox reaction with 2-Naphthol and enhancing the current peaks (see Supplementary Fig. 9b). Therefore, the Co₄Cu₁-ZIF@CB/GCE produced the highest peak current of 311 μ A when tested at pH 2 (see Fig. 7c). Long-term electrochemical cycling measurements were carried out under these optimized conditions, exhibiting a stable redox peak around $+0.20$ V over 50 cycles (see Supplementary Fig. 10a and 10b).

The sensing mechanism was schematically illustrated in Fig. 7d. In the electrochemical sensor for 2-Naphthol, metal centers play a crucial role in the sensing mechanism, acting as catalysts that facilitate the oxidation of 2-Naphthol. In the case of CoCu-ZIF, the incorporation of the secondary metal (Cu) enriches the variety of accessible oxidation states, as evidenced by the XPS analysis. The coherent shifts of Co 2p and Cu 2p indicate electronic coupling between Co³⁺/Co²⁺ and Cu²⁺/Cu⁺ centers. This leads to electron transfer between the metal centers, which enhances charge-transfer efficiency during oxidation, thereby improving the catalytic activity of the sensor. The detailed oxidation process of 2-Naphthol was analyzed based on the obtained linear relationship of peak potential (E_p) vs. pH (see Supplementary Fig. 9a) according to the Nernst equation shown in Eq. 1^{12,80}.

$$\frac{dE_p}{dpH} = -59.1 \frac{m}{n} \text{ mV pH}^{-1} (T = 298K) \quad (1)$$

where m and n are numbers of protons and electrons participating in the oxidation, respectively.

At the operating pH of 2, the measured slope of -30 mV pH⁻¹ results in m/n of ~ 0.5 . This m/n ratio suggests that the oxidation of 2-Naphthol involves a two-electron transfer process with approximately one proton, consistent with a metal-mediated oxidation mechanism. The net stoichiometry of $1\text{H}^+ + 2\text{e}^-$ indicates that oxidation of 2-Naphthol in this system most likely produces its oxidized form of 1,2-Naphthoquinone. The oxidation peak reflects the quantity of 2-Naphthol species oxidized into 1,2-Naphthoquinone, thereby determining the detection signal intensity.

Furthermore, the specific interaction of CoCu-ZIF@CB with 2-Naphthol is confirmed by the Fourier-transform infrared (FTIR) spectroscopy, where the obtained spectra are shown in Supplementary Fig. 11. 2-Naphthol is identified by four main peaks of C–H out-of-plane bending, phenol C–O stretching, C = C stretching, and O–H stretching at 844, 1217, 1595, and 3553 cm⁻¹, respectively. The CoCu-ZIF@CB spectra mainly show the characteristic peaks of the imidazole linker at 700–1500 cm⁻¹, with C = C band, aliphatic and aromatic C–H stretching, and O–H stretching at 1646, 2917, 3135, and 3447 cm⁻¹, respectively^{49,50}. The influence of carbon black is shown by the peak at 1517 cm⁻¹, identified as C = C stretching of aromatic compounds of carbon black overlapping with C = N stretching in CoCu-ZIF. After CoCu-ZIF@CB was treated to adsorb 2-Naphthol, new peaks appear at 809 and 1226 cm⁻¹ due to C–H out-of-plane bending and phenol C–O stretching from 2-Naphthol, with reduced intensity suggesting an interaction with the material surface. Compared to free 2-Naphthol, the C = C stretching peaks redshifted to 1566 cm⁻¹, suggesting that the π - π

interaction likely facilitates a binding of 2-Naphthol to the materials⁸¹. 2-Naphthol, CoCu-ZIF, and carbon black are similarly featured by conjugated π -electron systems due to their benzene ring, imidazole rings, and graphitic structure, respectively. Figure 7e illustrates the π - π stacking interactions between these three components, which drive the adsorption mechanism of the target analyte to the sensing surfaces, thus enhancing the electrochemical signal. A similar interaction has been exploited in the development of various sensors and adsorbents^{82–84}.

Sensing performance evaluation towards 2-Naphthol

After obtaining an optimal active material configuration for the electrode (Co₄Cu₁-ZIF@CB/GCE), different SWV-based characterizations (i.e., sensitivity, reproducibility, and selectivity) were carried out to evaluate its sensing performance towards 2-Naphthol. First, in the sensitivity test, the Co₄Cu₁-ZIF@CB/GCE sensor was exposed to 2-Naphthol with various concentrations (1 to 500 μ M) in 0.01 M PBS (pH 2) using potential windows of -0.60 to $+0.40$ V and a scan rate of 50 mV s⁻¹. The higher the 2-Naphthol concentration, the higher the peak current produced by the sensing system affected by the redox reaction of adsorbed 2-Naphthol (see Fig. 8a). The calibration plot between 2-Naphthol concentration and peak current in Fig. 8b shows a linear correlation for low (1–100 μ M) and high (100–500 μ M) concentrations with correlation coefficient values of $R^2 = 0.95$ ($y = 0.98x + 56.59$) and $R^2 = 0.95$ ($y = 0.37x + 126.99$), respectively. Two segments of linear ranges can result from the saturation of active sites at high concentrations of 2-Naphthol, thus decreasing the sensitivity indicated by the smaller slope. In addition, the adsorption activity of 2-Naphthol on the sensing surface at low concentration may form a monolayer system. Meanwhile, higher concentration possibly causes multilayer adsorption, which hinders additional adsorption⁸⁵. This behavior has been reported in numerous studies of the electrochemical analysis of Naphthol isomers and other analyte^{12,85–87}.

The limit of detection (LOD) is determined using the standardized equation of $\text{LOD} = 3 \times \text{SD}/S$, where SD is the standard deviation from the average of repeated blank measurements and S is the sensitivity that is equal to the slope of the linear regression of peak current vs. analyte concentration⁸⁸. By using the SD from three blank measurements (SD = 0.15), the LOD values of Co₄Cu₁-ZIF@CB/GCE, i.e., detectable concentration changes in the range of low and high 2-Naphthol concentrations are 0.45 μ M and 1.20 μ M with sensitivities of 0.98 μ A μ M⁻¹ and 0.37 μ A μ M⁻¹, respectively. The suggested safety level of 2-Naphthol in urine is 2.60 μ M⁸⁹. Therefore, with its superior sensitivity and an LOD that is almost six times lower than this threshold, the electrode modified with Co₄Cu₁@CB composite is applicable for health monitoring vs. 2-Naphthol exposure. Supplementary Table 5 summarizes the sensing performance of the carbon-black-coupled bimetallic CoCu-ZIF on GCE (Co₄Cu₁-ZIF@CB/GCE) in comparison with previously reported electrodes for 2-Naphthol detection. The results indicate that our sensor exhibits superior performance relative to the reported systems. Specifically, CoCu-ZIF@CB/GCE demonstrates higher sensitivity and a competitive LOD across a broad linear range, highlighting its applicability for both trace-level and high-concentration detection. In contrast, several previous studies achieved lower LODs but only within narrow linear ranges^{90,91}. Most of these earlier electrode designs primarily enhanced electrical conductivity by incorporating conductive polymers, carbon nanostructures, or noble metal nanoparticles. In comparison, our CoCu-ZIF@CB/GCE sensor uniquely integrates the conductivity enhancement provided by CB with dual redox-active sites from the Co–Cu bimetallic frameworks. This distinctive structural and electronic synergy effectively boosts the catalytic activity of the electrode toward 2-Naphthol oxidation, making it a promising platform for electrochemical sensing applications, competitive with previous approaches.

Second, to prove the process reproducibility of the electrodes, we have built five Co₄Cu₁-ZIF@CB/GCE samples from the as-prepared composite ink and exposed them to 100 μ M of 2-Naphthol (0.01 M PBS, pH 2). All five electrodes have demonstrated similar current responses of (148 ± 3) μ A (see

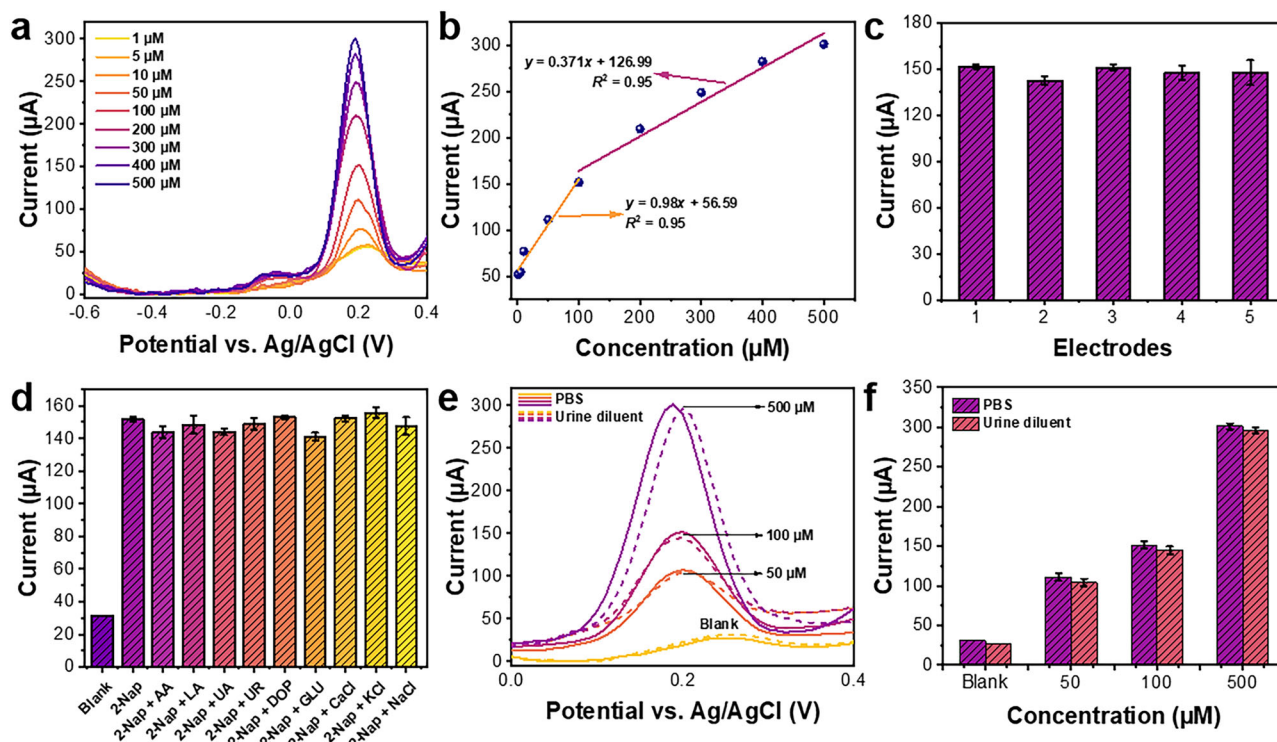


Fig. 8 | Sensing performance of carbon-black-coupled CoCu-ZIF composite on glassy carbon electrode towards 2-Naphthol. **a** Square wave voltammetry (SWV) response of a Co₄Cu₁-ZIF@CB/GCE sample towards different concentrations of 2-Naphthol. **b** Calibration plot of measured current response obtained from each prepared 2-Naphthol concentration. The linear regression is analysed for two groups of low (1–100 μM) and high (100–500 μM) 2-Naphthol concentrations. **c** Reproducibility test results showing the current responses of five Co₄Cu₁-ZIF@CB/GCE samples in 100 μM 2-Naphthol. **d** Cross-sensitivity assessment of a Co₄Cu₁-

ZIF@CB/GCE sample in 100 μM 2-Naphthol mixed with various 100 μM interference substances (i.e., ascorbic acid (AA), lactic acid (LA), uric acid (UA), urea (UR), dopamine (DOP), glucose (GLU), calcium chloride (CaCl₂), potassium chloride (KCl), and sodium chloride (NaCl)). **e**, **f** SWV response and respective bar chart of maximum current of a Co₄Cu₁-ZIF@CB/GCE sample during monitoring of 100 μM 2-Naphthol diluted in phosphate-buffered saline (PBS) and urine diluent, respectively. All measurements (except urine diluent shown in **f**) were conducted in 0.01 M PBS (pH 2).

Fig. 8c). The relative standard deviation (RSD) of 2.20% indicates lower measurement uncertainty compared to reported ZIF-based electrochemical sensors^{38,39,92}, demonstrating high precision in sensor response and overall sensing reliability.

Third, the Co₄Cu₁-ZIF@CB/GCE sample was tested to detect 2-Naphthol in the presence of possible background interference substances (see Fig. 8d–f). Figure 8d compares the sensor responses toward a mixed solution in PBS (0.01 M, pH 2) containing 100 μM 2-Naphthol and 100 μM of potential interfering substances commonly present in urine. These substances include ascorbic acid (AA), lactic acid (LA), uric acid (UA), urea (UR), dopamine (DOP), glucose (GLU), calcium chloride (CaCl₂), potassium chloride (KCl), and sodium chloride (NaCl). The presence of these interferents had a negligible influence on the sensor response, as indicated by a relative standard deviation (RSD) of 2.96%, demonstrating the high selectivity and accuracy of the sensor. Considering the linear relationship between current and concentration, this deviation corresponds to an approximate systematic error of 2.96 μM from the true 2-Naphthol concentration, which can be further corrected through calibration. Moreover, the interfering compounds exhibit oxidation peaks at distinct potentials, resulting in only minimal interference with the 2-Naphthol response observed at approximately 0.21 V^{93,94}. The selective ability of the sensor was also evaluated by detecting 2-Naphthol in non-biological urine diluent, which contains calcium chloride, magnesium chloride, potassium chloride, sodium chloride, sodium phosphate, sodium sulfate, urea, and creatinine, along with sodium azide as a preservative. Figure 8e, f shows the comparison of sensor response towards 2-Naphthol in PBS and urine diluent with concentrations of 50, 100, and 500 μM. Here, no significant difference was observed when the urine diluent buffer was used, as indicated by comparable current responses for 50 μM of 2-Naphthol in PBS and urine diluent, which

were (111 ± 4) μA and (104 ± 4) μA, respectively. Furthermore, we calculated the recovery of the sensor as the ratio of measured to added concentration after successively adding 50, 100, and 500 μM of 2-Naphthol to the urine diluent. From the detected recovery concentrations of 48.54, 89.83, and 466.33 μM, recovery percentage values of 97.08%, 89.83%, and 93.26%, respectively, were obtained. These high recovery values indicate the feasibility of Co₄Cu₁-ZIF@CB/GCE sensors in real sample analyses.

Conclusions

Bimetallic cobalt-and-copper-based zeolitic imidazolate framework (CoCu-ZIF) particles have been successfully integrated with carbon black (CB) and glassy carbon electrode (GCE) to serve as highly sensitive and selective electrochemical 2-Naphthol sensors. Among the contributing factors, the synergistic electronic interactions between Co³⁺/Co²⁺ and Cu²⁺/Cu⁺ have been found to play the most critical role in enhancing the electrochemical properties of the ZIF. A high Cu⁺ content increases carrier density, promoting internal charge redistribution and efficient electron transfer. Although CB has been required to further enhance the electrical conductivity of the composite, the CoCu-ZIF has been proven to play a crucial role in elevating 2-Naphthol detection due to its accessible dual redox-active sites and high surface area that actively promote redox reactions. The selectivity and limit of detection (LOD) of CoCu-ZIF@CB on GCE are within the safety threshold of 2-Naphthol, while featuring anti-interference capability and generating a stable detection response in challenging measurement conditions including synthetic urine. Moving forward, functionalizing the sensor surface with molecular recognition moieties like cyclodextrin or calixarene may further improve PAH selectivity. Additionally, bimetallic ZIF-based sensors show strong potential for multiplex PAH detection by targeting their distinct redox signatures.

Methods

Materials

The reagents including cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (ACS reagent $\geq 98\%$), $\text{K}_3\text{Fe}(\text{CN})_6$ (ACS reagent, $\geq 99.0\%$), and NafionTM perfluorinated resin solution (5 wt. %) were purchased from Sigma-Aldrich. Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) ($> 95.0\%$) and 2-MeIm ($> 98.0\%$) were purchased from Tokyo Chemical Industry. KCl (99.0%) and PBS 10X (pH 7.4) were obtained from Fujifilm Wako and Nacalai Tesque, respectively. The used electrodes including the GCE (diameter of 3 mm), a reference electrode (Ag/AgCl/saturated KCl), and a platinum counter electrode were acquired from ALS Japan. CB for GCE modification was obtained from Cabot Corporation. Sensing evaluation was performed using 2-Naphthol ($> 99.0\%$) from Tokyo Chemical Industry, with additional interference agents including Sigmatrix urine diluent, uric acid, ascorbic acid, glucose, and dopamine hydrochloride obtained from Sigma-Aldrich.

Synthesis of bimetallic CoCu-ZIF particles

CoCu-ZIF particles were synthesized through co-precipitation by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with a total mole of 2 mmol in 30 mL of methanol. Separately, 8 mmol of 2-MeIm was dissolved in another 30 mL of methanol. After both solutions were well mixed, the metal solution was transferred slowly to the 2-MeIm solution and stirred for 1 h at room temperature. The ZIF was obtained after 24 h of solution ageing, then the precipitate was thoroughly washed with methanol and dried at 60°C . In this work, the same methods were used to produce $\text{Co}_x\text{Cu}_y\text{-ZIF}$ with different precursor molar ratios of Co to Cu, where x and y are the molar ratios of Co and Cu, respectively. The produced sample variants include ZIF-67, $\text{Co}_4\text{Cu}_{0.5}\text{-ZIF}$, $\text{Co}_4\text{Cu}_1\text{-ZIF}$, $\text{Co}_4\text{Cu}_2\text{-ZIF}$, and $\text{Co}_4\text{Cu}_3\text{-ZIF}$.

Material characterizations

The phase and crystal structure of the materials were identified from XRD patterns obtained from an X-ray diffractometer, Rigaku MiniFlex 300/600, Japan, with a Cu anode source over a range of 2θ of 10° – 90° with a scan rate of 0.02° . In addition, FTIR spectroscopy, using a Prestige 21, Japan (KBr technique, at wavenumber range of $400 - 4000\text{ cm}^{-1}$) was conducted to confirm the formation and chemical properties of the CuCo-ZIF particles. Field emission scanning electron microscopy (FE-SEM) analysis using a Hitachi SU8000 with an acceleration voltage of 10.0 kV was carried out to investigate the material topography. This FE-SEM was integrated with a Bruker EDX spectrometer for elemental screening. XPS using an Ulvac PHI Quantes with Al K α source was performed to study the near-surface composition and elemental distribution of the materials. The binding energy scale was calibrated using the C 1s peak of adventitious carbon at 284.8 eV. Surface area, pore size, and pore volume were analyzed from nitrogen adsorption/desorption measurements using a Quantachrome Autosorb-1 in high-purity nitrogen gas (99.999%) at 77 K. Prior to nitrogen adsorption/desorption measurements, the samples were degassed by pre-heating at 150°C under flowing argon for 16 h. The analyses were performed using BET, BJH, and DFT methods.

Electrochemical measurements

Electrochemical measurements were conducted using a multichannel potentiostat (Biologic VMP3) with a standard three-electrode configuration comprising a glassy carbon working electrode (GCE, 3 mm diameter), Ag/AgCl (saturated KCl) reference electrode, and a platinum wire counter electrode. The electrolyte consisted of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KCl in 0.01 M PBS (pH 7.4). The GCE working electrodes were prepared by drop-casting 6 μL of a 4 mg/mL suspension of CoCu-ZIF (or composite) dispersed in deionized water, 2-propanol, and 5 wt% NafionTM (15:4:1 v/v) onto the pre-polished GCE and drying at 30°C for 20 min. Prior to electrochemical measurements, these modified electrodes were activated with 50 CV scans at 20 and 50 mV/s until a stable redox signal was observed. Final CVs were recorded in the potential window of -0.10 to $+0.55\text{ V}$ at a scan rate of 50 mV/s. EIS measurements were performed over 35 frequencies logarithmically spaced from 1 MHz to 0.01 Hz, with an AC

amplitude of 1 mV. For scan-rate studies, CVs were collected at 10–100 mV/s (step size: 10 mV/s) using the same potential window.

Sensing electrode preparation

Detection of 2-Naphthol was performed using a GCE modified with the optimized composite of carbon black-coupled CoCu-ZIF (CoCu-ZIF@CB), as illustrated in Fig. 1. A composite ink was prepared by dissolving CB and CoCu-ZIF in 1 mL of a mixed solvent comprising deionized water, 2-propanol, and 5 wt% NafionTM (15:4:1 v/v). After sonication for homogenization, 6 μL of this ink was drop-cast onto a pre-polished GCE and dried at 30°C for 20 min. The fabricated electrodes were evaluated using SWV to detect 500 μM of 2-Naphthol in 0.01 M PBS (pH 7.4). Prior to each SWV, 50 cycles of CV scans at 50 mV/s were performed in 0.01 M pure PBS (pH 7.4) to obtain a stable redox signal. Electrochemical study was performed on the electrodes with five different mass ratios of CB ($x\text{ mg}$) to CoCu-ZIF ($y\text{ mg}$) denoted as $x:y$ (i.e., 1:4, 2:4, 4:4, 4:2, and 4:1). In addition, the effect of pH of the analyte solution was also studied by change the pH of 0.01 M PBS using HCl as pH adjuster in the range of pH 2–7. The used potential window depended on the current peaks of 2-Naphthol on each measurement, i.e., -0.60 to $+0.00\text{ V}$ for mass ratios dependent measurement, and -0.60 to $+0.40\text{ V}$ for pH dependent measurement.

Setup for polycyclic aromatic hydrocarbon detection

PAH detection was conducted using 2-Naphthol with various concentrations (1, 5, 10, 50, 100, 200, 300, 400, and 500 μM) in 0.01 M PBS (pH 2). For each measurement, 20 cycles at 50 mV/s CV were conducted to obtain a stable signal. The detection response was obtained from the SWV signal measured at -0.60 to $+0.40\text{ V}$ with a scan rate of 50 mV/s. The SWV signal from different 2-Naphthol concentrations was used to determine sensor sensitivity and LOD (see Fig. 1b). Five different CoCu-ZIF@CB/GCE sensors fabricated from the same batch of ink were used to detect 100 μM of 2-Naphthol for evaluating reproducibility. The anti-interference ability of the sensors in heterogeneous solutions was assessed by measuring 2-Naphthol solutions of 100 μM (in 0.01 M PBS, pH 2) mixed with the interference compounds of ascorbic acid, lactic acid, uric acid, urea, dopamine, glucose, calcium chloride, potassium chloride, and sodium chloride. In addition, Sigmatrix urine diluent (5-fold dilution) was used as a buffer solution of 50, 100, and 500 μM of 2-Naphthol, which was measured to evaluate the sensor's recovery percentage.

Data availability

All data supporting the findings of this study are included in the Article and its Supplementary Information. Additional data are available from the corresponding authors upon reasonable request. Requests should be directed to Dr. Joel Henzie (henzie.joeladam@nims.go.jp), Prof. Dr. Erwin Peiner (e.peiner@tu-braunschweig.de), Dr.-Ing. Hutomo Suryo Wasisto (h.wasisto@biostark-ai.com), and Prof. Dr. Nugraha (nugraha@itb.ac.id), who are responsible for responding.

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Author contributions

C.W. and H.S.W. conceived the idea and concept. C.W. designed the experiments, formulated the materials, validated the methods, conducted

fabrication and characterization of CoCu-ZIF, interpreted the experimental results, created the figures (illustrations and graphs), wrote the initial manuscript (main), and revised the paper. H.S.W. and N.L.W.S. validated the methods, analyzed the obtained data, wrote the initial manuscript (support), and revised the paper. A.M., A.N., J.H., and N.N. provided input for the discussion of the results. J.H. provided research facilities and materials. E.P. revised the paper. Y.Y., J.H., H.S.W., N.N., and B.Y. led the project, supervised the work, and acquired the funding. All authors discussed the results and approved the final submitted manuscript.

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Competing interests

The authors declare no competing interests.

Inclusion and ethics statement

All collaborators of this study have fulfilled the criteria for authorship required by Nature Portfolio journals and have been included as authors, as their participation was essential for the design and implementation of the study. Roles, responsibilities, and contributions were agreed among collaborators ahead of the research and manuscript writing. This research was not severely restricted or prohibited in the setting of the researchers, and did not result in stigmatization, incrimination, discrimination, or personal risk to researchers. The references that are relevant and cited in this work not only come from our previous studies, but also include the reports from other research groups.

Additional information

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