Selective H$_2$O$_2$ conversion to hydroxyl radicals in the electron-rich area of hydroxylated C-g-C$_3$N$_4$/CuCo–Al$_2$O$_3$†

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The Fenton reaction has been explored extensively in different fields due to the generation of hydroxyl radicals (‘OH). However, the reaction requires strongly acidic conditions and excessive consumption of H$_2$O$_2$, which impedes its widespread application. Here, we report that twice the amount of ‘OH radicals as that of the reacted H$_2$O$_2$ was formed by the reaction of H$_2$O$_2$ with a type of nano–composite OH–CCN/CuCo–Al$_2$O$_3$ under nearly neutral conditions. The nano-composite was achieved by the co-incorporation of Cu and Co into γ-Al$_2$O$_3$, and the sequential complex formation of the σ-type Cu–O–C linkers between the surface Cu and the hydroxyl group of the tri-s-triazine ring in C-g-C$_3$N$_4$. From electron paramagnetic resonance spectra and density functional theory simulations, it was verified that an electron-rich area around Cu occurred due to the Cu–π interaction and the different electronegativities of Cu with Co and Al in OH–CCN/CuCo–Al$_2$O$_3$ which reacted with H$_2$O$_2$, resulting in two electron transfer processes. One process is from the electron-rich Cu center to H$_2$O$_2$ to form ‘OH, and the other is from H$_2$O to the N atom of OH–CCN to produce ‘OH. The catalyst shows extremely high activity for the degradation of various refractory organic pollutants in water under mild conditions with a high utilization efficiency of H$_2$O$_2$ (~90%). Our findings confirm that the construction of an electron-rich area is essential for overcoming the limitations of the classical Fenton process for environmental remediation and other applications.

1. Introduction

To date, the Fenton reaction has been extensively investigated in various fields and applications,1–9 since its establishment in 1894, due to the generation of highly aggressive hydroxyl radicals (‘OH) from the reaction of hydrogen peroxide (H$_2$O$_2$).1,10 Its widespread applications have been observed in the removal of toxic refractory organic pollutants from wastewaters and soils,3,4 material synthesis,1,5,6 medicine7 and polishing.8 In particular, the localized Fenton reaction exhibits a surprising effectiveness in cancer therapy without the need for an external energy input compared to other methods7 and in the production of ultra-smooth gold with a selective knockout of active sites, which is required in electrochemistry, microelectronics, and optics and for life-supporting medical implants.3,8a The Fenton process consists of the reaction of H$_2$O$_2$ with Fe$^{2+}$ or other reducing transition metallic ions in a strongly acidic solution.2 In practical applications, some of the drawbacks of this process include the need for stoichiometric amounts of metal salts required for the generation of ‘OH,11 the resulting metal sludge and strongly acidic conditions (pH = 2–3.5) required for most neutral treated systems,12,13 which result in processing problems during post-treatment. The development of heterogeneous Fenton catalysts has significantly addressed these problems. However, few of these catalysts exhibit high catalytic efficiency under nearly neutral mild conditions. Moreover, an excess of hydrogen peroxide (100-fold larger than the stoichiometric amount) is required to reach a suitable efficiency level in these materials,11 which is due to the necessary cycle of the reduction state (M$n^+$) and oxidation state (M$(n+m)^{n+m}$) of the metal for ‘OH formation. In the reaction, the reduction of M$(n+m)^{n+m}$ to M$n^+$ by the oxidizing H$_2$O$_2$ is the rate-limiting step,11,14 and it results in the conversion of excess H$_2$O$_2$ to O$_2$. Light, electricity, ultrasound and chelating agents have been widely used to improve the step reaction,13,16 resulting in an additional energy input and inconvenience for several applications.

Recently, we developed an efficient Fenton-like catalyst consisting of Ti, Cu and Al lattice-doped dandelion-like silica nanospheres,11 in which galvanic-like cells were formed by the negative charge nonuniformity of lattice oxygen due to different electronegativities of doped metals. Our findings...
indicate that it is important to construct a high electron density area around the active metal component in heterogeneous catalysts to achieve a high Fenton efficiency. It has been observed that molecular O₂ can trap the excess electrons on the surface of a fully oxidized metal oxide, producing superoxo (O₂⁻), peroxy (O₂O⁻) or dissociated (2 × O²⁻) forms. The redox potential (1.229 V vs. SHE) of O₂/H₂O is smaller than that of H₂O₂/H₂O (1.763 V), and thus, molecular H₂O₂ can also trap the excess electrons on metal oxides when H₂O₂ interacts with metal oxides.

Cation–π interactions are one of the most important intermolecular binding forces, which are relevant for aromatic recognition in chemical and biological processes. Charge transfer may be a particularly relevant parameter in cation–π interactions for transition-metal ions. The substitution of the hydroxyl group for the aromatic ring may enhance the cation–π interaction and increase the possibility of orbital interactions and charge transfer of π → cation (σ donation) and cation → π* (π back-donation). Graphitic carbon nitrides consist of 2D sheets of tri-s-triazine connected via tertiary amines, and they belong to the typical π-conjugated graphitic planes formed via sp² hybridization of carbon (C) and nitrogen (N) atoms and have become increasingly important in photocatalysis, heterogeneous catalysis and fuel cells.

In this study, a high electron density around Cu was achieved by doping both Co and Cu in the lattice of γ-Al₂O₃, and the sequential surface complex of Cu with hydroxyl on the aromatic ring of the carbon-doped g-C₃N₄, denoted as (OH–CCN/CuCo–Al₂O₃), was formed. The formation of the key σ-type bridge CO–Cu linker in the structure of the catalyst was verified and characterized using X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR) and extended X-ray absorption fine structure (EXAFS). Persistent pollutants are widely detected in various effluents and often lead to adverse ecotoxicological effects. Some prominent examples are phenols (such as phenol, chloroglucinol and 4-isopropylphenol), pharmaceuticals (such as ibuprofen, phenytoin and diphenhydramine), pesticides (such as 2-chlorophenol, 2,4-dichlorophenoxy-acetic acid and atrazine), and dyes (methyl orange, rhodamine B and methylene blue) as well as endocrine disrupting chemicals (such as bisphenol A). Thus, these refractory organic pollutants were selected to evaluate the activity and properties of the catalyst with H₂O₂ in aqueous solution. It was found that twice as much OH as the reacted H₂O₂ was generated in the OH–CCN/CuCo–Al₂O₃ suspension, resulting in an extremely high utilization efficiency of H₂O₂ for the rapid degradation and mineralization of refractory organic pollutants in water under mild conditions. Correspondingly, the interfacial electron transfer processes were monitored using the electron paramagnetic resonance (EPR) spectra, density functional theory (DFT) computation and in situ Raman spectra to verify that the excess unpaired electrons around Cu were responsible for the high efficiency of OH–CCN/CuCo–Al₂O₃. Our findings suggest that constructing an electron-rich layer is crucial for developing heterogeneous Fenton-like catalysts.

2. Experimental section

2.1. Chemicals and reagents

Horseradish peroxidase (POD, 99%), N,N-diethyl-p-phenylendiamine sulfate (DPD, 98%), 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO, 99%), 2-chlorophenol (≥99%), atrazine (≥99%) and ibuprofen (≥98%) were obtained from Sigma-Aldrich (St. Louis, USA). Bisphenol A (≥99%), diphenhydramine (≥99%), 2,4-dichlorophenoxyacetic acid (≥99%) and phenytoin (99%) were purchased from Acros (Geel, Belgium). Urea (USP grade) was obtained from Amresco (USA). Hydrogen peroxide (H₂O₂, 30%, w/w), aluminum isopropanoxide (Al(OiPr)₃, 98%), copper chloride dihydrate (CuCl₂·2H₂O, ≥99%), cobalt chloride hexahydrate (CoCl₂·6H₂O, ≥99%), and all the other chemicals (analytical grade) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Deionized water was used throughout this study.

2.2. Catalyst preparation

OH–CCN/CuCo–Al₂O₃ was synthesized through a two-step method. First, CuCo–Al₂O₃ was prepared using a modified evaporation-induced self-assembly process, according to a previously reported method. In a typical procedure, 4.2 g Al(OiPr)₃, 0.28 g CuCl₂·2H₂O, 0.2 g CoCl₂·6H₂O and 3.6 g hydrochloric acid solution were added dropwise to adjust the pH value to 5. The obtained solution was stirred at 50 °C for 3 h. Then, 0.1 mol L⁻¹ aqueous hydrochloric acid solution was added dropwise to adjust the pH to 3. After standing for 12 h, the mixture was evaporated at 100 °C in air to remove water and all other volatiles. Then, the solid was calcined in a muffle furnace at 600 °C in air for 6 h to remove the template. The obtained product was ground into powder, and it was referred to as CuCo–Al₂O₃. The Cu and Co contents in the samples were determined by ICP-OES (Optima 2000) after the samples were completely dissolved using nitric acid and hydrofluoric acid. The weight percentages of Cu and Co were calculated using the determined percentage of the Cu and Co contents in the samples. Following this procedure, various CuCo–Al₂O₃ samples with different Cu and Co contents were prepared, and the catalyst with 4.8 wt% Cu and 2.4 wt% Co exhibited the highest activity (Fig. S1a and S1b†). Therefore, this sample was selected as the solid precursor of OH–CCN/CuCo–Al₂O₃. As references, γ-Al₂O₃, Cu–Al₂O₃ and Co–Al₂O₃ were prepared using the same procedure. Second, OH–CCN/CuCo–Al₂O₃ was prepared through the in situ growth of g-C₃N₄ on the surface of CuCo–Al₂O₃ using urea as the precursor. Typically, 3.0 g urea and 1.0 g CuCo–Al₂O₃ were dissolved in 10 mL of water. The obtained solution was then dried overnight at 85 °C to obtain the solid precursors. The solid composite precursors were placed in a semi-closed alumina crucible with a cover and heated to 550 °C at a heating rate of 10 °C min⁻¹ in a muffle furnace, which was maintained for 2 h. After the thermal treatment and natural cooling, the resulting sample was collected for further use. Following this procedure, various OH–CCN/CuCo–Al₂O₃ samples with different dosages of urea in the synthesis procedure were prepared, and the catalyst prepared
using 3.0 g urea exhibited the highest activity (Fig. S1c†); this catalyst was referred to as OH–CCN/CuCo–Al2O3, and it was used for all of the subsequent experiments unless otherwise specified. The pristine g-C3N4, g-C3N4/Al2O3 and g-C3N4/Cu–Al2O3 were prepared using the same procedure without the addition of CuCo–Al2O3 and with the addition of γ-Al2O3 or Cu–Al2O3 instead of CuCo–Al2O3, respectively. As a reference, MCN/CuCo–Al2O3 was prepared using melamine as the precursor. The final load of g-C3N4 on MCN/CuCo–Al2O3 was almost the same as that of OH–CCN/CuCo–Al2O3. The basic information on some of the prepared samples is shown in Table S1.†

2.3. Characterization

Transmission electron microscope (TEM) and scanning electron microscope (SEM) images were obtained using a JEOL-2010 TEM and a SU 8020 FESEM, respectively. The Brunner–Emmet–Teller (BET) specific surface area, pore diameter and pore volume were obtained on a gas sorption analyzer (ASAP 2020 HD88) at the temperature of liquid nitrogen. Powder X-ray diffraction (XRD) patterns were recorded on a Scintag-XDS-2000 diffractometer with Cu Kα radiation (λ = 1.540598 Å) operating at 40 kV and 40 mA. EAXFS spectra were recorded at the beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. Cu foil, Cu2O and CuO were used as references. XPS data were recorded on an AXIS-Ultra instrument using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. FTIR was recorded on a Nicolet 8700 FTIR spectrophotometer (Thermo Fisher Scientific Inc., USA) in the range of 4000–400 cm⁻¹. EPR spectra of the solid samples were obtained using a Bruker model A300-10/12 electron paramagnetic resonance spectrometer. The detailed information of all the characterization studies is shown in the ESI.†

2.4. Procedures, analysis and calculation

15 refractory organic compounds, including bisphenol A (25 mg L⁻¹ and 100 mg L⁻¹), benzene (100 mg L⁻¹), phenol (100 mg L⁻¹), benzoic acid (100 mg L⁻¹), phloroglucinol (100 mg L⁻¹), 2-chlorophenol (50 mg L⁻¹), 4-isopropylphenol (100 mg L⁻¹), ibuprofen (30 mg L⁻¹), phenytoin (30 mg L⁻¹), diphenhydramine (30 mg L⁻¹), 2,4-dichlorophenoxycetic acid (100 mg L⁻¹), methyl orange (50 mg L⁻¹), rhodamine B (50 mg L⁻¹), methylene blue (80 mg L⁻¹) and atrazine (15 mg L⁻¹), were selected to evaluate the activity and properties of the catalyst. The initial concentration of some compounds was lower than 100 mg L⁻¹ due to their low solubility. The optimal dosages of the catalyst powder (0.8 g L⁻¹) and H2O2 (10 mM or 20 mM) were determined according to the best activity for 25 mg L⁻¹ BPA degradation at pH 7 (Fig. S2a and b†) and 100 mg L⁻¹ BPA degradation at pH 5 (Fig. S2c and d†). The optimal dosages were used in all the experiments unless otherwise specified. In a typical experiment, 50 mL of the pollutant aqueous solution (concentration range: 15 mg L⁻¹ to 100 mg L⁻¹) and 0.04 g of the catalyst powder were placed in a beaker. The pH value was adjusted using HCl solution. The suspensions were magnetically stirred for 30 min to establish the adsorption/desorption equilibrium between the pollutant and the catalyst at 35 °C. Then, H2O2 was added to the suspensions under magnetic stirring throughout the experiment. At given time intervals, 3 mL aliquots were collected and filtered through a Millipore filter (pore size 0.45 μm) for analysis. Then, the enzyme catalase was added to destroy the residual H2O2. The pollutants (except methyl orange, rhodamine B and methylene blue) were analyzed using a 1200 series HPLC (Agilent, U.S.A.) equipped with a UV detector and a ZORBAX Eclipse XDB-C18 column (4.6 × 150 mm, 5 μm). The mobile phase consisted of a mixture of methanol/water or a mixture of acetonitrile/water at a flow rate of 1 mL min⁻¹. Methyl orange, rhodamine B and methylene blue solutions were analyzed by recording variations at the wavelength of the maximum absorption using a Hitachi UV-3010 UV-visible spectrophotometer. The H2O2 concentration was determined using a DPD method, as previously reported in the literature. The total carbon (TC) and inorganic carbon (IC) were determined with a Shimadzu TOC-VCPH analyzer using high-temperature combustion. The total organic carbon (TOC) was calculated by TC minus IC automatically. The leaching of metallic ions was measured by ICP-OES on an OPTIMA 2000 (Perkin Elmer, U.S.A.). Each experiment was run in triplicate. The reported data are the arithmetic mean of three measured values. All of the information about the detection of 'OH and O2⁻• EPR signals, the measurement of in situ Raman spectra, the quantification of 'OH by the TPA probe method, the measurement and calculation of the turnover frequency (TOF), the calculation of the utilization efficiency of H2O2, and the computational methods of the density functional theory (DFT) is provided in the ESI.†

3. Results and discussion

3.1. Characterization of the catalysts

Fig. S3† shows the TEM and SEM images of the pristine g-C3N4, CuCo–Al2O3 and OH–CCN/CuCo–Al2O3. These images revealed that the pristine g-C3N4 possessed a wrinkled and fluffy microstructure stacked by nanosheets. CuCo–Al2O3 possessed a porous structure and pure surface. OH–CCN/CuCo–Al2O3 exhibited a fluffy surface and a porous structure surrounded by nanosheets, indicating that g-C3N4 was attached and dispersed on the surface of OH–CCN/CuCo–Al2O3. Fig. 1 shows the powder XRD patterns of different samples. In all the samples, the alumina substrate exhibited a typical γ-Al2O3 form. After doping with Cu and Co, no diffusion peaks corresponding to Cu or Co were observed for CuCo–Al2O3, which indicates that the copper/cobalt oxide crystals were not formed or the formation of small metal or metal oxide NPs (<4 nm) possessed a good dispersion. After g-C3N4 growth on the surface of γ-Al2O3 and CuCo–Al2O3 using urea as the precursor, two peaks appeared at 13.1° and 27.4°, which are assigned to the characteristic (100) and (002) planes of graphitic carbon nitride, respectively.24 Similarly, the same diffraction patterns of g-C3N4 were also observed on MCN/CuCo–Al2O3 from the melamine precursor. However, the supported g-C3N4 from different precursors showed distinctly different XPS spectra. In the XPS spectra of pristine g-C3N4, two C 1s peaks were observed at 284.8 eV and
288.1 eV (Fig. 2a), corresponding to the sp² C–C bonds and the sp²-hybridized C (N–C=N) in the aromatic skeleton rings of g-C₃N₄.¹⁴ The N 1s XPS could be fitted into three peaks at 398.6, 399.7 and 401.1 eV (Fig. 2b), corresponding to the N bonded to the carbon atoms (C–N) of triazine rings, the tertiary N in the form of N–(C)₃ and amino functional groups (C–N–H), respectively.²⁵ For MCN/CuCo–Al₂O₃, the C 1s (Fig. 2c) and N 1s (Fig. 2d) XPS spectra were almost the same as the spectra of the pristine g-C₃N₄ except that C=N (286.5 eV) was present, which indicates the presence of a typical carbon nitride structure. In contrast, for OH–CCN/CuCo–Al₂O₃, the peak intensity corresponding to C–C at 284.8 eV increased markedly (Fig. 2e), while the intensities for N–C=N (288.0 eV) and C=N–C (398.7 eV) significantly decreased (Fig. 2f). In addition, the atomic ratio of C to N of g-C₃N₄ on the surface of OH–CCN/CuCo–Al₂O₃ (0.79) and MCN/CuCo–Al₂O₃ (0.76). These results indicated that excess C atoms were incorporated into the tri-s-triazine of g-C₃N₄ in OH–CCN/CuCo–Al₂O₃, and they partially occupied and replaced the N atom, resulting in an increase of C–C and a decrease of N–C=N and C=N–C. In addition, a new peak at 286.1 eV for the C 1s spectra emerged in OH–CCN/CuCo–Al₂O₃ (Fig. 2e), which is ascribed to the C atoms of the aromatic ring bonded to the
hydroxyl groups (C–O–H/C–O-metal), while it did not appear in the pristine g-C3N4, g-C3N4/Al2O3 (Fig. S4†) and MCN/CuCo–Al2O3. The results indicated that the formation of C–O– is related to the urea precursor and the surface metal species (Cu, Co or Al), which is confirmed by the FTIR spectra of both the urea and melamine precursors on CuCo–Al2O3.

As shown in Fig. 3a, the peaks at 1686 cm−1 and 1627 cm−1 are assigned to the C=O stretching vibration and N–H bending vibration of urea, respectively. After urea was adsorbed on the surface of γ-Al2O3, the C=O peak shifted to 1670 cm−1, which indicated the reaction between C=O and Al. On the other hand, on CuCo–Al2O3, the C=O peak shifted to 1666 cm−1, which resulted from the complexation between C=O and Cu due to the larger stability constants of the Cu coordination than those of Al and Co. However, there was no significant shift for the N–H peak on the urea-adsorbed CuCo–Al2O3. The results indicated that the surface Cu of CuCo–Al2O3 was complexed with the oxygen atom and not the N atom of the urea precursor. In contrast, the characteristic peaks of melamine on the surface of CuCo–Al2O3 were completely consistent with the spectra of pure melamine (Fig. 3b), indicating that the metal species of CuCo–Al2O3 were not chelated with the melamine precursor. Therefore, upon further polymerization reaction, the C–O–Cu linker will be formed on OH–CCN/CuCo–Al2O3, but it would not be produced on MCN/CuCo–Al2O3. As expected, a new peak located at 1155 cm−1 was observed in OH–CCN/CuCo–Al2O3 (Fig. 3c), which was assigned to the C=O asymmetric stretching of hydroxyl groups connecting the aromatic ring, and the intensity of this peak increased with increasing g-C3N4 amounts (Fig. S5†), which confirmed the substitution of hydroxyl groups in the aromatic ring during the growth of g-C3N4 on the surface of CuCo–Al2O3 with urea as the precursor. In addition, the spectra of γ-Al2O3 displayed two absorption bands at 3439 cm−1 and 1639 cm−1 [Fig. 3c], which are ascribed to the stretching vibrations of OH [r(OH)] and the bending vibration of H–O–H [δ(HOH)] in the water molecules adsorbed on the surface of γ-Al2O3. In CuCo–Al2O3, the ρ(OH) shifted to a higher wavenumber (3455 cm−1), indicating the coordination of the adsorbed H2O with the Cu and Co species. This band shifted to 3450 cm−1 on OH–CCN/CuCo–Al2O3 and progressively shifted to lower wavenumbers with an increase in the loaded amount of g-C3N4 using urea as the precursor (Fig. S5†), which indicates that the coordination with the molecular H2O decreased. However, the ρ(OH) of MCN/CuCo–Al2O3 showed an extremely slight shift compared with that of CuCo–Al2O3 (Fig. 3d).

According to previous reports, the results confirmed that the surface Cu was complexed by σ bonding to the oxygen atom of the hydroxyl group connected with the C of the aromatic ring in g-C3N4 prepared using urea, which resulted in the formation of the C–O–Cu cross-linker from the combination of OH–CCN and CuCo–Al2O3. This is relatively different from that reported in several studies that the formation of metal–N is more likely in coordination compounds, which depends on the interaction of CuCo–Al2O3 with the precursor.

3.2. Extended X-ray absorption fine structure analysis of the catalysts

Fig. 4a shows the magnitude of the Fourier-transformed EXAFS signals at the Cu K-edge of the samples. Both the Cu–O shell at ~1.5 Å (no phase correction) and the other cation shells with a bond distance of 2.0–3.0 Å were observed for all of the
samples. OH–CCN/CuCo–Al2O3 was clearly different from Cu–Al2O3 and CuCo–Al2O3 in the second shells, which indicates that the loading of g-C3N4 on the surface would change the local environment of Cu. However, the Co K-edge EXAFS oscillations of OH–CCN/CuCo–Al2O3 almost completely coincided with those of CuCo–Al2O3 (Fig. 4b), which confirms that the surface Co was not complexed with g-C3N4 due to the higher complexation constant of Cu with –OH than that of Co. The results of the Cu K-edge EXAFS curve fitting (Fig. 4c and S6†) are shown in Table 1. The bond distances and coordination numbers of the Cu–Cu and Cu–O shells in Cu–Al2O3, CuCo–Al2O3 and OH–CCN/CuCo–Al2O3 are inconsistent with those in Cu foil, Cu2O and CuO, which indicates that the detected copper species were not in the form of Cu, Cu2O or CuO. The emergence of the Cu–O–Co bond. The CuCo bond. In addition, for OH–CCN/CuCo–Al2O3, the Cu–C shell with a bond distance of 2.58 Å and a coordination number of 0.8 emerged with the growth of g-

3.3. Formation of an electron-rich area around Cu

The EPR technique was used to obtain the electronic structural information of different samples in Fig. 5a. γ-Al2O3, g-C3N4, g–C3N4/Al2O3 and Co–Al2O3 did not display significant EPR signals. Cu–Al2O3, CuCo–Al2O3 and OH–CCN/CuCo–Al2O3 exhibit clear EPR signals with hyperfine coupling, which demonstrates the Cu(II) characteristic with I (nuclear spin) = 3/2 at room temperature. The g and A parameters of the spectrum are shown in Table S2.† For all the samples, the trend of $g_{||} > g_{\perp} > 2.0023(g_0)$ it was determined that the unpaired electron was localized in the $d^{2}_{x^2-y^2}$ orbital of Cu(II). The g-tensors and the signal shape clearly correspond to the six-coordinated Cu(II) with an octahedral geometry. Upon the introduction of Co, the $g_{\perp}$ value decreased from 2.1333 to 2.1163 (closer to $g_0$), and the EPR intensity increased significantly for CuCo–Al2O3. The lattice doping of Cu and Co would result in a heterogeneous electron cloud distribution of the lattice oxygen atom of γ-Al2O3 to form an electron-rich Cu center due to the higher electronegativity of Cu than those of Co and Al. Subsequently, as g–C3N4 was introduced on the surface of CuCo–Al2O3 with urea as the precursor, the $g_{\perp}$ value further decreased to 2.0995 for OH–CCN/CuCo–Al2O3 and decreased continuously as g–C3N4 increased on the surface of CuCo–Al2O3. Moreover, the EPR signal intensity of OH–CCN/CuCo–Al2O3 increased further compared with that of CuCo–Al2O3. The intensity of the EPR signal often indicates the amount of Cu(II) and the density of single electrons around the Cu sites. However, the atomic ratios of Cu(II) to Cu(0) in CuCo–Al2O3 (Fig. 5b) and OH–CCN/CuCo–Al2O3 (Fig. 5c) were 1.14 : 1 and 1.25 : 1, respectively, which suggests that the proportion of Cu(II) did not increase but reduced slightly after the loading of g–C3N4 on the surface of CuCo–Al2O3 with urea as the precursor. This result revealed that the enhancement of the EPR signal intensity is attributed to the increase of the electron density around Cu, which contributed to the Cu(II)–π interactions of the Cu–O–Cu bond on OH–CCN/CuCo–Al2O3.

3.4. DFT calculations of the electron density

To further demonstrate the role of the Cu–O–C bond in the increased electron density around Cu on OH–CCN/CuCo–Al2O3, the electron densities around C and N in the heterocycles of carbon-doped g–C3N4, O and Cu in the C–O–Cu linkers were investigated using DFT calculations based on similar parameters obtained from EXAFS. Fig. 6a shows an optimized geometry structure model of the carbon-doped g–C3N4 grown on the surface of CuCo–Al2O3. The dangling bonds of the O atoms connected to Cu in γ-Al2O3 were terminated with H atoms to obtain a neutral cluster. Due to the size and edge effects, the properties estimated with the finite-size model may vary to an extent from those in the real
system. However, it is expected that the results obtained with the current model would be qualitatively reliable in predicting the local chemical properties. The valence-electron density was analyzed using the Multiwfn package (Fig. 6b–d). The representative planes, including Cu–O1–C1 (doped C atom), O1–C1–C2 (local C atom) and O1–C1–N1, were investigated. Fig. 6b shows the two-dimensional valence-electron density color-filled maps of the carbon-doped g-C3N4 grown on the surface of the Cu-doped g-Al2O3 in the Cu–O1–C1 plane. The largest electron distribution area appeared around the Cu site, and its maximum valence-electron density was as high as 14.19 e\(^{-}/C0\)3 compared with the O atom (O1) in the Cu–O–C linker and the doped C atom (C1) in the heterocycles of the carbon-doped g-C3N4. In the O1–C1–C2 (Fig. 6c) and O1–C1–N1 planes (Fig. 6d), the electron distribution area and maximum valence-electron density (\(\Delta E_{0}^{d}\)) of O in the Cu–O–C linker were much greater than those of the doped C atom (C1), local C atom (C2) and N atom (N1) of the carbon-doped g-C3N4, which was due to the larger electronegativity of O than those of C and N. The DFT calculations exhibited the same results as the EPR determination for OH–CCN/CuCo–Al2O3, which confirms the formation of an electron-rich area around Cu.

### 3.5. Electron transfer mechanism in OH–CCN/CuCo–Al2O3 suspensions

BMPO-trapped EPR signals were detected in different air-saturated methanol/aqueous dispersions of the corresponding samples without adding H2O2. As shown in Fig. 7a, no signals were generated in g-Al2O3, g-C3N4, g-C3N4/Al2O3 and Co–Al2O3 methanol dispersions and the blank experiment. However, six characteristic peaks of BMPO–O2\(^{–}\) were observed in the methanol dispersions of Cu–Al2O3, CuCo–Al2O3 and OH–CCN/CuCo–Al2O3, and their intensities increased according to the same order as the solid EPR signal intensities, which

### Table 1 Curve fitting results of Cu K-edge EXAFS for various samples

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<td>CuCo–Al2O3</td>
<td>Cu–O</td>
<td>1.95</td>
<td>2.2</td>
<td>0.0035</td>
<td>−0.7</td>
<td>0.0094</td>
</tr>
<tr>
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<td>OH–CCN/CuCo–Al2O3</td>
<td>Cu–O</td>
<td>2.87</td>
<td>1.8</td>
<td>0.0035</td>
<td>−0.7</td>
<td>0.0094</td>
</tr>
</tbody>
</table>

* Bond distance.  
* Coordination number.  
* Debye–Waller factor.  
* Inner potential correction.  
* Residual factor.
reveals that the Cu center of OH–CCN/CuCo–Al2O3 possessed the most single electrons that reduced O2 to O2•⁻. The solid EPR signals (Fig. 7b) of the used Cu–Al2O3 and CuCo–Al2O3 decreased, while that of the used OH–CCN/CuCo–Al2O3 did not change, which indicates the transfer cycle of the electrons around the Cu center of OH–CCN/CuCo–Al2O3 and that no cycle occurred on Cu–Al2O3 and CuCo–Al2O3. Four characteristic peaks of BMPO–OH were observed in the OH–CCN/CuCo–Al2O3 aqueous suspension (Fig. 7c), but no such signals appeared in other sample suspensions. These phenomena suggested that the Cu center of OH–CCN/CuCo–Al2O3 donated electrons to O2 and simultaneously accepted electrons from H2O to produce ‘OH, forming an electron transfer cycle, which was predominantly contributed to the orbital interactions involving electron transfer of π → Cu (σ donation) and Cu → π* (π back-donation). The valence and conduction bands of g-C3N4 were mainly derived from the N 2p orbitals and the C 2p orbitals, respectively. As the N 2p orbitals were more positive than the energy level of OH−/C0 or H2O, the holes of the N 2p orbitals could react with water to produce ‘OH radicals. The results confirmed that on OH–CCN/CuCo–Al2O3, the donation of the unpaired electrons around the Cu center induced the formation of holes in the N 2p orbitals of OH–CCN, which trapped an electron from H2O, thereby maintaining the electron density around Cu.

In the presence of H2O2 (Fig. 8a and b), the ‘OH radicals were mainly generated, while the generation of O2•⁻ radicals was extremely small in the OH–CCN/CuCo–Al2O3 aqueous suspension under neutral conditions. The opposite phenomena occurred in the Co–Al2O3, Cu–Al2O3 and CuCo–Al2O3 dispersions with H2O2. These results indicated that H2O2 was predominantly reduced to ‘OH by the unpaired electrons around the Cu centers of OH–CCN/CuCo–Al2O3, while the decomposition of H2O2 followed the classic Fenton reaction mechanism that H2O2 was not only reduced to ‘OH, but also oxidized to large amounts of O2•⁻ in the Co–Al2O3, Cu–Al2O3 and CuCo–Al2O3 aqueous suspensions.

The interaction processes of different samples with H2O2 were observed by in situ Raman spectra. No significant peak appeared in the suspension of γ-Al2O3 with/without H2O2 (Fig. S7†), whereas, in the suspensions of Co–Al2O3 (Fig. 9a), Cu–Al2O3 (Fig. 9b) and CuCo–Al2O3 (Fig. 9c), a band appeared at 881–887 cm⁻¹, which was assigned to the O–O stretching for peroxo complexes of H2O2 with metal ions with the addition of H2O2, and the band gradually disappeared as the reaction time increased. These results verified that H2O2 directly reacted with the lattice Cu and Co and decomposed in these catalyst suspensions. In contrast, the characteristic peak did not appear in the OH–CCN/CuCo–Al2O3 suspension (Fig. 9d), confirming that H2O2 did not interact directly with
the lattice Cu and Co but was reduced by the electrons around the Cu center. All the evidence above confirmed that in the OH–CCN/CuCo–Al₂O₃ aqueous suspension, two electron transfer processes occurred from the electron-rich Cu center to H₂O₂ and from H₂O₂ to the N atom of OH–CCN, which generated approximately twice the amount of 'OH as that of the reacted H₂O₂ in the OH–CCN/CuCo–Al₂O₃ suspension.

3.6. Highly efficient generation of hydroxyl radicals

The generated 'OH was quantitatively measured in the OH–CCN/CuCo–Al₂O₃ aqueous dispersion with H₂O₂ under nearly neutral conditions using the terephthalic acid (TPA) probe method (the detailed information is provided in the ESI†). The concentration of the 'OH produced was approximately twice the amount of H₂O₂ consumption within a reaction time of 180 s, and the 'OH concentration remained higher than the H₂O₂ consumption until 1200 s (Fig. 10a). At the initial reaction stage, the 'OH predominantly reacted with TPA. Therefore, the amount of 'OH was accurately determined, as the tested TPA concentration was much larger than the produced 'OH concentration. As the reaction time increased, the increased amount of 'OH reacted with other substances, such as the intermediates of the reacted TPA, 'OH itself and H₂O₂, leading to the lower measured value. It was verified that the main active sites are the electron-rich Cu centers, and their amount depended on the surface Cu concentration, which was determined by the Langmuir adsorption isotherms of phenol on the surface of CuCo–Al₂O₃ due to the strong complexation of Cu and phenol (Fig. 10b). The equilibrium adsorption amount of phenol is qₑ = 7.14 × 10⁻⁶ mol g⁻¹, which is equal to the surface Cu concentration on OH–CCN/CuCo–Al₂O₃. Therefore, the turnover frequency (TOF) value of OH–CCN/CuCo–Al₂O₃, as defined by the turnover number of H₂O₂ into 'OH per second on the surface Cu center, was calculated to be 1.30 s⁻¹ under neutral conditions (a detailed calculation is provided in the ESI†). In particular, the obtained TOF value was lower than the actual value due to the reaction involving free radical chain reactions in solution. Nonetheless, this value was still 85 times higher than that (1.53 × 10⁻² s⁻¹) of the classic homogeneous Fenton reaction even under strongly acidic conditions. 32

3.7. Catalytic performance for refractory pollutant degradation

Pesticides, pharmaceuticals and dyes, which are highly toxic and difficult to degrade biologically, were selected to evaluate the activity and properties of the catalysts. For the degradation
of the endocrine-disrupting chemical bisphenol A (BPA), the tested samples exhibited different activities with H2O2 at the initial pH 7 (Fig. 11a). No significant BPA degradation was observed in the g-C3N4, g-Al2O3 and g-C3N4/Al2O3 suspensions. Approximately 19.5%, 57.0% and 78.0% of BPA was degraded within 30 min in Co–Al2O3, Cu–Al2O3 and CuCo–Al2O3 suspensions accompanied by 3.4%, 49.8% and 55.7% of TOC removal (Fig. 11b), respectively. Moreover, only 27.9% of BPA was degraded in the MCN/CuCo–Al2O3 suspension at the same time. Remarkably, 96.3% of BPA and 67.1% of TOC were simultaneously degraded in the OH–CCN/CuCo–Al2O3 suspension (prior to the addition of H2O2, about 4.8% of BPA and 3.4% of TOC were adsorbed on the surface of OH–CCN/CuCo–Al2O3). The rate of BPA degradation in the OH–CCN/CuCo–Al2O3 suspension was approximately 11, 5 and 2.2 times faster than those in the MCN/CuCo–Al2O3, Cu–Al2O3 and CuCo–Al2O3 suspensions, respectively (Fig. S8†). This result verified that BPA degradation was significantly enhanced by the formation of the electron-rich Cu center in OH–CCN/CuCo–Al2O3.

Compared with before the reaction, upon the introduction of H2O2, a significant amount of Co ions was released in the Co–Al2O3 (0.49 mg L−1) and CuCo–Al2O3 (0.46 mg L−1) suspensions (Fig. S9a†). The Cu2+ ions were 0.03 mg L−1 and 0.09 mg L−1 in the Cu–Al2O3 and CuCo–Al2O3 suspensions, respectively (Fig. S9b†). However, relatively small amounts of Cu (0.02 mg L−1) and Co (0.09 mg L−1) were released in the OH–CCN/CuCo–Al2O3 suspension. This result indicated that the abundant unpaired electrons around Cu reacted with H2O2 and not the lattice Cu and Co during BPA degradation, which was consistent with the characterization results given above. In contrast, the higher amount of Cu or Co release in the other suspensions upon the addition of H2O2 demonstrated that the lattice Cu and Co directly reacted with H2O2 following the classical Fenton reaction. In the OH–CCN/CuCo–Al2O3 suspensions, the
contribution of homogeneous Cu and Co ions was negligible (Fig. S10f). However, 10.3% and 24.0% of BPA degraded within 30 min of the homogeneous Fenton reaction for the highest concentration of released ions in the Co–Al₂O₃ and CuCo–Al₂O₃ suspensions, respectively. These results indicated that BPA degradation mainly resulted from the homogeneous Fenton reaction of the Co ion in the Co–Al₂O₃ suspension; about a third of the BPA degradation was attributed to the homogeneous Fenton reaction of Cu and Co ions in the CuCo–Al₂O₃ suspension, and almost all of BPA degradation was attributed to the solid catalyst in the OH–CCN/CuCo–Al₂O₃ suspension. The recyclability of OH–CCN/CuCo–Al₂O₃ was tested after being filtered, washed and dried. The activity of OH–CCN/CuCo–Al₂O₃ did not markedly decrease after 9 successive cycles of degradation testing (Fig. S11f) and remained at approximately 86% within 30 min in the continuous cycles, which suggested that OH–CCN/CuCo–Al₂O₃ was an effective and stable catalyst.

The utilization efficiency of H₂O₂ was defined as the ratio of the stoichiometric H₂O₂ consumption ([ΔH₂O₂]ₙ) for the mineralization of pollutants to the actual H₂O₂ consumption ([ΔH₂O₂]₁ₘ) in the reaction.⁴⁴ For the equivalent TOC removal (~70%), OH–CCN/CuCo–Al₂O₃ exhibited the highest utilization efficiency of H₂O₂ (90.1%) within the shortest reaction time (a detailed calculation is provided in the ESI and Table S3f), which was much higher than those in the CuCo–Al₂O₃ (78.8%) and Cu–Al₂O₃ (81.5%) suspensions. Furthermore, OH–CCN/CuCo–Al₂O₃ exhibited a higher advantage than many reported Fenton catalysts, such as Fe₃O₄ NPs, Cu₂O MPs, CuFeO₂ MPs, BiFeO₃, Au/Fe₂O₃ and Au–FeO₂/Al₂O₃, in the elimination of BPA with respect to the activity, reaction conditions and H₂O₂ efficiency (Table S4f). For example, the activity of OH–CCN/CuCo–Al₂O₃ is ~20 times greater than that of Fe₃O₄ NPs even at a reaction pH = 5.⁵ In addition, all the refractory compounds (initially 30, 50 or 100 mg L⁻¹) were substantially degraded along with an ~90% high utilization efficiency of H₂O₂ (Tables 2 and S3b); in particular, benzene, phenol, benzoic acid, phloroglucinol, 2-chlorophenol, ibuprofen and phenytoin could be completely degraded after a short time. For the extremely refractory atrazine (15 mg L⁻¹), the conversion could reach 73.6%. The degradation of maleic blue (MB) is regarded as a very difficult process using the classic Fenton method, and it could only be degraded by 21.1%.⁶ Here, however, the degradation of MB reached 60.7% with a high utilization efficiency of H₂O₂ (86.6%).

### 4. Conclusions

The OH–CCN/CuCo–Al₂O₃ composite was achieved by the Cu-O-C bond linking the hydroxylated carbon-doped g-C₃N₄ with Cu and Co co-substituted γ-Al₂O₃. A sufficient amount of unpaired electrons was produced around the Cu center by the incorporation of Co into Cu-Al₂O₃, and the subsequent formation of a surface complex of Cu with OH–CCN by the C–O–Cu linker. In the presence of H₂O₂, electron transfer processes were determined from the electron-rich Cu centers to H₂O₂ to form ‘OH, and from H₂O to the N atom of OH–CCN to produce ‘OH. Thus, twice the amount of ‘OH as that of the reacted H₂O₂ was generated in the OH–CCN/CuCo–Al₂O₃ suspension, which resulted in a high utilization efficiency of H₂O₂ (~90%) for the
rapid degradation and mineralization of refractory organic pollutants in water under mild conditions. The construction of an electron-rich area played an important role in the selective conversion of H₂O₂ to ·OH, and it exhibits remarkable potential in applications for environmental remediation, the chemical industry, medicine and polishing.

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Notes and references