Increased SO2 electrooxidation activity on a copper-nitrogen doped catalyst and its active sites analysis

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\textbf{A B S T R A C T}

It's a meaningful work to develop a highly active nonprecious SO2 electrooxidation catalyst, replacing the Pt-based ones. Here, a novel Cu-N doped carbon-based catalyst is synthesized by pyrolyzing the imidazole chelated copper ions on the chitosan modified carbon BP2000. During the preparation, metallic Cu is developed and encapsulated in the carbon lattices, and transformed into the CuNx structures on the catalyst surface, simultaneously. Metallic Cu plays significant role in the doping and developing of active sites, which have vital effects on the catalysis activity. The prereduction of Cu\textsuperscript{2+} by NaBH\textsubscript{4} during the preparation of Doping(I)-Cu@N-C makes great contribution to the development of metallic Cu, which highly dispersive anchor in the carbon lattices. This as-synthesized Doping(I)-Cu@N-C catalyst exhibits excellent SO2 electrooxidation activity. Its SO2 oxidation currents are remarkably increased with the elevation of applied potentials, and the oxidation performances prominently surpass the commercial Pt/C, when the potential is above 0.822 V. The peak SO2 oxidation current (i_p) of Doping(I)-Cu@N-C is 7.17 mA cm\textsuperscript{-2} @ 0.684 V, much higher than the 3.03 mA cm\textsuperscript{-2} @ 0.584 V of Pt/C with the same mass loading. In the chronoamperometry tests under 1.2 V, the terminal oxidation current of Doping(I)-Cu@N-C was 1.74 times as high as that of Pt/C, indicating that this prepared catalyst also displays much better SO2 electrooxidation activity than Pt/C under constant applied potentials.

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\textbf{I n t ro d u c t i o n}

Sulfur dioxide, usually coming from effluents discharged by power plants and industrial boilers, is not only hazardous to people’s health but also detrimental to the environment [1,2]. Flue gas desulfurization technologies are normally used to control the emission of SO2 [3]. However, conventional desulfurization technologies have prominent shortcomings such as the large amount usage of chemical reagents, production of secondary pollutants and expensive operation costs. SO2 electrooxidation displays the advantageous high efficiency, compacted facility, low operation costs and environmentally friendly processes [4–10]. What’s more, with perspective applications in energy conversion, flue gas
desulfurization, corrosion, electrogenerative and catalysis, SO₂ electrooxidation has gained many attentions in the past several decades [7,11–13].

Generally, the electrooxidation of SO₂ usually took place on the anodic electrodes under certain applied potentials [9,14,15]. For instance, a SO₂ absorption and electrochemical oxidation process was conducted by Umar Tezcan Ün et al. with the platinum expanded mesh anode in the sulfuric acid electrolyte [16]. And a gaseous SO₂ electrooxidation method was proposed by Zhai et al., showing positive prospect towards disposing the low concentration SO₂ with Pt/C catalysts [17,18]. With notable desulfurization performances, many efforts were paid to search for the robust SO₂ electrooxidation catalysts [7,13,15,19–22]. Most of the investigations focused on the precious metal catalysts, such as Pt [23,24], Pd [25], Au [26,27], Ru [6], as well as their alloys [11,28]. However, the surface oxide species of precious metals evidently blocked their active sites in high oxidation potential regions, resulting in remarkable decrease of SO₂ oxidation activities on precious metal catalysts [20,21,29–31]. In addition, these precious metals showed less competitive in the application of SO₂ electrooxidation for economic reasons. So it’s a meaningful work to develop the non-precious substituent catalyst for SO₂ electrooxidation.

M-N-C catalysts were extensively applied to the 2 e⁻ or 4 e⁻ processes of ORR, HOR etc. reactions [32–39]. SO₂ electrooxidation was a 2 e⁻ transfer reaction on the anodic electrodes. And it was a feasible attempt and economic replacement to the catalysis of SO₂ with M-N-C catalysts. What’s more, characteristics and intrinsic activities of carbon catalysts and M-N-C catalysts for the electrooxidation of SO₂ were seldom reported. Nevertheless, the carbon catalyst was one of the promising candidates for SO₂ electrooxidation, as they are low in cost, easily accessible, and the N-doped structures exhibit obvious SO₂ oxidation activity [40]. Non-precious catalysts based on the pyrolysis of metal-nitrogen precursors were recognized as another better alternatives. Our previous work explored the Fe-N doped catalyst with good SO₂ electrooxidation performances [41]. The understanding of M-N-C catalysts applying to SO₂ electrooxidation would have profound effects on environmental protection and desulfurization.

In this work, we applied a prereduction method to prepare the nanoparticle encapsulated Cu-N doping carbon-based catalyst, which had numerous highly dispersive metal particles embedded in the carbon lattices. A probe molecular was selected to study the surface active composites for SO₂ electrooxidation. What’s more, the influences of metallic Cu for the development of active composites and active structures were also investigated by comparing the samples prepared through different synthesis methods. Thus, the objective of this work was to develop an excellent nonprecious SO₂ electrooxidation catalyst and clarify the influential active factors of Cu-N doping catalyst for the electrooxidation of SO₂.

**Experimental**

**Main materials**

Soluble chitosan, obtained from Henan Weidao Chemical Reagent Factory, was a nontoxic food grade reagent, which makes a positive contribution to the development of a cleaner and healthier catalyst preparation process. Chitosan was beneficial for the dispersion and sequestration of Cu²⁺ on the carbon support of BP2000 with its abundant nitrogen and oxygen functional groups. BP2000 was originally sourced from the commercial product from Carbot. CuCl₂ was provided by the Tianjin Damao Chemical Reagent factory. Imidazole was purchased from Tianjin Guangfu fine chemical research institute. NaBH₄ was offered by the Sinopharm Chemical Reagent Co. Ltd.

**Catalyst synthesis**

To study the effects of Cu for the development of Cu-N doping catalyst and formation of active sites, a group of copper-nitrogen doped carbon catalysts were prepared and characterized. Doping (I)-Cu@N-C was the sample prepared with prereduction by the NaBH₄, aiming at clarifying the function and influence of metallic Cu in the active site development. A Doping (II)-Cu@N-C catalyst was prepared by the directly carbonization reduction, during which active sites were developed for the catalysis of Cu that formed through carbonization reduction. For comparison, pyrolysis of carbon support (BP2000) was also prepared following the same carbonization procedures.

**Synthesis of doping (I)-Cu@N-C**

0.5 g soluble chitosan was dispersed in 168 mL deionized water, then 0.1 g carbon BP2000 was added, following with a vigorously ultrasonic process for 2 h. The mixture was adjusted to 9, then the mixture was applied to the oil bath under 55 °C for 3 h. Subsequently, the pH was adjusted to 6 – 7, followed by adding 0.1 g imidazole and 50 mL 0.05 M CuCl₂. This new mixture was kept and stirred under 60 °C for another 3 h. The obtained suspension mixture was blended with 100 mL NaBH₄ ethanol solution with the final concentration of 0.02 M, stirring for another 3 h in the ice-water bath. The final suspension was gathered by centrifugation, washing and desiccation. Ultimately, the precursor was placed and pyrolyzed in a tube furnace for carbonization in the inert gas of Ar with the first ramping temperature of 5 °C min⁻¹ to 450 °C holding at 450 °C for 1 h and the second ramping temperature of 1 °C min⁻¹ to 700 °C holding at 700 °C for 1 h to complete the pyrolysis process. The furnace was cooled down naturally. This was the Doping(I)-Cu@N-C catalyst sample.

**Synthesis of doping (II)-Cu@N-C**

0.5 g soluble chitosan was dispersed in 168 mL deionized water, then 0.1 g carbon BP2000 was added, followed by a vigorously ultrasonic process for 2 h. The mixture was adjusted to 9, then it was transferred to an oil bath pan (55 °C), holding for 3 h to have the carbon supports well modified with the N and O functionalized chitosan. Subsequently, the mixture pH was adjusted to 6 – 7, followed by adding 0.1 g imidazole and 50 mL 0.05 M CuCl₂. This new mixture was under oil bath at 60 °C for another 3 h. Afterwards, the suspension was gathered by centrifugation, washing and desiccation. Finally, the above precursor was placed in a tube furnace for pyrolysis under Ar following the same carbonization pyrolysis process with the above sample. The furnace
was cooled down naturally to the ambient temperature. After grinding, the catalyst was the Doping(II)-Cu@N-C sample.

Preparation of the carbon catalyst BP
Carbon BP2000 was placed in the tube furnace for pyrolysis under Ar with the first ramping temperature of 5 °C min⁻¹ to 450 °C holding at 450 °C for 1 h and a second ramping temperature of 1 °C min⁻¹ to 700 °C holding at 700 °C for 1 h to complete the pyrolysis process. The final product was the sample of BP catalyst.

Physical characterization

Morphology characteristics of the catalysts were examined by the transmission electron microscopy (TEM) on a JEOL JEM-2000EX microscope instrument. Samples were well dispersed by dropping their isopropyl alcohol dispersive suspension onto the Cu grids, followed by drying in air. The high-resolution TEM morphologies, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and element mappings were characterized and recorded by a Tecnai G2 F20-TWIN transmission electron microscope under 200 kV. X-ray diffraction (XRD) patterns were obtained on a D/max-2500PC diffractometer with Cu Kα (λ = 1.54 nm) radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an imaging photoelectron spectrometer of Thermo Scientific ESCAlab 250Xi with a monochromatic Al Kα X-ray source (1486.6 eV).

Electrochemical characterization

SO₂ electrooxidation performances of the prepared catalysts were characterized and compared on a rotating disk electrode in the typical three-electrode cell system on an electrochemical workstation (CHI Instruments: CHI 730D, Chenhua Co., China). In the system, the working electrode was evenly coated with a quantitative well-dispersed catalyst suspension on a glass carbon electrode (GCE, 4 mm) forming the uniform catalyst film. Catalyst loadings were 0.379 mg cm⁻² for all the tests. A platinum foil was used as the counter electrode, and a saturated calomel electrode was served as the reference electrode (SCE). Background electrolyte in tests was 0.5 M H₂SO₄. SO₂ was generated by dissolving appropriate amount of solid Na₂SO₃ in N₂ bubbling deoxygenated 0.5 M H₂SO₄ with the concentration of 1 g L⁻¹. In this paper, the catalytic activities of the prepared catalysts were determined and compared with cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) on the RDE system. Catalytic activity of the commercial 20% Pt/C with the same mass loading served as the reference sample.

Results and discussion

Characterization of doping (I)-Cu@N-C

Physical characterizations of Doping(I)-Cu@N-C were examined and displayed in Fig. 1. Transmission electron microscopy (TEM) observations of the as-synthesized Cu-N doped Doping(I)-Cu@N-C catalyst indicated that some leopard-stripe-like substances were developed among the carbon particles (Fig. 1(e)), which was the gather of dense nanoparticles as shown in the enlarged images (Fig. 1(f)). High-resolution TEM (HRTEM) images showed that numerous well-dispersed nanoparticles were successfully embedded in the carbon lattices both on the carbon particles and in the developed leopard-stripe-like parts (Fig. 1(g, h, j, k)). A special section was selected and the corresponding elemental mapping demonstrated the presence of C, N, O, and Cu in catalyst. Notably, the N element was homogeneously in combination with the C. The O element was also well combined with C with more condensed distribution at the nanoparticle section on the catalyst. The Cu signal was highly overlaid with the N, suggesting that the Cu species was stabilized by N coordination with the active metal-nitrogen sites. As for the aggregated particle section, the particle was proved to be made up of Cu (Fig. 1 (a)). The corresponding SAED pattern of the particle displayed the regularly unambiguous Bragg diffraction spots of Cu (Fig. 1 (c)), suggesting the long range ordered high crystallinity structures. However, the interlayer lattice spacing was difficult to identify because of the thick and overlapped structures of Cu (Fig. 1 (k)). Importantly, the high-angle annular dark-field scanning TEM (HAADF-STEM) further indicated the widely distributed Cu existed in the carbon/nitrogen matrix for the wide distribution of the bright spots of metal, meeting the Bragg conditions (Fig. 1(b)). For the less dense region, the SAED image displayed the dispersive annular pattern, attributing to the dispersive small particles in carbon matrix and their random orientation (Fig. 1 (d)). XRD measurements further verified the existence of metallic Cu in the catalyst with strong diffraction peaks of the (111), (200), (220) and (311) planes of metallic Cu at 43.3°, 50.6°, 74.2°, and 89.5°, respectively (JCPDS no. 03-1005). Therefore, we can conclude from the above physical characterizations that Cu species are well-dispersed incorporating into the carbon layers with the well doping N element.

X-ray photoelectron spectroscopy measurements were applied to study the chemical environment and configuration structures of the doping elements in the Doping(I)-Cu@N-C catalyst (Fig. 2). The spectra showed the successfully doped N, Cu elements in catalyst, as well as the configuration structures of Cu, O, and N. This observation was in agreement with the elemental mappings, corroborating the high degree graphitic carbon doped and combined with the N, Cu elements. N 1s spectra illustrated the well combination of N and C elements in the structures of pyridine N, pyrrolic N and quaternary N, as well as the strong interaction of N and Cu elements, which demonstrated the possible CuNₓ active sites in catalyst. Deconvolution of N 1s spectrum revealed the N-functionalized carbon, in which the nitrogen atoms are anchored within the carbon backbone with specific microstructures. In literature, active sites in typical M-N-C catalysts were usually made up of metals coordinating to nitrogen atoms, presenting as pyrrole or pyridine moieties, or covalently attached at edges of graphitic structures, and sited as the pyridinic N with the protonated nitrogen bonded to metals [42–44]. Such as the transition metals coordinated to pyrrolic nitrogen and pyridinic nitrogen, interacting with one protonated nitrogen [45,46]. The metal facilitated the incorporation of various nitrogen sites into the carbon matrix with
the strong Lewis basicity [47]. N atom was quite negative because they had more electronegative and strong electron accepting ability than carbon atoms. Most of the compensating positive charges were distributed on the adjacent carbon atoms [48], which created the net positive charge centers on the adjacent carbon atoms, readily facilitating the adsorption of substances with lone pair electrons and consequently increasing the catalytic activity toward SO2 electrooxidation. Nitrogen-doping was recognized as one of the most effective strategies to create active sites in the carbon catalyst [49]. The O1s spectra elucidated the existence of C=O and O-C=O on catalyst, which enhanced the interaction of reactants and facilitated the transport of electrolytes for the better wettability and hydrogen-bond property of the catalyst. H2O is significant for the electrooxidation of SO2, and the oxygen-containing functional groups on catalyst can benefit the catalysis process. To further confirm the states of Cu-N in catalyst, the Cu 2p spectrum was analyzed (Fig. 2(c)). Binding energy ranges of Cu2p3/2 and Cu2p1/2 were usually observed at 930–937 eV and 950–957 eV, respectively, with a satellite peak locating at around 942 eV. The binding energies of Cu2p3/2 at 934.42 eV and Cu2p1/2 at 954.27 eV with a splitting energy of 19.85 eV between the two particular peaks were in agreement with the standard spectrum of Cu2+. Besides, the strong shake-up satellite peak of Cu2p3/2 appearing at 942.37 eV confirmed the existence of Cu2+. While the deconvolution curves of Cu2p3/2 at 932.47 eV and Cu2p1/2 at 952.39 eV were originated from tetrahedral Cu+ ions (or Cu0; it’s difficult to differentiate between the Cu0 and Cu+ on the basis of only Cu2p spectrum, due to their quite close binding energies from 932.0 to 933.0 eV). However, the possibility of Cu0 on the surface of catalyst was rather low, because the catalyst was preserved under air. The separated binding energy of Cu2p3/2 and Cu2p1/2 for the Cu+ was 19.86 eV, confirming the existence of Cu (I). What’s more, the Auger analysis is commonly used to complement the Cu2p deconvolution analysis with the information of Cu0, and the kinetic energy of Cu0 is 918.2 eV. In our catalyst, the Auger spectrum primarily denoted the presence of Cu+ at 914.69 eV and Cu2+ at 917.82 eV with no Cu0 existence on the catalyst surface. Nonetheless, the Cu+ had a relatively higher content than the Cu2+ on the catalyst. The above investigations are very significant because the CuNx sites on catalyst surface are the active structures for SO2 electrooxidation. Coordinating with nitrogen on the catalyst surface can stabilize the metal in the acidic conditions.
SO₂ electrooxidation activity

The SO₂ electrooxidation activity of Doping (I)-Cu@N-C was first displayed and compared with the linear sweep voltammetry (LSV) in 1 g L⁻¹ Na₂SO₃ (0.5 M H₂SO₄ background electrolyte, N₂) on the rotating disk electrode. For comparison, 20% Pt/C (JM) was applied to perform under the same conditions. As shown in Fig. 3(a), the onset oxidation potential of Doping (I)-Cu@N-C is only 35.4 mV higher than the commercial Pt/C. What’s more, above 0.822 V, the SO₂ electrooxidation performances on Doping (I)-Cu@N-C are remarkably elevated than the Pt/C. The one half of the intersection point current for the Doping (I)-Cu@N-C is 0.659 V, while the corresponding potential for Pt/C is only 92 mV lower. Thus, the SO₂ electrooxidation activity of Doping (I)-Cu@N-C is only slightly lower than Pt/C before 0.822 V, and its oxidation performances prominently surpass Pt/C above 0.822 V and obviously increase with the elevation of oxidation potentials. In the higher oxidation potential region, its SO₂ oxidation activity is obviously higher than the reported catalyst. To further clarify the SO₂ electrooxidation activity on Doping (I)-Cu@N-C, cyclic voltammograms (CV) were conducted at a scanning rate of 50 mV s⁻¹ in 1 g L⁻¹ Na₂SO₃ (Fig. 3 (b)). The peak current (iₚ) of SO₂ oxidation for the Doping (I)-Cu@N-C is 7.17 mA cm⁻² @ 0.684 V much higher than the 3.03 mA cm⁻² @ 0.584 V for Pt/C, indicating the excellent SO₂ electrooxidation activity of this as-synthesized Doping (I)-Cu@N-C catalyst. SO₂ electrooxidation were typically carried out under certain

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Fig. 2 – XPS analysis of the resultant catalyst Doping (I)-Cu@N-C. (a) high resolution N 1s spectrum; (b) high resolution O 1s spectrum; (c) high resolution Cu 2p spectrum; (d) Cu LM2 Auger spectra.

Fig. 3 – SO₂ electrooxidation activity tests. (a) LSV measurements of Doping (I)-Cu@N-C and 20% Pt/C in 1 g L⁻¹ Na₂SO₃ (0.5 M H₂SO₄, N₂; background electrolyte) under 1600 r min⁻¹ at the scanning rate of 5 mV s⁻¹. (b) CV curves of Doping (I)-Cu@N-C and 20% Pt/C at a scanning rate of 50 mV s⁻¹ in 1 g L⁻¹ Na₂SO₃ (background electrolyte H₂SO₄). (c) Chronoamperometry tests of Doping (I)-Cu@N-C and 20% Pt/C in 1 g L⁻¹ Na₂SO₃ and 0.5 M H₂SO₄, respectively; 1600 r min⁻¹.
applied potentials, catalyst activities were also examined under a selected potential in our experiment. The chronocoulometry (CA) tests were conducted under 1.2 V in 0.5 M H₂SO₄ (without S(IV)) and the 1 g L⁻¹ Na₂SO₃ (0.5 M H₂SO₄, with S(IV)), respectively, on the Doping (I)-Cu@N-C and Pt/C catalysts (Fig. 3(c)). There was no obvious difference on the Doping (I)-Cu@N-C and Pt/C in 0.5 M H₂SO₄, displaying the background currents close to zero at 1.2 V. However, in SO₂ electrooxidation tests, the terminal oxidation current of Doping (I)-Cu@N-C was 1.74 times as much as that of Pt/C. So when carried out under 1.2 V, the prepared Doping (I)-Cu@N-C catalyst displays much better SO₂ electro-oxidation activity than the commercial Pt/C with the same catalyst loadings. In a word, this prepared Doping (I)-Cu@N-C sample is an excellent non-precious SO₂ electrooxidation catalyst.

In order to demonstrate the kinetic activity of Doping (I)-Cu@N-C, we investigated its electrochemical performances with CV under different scanning rates (Fig. 4(a)) and LSV under different rotating rates (Fig. 4(b)). Furthermore, the characteristics were analyzed (Fig. 4 (c) and (d)) and also summarized on the basis of the Koutecky-Levich (K-L) equation (Fig. 4 (e)). It was obvious that the peak potential of SO₂ electrooxidation slightly shifted to more positive potentials with the elevation of scanning rates, and the plot of \( E_p \) and log (\( \omega \)) was nearly linear, demonstrating the irreversible process of SO₂ electrooxidation on this catalyst. What’s more, the similar linear relationship between \( i_p \) and \( \omega^{1/2} \) indicated the diffusion controlling process of SO₂ electrooxidation on catalyst. With the increasing of rotating speeds, SO₂ oxidation currents rise obviously due to the shortened diffusion distances at higher rotating rates. The corresponding K-L plot at 1.2 V displayed fairly well linearity, and the kinetic-limiting current of Doping (I)-Cu@N-C deriving from the K-L plot was 53.08 mA cm⁻² @1.2 V, further demonstrating that this as-prepared Cu-N doped catalyst was an excellent SO₂ electro-oxidation sample. Thus, Doping (I)-Cu@N-C catalyst exhibited a highly comparable activity to Pt/C, indicating the great potential for application.

**Role of Cu in catalyst and identification of active sites**

Investigating the role of doped metal in the development of active sites was one of the most meaningful work to acquaint with the metal-nitrogen doped SO₂ electrooxidation catalyst. Experiments were designed to investigate the effects of doping metal on the formation of active sites, which was important for figuring out the workable strategies to enhance the catalytic activity of the SO₂ electrooxidation catalysts. The compositions and structures were characterized and identified by XPS and XRD measurements. As illustrated in Fig. 1 (d), there are three kinds of nonprecious SO₂ electrooxidation catalysts prepared and tested for comparison. The Doping(I)-Cu@N-C was prepared by the prereduction of Cu ions to the colloidal sol Cu with NaBH₄ and then going through the carbonization process. The Doping(II)-Cu@N-C was prepared through directly carbonization reduction. Though prepared with different methods, Doping(I)-Cu@N-C and Doping(II)-Cu@N-C were all doped with metallic Cu. However, the prereduction by NaBH₄ can provide more metallic Cu with the intensified XRD patterns (Fig. 1 (d)), which enhance the doping process and active sites development. The composites comprise of graphitic carbon with obvious evidence of the wide-angle peak at around 25° in the XRD pattern, corresponding to the (002) lattice of graphitic carbon. The strong Cu signals and weak C signals were observed simultaneously.

![Fig. 4](image-url) – Kinetic activity analysis of Doping (I)-Cu@N-C. (a) CV curves of Doping (I)-Cu@N-C in 1 g L⁻¹ Na₂SO₃ under different scanning rates. (b) LSV measurements of Doping (I)-Cu@N-C in 1 g L⁻¹ Na₂SO₃ under different rotating rates. (c) \( I_p \sim \omega^{1/2} \). (d) \( E_p \sim \log (\omega) \). (e) K-L analysis at 1.2 V; \( i \sim \omega^{-1/2} \).
indicating the encapsulated structures in the carbon lattice or carbon shells. Their chemical composition and element bonding configurations were compared and verified by XPS (Fig. 5). Both methods produced the metallic Cu during the preparation, but the NaBH₄ prereduction process developed much earlier, providing better catalysis for the development of active sites. So the contents of Cu, N were higher in the Doping(I)-Cu@N-C than the Doping(II)-Cu@N-C catalyst. Therefore, the prereduction method can provide the better Cu-N doping in catalyst, exhibiting the much better SO₂ electrooxidation performance (Fig. 3(c)).

According to the XPS analysis, the doped Cu were in the combining state (Cu⁺ and some Cu²⁺) on the N-C matrix surface, implying the formation of CuNx active structures. To evaluate the influences of these structures in the Cu-N doped catalyst, a molecular probe of 2, 2'-bipyridine was used to occupy the 3d orbital of Cu in the CuNx active site on catalyst surface to identify the influence of CuNx structures for SO₂ electrooxidation as well as the differences of active structures on the prepared catalysts with different synthesis methods (Fig. 6). The 2, 2'-bipyridine can occupy the 3d metal center of Cu with its strong steric hindrance of the aromatic rings of

![Fig. 5](image1)

**Fig. 5 — XPS comparison of Doping (I)-Cu@N-C, Doping (II)-Cu@N-C and BP. (a) high resolution N 1s spectrum; (b) high resolution O 1s spectrum; (c) high resolution Cu 2p spectrum; (d) Cu LM2 Auger spectra.**

![Fig. 6](image2)

**Fig. 6 — Active site recognition. (a) Chronoamperometry tests of Doping (I)-Cu@N-C and Doping (II)-Cu@N-C in 1 g L⁻¹ Na₂SO₃ at 1.2 V; before and after the 2, 2'-bipyridine occupation. (b) LSV measurements of Doping (I)-Cu@N-C and Doping (II)-Cu@N-C in 1 g L⁻¹ Na₂SO₃ before and after the 2, 2'-bipyridine occupation.**
bipyridine, ligating the interaction of SO₂ and metal center in the axial direction. The CA-1.2 V SO₂ electrooxidation currents of Doping (I)-Cu@N-C was much higher than the Doping(II)-Cu@N-C. The oxidation currents on both catalysts were remarkably dropped after being covered by the 2, 2'-bipyridine (Fig. 6 (a)). However, the higher SO₂ electrooxidation activity was achieved on Doping (I)-Cu@N-C sample, because the prereduction process provided more metallic Cu in the carbonization process, catalyzing the active sites formation and Cu-N doping. There are more CuNx active sites formed on the Doping (I)-Cu@N-C catalyst (Fig. 6), and these CuNx active sites play important role in SO₂ catalysis as proved in the molecular probe test. In the potential dynamic tests, we got the similar conclusion (Fig. 6 (b)). The Doping(II) -Cu@N-C catalyst produced less active sites, which might be influenced by the hysteresis formation of Cu in the carbonization reduction process, hindering the development of active sites.

Thus, we conclude that the presence of metallic Cu plays important roles on the development of CuNx active sites and doping of Cu, N elements. The encapsulated nanoparticle Cu under graphitic carbon shells can activate the C-N surface, forming the CuNx active structures on the catalyst surface and displaying excellent catalysis activities towards SO₂ electro-oxidation. The prereduction method is superior to the direct carbonization reduction process in developing of CuNx active sites, and the metallic Cu plays a significant role in preparing Cu-N doped catalyst.

Conclusion

In summary, we synthesized a novel Cu-N doping nanoparticle encapsulated SO₂ electrooxidation catalyst via a prereduction method. Metallic Cu plays a significant role in the active site development and Cu-N doping in the catalyst. The CuNx structures and the coordination of N, C elements are believed to be the effective factors to enhance SO₂ electro-oxidation. Moreover, the majority of Cu are highly dispersive and well-encapsulated in the carbon lattice, catalyzing the formation of CuNx active sites on the surface. This prepared Doping(II)-Cu@N-C demonstrates obviously enhanced SO₂ electrooxidation activity in H₂SO₄. With the same mass loading, its SO₂ electrooxidation activity surpasses Pt/C above the 0.822 V. In general, we find that metallic Cu contributes to the catalysis of Cu-N doping and CuNx active site development. The prereduction method is a better way to dope and develop the active sites in the Cu-N doping catalyst. The outstanding catalytic performances are ascribed to the formation of CuNx structures and effective doping of Cu, N elements, making Doping (I)-Cu@N-C an excellent SO₂ electrooxidation catalyst.

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