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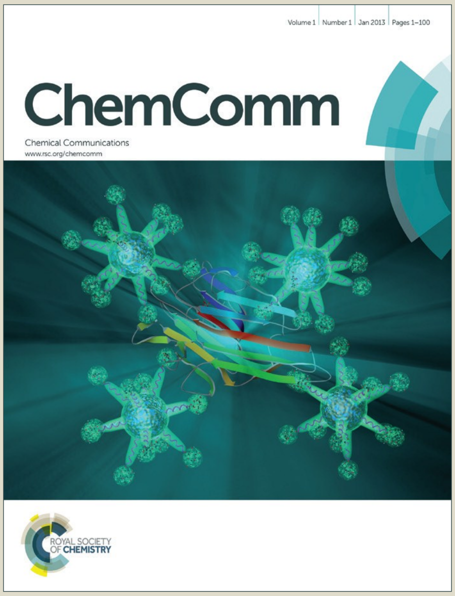

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Chloride Accelerated Fenton Chemistry for Ultrasensitive and Selective Colorimetric Detection of Copper

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A highly selective, ultrasensitive (visual and instrumental detection limits of 40 nM and 0.1 nM, respectively), environmentally-friendly, simple and rapid colorimetric sensor was developed for detection of copper(II) in water. This sensor is based on a novel signal-amplification mechanism involving reactive halide species (RHSs) including chloride or bromide which accelerate copper Fenton reactions oxidizing the chromogenic substrate to develop colour. The results of this study expand our understanding of copper-based Fenton chemistry.

Copper(II), an essential cofactor of many metalloenzymes catalyzing numerous metabolic reactions, is also capable of enhancing hydroxyl radical production from hydrogen peroxide, a property implicated in the progression of neurodegenerative disorders including Alzheimer's, Parkinson's, and Wilson's diseases with long-term exposure to even trace levels.[1] Due to its environmental and biological importance, the past decades have witnessed a large number of reports on the design of Cu(II) sensors with improved simplicity.[2] To achieve good sensitivity, a variety of signal amplification strategies were adopted in the sensor design. For example, transducing materials with high extinction coefficients or optoelectronic properties were introduced such as gold nanoparticles[2a-c] and quantum dots[2d-f] for designing colorimetric and fluorescence sensors, respectively. The role that copper plays in the signal development is a critical determinant of sensitivity. When copper serves as the reactant, usually the chemsensor generates signal in a defined stoichiometric ratio to Cu(II) (usually 1:1),[3] thus limiting sensitivity. In contrast, when copper is used as a catalyst in the colour-producing reaction, sensor sensitivity and selectivity can be dramatically improved via catalytic signal amplification. For example, Cu(II) assisted with peptide,[2f] DNAzyme,[2g-i] GpG DNA duplex,[2j] metalloenzyme,[2k] and organic dyes[2l, 2m] have been used to catalyze various colour developing reactions, including DNA cleavage,[2c, 2g, 2i] spirolactam ring-opening, hydrolysis of α-amino acid esters,[2n, 2o] oxidative cyclization of azoaromatics,[2p] cysteine oxidation,[2b, 2q] the azide alkyne Huisgen cyclo-addition reaction,[2a, 2v] and Fenton reactions.[2c, 2l] Nevertheless, most approaches are not time- and cost-effective or require use of toxic chemicals. To address these issues, herein we report a highly efficient yet simple colorimetric assay for copper(II) in water. To the best of our knowledge, this is the simplest, most cost-effective and environmental friendly method to detect this metal.

Our method is based on the discovery that chloride (or bromide, as discussed later) ions can significantly accelerate the copper-based Fenton reaction, with colorimetric quantification via a widely used chromogenic substrate 3,3',5,5'-tetramethylbenzidine (TMB). TMB can be used to detect copper based on Fenton chemistry (referred to as Cu-Fenton) even without the assistance of halide anions. When H_2O_2 was added (final concentration 750 mM) to the MES buffer (1 mM, pH 5.5) containing Cu(II) and TMB (0.5 mM), the bluish oxidized TMB (ox-TMB, with maximal light absorbance at 652 nm, *i.e.*, A_{652}) was generated, facilitating a colorimetric assay with a limit of detection (LOD, 3σ) of ~ 200 nM (Fig. S1) and visual LOD of ~2 μM (Fig. 1a), which is 10 times lower than the drinking water limit set by the U.S. Environmental Protection Agency (1.3 ppm, or 20 μM). However, this approach is not practically useful due to compromised selectivity (Fig. S2) as at micromolar concentrations, other metal ions such as Fe(II), Cr(III), Ag(I) and Au(III) can also facilitate TMB oxidation via Fenton chemistry (Fe and Cr) or by direct oxidation (Ag and Au).

We noticed that the sensitivity of the aforementioned copper assay could be significantly enhanced in the presence of chloride ions (referred to as "chloride-accelerated Cu-Fenton" or "CA Cu-Fenton"). When 250 mM NaCl was introduced into the reaction system (containing Cu(II), H_2O_2, and TMB in MES buffer), the developed chromogen colour intensity (A_{652}) was amplified ~ 100 times (*i.e.*, 0.5120 ± 0.0084 vs. 0.0055 ± 0.0009 without NaCl, *n* = 3, Fig. 1b). This dramatic signal amplification endows the assay with high sensitivity for visual detection of ppb levels of waterborne copper. When using 100 mM NaCl in a 10-min assay, the LOD was 40 nM (Fig. 1c) by naked eye and 0.11 nM using a microplate-reader (Fig. S3 and S4) with the dynamic range up to 750 nM (Fig. 1b and S4). Such signal amplification was attributable to chloride anions rather than sodium cations upon comparisons of NaCl, KCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, CH_3COONa (NaAC), $NaNO_3$, NaH_2PO_4 on color development (Fig. S5).

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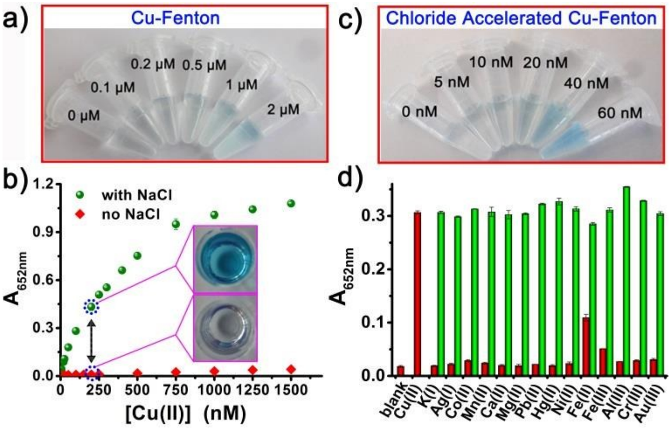


Fig. 1 (a) Colorimetric assay of Cu(II) based on Cu-Fenton chemistry. (b) Absorbance of ox-TMB catalyzed by different concentration of Cu(II) in the presence/absence of 100 mM NaCl. Inset: representative photographs of 200 nM Cu(II) catalyzed TMB oxidation with or without NaCl (100 mM). (c) The colorimetric assay of Cu(II) based on chloride-accelerated (CA) Cu-Fenton reaction. NaCl =100 mM. (d) The selectivity of the assay for Cu(II) relative to other metal cations (red bars) and the interference of these metal ions (green bars) in 2 mM MES buffer containing 100 mM NaCl, where the concentration of Cu(II) was 0.1 μM, of Cr(III) and Au(III) was 1 μM, and other metal ions were 10 μM. Error bars represent standard deviations from three repeated experiments.

In addition, the selectivity of the assay against other metal ions was excellent (Fig. 1d). Based on the calculation of Liu,[2g] signal intensity produced by Cu(II) is ~1000 times higher than that of Co(II), Mn(II), Ca(II), Mg(II), Pb(II), Hg(II), Ni(II), Al(III) and K(I), and ~800 times that of Fe(III), and 300 times that of Fe(II), and Ag(I) and ~ 50 times that of Cr(III) and Au(III). The interference of both competing metal ions (Fig. 1d) and anions (Fig. S6) with the colorimetric assay was insignificant, indicating great potential for practical applications. These results demonstrate that chloride ions not only amplify assay sensitivity, but also enhance selectivity for Cu(II) relative to other metal ions.

Signal amplification as a function of Cl^- and Cu(II) concentrations demonstrates a synergistic catalytic effect of chloride with copper on TMB oxidation by H_2O_2 to amplify developed chromogen intensity with increased chloride concentration (Fig. 2a). However, high chloride concentrations alone also result in elevated background noise (Fig. 2a, when [Cu(II)] = 0). In addition, we observed that the bluish ox-TMB aggregated over time with high NaCl concentrations (e.g. > 250 mM over 10 min), which affected assay quantitation. The LODs over chloride concentrations are shown in Fig. S3. Since optimal sensitivity (0.11 nM) can be achieved with 100 mM NaCl, we chose this concentration for signal amplification in all further experiments.

Next, we evaluated the role of pH and H_2O_2 concentration on signal amplification, which was optimal (40.5 times) under pH 5.5 for CA Cu-Fenton (Fig. S7), while Fenton reactions based on Fe(II) or Fe(III) are under pH 3.[4] Although higher concentrations of H_2O_2 increased TMB oxidation with even low concentration of Cu, this enhancement was much more significant in the presence of higher concentrations of Cu(II) (Fig. S8). We further discovered chloride-based signal amplification is fairly universal, enhancing other chromogenic reagents, including 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), o-phenylenediamine (OPD), guaiacol, o-dianisidine (ODA), and diaminobenziidine (DAB) (Fig. S9). However, signal amplification

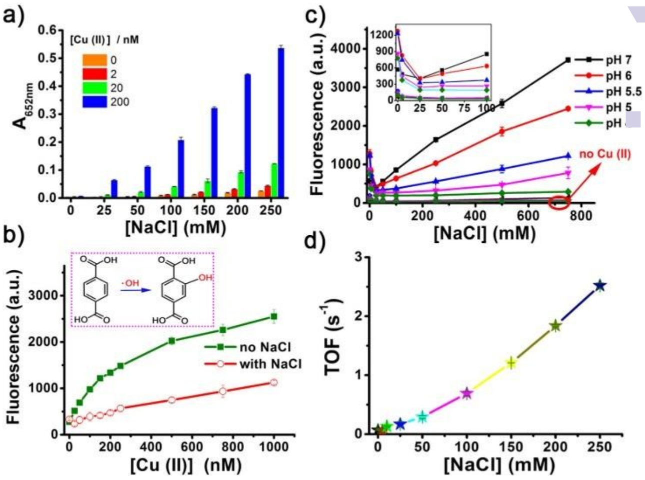
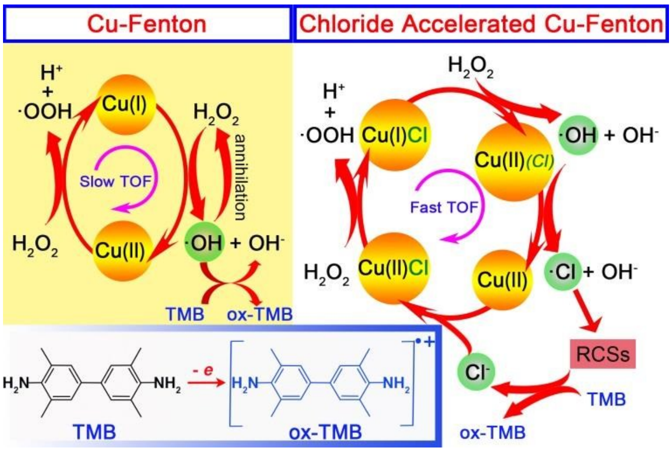


Fig. 2 (a) TMB oxidation catalyzed by CA Cu-Fenton with varying Cu(II) (0-200 nM) and NaCl concentrations (0-250 mM). (b) The hydroxyl radical yield detected with terephthalic acid (TPA) as a function of Cu(II) concentration (0-1000 nM) with or without 100 mM NaCl. Inset: Hydroxylation of TPA with ·OH to form fluorescent product 2-hydroxyterephthalic acid. (c) Effect of NaCl concentration (0-750 mM) on the ·OH production under different pHs (4-7) in the CA Cu-Fenton system; the system without Cu(II) served as the control. Inset: the ·OH production with ≤ 100 mM NaCl. (d) Turnover frequency (TOF) of CA-Cu-Fenton reaction with different concentrations (0-250 mM) of NaCl and 2 nM Cu(II). Error bars represent standard deviations from three repeated experiments.

magnitude differs for each chromogen. TMB is a promising substrate due to its low cost, high sensitivity, non-toxic nature (according to the Globally Harmonised System) and ease of unaided visual detection with its bluish oxidized properties.

Copper(II) is an established Fenton catalyst that can react with oxygen or peroxide to generate highly reactive oxygen species (ROS), such as superoxide anion ($·O_2^-$) and hydroxyl radical (·OH).[5] We intuitively expected ·OH, as the most reactive ROS, to be responsible for directly oxidizing TMB to generate the bluish product, since this was true when no NaCl was added. Without NaCl, TMB oxidation-induced colour development is positively correlated with Cu(II) and ·OH concentrations produced by the Cu-Fenton reaction, as determined by terephthalic acid (TPA), a sensitive substrate that quantitatively reacts with ·OH to form a hydroxylated product (TPA-OH) with strong fluorescence properties[6] (Inset, Fig. 2b). However, when we measured the ·OH yields in the system with added NaCl (25 mM) at pH 5.5, the amount of ·OH decreased to ~ 30% of its initial value prior to NaCl addition (blue line, Fig. 2c and inset). With addition of 250 mM NaCl, ·OH yields increased slowly to ~ 40% of its initial levels. Nevertheless, there was a clear decrease in net ·OH generation in the presence of Cl^- (Fig. 2b and c), despite more ox-TMB production in the presence of Cl^- anions (Fig. 1b and 2a). Meanwhile, the TMB oxidation was nearly unaffected by the presence of well-established ·OH scavengers such as propanol, mannitol or tert-butyl alcohol (TBA) (Fig. S10). Collectively, the experimental evidence suggests ·OH is not the primary ROS responsible for TMB oxidation in the presence of Cl^-.

Chloride anions are well demonstrated scavengers of ·OH and are consequently easily oxidized to form chloride atoms (·Cl) subsequent to the formation of dichloride anion radicals ($·Cl_2^-$),[7] as shown in Scheme S1. Since ·Cl (E°(·Cl/Cl^-) = 2.41 V) and $·Cl_2^-$ (E°($·Cl_2^-/2Cl^-$) = 2.09 V) are much less reactive than ·OH (E°(·OH



Scheme 1 The mechanism of Cu-Fenton and chloride accelerated Cu-Fenton reaction on the oxidation of TMB.

H^+/H_2O) = 2.73 V),[8] their steady-state concentrations should be significantly higher than that of ·OH.[7a-c] Further, the spontaneous self-coupling annihilation products of chloride radicals such as chlorine ($Cl_{2(aq)}$) or hypochlorous acid (Scheme S1), can themselves oxidize TMB to OX-TMB;[9] however, the self-annihilation of ·OH generates H_2O_2 (Scheme S1), which hardly oxidize TMB even in 3 M over 40 min (Fig. S11). Consequently, it is reasonable to conclude that chloride radicals may be largely responsible for the observed TMB oxidation. To verify this hypothesis, the NaCl effect on TMB oxidation in a photo-Fenton reaction system was evaluated with ·OH generated by UV induced homolysis of H_2O_2 (H_2O_2 + UV → 2 ·OH).[10] In the presence of NaCl, chloride radicals were generated by ·OH oxidation.[11] The ·OH yield decreased with increasing NaCl (Fig. S12), while ox-TMB increased by 50% (A_{652} increasing from 0.2 to 0.4) at 100 mM NaCl (Fig. S13). While this result supports the theory that the reactive chloride species (RCSs) enhanced TMB oxidation, such enhancement was far less than the 40-time signal amplification in the CA Cu-Fenton, demonstrating the existence of additional signal amplifying mechanisms.

We hypothesize the mechanism is due to the enhanced catalytic activity of Cu(II) when complexed with chloride ions (Scheme 1). As J. Perez-Benito described, chloride ions can enhance the Cu(II)-catalyzed decomposition of H_2O_2 by decreasing the activation energy.[12] The main complex in our 100 mM NaCl system is $[CuCl]^+$ based both on our calculations (Fig. S14) and data (Fig. S15) demonstrating increased absorbance (λ = 250 nm) with increasing concentrations of NaCl added to a 0.2 mM Cu(II) solution, consistent with previous work.[13] The positive correlation between chloride concentration and initial rate of TMB oxidation (Fig. S16) or the turnover frequency (TOF, Fig. 2d) is further evidence of the synergistic catalytic activity of copper and chloride. Cl^- binding to Cu(I) is much stronger than to Cu(II), resulting in higher standard redox potential (e.g., $E^{\circ}(CuCl_2/CuCl_2^-)$ = 0.567 V; $E^{\circ}(CuCl^+/CuCl^0)$ = 0.330 V) than that of Cu(II)/Cu(I) (0.153 V),[14] facilitating the Cu(II) → Cu(I) transformation,[15] which is assumed to be the rate limiting step in Cu-Fenton,[5a] which commensurately increases Cu(II) → Cu(I) → Cu(II) cycling to more rapidly generate ·OH. Actually, the catalytic activity of Cl^- demonstrated in reducing Cu(II) → Cu(I) in electrodeposition and oxidation of dopamine and ascorbic acid,[16] may contribute to accelerated Cu-Fenton cycling. Further, the formation of $[Cu(Cl)_x(H_2O_2)_y]^{2-x}$ and $[Cu(Cl)_x(H_2O_2)_y]^{1-x}$ complexes may facilitate generation of RCSs *in situ* (i.e., ·Cl is directly generated from the complexes via inner sphere electron-transfer from ·OH). This would significantly increase RCSs generation rate relative to the oxidation of chloride ions by ·OH via outer sphere electron-transfer in bulk solution, given that the reaction is virtually diffusion-rate controlled and both ·OH and ·Cl are short-lived species with limited migration capability in buffer.[7e, 7g, 7] Experimental evidence demonstrates more ·OH were generated with increasing NaCl concentrations at both pH 6 and 7 (Fig. 2c) with ·OH yield increased by ~ 7 times in 750 mM NaCl under pH 7. At lower pHs, there was no net increase in ·OH yield, which can be attributed to the higher oxidizing capability (i.e., higher E°) of ·OH in acidic solutions and thus more complete transformation to RCSs.[7b, 8, 11] The existence of RCSs was substantiated with the observation of significant amounts of chlorinated cinnamyl alcohol (i.e., 2-chloroacetophenone) in the Mass Spectrometry experiment (Fig. S17); in the CA Cu-Fenton system with 250 mM NaCl added, chlorinated products were generated but oxidized product dominated, while only oxidized product was detected in the Cu-Fenton system when NaCl was absent.

Chloride anions played two main roles in the system. First, chloride ions served as a co-catalyst by complexing with copper to catalyze the decomposition of H_2O_2. Second, chloride ions serving as the reductant (or the scavenger of ·OH) were oxidized to form RCSs, which further oxidized TMB to ox-TMB. By virtue of these dual functions (evidenced by the apparent reaction order of Cl^- being 0.9, Fig. S18), chloride anions amplified the colorimetric assay signal dramatically.[18] Comparing the effect of Cl^- with other halogen anions (F^-, Br^-, I^-) on the assay, Br^- could provide larger signal amplification than Cl^- (Fig. S19), but F^- was not effective due to its extremely high reduction potential (E°(·F/F^-) = 3.6 V).[8] I^- was not considered due to redox reactions with Cu(II).[19] Both Cl^- and Br^- have been shown to be weak activator of H_2O_2 decomposition, possibly through cycling of halogen anions and halogen atoms (X^- ↔ ·X),[20] although the catalytic activity of either X^- or Cu(II) alone was negligible compared to CuX^+ complexes in our system (Fig. 2a). The reactive halogen species produced further oxidize TMB resulting in the colour development, but also accounting for background A_{652} in the absence of Cu(II) (Fig. 2a). In the assay, we used Cl^- instead of Br^- to reduce background noise (Fig. S19). Herein, the halogen atoms are radicals[21] with high reactivity towards other organic compounds, including the oxidation of TMB and/or halogenation of organic molecules, especially olefinic compounds such as cinnamyl alcohol.

Our conclusion that Cl^- accelerates Cu-Fenton appears to contradict the established inhibition effect of Cl^- on pollutant degradation in Fenton chemistry. Such an apparent discrepancy can be attributed to two reasons: first, it is much more difficult to degrade most organic compounds than to oxidize TMB (E°(ox-TMB/TMB) = 0.27 V),[22] so RCSs (·Cl and ·Cl_2^-) can oxidize TMB easily, while not noticeably degrading nor mineralizing pollutants such as atrazine and 4-nitrophenol,[7b, 7d] which can only be achieved by high energy ROSs such as ·OH. Due to the scavenging effect of Cl^- on ·OH, inhibition of pollutant degradation by ·OH is inevitable. Further, the previous pollutant degradation experiment was performed in acidic buffer (pH < 3-4), where ·OH to ·Cl conversion predominates, ensuring the low steady state concentration of ·OH (Fig. 2c). We noticed similar effects on Fe(II)-based Fenton chemistry (data not shown) with a systematic investigation undergoing.

As copper historically and currently enjoys widespread use in household water supply lines, corrosion can result in drinking water contaminated with trace amounts of copper, particularly with infrequent use as water can interact with pipes for longer durations. To demonstrate the feasibility of our colorimetric assay, we evaluated copper ions in tap water with our method followed by validation with inductively coupled plasma mass spectrometry (ICP-MS). Quantitation for both methods was obtained by calibration using the standard addition method (detailed in the Experimental session). The determined copper concentration with our method (*n* = 5) was 4.50 (±0.23) µM, consistent with that obtained with the ICP-MS, i.e., 4.26 (±0.12), (t-test 2.07; <2.31 at 95% confidence level, Fig. S20).

In summary, a highly sensitive colorimetric chemosensor was developed for Cu(II) in water samples, demonstrating promise for a variety of applications due to its simplicity, accuracy, cost- and time-effectiveness. The mechanism underlying this sensor is the copper catalyzed oxidation of chloride anions by H_2O_2, the halogen contribution to which may enhance our understanding of Cu-Fenton chemistry. Given the common presence of Cl^- and Br^- in natural marine and treated water systems, industrial processes, and other *in vivo* and *in vitro* scenarios, our results have wide implications for toxicological, environmental studies and engineering, and marine biology.

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