Single Atomic Cu-N₂ Catalytic Sites for Highly Active and Selective Hydroxylation of Benzene to Phenol

HIGHLIGHTS
- Single-atom Cu catalyst on HCNS with unique Cu-N₂ moieties was synthesized.
- Cu-N₂ shows 3.4 times turnover number of Cu-N₃ for benzene hydroxylation.
- Unique Cu-N₂ coordination state leads to lower energy barrier for H₂O₂ activation.
- It paves a new avenue to design single-atom catalysts by tuning coordination state.

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Single Atomic Cu-N\(_2\) Catalytic Sites for Highly Active and Selective Hydroxylation of Benzene to Phenol

Ting Zhang\(^{1,5}\), Xiaowa Nie\(^{1,5}\), Weiwei Yu\(^{1}\), Xinwen Guo\(^{1}\), Chunshan Song\(^{1,2}\), Rui Si\(^{3,}\)*, Yuefeng Liu\(^{4,}\)* and Zhongkui Zhao\(^{1,6,}\)*

**SUMMARY**

Searching for an efficient single-atom catalyst for benzene hydroxylation to phenol is of critical importance, but still remains a challenge. Herein, a single-atom catalyst with unique Cu-N\(_2\) moieties (Cu\(_1\)-N\(_2\)/HCNS) was prepared and confirmed by HAADF-STEM and EXAFS. Turnover number (TON) over Cu\(_1\)-N\(_2\)/HCNS (6,935) is 3.4 times of Cu\(_1\)-N\(_3\)/HCNS (2,034) under the same reaction conditions, and both exhibit much higher phenol selectivity (close to 99%) and stability compared with Cu nanoparticles and nanoclusters. Experiments and DFT calculations reveal that atomically dispersed Cu species are active sites for benzene hydroxylation to phenol, and the Cu-N\(_2\) is more active than Cu-N\(_3\) owing to its much lower energy barrier concerning the activation of H\(_2\)O\(_2\) led by its unique coordination state of local atomic structure. We envision that this work opens a new window for modulating coordination environments of single metallic atoms in catalysis design.

**INTRODUCTION**

Activation of aromatic C-H bonds has been one of the most active research topics, yet long-standing challenge remains (Leitch and Frost, 2017; Sambiagio et al., 2018; Shan et al., 2018). Phenol is widely used as a versatile intermediate for phenolic resin, pharmaceuticals, agrochemicals, etc. (Bai et al., 2006; Wang et al., 2012). However, the current technology for phenol production by three-step cumene process generates large amounts of chemical waste and low-value by-product (Tsuji et al., 2017; Morimoto et al., 2015; Chen et al., 2009). Catalytic direct selective oxidation of benzene with H\(_2\)O\(_2\) as oxidant is an acceptable passway for efficient and clean phenol production (Ivanchikova et al., 2014; Su et al., 2017; Evtushok et al., 2018; Xia and Tang, 2012; Szécsényi et al., 2018). In this regard, heterogeneous catalytic hydroxylation of benzene with H\(_2\)O\(_2\) to phenol is highly desirable (Zhang et al., 2017a, 2017b; Deng et al., 2015; Zhu et al., 2018; Yang et al., 2013; ElMetwally et al., 2018; Han et al., 2017). Although numerous efforts of designing such catalytic system have been made and considerable achievements have been obtained, it still remains a challenge (Balducci et al., 2003). Nitrogen-doped carbon materials have been found to be active for hydroxylation of benzene with H\(_2\)O\(_2\) under mild condition yet shows low catalytic activity (Yang et al., 2013). Metal-doped carbon nitride shows an improved activity for hydroxylation of benzene with H\(_2\)O\(_2\) to phenol but still remains unsatisfactory (Chen et al., 2009; Di et al., 2010; Xu et al., 2018; Zhang et al., 2018a, 2018b; Hosseini et al., 2018). Therefore, developing efficient catalysts for benzene hydroxylation with H\(_2\)O\(_2\) to phenol is of great urgency.

Owing to enhanced intrinsic activity and selectivity toward targeted product and maximized utility of metal atoms (Dvořák et al., 2016; Kwon et al., 2017; Chen et al., 2018a, 2018b; Yamaguchi et al., 2017; Li et al., 2018a, 2018b; Malonzo et al., 2016; Liang et al., 2015), single-atom catalyst (SAC) has been emerging as an attractive frontier in heterogeneous catalysis (Qiao et al., 2011; Mitchell et al., 2018; Chen et al., 2018a, 2018b; Thomas et al., 2005; Yamashita et al., 2018). Up to now, SAC has been broadly applied to thermo-, electro-, and photo-catalysis owing to its extraordinary catalytic performance from the unique electronic properties of single atomic sites (Zhang et al., 2018a, 2018b; Gao et al., 2016; bin Mohd Yusoff et al., 2015; Yang et al., 2016; Cheng et al., 2018). Especially for the activation of C-H bonds, SAC shows extraordinary catalysis (Marcinkowski et al., 2018; Yuan et al., 2018; Yamaguchi et al., 2018). Single-atom Fe/Ni/Co materials are proved to be efficient for benzene hydroxylation with H\(_2\)O\(_2\) to phenol (Ivanchikova et al., 2014; Su et al., 2017; Evtushok et al., 2018; Wang et al., 2015). However, the activity and selectivity are far from their applications. Our previous work shows that single atomic Cu-N\(_3\) sites...
have extraordinary phenol selectivity with H$_2$O$_2$ as oxidant, yet the activity still remains to be improved (Zhang et al., 2018a, 2018b). Therefore, developing single-atomic Cu catalysts with increased activity for benzene hydroxylation with H$_2$O$_2$ is desirable. In homogeneous catalysis, the design of ligands plays crucial roles in tuning activity by modulating the coordination states of central metal atoms (Morimoto et al., 2015). Also for heterogeneous catalysis, as reported by references Evtushok et al., 2018; Liu et al., 2017; Jiang et al., 2018; Han et al., 2018, the coordination states of metal atom in SAC significantly affect the catalytic performance. Considering this, modulating coordinated state of single-atom Cu-N$_x$ moieties on hollow carbon nitride microsphere (HCNS) can be a sapiential approach to develop an excellent single-atom catalyst for benzene hydroxylation to phenol.

Herein, a single-atom Cu catalyst isolated on HCNS with unique Cu-N$_2$ moieties (Cu$_1$-N$_2$/HCNS) has been successfully prepared by a facile chemical reduction deposition-acid leaching (CRD-AL) method (see Scheme 1), confirmed by extended X-ray absorption fine structure (EXAFS) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Surprisingly, Cu$_1$-N$_2$/HCNS exhibits 3.4 times turnover number (TON) (6,935) of Cu$_1$-N$_3$/HCNS (2,034) toward benzene hydroxylation to phenol; besides, both single-atom catalysts demonstrate much higher selectivity and stability than Cu nanoparticles or nanoclusters. HAADF-STEM, EXAFS, and kinetic results reveal that the single-atom Cu species are catalytic active sites for benzene hydroxylation to phenol and Cu-N$_2$ is extremely more active than Cu-N$_3$ owing to its unique local atomic structure.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Cu$_1$-N$_2$/HCNS Catalyst

In this paper, a single-atom Cu catalyst isolated on HCNS with unique Cu-N$_2$ moieties (Cu$_1$-N$_2$/HCNS) has been successfully prepared by a facile CRD-AL method. Typically, 0.14 g of HCNS carrier (Jun et al., 2013a, 2013b) was first ultrasonically dispersed in 20 mL of Cu(NO$_3$)$_2$ aqueous solution (2 mmol L$^{-1}$). Then, the Cu species were deposited on HCNS surface with 1 mL of NaBH$_4$ (0.5 mol L$^{-1}$) as reductant. After stirring for 4 h at room temperature, solid sample was collected by centrifugation and washed with DI water and ethanol three times, respectively. Subsequently, the solid sample was dried at 60°C for 12 h. For now, the obtained dry solid catalyst is denoted as Cu NC/HCNS (1.14 wt% Cu, inductively coupled plasma-atomic emission spectrometry [ICP-AES]). To get single-atom catalyst Cu$_1$-N$_2$/HCNS, 0.01 g of Cu NC/HCNS was further treated with 10 mL of dilute HNO$_3$ solution for 4 h at room temperature. The solid was centrifuged, washed with DI water and ethanol three times, respectively. The CuO nanoclusters are easily eliminated, whereas the single atoms anchored by the support are stable (Liu et al., 2018). Although metallic Cu can be oxidized, the Cu$^{2+}$ captured by N atoms on HCNS can be in situ reduced and single-atomic Cu coordinated with neighboring N atoms formed. The method applied in this work is different from the pre-assembly method for Cu-N$_3$ in our former report (Zhang et al., 2018a, 2018b). For Cu$_1$-N$_2$/HCNS catalyst, the Cu species were deposited on the pre-formed HCNS, followed by
acid-leaching treatment; CuOx clusters were removed while the single-atomic Cu was anchored by two neighboring N atoms and formed the Cu-N2 sites, whereas for the Cu1-N3/HCNS catalyst, the Cu2+ ions were pre-coordinated with melamine to form Cu-Mel complex and the Cu atoms were isolated in the supermolecular assemblies; subsequently, Cu-N3 sites were in situ formed during thermal polymerization.

X-ray powder diffraction (XRD) patterns of Cu NC/HCNS and Cu1-N2/HCNS catalysts (see Figure S1) display the characteristic peaks at 12.9° and 27.4°, assigned to (100) and (200) crystal faces of g-C3N4, respectively (Zhao et al., 2018), indicating deposition and acid leaching have no influence on the crystal property of g-C3N4 support. Field emission scanning electron microscopy and transmission electron microscopy (see Figures 1A, 1B, 1E, 1F, and S2A) are applied for characterization toward the morphology of as-prepared catalysts. It is shown that Cu1-N2/HCNS and Cu NC/HCNS catalysts feature a regular hollow spherical structure (Zhang et al., 2018a, 2018b; Jun et al., 2013a, 2013b). Textural properties (see Figure S3 and Table S1) indicate that the micro-structure of HCNS is maintained after loading Cu atoms. The porous hollow micro-/nano-structures have benefit for the catalytic reaction by improving accessibility of catalytic sites to reactants (Zhang et al., 2018a, 2018b; Harmer et al., 1996; Matei et al., 2013; Li et al., 2018a, 2018b). Furthermore, the textural properties of CN1-N2/HCNS and Cu1-N3/HCNS are similar. Also, our former research indicates that the elemental composition of Cu1-N3/HCNS is the HCNS support (molar ratio of N/C = 1.5) (Zhang et al., 2018a, 2018b). The addition of trace Cu-melamine complex (0.85 wt% Cu in the final Cu1-N3/HCNS catalyst) shows inconspicuous effect on the textural properties of Cu1-N3/HCNS catalyst compared with the HCNS support.

For further observation of metal species dispersed on g-C3N4 support, HAADF-STEM experiments were performed and the obtained images are displayed in Figures 1C, 1D, 1G, and 1H. No obvious metallic nanoparticles can be observed both on Cu NC/HCNS and Cu1-N2/HCNS. XRD patterns (see Figure S1) also exhibit no characteristic peak corresponding to Cu nanoparticles. However, HAADF-STEM image (see Figure 1D) of Cu NC/HCNS displays the existence of nanoclusters less than 2 nm. The fitting results (see Table S2) toward R-space EXAFS spectrum (see Figure S4) of Cu NC/HCNS are matched well with CuO clusters, i.e., first shell of Cu-O at 1.92 Å with CN = 2.9 and second shell of Cu-Cu (originated from Cu-O-Cu) at 2.87 Å with 0.4 of coordination (CN). Besides, X-ray photoelectron spectroscopy (XPS) of O 1s spectrum (see Figure S5A) reveals the existence of lattice O2− species and the N 1s XPS spectrum (see Figure S5B) displays no obvious peak assigned to Cu-N species, further proving the CuO clusters on the Cu NC/HCNS. For clear observation, the raw and enlarged image of Figure 1D is given in Figure S2B. Concerning Cu1-N2/HCNS catalyst, single Cu atoms are clearly identified as bright spots (highlighted by green circles) isolated on g-C3N4 surface by HAADF-STEM image (see Figure 1I). The Cu content of Cu1-N2/HCNS is ca. 0.23 wt% determined by inductively coupled plasma-atomic emission spectroscopy.

Figure 1. Characterization of As-prepared Samples
(A and B) Scanning electron microscopy (SEM) (A) and transmission electron microscopy (TEM) (B) images of Cu NC/HCNS catalyst. (C and D) HAADF-STEM images of Cu NC/HCNS catalyst, the Cu clusters are highlighted by yellow circles. (E and F) SEM (E) and TEM (F) images of Cu1-N2/HCNS catalyst. (G and H) HAADF-STEM images of Cu1-N2/HCNS catalyst, the single Cu atoms are highlighted by green circles.
The amount of active Cu sites in single-atom Cu1-N2/HCNS catalyst is determined by KSCN titration method, and the results are shown in Figure S6. The result indicates that, for Cu1-N2/HCNS catalyst, about 80% of the loaded Cu atoms serve as active sites (0.029 mmolCu/gCat.) (see Figure S6A), whereas for Cu1-N3/HCNS, about 60% of the loaded Cu atoms serve as active sites (0.080 mmolCu/gCat.) (see Figure S6B).

Heteroatom, like N atoms, in carbon matrix have been proved to be efficient anchoring sites for stabilizing metal atoms (Zhang et al., 2018a, 2018b; Liu et al., 2018; Qu et al., 2018). g-C3N4 features abundant N content and chemical stability (Liu et al., 2016) and, therefore, has been considered as an ideal support for single-atom catalysts (Zhang et al., 2018a, 2018b). For understanding the electronic character of the developed Cu1-N2/HCNS catalyst, X-ray photoelectron spectroscopy (XPS) was carried out (see Figures 2 and S7). XPS survey spectrum of Cu1-N2/HCNS (see Figure S7A) displays the characteristic peaks of C, N, O, and Cu. The deconvoluted O 1s spectrum (see Figure S7B) shows no O2− species, proving the complete etching of CuO clusters. C 1s spectrum (see Figure S7B) reveals the major content of C-C, N-C=N moieties. The Cu 2p XPS spectra (see Figure 2C) show that the characteristic peak of Cu+ 2p3/2 shifts to 932.8 eV in single-atom Cu1-N2/HCNS compared with that of CuNC/HCNS, further confirming the strong interaction between single Cu atoms and the g-C2N4 matrix.

To further investigate the electronic properties and coordination environment of Cu1-N2/HCNS, X-ray absorption near-edge spectroscopy (XANES) and EXAFS measurements were performed. Cu K-edge XANES profiles for the measured sample and the related references (Cu foil, Cu2O, and CuO) are shown in Figure 2D. Cu1-N2/HCNS exhibits an energy absorption edge between Cu+ (Cu2O) and Cu2+ (CuO) standards in the range of E0 (around 8,979 eV), and the corresponding oxidation state of copper is determined as +1.5 via linear combination fitting (Krenkel et al., 2011). This observation agrees with the related XPS results (see Figure 2C). EXAFS spectra (see Figure 2E) for Cu1-N2/HCNS only displays a prominent peak at approximately 1.9 Å, and no significant contribution for metallic Cu or oxidized CuO clusters at longer distances above 2.5 Å is observed, revealing the atomic dispersion of isolated Cu atoms throughout HCNS matrix. XANES is the nowadays the most direct and efficient technology for the characterization concerning atomic structure of single-atom catalyst. The XANES spectra of central atoms with different coordination numbers or ligands usually display distinct difference in adsorption curves (Kau et al., 1987; Sorrell and Malachowski, 1983; Sorrell et al., 1982). The near-edge of Cu1-N2/HCNS and Cu1-N3/HCNS (see Figure 2F) features obviously different shapes, implying the possible difference in coordination environment of single-atom Cu moieties. The Cu K-edge spectrum of Cu1-N2/HCNS is similar to that of the compound Cu(pz)BF4, in which the central Cu ion is coordinated with N2O-ligation (Kau et al., 1987; Sorrell and Malachowski, 1983). However, Cu1-N3/HCNS catalyst shows a similar Cu K-edge spectrum to compound [Cu2(mxyN6)](BF4)2, in which the central Cu ion is coordinated with N2-ligation (Kau et al., 1987; Sorrell et al., 1982). This difference in the adsorption curve of XANES spectra indicates that the local atomic structure of single Cu atoms over Cu1-N2/HCNS differs from that over Cu1-N3/HCNS. To further obtain the structural parameters of copper in Cu1-N2/HCNS, we conducted EXAFS fitting in R space (see Figure 2G) via a possible structural model presented in Figure 2F. Two nitrogen atoms are coordinated with isolated copper center, which is also capped by adsorbed oxygen-containing molecule (O2 and/or H2O and/or CO2) to form saturated structure for its stable existence. Table S3 shows that the bond length of Cu-N is determined to be 1.92 Å, plus a minor Cu-O shell at 1.96 Å with the coordination number of ca. 1. All these results are well consistent with the hypothesized structural model (see Figure 2F) in the density functional theory (DFT) calculation. For comparison of the reaction mechanism of H2O2 activation over Cu1-N2/HCNS and Cu1-N3/HCNS, the structure model of Cu-N3 has been constructed and optimized via DFT according to the EXAFS fitting results (see Figures 2F, S4D, and S4E and Table S2) and displayed in Figures 2H and 2J.

Catalytic Evaluation

As a critically important chemical transformation, aromatic C-H bond activation has been one of the most active research topics (Morimoto et al., 2015; Marcinkowski et al., 2018; Shilov and Shul’pin, 1997; Labinger and Bercaw, 2002; Wencel-Delord; Glorius, 2013). Herein, benzene hydroxylation with H2O2 to phenol was performed as a model reaction to evaluate the catalytic performance of the developed Cu1-N2/HCNS catalyst (see Figure 3 and Table S4). For comparison, Cu NC/HCNS, Cu NP/HCNS, and our previously reported

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Figure 2. X-Ray Spectroscopy Analyses of single-atom catalyst

(A) The O 1s XPS spectrum of Cu\textsubscript{1}-N\textsubscript{2}/HCNS single-atom catalyst.

(B) The N 1s XPS spectra of single-atom Cu\textsubscript{1}-N\textsubscript{2}/HCNS catalyst and HCNS support.

(C) Cu 2p XPS spectra of Cu\textsubscript{1}-N\textsubscript{2}/HCNS single-atom catalyst and Cu NC/HCNS nanocluster catalyst.

(D and E) Normalized Cu K-edge XANES spectra (D) and $k^3$-weighted Fourier transform spectra (E) from Cu K-edge EXAFS of Cu foil, CuO, Cu$_2$O, and Cu\textsubscript{1}-N\textsubscript{2}/HCNS.

(F) The comparison of normalized Cu K-edge XANES spectra of Cu\textsubscript{1}-N\textsubscript{2}/HCNS and Cu\textsubscript{1}-N\textsubscript{3}/HCNS (Zhang et al., 2018a, 2018b).

(G and H) The corresponding EXAFS fitting curves of Cu\textsubscript{1}-N\textsubscript{2}/HCNS (G) and Cu\textsubscript{1}-N\textsubscript{3}/HCNS (H).

(I and J) The models of Cu–N\textsubscript{2} sites in Cu\textsubscript{1}-N\textsubscript{2}/HCNS (I) and the model of Cu–N\textsubscript{3} sites in Cu\textsubscript{1}-N\textsubscript{3}/HCNS (J), orange, Cu; gray, C; blue, N; red, O.
Cu1-N2/HCNS (Zhang et al., 2018a, 2018b) were chosen as benchmark under the same reaction conditions. The results show that only trace benzene is converted without catalyst (Blank) or over bare HCNS support. Like our previously reported Cu1-N2/HCNS (Zhang et al., 2018a, 2018b), the developed single atomic Cu1-N2/HCNS catalyst exhibits much higher selectivity and stability than Cu nanoparticles and nanoclusters for benzene hydroxylation to phenol. More interestingly, Cu1-N2/HCNS catalyst exhibits 3.4 times TON (6,935) of Cu1-N2/HCNS (2,034) under the same reaction conditions. From Table S4, under the same reaction conditions, 70.9% of benzene conversion with 91.3% of phenol selectivity over Cu1-N2/HCNS catalyst can be achieved, whereas only 15.6% of conversion over Cu1-N2/HCNS can be obtained, although it shows 99.3% of slightly higher selectivity. In fact, the more than 99.9% of selectivity is also obtained in the absence of catalyst or over the bare HCNS support. Furthermore, the developed Cu1-N2/HCNS catalyst also shows much superior catalytic performance to the previously reported single-atom catalysts (Table S4), owing to the atomically dispersed Cu-N2 moieties and the promoted accessibility of single Cu active sites by the porous hollow structure. Beyond the remarkable catalytic performance, the Cu1-N2/HCNS catalyst also shows high recycling stability and reusability. Figure 3B displays no obvious decrease in benzene conversion over Cu1-N2/HCNS after four cycles.

It has been revealed that the reaction parameters, such as molar ratio of H2O2 to benzene, reaction temperature, and type of catalyst, may affect the performance of liquid phase benzene oxidation over heterogeneous catalysts with H2O2 as oxidant (Evtushok et al., 2018; Acharyya et al., 2014). Data in Table S4 (Entry 3 and 12) demonstrate that the reaction temperature has an effect on the catalytic activity and selectivity of benzene oxidation over Cu1-N2/HCNS. When the reaction is carried out at 25°C, higher benzene TON compared with references is obtained, yet the phenol selectivity shows a disadvantage (see Table S4, Entry 12, 13, and 14). Surprisingly, after the reaction is carried out at 60°C (see Table S4, Entry 3), improved phenol selectivity with enhanced catalytic activity is obtained. The aforementioned results indicate that a higher reaction temperature (60°C) may be beneficial for the improving of phenol selectivity over Cu1-N2/HCNS. This phenomenon is different from the reported results that high temperature leads to decreased phenol selectivity over single-atom Co-ISA/CNS catalyst (Evtushok et al., 2018).

Figure 3B gives the effect of molar ratio of H2O2 to benzene in liquid phase benzene oxidation over the Cu1-N2/HCNS catalyst. The results clearly show that increasing the molar ratio of H2O2 to benzene (less than 10) leads to higher benzene conversion with invariable H2O2 utilization and phenol selectivity. However, when the molar ratio of H2O2 to benzene is further increased to 15, the benzene conversion displays no more observable increment, yet the H2O2 shows striking decrease.

From the aforementioned description, both the Cu1-N2/HCNS developed in this work and the Cu1-N3/HCNS reported in our previous work feature the single-atom catalyst, however, with different local atomic structures of Cu atoms. Different coordination environment of single-atom Cu catalyst results in quite distinct catalytic performance for liquid phase benzene oxidation (see Table S4, Entry 3 and 4). As previously reported (Ivanchikova et al., 2014; Su et al., 2017; Evtushok et al., 2018), the reaction pathway for benzene oxidation to phenol by H2O2 usually can be abstracted into two steps, including the first H2O2 decomposition for the formation of active oxygen species and the subsequent oxidation of benzene to phenol. The much different catalytic activity clearly displays that the benzene conversion is directly related to the H2O2 conversion since a similar H2O2 utilization efficiency over Cu1-N2/HCNS, Cu1-N3/HCNS, and Cu NC/HCNS catalysts can be observed (see Table S4, Entry 3, 4, and 5). This phenomenon implies that the different catalytic performance over diverse catalysts may derive from their discrepant abilities for the activation of H2O2.
DFT Calculations for Reaction Mechanism

To compare the activity of Cu1-N2/HCNS and Cu1-N3/HCNS catalysts toward H2O2 adsorption and activation, DFT calculations were performed to identify intermediates and reaction pathways. The minimum energy pathways for H2O2 adsorption and dissociation on the Cu-N2 and Cu-N3 sites are illustrated in Figures 3C–3F, respectively, with all optimized structures included. On the Cu1-N2/HCNS catalyst, the H2O2 oxidant is initially adsorbed by the active Cu site with the O-Cu2 distance of 1.90 Å. In the meantime, multiple hydrogen bonds are formed between the H atoms of H2O2 and N atoms of the catalyst, resulting in an activation of the O-O bond to 1.51 Å from 1.48 Å in gas phase. The binding energy of H2O2 is calculated to be −0.89 eV on the Cu-N2 site. The activated H2O2* can be easily transformed into the active O* species by releasing a water molecule, with an energy barrier of only 0.42 eV and a reaction energy exothermic by −0.95 eV. As shown in the transition state configuration (see Figures 3C and 3D), the O-O bond length elongates to 1.68 Å from 1.51 Å, whereas the O1-H2 distance contracts to 1.75 Å from 2.00 Å in the adsorbed state, indicating that the O-O bond cleavage and O-H bond formation tend to occur concurrently in the H2O2 dissociation step. The Cu site still coordinates to the O2 atom strongly, with a bond length of 1.82 Å in the transient state (TS). In the dissociated state, a H2O molecule is formed, which is H-bonded to the active O* species with the H2-O2 distance of 1.60 Å. Then, the formed active O* species over the Cu-N2 site is ready to react with benzene to form phenol.

On the Cu1-N3/HCNS catalyst (see Figures 3E and 3F), the H2O2 molecule is still adsorbed over the Cu site, but the Cu-O interaction is weaker than that adsorption on the Cu-N2 site, as evidenced by the longer distance of Cu-O2 (2.58 Å) and the weaker binding energy of H2O2 (−0.52 eV, see Figure 3F). Although hydrogen bonds are formed between the H atoms of H2O2 and N atoms of the catalyst, we did not observe obvious activation of H2O2 upon adsorption on the Cu-N3 site owing to the weak interaction with Cu, and the O-O bond length does not change compared with that in gas phase molecule. In the formation of active O* species, Cu interaction with the O2 atom is still weak in the transition state, with the Cu-O2 bond length of 2.20 Å. This bond length is 0.38 Å longer than that in the transition state generated over the Cu-N2 site, indicating an unstable transition state for active O* formation over the Cu-N3 site. Although the elementary pathways for H2O2 adsorption and dissociation are similar over Cu1-N2/HCNS and Cu1-N3/HCNS catalysts, the energy barrier of H2O2* dissociation to O* is up to 1.16 eV on the Cu-N3 site, with an unfavorable reaction energy of 0.86 eV.

Comparing the energy pathways for H2O2 adsorption and dissociation on the two single-atom catalysts, clearly, the Cu1-N2/HCNS is catalytically more active for both H2O2 activation and active O* species formation, which would be a superior candidate for benzene oxidation than the Cu1-N3/HCNS catalyst.

To supplement the DFT results, the comparative trials were rationally designed and carried out (see Figure S9). The excess benzene versus H2O2 was used to ensure that the in situ formed active oxygen from H2O2 is rapidly consumed. The results indicate that Cu1-N2/HCNS shows a higher H2O2 activation rate with higher benzene conversion than Cu1-N2/HCNS catalyst, firmly demonstrating that the much higher activity of Cu1-N2/HCNS for selective oxidation of benzene compared with Cu1-N3/HCNS catalyst may originate from its higher H2O2 activation ability.

Kinetic Studies of Benzene Oxidation

To get further experimental insight into the much superior catalytic performance of the developed single-atom Cu1-N2/HCNS catalyst, kinetic studies of benzene oxidation were carried out in a kinetic controlled regime. From Figures 3G and S10 and Table S5, the two single-atom catalysts exhibit a lower apparent activation barrier (Ea) than that of supported nanocluster (Cu NC/HCNS) and nanoparticle (Cu NP/HCNS) catalysts for the benzene oxidation reaction. Moreover, the single atomic Cu1-N2/HCNS catalyst demonstrates much lower Ea and much higher pre-exponential factor (A) concerning benzene oxidation than Cu1-N2/HCNS, originating from the different properties of Cu-N2 catalytic sites and Cu-N3 moieties. As a consequence, the Cu1-N2/HCNS catalyst displays much higher TON for benzene selective oxidation to phenol in comparison with other catalysts (see Figure 3A and Table S4).

From the reaction results for selective oxidation of benzene shown in Table S4, the developed single atomic Cu1-N2/HCNS catalyst exhibits a much higher selectivity toward phenol than Cu NC/HCNS and
Cu NP/HCNS catalysts. From our previous finding (Zhang et al., 2018a, 2018b), quinone confirmed by mass spectrometry, as the detected by-product, possibly results from the deep oxidation of as-formed phenol over Cu1-N2/HCNS catalyst. Therefore, kinetic studies of phenol oxidation over Cu1-N2/HCNS, Cu NC/HCNS, and Cu NP/HCNS catalysts were carried out to explore the origin of the higher selectivity of Cu1-N2/HCNS than the other two. As shown in Figures 3H and S11, and Table S5, Cu1-N2/HCNS exhibits a slightly lower $A$ than Cu NC/HCNS and Cu NP/HCNS for phenol oxidation to quinone, indicating the unfavorable for phenol oxidation. Furthermore, as shown as earlier, Cu1-N2/HCNS exhibits much lower $E_a$ with much higher $A$ for benzene oxidation than Cu NC/HCNS and Cu NP/HCNS (Table S5). As a consequence, Cu1-N2/HCNS exhibits much higher selectivity for hydroxylation of benzene to phenol than Cu NC/HCNS and Cu NP/HCNS catalysts.

In other words, the extremely higher activity of Cu1-N2/HCNS compared with Cu1-N3/HCNS originates from its much higher H$_2$O$_2$ activation and lower $E_a$ with much higher $A$ for benzene oxidation. The much higher phenol selectivity of Cu1-N2/HCNS compared with Cu NC/HCNS and Cu NP/HCNS derives from the much lower $E_a$ with much higher $A$ for benzene oxidation but the comparable $E_a$ with slightly lower $A$ for phenol oxidation to quinone.

The developed Cu1-N2/HCNS catalyst in this work shows high recycling stability and reusability. ICP and XPS results indicate the Cu content of the used catalyst is similar to that of the fresh catalyst (Table S6), demonstrating that the single Cu atoms are firmly anchored on HCNS owing to the strong coordination of Cu-N bond (see Figures 4A and 4B). More interestingly, the phenol selectivity increases from 91.5% to 97%-99% from the second cycle (see Figure 3B). The XANES profile of Cu1-N2/HCNS-used (see Figures 4C, 4D, and S12) determines a slight increase of oxidation state of Cu from $+1.5$ to $+1.7$ (see Table S3), correlating to the larger CN value of Cu-O from 0.9 to 1.4 via EXAFS fit, indicating the possible oxidation of Cu by H$_2$O$_2$ during the reaction process thus inducing the variation of local atomic structure of single-atom Cu. The increased phenol selectivity may result from the variation of the local atomic structure of

![Figure 4. X-Ray Spectroscopy Analyses of the Used Single-Atom Catalyst](image_url)

(A) Cu 2p XPS spectrum of Cu1-N2/HCNS-used.
(B) N 1s XPS spectrum of Cu1-N2/HCNS-used.
(C) Normalized Cu K-edge XANES spectra of Cu foil, CuO, Cu$_2$O, and Cu1-N2/HCNS-used.
(D) The $k^3$-weighted Fourier transform spectra from Cu K-edge EXAFS.
single Cu atom. To verify this hypothesis, the controlled experiment was performed. Figure 3B shows that the phenol selectivity increases to 97% over the H2O2 pretreated Cu1-N2/HCNS, firmly proving our aforementioned hypothesis. The developed Cu1-N2/HCNS catalyst shows outstanding catalytic performance for hydroxylation of benzene to phenol, and more than 70% of benzene conversion with close to 99% of phenol selectivity has been obtained.

Conclusions
In summary, we present a facile reduction deposition-acid leaching strategy for preparing the single atomic Cu1-N2/HCNS catalyst. Owing to the unique local atomic structure of Cu atom center, the single-atom Cu-N2 catalytic sites are far superior to Cu-N3 sites with the former showing 3.4 times higher TON for benzene hydroxylation to phenol compared with the latter under the same reaction conditions. Moreover, Cu1-N2/HCNS catalyst demonstrates much higher selectivity (close to 99%) and stability than Cu nanoparticles and nanoclusters. The unique Cu-N2 sites anchored on the g-C3N4 surface are responsible for the outstanding catalytic properties concerning activity, selectivity, and stability for benzene hydroxylation to phenol, and the unique Cu-N2 is extremely more active than Cu-N3 owing to its much lower energy barrier regarding H2O2 activation owing to the unique coordination state of local atomic structure, confirmed by the results from experiments and DFT calculations. This work not only generates an efficient benzene hydroxylation catalyst for phenol production, but also presents a facile and efficient method for modulating coordination environment of single metallic atoms to design excellent catalysts.

Limitations of the Study
In this paper, we have proved that single-atom catalyst with Cu-N2 sites shows extremely high activity than Cu-N3 sites for benzene hydroxylation with H2O2 to phenol. However, our current evaluation system needs a large amount of H2O2 for a high benzene conversion, which results in a relatively low utilization of H2O2 because of its invalid decomposition.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.11.010.

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AUTHOR CONTRIBUTIONS
T.Z. conceived and performed the experiments, collected and analyzed data, and wrote the paper. X.N. conducted the density functional theory calculation, analysis, and also wrote this section. W.Y. participated in the synthesis of materials. X.G. participated in the data analysis and discussions. C.S. participated in the data analysis and discussions and also revised the paper. R.S. performed XAS measurement and participated in the XAS data analysis and wrote this section. Y.L. conducted the HAADF-STEM studies. Z.Z. conceived the idea, supervised the project work, and led the data analysis and discussion, and prepared and finalized the paper. All the authors commented on the manuscript and have given approval to the final version of the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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REFERENCES

Acharya, S.S., Ghosh, S., and Bal, R. (2014). Fabrication of three-dimensional (3D) raspberry-like copper chromite spinel catalyst in a facile hydrothermal route and its activity in selective hydroxylation of benzene to phenol. ACS Appl. Mater. Interfaces 6, 14451–14459.

Bal, R., Tada, M., Sakai, T., and Iwasa, Y. (2006). Direct phenol synthesis by selective oxidation of benzene with molecular oxygen on an ionic-thermal-N/Re cluster/zeolite catalyst. Angew. Chem. Int. Ed. 45, 448–452.

Balducci, L., Bianchi, D., Bortolo, R., D’Alloisio, R., Ricci, M., Tassanini, R., and Ungarelli, R. (2003). Direct oxidation of benzene to phenol with hydrogen peroxide over a modified titanium silicate. Angew. Chem. Int. Ed. 42, 4957–4960.

bin Mohd Yusoff, A.R., Kim, D., Schneider, F.K., da Silva, W.J., and Jang, J. (2015). Au-doped single layer graphene nanoribbons for a record-high efficiency ITO-free tandem polymer solar cell. Energy Environ. Sci. 8, 1523–1537.

Chen, X., Zhang, J., Fu, X., Antonietti, M., and Wang, X. (2009). Fe–Co₃O₄-Catalyzed oxidation of benzene to phenol using hydrogen peroxide and visible light. J. Am. Chem. Soc. 131, 11658–11659.

Chen, Z., Vorobyeva, E., Mitchell, S., Fako, E., Ortuno, M.A., López, N., Collins, S.M., Midgley, P.A., Richard, S., Vile´, G., and Perez-Ramı´rez, J. (2018a). A heterogeneous single-atom palladium catalyst surpassing homogeneous systems for Suzuki coupling. Nat. Nanotechnol. 13, 702–707.

Chen, Y., Ji, S., Chen, C., Peng, Q., Wang, D., and Li, Y. (2018b). Single-atom catalysts: synthetic strategies and electrochemical applications. Joule 2, 1242–1264.

Cheng, C., Li, S., Xia, Y., Ma, L., Nie, C., Roth, C., and Thomas, A. (2013b). From melamine-derived 2D-NH₂ to 3D-NH₂: transformation of benzene to phenol using dioxygen as an oxygen source and water as an electron source in the presence of a cobalt catalyst. Chem. Sci. 8, 7119–7125.

Han, Y., Wang, Y., Xu, R., Chen, W., Zheng, L., Han, A., Zhu, Y., Zhang, J., Zhang, H., Luo, J., et al. (2018). Electronic structure engineering to boost oxygen reduction activity by controlling the coordination of the central metal. Energy Environ. Sci. 11, 2384–2382.

Harmer, M.A., Farneth, W.E., and Sun, Q. (1996). High surface area nano resin/silica nanocomposites: a new class of solid acid catalyst. J. Am. Chem. Soc. 118, 7708–7715.

Hosseini, S.M., Ghaci, M., Kulinch, S.A., Wunderlich, W., Farokhpour, H., Saraji, M., and Shahvar, A. (2018). Au-Pd@g-C₃N₄ as an efficient photocatalyst for visible-light oxidation of benzene to phenol: experimental and mechanistic study. J. Phys. Chem. C 122, 27477–27485.

Ivanichkova, I.D., Maksimchuk, N.V., Maksimovskaya, R.I., Maksimov, G.M., and Khodkeeva, O.A. (2014). Highly selective oxidation of aliphatic hydrocarbons to α-keto-aldehydes by highly dispersed polyoxometalate and N-doped graphitic carbon nitride as an efficient photocatalyst for visible-light oxidation of carbon dioxide. J. Am. Chem. Soc. 138, 6292–6297.

Jun, Y., Park, J., Lee, S.U., Thomas, A., Hong, W.H., and Stucky, G.D. (2013a). Three-dimensional macroscopic assemblies of low-dimensional carbon nitrides for enhanced hydrocarbon evolution. Angew. Chem. Int. Ed. 52, 11083–11087.

Jun, Y., Lee, E.Z., Wang, X., Hong, W.H., Stucky, G.D., and Thomas, A. (2013b). From melanin- and supramolecular aggregates to carbon nitride hollow spheres. Adv. Funct. Mater. 23, 3661–3667.

Kao, L.S., Spira-Solomon, D.J., Pennen-Hahn, J.E., Hodgson, K.O., and Solomon, E.I. (1987). X-ray absorption edge determination of the oxidized state and coordination number of copper: application to the type 3 site in Rhizoctonia cerealis and its reaction with oxygen. J. Am. Chem. Soc. 109, 6433–6442.

Kwon, Y., Kim, T.Y., Kwon, G., Yi, J., and Lee, H. (2017). Selective activation of methane on single-atom catalyst of rhodium dispersed on zirconia for direct conversion. J. Am. Chem. Soc. 139, 17694–17699.

Labinger, J.A., and Bercaw, J.E. (2002). Understanding and exploiting C–H bond activation. Nature 417, 507–514.

Leitch, J.A., and Frost, C.G. (2017). Ruthenium-catalysed activation for remote meta-selective C–H functionalization. Chem. Soc. Rev. 46, 7145–7153.

Li, F., Han, G., Noh, H., Kim, S., Lu, Y., Jeong, H.Y., Fu, Z., and Baek, J. (2018a). Boosting oxygen reduction catalysis with abundant copper single atom active sites. Energy Environ. Sci. 11, 2263–2269.

Li, Y., Liu, X., Zhang, Z., Zhao, S., Tian, G., Zheng, J., Wang, D., Shi, S., and Russell, T.P. (2018b). Adaptive structured pickering emulsions and porous materials based on cellulose nanoscaffold. Angew. Chem. Int. Ed. 57, 13560–13564.

Liang, H., Bruller, S., Dong, R., Zhang, J., Feng, X., and Mullen, K. (2015). Molecular metal–N₉ centres in porous carbon for electrocatalytic hydrogen evolution. Nat. Commun. 6, 7992.

Liu, J., Wang, H., and Antonietti, M. (2016). Graphitic carbon nitride “Reloaded”: emerging applications beyond (photo) catalysis. Chem. Soc. Rev. 45, 2308–2326.

Liu, W., Zhang, L., Liu, X., Liu, X., Yang, X., Miao, S., Wang, W., Wang, A., and Zhang, T. (2017). Discriminating catalytically active Fe₅N₆ species of atomically dispersed Fe₅N₆ catalyst for selective oxidation of the C–H bond. J. Am. Chem. Soc. 139, 10790–10798.

Liu, W., Chen, Y., Qi, H., Zhang, L., Yan, W., Liu, X., Yang, X., Miao, S., Wang, W., Liu, C., et al. (2018). A durable nickel single-atom catalyst for hydrogenation reactions and cellulose valorization under harsh conditions. Angew. Chem. Int. Ed. 57, 7071–7075.

Malonzo, C.D., Shaker, S.M., Ren, L., Prinslow, S.D., Platero-Prats, A.E., Gallington, L.C., Borycz, J., Thompson, A.B., Wang, T.C., Farha, O.K., et al. (2016). Thermal stabilization of metal-organic framework-derived single-site catalytic clusters through nanocasting. J. Am. Chem. Soc. 138, 2739–2748.

Marcinkowski, M.D., Darby, M.T., Liu, J., Wimble, J.M., Lucco, F.R., Lee, S., Michaelides, A., Flynnter-Stephanopoulos, M., Stamatakis, M., and Sykes, E.C.H. (2018). Pt/Cu single-atom alloys as coke-resistant catalysts for efficient C–H activation. Nat. Chem. 10, 325–332.

Matei, F., Jiménez-Borja, C., Canales-Vázquez, J., Brossa, S., Dorado, F., Valverde, J.L., and Cuenca, D. (2013). Enhanced selective combustion of palladium catalysts...
deposited on highly porous supports. Appl. Catal. B Environ. 132-133, 80–89.

Mitchell, S., Vorobyeva, E., and Pérez-Ramírez, J. (2018). The multifaceted reactivity of single-atom heterogeneous catalysts. Angew. Chem. Int. Ed. 57, 15316–15329.

Morimoto, Y., Bunno, S., Fujieda, N., Sugimoto, H., and Itoh, S. (2015). Direct hydroxidation of benzene to phenol using hydrogen peroxide catalyzed by nickel complexes supported by pyridylaldehyde ligands. J. Am. Chem. Soc. 137, 5867–5870.

Qiao, B., Wang, A., Yang, X., Allard, L.F., Jiang, Z., Cui, Y., Liu, J., Li, J., and Zhang, T. (2011). Single-atom catalysis of CO oxidation using Pt/FeOx. Nat. Chem. 3, 634–641.

Qu, Y., Li, Z., Chen, W., Lin, Y., Yuan, T., Yang, Z., Zhao, C., Wang, J., Zhao, C., Wang, X., et al. (2018). Direct transformation of bulk copper into copper single sites via emitting and trapping of atoms. Nat. Catal. 1, 781–786.

Sambiasi, C., Schönbauer, D., Blieck, R., Daou-Huy, T., Pototschnig, G., Schaaf, P., Wiesinger, T., Zia, M.F., Wencel-Delord, J., Besset, T., et al. (2018). Comprehensive overview of directing groups applied in metal-catalysed C-H functionalisation. Chem. Soc. Rev. 47, 6603–6743.

Shan, C., Zhu, L., Qu, L., Bai, R., and Lan, Y. (2018). Mechanistic view of Ru-catalyzed C-H bond activation and functionalization: computational advances. Chem. Soc. Rev. 47, 7552–7576.

Shilov, A.E., and Shul’pin, G.B. (1997). Activation of C-H bonds by metal complexes. Chem. Rev. 97, 2879–2932.

Sorrell, T.N., and Malachowski, M.R. (1983). Mononuclear three-coordinate copper (I) complexes: synthesis, structure, and reaction with carbon monoxide. Inorg. Chem. 22, 1883–1887.

Sorrell, T.N., Malachowski, M.R., and Jameson, D.L. (1982). Synthesis, structure, and reactivity of a bimolecular three-coordinate copper (I) complex. Inorg. Chem. 21, 3250–3252.

Su, Y., Han, Z., Zhang, L., Wang, W., Duan, M., Li, X., Zheng, Y., Wang, Y., and Lei, X. (2017). Surface hydrogen bonds assisted mesoporous WO3 photocatalysts for high selective oxidation of benzylalcohol to benzaldehyde. Appl. Catal. B Environ. 217, 108–114.

Szocsényi, Á., Li, G., Gasscon, J., and Pidko, E.A. (2018). Mechanistic complexity of methane oxidation with H2O2 by single-site Fe/ZSM-5 catalyst. ACS Catal. 8, 7961–7972.

Thomas, J.M., Raja, R., and Lewis, D.W. (2005). Single-site heterogeneous catalysts. Angew. Chem. Int. Ed. 44, 6456–6482.

Tsui, T., Zaoputra, A.A., Hitomi, Y., Miera, K., Ogura, T., Shiota, Y., Yoshizawa, K., Sato, H., and Koder, M. (2017). Specific enhancement of catalytic activity by a dicopper core: selective hydroxylation of benzene to phenol with hydrogen peroxide. Angew. Chem. Int. Ed. 56, 7779–7782.

Wang, Y., Wang, X., and Antonietti, M. (2012). Polymeric graphitic carbon nitride as a heterogeneous organocatalyst: from photochemistry to multipurpose catalysis to sustainable chemistry. Angew. Chem. Int. Ed. 51, 68–89.

Wang, D., Wang, M., and Li, Z. (2015). Fe-based metal-organic frameworks for highly selective photocatalytic benzene hydroxylation to phenol. ACS Catal. 5, 6852–6857.

Wencel-Delord, J., and Glorius, F. (2013). C-H bond activation enables the rapid construction and late-stage diversification of functional molecules. Nat. Chem. 5, 369–375.

Xia, Y., and Tang, Z. (2012). Monodisperse hollow supraparticles via selective oxidation. Adv. Funct. Mater. 22, 2585–2593.

Xu, J., Chen, Y., Hong, Y., Zheng, H., Ma, D., Xue, B., and Li, Y. (2018). Direct catalytic hydroxylation of benzene to phenol catalyzed by vanadia supported on exfoliated graphitic carbon nitride. Appl. Catal. Gen. 59, 31–39.

Yamaguchi, S., Kamiya, K., Hashimoto, K., and Nakanishi, S. (2017). Ru atom-modified covalent triazine framework as a robust electrocatalyst for selective alcohol oxidation in aqueous electrolytes. Chem. Commun. (Camb.) 53, 10437–10440.

Yamaguchi, S., Suzuki, A., Togawa, M., Nishibori, M., and Yahiro, H. (2017). Specific enhancement of catalytic activity by a dicopper core: selective hydroxylation of benzene to phenol with hydrogen peroxide. Angew. Chem. Int. Ed. 56, 7779–7782.

Yamashita, H., Mori, K., Chen, W., Cao, T., Zheng, L., Dong, J., Zhang, J., Zhang, M., Han, Y., et al. (2018). A cocoon silk chemistry strategy to ultra thin N-doped carbon nanosheets with metal single-site catalysts. Nat. Commun. 9, 3861–3869.
Supplemental Information

Single Atomic Cu-N₂ Catalytic Sites for Highly Active and Selective Hydroxylation of Benzene to Phenol

Ting Zhang, Xiaowa Nie, Weiwei Yu, Xinwen Guo, Chunshan Song, Rui Si, Yuefeng Liu, and Zhongkui Zhao
Figure S1. The XRD Patterns of Cu NC/HCNS and Cu$_1$N$_2$/HCNS, related to Figure 1.
Figure S2. (A) SEM Image of Single-atom Cu_{1-N}_2/HCNS Catalyst and (B) HAADF-STEM image of Cu NC/HCNS, related to Figure 1.
Figure S3. Nitrogen Physisorption Analysis of Single-atom Cu$_1$-N$_2$/HCNS Catalyst, Cu$_1$-N$_2$/HCNS Catalyst and HCNS Support, related to Figure 1.
(A) Isotherms curves
(B) Pore size distribution curves
Table S1. Textural Properties of Single-atom Cu$_{1}$-N$_{2}$/HCNS Catalyst and HCNS Support, related to Figure 1.

| Entry | Sample            | $S_{\text{BET}}$ (m$^2$·g$^{-1}$) | $V_{\text{BJH}}$ (cm$^3$·g$^{-1}$) | $V_{\text{Total}}$ (cm$^3$·g$^{-1}$) |
|-------|-------------------|-----------------------------------|-----------------------------------|-------------------------------------|
| 1     | HCNS              | 57                                | 0.64                              | 0.64                                |
| 2     | Cu$_{1}$-N$_{2}$/HCNS | 65                                | 0.67                              | 0.67                                |
| 3     | Cu$_{1}$-N$_{3}$/HCNS | 84                                | 0.82                              | 0.82                                |
Figure S4. XAFS Analysis, related to Figure 1.
(A) Normalized Cu K-edge XANES spectra of Cu foil, CuO, Cu$_2$O and Cu NC/HCNS.
(B) The $k^3$-weighted Fourier transform spectra from Cu K-edge EXAFS.
(C) The corresponding EXAFS fitting curve of Cu NC/HCNS.
(D) Normalized Cu K-edge XANES spectra of Cu foil, CuO, Cu$_2$O and Cu$_{1-N_3}$/HCNS.
(E) The $k^3$-weighted Fourier transform spectra from Cu K-edge EXAFS of Cu foil, CuO, Cu$_2$O and Cu$_{1-N_3}$/HCNS.
Figure S5. XPS analysis of Cu NC/HCNS catalyst, related to Figure 1.
(A) O 1s XPS spectrum.
(B) N 1s XPS spectrum.
### Table S2. EXAFS fitting data for Cu NC/HCNS catalyst, related to Figure 1.

| Sample          | Cu-N (O) $^a$ | Cu-Cu $^a$ | $\sigma^2$ (Å$^2$) $^c$ | $\Delta E_0$ (eV) | Valence |
|-----------------|---------------|------------|--------------------------|-------------------|---------|
| Cu NC/HCNS      | 1.92±0.01(O)  | 2.87±0.04  | 0.007±0.001(N,O)         | 7.6±0.9           | +1.6    |
| Cu$_1$N$_3$/HCNS | 1.96±0.01(N)  | 3.3±0.3    | 0.007±0.001(N)           | 10.8±1.3          | +1.6    |

$^a$Bond distance;
$^b$Coordination number;
$^c$Debye-Waller factor;
$^d$Inner potential correction.

Cited from Ref. (Zhang et al., 2018)
Before the reaction carried out, single-atom catalyst was treated with certain amount of KSCN in water solution for 2 h. The amount of KSCN was calculated according to the total Cu content from ICP result. The following reaction was performed under following conditions: benzene (0.4 mL), H₂O₂ (6 mL) and acetonitrile (3 mL), 60 °C for 0.5 h.
Figure S7. XPS analysis of Cu$_{1}$N$_{2}$/HCNS catalyst, related to Figure 2.
(A) The survey XPS spectrum.
(B) The C 1s XPS spectrum.
Table S3. EXAFS fitting data for the fresh and used Cu$_{1}$-N$_2$/HCNS single-atom catalyst, related to Figure 2 and Figure 4.

| Sample          | Cu-N/O   | Cu-Cu   |          |          |          | Valence |
|-----------------|----------|---------|----------|----------|----------|---------|
|                 | $R$ (Å)$^a$ | CN$^b$  | $R$ (Å)$^a$ | CN$^b$  | $\sigma^2$ (Å$^2$)$^c$ | $\Delta E_0$ (eV) |       |
| Cu$_{1}$-N$_2$/HCNS | 1.92±0.03(N) | 2.0(N) | -        | -        | 0.007±0.001(N,O) | 7.6±0.9 | +1.5   |
|                 | 1.96±0.05(O) | 0.9±0.4(O) | -        | -        | -        | -       |         |
| Cu$_{1}$-N$_2$/HCNS-used$^e$ | 1.94±0.07(N) | 2.0(N) | -        | -        | 0.007±0.001(N,O) | 7.6±0.9 | +1.7   |
|                 | 1.97±0.07(O) | 1.4±1.0(O) | -        | -        | -        | -       |         |

$^a$Bond distance.
$^b$Coordination number.
$^c$Debye-Waller factor.
$^d$Inner potential correction.
$^e$The sample was recovered after one reaction cycle.
Table S4. Catalytic Performance of Various Catalysts for Direct Hydroxylation of Benzene to Phenol, related to Figure 3.

| Entry | Sample       | Temp. (°C) | Time (h) | Conv. (%) | Benzene | H₂O₂ | TON of | Sel. (%) | of Phenol | p-benzoquinone | others | Utilization of H₂O₂ | Ref.         |
|-------|--------------|------------|----------|-----------|---------|------|--------|----------|-----------|-----------------|---------|---------------------|-------------|
| 1ᵃ    | Blank        | 60         | 12       | 1.5       | -       | -    | -      | >99.9    | -         | -               | -       | -                   |             |
| 2ᵃ    | HCNS         | 60         | 12       | 5.2       | -       | -    | -      | >99.9    | -         | -               | -       | -                   |             |
| 3ᵇ    | Cu₁-N₂/HCNS  | 60         | 2.5      | 70.9      | 47.3    | 6935 | -      | 91.1     | 8.9       | <0.1            | 15      | This work           |             |
| 4ᵇ    | Cu₁-N₂/HCNS  | 60         | 2.5      | 15.6      | 11.6    | 2034 | -      | 99.3     | 0.7       | <0.1            | 14      | This work           |             |
| 5ᵇ    | Cu NC/HCNS   | 60         | 2.5      | 44.7      | 25.5    | 3489 | -      | 73.0     | 27.0      | <0.1            | 16      | This work           |             |
| 6ᵇ    | Cu NP/HCNS   | 60         | 2.5      | 41.4      | -       | 3231 | 70.9   | 29.1     | <0.1       | -               | -       | -                   |             |
| 7ᵇ    | Cu₁-N₂/HCNS  | 60         | 12       | 76.8      | -       | -    | 91.5   | 8.5      | <0.1       | -               | -       | This work           |             |
| 8ᵇ    | Cu₁-N₂/HCNS  | 60         | 3.5      | 89.3      | -       | 2783 | 90.5   | 9.5      | <0.1       | -               | -       | This work           |             |
| 9ᵇ    | Co-ISA/CNS   | 60         | 24       | 82.0      | -       | <722 | 86.0   | -        | -         | -               | -       | Zhu er al., 2018    |             |
| 10ᵇ   | [Ni(tpea)]²⁺ | 60         | 216      | 7.5       | -       | 749  | 99.0   | -        | -         | -               | -       | Morimoto, 2015      |             |
| 11ᵇ   | SA-Fe/CN     | 60         | 24       | 45        | -       | 786  | 94.0   | -        | -         | -               | -       | Zhang et al., 2017  |             |
| 12ᵇ   | Cu₁-N₂/HCNS  | 25         | 24       | 81.2      | -       | 2531 | 86.6   | 13.4     | <0.1       | -               | -       | This work           |             |
| 13ᵇ   | Co-ISA/CNS   | 25         | 24       | 53.0      | -       | <511 | 93.0   | -        | -         | -               | -       | Zhu et al., 2018     |             |
| 14ᵇ   | FeN₄/GN-2.7  | 25         | 24       | 23.4      | -       | 44   | 80.0   | -        | -         | -               | -       | -                   |             |

ᵃReaction conditions: 0.013 mol% active copper, molar ratio of H₂O₂ to substrate is 10:1, 0.5 mL of benzene, 6 mL of CH₃CN.
ᵇReaction conditions: 50.0 mg catalyst, 0.4 mL benzene, 6 mL H₂O₂ (30 wt%), 3 mL CH₃CN.
Figure S8. Effect of the Molar Ratio of H$_2$O$_2$ to Benzene in Benzene Oxidation over Cu$_{11}$N$_6$/HCNS Catalyst, related to Figure 3.

Reaction conditions: 20 mg catalyst, 0.5 mL benzene, 6 mL CH$_3$CN, and different amount of H$_2$O$_2$ (30%) at 60 °C for 2.5 h.
Figure S9. Comparative Trials for $\text{H}_2\text{O}_2$ Decomposition in Benzene Oxidation over Cu$_x$-N$_y$/HCNS Catalyst, related to Figure 3.

Reaction conditions: 0.0065 mol% active copper, 1.0 mL benzene (11 mmol), 0.52 mL $\text{H}_2\text{O}_2$ (30%) (5.5 mmol), and 6 mL CH$_3$CN at 60 °C.
Figure S10. The Kinetic Data Concerning Variation of Benzene Concentration as a Function of Reaction Time at Different Temperatures in the Kinetic Controlled Regime, related to Figure 3. Reaction conditions: 20 mg of Cat., 0.20 mL of benzene, 3.0 mL of H₂O₂ (30 wt%), 6 mL of CH₃CN. The data of Cu₁-N₂/HCNS and Cu NP/HCNS is cited from Ref. (Zhang et al., 2018).
Figure S11. The Kinetic Data Concerning Variation of Phenol Concentration as a Function of Reaction Time at Different Temperatures in the Kinetic Controlled Regime, related to Figure 3. Reaction conditions: 20 mg of Cat., 0.20 mL of phenol, 3.0 mL of H$_2$O$_2$ (30 wt%), 6 mL of CH$_3$CN. The data of Cu NP/HCNS is cited from Ref. (Zhang et al., 2018).
Table S5. The Comparison of Kinetic Parameters of Benzene Oxidation and Phenol Oxidation over Various Catalysts, related to Figure 3.

| Reaction          | $E_a$ (kJ mol$^{-1}$) | $A_{Cu1-N3/HCNS}$ | $A_{Cu NC/HCNS}$ | $A_{Cu NP/HCNS}$ | $A_{Cu1-N2/HCNS}$ | $A_{Cu NP/HCNS}$ |
|-------------------|-----------------------|--------------------|------------------|------------------|-------------------|------------------|
| Benzene oxidation | 18                    | 27                 | 52               | 53               | 1/8.0             | 1/1.2            |
| Phenol oxidation  | 31                    | 40                 | 35               | 34               | -                 | 1.2/1            |

*From Ref. (Zhang et al., 2018).*
### Table S6. Surface Component of Cu1-N2/HCNS Before and After Reaction\(^a\), related to Figure 4.

| Sample                  | C\(^b\) (At. %) | N\(^b\) (At. %) | O\(^b\) (At. %) | Cu\(^c\) (At. %) | Cu\(^c\) (wt %) |
|-------------------------|------------------|------------------|------------------|------------------|------------------|
| Cu1-N2/HCNS             | 41.84            | 56.13            | 1.78             | 0.25             | 0.23             |
| Cu1-N2/HCNS-used        | 45.72\(^d\)      | 49.10\(^d\)      | 4.93\(^d\)       | 0.25\(^f\)       | 0.21\(^e\)       |

\(^a\)Reaction conditions: 20 mg of Cat., 6 mL of CH3CN, 5.2 mL of H2O2, 0.5 mL of benzene, 60 °C for 12 h.
\(^b\)XPS results.
\(^c\)ICP-AES results.
\(^d\)The solid catalyst was recovered after 1 cycle.
\(^e\)The solid catalyst was recovered after 4 cycles.
Figure S12. The Corresponding EXAFS Fitting Curve of Cu$_1$-N$_2$/HCNS-used Catalyst, related to Figure 4.
Transparent Methods

Chemicals
Melamine, cyanuric acid, copper nitrate hydrate \((\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O})\), acetonitrile \((\text{CH}_3\text{CN})\), \(n\)-tetradecane and chloroform \((\text{CH}_3\text{Cl})\) were supplied by Tianjin Fuyu Fine Chemical Co., Ltd. Copper(II) acetate monohydrate \((\text{Cu(OAc)}_2\cdot\text{H}_2\text{O})\), dimethyl sulfoxide \((\text{DMSO})\) and \(\text{H}_2\text{O}_2\) (30\%) were purchased from Damao Chemical Reagent Factory. Polyvinylpyrrolidone \((\text{PVP-K30})\) and potassium rhodanate \((\text{KSCN})\) were obtained from Sigma. Nitric acid \((\text{HNO}_3, \ 65\text{~}~\text{to}~\text{68 wt}\%)\), sodium hydroxide \((\text{NaOH})\) and sodium borohydride \((\text{NaBH}_4)\) were supplied by Tianjin Guangfu Technology Development Co., Ltd. All the chemical reagents were analytical grade and directly used without further purification.

Preparation of Hollow Carbon Nitride Spheres (HCNS)
The hollow carbon nitride spheres (HCNS) was prepared corresponding to reference (Jun, 2013; Jun, 2013). Typically, 0.5 g of melamine and 0.51 g of cyanuric acid were ultrasonically dissolved in 20 mL and 10 mL of DMSO, respectively. After that, the two DMSO solutions were mixed together to obtain the white precipitates. As a consequence, the resulting solid was recovered by filtering and washing with ethanol. Finally, the HCNS was obtained by the drying at 50 °C with the subsequent calcination at 550 °C for 4 h with the heating rate under nitrogen atmosphere.

Preparation of \(\text{Cu}_1\text{-N}_3/\text{HCNS}\) Catalyst
For comparison, the supported \(\text{Cu}_1\text{-N}_3\) catalyst on HCNS was prepared according to our previous report (Zhang et al., 2018). Typically, the designed amount of \(\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}\) was firstly mixed with melamine in DMSO and magnetic stirring for 10 min, the DMSO dissolved cyanuric acid was added and keep stirring for 10 min. Solid sample was obtained by filtration and washed with water and ethonal. Dried solid was calcinated under \(\text{N}_2\) atmosphere at 550 °C for 4 h. The final obtained solid catalyst was denoted as \(\text{Cu}_1\text{-N}_3/\text{HCNS}\). The Cu content is 0.85 wt\% determined by ICP-AES.

Preparation of \(\text{Cu NP/HCNS}\) Catalyst
For comparison, the supported Cu nanoparticle catalyst on HCNS was prepared by a modified adsorption method (Nishimura, 2010). Typically, a) 0.12 g of PVP-K30 was dissolved in 5 mL of \(\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}\) aqueous solution (0.02 M) under \(\text{N}_2\) atmosphere. b) 1 mL of reductant (1.2 mmol \text{NaBH}_4 and 1.0 mmol \text{NaOH}) was injected and the system was stirring for 12 h. c) 0.5 g of HCNS was added and kept stirring for 4 h. d) Solid sample was recovered by centrifugation and washed with water for 3 times, ethanol for 1 times, respectively. The solid catalyst was dried and denoted as \(\text{Cu NP/HCNS}\). The Cu content is 0.85 wt\% determined by ICP-AES.

Characterization of Catalysts
Low-magnification field emission scanning electron microscopy (FESEM) images were recorded by a FEI QUANTA 450 scanning electron microscopy. The transmission electron microscopy (TEM), high-resolution TEM, HAADF-STEM images were collected on a JEOL-ARM200F FETEM with 200kV of electron acceleration energy. X-ray photoelectron spectra (XPS) were recorded on an Al Kα radiated Thermo VG ESCALAB250 instrument. The binding energy (BE) was calibrated by C 1s peak at 284.6 eV as the internal standard, and the deconvolution of spectra were carried out using the XPS PEAK 41 program with Gaussian function after subtracted by a Shirley background. Cu content was.
determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Nitrogen adsorption-desorption isotherms were recorded by 3H-2000PSI system of Beishide apparatus at 77 K. A degas process was performed at 140 °C for 6 h before the test. Brunauer-Emmett-Teller (BET) model was applied for the analysis of the porosity with the pore volume measured at P/P₀ = 0.99 point. The mesopore size distribution was calculated by BJH method from adsorption branch.

**N₂O Titration Experiment**

The content of surface active Cu atoms of Cu-NP/HCNS was determined by N₂O titration method on a Builder PCA-1200 apparatus equipped with a thermal conductor detector (TCD). (Zhang et al., 2018; Nishimura, 2010) Typically, a quartz “U” tube loaded with 100 mg sample of Cu-NP/HCNS was equipped and was firstly pretreated with Ar at 300 °C for 0.5 h. After the sample was reduced by 10 % H₂/Ar at 250 °C for 0.5 h, the tube was purged with Ar at 35 °C for 0.5 h. Subsequently, the sample was oxidized with N₂O for a period of time. When the TCD baseline stays steady, N₂O was replaced by Ar and the tube was purged for another 0.5 h. Later, the sample was reduced under 10 % H₂/Ar atmosphere at 200 °C for 0.5 h with a heating rate of 10 °C/min. The surface consumed H₂ was 3.4 × 10⁻³ mmol calculated through calibration, and the dispersity of Cu active sites was 26 %.

**KSCN Titration Experiment**

To determine the amount of exposed active Cu on the surface of the single-atom catalysts, KSCN titration method was applied. Typically, 50 mg single-atom catalyst was firstly loaded in a 50 mL flask. Then, a special equivlent of KSCN with 10 mL DI water was added. After magnetic stirring for 2 h, the solid catalyst was separated by centrifugation. Subsequently, the solid catalyst was transferred into the reaction system consist of benzene (0.4 mL), H₂O₂ (6 mL) and acetonitrile (3 mL). The following reaction was performed at 60 °C for 0.5 h.

**XAFS Analysis**

The X-ray absorption fine structure (XAFS) spectra at Cu K (E₀= 8979.0 eV) edge was performed at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under “top-up” mode with a constant current of 260 mA. The XAFS data were recorded under fluorescence mode with a Lytle-type ion chamber. The energy was calibrated accordingly to the absorption edge of pure Cu foil. Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as function of energies μ(E) were processed by background subtraction and normalization procedures, and reported as “normalized absorption” with E₀ = 8979.0 eV for all the tested samples and Cu/Cu₂O/CuO standard. Based on the normalized XANES profiles, the molar fraction of Cu²⁺/Cu⁺/Cu⁰ can be determined by the linear combination fit (Kuld, 2014) with the help of various references (Cu foil for Cu⁰, Cu₂O for Cu⁺ and CuO for Cu²⁺). For the extended X-ray absorption fine structure (EXAFS) part, the Fourier transformed (FT) data in R space were analyzed by applying first-shell appromiate model for Cu-N, Cu-O and Cu-Cu contributions. The passive electron factors, S₀², were determined by fitting the experimental data on Cu foil and fixing the coordination number (CN) of Cu-Cu to be 12, and then fixed for further analysis of the measured samples. The parameters describing the electronic properties (e.g., correction to the photoelectron energy origin, E₀) and local structure environment including CN, bond distance (R) and Debye-Waller factor around the absorbing atoms were allowed to
vary during the fit process. The fitted ranges for $k$ and $R$ spaces were selected to be $k = 3-10$ Å$^{-1}$ (Cu$_{1}$-N$_{2}$/HCNS) or 3-12 Å$^{-1}$ (Cu NC/HCNS) with $R = 1.0-3.0$ Å ($k^3$ weighted).

**Computational Methods**

The Vienna *ab initio* simulation package (VASP) was applied for all spin-polarized DFT calculations, with the ion cores represented by the projector augmented wave (PAW) potentials ([Blöchl, 1994]; [Kresse, 1996]; [Kresse, 1999]). The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional ([Kresse, 1999]) was used to calculate the electronic exchange-correlation energy. A 400 eV of the cutoff energy was used for plane-wave basis set. Structure optimizations were conducted using a damped molecular dynamics method until the forces on all atoms were less than 0.02 eV/Å. Transition states were searched using the climbing image nudged elastic band (CI-NEB) method ([Pdrew, 1996]; [Henkelman, 2000]), and each transition state was confirmed to have a single imaginary vibrational frequency along the reaction coordinate. A periodic monolayered $g$-C$_3$N$_4$ model in a $2 \times 2$ supercell was constructed and the optimized lattice parameters were calculated to be $a = b = 14.32$ Å and $c = 10.00$ Å. A $2 \times 2 \times 1$ $k$-point sampling within the Monkhorst-Pack scheme was employed for structural relaxations. The vacuum thickness was set to 10 Å to avoid interactions between repeating slabs. To compare the reactivity of benzene oxidation between the Cu$_{1}$-N$_{2}$/HCNS and Cu$_{1}$-N$_{3}$/HCNS catalyst, the C atom at different locations were separately replaced by a single Cu atom to model the Cu-N$_{2}$ and Cu-N$_{3}$ sites, as illustrated in Figure 2i and j. The binding energy of adsorbate was calculated by subtracting the energies of the isolated adsorbate in gas phase and the bare catalyst from the total energy of the adsorbed system.

**Catalytic Performance Test**

Selective oxidation of benzene to phenol was performed as the probe evaluation for catalytic performance test. Typically, a certain amount of catalyst (0.046 mg of active Cu atoms, 6 mL of CH$_{3}$CN, 0.5 mL of benzene and 5.2 mL of H$_{2}$O$_{2}$ (30 wt%)) were mixed in a 50 mL round-bottom glass flask and sealed carefully. Then the reaction was carried out at 60 °C in a water bath kettle with magnetic stirring for a period of time. After the reaction was accomplished and the system cooled to room temperature, products was extracted by dichloromethane, and n-tetradecane was injected as internal standard. The final products was analyzed by Fuli 9790II gas chromatograph equipped with a 30 m × 0.32 mm × 0.50 µm SE-54 capillary column and a flame ionization detector (FID).

Turnover number (TON) was calculated as the following formula:

$$TON = \frac{\Delta n_{\text{Benzene}}}{n_{\text{Cu}}}$$

$\Delta n_{\text{Benzene}}$: Converted benzene, mol; $n_{\text{Cu}}$: Amount of active Cu sites, mol.

**Kinetic Studies**

In order to explain the origin of the extraordinary catalytic performance of the Cu$_{1}$-N$_{2}$/HCNS catalyst for benzene selective oxidation to phenol, the kinetic studies were performed concerning benzene oxidation and phenol oxidation over diverse catalysts in the temperature range of 20-60 °C within a kinetic controlled regime. Reaction conditions: 20 mg of catalyst, 0.20 mL of benzene, 3.0 mL of H$_{2}$O$_{2}$ (30 wt%), 6 mL of CH$_3$CN, carried out for 1.5 h at 20 °C, 30 °C 40 °C and 60 °C, respectively. The reaction rate ($r$) was calculated by dividing the number of the reacted benzene (phenol) by the
reaction time and the number of the supported active Cu atoms on HCNS. By plotting \( \ln r \) as a function of \( 1/T \), an Arrhenius plot was achieved. With the slope and intercept of Arrhenius plot, the apparent activation barrier \( (E_a) \) and pre-exponential factor \( (A) \) for benzene oxidation and phenol oxidation over the catalysts were achieved.

**Recyclability Test**
To test the stability of single-atom Cu\(_{1-}\)N\(_2\)/HCNS catalyst for benzene selective oxidation to phenol, the recycling experiment was performed. Typically, 20 mg of fresh Cu\(_{1-}\)N\(_2\)/HCNS catalyst was applied in a 50 mL round-bottom glass flask. 6 mL CH\(_3\)CN, 5.2 mL H\(_2\)O\(_2\) and 0.5 mL benzene was added and the flask was sealed carefully. The reaction was carried out at 60 °C for 12 h. After one cycle of reaction, solid catalyst was recovered by centrifugation, washed with ethanol and dried. The recovered catalyst was used for the next cycle. Products were analyzed by gas chromatograph.

**Controlled experiments**
To investigate the origin of the phenol selectivity increment over the recovered single-atom Cu\(_{1-}\)N\(_2\)/HCNS catalyst, a rational controlled experiment was performed. Fresh Cu\(_{1-}\)N\(_2\)/HCNS catalyst was firstly pretreated with hydrogen peroxide under the same condition as catalytic performance test except benzene was absent. Subsequently, solid catalyst was recovered by centrifugation, washed with ethanol for 3 times and dried. Then, 20 mg of hydrogen peroxide pretreated catalyst was applied in benzene selective oxidation to phenol as the same procedure in recycling test part. The final products were analyzed by gas chromatograph.

**Comparative Trials of H\(_2\)O\(_2\) Activation over Cu\(_{1-}\)N\(_2\)/HCNS and Cu\(_{1-}\)N\(_3\)/HCNS**
Typically, a certain amount of catalyst (0.046 mg of active Cu atoms, 6 mL of CH\(_3\)CN, 1.0 mL of benzene and 0.52 mL of H\(_2\)O\(_2\) (30 wt%) were mixed in a 50 mL round-bottom glass flask and sealed carefully. Then the reaction was carried out at 60 °C in a water bath kettle with magnetic stirring for a period of time. After the reaction was accomplished and the system cooled down to room temperature, products was extracted by dichloromethane. The remained H\(_2\)O\(_2\) was titrated by indirect iodometry method.

The conversion of H\(_2\)O\(_2\) was calculated according to the following formula:

\[
X_{H_2O_2} = 100\% \times \frac{n_{0,H_2O_2} - n_{1,H_2O_2}}{n_{0,H_2O_2}}
\]

\(X_{H_2O_2}\): H\(_2\)O\(_2\) conversion;

\(n_{0,H_2O_2}\): the initial molar quantity of H\(_2\)O\(_2\);

\(n_{1,H_2O_2}\): the final molar quantity of H\(_2\)O\(_2\) after reaction.

The effective utilization rate of of H\(_2\)O\(_2\) \((U_{H_2O_2})\) was calculated according to the following formula:

\[
U_{H_2O_2} = 100\% \times \frac{\Delta n_{Benzene}}{\Delta n_{H_2O_2}}
\]

\(\Delta n_{Benzene}\): Converted benzene, mol;

\(\Delta n_{H_2O_2}\): Converted H\(_2\)O\(_2\), mol.
Supplemental References

Zhang, T., Zhang, D., Han, X., Dong, T., Guo, X., Song, C., Si, R., Liu, W., Liu, Y. & Zhao, Z. (2018). Preassembly Strategy to Fabricate Porous Hollow Carbonitride Spheres Inlaid with Single Cu–N₃ Sites for Selective Oxidation of Benzene to Phenol. J. Am. Chem. Soc. 140, 16936-16940.

Zhu, Y., Sun, W., Luo, J., Chen, W., Cao, T., Zheng, L., Dong, J., Zhang, J., Zhang, M., Han, Y., Chen, C., Peng, Q., Wang, D. & Li, Y. (2018). A Cocoon Silk Chemistry Strategy to Ultrathin N-doped Carbon Nanosheet with Metal Single-site Catalysts. Nature Commun. 9, 3861-3869.

Morimoto, Y., Bunno, S., Fujieda, N., Sugimoto, H. & Itoh, S. (2015). Direct Hydroxylation of Benzene to Phenol Using Hydrogen Peroxide Catalyzed by Nickel Complexes Supported by Pyridylalkylamine Ligands. J. Am. Chem. Soc. 137, 5867-5870.

Zhang, M., Wang, Y., Chen W., Dong, J., Zheng, L., Luo, J., Wan, J., Tian, S., Cheong, W., Wang, D. & Li, Y. (2017). Metal (Hydr)oxides@Polymer Core-Shell Strategy to Metal Single Atom Materials. J. Am. Chem. Soc. 139, 10976-10979.

Deng, D., Chen, X., Yu, L., Wu, X., Liu, Q., Liu, Y., Yang, H., Tian, H., Hu, Y., Du, P., Si, R., Wang, J., Cui, X., Li, H., Xiao, J., Xu, T., Deng, J., Yang, F., Duchesne, P. N., Zhang, P., Zhou, J., Sun, L., Li, J., Pan, X., & Bao, X. (2015). A Single Iron Site Confined in a Grapheme Matrix for the Catalytic Oxidation of Benzene at Room Temperature. Sci. Adv. 1, No. e1500462.

Jun, Y., Park, J., Lee, S. U., Thomas, A., Hong, W. H. and Stucky, G.D. (2013). Three-Dimensional Macroscopic Assemblies of Low-Dimensional Carbon Nitrides for Enhanced Hydrogen Evolution. Angew. Chem. Int. Ed. 52, 11083-11087.

Jun, Y., Lee, E.Z., Wang, X., Hong, W.H., Stucky, G.D. and Thomas, A. (2013). From Melamine-Cyanuric Acid Supramolecular Aggregates to Carbon Nitride Hollow Spheres. Adv. Funct. Mater. 23, 3661-3667.

Nishimura, S., Takagaki, A., Maenosono, S. and Ebitani, K. (2010). In Situ Time-Resolved XAFS Study on the Formation Mechanism of Cu Nanoparticles Using Poly(N-vinyl-2-pyrrolidone) as a Capping Agent. Langmuir 26, 4473-4479.

Kuld, S., Conradsen, C., Moses, P.G., Chorkendorff, I. and Sehested, J. (2014). Quantification of Zinc Atoms in a Surface Alloy on Copper in an Industrial-Type Methanol Synthesis Catalyst. Angew. Chem. 126, 6051-6055.

Blöchl, P.E. (1994). Projector augmented-wave method. Phys. Rev. B 50, 17953-17979.

Kresse, G. and Furthmüller, J. (1996). Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comp. Mater. Sci. 6, 15-50.

Kresse, G. and Joubert, D. (1999). From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758-1775.
Perdew, J.P., Burke, K. and Ernzerhof, M., (1996). Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77, 3865-3868.

Henkelman, G., Uberuaga, B. P. and Jónsson, H., (2000). A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. 113, 9901-9904.