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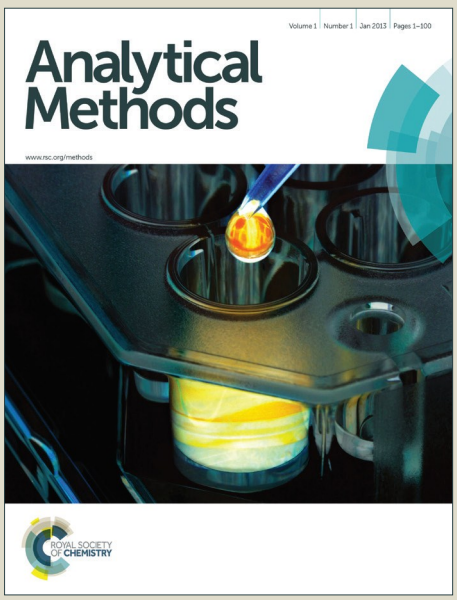

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Synthesis of Copper Sulfide Nanorods as Peroxidase Mimics for Colorimetric Detection of Hydrogen Peroxide

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Abstract

Copper sulfide (CuS) nanorods were synthesized via one-pot hydrothermal approach. The CuS nanorods exhibited intrinsic peroxidase-like activity. The CuS nanorods showed high catalytic activity, good stability and dispersion in water. Further, CuS nanorods were used as peroxidase mimetics for colorimetric detection of hydrogen peroxide. This method is simple, inexpensive, highly sensitive, and selective for H_2O_2 detection with a linear range 1.0×10^{-6} - 1.0×10^{-3} mol L^{-1} with a detection limit of 1.1×10^{-7} mol L^{-1}. The color change observable by the naked eyes based on the oxidation of o-phenylenediamine (OPD) is the principle for the sensing of H_2O_2 level.

Keywords: Peroxidase mimetics; Copper sulfide; Nanorods; Colorimetric; Hydrogen peroxide

1. Introduction

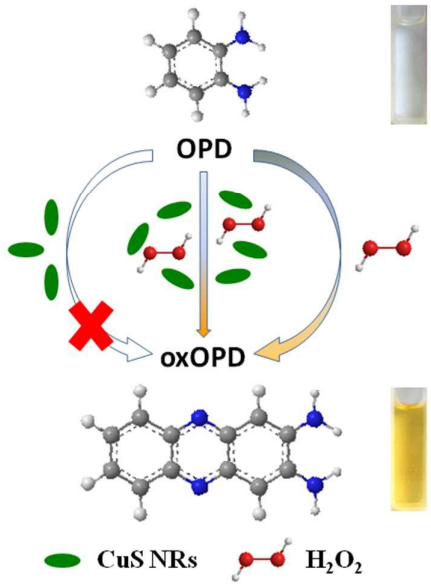
Colorimetric biosensing has attracted considerable attractive because of its low cost, practicality and simplicity.[1, 2] However, a key challenge in developing colorimetric sensors is transforming the detection events into color changes. Since color changes can be observed by the naked eye, a colorimetric sensor does not require expensive or sophisticated instruments and can be applied to real-time and on-site analysis.[3-6] In recent years, enzyme-based colorimetric biosensing has become more attractive due to its excellent properties such as high substrate specificities and high catalytic efficiency under mild conditions. [7] Natural enzymes, especially horseradish peroxidase (HRP)，which is one kind of protein that can catalyze some substrates such as 3,3′,5,5′-tetramethylbenzidine (TMB), o-phenylenediamine (OPD), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) to the corresponding oxidized products.[8] It is incredibly efficient and a highly specific under mild conditions. It can activate hydrogen peroxide to perform a variety of chemical reactions such as oxidation, which has been extensively investigated and applied in many different areas.[9] However, the practical applications of native enzymes are inevitably restricted due to their limited natural sources, complicated and high-cost purification processes, and loss of bioactivity in harsh chemical environments. Therefore, more and more attention has been paid to the construction of efficient enzyme mimics, which possess significant advantages such as low-cost of preparation, simple storage, flexibility in composition and structure design.[10, 11]

Recently, colorimetric biosensor based on enzyme mimics has become an increasingly important focus for the researchers. The rapid development of nanotechnology has opened a promising field towards the fabrication of enzyme mimics. Nanoparticles exhibited versatile excellent properties such as catalytic, optical, and electronic properties because of their small size, various morphology, and different composition.[12] Since the first report of Fe_3O_4 magnetic nanoparticles (MNPs) possessing intrinsic peroxidase-like activity,[13] a variety of inorganic nanomaterials with peroxidase-like activity came into sight，including metal oxide nanomaterials,[14, 15] sulfide nanomaterials,[16] metal nanomaterials,[17-19] carbon nanomaterials,[20, 21] These nanoparticles based mimics could be potentially effective employed in colorimetric biosensors.

Copper sulfide (CuS), as one of the most important metal chalcogenide semiconductors, has been the focus of considerable attention not only because of its excellent electrical, optical, physical and chemical properties but also its potential applications in many fields, such as photocatalysis,[22-24]

solar-cell devices,[25] optical limiting[26] and biosensors.[9, 27] Recently, a series of three-dimensional CuS with hierarchical structures have been proved to own intrinsic peroxidase-like catalytic activity similar to Fe_3O_4 magnetic nanoparticles.[28] This finding of peroxidase activity paves a new avenue for exploring the sensing applications of CuS nanoparticles and improving the development of practical applications. In particular, the properties of materials could be tuned by adjusting the structure, morphology, stoichiometric composition and valence state, therefore, it's of great significance in researching various of morphology of CuS nanoparticles.

It is well-known that hydrogen peroxide (H_2O_2) is produced stoichiometrically during the oxidation of glucose by dissolved oxygen in the presence of glucose oxidase (GOx).[29] In fact, the determination of trace H_2O_2 itself is also very important and necessary in environmental and clinical analysis. Many methods such as spectrofluorometry,[30, 31]electroanalysis[32-35] and chemluminescence[36] have been developed for detection of H_2O_2, however, these methods have disadvantages such as requiring expensive or sophisticated instruments and cannot be applied to real-time and field analysis. Nanoparticles as enzyme mimics-based colorimetric biosensors have emerged as an important tool for the real-time and on-site detection of H_2O_2.



Scheme 1 Schematic representation of the colorimetric detection of hydrogen peroxide based copper sulfide nanorods as peroxidase mimetics.

Herein, copper sulfide nanorods were synthesized and used for the colorimetric detection of H_2O_2. The CuS nanorods were prepared via a hydrothermal method. The as-prepared CuS nanorods

exhibited good catalytic property, stability, dispersibility compared to the natural enzymes. The CuS nanorods were then used as peroxidase mimetics for colorimetric detection of H_2O_2. As shown in Scheme 1, the color change observable by the naked eyes based on the oxidation of o-phenylenediamine (OPD) is the principle for the sensing of H_2O_2 level.

2. Experimental section

2.1. Chemicals and materials

Copper chloride dehydrate($CuCl_2 \cdot 2H_2O$), sodium sulfide($Na_2S \cdot 9H_2O$), poly(vinylpyrrolidone) (PVP), sodium acetate (NaAc), acetic acid (HAc) and hydrogen peroxide (H_2O_2, 30%) were purchased from commercial sources. 3,3′,5,5′-tetramethylbenzidine (TMB), o-phenylenediamine (OPD) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) were purchased from Sigma-Aldrich. All other chemicals were of analytical reagent grade and used without further purification. Deionized water was used throughout the experiment.

2.2. Synthesis of CuS nanorods

CuS nanorods were synthesized via hydrothermal method according to the reported method and slightly modified.[35] $CuCl_2$ (0.025 mmol) was dissolved in deionized water (10 mL) containing PVP (8 mg), and the solution was magnetically stirred to form a homogeneous solution. Then, 10 mL of the $Na_2S \cdot 9H_2O$ aqueous solution (0.075 mmol) was added into the above solution followed by further stirring for 30min to form a homogeneous light yellow solution and was then transferred to a 50 mL Teflon-lined stainless steel autoclave. After heating at 180 ℃ for 24 h and naturally cooling to room temperature, the resulting suspension was centrifuged for 10 min at 12000 rpm and washed with water for three times, and dried at 60 °C for 12 h to obtain the CuS nanorods.

2.3. Peroxidase-like activity measurements

The peroxidase-like activity of the CuS nanorods was investigated through the catalytic oxidation of the peroxidase substrate o-phenylenediamine in the presence of H_2O_2. The detail as following: 40μL of 20 mM OPD, 10 μL of the CuS nanorods stock solution (500 μg mL^{-1}), and 100 μL of 1mM H_2O_2 were added into 850 μL of 0.2 M acetate buffer (pH = 4.0), then the mixed solution was incubated at 45 °C by water bath for 10min. After that, the resulting solution was diluted with water, mixed and used for the absorption spectroscopy measurement. It took about 30 seconds to do the measurement.

2.4. Hydrogen peroxide determination

The determination of hydrogen peroxide was carried out similar to above description: at first, 40μL

of 20 mM OPD, 10 μL of 500 μg mL^{-1} CuS nanorods solution, and 100μL of H_2O_2 with different concentrations were mixed in 850 μL of 0.2 M acetate buffer (pH = 4.0) and incubated at 45 °C for 10 min, then the resulting solution was diluted with water for the absorption spectroscopy measurement.

3. Results and discussion

3.1. Characterization of CuS nanorods

Hydrothermal heating often provides more homogenous nucleation and decreases the crystallization time for the synthesis of uniform nanostructure materials.[37] Herein, the CuS nanorods were synthesized from a common cupric salt as copper source and PVP as the capping agent through hydrothermal approach.

The size and morphology of CuS nanorods were investigated by transmission electron microscopy (TEM, see Fig. 1). The TEM image in Fig. 1 indicated that the true shape of as-prepared CuS is a kind of nanorod with average diameter of 20 nm and length of 60-100 nm.

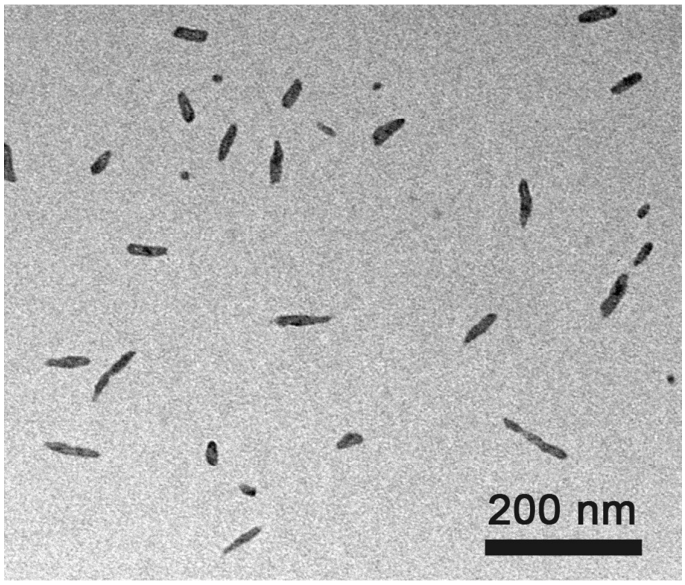


Fig. 1 TEM image of as-synthesized CuS nanorods.

The crystallinity and phase purities of CuS nanorods were examined by the X-ray diffraction (XRD) technique. The diffraction patterns (see Fig. 2A) of the crystalline products indicated that all the diffraction peaks can be indexed to the hexagonal phase of the covellite structure (JCPDS No. 6-464) with the P63/mmc space group and a primitive hexagonal unit cell with a=b=3.79A and c=16.34A. No other characteristic peaks of impurities, such as $Cu_{1.8}S$, $Cu_{1.96}S$, Cu_2S or CuO, were detected. The strong intensity of the (110), (102), (103) and (006) planes indicates that they are the

dominant crystal faces of the formed CuS nanostructures.

As shown in Fig. 2B, UV-Vis absorption spectrum was also used to characterize CuS nanorods. The nanorods showed obvious absorbance around 230 nm as well as slight absorption around 380nm. This result suggested that CuS nanorods really were nano-sized. The inset of Figure 2B shows the photograph of CuS nanorods dispersed in water. From this picture, the as-prepared CuS nanorods possess good dispersibility in water and no any aggregation was observed.

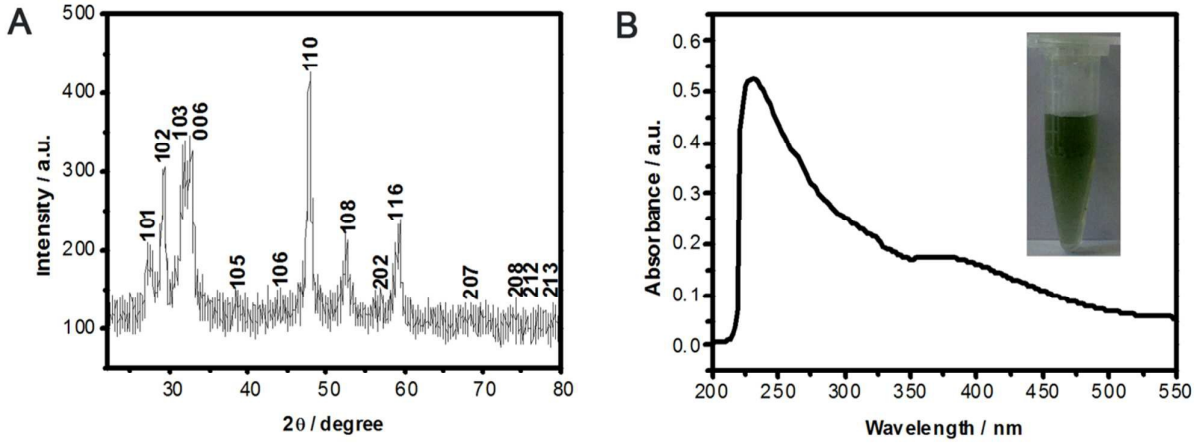


Fig. 2 (A) XRD and (B) UV-vis spectra of of as-synthesized CuS nanorods. Inset of B is the photograph of CuS nanorods dispersed in water.

3.2. Peroxidase-like catalytic activity of CuS Nanorods

The catalytic activity of the as-prepared CuS nanorods was investigated by using OPD as the substrate in the presence of H_2O_2. In general, OPD can be oxidized by H_2O_2 to produce a yellow product (oxOPD) and the reaction is catalyzed by peroxidase such as horseradish peroxidase (HRP). In this experiment, the OPD is completely oxidized in the presence of CuS nanorods similar to that using HRP as catalyzer. As shown in Fig. 3A, in absence of CuS nanorods (b), the solution of OPD just arise slight color change seemingly to be pale yellow. While added the CuS Nanorods in the mixture of OPD and H_2O_2 (c), the solution take place obviously change and turn into a yellow solution. However, in absence of H_2O_2 (a), the solution haven't any change although there having catalyzer existence. These phenomena indicate that the CuS nanorods indeed exhibit peroxidase-like activity. Accordingly, the results of above were also confirmed by spectrophotometer, which was used to monitor the absorbance of the mixture solutions dynamically. What's more, by the dynamic absorbance monitoring, the result showed that oxOPD owing maximum absorption around 450 nm was gotten (as shown in Fig. 3B).

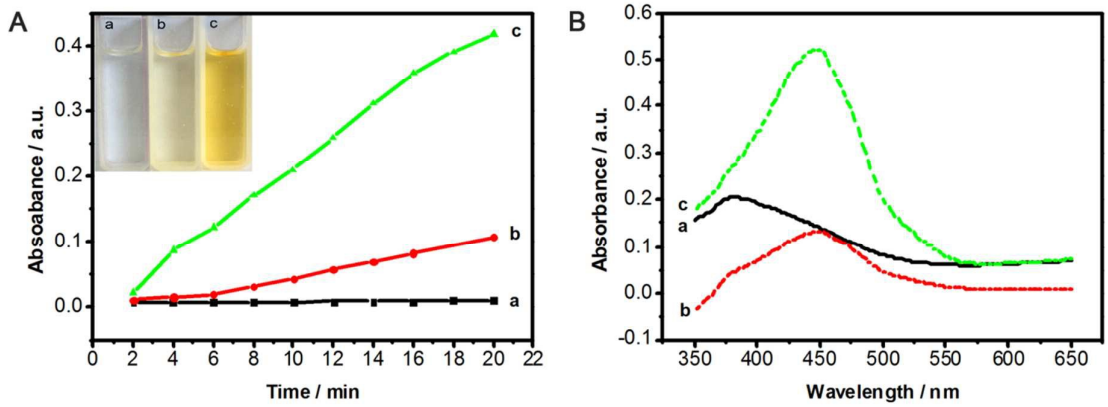


Fig. 3 (A) Time- and (B) wavelength-dependent absorbance changes of OPD at 450 nm in different reaction systems: (a) OPD + CuS nanorods, (b) OPD + H_2O_2, and (c) OPD + CuS nanorods + H_2O_2 in a pH 4.0 HAc-NaAc buffer (0.1 M) at room temperature. Inset shows the color change of different samples.

It is important to rule out the possibility that the observed peroxidase-like catalytic activity is caused by copper ions leaching from CuS nanorods in the solution. To test this, leaching solution was obtained by incubating CuS nanorods in the reaction buffer (pH 4.0) for 10 min and then removed the CuS nanorods from solution by centrifugation. As shown in Figure 4, absorbance at 450 nm increases continuously during the reaction process in the presence of CuS nanorods. However, there is no any change in the absorbance when the leaching solution was used instead of CuS nanorods under the same reaction conditions (b). These experimental results reveal that the observed peroxidase-like activity can be attributed to intact nanorods.

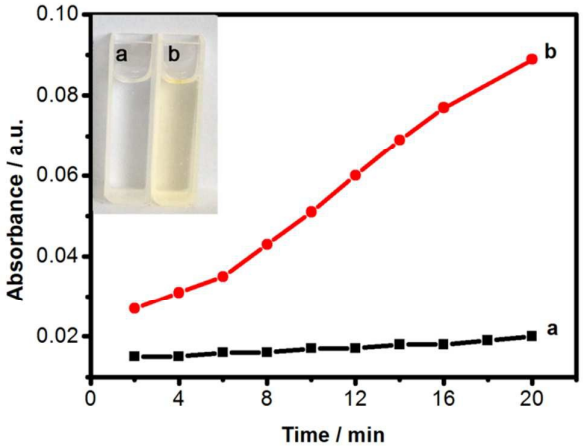


Fig. 4 Time-dependent absorbance evolution of OPD oxidation system at 450 nm in the presence of CuS nanorods (a) and leaching solution (b). Inset shows the color change of different samples.

Besides OPD, it is well-known that TMB and ABTS are also typical substrates of peroxidase catalytic oxidation reaction. What's more, anyone of them will get color change in the present of peroxidase (e.g. HRP). Hence, TMB and ABTS were also employed to verify the catalytic performance of CuS nanorods as peroxidase mimetics. As shown in Fig. 5, OPD was oxidized and the solution changed into yellow. Accordingly, in the present of H_2O_2 and CuS nanorods, the solution of TMB was oxidized into blue solution; the ABTS was oxidized into green solution. These phenomenons entirely prove that CuS Nanonrods possess peroxidase-like activity.

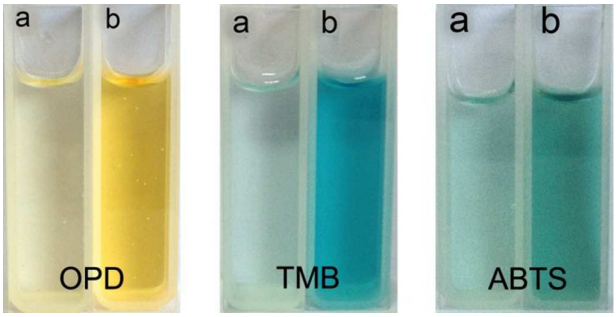


Fig. 5 Images of oxidation color reaction of OPD, TMB, and ABTS by H_2O_2 before and after by the catalysis of CuS nanorods, respectively.

3.3. Optimization of detection conditions

The catalytic activity of CuS nanorods depends on some key factors, such as pH, the volume of CuS nanorods, concentration of OPD and H_2O_2. Therefore, these factors are optimized in this experiment. The CuS nanorods would be unstable when pH is low than 3.0. However, if the pH is too high, H_2O_2 tends to decompose into H_2O and O_2 rather than ROS.[38] Therefore, the effect of pH on the CuS nanorods-based catalytic activity by adopting 0.2 M of NaAc buffer solutions with pH values in the range of 3.0-7.0 was investigated. As the pH of solution increased, the absorbance increased and then decreased sharply, which can be seen from Fig. 6A. The maximum of absorbance is obtained at pH 4.0. Thus, pH 4.0 was selected for the following assay.

CuS nanorods as peroxidase mimetics, its volume conspicuously affects the absorbance of oxidation colour reaction of OPD. As the concentration of CuS nanorods increased, the absorbance of solution increased rapidly and then reached a platform relatively above 50 μg mL^{-1}, which is shown in Fig. 6B. Therefore, the optimal concentration of CuS nanorods was selected at 50 μg mL^{-1}. Similarly, the OPD solution with concentration of 0.8 mM was selected in oxidation colour reaction according the result shown in Fig. 6C.

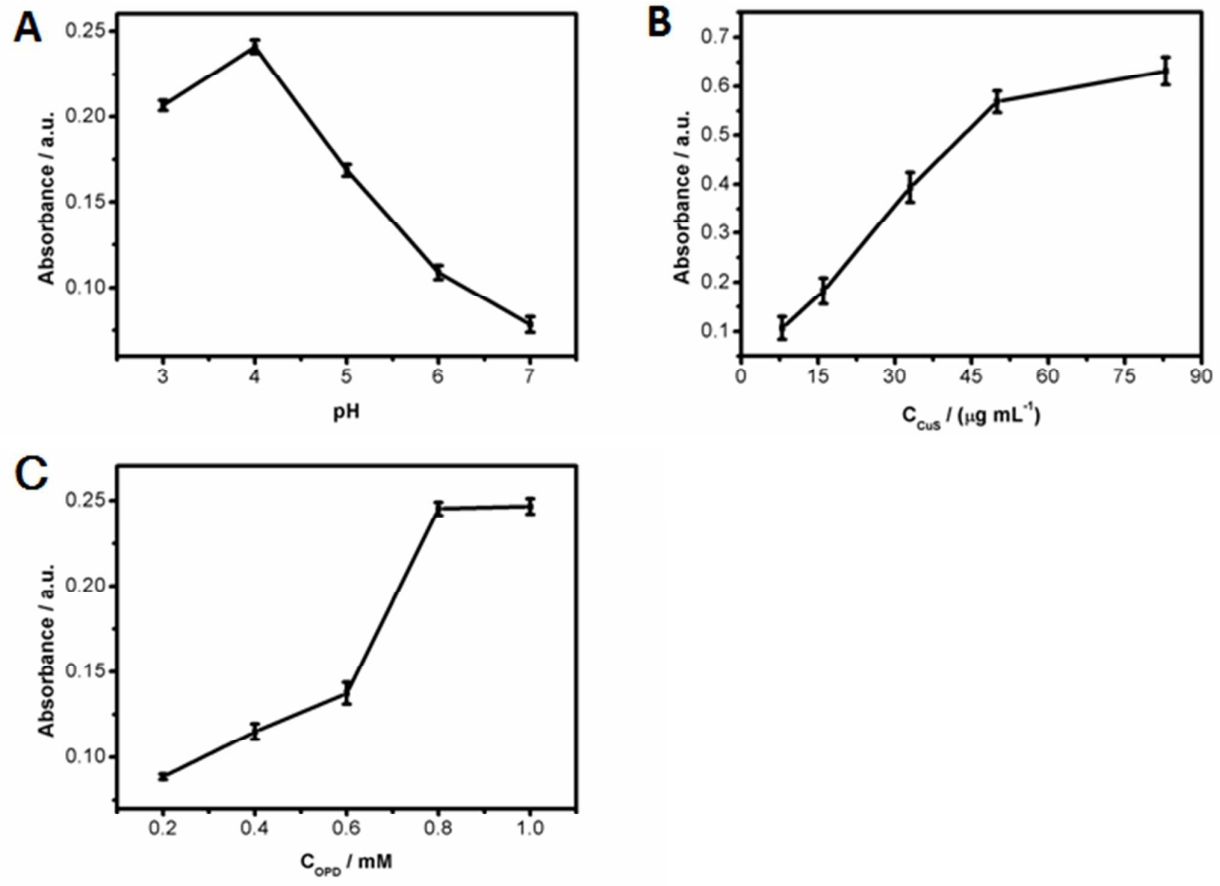
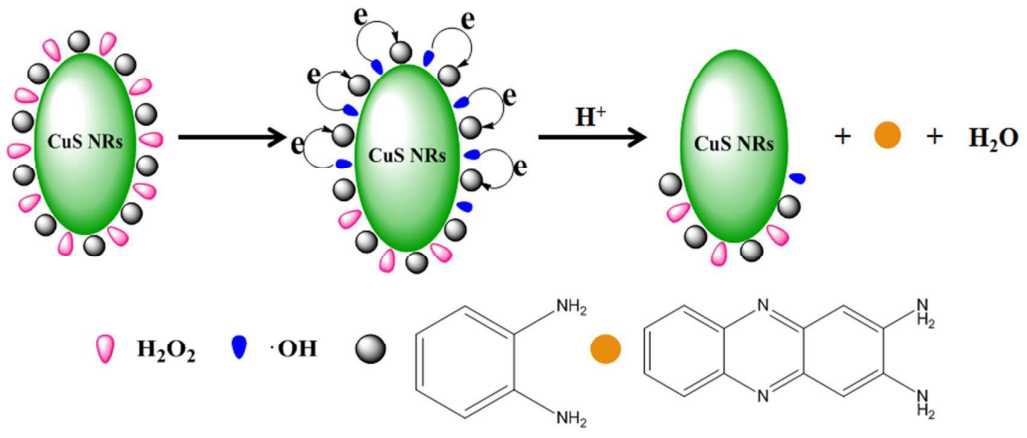


Fig. 6 Effects of (A) pH, (B) concentration of CuS nanorods, (C) Concentration of OPD on the absorbance in the color reaction with the H_2O_2 concentration of 0.1 mM.

3.4. Mechanism of Peroxidase-Like Activity of CuS Nanorods



Scheme 2. The possible catalytic mechanism of CuS nanorods.

A possible catalytic mechanism of CuS was presented in Scheme 2. First, H_2O_2 molecules were

adsorbed on the surface of CuS and then activated by the bound Cu^{2+} to generate the ·OH, and the generated ·OH was stabilized by CuS nanorods via partial electron exchange interaction.[39] Second, OPD was oxidized by ·OH to form a yellow color product. The yellow signal comes from the charge transfer complex, consisting of a cation free radical and OPD.[40]

3.5 Analytical application in determination of H_2O_2

In order to demonstrate the performance of the proposed method, as-prepared CuS nanorods was employed to detect H_2O_2 by colorimetric assay in this work. As displayed in Fig. 7A, a clear change from light yellow to dark yellow could be obviously differentiated by the naked eyes when the concentration of H_2O_2 is more than 0.05 mM. Under the optimal detection conditions, the catalytic ability of the CuS nanorods on OPD oxidation in the presence of various concentration of H_2O_2 was investigated. The UV–vis spectra of the different concentration of H_2O_2 solutions are shown in Fig. 7B. It can be evidently observed that the absorbance increased gradually with the increasing of H_2O_2 concentration.

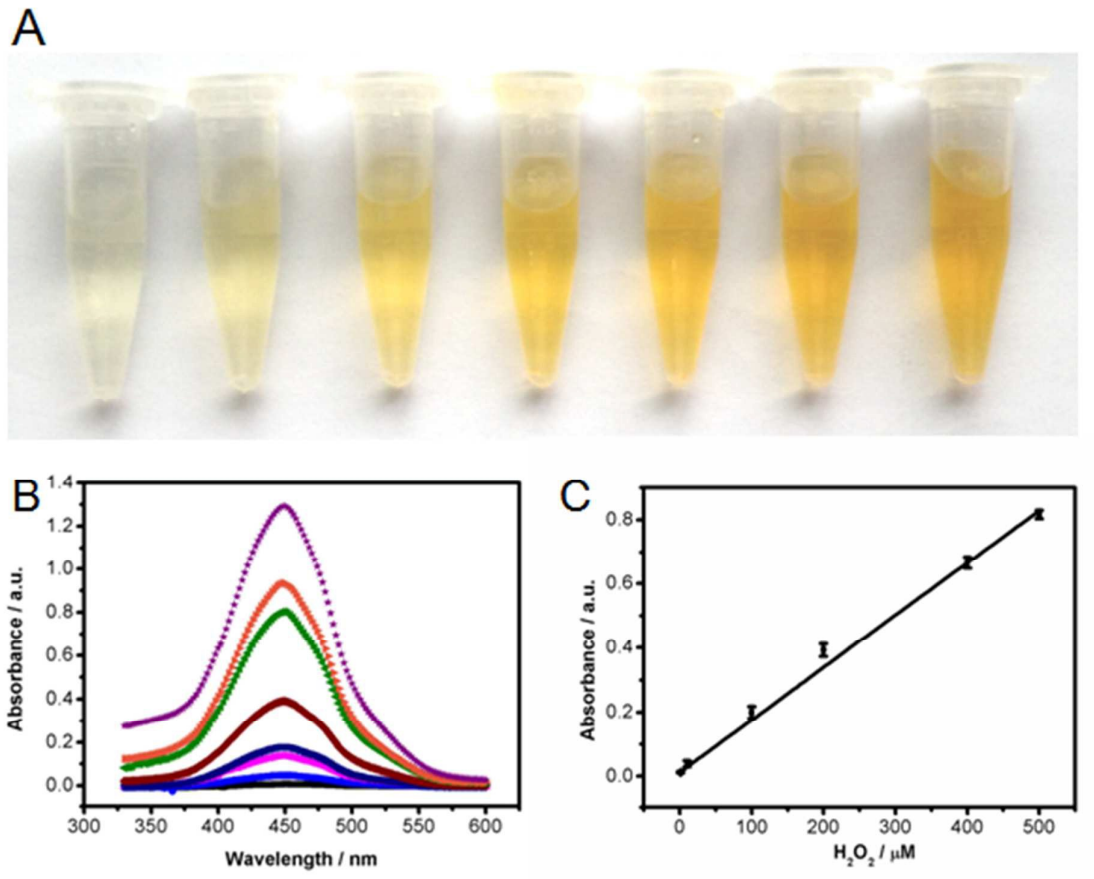


Fig. 7 (A) Photographs of OPD and CuS nanorods mixed solution in the different amounts of H_2O_2; (B) UV–Vis

spectra of OPD–H_2O_2 system catalyzed by CuS nanorods. The mixing sample was incubated at 45 °C for 10 min, then the absorption spectroscopy of the resulting solution was measured. curves from bottom to up represent 0.001, 0.01, 0.05, 0.1, 0.2, 0.4, 0.5 and 1.0 mM, respectively; (C) Calibration curve for the H_2O_2 colorimetric sensor.

The calibration plots (Fig. 7C) showed good linear relationship between the absorbance and the concentration of H_2O_2 in the range from 0.001 to 2.0 mM with a limit of detection 1.1×10^{-7} mol L^{-1}. The linear regression equation was y=0.00157x+0.03294 with a linear regression coefficient of 0.9929. These results exhibited that the proposed colorimetric method was able to sensitively detect H_2O_2 over a relatively wider concentration range with a lower detection limit.

Table 1 summarizes the detection limit of our method and other nanoparticles-based colorimetric detection of H_2O_2.[8, 17, 41-45] From Table 1, compared with the other studies utilizing different nanoparticles including Fe_3O_4, Pt, FeSe, Co_3O_4 Fe_3O_4@MSN, our method showed a lower limit of detection, which could be attributed to the excellent catalytic property of CuS nanorods to OPD substrate.

Table 1 Comparison of other nanoparticle-based preoxidase mimetric for colorimetric determination of hydrogen peroxide (H_2O_2)

Materials used	Substrate used	Linear range	Detection limit	Reference
Fe_3O_4	DPD	0.5-150 μmol L^{-1}	0.25 μmol L^{-1}	41
HRP-Cu^{2+}complex	OPD	1-500 μmol L^{-1}	0.5 μmol L^{-1}	8
rGO–CFs	TMB	2-100 μmol L^{-1}	0.3 μmol L^{-1}	42
Pt	TMB	50-3000 μmol L^{-1}	7.9 μmol L^{-1}	17
FeSe	TMB	2-30 μmol L^{-1}	0.5 μmol L^{-1}	43
Fe_3O_4@MSN	TMB	1.0-100 μmol L^{-1}	1.0 μmol L^{-1}	44
Co_3O_4	TMB	0.05-25 mmol L^{-1}	10 μmol L^{-1}	45
CuS nanorods	OPD	0.001-1.0 mmol L^{-1}	0.11 μmol L^{-1}	This work

3.6. Selectivity, reproducibility and stability of the method

The selectivity of this method for detection of H_2O_2 was investigated by using glucose, dopamine, ascorbic acid and uric acid as the potential interferences. The results showed that the interfering species cannot induce the color change in the absence of H_2O_2, indicating a high selectivity of our method.

The developed method for the determination of H_2O_2 showed a good reproducibility. The absorbance of Ox-OPD was examined in the presence of 1.0 μM H_2O_2 and CuS nanorods for

replicate five assays. A relative stand deviation was found to be 3.6%.

The stability of the CuS nanorods in wide temperature ranges is crucial to extend their applications. As inorganic materials, CuS nanorods were expected to be more stable than natural enzymes. As for HRP, after treatment at temperatures greater than 40°C for 2h, the enzyme activity dramatically declines. In contrast, CuS nanorods were stable when they were incubated at a wide range of temperatures (20-90°C) for 2h. The stability of CuS nanorods makes them suitable for a broad range of applications in the biomedicine and environmental chemistry fields.

4. Conclusions

The copper sulfide nanorods as a novel peroxidase mimetics was successfully developed in this work. In the presence of H_2O_2, CuS nanorods could catalyze the oxidation of peroxidase substrate OPD to produce a kind of yellow substance, which demonstrates CuS nanorods possessing intrinsic peroxidase-like activity. The CuS nanorods was exploited as a new type of peroxidase for detection H_2O_2 through a simple, cheap and sensitivity colorimetric method. The copper sulfide nanorods as peroxidase mimetics show several advantages over natural enzymes, such as low-cost, ease of preparation, and stability, which open up a wide range of new potential applications of CuS nanorods in environmental chemistry, biotechnology and medical diagnostics.

Acknowledgement

We greatly appreciate the support of the National Natural Science Foundation of China (No: 21365016, 21265014). This work is also supported by Enhance Comprehensive Strength Project of Ningxia University (8016-18).

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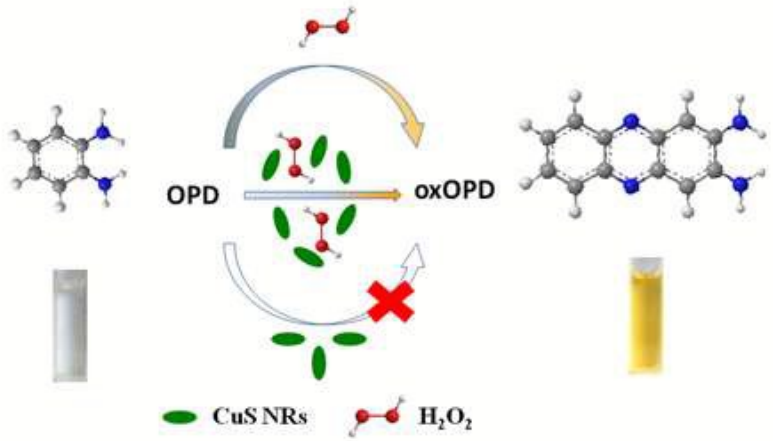
Graphical abstract



Copper sulfide (CuS) nanorods were synthesized and used as peroxidase mimics for colorimetric detection of H_2O_2.