An effective and rapid method for the detection of hydrazine hydrate is urgently needed as a result of its high toxicity and extensive use. Here, copper nanoparticles supported on carbon (written as: Cu NP/C) and copper oxide polycrystalline solids (written as: CuO PS), synthesized by calcining the same metal–organic framework at high temperature, were respectively used as electrode materials for electrochemical sensing hydrazine. The results show that the prepared Cu NP/C exhibits a better performance with a sensitivity of 0.1726 mA (mmol/L)\(^{-1}\), a wider linear range of 0.1–2.4 mM and a lower detection limit of 0.0014 mmol \(\cdot\) L\(^{-1}\), compared to the obtained CuO PS. This can be reasonably explained by the lower copper valence state and its interaction with the carbon supports in Cu NP/C. Furthermore, the good selectivity and anti-interference ability from the Cu NP/C are also acquired for electrochemical detection of hydrazine.

1 | INTRODUCTION

Hydrazine with high power density, strong reducing property and corrosivity has been widely used as reducing agents, foaming agents, pesticides and fuels in the applications of industry, agriculture, medicine and energy [1, 2]. However, the high toxicity makes it a serious pollutant in water and soil [3]. As it is documented, hydrazine can be absorbed by the body through the respiratory tract or the skin, which will seriously damage our liver, lungs, kidneys and the central nervous system, even cause cancer [4]. Therefore, a highly sensitive method for hydrazine sensing is extremely urgent to ensure the sustainable development of mankind [5].

At present, many analytical methods have been put forward, including, spectrophotometry, titrimetry, chromatography [6]. Among them, the electrochemical analysis provides an unquestionable prospect for the detection of hydrazine, benefiting from the advantages of fast response time, low cost, good selectivity, broad linear detection range and easy operation [7]. As we know, the electrochemical sensing performance is generally determined by the electrode modified materials, and a great deal of materials have been investigated for detecting hydrazine, for instance, precious metal materials, transition metal oxides, two-dimensional carbon materials and so on. As the more prominent one, copper-based materials have received much attention in point of the unique orbital occupation, abundant storage and low-cost. As previously reported, Reza Ojani et al. realized that copper oxide nanoparticles combined with ionic liquid achieved a good performance for electrochemical detection of hydrazine [8]. Razium Ali Soomro et al. reported the CuO nanostructures with large surface area enhanced the conductivity, achieved the detection of hydrazine hydrate in tap water [9]. By optimizing the mass ratio of copper oxide to mesoporous carbon, Zhang et al. presented a leaf-like copper oxide decorated on worm-like mesoporous carbon, showing a sensitivity of 0.00487 \(\mu\)A\(\cdot\)\(\mu\)M\(^{-1}\) for hydrazine sensing [10]. For all this, copper-based materials have yet to be constructed into real sensors and the improvement of hydrazine sensing performance is still necessary.

In recent years, a metal-organic framework (MOF) ([Cu\(_3\)(BTC)\(_2\)(H\(_2\)O)\(_3\)]\(_n\), HKUST-1), consisting of trimesic acid and copper nodes, has been emerging as a new multifunctional and porous material [11]. With the advantages of the large specific surface area, adjustable morphology and high active surface site, HKUST-1 and its derivatives have been widely implemented in gas storage and separation, energy and sensors [12]. For example, Li et al. presented an electrochemical sensor based on HKUST-1 for the detection of dopamine, which has good electrocatalytic activity and high selectivity [13]. Xu et al. demonstrated that low concentration
of xylene could be detected through the interaction between HKUST-1 and xylene [14]. Kowsar Majid et al. synthesized HKUST-1 by microwave-assisted method, showing excellent stability and a low detection limit for electrochemical sensing of acetaminophen (AC) and dopamine (DA) [15]. Lin et al. synthesized a nanocomposite of graphene fragments and HKUST-1 used for electrochemical sensing of hydrogen peroxide with high performance [16]. Nevertheless, whether the HKUST-1 derivatives can achieve efficient electrochemical detection of hydrazine is still unexplored. Thus, in this work, copper nanoparticles supported on carbon substrate (Cu NP/C) and copper oxide polycrystalline solids (CuO PS), obtained through the pyrolysis of the \([\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n\) (HKUST-1, BTC = 1,3,5-benzenetricarboxylate), were respectively examined for the detection of hydrazine. From the electrochemical results, it is found that the Cu NP/C exhibits better performance, compared to CuO PS and most of the previously reported materials. Specifically, the sensitivity and detection of limit from Cu NP/C is determined to be 0.1726 mA (mmol/L)^{-1} and 0.0014 mmol-L^{-1}, respectively. Furthermore, good selectivity is also obtained.

## EXPERIMENTAL SECTION

### 2.1 Reagents

Copper nitrate (Cu(NO_3)_2⋅3H_2O, AR), 1,3,5-benzenetricarboxylic acid (H_3BTC, 98%), ethanol (C_2H_5OH, 99.8%), hydrazine hydrate (N_2H_4⋅H_2O, AR, 80%), urea (CO(NH_2)_2, AR, 99%), dicyandiamide (DCD, 96%), ammonium acetate (NH_4OAc, AR), melamine (C_3H_6N_6, 99%), and ammonium carbonate ((NH_4)_2CO_3, AR, 30% NH_3 basis), all the reagents were purchased from Aladdin.

### 2.2 Instruments

X-ray diffraction (XRD) measurements were performed on a Rigaku Dmax 2500 Powder Diffractometer equipped with Cu-Kα radiation (λ = 0.15406 nm). The Fourier transform infrared spectra (FT-IR) in the range of 600–4000 cm^{-1} were recorded from the IS50 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were executed on an AVG Thermo ESCALAB 250 spectrometer (VG scientific) running at 120 W. The morphologies of the two derivatives were characterized by Hitachi S4800 scanning electron microscope (SEM) with a working accelerating voltage of 20 kV. The transmission electron microscopy (TEM) images were obtained on the Tecnai G2 F20. Raman spectra were measured in the inVia Qontor (Renishaw, UK) system at a wavelength of 532 nm.

### 2.3 Synthesis of Cu NP/C and CuO PS

Firstly, the precursor of \([\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n\) was synthesized by following the previously reports with a little modifications [17, 18]. Typically, 4.5 mmol (1.087 g) of Cu(NO_3)_2⋅3H_2O was dissolved in 15 mL deionized water. At the same time, 2.5 mmol (0.525 g) of 1,3,5-benzenetricarboxylic acid was dissolved in 15 mL ethanol. Then, the two solutions were mixed. After stirring for 30 min, the mixture was transferred to a 50 mL Teflon-lined autoclave and heated to 120°C for 12 h. When the system cooled down to room temperature, a blue solid powder as \([\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n\) product was obtained by centrifugal separation, washed three times with ethanol and dried at 70°C for 12 h under vacuum condition [11]. For the synthesis of Cu NP/C, 300 mg sample of \([\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n\) was calcined at 1000°C in a tube furnace in Ar atmosphere for 3 h with a heating rate of 5°C/min. To obtain CuO PS, the experimental procedures were almost the same to that of Cu NP/C except for the calcination in air.

### 2.4 Electrochemical measurements

All electrochemical measurements were carried out on a CHI 760E electrochemical workstation with a standard three-electrode system at room temperature. Before the experiments, a piece of carbon paper (5 mm × 5 mm) was rinsed with water/ethanol and dried at 60°C. The catalyst ink was prepared by mixing the materials, ethanol, and Nafion (5%) in a certain proportion. The preparation of working electrode was completed by dropcasting the catalyst ink onto the above cleaned carbon paper with a loading of 4.8 mg/cm². Ag/AgCl (in saturated KCl) electrode and a graphite rod were used as reference electrode and counter electrode, respectively. For the electrochemical tests, cyclic voltammetry and linear sweep voltammetry (LSV) were used to quantitatively evaluate the sensing potential of prepared materials toward hydrazine. Chronoamperometry was conducted to quantitatively determine the sensing performance of materials. Through the whole process, 0.1 M KOH was chosen as the electrolyte.

## RESULTS AND DISCUSSION

### 3.1 Characterization of \([\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n\) (Cu-MOF)

As reported, copper ions coordinated with the oxygen atom from trimesic acid in hydrothermal condition resulted in the formation of HKUST-1 polyhedrons. During the subsequent high temperature annealing process, in one case, copper (II) atoms in HKUST-1 were reduced to zero valent atoms by carbon atoms, which migrated and aggregated into larger copper nanoparticles with the emission of carbon dioxide and water vapour under the protection of inert argon gas. This is the formation of Cu NP/C composites. In another case, the coordination interaction of copper with the oxygen atoms became the stronger chemical bond with the loss of organic ligands when calcined in air, leading to the formation of CuO PS. Herein, the precursor materials were analyzed by XRD pattern and FT-IR. As shown in Figure 1(a), all the diffraction peaks are sharp,
FIGURE 1  The as-synthesized \([\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n\): (a) X-ray diffraction pattern; (b) infrared spectra

matching well with the face-centred cubic structure of the Cu-MOF and consistent with results from the literature reports [19]. The other signal peaks were not observed, indicating the pure phase and good crystallinity of \([\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n\). The FTIR spectrum of the synthesized Cu-MOF is shown in Figure 1(b). The absorption peak around 1651 cm\(^{-1}\) is assigned to the asymmetric stretching vibration of carboxylate, while the signals at 1448 and 1372 cm\(^{-1}\) were attributed to the symmetrical stretching vibrations. A wide stretching vibration band in the range of 3800–2700 cm\(^{-1}\) was caused by the OH groups originating from water molecules. Furthermore, the detected bands at 1105 and 729 cm\(^{-1}\) can be attributed to the existence of C-O stretching vibration and C-H bending vibration, respectively [20]. This result shows the carboxylic acid is involved in the Cu-MOF, agreeing well with the results of other reported FTIR spectra [21].

3.2 Characterizations of Cu NP/C and CuO PS

The XRD patterns of Cu NP/C and CuO PS are shown in Figure 2(a). The black curve belongs to the XRD pattern of Cu NP/C. The characteristic diffraction peaks at 43.7°, 50.7°, and 74.3° correspond to the (111), (200), and (220) planes of the metallic copper (PDF#04-0836) [22]. This indicates the existence of metal copper nanoparticles. For the red line from CuO PS, the main characteristic diffraction peaks coincide with the peaks of the copper oxide standard (PDF#48-1548) [23]. The 2θ values at 32.6°, 35.7°, 38.9°, 49.0°, 53.6°, 58.3°, 61.7°, 66.2°, 68.4°, 72.3° and 74.9° are from the (110), (002), (111/200), (−202), (020), (202), (−113), (−311), (220), (311) and (−222) facet of CuO crystal [12]. The pure copper oxide of this product can be demonstrated by no impurity peaks in the pattern.

To visualize the morphologies and structures of two materials, SEM and TEM were conducted. For the Cu NP/C, the SEM image in Figure 2(b) presents that numerous spherules are randomly dispersed on the carbon sheets, indicating the formation of targeted composites consisting of copper nanoparticles and carbon sheets. In Figure 2(c), the TEM image reveals that a buffer layer of porous and thin graphite sheet exists between Cu nanoparticles and thick carbon substrates, which will contribute to the efficient electron transfer in composites. For the CuO PS, Figure 2(d) displays the distinct lamellar structure despite the polycrystalline features. The corresponding elemental mapping images of Cu NP/C are exhibited in Figure 3(a,b), displaying the copper and carbon in the composites. In addition, the Raman spectra of Cu NP/C and CuO PS were collected to identify the composition. In Figure 3(a), the peak at 1350 cm\(^{-1}\) and 1600 cm\(^{-1}\) from Cu NP/C can be determined to the D and G band of carbon, respectively [24]. To our knowledge, the G band and the D band are respectively related to the relative motion of the sp\(^2\) carbon atoms and the breathing mode of the carbon rings [25, 26]. The ratio of D to G band is calculated to be 0.92, illustrating the co-existence of amorphous and graphitic carbon.
The Raman spectrum of CuO PS is shown in Figure 3(b). The signals at 295 cm$^{-1}$, 343 cm$^{-1}$, and 628 cm$^{-1}$ are attributed to Ag and Bg of CuO [27]. This declares the main composition of CuO again.

To get insight into the electronic structures of two samples, X-ray photoelectron energy spectrum (XPS) experiments were carried out. Figures 4(a) and 4(b) are, respectively, the full XPS survey spectrum of Cu NP/C and CuO PS, showing the existence of Cu and O in samples. For the deconvoluted XPS spectra of Cu 2p in Figure 4(c), the peaks positioned at 932.7 and 952.56 eV are resulted from Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ of metallic Cu. The binding energies located at 934 and 954 eV are ascribed to the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ of Cu$^{2+}$. This suggests the presence of copper oxide on the surface of Cu nanoparticles in Cu NP/C materials, which can be explained by the interaction of copper with oxygen in buffer layers and carbon support [28–30].

In Figure 4(d), the XPS spectrum of Cu 2p from the CuO PS presents two peaks at 934.7 and 954.1 eV, corresponding to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ of Cu(II). The two peaks belonging to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ of Cu$^{2+}$ were found at 932.2 and 952.2 eV, respectively [31, 32]. Compared with each other, it can be concluded that the valence of copper in Cu NP/C is much lower than that in CuO PS. It is worth to mention that the satellite peaks at 962.7 and 943.2 eV are typical features of copper oxide [33].

### 3.3 Electrochemical properties of Cu NP/C and CuO PS

Herein, the Cu NP/C and CuO PS were evaluated for electrochemical sensing hydrazine in 0.1 M KOH. The bare carbon paper was used as a comparison. As shown in Figure 5(a), the typical cyclic voltammetric curve (CV) from Cu NP/C shows a significantly higher current density than that from CuO PS and carbon paper in 6 mM hydrazine hydrate solution. This suggests the best electrochemical performance of the Cu NP/C among three samples. Figure 5(c) reveals the influence of scanning rates on the electrocatalytic oxidation of hydrazine hydrate on Cu NP/C modified-electrode. Intuitively, the response current is increasing with the scan rate changing from 10, 30, 50, 70 to 90 mV/s. The linear relationship between response currents $j_p$ and scan rate $v^{1/2}$ in Figure 5(d) is expressed as: $j_p = 0.651 v^{1/2} - 0.745$ (related coefficient: $R^2 = 0.995$), illustrating a diffusion control process of hydrazine oxidation on the Cu NP/C modified-electrode [34]. To qualitatively investigate the relationship between current density and concentration, cyclic voltammetry and LSV were performed in the electrolyte with different concentrations of hydrazine hydrate (0, 2, 4, 6, 8, 10 mM). As shown in Figures 5(b) and 6(a), the current densities from CV and LSV clearly increase with the hydrazine concentration ranging from 0 to 10 mM.

To accurately reveal the sensing performance of Cu NP/C and CuO PS, the amperometric (I-t) method was applied in 0.1 M KOH solution. According to the peak values in LSV curves, a potential of 0.45 V was chosen. In Figure 6(b), the current densities from Cu NP/C stepwisely enhance with the concentration of hydrazine hydrate continuously increasing from 0.1 to 2.4 mM. For the CuO PS, it also shows the similar changes in current density, but the degree of change is much smaller and the sensing saturation was quickly reached. Therefore, compared to CuO PS, the Cu NP/C material shows a more powerful sensing capability to hydrazine hydrate. Further linear fitting in Figure 6(c) presents the calibration curve between the hydrazine hydrate concentrations and the response current: $y = 0.6904 x + 0.2449$ (related coefficient: $R^2 = 0.999$) and a sensitivity of 0.1726 mA (mmol/L)$^{-1}$ for Cu NP/C. The limit...
of detection (LOD) was calculated to be 0.0014 mM based on the triple signal-to-noise ratio (LOD = 3σ/q)[4]. However, for the CuO PS, the correlativity of hydrazine hydrate concentrations and current density follows two different linear relationships. In the low concentrations range from 0.1 to 1.0 mM, the linear curve is fitted as: $y = 0.3653x + 0.0051$ (related coefficient: $R^2 = 0.997$) with a sensitivity of 0.0913 mA (mmol/L)$^{-1}$. In the range of 1.0 to 1.6 mM, the linear regression curve is indicated as: $y = 0.1782x + 0.183$ (related coefficient: $R^2 = 0.998$) with a sensitivity of 0.0446 mA (mmol/L)$^{-1}$. The LOD was calculated to be 0.0041 mM for CuO PS. Therewith, the obtained sensitivity and LOD of Cu NP/C are much superior to that of CuO PS and most of previous reported materials, as shown in Table 1.

Herein, for the excellent sensing performance of present Cu NP/C, the reasonable explanations can be tentatively attributed to: (1) the lower copper valence in Cu NP/C (as analyzed in XPS) contributes to the dehydrogenation involved in the mechanism of hydrazine oxidation [35]. It can be provided that the electron density around element copper in Cu NP/C is much higher than that in CuO PS. This means the easier interaction between copper and hydrogen prompts the electron transport and formation of intermediates. (2) Porous carbon support provides favourable mass/electron transport and larger capacitance of 38 mF/cm$^{-2}$, benefiting to the electrochemical reactions. (3) The interaction of Cu NP and carbon improves the electron transport channel, decreasing the electrochemical impedance and enhancing the reaction efficiency. As reported, the smaller the charge/electron transfer resistance, the faster the electrochemical reactions. [36]

Selectivity is another critical factor for the sensing ability of materials. Herein, several nitrogenous substances were chosen to perform interference experiment, as shown in Figure 6(d). Apparently, the response current density of 0.1 mM hydrazine hydrate has no observable changes when the interfering substances including dicyandiamide (DCD), urea, NH$_4$OAc, (NH$_4$)$_2$CO$_3$ and melamine with a concentration of 0.1 mM were added in sequence. Moreover, despite the co-existence of these interferences in the electrolyte, the subsequent detection of hydrazine is also not influenced. In all, the present Cu NP/C shows excellent sensitivity and remarkable selectivity for electrochemical sensing hydrazine hydrate.

### 4 CONCLUSION

In summary, the sensing performance of Cu NP/C is better than that of CuO PS because the carbon-loaded copper nanoparticles possess stronger electron transport capacity and larger specific surface area. According to the amperometric tests, the LOD was calculated to be 0.0014 and 0.0041 mmol-L$^{-1}$ with a sensitivity of 0.1726 and 0.0913 mA (mmol/L)$^{-1}$ for the Cu NP/C and CuO PS, respectively. We hope the present Cu NP/C can provide a thought for sensing hydrazine hydrate and the superior sensing performance can provide a different way for following application of MOF and their derivatives.

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