Electronic Supplementary Information (ESI)

Cu-curcumin nanozyme for detection of Cr(VI) through off-on strategy of peroxidase mimicking activity

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Materials and reagents

Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), curcumin, thiourea ($CS(NH_2)_2$), barium chloride ($BaCl_2$), calcium chloride anhydrous ($CaCl_2$), lead chloride ($PbCl_2$) and ethylenediaminetetraacetic acid (EDTA) were purchased by Shanghai Macklin Biochemical Technology Co. Potassium chloride (KCl), 3,3′,5,5′-tetramethylbenzidine (TMB), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and p-benzoquinone (PBQ) were purchased from Shanghai Aladdin Biochemical Technology Co. Sodium chloride (NaCl), nickel(II) chloride ($NiCl_2$), zinc chloride ($ZnCl_2$), manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and L-histidine (L-his) were obtained by Anegi Chemicals & 3A (Anhui Zesheng Technology Co., Ltd.). Isopropanol (IPA) was acquired from Tianjin Komeo Chemical Reagent Co. Glycol was supplied from Tianjin Fuyu Fine Chemical Co. Hydrogen peroxide (30% H_2O_2) was received from Luoyang Chemical Reagent Factory. 8-Hydroxyquinoline (8-HQ) was purchased in Shanghai Reagent Factory. Potassium dichromate ($K_2Cr_2O_7$) was purchased from Jiaozuo Xinan Technology Co.

Instruments and characterizations

Transmission electron microscopy (TEM) images were obtained with a -TWINTMP (FEI, USA) at an accelerating voltage of 200 kV to observe the morphology of the samples. X-ray diffraction (XRD) images were acquired with an x-ray diffractometer from PANalytical (Netherlands) and were used to analyze the crystalline structure of the materials. Fourier Transform Infrared Spectroscopy (FTIR) images were obtained with Bruker Vertex 70 for obtaining information on the chemical

bonding and for qualitative analysis. X-ray Photoelectron Spectroscopy (XPS) measurements were carried out on an AXIS SUPRA (Shimadzu, Japan) for analyzing the surface composition of the material in terms of its chemical state. UV-Vis absorption spectra were recorded at room temperature by UV-2550 spectrophotometer (Shimadzu, Japan). Quantitative analysis was performed by monitoring the absorbance of oxidized TMB (oxTMB) at 652 nm.

Steady-state kinetic analysis of Cu-curcumin hybrid nanozyme

The optimal conditions had been achieved for the steady-state kinetic experiments. Either H_2O_2 concentration was set at 3 mM and the TMB concentration was adjusted, or the TMB concentration was maintained at 0.5 mM and H_2O_2 concentration was modulated. And then the absorbance was measured by time-scanning operation to obtain the corresponding initial velocity. The maximum initial velocity (V_{max}) and the Michaelis-Menten constant (K_m) were obtained according to the Lineweaver-Burk equation (1),

$$V = (V_{max} * [S]/(K_m + [S]) \quad (1)$$

Where V is the initial reaction rate, V_{max} is the maximum reaction rate, [S] is the substrate (TMB or H_2O_2) concentration, and K_m is the Michaelis constant.

Inkjet printing of paper-based devices

The paraffin was injected into a clean HP printer cartridge. The pattern of the hydrophobic barrier for the paper devices were designed using CorelDraw X6 software and printed 15 times on single side of Whatman(R) filter paper. The printed paper placed

on a hot air oven at 100 °C for 15 min, and the creation of delimited detection zones with hydrophobic paraffin barriers.

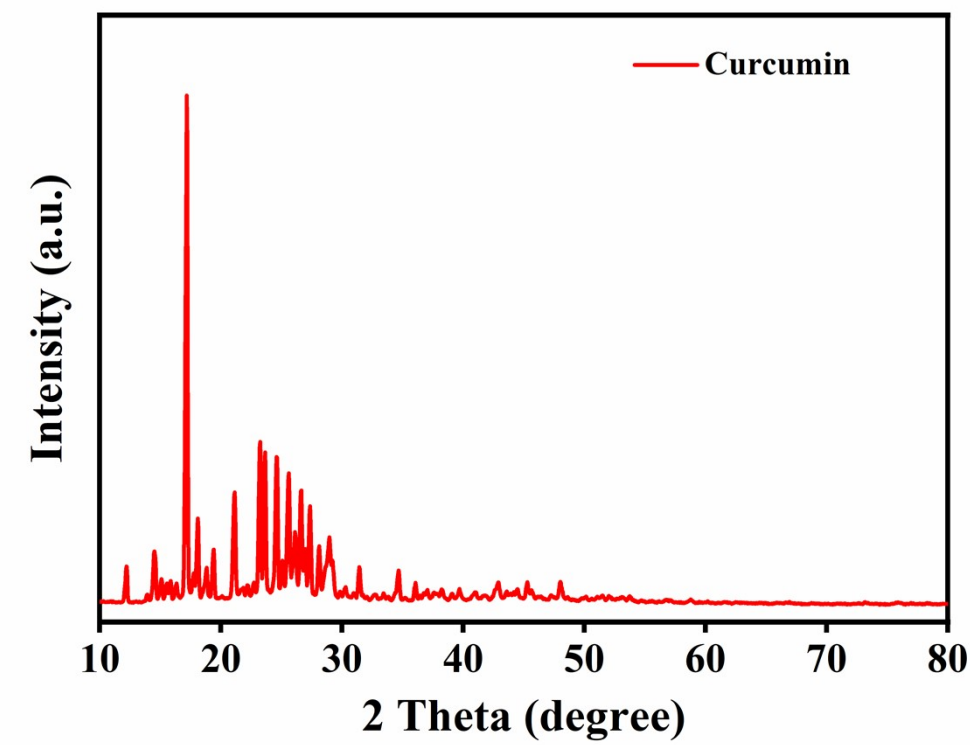

Fig. S1. The XRD spectra of curcumin.

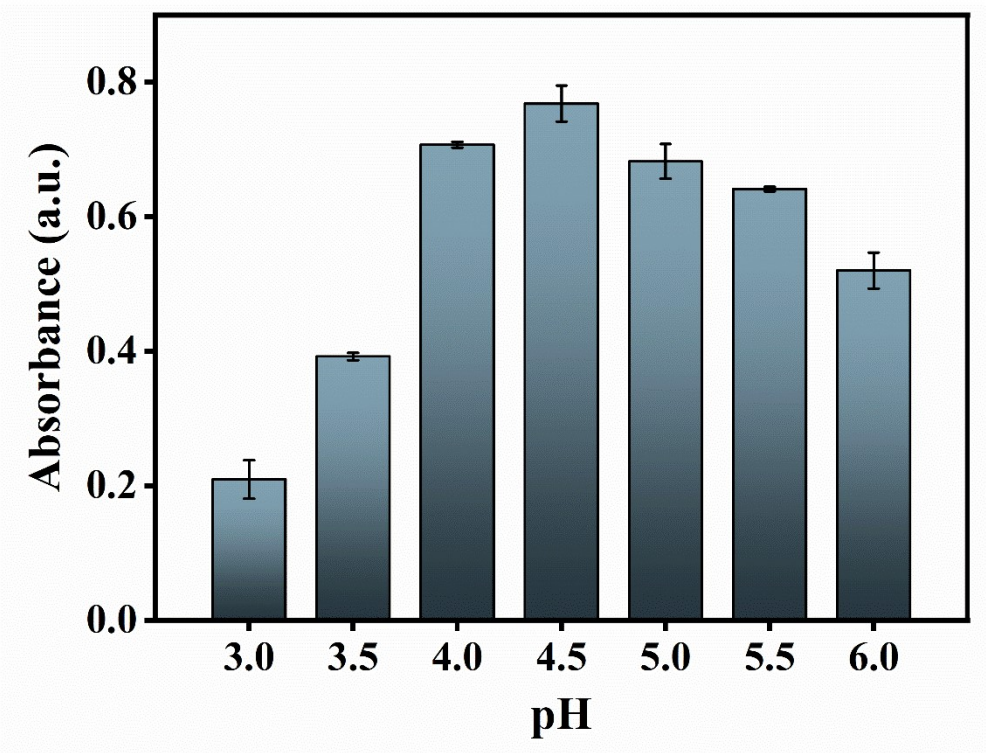

Fig. S2. The effect of pH on the peroxidase-mimic activity of Cu-curcumin nanozyme.

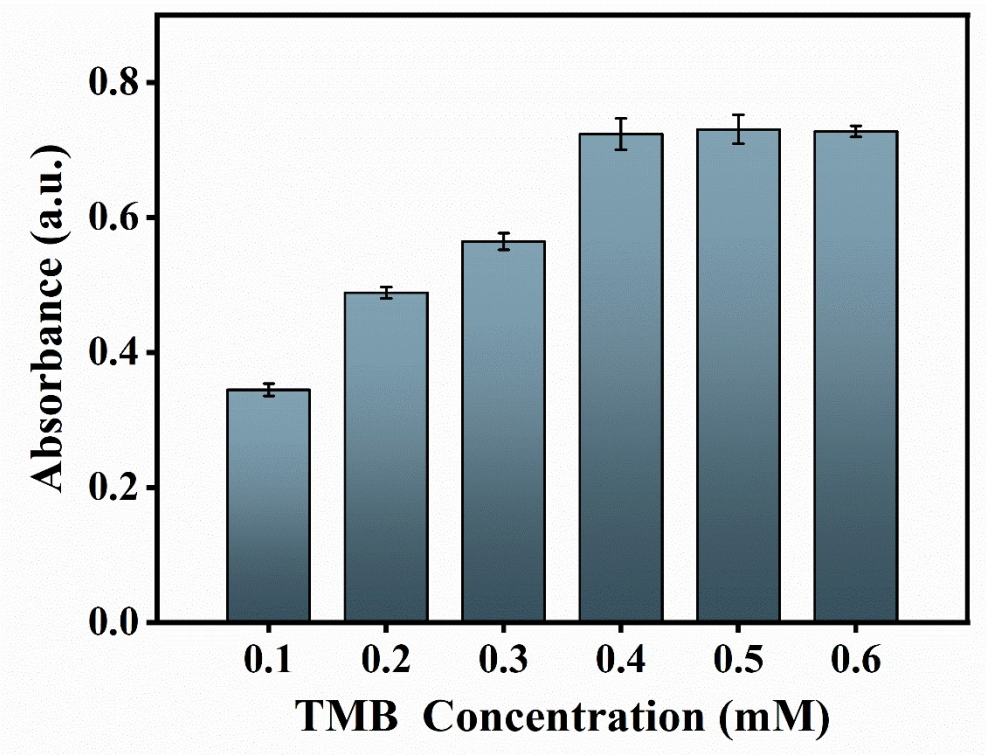

Fig. S3. The effect of TMB concentration on the peroxidase-mimic activity of Cu-curcumin nanozyme.

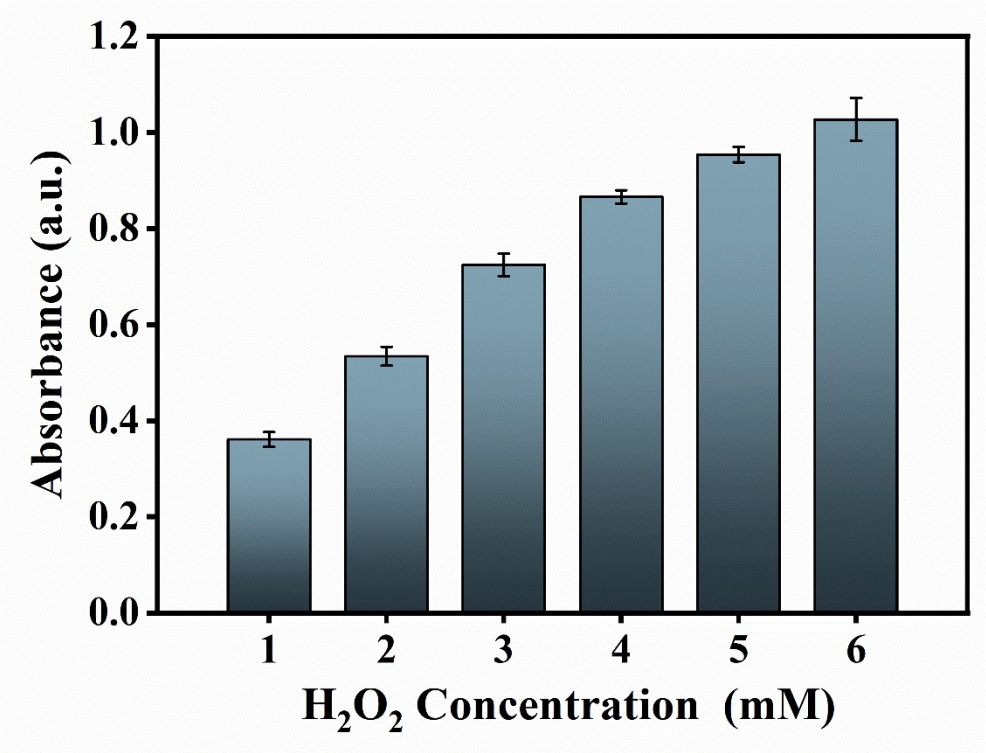

Fig. S4. The effect of H_2O_2 concentration on the peroxidase-mimic activity of Cu-curcumin nanozyme.

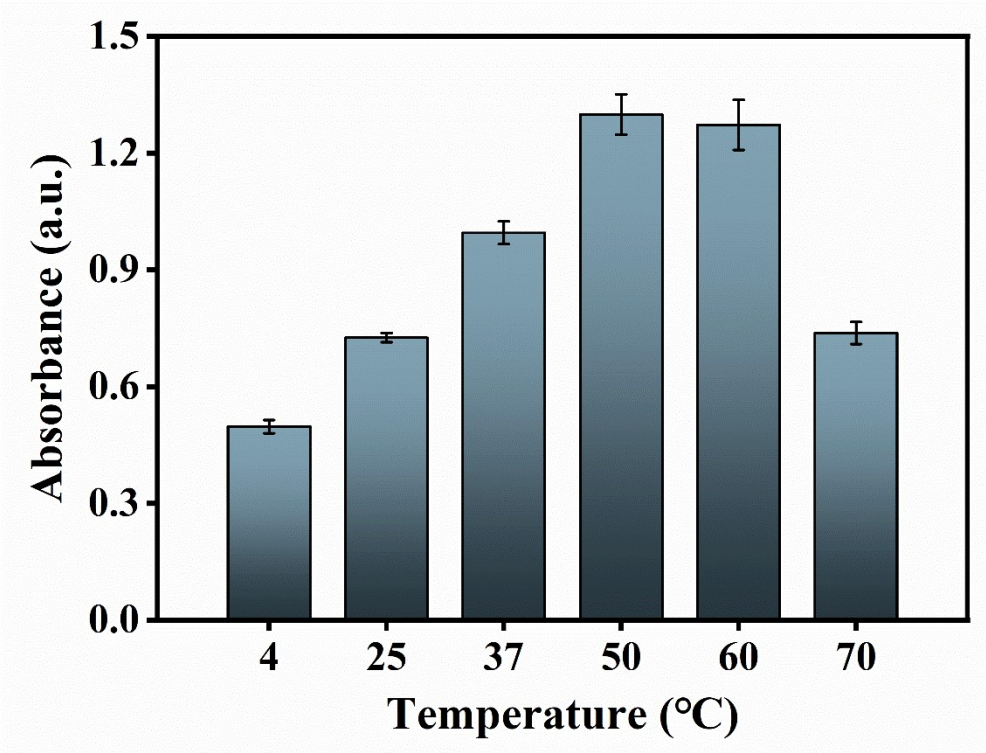

Fig. S5. The effect of temperature on the peroxidase-mimic activity of Cu-curcumin nanozyme.

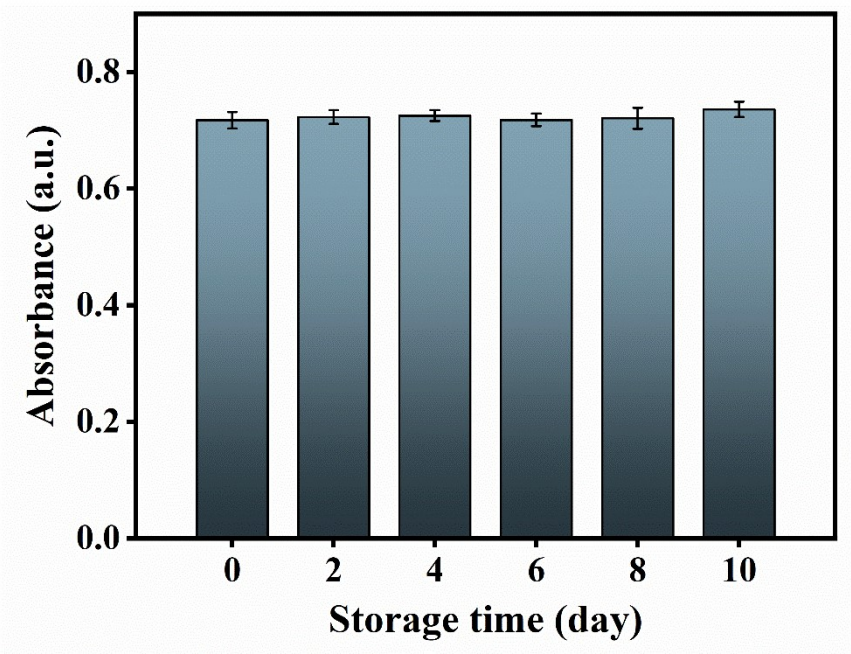

Fig. S6. The stability investigation of Cu-curcumin stored for different period (0 day, 2 day, 4 days, 6 days, 8days and 10 days).

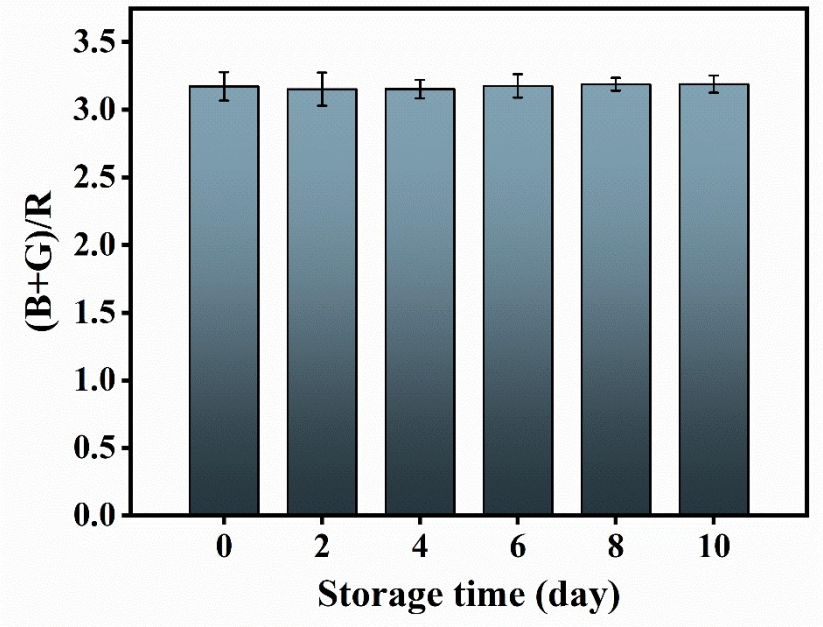

Fig. S7. The stability investigation of Cu-curcumin nanozyme-based paper sensor stored for different period for 35 μM Cr(VI) assay (0 day, 2 days, 4 days, 6 days, 8 days, and 10 days).