



Full Length Article

Formation of high-valent cobalt-oxo phthalocyanine species in a cellulose matrix for eliminating organic pollutants



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ABSTRACT

The selective elimination of recalcitrant organic pollutants in high backgrounds of complex constituents has proven a significant challenge. Inspired by the naturally occurring oxidation reactions catalyzed by metalloporphyrin-based enzymes, where the target substrates can be oxidized selectively due to the specific enzyme environment and the axial fifth ligands of metalloporphyrins, we developed a bioinspired catalytic system based on cellulosic fiber-bonded cobalt phthalocyanine for capturing and oxidizing dyes by H₂O₂ activation in the presence of high additive concentrations. In this system, the cellulosic fibers provided the amorphous regions, functioning as cavities in the same manner as the protein backbones of enzymes for the selective accessibility of dyes; cobalt phthalocyanine was introduced as the catalytic entity; and linear alkylbenzene sulfonate (one of the most widespread surfactants in industrial and domestic wastewater) was employed as the fifth ligand to help generate high-valent cobalt-oxo intermediates by the heterolytic cleavage of the peroxide O–O bond. According to detailed density functional theory calculations, the spin populations are predominantly located around the cobalt-oxo center, achieving an electrophilic attack on the electron-rich azo bond and the aromatic ring of the target model dyes.

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1. Introduction

The growing pollution in aqueous environments, which can lead to serious and long-term threats to human health, is one of the most pervasive global problems. Most discharged recalcitrant pollutants are found at trace levels in high backgrounds of readily handled and biodegradable constituents [1,2]. The elimination of these microcontaminants has always been a great challenge in water purification and has garnered increased concern worldwide [3–7]. Although many oxidation methods have been developed for eliminating organic pollutants [8–10], target pollutants are often inefficiently oxidized in the presence of organic and inorganic matrices that are a thousand to a million fold more abundant [1]. Thus, a desirable oxidation system for removing recalcitrant pollutants must be shielded from the interference of external

complicated constituents or employ these constituents to promote the elimination of the target contaminants.

Coordination complex catalysts such as metalloporphyrins (MPs) and metallophthalocyanines (MPCs) have been extensively studied as mimic enzyme catalysts for activating O₂, H₂O₂ or other peroxides to facilitate the elimination of organic pollutants [11–15]. Among the reactions using H₂O₂ as the oxidant, the generation of hydroxyl radicals (•OH) and metal-oxo-based intermediates, corresponding to the homolytic and heterolytic cleavage of the peroxide O–O bond [16–18], have proven most effective in oxidizing organic contaminants. However, in high backgrounds of complicated constituents, both of these active species inevitably react with the high-concentration and easily handled constituents or the free coordination catalysts in homogeneous systems, leading to the inefficient oxidation of low-concentration recalcitrant contaminants [19] or the oxidative destruction of the catalysts themselves [16]. As a potent H-atom abstractor, •OH is theoretically able to move freely and react with all organic matter involving high-concentration constituents, as the O–H bond of water is stronger than nearly all C–H bonds [20]. In contrast, the supported coordination complexes may exhibit good stability toward the autooxidation of

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catalytic entities when the reactions are dominated by metal-oxo based intermediates, as the coordination complex in this case has been covalently anchored to the support, thereby minimizing the possibility of autooxidation. Therefore, effective strategies for designing catalytic systems based on coordination complexes should control the reaction channels of H_2O_2 activation without generating $\bullet\text{OH}$ [20,21]; the heterolytic cleavage of the O–O bond is more desirable for the catalytic systems of coordination complexes.

Notably, in most enzymatic reactions, the target substrate is selectively captured in a region that contains active sites, followed by the rapid oxidation of the substrate. The catalytic entity, cofactors and protein backbone represent the heart of enzyme-catalyzed systems. In such systems, the protein backbone provides the steric environment for the substrate to become attached to the active sites and protects the active sites against external interference, while cofactors (such as the axial ligands in metalloporphyrin-based enzymatic reactions) determine the reaction channels [22–24]. For example, horseradish peroxidase presents peroxidase-like activity in the presence of the imidazole ligand of a histidine residue, while catalase presents catalase-like activity when presented with the phenolate ligand of a tyrosine residue. Generally, the high oxidation states of the central transition metal ions tend to become stabilized in MPs, while the phthalocyanine ligand tends to stabilize the lower oxidation states of metals, implying that high oxidation states of MPcs have stronger oxidizing abilities than those of MPs [18]. Both high-valent metal-oxo species and $\bullet\text{OH}$ have been previously reported in MPcs-activated H_2O_2 systems. However, few studies have focused on the precise control of O–O bond cleavage by introducing the fifth ligand into such a system.

In the present paper, we report a bioinspired strategy for removing organic contaminants in high backgrounds of complicated constituents as exemplified by the elimination of recalcitrant dyes from dyeing effluents, of which several billion tons are produced annually, containing massive amounts of organic and inorganic additives (concentrations 100–1000 times higher than those of dyes). These additives are necessary to improve dye penetration into fibers during the dyeing process through hydrophobic and electrostatic interactions [25]. Therefore, the degradation of dye effluents remains a significant problem and has recently attracted a great deal of attention [26–29]. In this work, a bioinspired catalytic system based on cellulosic fiber-bonded cobalt phthalocyanine (CoPc-F, Scheme S1A) was developed to eliminate dyes by H_2O_2 activation, using the enzyme mimic catalyst cobalt phthalocyanine (CoPc) as the catalytic entity. Compared with iron phthalocyanine, CoPc derivatives have better chemical stability and are more affordable [30]. Linear alkylbenzene sulfonate (one of the most widespread surfactants in dye effluents) was employed as the fifth ligand to control the reaction channel of O–O bond cleavage. As an important applied form of cellulose (the most abundant biomaterial on earth), cellulosic fibers could play the role of the protein backbones in enzymes, as their swelling properties facilitate dye penetration and their amorphous regions function as cavities that introduce catalytic entities and cofactors to generate active sites, thereby creating an enzyme-like environment with regioselectivity for organic dyes. The catalytic oxidation of azo dyes (accounting for 60%–70% of all organic dye production worldwide [31,32]) was conducted in the presence of several typical additives with high concentrations. The generated active species and oxidation pathway of C.I. Acid Red 1 (AR1, employed as the major model) are presented as determined through in situ electron paramagnetic resonance (EPR), density functional theory (DFT) calculations and ultra-performance liquid chromatography/high-definition mass spectrometry.

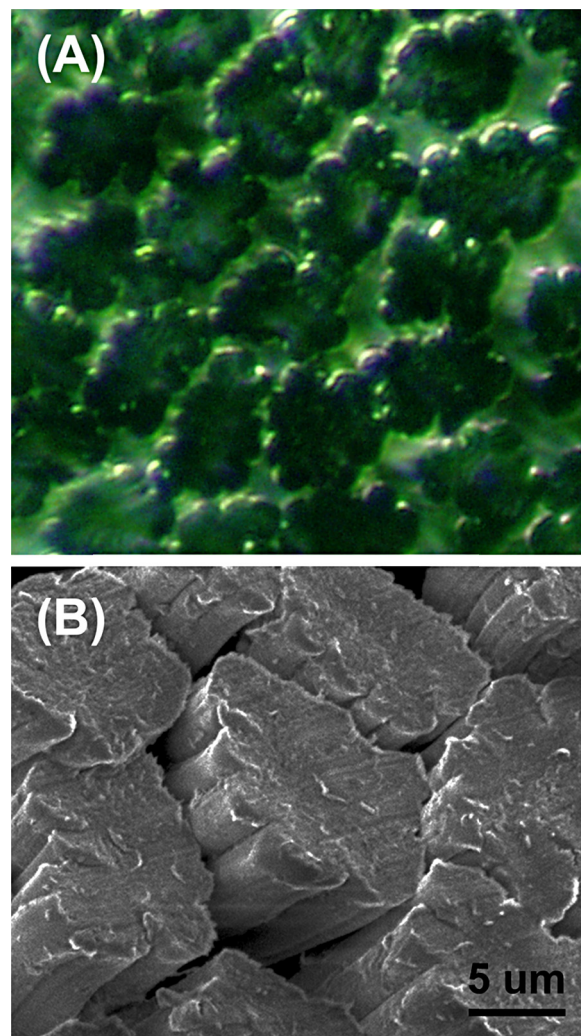


Fig. 1. Photomicrograph (A) and SEM (B) of the CoPc-F cross section.

2. Experimental

2.1. Materials

Cellulosic fibers were supplied by Fulida Co., Ltd. (Zhejiang, China). AR1 and C.I. Acid Orange 7 (AO7) were purchased from Acros and were used without further purification. C.I. Reactive Red 2 (RR2) and C.I. Reactive Blue 19 (RB19) were commercial compounds and were used without further purification. Sodium linear-dodecylbenzenesulfonate (LAS) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. The spin-trap reagent, 5,5-dimethyl-pyrroline-oxide (DMPO), was reagent grade and was purchased from Tokyo Chemical Industry Co., Ltd. Poly(ethylene glycol) (PEG, $M_w = 1000$), urea and H_2O_2 (9.7 M) were purchased from Sinopharm Chemical Reagent Co., Ltd. CoPc-F was synthesized by covalently immobilizing cobalt tetra(2,4-dichloro-1,3,5-triazine)aminophthalocyanine to the cellulosic fibers according to previously described methods [30]. Water-soluble cobalt tetra(*N*-carbonylacrylic)aminophthalocyanine (CoMPc, Scheme S1B) was synthesized by modifying cobalt tetraaminophthalocyanine with maleic anhydride according to a previously reported method [33]. The content of CoPc in CoPc-F was calculated to be $7.2 \mu\text{mol/g}$ using an atomic absorption spectrometer (Thermo Sollar M6). As seen in the photomicrograph cross section of CoPc-F (Fig. 1A, obtained using an Olympus 1X71 at $\times 400$ magnification), the green CoPc was loaded uniformly to the interiors of the cellulose fibers. The

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