

Chemical redox-cycling based colorimetric and smartphone dual-channel sensing platform for phenol detection by using bifunctional copper-based metal-organic frameworks

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Abstract

A dual-functional copper-based metal-organic frameworks (Cu-MOFs) nanomaterial was designed to constructed chemical redox-cycling based colorimetric and smartphone dual-channel analysis strategy for highly sensitive determination of phenol. During the redox-cycling detection system, colorless 4-aminoantipyrine (4-AAP) was served as the color-generating substrate. In this colorimetric system, the bifunctional Cu-MOFs played two important roles. On the one hand, Cu-MOFs were exploited as nanozyme to catalyze colorless phenol and 4-AAP with H_2O_2 to initiate the oxidative coupling reaction, generating deep red quinone imine product. On the other hand, Cu^{2+} and Cu^+ of the Cu-MOFs could trigger the Fenton-like reaction-driven chemical redox-cycling amplification, resulting in more deep red quinone imine product. Drawing on the interesting findings, a highly sensitive colorimetric assay was built for visual phenol detection. There was a good linear correlation between the absorption response and phenol concentrations over the range of 10 nM to 20 μM , achieved the limit of detection (LOD) as low as 2 nM. Noteworthily, RGB color model analytical technique was introduced to realize quantitative phenol detection via smartphone combination. The obtained results were in high agreement with those derived from the colorimetric method. Moreover, it was realized phenol determination in tap and river water samples. The dual-channel sensing strategy holds great potential in measuring and monitoring phenols content for water pollution control and food safety.

Introduction

Phenol as a class of important aromatic derivatives, were extensively utilized in industrial fields including textiles, dye synthesis, pharmaceuticals, petrochemicals, and other sectors [1–3]. Nevertheless, phenolic compounds were generally characterized by high toxicity, poor biodegradability, and strong bioaccumulation potential. Therefore, phenolic compounds became one of the most harmful pollutants and might cause great harm to the ecological environment. For example, as a paradigm phenolic contaminant, phenol was susceptible to bioaccumulation via the food chain even at minimal concentrations [4]. The phenolic pollutants could permeate into the bloodstream of human cells, and pose a serious threat to the endocrine, reproductive and nervous systems, and even cause damages to human organs including the lungs and kidneys [4–6]. Moreover, the maximum allowable level of volatile phenols (as phenol) in drinking water is no more than 0.002 mg/L (about 21 nM), according to the Standards for Drinking Water Quality Standard of China (GB 5749 – 2022). Thus, it is great importance to exploit rapid and highly sensitive technologies for phenol detection.

Up to date, a variety of methodologies have been developed for phenol or phenolic compounds detection, such as chromatography [7, 8], mass spectrometry [9, 10], electrochemistry [11, 12], colorimetry [13, 14], and fluorometry [15–17]. Among these, chromatography and mass spectrometry could offer high accuracy, sensitivity and excellent phenolic compound analysis performance. However, these methods relied on large-scale precision instruments, with high costs for equipment acquisition and maintenance. Additionally, sample pretreatment and operational procedures were cumbersome, making them difficult to fulfill the requirements of rapid and on-site detection. In contrast, colorimetry

was highly favored in biological and environmental analysis due to its low cost, simplicity of operation, and directly visualizable readout [18–20].

Until now, several colorimetric sensing systems have been developed for the detection of phenol and its derivatives. For instance, polyoxometalate coordination polymers based colorimetric methods have been successfully established [21–24]. However, their synthesis required precise regulation of multiple reaction parameters and exhibited strong dependence on the reaction environment. Additionally, the catalytic activity declined significantly toward phenolic derivatives with large steric hindrance. Wang et al. proposed immobilizing cytochrome c in a UCST-pH dual-responsive polymer to impart reversible insoluble-soluble properties, enabling highly sensitive phenol detection [25]. However, the system required precise temperature control to achieve the reversible transition between micellar and soluble states. This constraint limits its practical application in on-site rapid detection scenarios. Recently, nanozymes have emerged as a research hotspot in the fields owing to their unique enzyme-mimetic activities. Various nanomaterials as nanozymes have been employed for colorimetric phenol detection, including Fe_3O_4 nanoparticles, hierarchically porous MoS_2 particles, manganese-based spinel oxides, FeCoZn triatomic nanozymes, and Sn single-atom nanozymes [5, 26–28]. However, some nanozymes suffered from insufficient detection sensitivity, making it difficult to accurately quantify low-concentration phenolic pollutants. Meanwhile, several sensing systems rely on complicated operations or specialized instruments, failing to meet the demands of on-site rapid detection. Thus, it would be great to come up with low cost and on-site colorimetric strategy for low-concentration phenol detection.

Due to its rapid spread and advances in image processing, smartphones have boosted analytical chemistry, turning them into powerful platforms for sensing applications [29, 30]. The smartphone featured portability, low cost, easy operation, and advanced imaging and computing capabilities [31, 32]. In addition, the smartphone exhibited excellent suitability for resource-limited on-site detection and reduced reliance on expensive and bulky instruments. Very recently, the integration of colorimetric assay with smartphones has established a new paradigm for biosensing or sensing, and analytical detection [33, 34]. Smartphone cameras captured color changes in chemical reactions, and RGB colorimetry with image-processing algorithms enabled rapid, direct, and accurate quantification of target analytes. This integrated strategy has shown remarkable versatility and potential in a wide range of applications, emerging as an important trend in sensing research in recent years.

In recent years, chemical redox-cycling reactions have garnered extensive attention in the field of analytical and bioanalytical chemistry due to their remarkable signal amplification capability. Such redox-cycling reaction has been successfully employed to construct various biosensors, such as photoelectrochemical biosensors, electrochemical biosensors, and fluorescent biosensors [35–38]. In our previous reported work, an ultrasensitive fluorescent split-type immunosensor was successfully developed through integrating Fenton-like reaction and chemical redox-cycling. And this sensor was used to achieve the ultrasensitive detection of interleukin-6 (IL-6) [37]. With the aid of this cyclic amplification mechanism, the response signal of the target analyte was greatly amplified.

Drawing inspiration from the above smartphone and chemical redox-cycling, a new kind of bifunctional Cu-MOFs nanomaterial was designed and fabricated colorimetric and smartphone dual-channel sensing platform for phenol detection. In the sensing system, bifunctional Cu-MOFs played two important roles. On the one hand, Cu-MOFs were exploited as nanozyme to catalyze colorless phenol and 4-AAP with H_2O_2 to initiate the oxidative coupling reaction, generating deep red quinone imine product. On the other hand, Cu^{2+} and Cu^+ of the Cu-MOFs could trigger the Fenton-like reaction-driven chemical redox-cycling strategy, resulting in more and more deep red quinone imine product. Based on the dual-path chromogenic mechanism, a colorimetric assay capable of highly sensitive and selective was established for the visual phenol detection. Meanwhile, by virtue of RGB color space analysis, a smartphone-enabled detection channel was further realized for phenol assay under sunlight. The results demonstrated a favorable linear correlation between color changes and phenol concentrations. Furthermore, the dual-channel sensing system has been extended for quantification assay of phenol content in real tap and river water samples.

Experimental

Preparation of Cu-MOFs materials

The Cu-MOFs was prepared by a one-pot method. In the preliminary step, 50 mL anhydrous methanol was adopted as the reaction medium. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.9 g) and PVP (0.4 g) were completely dissolved in this solvent to prepare a transparent and blue solution 1. Separately, 0.43 g of 1, 3, 5-benzenetricarboxylic acid (BTC) was dissolved evenly in another 50 mL portion of anhydrous methanol, forming a limpid colorless solution 2. The above colorless solution 2 was then gradually added dropwise into the blue solution 1 under gentle operation. The resultant mixture turned deep blue and gradually became turbid afterward. The obtained mixed system was further kept standing for maturation treatment at a constant temperature of 27°C , with the whole standing period maintained for 24 h. The resulting crude suspension was subjected to centrifugation at 10 000 rpm for 15 min. The collected solid sediments were rinsed repeatedly with anhydrous methanol in three cycles to eliminate residual impurities. Afterwards, the purified precipitates were transferred into a vacuum drying chamber and kept at 80°C for an entire night. Ultimately, Cu-MOFs nanoscale materials were successfully prepared.

Protocol for colorimetric detection of phenol

The detailed protocols for colorimetric detection of phenol were carried out as follows. Specifically, 20 μL Cu-MOFs (0.2 mg/mL), 20 μL H_2O_2 (5 mM), 20 μL phenol solutions at varied concentrations and 20 μL 4-AAP (2 mM) were mixed with 40 μL 50 mM Tris-HCl buffer (pH 7.5) and 80 μL ultrapure water. The resulting mixture was incubated at 37°C for 25 min. In the final step, the UV-Vis absorbance spectra of the resulting solution was measured by using a U-3900 spectrophotometer. Identical experimental approaches were employed to optimize some key reaction parameters, such as Cu-MOFs

concentrations, H_2O_2 concentrations and reaction time. Meanwhile, in order to evaluate its selectivity, phenol was replaced by phenol analogs and potential interfering substances.

Procedure for smartphone channel sensing of phenol

In the smartphone channel detection procedure, the above obtained solution was successively transferred into 8-well microplate strips. All sample images were acquired under sunlight with an iPhone 14 smartphone. Then, chromatic RGB signals of all specimens were attained with the “Color Grab” smartphone application (APP). Finally, a calibration curve suitable for the quantitative detection of phenol was established via analyzing the correlation between the R/G ratio and phenol concentrations.

Protocol of real water samples assay

Practical sample analysis adopted two categories of real water samples, namely tap water and river water gathered from Xinyang City, China. Firstly, the collected water samples underwent filtration treatment, followed by 50-fold dilution by using ultrapure water. Then phenol standard solutions at concentrations of 100.0 nM, 200.0 nM and 500.0 nM were individually spiked into the pretreated diluted water samples. Finally, UV-Vis absorption measurement was performed and the intensity at 505 nm was recorded.

Results and discussion

Principle of dual-channel sensing platform

Scheme 1 illustrated the principle of chemical redox-cycling based colorimetric and smartphone dual-channel sensing platform by using bifunctional Cu-MOFs nanomaterials. The bifunctional Cu-MOFs played two important roles in this study. One was that Cu-MOFs were exploited as nanozyme to catalyze the colorless phenol and 4-AAP with H_2O_2 to initiate the oxidative coupling reaction, generating deep red quinone imine product. The other was that Cu^{2+} and Cu^+ of the Cu-MOFs could trigger the Fenton-like reaction-driven chemical redox-cycling amplified strategy. In the redox-cycling system, on the one hand, Cu^{2+} ions could oxidize phenol to produce Cu^+ ions and quinoid radicals intermediates. On the other hand, the produced Cu^+ ions were reacted with the introduced H_2O_2 to induce a Fenton-like reaction to form Cu^{2+} ions and $\cdot\text{OH}$ groups, which triggering a redox cycle. Both the produced $\cdot\text{OH}$ groups and recycled Cu^{2+} ions took place the oxidation reaction of phenol to generate quinoid radicals intermediates. The dual-pathway generated quinoid radicals intermediates further proceed with 4-AAP to induce the oxidative coupling reaction, and form more deep red quinone imine products, which had distinct characteristic absorption intensity at 505 nm. Accordingly, the quantitative detection of phenol can be achieved by virtue of the absorbance response differences of chromogenic method. Meanwhile, by using RGB color space analysis, a smartphone sensing platform was developed for on-site rapid and

quantitative detection of phenol. As a result, a colorimetric and smartphone dual-channel sensing platform was established for sensitive and selective determination of phenol on the basis of bifunctional Cu-MOFs mediated chemical redox-cycling.

Scheme 1 Schematic illustration of colorimetric and smartphone dual-channel sensing platform for phenol detection.

Characterization of Cu-MOFs

Morphology of synthesized Cu-MOFs was initially analyzed by using scanning electron microscopy (SEM) characterization. Figure 1A indicated that the prepared Cu-MOFs exhibited a regular octahedral structure. And the SEM images revealed that the synthesized Cu-MOFs material had uniform morphological characteristics with no obvious agglomeration. Figure 1B displayed the average size of the synthesized Cu-MOFs was $1.35 \pm 0.31 \mu\text{m}$, showing the uniform size distribution. In addition, X-ray diffraction (XRD) analysis was performed to verify the successful synthesis and intact crystal structure of the Cu-MOFs. As showed in Fig. 1C, a series of sharp characteristic diffraction peaks appeared in the XRD pattern. A distinct well-recognized crystalline diffraction peak was observed at 12° , and no obvious impurity peaks were detected. This was consistent with the standard XRD pattern of Cu-MOFs reported in the literature [39], confirming that the synthesized Cu-MOFs material had excellent crystallinity and high purity. The full XPS spectrum (Fig. 1D) showed four characteristic peaks corresponded to the characteristic binding energies of Cu 2p, O 1s, N 1s, and C 1s, respectively. As indicated in inset of Fig. 1D, high-resolution XPS spectrum of Cu 2p peaks present at 954.48 eV and 934.58 eV was for Cu (II), as well as 952.68 eV and 932.98 eV was for Cu (I). It confirmed the as-synthesized Cu-MOFs were composed of a mixture of Cu^+ and Cu^{2+} species. Moreover, the presence of two observed satellite peaks could be attributed to electronic shakeup processes. Significantly, the presence of $\text{Cu}^+/\text{Cu}^{2+}$ redox pairs opened up opportunity to employ Cu-MOFs in triggering a Fenton-like reaction, thereby enabling a chemical redox-cycling amplified colorimetric system.

Evaluation of chemical redox-cycling based colorimetric system

In order to test the feasibility of the chemical redox-cycling colorimetric strategy, UV-Visible absorption spectra was performed by investigating the reaction systems with different compositions. As shown in Fig. 2A, when the reaction system contained only 500 μM H_2O_2 , 100 μM phenol, and 200 μM 4-AAP (H_2O_2 -4-AAP-phenol system, curve a), no significant characteristic absorption peak was detected at 505 nm. It indicated that H_2O_2 alone could not induce the oxidation reaction of 4-AAP and phenol to produce the quinone imine product, which with characteristic absorption at 505 nm. Similarly, the system composed of 100 μM Cu^{2+} , 100 μM phenol, and 200 μM 4-AAP exhibited only a weak absorption signal at 505 nm (Cu^{2+} -4-AAP-phenol system, curve b in Fig. 2A). It was also confirmed that the chemical oxidation of phenol by Cu^{2+} alone was insufficient to generate an adequate amount of quinoid radicals

intermediate for coupling reaction with 4-AAP. As expected, when Cu^{2+} and H_2O_2 coexisted (Cu^{2+} - H_2O_2 -4-AAP-phenol system), a remarkable absorption peak was observed at 505 nm (curve c in Fig. 2A). It was demonstrated that the Cu^{2+} - H_2O_2 -4-AAP-phenol system successfully triggered the chemical redox-cycling via Fenton-like reaction to produce a large number of quinoid radicals intermediates, following reacted with 4-AAP to generate more and more deep red quinone imine product, and leading to a strong absorption intensity at 505 nm. Moreover, the kinetic behaviors of the three reaction systems were also investigated. Specifically, the dependence of the absorption intensity on reaction time was explored. As shown in Fig. 2B, both H_2O_2 -4-AAP-phenol system and Cu^{2+} -4-AAP-phenol system did not lead to obvious absorption intensity at 505 nm (curve a and b), with increasing reaction time from 0 to 40 min. Magically, the absorption intensity of Cu^{2+} - H_2O_2 -4-AAP-phenol system was significantly enhanced within 5 min. It was confirmed that the oxidation rate of phenol was remarkably improved in the Cu^{2+} - H_2O_2 -4-AAP-phenol system.

To ensure the excellent performance of chemical redox-cycling based colorimetric system, some key reaction conditions were systematically optimized, including pH value, Cu^{2+} concentrations, and H_2O_2 concentrations. At first, the effect of different pH values on absorption intensity at 505 nm of the system was investigated, by using Tris-HCl buffer solution as the reaction medium. As shown in Fig. S1, the maximum absorption intensity was observed at pH 7.5. It indicated that pH 7.5 was most favorable for the chemical redox-cycling system. Therefore, Tris-HCl buffer solution with pH 7.5 was determined as the optimal reaction medium. Secondly, the effect of Cu^{2+} concentrations on absorption intensity was shown in Fig. S2. With Cu^{2+} concentrations increasing progressively across the range of 0 to 100 μM , the absorption intensity of the system was significantly enhanced. When the Cu^{2+} concentrations were exceeded 100 μM , the absorption intensity was no longer improved, even showed decreasing trend. Thirdly, the dependence of the absorption intensity on H_2O_2 concentrations was shown in Fig. S3. As the H_2O_2 concentrations varied in the range of 0 to 500 μM , the absorption intensity showed a continuous enhancement and reached saturation at 500 μM . After that, with the further increasing H_2O_2 concentrations, no obvious change was observed in the absorption intensity.

Feasibility and optimization of Cu-MOFs based colorimetric system for phenol

Inspired above Cu^{2+} -mediated chemical redox-cycling system, Cu-MOFs was explored to construct colorimetric platform for phenol detection by dual-path signal conversion strategy. The feasibility of Cu-MOFs based colorimetric system for phenol assay was firstly investigated. As shown in Fig. 3A (curve a), no characteristic absorption peak of the quinone imine product was detected at 505 nm when the system was absence of phenol. It indicated that the oxidative coupling reaction did not occur. However, a distinct absorption peak was observed at 505 nm while phenol was present in this colorimetric system (curve b in Fig. 3A). The results confirmed that Cu-MOFs could efficiently trigger the formation of deep

read quinone imine product. Compared with the Cu^{2+} -mediated chemical redox-cycling system alone (curve c in Fig. 2A), the absorption signal of the Cu-MOFs based colorimetric system was stronger under the same conditions. It suggested that Cu-MOFs could also be used as nanozyme to catalyze phenol and 4-AAP to induce oxidative coupling reaction, except for Cu^{2+} -triggered chemical redox-cycling. Additionally, the kinetic behaviors of the Cu-MOFs based colorimetric system were also studied through collecting the absorption intensity value at 505 nm under different incubation time. As displayed in Fig. 3B (curve b), a remarkable absorption increasement in the 505 nm was observed with incubation time increasing from 0 to 25 min. And it became stable after 25 min (curve b in Fig. 3B).

Figure 3. (A) UV-Visible absorption spectra of the Cu-MOFs based colorimetric system in the absence (a) and presence of 100 μM phenol. (B) Relationship between reaction time and absorbance at 505 nm in the absence (a) and presence of 100 μM phenol.

Some key reaction conditions of Cu-MOFs based colorimetric system were evaluated and optimized, such as Cu-MOFs concentrations and H_2O_2 concentrations. As shown in Fig. 4A, with the increasement of Cu-MOFs concentrations from 0 to 0.02 mg/mL, a gradual absorption enhancement in the 505 nm was obtained. When Cu-MOFs concentration was exceeded 0.02 mg/mL, the absorption intensity was no longer increased and even decreased. And the absorption intensity reached a maximum at 0.02 mg/mL. Therefore, 0.02 mg/mL of Cu-MOFs concentrations was determined as the optimal concentration. The effect of H_2O_2 concentrations on the absorption signal response was shown in Fig. 4B. As the concentration increased from 0 to 500 μM , the absorption intensity continuously increased and reached plateau at 500 μM . Therefore, 500 μM of H_2O_2 concentrations was determined as the optimal concentration.

Figure 4. (A) Relationship between concentration of Cu-MOFs and absorbance intensity. (B) Absorbance intensity versus the H_2O_2 concentrations.

Cu-MOFs based colorimetric channel for phenol detection

Thanks to chemical redox-cycling strategy mediated bifunctional Cu-MOFs, a new colorimetric channel was established to realize phenol quantitative detection. UV-Vis absorption spectra of the system, recorded at varying concentrations of phenol, was presented in Fig. 5A. And the absorption signal at 505 nm of the system was observed to increase gradually with the phenol concentrations range from 0.01 μM to 200 μM . Quantitative analysis showed that a good linear correlation between phenol concentrations from 10 nM to 20 μM and absorption intensity was observed ($R^2 = 0.9935$, Fig. 5B). The calculated limit of detection (LOD) of the method was determined to be 2 nM, derived from the 3σ rule ($S/N = 3$). Compared with the reported colorimetric phenol detection technologies, the analytical performance of the method was greatly improved, with LOD reduced by 1–3 orders of magnitude (shown in Table 1) [5, 6, 17, 40–42]. Furthermore, as the phenol concentrations increased from 0 to 200 μM , it caused the color to shift gradually from colorless to pink and finally to deep red. A distinct concentration-dependent color gradient was observed in Fig. 5C. It provided a foundation for visual quantitative

determination of phenol by naked-eye. Moreover, RGB color intensity data captured via the “Color Grab” APP was found to be highly consistent with the visual color evolution pattern (Fig. 5D).

Figure 5. (A) UV-Visible absorption spectra of sensing system in the presence of different concentrations of phenol. (B) Linear correlation between absorption intensity at 505 nm and phenol concentrations. (C) Optical photographs of the colorimetric system responding to different phenol concentrations. (D) RGB color with varying concentrations of phenol via the “Color Grab” application.

Table 1
Comparison of different colorimetric methods for phenol detection.

Sensing materials	Linear range (μM)	LOD (nM)	References
Fe ₃ O ₄ NPs	1.67–1200	3790	[5]
Co-MOF-74 based Co ₃ O ₄	0.5–300	1020	[6]
N, Cu-CQDs	1-100	120	[17]
UiO-67-Cu ²⁺	0.1–200	61	[40]
Cu-Mn MOF	1–40	159	[41]
CAT-Fe ₃ O ₄ @ZIF-8	5-100	700	[42]
Cu-MOFs	0.01-20	2	this work

In order to assess the selectivity of this sensing platform for phenol detection, the response behaviors of phenol analogs and potential interfering substances were also investigated. Firstly, the ability to distinguish phenol analogs was evaluated, including *o*-aminophenol, *o*-nitrophenol, resorcinol, 3-aminophenol, *p*-nitrophenol, and phenol. As shown in Fig. 6A, significant differences were observed in the characteristics of UV-Vis absorption peaks generated by different phenolic compounds in the colorimetric system. Effective discrimination of structural analogs could be achieved through the specificity of absorption spectra. Meanwhile, obvious color differences were presented among various phenol analogs, only target phenol could produce deep red color (Fig. 6B). This provided a visual basis for the naked-eye identification of different phenolic pollutants. As illustrated in Fig. 6C, a smartphone device was utilized to capture and process images of colorimetric system comprising different phenol analogs. The derived RGB color data exhibited excellent consistency with the results of visual characterization.

Figure 7. (A) Absorbance of Cu-MOFs based colorimetric channel in the presence of phenol and potential interfering substances. (B) Photographs of phenol and potential interfering substances detected by colorimetric channel. (C) RGB color of phenol and potential interfering substances.

The influence of potential interfering substances on phenol detection was further evaluated. As shown in Fig. 7A, when phenol was added into the Cu-MOFs based colorimetric system, a strong UV-Vis

absorption peak was appeared at 505 nm. However, no obvious absorption signal was generated by other interfering substances with the same concentration. Color change assays showed that the system with phenol was significantly converted from colorless to deep red, while no noticeable color effect was caused by other interfering substances (Fig. 7B). Image collection and processing of colorimetric systems with other interfering substances were synchronously performed via a smartphone, with corresponding RGB color data shown in Fig. 7C. The results indicated that the colorimetric method exhibited good selectivity for phenol. In a word, it could effectively resist the interference from structural analogs and common coexisting substances.

Cu-MOFs based smartphone channel for phenol detection

To address the practical requirement for on-site and rapid phenol analysis, Cu-MOFs based smartphone readout channel was developed for visual detection of phenol. Under sunlight irradiation conditions, images of colorimetric system with different phenol concentrations were recorded using an iPhone 14 smartphone loaded with the “Color Grab” APP. Subsequent quantitative analysis was performed following transformation of the obtained image data into RGB numerical values. Corresponding RGB images of the reacted solution captured by smartphone were shown in Fig. 8A and 8B. In the RGB detection channel, a bimodal linear correlation between the R/G ratio and phenol concentrations was obtained across the 0.01–20 μM range. Specifically, for phenol concentrations between 0.01 and 0.5 μM , the linear relationship equation was fitted as $Y_1 = 1.1355 + 0.2123C_{\text{phenol}}$, $R^2 = 0.9857$ (showed in Fig. 8C). For the concentration range of 0.5–20 μM , the linear fitting equation was established as $Y_2 = 1.2374 + 0.0124C_{\text{phenol}}$, $R^2 = 0.9965$ (displayed in Fig. 8D). Based on this linear relationship, the limit of detection (LOD) of the smartphone channel for phenol was 3 nM. It confirmed the constructed smartphone readout channel platform could meet the practical needs for its on-site rapid detection.

Figure 8. (A) RGB detection channel within phenol concentration from 0.01 to 0.5 μM . (B) RGB detection channel within phenol concentration from 0.5 to 20 μM . (C) Linear plot of RGB color value (R/G) versus phenol concentration from 0.01 to 0.5 μM . (D) Linear plot of RGB color value (R/G) versus phenol concentration from 0.5 to 20 μM .

Analysis of phenol in real water samples

To verify the practical application feasibility and reliability of this colorimetric sensing system, spiked recovery experiments of phenol were carried out in real water (tap and river water) samples. After pretreatment, the water samples were diluted by 50-fold. Phenol standard solutions at final concentrations of 100.0 nM, 200.0 nM, and 500.0 nM were added separately. The established Cu-MOFs based colorimetric channel detection method was employed for phenol quantitative analysis. The experimental results were presented in Table 2. The spiked recoveries in real water samples fell within range of 92.8% to 109.1%. The relative standard deviations (RSD) were no more than 6.5%. These results indicated that the method exhibited good accuracy and precision. It could meet the requirements for phenol quantitative analysis in real tap water and river water samples.

Table 2
Recovery of phenol detection in tap water, river water samples (n = 3).

Samples	Added (nM)	Found (nM)	Recovery (%)	RSD (%)
	0	-	-	-
	100.0	92.81	92.8	5.7
Tap water	200.0	206.9	103.5	4.8
	500.0	486.2	97.2	4.3
	0	-	-	-
River water	100.0	109.1	109.1	5.3
	200.0	215.5	107.8	6.5
	500.0	518.4	103.7	4.6

Conclusions

In conclusion, a novel dual-channel sensing platform combining colorimetric and smartphone channels, was developed for phenol detection with high sensitivity and selectivity, by using bifunctional Cu-MOFs mediated chemical redox-cycling strategy. The bifunctional Cu-MOFs played two important roles in this study. Compared with other reported colorimetric methods, the analytical performance of the assay was greatly improved, with LOD reduced by 1–3 orders of magnitude. By color changes from colorless to deep red, a smartphone based RGB color model analytical method was developed for a on-site visual quantification detection of phenol. The dual-channel method offered simplicity, ease of operation, low-cost and reliability, and successfully applied for phenol assay in real water samples. Thanks to the Cu-MOFs mediated chemical redox-cycling, the dual-channel sensing strategy holds great potential in quantifying and monitoring phenols for water pollution control and food safety.

Declarations

Ethical approval

This research did not involve human or animal samples.

AI disclosure

The authors declare that no Artificial Intelligence (AI) tools were used in the preparation of the manuscript, including figures and graphical abstracts.

Conflict of interest

The authors declare no competing interests.

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Author Contribution

Qian-Yue Xu: Methodology, Formal analysis, Data curation, Investigation, Visualization, Writing - original draft. Si-Yu Xie: Methodology, Formal analysis, Data curation, Investigation. Hai-Bo Wang: Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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Data availability

No datasets were generated or analysed during the current study.

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Figures

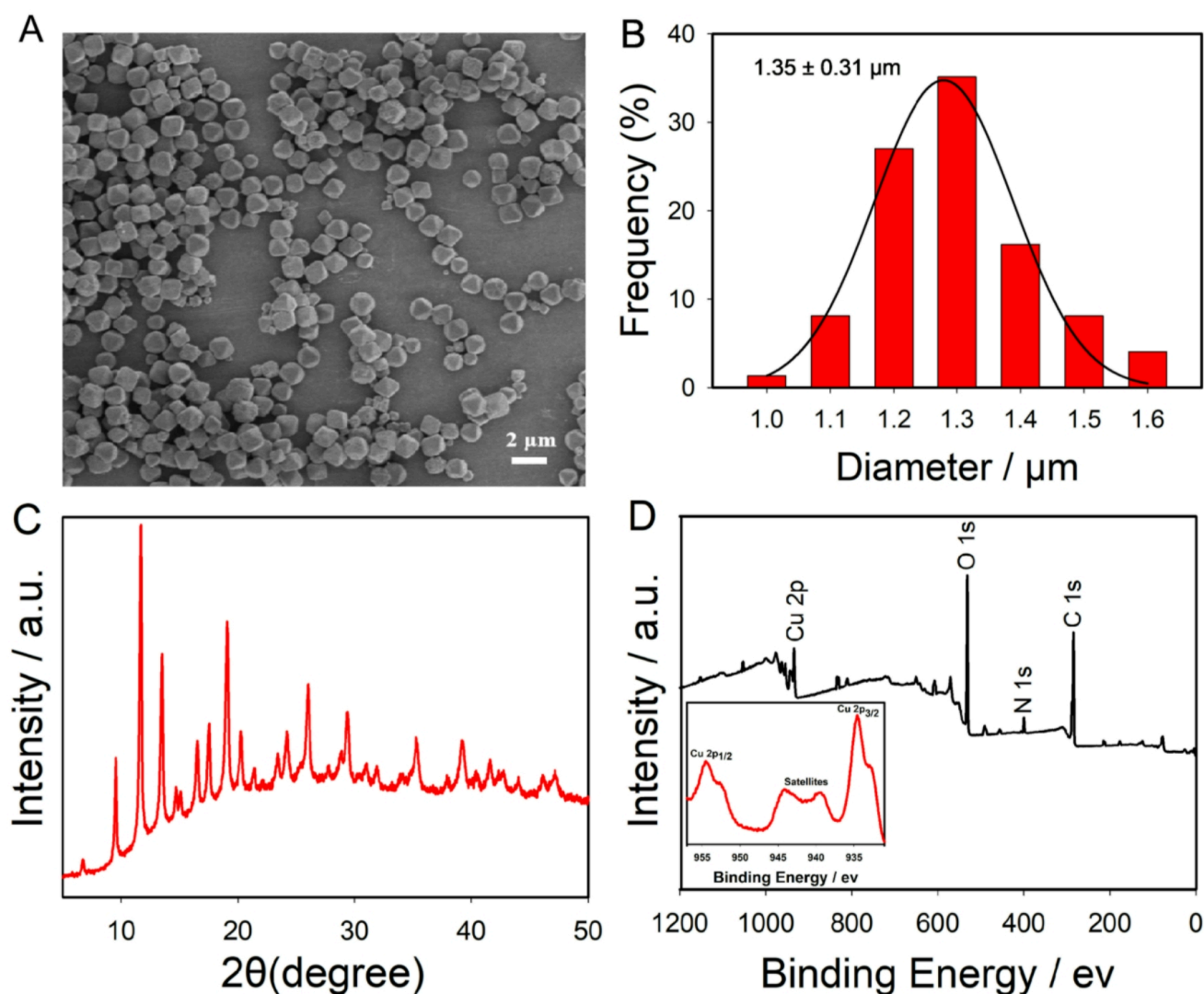


Figure 1

(A) SEM image of Cu-MOFs. (B) Size distribution of Cu-MOFs. (C) XRD pattern of Cu-MOFs. (D) XPS spectra of the Cu-MOFs. Inset is high resolution XPS of Cu 2p.

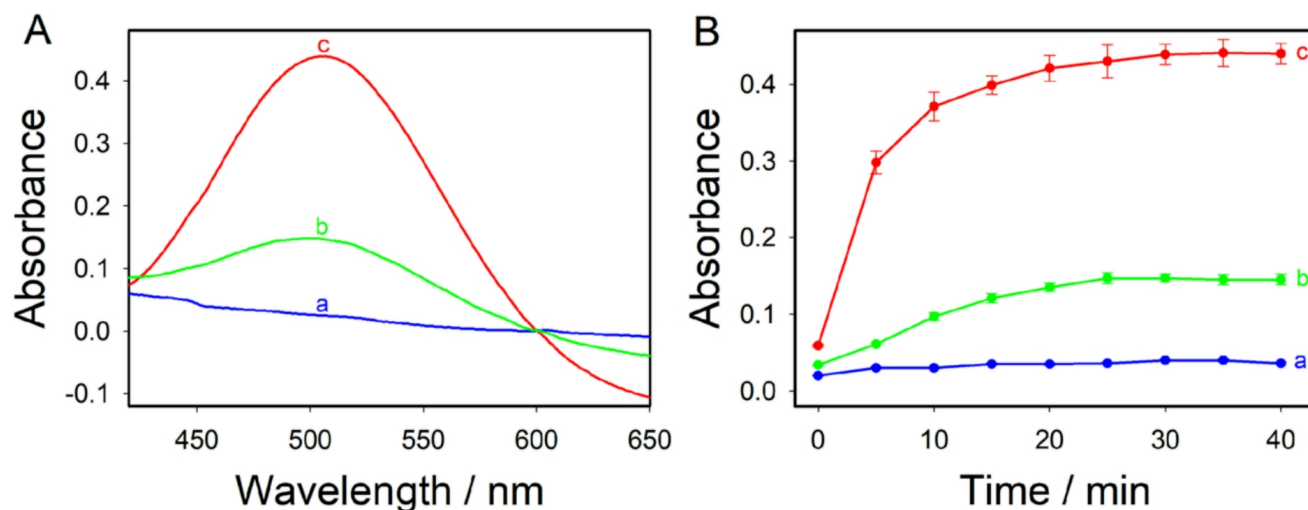


Figure 2

(A) UV-Visible absorption spectra of the 500 μM H_2O_2 + 100 μM phenol + 200 μM 4-AAP (a), 100 μM Cu^{2+} + 100 μM phenol + 200 μM 4-AAP (b), 100 μM Cu^{2+} + 500 μM H_2O_2 + 100 μM phenol + 200 μM 4-AAP (c). (B) The kinetic behaviors of 500 μM H_2O_2 + 100 μM phenol + 200 μM 4-AAP (a), 100 μM Cu^{2+} + 100 μM phenol + 200 μM 4-AAP (b), and 100 μM Cu^{2+} + 500 μM H_2O_2 + 100 μM phenol + 200 μM 4-AAP (c).

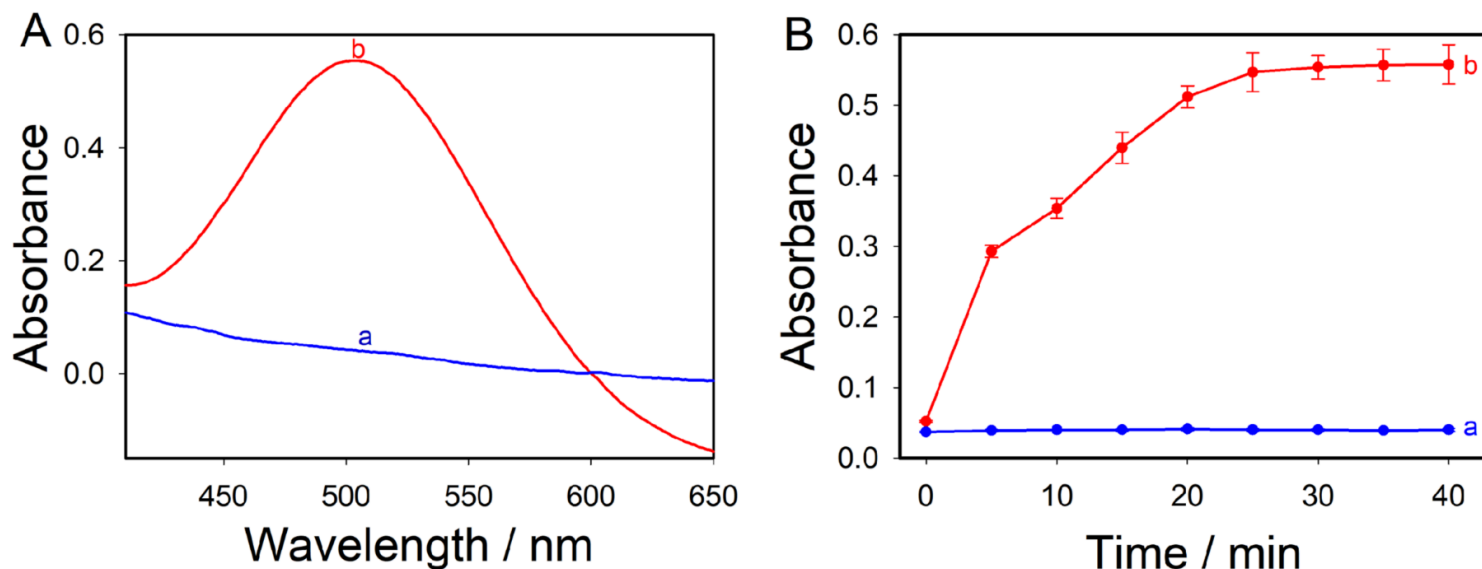


Figure 3

(A) UV-Visible absorption spectra of the Cu-MOFs based colorimetric system in the absence (a) and presence of 100 μM phenol. (B) Relationship between reaction time and absorbance at 505 nm in the absence (a) and presence of 100 μM phenol.

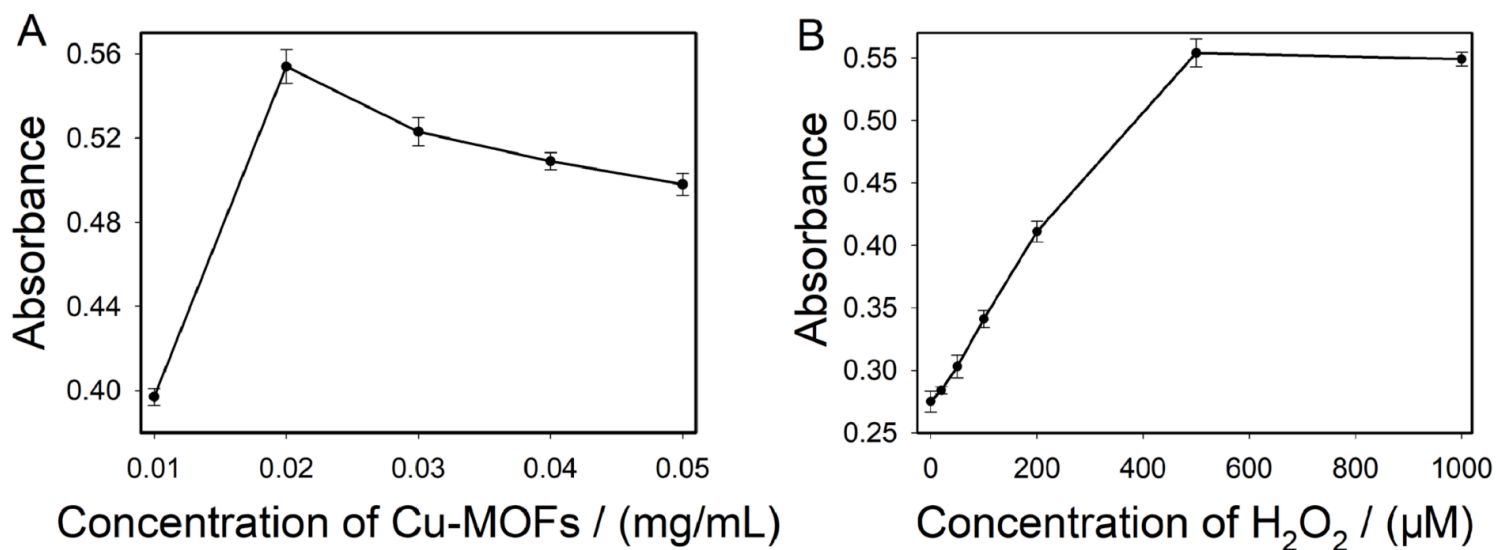


Figure 4

(A) Relationship between concentration of Cu-MOFs and absorbance intensity. (B) Absorbance intensity versus the H_2O_2 concentrations.

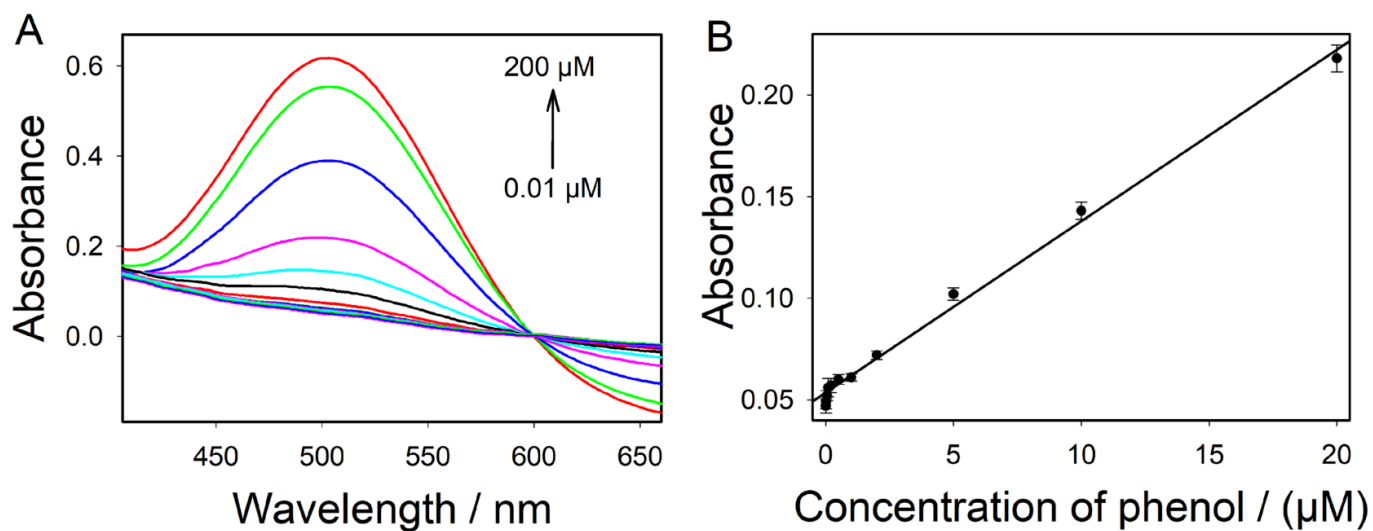


Figure 5

(A) UV-Visible absorption spectra of sensing system in the presence of different concentrations of phenol. (B) Linear correlation between absorption intensity at 505 nm and phenol concentrations. (C) Optical photographs of the colorimetric system responding to different phenol concentrations. (D) RGB color with varying concentrations of phenol via the “Color Grab” application.

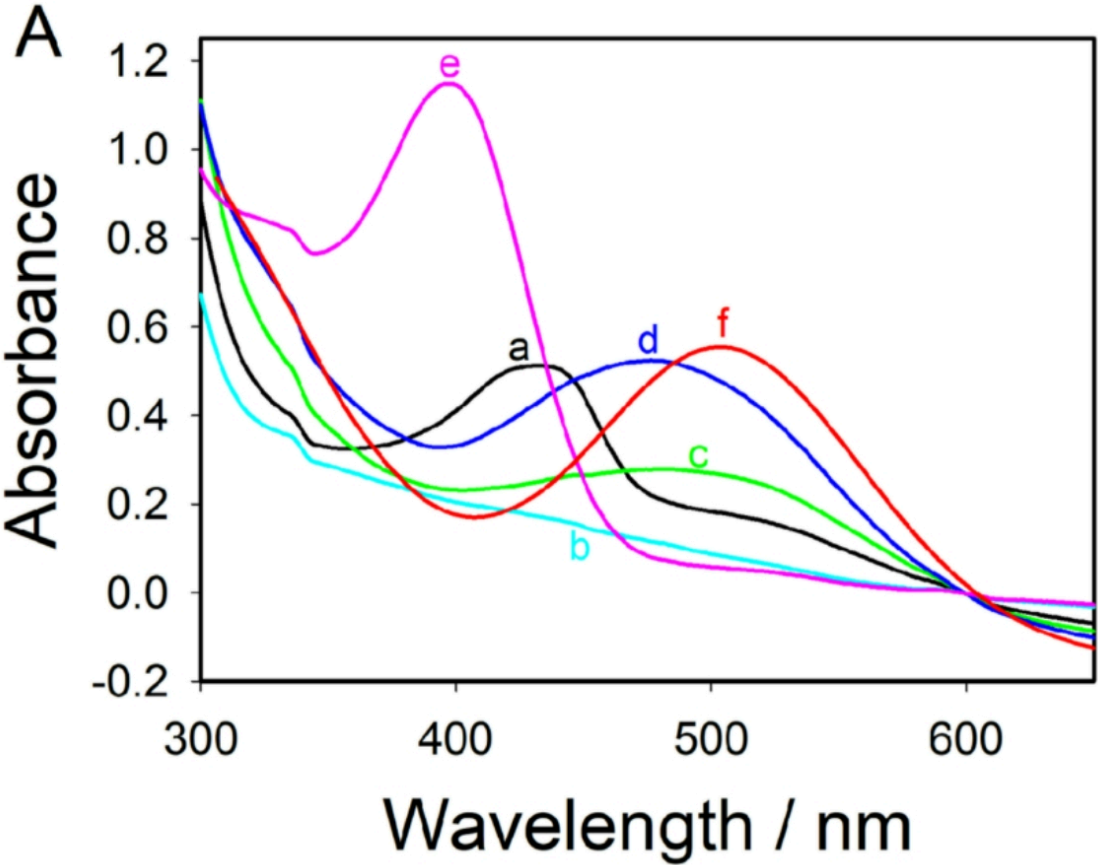


Figure 6

(A) The UV-Visible absorption spectra of Cu-MOFs based colorimetric channel in the presence of phenol and its analogues, including *o*-aminophenol (a), *o*-nitrophenol (b), resorcinol (c), 3-aminophenol (d), *p*-nitrophenol (e), phenol (f). (B) Photographs of phenol and its analogues detected by colorimetric channel. (C) RGB color of phenol and its analogues.

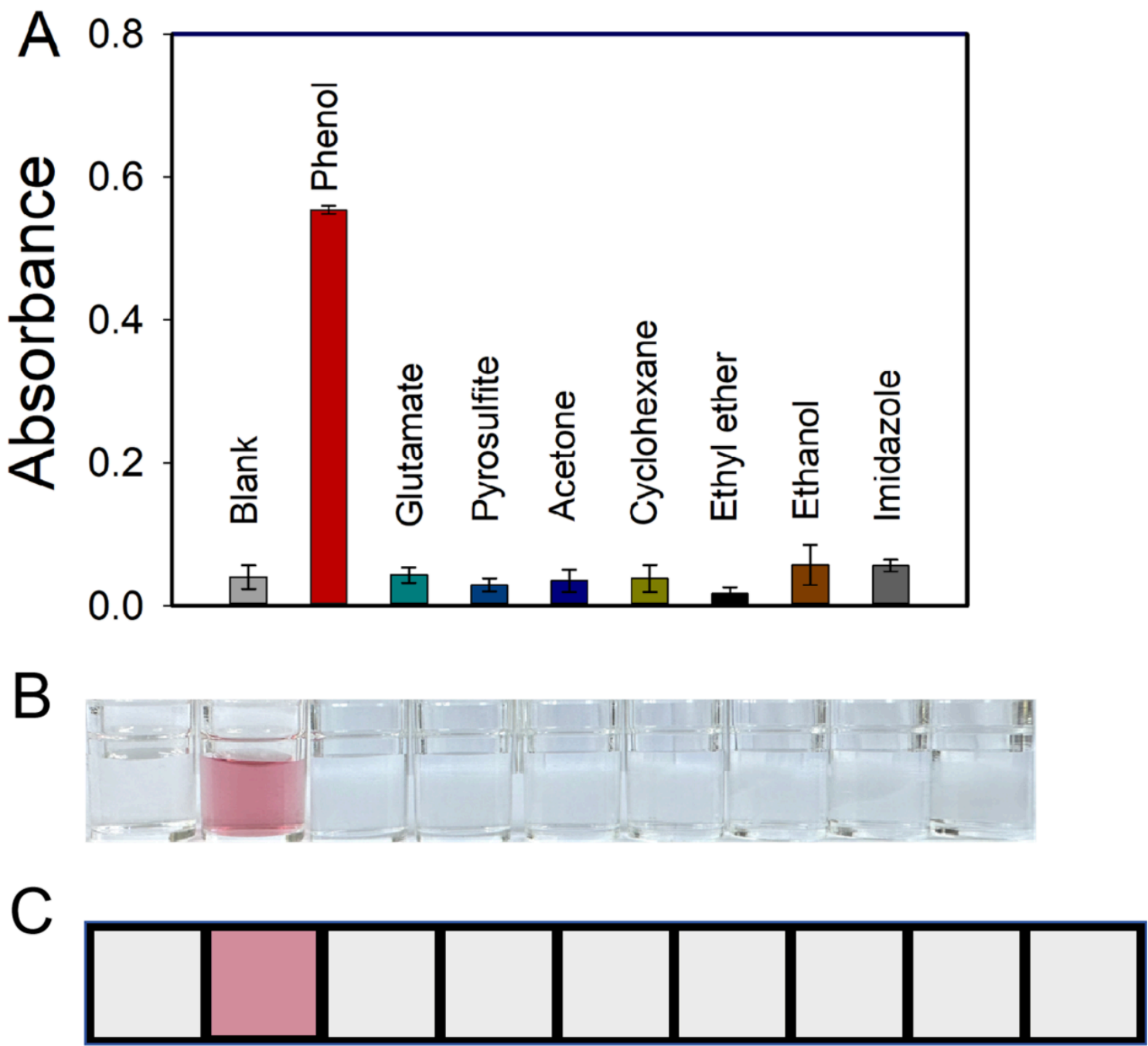


Figure 7

(A) Absorbance of Cu-MOFs based colorimetric channel in the presence of phenol and potential interfering substances. (B) Photographs of phenol and potential interfering substances detected by colorimetric channel. (C) RGB color of phenol and potential interfering substances.

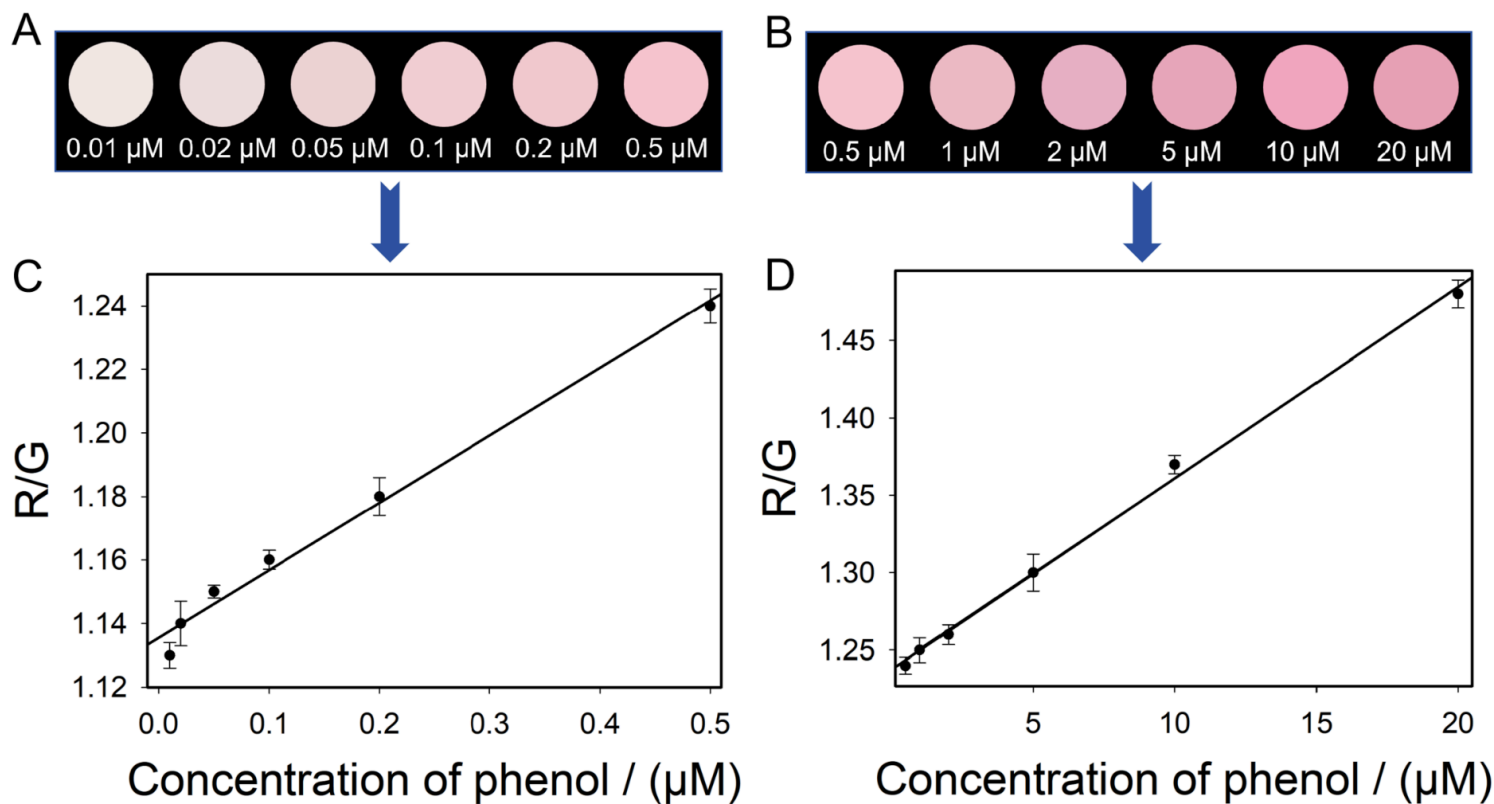


Figure 8

(A) RGB detection channel within phenol concentration from 0.01 to 0.5 μM . (B) RGB detection channel within phenol concentration from 0.5 to 20 μM . (C) Linear plot of RGB color value (R/G) versus phenol concentration from 0.01 to 0.5 μM . (D) Linear plot of RGB color value (R/G) versus phenol concentration from 0.5 to 20 μM .

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