Cite this: *J. Mater. Chem. A*, 2017, 5, 7153

Selective H_2O_2 conversion to hydroxyl radicals in the electron-rich area of hydroxylated C-g- C_3N_4 /CuCo- Al_2O_3 [†]

Lai Lyu,^{ab} Lili Zhang,^a Guangzhi He,^{©c} Hong He^{bc} and Chun Hu^{©d}*^{ab}

The Fenton reaction has been explored extensively in different fields due to the generation of hydroxyl radicals ($\cdot\text{OH}$). However, the reaction requires strongly acidic conditions and excessive consumption of H_2O_2 , which impede its widespread application. Here, we report that twice the amount of $\cdot\text{OH}$ radicals as that of the reacted H_2O_2 was formed by the reaction of H_2O_2 with a type of nano-composite OH-CCN/CuCo- Al_2O_3 under nearly neutral conditions. The nano-composite was achieved by the co-incorporation of Cu and Co into $\gamma\text{-Al}_2\text{O}_3$, and the sequential complex formation of the σ -type Cu-O-C linker between the surface Cu and the hydroxyl group of the tri-s-triazine ring in C-g- C_3N_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_2O_3 , which reacted with H_2O_2 , resulting in two electron transfer processes. One process is from the electron-rich Cu center to H_2O_2 to form $\cdot\text{OH}$, and the other is from H_2O to the N atom of OH-CCN to produce $\cdot\text{OH}$. 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_2O_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.

Received 21st February 2017
Accepted 10th March 2017

DOI: 10.1039/c7ta01583f

rsc.li/materials-a

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 ($\cdot\text{OH}$) from the reaction of hydrogen peroxide (H_2O_2).^{3,10} 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.^{8,9} The Fenton process consists of the reaction of H_2O_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 $\cdot\text{OH}$,^{3,11} the resulting metal sludge and strongly acidic conditions ($\text{pH} = 2\text{--}3.5$) 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 ($\text{M}^{(n+m)+}$) of the metal for $\cdot\text{OH}$ formation. In the reaction, the reduction of $\text{M}^{(n+m)+}$ to M^{n+} by the oxidizing H_2O_2 is the rate-limiting step,¹⁴ and it results in the conversion of excess H_2O_2 to O_2 . Light, electricity, ultrasound and chelating agents have been widely used to improve the step reaction,^{15,16} 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,¹⁷ in which galvanic-like cells were formed by the negative charge nonuniformity of lattice oxygen due to different electronegativities of doped metals. Our findings

^aKey Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: huchun@rcees.ac.cn; Fax: +86-10-62923541; Tel: +86-10-62849628

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

^cState Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ta01583f

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 O_2 can trap the excess electrons on the surface of a fully oxidized metal oxide, producing superoxo (O_2^-), peroxo (O_2^{2-}) or dissociated ($2 \times O^{2-}$) forms.¹⁸ The redox potential (1.229 V vs. SHE) of O_2/H_2O is smaller than that of H_2O_2/H_2O (1.763 V), and thus, molecular H_2O_2 can also trap the excess electrons on metal oxides when H_2O_2 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.¹⁹ 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 $\pi \rightarrow$ cation (σ donation) and cation $\rightarrow \pi^*$ (π back-donation). Graphitic carbon nitrides ($g-C_3N_4$) consist of 2D sheets of tri-*s*-triazine connected *via* tertiary amines, and they belong to the typical π -conjugated graphitic planes formed *via* sp^2 hybridization of carbon (C) and nitrogen (N) atoms and have become increasingly important in photocatalysis, heterogeneous catalysis and fuel cells.²⁰

In this study, a high electron density around Cu was achieved by doping both Co and Cu in the lattice of $\gamma-Al_2O_3$, and the sequential surface complex of Cu with hydroxyl on the aromatic ring of the carbon-doped $g-C_3N_4$, denoted as (OH-CCN/CuCo- Al_2O_3), was formed. The formation of the key σ -type bridge C-O-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.¹⁴ Some prominent examples are phenols (such as phenol, phloroglucinol and 4-isopropylphenol), pharmaceuticals (such as ibuprofen, phenytoin and diphenhydramine), pesticides (such as 2-chlorophenol, 2,4-dichlorophenoxyacetic acid and atrazine), and dyes (methyl orange, rhodamine B and methylene blue) as well as endocrine disrupting chemicals (such as bisphenol A).¹⁷ Thus, these refractory organic pollutants were selected to evaluate the activity and properties of the catalyst with H_2O_2 in aqueous solution. It was found that twice as much $\cdot OH$ as the reacted H_2O_2 was generated in the OH-CCN/CuCo- Al_2O_3 suspension, resulting in an extremely high utilization efficiency of H_2O_2 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- Al_2O_3 . Our findings suggest that constructing an electron-rich area is crucial for developing heterogeneous Fenton-like catalysts.

2. Experimental section

2.1. Chemicals and reagents

Horseradish peroxidase (POD, 99%), *N,N*-diethyl-*p*-phenylenediamine sulfate (DPD, 98%), 5-*tert*-butoxycarbonyl-5-methyl-1-pyrroline-*N*-oxide (BMPO, 99%), 2-chlorophenol ($\geq 99\%$), atrazine ($\geq 99\%$) and ibuprofen ($\geq 98\%$) were obtained from Sigma-Aldrich (St. Louis, USA). Bisphenol A ($\geq 99\%$), diphenhydramine ($\geq 99\%$), 2,4-dichlorophenoxyacetic acid ($\geq 99\%$) and phenytoin (99%) were purchased from Acros (Geel, Belgium). Urea (USP grade) was obtained from Amresco (USA). Hydrogen peroxide (H_2O_2 , 30%, w/w), aluminum isopropoxide ($Al(O^iPr)_3$, 98%), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, $\geq 99\%$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, $\geq 99\%$), glucose 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- Al_2O_3 was synthesized through a two-step method. First, CuCo- Al_2O_3 was prepared using a modified evaporation-induced self-assembly process, according to a previously reported method.²¹ In a typical procedure, 4.2 g $Al(O^iPr)_3$, 0.28 g $CuCl_2 \cdot 2H_2O$, 0.2 g $CoCl_2 \cdot 6H_2O$ and 3.6 g glucose were dissolved in 60 mL of deionized water. The mixed 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 value to 5. The obtained solution was continuously stirred for 5 h. 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- Al_2O_3 . 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- Al_2O_3 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 b†). Therefore, this sample was selected as the solid precursor of OH-CCN/CuCo- Al_2O_3 . As references, $\gamma-Al_2O_3$, Cu- Al_2O_3 and Co- Al_2O_3 were prepared using the same procedure. Second, OH-CCN/CuCo- Al_2O_3 was prepared through the *in situ* growth of $g-C_3N_4$ on the surface of CuCo- Al_2O_3 using urea as the precursor. Typically, 3.0 g urea and 1.0 g CuCo- Al_2O_3 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- Al_2O_3 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 K α radiation ($\lambda = 1.540598$ Å) operating at 40 kV and 40 mA. EXAFS 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 K α 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-dichlorophenoxyacetic 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 μ m) 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 $\times$ 150 mm, 5 μ m). 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.²² The total carbon (TC) and inorganic carbon (IC) were determined with a Shimadzu TOC-V_{CPH} 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 $\cdot$ OH and O₂^{•−} EPR signals, the measurement of *in situ* Raman spectra, the quantification of $\cdot$ 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 diffraction 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.²³ 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

Fig. 1 XRD patterns of various samples.

288.1 eV (Fig. 2a), corresponding to the sp^2 C-C bonds and the sp^2 -hybridized C (N-C=N) in the aromatic skeleton rings of $g-C_3N_4$.²⁴ 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-C) 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- Al_2O_3 , the C 1s (Fig. 2c) and N 1s (Fig. 2d) XPS spectra were almost the same as the spectra of the pristine $g-C_3N_4$ 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- Al_2O_3 , 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 $g-C_3N_4$ on the surface of OH-CCN/CuCo- Al_2O_3 (1.21) is much higher than those of the pristine $g-C_3N_4$ (0.79) and MCN/CuCo- Al_2O_3 (0.76). These results indicated that excess C atoms were incorporated into the tri-s-triazine of $g-C_3N_4$ in OH-CCN/CuCo- Al_2O_3 , 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- Al_2O_3 (Fig. 2e), which is ascribed to the C atoms of the aromatic ring bonded to the

Fig. 2 XPS spectra in (a) C 1s and (b) N 1s for $g-C_3N_4$; in (c) C 1s and (d) N 1s for MCN/CuCo- Al_2O_3 ; and in (e) C 1s and (f) N 1s for OH-CCN/CuCo- Al_2O_3 .

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 [ν (OH)] and the bending vibration of H-O-H [δ (HOH)] in the water molecules adsorbed on the surface of γ -Al₂O₃.²⁶ In CuCo-Al₂O₃, the ν (OH) shifted to a higher wave-number (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 ν (OH) of MCN/CuCo-Al₂O₃ showed an extremely slight shift compared with that of CuCo-Al₂O₃ (Fig. 3d). According to previous reports,^{14,19} these 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,^{27,28} 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

Fig. 3 FTIR spectra for the various samples. (a) The FTIR spectra of the urea precursor growing on the substrate materials in the catalyst-prepared phase. (b) The FTIR spectra of the melamine precursor growing on the substrate materials in the catalyst-prepared phase. (c) and (d) The FTIR spectra of the prepared samples.

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-Al shell in these samples indicated that the copper species were incorporated into the alumina lattice, forming the Cu-O-Al bond. The Cu-Co shells (belonging to the second shells) were observed in CuCo-Al₂O₃ and OH-CCN/CuCo-Al₂O₃, and their presence suggests the backscattering from Co to Cu and the generation of the Cu-O-Co 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-

C₃N₄ on the surface of CuCo-Al₂O₃, thereby confirming the formation of the Cu-O-C bond on the surface of OH-CCN/CuCo-Al₂O₃. No Cu-N shell was observed in OH-CCN/CuCo-Al₂O₃.

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 $g_{\parallel} > g_{\perp} > 2.0023(g_e)$ indicated that the unpaired electron was localized in the d_{x²-y²} orbital of Cu(II).²⁹ The g-tensors and the signal shape clearly correspond to the six-coordinated Cu(II) with an octahedral geometry.²⁹ Upon the introduction of Co, the $g_{\perp}$ value decreased from 2.1333 to 2.1163 (closer to g_e), 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(I) to Cu(II) 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-C 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 the Cu-doped γ-Al₂O₃ through the connection of C-O-Cu using the B3LYP functional and Gaussian 09 package. 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

Fig. 4 Fourier transforms of k^3 -weighted EXAFS oscillations obtained at the (a) Cu K-edge and (b) Co K-edge of the various samples. (c) The EXAFS curve fitting for the Cu K-edge of OH-CCN/CuCo-Al₂O₃.

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

Entry	Sample	Shell	R^a (Å)	CN ^b	σ^{2c} (Å ²)	ΔE_0^d (eV)	R_f^e
1	Cu	Cu–Cu	2.54	10.9	0.0085	−8.2	0.0090
2	Cu ₂ O	Cu–O	1.84	1.6	0.0034	−3.2	0.0157
		Cu–Cu	2.97	1.2	0.0034	−3.2	
		Cu–O	3.47	5.2	0.0034	−3.2	
3	CuO	Cu–O	1.95	2.2	0.0035	−0.7	0.0094
		Cu–O	2.87	1.8	0.0035	−0.7	
		Cu–Cu	2.94	0.3	0.0035	−0.7	
4	Cu–Al ₂ O ₃	Cu–O	1.94	3.2	0.0070	−4.8	0.0109
		Cu–Cu	3.07	0.5	0.0070	−4.8	
		Cu–Al	3.64	0.4	0.0070	−4.8	
5	CuCo–Al ₂ O ₃	Cu–O	1.94	3.3	0.0075	−5.7	0.0124
		Cu–Cu	2.99	0.5	0.0075	−5.7	
		Cu–Co	3.11	0.6	0.0075	−5.7	
		Cu–Al	3.65	0.3	0.0075	−5.7	
6	OH–CCN/CuCo–Al ₂ O ₃	Cu–O	1.94	3.1	0.0055	−5.9	0.0059
		Cu–C	2.58	0.8	0.0055	−5.9	
		Cu–Cu	2.96	0.4	0.0055	−5.9	
		Cu–Al	3.43	0.5	0.0055	−5.9	
		Cu–Co	3.44	0.7	0.0055	−5.9	

^a Bond distance. ^b Coordination number. ^c Debye–Waller factor. ^d Inner potential correction. ^e Residual factor.

Fig. 5 (a) EPR spectra of all of the fresh solid samples. XPS spectra in Cu 2p_{3/2} for (b) CuCo–Al₂O₃ and (c) OH–CCN/CuCo–Al₂O₃.

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 γ -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 Å^{−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 (~ 3.95 e Å^{−3}) 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 γ -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

Fig. 6 The structure (a) and two-dimensional valence-electron density color-filled maps of carbon-doped $g\text{-C}_3\text{N}_4$ growing on the surface of Cu-doped $\gamma\text{-Al}_2\text{O}_3$ through the connection of C–O–Cu: (b) the valence-electron density map in the Cu–O1–C1 plane; (c) the valence-electron density map in the O1–C1–C2 plane; (d) the valence-electron density map in the O1–C1–N1 plane. Cyan, violet, red, orange, and white circles denote C, N, O, Cu, and H atoms, respectively. The valence-electron density is given in $\text{e } \text{\AA}^{-3}$.

reveals that the Cu center of OH–CCN/CuCo– Al_2O_3 possessed the most single electrons that reduced O_2 to $\text{O}_2^{\cdot-}$. The solid EPR signals (Fig. 7b) of the used Cu– Al_2O_3 and CuCo– Al_2O_3 decreased, while that of the used OH–CCN/CuCo– Al_2O_3 did not change, which indicates the transfer cycle of the electrons around the Cu center of OH–CCN/CuCo– Al_2O_3 and that no cycle occurred on Cu– Al_2O_3 and CuCo– Al_2O_3 . Four characteristic peaks of BMPO– $\cdot\text{OH}$ were observed in the OH–CCN/CuCo– Al_2O_3 aqueous suspension (Fig. 7c), but no such signals appeared in other sample suspensions. These phenomena suggested that the Cu center of OH–CCN/CuCo– Al_2O_3 donated electrons to O_2 and simultaneously accepted electrons from H_2O to produce $\cdot\text{OH}$, forming an electron transfer cycle, which was predominantly contributed to the orbital interactions involving electron transfer of $\pi \rightarrow \text{Cu}$ (σ donation) and $\text{Cu} \rightarrow \pi^*$ (π back-donation).¹⁹ The valence and conduction bands of $g\text{-C}_3\text{N}_4$ were mainly derived from the N 2p orbitals and the C 2p orbitals, respectively.³⁰ As the N 2p orbitals were more positive than the energy level of OH^- or H_2O , the holes of the N 2p orbitals could react with water to produce $\cdot\text{OH}$ radicals. The results confirmed that on OH–CCN/CuCo– Al_2O_3 , 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 H_2O , thereby maintaining the electron density around Cu.

In the presence of H_2O_2 (Fig. 8a and b), the $\cdot\text{OH}$ radicals were mainly generated, while the generation of $\text{O}_2^{\cdot-}$ radicals was extremely small in the OH–CCN/CuCo– Al_2O_3 aqueous dispersion under neutral conditions. The opposite phenomena occurred in the Co– Al_2O_3 , Cu– Al_2O_3 and CuCo– Al_2O_3 dispersions with H_2O_2 . These results indicated that H_2O_2 was predominantly reduced to $\cdot\text{OH}$ by the unpaired electrons around the Cu centers of OH–CCN/CuCo– Al_2O_3 , while the decomposition of H_2O_2 followed the classic Fenton reaction mechanism that H_2O_2 was not only reduced to $\cdot\text{OH}$, but also oxidized to large amounts of $\text{O}_2^{\cdot-}$ in the Co– Al_2O_3 , Cu– Al_2O_3 and CuCo– Al_2O_3 aqueous suspensions.

The interaction processes of different samples with H_2O_2 were observed by *in situ* Raman spectra. No significant peak appeared in the suspension of $\gamma\text{-Al}_2\text{O}_3$ with/without H_2O_2 (Fig. S7†), whereas, in the suspensions of Co– Al_2O_3 (Fig. 9a), Cu– Al_2O_3 (Fig. 9b) and CuCo– Al_2O_3 (Fig. 9c), a band appeared at $881\text{--}887\text{ cm}^{-1}$, which was assigned to the O–O stretching for peroxo complexes of H_2O_2 with metal ions^{14,31} with the addition of H_2O_2 , and the band gradually disappeared as the reaction time increased. These results verified that H_2O_2 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– Al_2O_3 suspension (Fig. 9d), confirming that H_2O_2 did not interact directly with

Fig. 7 (a) BMPO spin-trapping EPR spectra for HO₂•/O₂•- in various methanol dispersions without H₂O₂. (b) EPR spectra of the various solid samples before and after the reaction with O₂. (c) BMPO spin-trapping EPR spectra for •OH in various aqueous suspensions without H₂O₂.

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 H₂O 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 $q_e = 7.14 \times 10^{-6} \text{ mol g}^{-1}$, 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 ($1.53 \times 10^{-2} \text{ s}^{-1}$) 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

Fig. 8 BMPO spin-trapping EPR spectra for (a) •OH in various aqueous suspensions and (b) HO₂•/O₂•- in various methanol dispersions in the presence of H₂O₂.

Fig. 9 *In situ* Raman spectra of (a) Co-Al₂O₃, (b) Cu-Al₂O₃, (c) CuCo-Al₂O₃ and (d) OH-CCN/CuCo-Al₂O₃ aqueous dispersions recorded at different times after adding H₂O₂.

Fig. 10 (a) The measurement of the generation of $\cdot\text{OH}$ using the TPA method (initial TPA 665 mg L⁻¹). (b) Adsorption isotherms of phenol on CuCo-Al₂O₃ (initial phenol: 2–150 mg L⁻¹, adsorbent addition: 0.4 g L⁻¹, pH 7).

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, γ -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

Fig. 11 (a) Degradation of BPA in various suspensions with H₂O₂. (b) TOC removal during the degradation of BPA in various suspensions (initial pH 7, initial BPA 0.1 mM, initial H₂O₂ 10 mM, catalyst 0.8 g L⁻¹).

contribution of homogeneous Cu and Co ions was negligible (Fig. S10†). 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. S11†) 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]_s) for the mineralization of pollutants to the actual H₂O₂ consumption ([ΔH₂O₂]_A) in the reaction.¹⁴ 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 S3a†), 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-Fe₂O₃/Al₂O₃, in the elimination of BPA with respect to the activity, reaction conditions and H₂O₂ efficiency (Table S4†). For example, the activity of OH-CCN/CuCo-Al₂O₃ is ~20 times greater than that of Fe₃O₄ NPs even at a reaction pH = 5.³³ 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 methylene blue (MB) is regarded as a very difficult process using the classic Fenton method, and it could only be degraded by 21.1%.¹² Here, however, the

Table 2 Degradation of various refractory organic compounds in the OH-CCN/CuCo-Al₂O₃ suspension^a

Entry	Contaminants	Initial conc. (mg L ⁻¹)	Time (min)	Conv. ^b (%)	η[H ₂ O ₂] ^c (%)
1	Benzene	100	30	100	94.5
2	Phenol	100	30	100	93.0
3	Benzoic acid	100	30	100	92.4
4	Phloroglucinol	100	30	100	92.5
5	Bisphenol A	100	30	93.3	93.4
6	2-Chlorophenol	50	30	100	92.4
7	4-Isopropylphenol	100	30	94.0	92.0
8	Ibuprofen	30	30	100	91.1
9	Phenytoin	30	30	100	91.5
10	Diphenhydramine	30	30	97.7	90.3
11	2,4-Dichlorophenoxyacetic acid	100	30	89	92.3
12	Methyl orange	50	30	98.0	90.3
13	Rhodamine B	50	30	99.9	92.9
14	Methylene blue	80	30	60.7	86.6
15	Atrazine	15	30	73.6	80.3

^a Reaction conditions: initial [H₂O₂] = 0.02 mol L⁻¹, catalyst 0.8 g L⁻¹, initial pH = 5, 308 K. ^b The conv. represented the destruction of each organic compound. ^c η[H₂O₂] represents the utilization efficiency of H₂O₂.

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, two 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 H_2O_2 to $\cdot\text{OH}$, and it exhibits remarkable potential in applications for environmental remediation, the chemical industry, medicine and polishing.

Acknowledgements

This work was supported by the National Key Research and Development Plan (2016YFA0203200) and the National Natural Science Foundation of China (Grant No. 51538013 and 21407165). We thank the BL14W1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF, China) for providing the beamline.

Notes and references

- G. Feng, P. Cheng, W. Yan, M. Boronat, X. Li, J.-H. Su, J. Wang, Y. Li, A. Corma, R. Xu and J. Yu, *Science*, 2016, **351**, 1188–1191.
- G. Z. Chen, *Angew. Chem., Int. Ed.*, 2010, **49**, 5413–5415.
- S. Navalon, R. Martin, M. Alvaro and H. Garcia, *Angew. Chem., Int. Ed.*, 2010, **49**, 8403–8407.
- K. A. Sashkina, V. S. Labko, N. A. Rudina, V. N. Parmon and E. V. Parkhomchuk, *J. Catal.*, 2013, **299**, 44–52.
- X. Zhou, Y. Zhang, C. Wang, X. Wu, Y. Yang, B. Zheng, H. Wu, S. Guo and J. Zhang, *ACS Nano*, 2012, **6**, 6592–6599.
- R. Martín, M. Álvaro, J. R. Herance and H. García, *ACS Nano*, 2010, **4**, 65–74.
- W.-P. Li, C.-H. Su, Y.-C. Chang, Y.-J. Lin and C.-S. Yeh, *ACS Nano*, 2016, **10**, 2017–2027.
- A. M. Nowicka, U. Hasse, M. Hermes and F. Scholz, *Angew. Chem., Int. Ed.*, 2010, **49**, 1061–1063.
- A. M. Nowicka, U. Hasse, G. Sievers, M. Donten, Z. Stojek, S. Fletcher and F. Scholz, *Angew. Chem., Int. Ed.*, 2010, **49**, 3006–3009.
- H. J. H. Fenton, *J. Chem. Soc., Dalton Trans.*, 1894, **65**, 899–910.
- S. Navalon, M. de Miguel, R. Martin, M. Alvaro and H. Garcia, *J. Am. Chem. Soc.*, 2011, **133**, 2218–2226.
- X. Yang, X. Xu, J. Xu and Y. Han, *J. Am. Chem. Soc.*, 2013, **135**, 16058–16061.
- N. N. Tušar, D. Maučec, M. Rangus, I. Arčon, M. Mazaj, M. Cotman, A. Pintar and V. Kaučič, *Adv. Funct. Mater.*, 2012, **22**, 820–826.
- L. Lyu, L. Zhang, Q. Wang, Y. Nie and C. Hu, *Environ. Sci. Technol.*, 2015, **49**, 8639–8647.
- N. Wang, L. Zhu, M. Lei, Y. She, M. Cao and H. Tang, *ACS Catal.*, 2011, **1**, 1193–1202.
- M. Hartmann, S. Kullmann and H. Keller, *J. Mater. Chem.*, 2010, **20**, 9002–9017.
- L. Lyu, L. Zhang and C. Hu, *Environ. Sci.: Nano*, 2016, **3**, 1483–1492.
- M. Setvín, U. Aschauer, P. Scheiber, Y.-F. Li, W. Hou, M. Schmid, A. Selloni and U. Diebold, *Science*, 2013, **341**, 988–991.
- A. Lagutschenkov, R. K. Sinha, P. Maitre and O. Dopfer, *J. Phys. Chem. A*, 2010, **114**, 11053–11059.
- X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76–80.
- B. Xu, T. Xiao, Z. Yan, X. Sun, J. Sloan, S. L. González-Cortés, F. Alshahrani and M. L. H. Green, *Microporous Mesoporous Mater.*, 2006, **91**, 293–295.
- H. Bader, V. Sturzenegger and J. Hoigne, *Water Res.*, 1988, **22**, 1109–1115.
- H. Li, S. Gan, H. Wang, D. Han and L. Niu, *Adv. Mater.*, 2015, **27**, 6906–6913.
- X. Li, X. Dai, J. Takahashi, N. Li, J. Jin, L. Dai and B. Dong, *Bioresour. Technol.*, 2014, **159**, 412–420.
- J. Zhang, M. Zhang, C. Yang and X. Wang, *Adv. Mater.*, 2014, **26**, 4121–4126.
- Ž. Mitić, G. S. Nikolić, M. Cakić, P. Premović and L. Ilić, *J. Mol. Struct.*, 2009, **924–926**, 264–273.
- R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner and M. Beller, *Science*, 2013, **342**, 1073–1076.
- X. Zou, R. Silva, A. Goswami and T. Asefa, *Appl. Surf. Sci.*, 2015, **357**, 221–228.
- R. R. Cheng, Z. L. Wu, Y. L. Hou, J. Dong, J. Z. Cui and B. Zhao, *Inorg. Chem. Commun.*, 2015, **51**, 95–98.
- T. Xiong, W. Cen, Y. Zhang and F. Dong, *ACS Catal.*, 2016, **6**, 2462–2472.
- S. Bordiga, A. Damin, F. Bonino, G. Ricchiardi, C. Lamberti and A. Zecchina, *Angew. Chem., Int. Ed.*, 2002, **41**, 4734–4737.
- X. Huang, X. Hou, J. Zhao and L. Zhang, *Appl. Catal., B*, 2016, **181**, 127–137.
- X. Zhang, Y. Ding, H. Tang, X. Han, L. Zhu and N. Wang, *Chem. Eng. J.*, 2014, **236**, 251–262.