Enhanced Fenton-catalytic efficiency by highly accessible active sites on dandelion-like copper–aluminum–silica nanospheres for water purification†

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A novel Fenton catalyst consisting of dandelion-like copper–aluminum–silica nanospheres (DCAS Ns) was successfully prepared via a hydrothermal process for the first time. This catalyst exhibited exceptionally high activity and stability for the degradation and mineralization of various refractory pollutants, as demonstrated with phenol, pharmaceuticals, pesticides, dyes and endocrine disrupting chemicals at neutral pH. The reaction rate was 5.2–13.4 times higher than that of the conventional Fenton catalysts. Moreover, the utilization efficiency of H₂O₂ was as high as 86.7%. According to the characterization, DCAS Ns possessed a unique fibrous structure arranged in three dimensions to form nanospheres, just like dandelion flowers. Cu and Al were co-incorporated into the framework of the fibrous silica nanospheres with Si–O–Cu and Al–O–Cu, resulting in great exposure, significant accessibility and high stability of the surface Cu, which were responsible for the outstanding Fenton catalytic performance of DCAS Ns. In addition, the formation of [Cu₃+–O–AP] complexes inhibited the generation of HO₂⁻/O₂⁻ and O₂ and promoted the generation of 'OH during the Fenton reaction, resulting in the high utilization efficiency of H₂O₂ in the DCAS Ns Fenton system. These findings thus provide a new insight into the design and application of high-efficiency Fenton catalysts for water purification.

Introduction

Industrial processes generate increasing amounts of wastewater which is contaminated with a series of nonbiodegradable and persistent organic compounds that are often released into the water environment. Some of these compounds including phenols, pesticides, pharmaceuticals, dyes as well as endocrine disrupting chemicals adversely affect human health through food chains or environmental cycles. The development of effective and practical techniques for the removal of organic pollutants in drinking- and waste-water has attracted worldwide attention over the past decades.

The Fenton process is an especially powerful method among various advanced oxidation processes (AOPs), since it does not require any special equipment or energy input and can rapidly and nonselectively degrade various organic pollutants with the highly aggressive free hydroxyl radical ('OH) which is produced in the Fenton reaction. The main limitations of the classical homogeneous Fenton reaction are the consumption of stoichiometric amounts of iron, the accumulation of iron-containing sludge, the requirement of very low pH values (2–3) for which large quantities of acid are needed, and the requirement of a neutralization step of effluent and sludge disposal. To solve or minimize these problems, heterogeneous Fenton catalysts, such as metal oxides and supported transition metal solids, have been developed as alternatives to the homogeneous Fenton process. These catalysts avoid the need for large amounts of reducing metal ions and reduce recovery costs. However, most of these catalysts still exhibited several deficiencies: (i) low activity at neutral pH, (ii) poor stability due to the serious leaching of active metals and (iii) low utilization efficiency of H₂O₂.

To improve the activity, some researchers developed porous supports which enlarged the specific surface area of the catalysts and increased the exposure of active components on the surface of the supports. Although the large specific surface area of the porous catalysts increases the activity to a certain extent, the effective utilization of the specific surface area is actually very low, because it is difficult for the pollutants to reach their complex internal channel and come into contact with the pore wall due to the steric effect. The poor accessibility to these active sites inside the pores limits their applications. To inhibit the release of the active component and improve the
stability of the catalysts, the in situ doping synthesis method has been developed.18,19 Although the chemical bonds formed fix the active component in this process, a large number of active sites are wrapped in the bulk of the catalyst without direct exposure to the pollutants or H2O2, decreasing the activity and efficiency of the catalyst. Therefore, it is necessary to develop highly active and stable Fenton catalysts with large effective surface area and good accessibility.

Herein, a novel fibrous Fenton catalyst consisting of dandelion-like copper–aluminum–silica nanospheres (DCAS Ns) fabricated via a hydrothermal method is described. DCAS Ns show very high activity, stability and utilization efficiency of H2O2 for the degradation of various refractory pollutants, as demonstrated with phenol, pharmaceuticals, pesticides, dyestuffs and endocrine disrupting chemicals in the Fenton process at neutral pH. Our findings suggest that the outstanding catalytic performance of DCAS Ns is due to their unique dandelion-like structure with high exposure and accessibility of the active sites and the special local environment of Cu that is incorporated in the fibrous structure of Al-doped silica nanospheres according to the transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS) measurements and UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS).

Experimental section

Chemicals

BPA (≥99%), 2,4-dichlorophenoxyacetic acid (≥99%), diphenylamine (≥99%), phenytoin (99%) and antipyrine (99%) were obtained from Acros (Geel, Belgium). Sulfamethoxazole (≥99%), ciprofloxacin (≥98%), ibuprofen (≥98%), 2-chlorophenol (≥99%), cetylpyridinium bromide hydrate (CBH, 98%), catalase from bovine liver (2000–5000 units per mg protein), N,N-dimethyl-p-phenylenediamine sulfate (DPP, 98%) and horseradish peroxidase (POD) were purchased from Sigma-Aldrich (St Louis, United States). Methylene blue (≥98.5%), cyclohexane (≥99.5%), n-pentanol (≥98.5%), tetrathyl orthosilicate (TEOS, 99%), aluminum isopropoxide (Al(OiPr)3, 98%), cetyltrimethyl ammonium bromide (CTAB, 99%), hydrogen peroxide (H2O2, 30%, w/w), copper nitrate trihydrate (Cu(NO3)2·3H2O, ≥99%), copper chloride dihydrate (CuCl2·2H2O, ≥99%), sodium metasilicate nonahydrate (Na2SiO3·9H2O, ≥99%), aluminum nitrate nonahydrate (Al(NO3)3·9H2O, ≥99%), phenol, urea and glucose were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All of the other chemicals were of analytical grade. Deionized water was used throughout this study.

Catalyst synthesis

For the preparation of DCAS Ns, a hydrothermal process was used. In a typical synthesis, TEOS (5.4 mL) was dissolved in a solution of pentanol (3.0 mL) and cyclohexane (50 mL). A stirred solution of urea (1.0 g) and CBH (2.0 g) in deionized water (60 mL) was then added. After 60 min stirring, a mixed solution (20 mL) of Cu(NO3)2·3H2O and Al(NO3)3·9H2O was added in accordance with the different Si/Cu and Si/Al ratios. The resulting mixture was continuously stirred for 60 min at 45 °C and then placed in a Teflon-lined steel autoclave and heated at 120 °C for 5 h. After natural cooling, the obtained product was filtered, washed with deionized water and acetone several times. Finally, the as-synthesized material was dried at 70 °C for 12 h and calcined at 550 °C for 6 h in a muffle furnace to obtain the product DCAS Ns. The amounts of Cu and Al in the sample were determined by ICP-OES (Optima 2000) after the sample was completely dissolved using nitric acid and hydrofluoric acid. Then, the weight percentages of Cu and Al were calculated. Following this procedure, various catalysts with different Cu and Al contents were prepared. The catalyst (Si/Cu = 50, Si/Al = 50) with 1.07 wt% Al and 1.91 wt% Cu exhibited the highest activity and stability (Fig. S1†), which is referred to as DCAS Ns and used for all of the subsequent experiments unless otherwise specified. As references, DS Ns (without Cu and Al), DAS Ns (without Cu and with 1.02 wt% Al), and DCS Ns (without Al and with 1.89 wt% Cu) were prepared using the same procedure.

In addition, Cu-MCM-41 (Cu-doped mesporous silica) and Cu-γ-Al2O3 (Cu-doped mesoporous γ-Al2O3) with equivalent Cu contents (ca. 1.90 wt%) were also prepared. Cu-MCM-41 was synthesized using a modified hydrothermal method.20 Na2SiO3·9H2O (8.53 g) and Cu(NO3)2·3H2O (0.15 g) were dissolved in deionized water (100 mL) stirring at room temperature. CTAB (2.73 g), dissolved in deionized water (25 mL), was added to the above solution and stirred for 60 min. The pH of the mixture was adjusted to 10.8 by using HCl (0.1 M) to form a gel. After stirring for 60 min, the gel was transferred to a Teflon-lined steel autoclave and heated at 145 °C for 48 h. After the reaction, the autoclave was naturally cooled, and the obtained product was collected by filtration, washed with distilled water, and dried at 110 °C for 12 h. Finally, crystallization and template removal were carried out in a muffle furnace at 550 °C for 6 h. Mesoporous Cu-γ-Al2O3 was prepared using a modified evaporation-induced self-assembly method as described in previous reports.19,21 Al(OiPr)3 (4.2 g), CuCl2·2H2O (0.08 g) and glucose (3.6 g) were dissolved in 50 mL of deionized water. The mixed solution was stirred at 45 °C for 1 h. After adjusting the pH to 5.5 (HCl 0.1 M), the solution was vigorously stirred for 24 h. Then, the mixture was heated at 100 °C in open air to remove water and other volatiles. The resulting solid was calcined in a muffle furnace at 600 °C for 6 h to remove the template. Finally, the obtained product was washed with deionized water and dried at 100 °C for 12 h.

Characterization

The TEM images of the various samples were obtained using a JEOL-2010 microscope operating at 200 kV. The FESEM images of the various samples were collected on a SU8020 instrument (Hitachi), which was operated at the accelerating voltage of 20 kV and the detector current of 10 mA. N2 adsorption and desorption isotherms were collected on a gas sorption analyzer (ASAP 2020 HD88) at the temperature of liquid nitrogen. The samples were previously outgassed for 30 min at
150 °C and then heated for 180 min at 350 °C. The specific surface areas were calculated from the isotherms using the BET method. The XPS analysis was performed on an AXIS-Ultra instrument using monochromatic Al Kz radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. The binding energies were calibrated using the C 1s hydrocarbon peak at 284.8 eV to compensate for surface charge effects. Auger electron spectroscopy (AES) was performed on an AXIS-Ultra instrument from Kratos. The UV-Vis DRS was recorded on a Hitachi U-3900 spectrophotometer. The extended X-ray absorption fine structure (EXAFS) spectra were recorded at the beam lines BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. Cu foil, Cu2O and CuO were used as references. The DCS Ns and DCAS Ns samples were sealed between two layers of adhesive PVC tape. The Cu K-edge (8.979 keV) EXAFS spectra of the samples were collected under ambient conditions in transmission mode. The parameters for EXAFS measurements, data collection modes and error calculations were all controlled according to guidelines set by the International XAFS Society Standards and Criteria Committee. The resulting EXAFS data were analyzed by the REX2000 program (Rigaku Co.). EXAFS oscillations $\chi(k)$ were extracted using spline smoothing and weighted by $k^3$ to compensate for the diminishing amplitude in the high $k$ range. The filtered $k^3$ weighted $\chi(k)$ were Fourier transformed (FT) to $R$ space in the $k$ range of 2 to 10 Å$^{-1}$. A nonlinear least-squares algorithm was applied to the EXAFS fitting with phase correlation in the $R$ space between 1.0 and 3.5 Å for the Cu K-edge. The structural parameters of the samples were obtained via the curve fitting procedures using FEFF8.4 code.

Results and discussion

Catalyst characterization

As shown in Fig. 1, the three samples (DS Ns, DCS Ns and DCAS Ns) exhibited well-defined and ordered fibers arranged in three dimensions to form spheres, just like dandelion flowers, in the TEM and FESEM images. The fiber interval became smaller in DCS Ns, while it became larger and a more loose fibrous structure appeared in DCAS Ns, which could be attributed to the larger radius of Al than that of Si. Obviously, with the introduction of Cu and Al, the size of fibrous spheres reduced, and it was the smallest for DCAS Ns, indicating the incorporation of Cu and Al that resulted in greater dispersion of the nanoparticles. However, excessive Al would destroy the fiber structure of the material (Fig. S4†). The BET surface areas of DS Ns, DCS Ns and DCAS Ns were 386, 356 and 488 m$^2$ g$^{-1}$, respectively (Table 1). Both Cu-MCM-41 and Cu-$\gamma$-Al$_2$O$_3$ possessed mesoporous structures (Fig. S5†) with BET surface areas of 1027 and 215 m$^2$ g$^{-1}$, respectively. By the XPS analysis, the surface Cu concentration was 0.70 wt%, 1.46 wt%, 1.16 wt% and 1.38 wt% for Cu-$\gamma$-Al$_2$O$_3$, Cu-MCM-41, DCS Ns, and DCAS Ns, respectively, while their Cu concentrations in the bulk were all approximately 1.90 wt% by ICP-OES measurements. This result indicated that more copper sites were exposed on the surface of Cu-MCM-41, DCS Ns and DCAS Ns than that of Cu-$\gamma$-Al$_2$O$_3$. The surface Cu concentration of DCAS Ns was higher than that of DCS Ns for the same bulk concentration, indicating the introduction of Al that enhanced the Cu exposure to the surface of the material.

The valence states of Cu on the surface of DCS Ns and DCAS Ns were characterized by XPS. As shown in Fig. 2a, the binding energy peak at 935.8 eV and the appearance of a shake-up satellite line at ca. 943.8 eV were attributed to the 2$p_{3/2}$ core level of Cu$^{2+}$ in DCS Ns. The peak at 933.2 eV corresponded to the reduction state copper species, and the auger parameters at 1847.5 eV confirmed that the reduction state copper species was Cu$. The fitting of the two peaks revealed that both Cu$^+$ and Cu$^{2+}$ existed on the surface of DCS Ns with a Cu$^+$ to Cu$^{2+}$ atomic ratio of 0.8 : 1. Similarly, both Cu$^+$ and Cu$^{2+}$ also existed on the surface of DCAS Ns (Fig. 2b), and the atomic ratio of Cu$^+$ to Cu$^{2+}$ was analyzed by recording variations at the wavelength of maximum absorption using a Hitachi UV-3010 UV-visible spectrophotometer. The total carbon (TC) and inorganic carbon (IC) were determined using a Shimadzu TOC-VCPH analyzer using high-temperature combustion, and the total organic carbon (TOC) was automatically calculated by TC minus IC. The concentration of H$_2$O$_2$ was determined using a DPD method, as previously reported in the literature.

The leaching of metallic ions during the reaction was analyzed by ICP-OES on an OPTIMA 2000 (Perkin Elmer, USA). The reusability of DCAS Ns was tested by recovering the catalyst through filtration. The remaining solid was washed with deionized water, dried at 70 °C and reused in the following cycle. The GC-MS analysis was carried out on an Agilent 6890 GC/5973 MSD with a DB-5 MS capillary column. The BMPO trapped ESR spectra were recorded using a Bruker A300-10/12 ESR spectrometer. The details about GC-MS and ESR procedures are provided in the ESI†.
on the surface of DCAS Ns was 1.9 : 1, greater than that of DCS Ns. This result indicated that the introduction of Al has changed the existing state of Cu, greatly increasing the proportion of Cu$^+$ on the surface of DCAS Ns, which is useful for heterogeneous Fenton reaction. Notably, the Cu 2p$_{3/2}$ binding energy (935.8 eV) for Cu$^{2+}$ in DCS Ns and DCAS Ns was much higher than that in pure CuO (933.8 eV), indicating that the high electron affinity of silicon resulted in the movement of electrons from copper to silicon.$^{26}$ This is the evidence for the formation of Si–O–Cu in the framework of the samples. The stable existence of Cu$^+$ in the framework of the solid has been previously reported in other Cu-doped materials prepared by a similar one-pot method,$^{19,25}$ where the disperse Cu doping in the matrix caused the emergence of the intrinsic defects, such as oxygen vacancies ($\nu_O$). The intensity of O 1s peak (ca. 533 eV) in DCS Ns and DCAS Ns significantly decreased compared to the one in DS Ns and DAS Ns (Fig. 2c), which was due to the increased amount of $\nu_O$ upon Cu doping. The excess electrons may be introduced from the increased $\nu_O$ due to charge compensation, some of which at nearby primarily stimulated the reduction of Cu$^{2+}$ species to Cu$^+$ species.$^{27}$ In addition, the Al 2p binding energy (75.0 eV) for DAS Ns (Fig. 2d) was much higher than that for pure Al$_2$O$_3$ (74.1 eV)$^{28,29}$ indicating that the aluminum was in the framework of DAS Ns, not in the form of Al$_2$O$_3$. For DCAS Ns, in addition to the peak of the Al 2p binding energy (75.0 eV), another peak at 77.4 eV was observed, which was assigned to the Cu 3p$_{3/2}$ binding energy of Cu$^+$,$^{29}$ indicating that the local environments of Al and Cu were influenced by each other in the framework of DCAS Ns.

Fig. 3a shows the Fourier transforms of $\chi^2$-weighted EXAFS oscillations from various samples at the Cu K-edge. A peak at ~1.4 Å (no phase correction) was observed over all samples, which was assigned to a Cu–O shell.$^{30}$ The bond distance in the range of 2.2–3.0 Å indicated the existence of an ordered cation shell beyond the oxygen shell,$^{31}$ which was due to the back-scattering from other adjacent atoms, such as Cu, Si and Al. In order to obtain the local coordination structure of Cu species in DCS Ns and DCAS Ns catalysts, curve fitting was performed, with the results shown in Fig. 3b and c and Table 2. A Cu–Cu shell with a bond distance of 2.54 Å and a coordination number of 10.9 was found on copper foil. Cu–O and Cu–Cu shells with different bond distances and coordination numbers were found on Cu$_2$O and CuO samples. DCS Ns possessed a Cu–O shell with a bond distance of 1.93 Å and a coordination number of 3.4, which were different from the bond distance and the coordination numbers of Cu$_2$O and CuO samples. This result indicated that the copper in the structure of DCS Ns was not in the form of Cu$_2$O or CuO.$^{32}$ In the second shells, besides the Cu–Cu shell with a bond distance of 2.88 and a coordination number of 0.6, the Cu–Si shell with a bond distance of 3.17 and a coordination number of 1.5 was also observed, confirming that Cu was incorporated into the silica framework,$^3$ forming Si–O–Cu bonds. As for DCAS Ns, the Cu–Al shell with a bond distance of 3.15 Å emerged with the introduction of Al and the bond distance and coordination number of the Cu–Si shell changed to 3.20 and 0.4, respectively. The results indicated that the incorporation of Al affected the local environment of the copper, and the position of Si was partly replaced by Al, forming Al–O–Cu bonds.

Fig. 4 gives a comparison of the UV-Vis DRS spectra of the four samples. No significant absorption peak was observed for the DS Ns and DAS Ns samples. However, the DCS Ns sample shows a single strong absorption peak at ca. 220 nm, assigned to the charge transfer transitions of isolated Cu$^{2+}$ in coordination with lattice oxygen,$^{31}$ confirming the formation of Si–O–Cu in the framework of the DCS Ns sample.$^{18,33}$ As for the DCAS Ns, besides the obvious absorption peak of Si–O–Cu (220 nm), a very broad absorption in the range of 500–800 nm was observed, which was attributed to the d–d transition of Cu$^{2+}$ in the pseudo-octahedral ligand oxygen environment,$^{33,35}$ indicating the formation of Al–O–Cu in DCAS Ns. These results are in good agreement with the EXAFS results.

Table 1 BET surface area and metal content information of various samples

<table>
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<tr>
<th>Catalyst</th>
<th>BET surface area/m$^2$ g$^{-1}$</th>
<th>Al content/wt%</th>
<th>Bulk Cu content/wt%</th>
<th>Surface Cu content/wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS Ns</td>
<td>386</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DCS Ns</td>
<td>336</td>
<td>—</td>
<td>1.89</td>
<td>1.16</td>
</tr>
<tr>
<td>DAS Ns</td>
<td>607</td>
<td>1.02</td>
<td>—</td>
<td>—</td>
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<tr>
<td>DCAS Ns</td>
<td>488</td>
<td>1.07</td>
<td>1.91</td>
<td>1.38</td>
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<td>Cu-MCM-41</td>
<td>1027</td>
<td>—</td>
<td>1.90</td>
<td>1.46</td>
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<tr>
<td>Cu-$\gamma$-Al$_2$O$_3$</td>
<td>215</td>
<td>—</td>
<td>1.92</td>
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</table>
Catalytic performance

The Fenton catalytic activity of the catalysts prepared in this study was assessed for the degradation of BPA with \( \text{H}_2\text{O}_2 \) at nearly neutral pH and room temperature. In the adsorption/desorption equilibrium stage (without \( \text{H}_2\text{O}_2 \)), 5.7/0.5%, 7.1/0.4%, 7.4/0.5%, 2.5/0.3% and 6.0/0.6% of BPA (23 mg L\(^{-1}\)) was adsorbed on the surface of DAS Ns, DCS Ns, DCAS Ns, Cu-\( \text{g}\)-\( \text{Al}_2\text{O}_3 \) and Cu-MCM-41, respectively. In the Fenton reaction stage (Fig. 5a), no significant degradation of BPA was observed in DAS Ns suspension. The degradation of BPA within 120 min was 47.1% and 80.5% in the Cu-\( \text{g}\)-\( \text{Al}_2\text{O}_3 \) and Cu-MCM-41 suspensions, respectively. However, both DCS Ns and DCAS Ns exhibited similar activity that approximately 98% of BPA was removed within 60 min. All of the reactions were fitted with pseudo-first-order kinetics (Fig. S6†). The kinetic constants in DCAS Ns suspension were approximately 13.4 and 5.2 times larger than those in Cu-\( \text{g}\)-\( \text{Al}_2\text{O}_3 \) and Cu-MCM-41 suspensions, respectively. In addition, after a reaction of 180 min, the TOC removal (Fig. 5b) was only 38.3% and 12.6% in the Cu-\( \text{g}\)-\( \text{Al}_2\text{O}_3 \) and Cu-MCM-41 suspensions, respectively, while approximately 70% of TOC removal was observed in the DCS Ns and DCAS Ns suspensions, which were much higher than the 10% to 30% TOC removal for BPA degradation in most of the reported Fenton processes under similar conditions.\(^{26,27}\) The changes of concentrations of the residual Cu in the solutions of DCS Ns and DCAS Ns during the Fenton process are shown in Fig. S7†.
At the end of the reaction, the concentrations of the total dissolved Cu were 0.55 and 0.19 mg L\(^{-1}\) in the DCS Ns and DCAS Ns suspensions, respectively, and no leaching of Al ions from DCAS Ns was detected. The amount of released Cu was much lower than the limits set by EU directives (<1.3 mg L\(^{-1}\)) and USA regulations (<1.3 mg L\(^{-1}\)). Moreover, only 13% of BPA was removed within 120 min by the homogeneous Fenton reaction (Cu\(^{2+}\) concentration 0.2 mg L\(^{-1}\)), which was much lower than that in the DCAS Ns suspension. The results indicated that the catalytic contribution of the released ions was not evident and the Cu in the framework of the material was the predominant active component for this Fenton reaction.

Based on the above analysis, in Cu-\(\gamma\)-Al\(_2\)O\(_3\), most of the Cu was incorporated in the bulk, as shown in Fig. 6a, these Cu could not directly come into contact with the pollutants or H\(_2\)O\(_2\), leading to very low efficiency and activity. Cu-MCM-41, as a typical multiporous material, possesses the largest specific surface area and the highest exposed surface Cu. However, the activity of Cu-MCM-41 is much lower than that of DCS Ns and DCAS Ns although they have smaller specific surface areas. This result indicated that the specific surface area and exposed active components of the multiporous material have not been fully utilized due to the complex internal channel of the material, the viscous resistance of the solution and the steric effect between the material and pollutants or H\(_2\)O\(_2\) (Fig. 6b). In contrast, DCS Ns and DCAS Ns possess the well-defined and ordered dandelion-like fibers arranged in three dimensions to form spheres (Fig. 6c), which allowed easy access to the exposed active components for the pollutants and H\(_2\)O\(_2\). The high accessibility finally resulted in high utilization of the active sites and the high activity of DCS Ns and DCAS Ns.

DCS Ns and DCAS Ns with equal Cu contents exhibited similar high activities for BPA degradation. However, the release of Cu in the DCAS Ns suspension was significantly lower than that in the DCS Ns suspension. In addition, the cycle tests showed that the activity of DCAS Ns did not markedly decrease, and the degradation of BPA remained at approximately 95% within 90 min after 8 cycles (Fig. 7a). Moreover, it was observed that Cu(n) leaching from DCAS Ns became less and less, less than 0.1 mg L\(^{-1}\) over the reuse cycles (Fig. S8a†). In contrast, the activity of DCS Ns for BPA degradation markedly decreased that only 67.2% of BPA was removed at 90 min in the 8th cycle (Fig. 7b) and the release of Cu(n) was maintained at a relatively high level over the reuse cycles (Fig. S8b†). These results indicated that the surface Cu was firmly immobilized in the framework of DCAS Ns by Al–O–Cu, resulting in the high stability of the catalyst. In addition, DCAS Ns, the dandelion-like silica nanospheres, could be uniformly suspended in water without any external agitation (Fig. S9†). These results suggested that the DCAS Ns was very potential for industrial application as a heterogeneous Fenton catalyst.

![UV-Vis DRS of DS Ns, DAS Ns, DCS Ns and DCAS Ns.](image-url)  

![BPA degradation and TOC removal in different suspensions with H\(_2\)O\(_2\). Reaction conditions: initial pH 7, initial BPA concentration 23 mg L\(^{-1}\), initial H\(_2\)O\(_2\) concentration 10 mM and catalyst concentration 1.0 g L\(^{-1}\).](image-url)  

**Table 2** Curve fitting results of Cu K-edge EXAFS for various samples

<table>
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<tr>
<th>Sample</th>
<th>Shell</th>
<th>(R^a) (Å)</th>
<th>CN(^b)</th>
<th>(\sigma^c) (Å(^2))</th>
<th>(\Delta E_0^d) (eV)</th>
<th>(R_e^e)</th>
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<tr>
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</tbody>
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\(^a\) Bond distance. \(^b\) Coordination number. \(^c\) Debye-Waller factor. \(^d\) Inner potential correction. \(^e\) Residual factor.
To further study the adaptability and activity of the catalyst for different compounds, a series of refractory organic pollutants including phenols, pesticides, pharmaceuticals, dyes as well as endocrine disrupting chemicals were degraded in the DCAS Ns suspensions at neutral pH and room temperature. As listed in Table 3, all the refractory compounds were substantially degraded at 30 min, especially phenol, phenytoin, diphenhydramine, ciprofloxacin, 2-chlorophenol and bisphenol A (10 mg L\(^{-1}\)), which could be completely removed at 60 min. Even for the extremely refractory antipyrine and sulfamethoxazole, the conversion could reach 68.3% and 79.5%, respectively, within 60 min. The selection of a lower catalyst concentration (0.4 g L\(^{-1}\)) for methylene blue removal was due to the strong adsorption of DCAS Ns for methylene blue. Prior to the addition of H\(_2\)O\(_2\), approximately 50% of methylene blue (50 mg L\(^{-1}\)) was adsorbed on the surface of DCAS Ns (0.4 g L\(^{-1}\)), indicating a good accessibility of DCAS Ns for methylene blue. In the presence of H\(_2\)O\(_2\), 92.5% of methylene blue was decolorized within 30 min, and 73.5% of TOC was removed within 120 min. In order to clarify that the removal of methylene blue is mainly due to the Fenton catalysis, UV-Vis DRS spectra of the used DCAS Ns with different reaction times were recorded (Fig. S10†). With the reaction time, the absorption peak (664 nm) of the methylene blue adsorbed on the surface of DCAS Ns gradually weakened, which indicated that the methylene blue on the material surface and in the solution were simultaneously degraded by the Fenton catalysis rather than adsorption only.

Fig. 6 Schematic illustration of pollutants or H\(_2\)O\(_2\) in contact with (a) the catalyst with the active component in the bulk, (b) the multiporous catalyst and (c) DCAS Ns. Every picture is a 3/4 sphere cutting diagram.

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**High utilization efficiency of H\(_2\)O\(_2\)**

The utilization efficiency of H\(_2\)O\(_2\) is defined as the ratio of the stoichiometric consumption of H\(_2\)O\(_2\) (\([\Delta H_2O_2]_S\)) for the mineralization of pollutants to the actual consumption of H\(_2\)O\(_2\) (\([\Delta H_2O_2]_A\)) in the Fenton reaction.\(^{44}\) The details are shown in the ESI, Table S1.† In the DCAS Ns suspensions, the utilization efficiency of H\(_2\)O\(_2\) was maintained at more than 86.7% prior to the complete disappearance of BPA (Fig. 8a), which was much higher than that of 10% to 60% in the reported Fenton processes under similar conditions.\(^{45}\) During the catalytic degradation of BPA, several intermediates including aliphatic acids, alcohols and aromatic products (i.e., 4-isopropylphenol, 4-hydroxybenzoic acid, hydroquinone, 2,4-dihydroxybenzoic acid and 4-hydroxyacetophenone) were generated in the DCAS Ns system at 15 min (Table S2†). Interestingly, almost all the aromatic products were detected on the surface of DCAS Ns and few of them were detected in the aqueous solution. These aromatic products complexed with the surface Cu of the DCSA Ns and might influence the generation of the reactive oxygen species (ROS). So the ESR spin-trap technique (with BMPO) was employed to detect the nature of the ROS generated in various DCAS Ns samples with H\(_2\)O\(_2\) (Fig. 8b). The ‘OH intensity in the suspensions of DCAS Ns adsorbed BPA and those used after 15 min of Fenton reaction with BPA was much higher than that of the suspensions of fresh DCAS Ns. In contrast, little HO\(_2^-\)/O\(_2^-\) was detected in the BPA-adsorbed and 15 min-used DCAS Ns suspensions, while the fresh DCAS Ns exhibited a higher HO\(_2^-\)/O\(_2^-\) intensity. These results indicated that the complexation between the Cu species on the surface of the DCAS Ns and the pollutants or their intermediate products promoted the generation of ‘OH and prevented the formation of HO\(_2^-\)/O\(_2^-\). Based on the experimental results and a review of the literature,\(^6,10,40,41\) a heterogeneous Fenton catalytic process of DCAS Ns is

Fig. 6 Schematic illustration of pollutants or H\(_2\)O\(_2\) in contact with (a) the catalyst with the active component in the bulk, (b) the multiporous catalyst and (c) DCAS Ns. Every picture is a 3/4 sphere cutting diagram.

Fig. 7 Reusability of (a) DCAS Ns and (b) DCS Ns for the degradation of BPA. Reaction conditions: initial pH 7, initial BPA concentration 23 mg L\(^{-1}\), initial H\(_2\)O\(_2\) concentration 10 mM and catalyst concentration 1.0 g L\(^{-1}\).
proposed (Table 4). Due to the high accessibility of the active sites in DCAS Ns, large amounts of pollutants and H2O2 were gathered around or adsorbed on the fiber surface. On the site of Cu+, H2O2 reacted with Cu+ and was converted into OH and OH− (eqn (1)). Meanwhile, Cu+ was oxidized to Cu2+ by H2O2. On the site of Cu2+, most of the aromatic products (AP–OH) complexed with the Cu2+, forming Cu2+-O–AP complexes (eqn (4)). These complexes prevented H2O2 from reacting with Cu2+ and inhibited the conventional reduction of Cu2+ to Cu+ (eqn (2) and (3)), preventing the formation of HO2•/O2•− and O2. In contrast, the Cu2+-O–AP complexes directly interacted with H2O2 (eqn (5)), not only carrying out the reduction of Cu2+ to Cu+ but also producing a hydroxylation product and another OH, resulting in the high utilization efficiency of H2O2.

Table 4 Possible reaction process in the DCAS Ns suspension

\[
\begin{align*}
\text{Cu}^+ + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{2+} + \cdot\text{OH} + \text{OH}^- \quad (1) \\
\text{Cu}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^+ + \text{HO}_2^- + \text{H}^+ \quad (2) \\
\text{Cu}^{2+} + \text{HO}_2^- & \rightarrow \text{Cu}^+ + \text{O}_2 + \text{H}^+ \quad (3) \\
\text{Cu}^{2+} + \text{AP}–\text{OH} & \rightarrow \text{[Cu}^{2+}–\text{O–AP]} + \text{H}^+ \quad (4) \\
\text{[Cu}^{2+}–\text{O–AP]} + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^+ + \text{HO–AP–OH} + \cdot\text{OH} \quad (5)
\end{align*}
\]

Conclusions

In this work, dandelion-like copper–aluminum–silica nanospheres (DCAS Ns) with a large specific surface area and significant accessibility were fabricated using a hydrothermal process successfully. The introduction of Al loosened the fibers and increased the exposure of Cu on the surface of DCAS Ns. Cu and Al were co-incorporated into the framework of DCAS Ns by chemical bonding of Si–O–Cu and Al–O–Cu, which is unambiguously confirmed by EXAFS and UV-Vis DRS. DCAS Ns showed very high activity and stability for the degradation and mineralization of refractory organic pollutants in the presence of H2O2 under nearly neutral pH conditions. All of the refractory compounds were substantially degraded at 30 min, and the reaction rate was 5.2–13.4 times higher than that of the conventional Cu-based porous materials. The TOC removal reached 70% within 180 min and the utilization efficiency of H2O2.
H$_2$O$_2$ was maintained at more than 86.7% prior to the complete disappearance of BPA in the DCAS Ns suspension. In addition, the released Cu in the DCAS Ns suspension was only 0.19 mg L$^{-1}$, much lower than that in the DCS Ns suspension (0.55 mg L$^{-1}$). The comparison of the structure and activity of Cu-MCM-41, Cu-$\gamma$-Al$_2$O$_3$ and DCAS Ns revealed that the large specific surface areas of DCAS Ns and Cu-MCM-41 led to the vast majority of active sites exposed to the surface of the materials, and the special structure of DCAS Ns significantly enhanced the accessibility for the contaminants and H$_2$O$_2$ to the active sites, which eventually led to the enhanced Fenton catalytic activity for the degradation of various refractory organic pollutants in the DCAS Ns suspensions. The comparison of the local environment of Cu and the reusability of DCAS Ns and DCAS Ns revealed that the incorporation of Al affected the local environment of Cu, and the position of Si was partly replaced by Al, forming Al-O-Cu bonds, which enhanced the stability of DCAS Ns. The formation of Cu$^{2+}$/O$_2$ and promoted the generation of HO$_2$. The synergic effects of the highly accessible active sites in the framework of the dandelion-like structure and special complexation between Cu$^{2+}$ and the aromatic products resulted in the exceptionally high activity and stability of DCAS Ns and high utilization efficiency of H$_2$O$_2$.

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Notes and references