Convenient colorimetric assay for Cr(VI) detection based on the nanozyme Cu-4PDA-NH₂ with oxidoreductase-like activity

Xixingchi Chen^{a,b}, Jiakang Hu^{a,b}, Xuesong Wang^{a,b}, Qing Han^{a,b}, Chen

Chen^{a,b}, Haozhe Xu^{a,b}, Chenyu Liao^{a,b}, Yalin Wang^{a,b}, Yongxin Li^{a,b,*}

^aKey Laboratory of Groundwater Resources and Environment (Jilin University), Ministry of Education, College of New Energy and Environment, Jilin University, Changchun 130021, P. R. China.

^bJilin Provincial Key Laboratory of Water Resources and Water Environment, College of New Energy and Environment, Jilin University, Changchun 130021, P. R. China.

*Corresponding author.

E-mail address: liyongxin@jlu.edu.cn

Supplementary Information

Materials and reagents

All chemicals were of analytical grade and were used without further purification. Potassium dichromate (K₂Cr₂O₇), sodium hypochlorite (NaClO), sodium nitrite (NaNO₂), sodium nitrate (NaNO₃), sodium sulfide (Na₂S), sodium sulfite (Na₂SO₃), sodium thiosulfate (Na₂S₂O₃), sodium hydroxide (NaOH), glacial acetic acid (CH₃COOH), sulfuric acid (H₂SO₄), sodium carbonate (Na₂CO₃), sodium hydrogen carbonate (NaHCO₃), sodium acetate (CH₃COONa), potassium iodide (KI), potassium nitrate (KNO₃), potassium fluoride (KF), potassium bromide (KBr), Potassium permanganateiron (KMnO₄), trichloride (FeCl₃), iron(II) chloride (FeCl₂), aluminium potassium sulfate dodecahydrate (Al₂(SO₄)₃), manganese chloride (MnCl₂), zinc chloride (ZnCl₂), magnesium chloride hexahydrate (MgCl₂), cobalt (II) chloride hexahydrate (CoCl₂), copper (II) chloride dehydrate (CuCl₂·2H₂O), potassium chloride (KCl), calcium chloride anhydrous (CaCl₂), mercury(II) chloride (HgCl₂), chromium(III) chloride hexahydrate (CrCl₃), nickel(II) chloride hexahydrate (NiCl₂), hydrochloric acid (HCl), cadmium chloride hemi(pentahydrate) (CdCl₂), 3,3',5,5'tetramethylbenzidine (TMB), 2,4-dichlorophenol (2,4-DP), 4-aminoantipyrine (4-AP), 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), tert-Butanol, 1, 4benzoquinone were purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Sodium chloride (NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 3-Amino-4-pyridazinecarboxylic Acid (4PDA-

NH₂) were purchased from Bidepharm (Shanghai, China). The solution used in the experiment was Wahaha pure water.

Characterization

PH measurements were made using a PHS-3 C pH meter (Shanghai, China) following standard protocols. Scanning electron microscope (SEM) images were acquired using a field emission scanning electron microscope JSM-7900 F (Japan). UV-visible spectroscopic measurements were performed on a Mapada UV-670 spectrophotometer (Shanghai, China) following established procedures. Centrifugal processing was performed using a HC-2062 high-speed centrifuge (Hefei, China). The Fourier transform infrared (FTIR) spectra of the materials in the range of 4000-400 cm⁻¹ were carried out on a SHIMADZU IRTracer-100 FTIR spectrometer (Japan). The zeta potential was collected from a Zetasizer Nano ZS (Malvern, UK).



Supplementary Figures

Fig. S1. (A) SEM image; (B) EDS layered images; (C-F) elemental mapping of Cu-

4PDA-NH₂. [C (pink), N (red), O (orange), and Cu (blue)]



Fig. S2. Comparison of catalytic activity between the presence and absence of Cu-4PDA-NH_{2.}



Fig. S3. (A) The effect of 1, 4-Benzoquinone and tert-Butanol on the reaction system.

(B) Catalytic reaction of Cu-4PDA-NH₂ in air, N₂, and O₂.



Fig. S4. Zeta potential measurements of Cu-4PDA-NH₂.



Fig. S5. (A) UV-vis absorption spectra of catalytic activity of ABTS in different reaction systems; (B) Chemical structure of ABTS.



Fig. S6. Comparison of TMB and ABTS catalyzed by Cu-4PDA-NH₂.



Fig. S7. Relative activity of different concentrations of Cu-4PDA- NH_2 in 500 mM NaCl and pure water.



Fig. S8. The change in catalytic activity of Cu-4PDA- NH_2 over a 7-day period.