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Ag⁺ colorimetric sensor based on graphene oxide/nano-platinum composite



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Abstract

With the development of society, pollution accidents occur more frequently, and the effects of toxic substances containing silver on human health and environment are increasingly extensive. Therefore, the real-time on-site monitoring of silver ions is urgently needed. Based on the catalase-like properties of graphene/nano-platinum composites and the coupling effect between Pt and Ag⁺, a simple, unlabeled colorimetric sensing method is proposed to achieve the quantitative detection of Ag⁺. Under optimal conditions, the detection range of Ag⁺ by this colorimetric sensing method is 0.5–1000 μ M, and the detection limit is 0.5 μ M, which is lower than the previously reported detection limit of unlabeled Ag⁺ colorimetric sensing method, showing higher sensitivity and detection range. Under the same conditions, the sensor has almost no response to interference ions, showing good specific recognition ability. In addition, the colorimetric sensing method can be used to detect Ag⁺ in actual water samples, serving as a new paradigm for visual detection of Ag⁺.

Keywords Graphene oxide, Nano-platinum, Ag⁺ detection, Catalase, Wastewater

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Introduction

With the development of industry, environmental problems have become the focus of public concern. Heavy metal ions that cannot be naturally degraded are extremely destructive to nature and human health, and are one of the representative pollutants that cause ecological and environmental problems. Ag⁺ is used in sterilization, purification and deodorization, but if used improperly, it may accumulate in the body and cause argentosis, serious damage to the cell membrane through extracellular mechanisms, skin irritation, stomach pain, organ edema and even death (Khodaparast et al. 2021). Therefore, it is urgent to establish a rapid, sensitive, reliable and low-cost Ag⁺ detection technology. This is of vital significance for food safety, biomedical prevention and environmental protection.

At present, the most commonly used silver ion detection methods include atomic fluorescence spectrometry (Ksa et al. 2019), atomic absorption/emission spectrometry (Yang et al. 2017; Kumar et al. 2019; Karandashev et al. 2019; Winkler. 2020), and inductively coupled plasma mass spectrometry (Shaban et al. 2017). Although these traditional detection methods have high sensitivity and specificity, they have many shortcomings, such as expensive instruments, high operating costs, lack of portability, cumbersome procedures, long time consuming, and strict requirements

for operators. In addition, because of the dependence on detection equipment, traditional detection methods are difficult to use in on-site detection, and practicability is poor. Therefore, the development of a rapid, convenient, low-cost, simple and reliable methods that are convenient for on-site detection is the current research hotspot in the field of Ag⁺ detection.

Colorimetric sensing method has the advantages of visual detection results, simple operation, and rapid response. It has been widely concerned and developed rapidly, and can achieve rapid and real-time detection of objects (Zhao et al. 2020; Wu et al. 2019; Yha et al. 2020). Among nanomaterials, graphene and its derivatives have good catalytic performance and have unique layered structure, large specific surface area and active groups on the surface to provide modified active sites for loading other nanomaterials. Consequently, it can be used as a good support material to prepare nanocomposites and has been widely used in the field of colorimetric sensing and detection (Vinotha et al. 2021; Minh et al. 2020; Boruah et al. 2020). Therefore, in this study, graphene oxide has been used as the carrier, and chloroplatinic acid as the precursor to synthesize nanometer catalytic materials with stable structure and high catalytic efficiency, to build a colorimetric sensing detection platform, and to realize the visualization and rapid on-site detection of Ag⁺.

Materials and methods

Chemicals

Silver nitrate (AgNO₃), citric acid (C₆H₈O₇), disodium hydrogen phosphate (Na_2HPO_4), hydrogen peroxide (H_2O_2) , chloroplatinic acid (H_2PtCl_6) and 3,3',5,5'-tetramethylbenzidine (TMB) were purchased from Tianjin Daimao Chemical Reagent Co. Ltd. (China), and graphene oxide was purchased from Shenzhen Qihang Technology Co. Ltd. (China). All metal salt solutions (0.1 M) were prepared from the corresponding metal salts in deionised water. All glassware was cleaned by rinsing several times with tap water and then, re-rinsing with de-high purity water. High purity water obtained using a water purifier (WP-UPT-20, China) was used for reagents preparation. 0.1 N Hydrochloric acid and 0.1 N sodium hydroxide, both analytical grade and obtained from Tianjin Damao Chemical Reagent Co. Ltd. (China), were used to adjust the pH.

Synthesis of GO/PtNPs

1.25 mL of graphene oxide (0.5 mg/L) and 0.3 mL of H_2PtCl_6 solution (10 mM) were mixed homogeneously with 10 mL of ultrapure water. Then, the pH of the system was adjusted to 9.5 with sodium hydroxide (0.1 mol/L) before added with ultrapure water to 12.5 mL. The mixture was then sonicated for 6 h prior to transferring to a hydrothermal reactor (LC-KH-50, LICHEN, China) at 180 °C for 8 h. From this process, a graphene oxide nanoplatinum composites (GO/PtNPs) were obtained.

The parameters (pH of the mixture, concentration of H_2PtCl_6 solution, synthesis temperature and synthesis time) affect the size, shape, dispersion and catalytic ability of GO/PtNPs. Therefore, the parameters were varied in order to determine the ideal conditions. The effects of pH of the mixture solution (8, 8.5, 9, 9.5, 10, 10.5), concentration of H_2PtCl_6 solution (0.08, 0.16, 0.24, 0.32, 0.4 mM), synthesis temperature (150, 160, 170, 180, 190, 200 °C) and reaction time (6, 7, 8, 9, 10 h) on GO/PtNPs synthesis were investigated.

5 μ L of the synthesized GO/PtNPs, 40 μ L of TMB (1 mM), and 4 μ L of H₂O₂ (10 M) were mixed and then, fixed to 2000 μ L with citrate buffer solution at pH=5. The absorbance values were measured using a UV-1750 spectrophotometer (Shimadzu, Japan) at 652 nm after 5 min of reaction.

Characterization of the synthesized GO/PtNPs

UV–Vis spectra were obtained using a UV-1750 spectrophotometer from Shimadzu Co. Ltd. of Japan. Fullwavelength scans of graphene and graphene/platinum nanoparticles were performed at 200 nm and 700 nm, respectively, at room temperature. Fourier Transform Infra-Red (FTIR) spectroscopy was performed with a NicoletiS5 (USA) in the range of 4000–400 cm⁻¹ to observe the changes in the surface groups of GO and GO/PtNPs. LabRAM HR confocal micro-Raman spectrometer (France) was used to analyze the changes in GO surface defects before and after synthesis. The crystal structures of GO and GO/PtNPs were evaluated using a PANalytical X-pert3-ray diffractometer (XRD) (Netherlands). The shape and size analyses of the prepared GO/ PtNPs were identified using a JEOL-JEM2100F (Japan) transmission electron microscope (TEM) at 200 kv. An SM-7500F (Japan) X-ray energy spectrometer (EDS) was used for the elemental studies.

Study of catalytic kinetic parameters of GO/PtNPs

A fixed amount of GO/PtNPs (ideal value from synthesis experiment), H_2O_2 and TMB was placed in a 5 mL test tube. The concentration of H_2O_2 and TMB was varied at 0.005–0.04 M and 0.01–1.5 mM, respectively. Then, citrate buffer solution with pH varied between 2.2 and 8, was added to 2000 µL. The absorbance values were measured using a UV-1750 spectrophotometer (Shimadzu, Japan) at 652 nm. The measurement time was also varied between 1 and 30 min.

Detection ability of the synthesized GO/PtNPs for Ag⁺ ions *Specificity and anti-interference analysis*

Ag⁺, Zn²⁺, Cr⁶⁺, Cu²⁺, Ni²⁺, Al³⁺, Cd²⁺ and Ca²⁺ solutions were added to 1000 μ L citric acid buffer solution with pH 5 and 2 μ L GO/PtNPs solution. After well-mixed for 10 min, 4 μ L H₂O₂ (10 M) and 40 μ L TMB (1 mM) were added to the system and fixed to 2000 μ L with a citric acid buffer solution at pH 5. The absorbance values were measured using a UV-1750 spectrophotometer (Shimadzu, Japan) at 652 nm after reaction for 5 min.

Sensitivity analysis

2 μ L GO/PtNPs was mixed with Ag⁺ solution of 0.5– 1000 μ M and citric acid buffer solution of 1000 μ L and pH=5 until homogeneous for 10 min. Then, 4 μ L H₂O₂ (10 M) and 40 μ L TMB (1 mM) were added to 2000 μ L in citric acid buffer solution with pH 5. After reaction for 5 min, absorbance values were measured at 652 nm, and standard curves were drawn.

Spike-and-recovery experiment

The practicability of the proposed method was studied by adding different concentrations of Ag^+ to various environmental water samples (i.e., tap water, pond water and river water). Tap water samples were collected from the municipal pipe network in Jinan, Shandong Province, China; pond water was collected from Jinan, Shandong Province, China; and river water samples were collected from Xiuyuan River in Jinan, Shandong Province, China. The collected water samples were filtered through a filter membrane with a pore size of 0.22 μ m, and Ag⁺ (1, 10, 100, 500 μ M) standard solutions were added to the actual water samples. The proposed colorimetric sensing method based on graphene/nano-platinum was used for determination, the experimental results were recorded, and the recovery rate was calculated.

Results and discussion

GO/PtNPs characterization

TEM characterization analysis

Graphene oxide thin/nano-platinum composites were synthesized by one-step hydrothermal reaction in a solution. In this process, the chloroplatinic acid precursor is directly reduced to Pt NPs, which is anchored on the graphene surface mainly through defects and oxygen functional groups (Satar et al. 2019; Zhao et al. 2021). It is worth noting that due to the residual oxygen-containing groups on the graphene surface, the obtained hybrid can form a well-dispersed aqueous colloid with good stability (Shuang et al. 2017), which is conducive to its application in colorimetric sensing detection. Figure 1 (A) and (B) shows that platinum clusters were fixed on the surface of graphene oxide. The Pt NPs are nearly spherical, distributed between graphene oxide sheets, with particle sizes ranging from 2 to 3 nm. Figure 1C shows the lattice stripes of Pt NPs, whose average crystal plane spacing is 0.2 nm, that is 2.0 Å, corresponding to the {200} and {111} sides of the platinum face-centered cubes.

Raman characterization analysis

Raman spectrum analysis also confirmed the formation of Pt NPs on the graphene sheets (Fig. 2). It can be seen from Fig. 2 that graphene oxide has two characteristic peaks in the range of $1200-1800 \text{ cm}^{-1}$, namely the D peak at 1369 cm^{-1} and the G peak at 1614 cm^{-1} . The D peak represents the disorder-induced feature of carbon materials as the ordered structure of graphene is destroyed after oxidation (Tamalampud et al. 2019). The



Fig. 2 Raman spectra of GO and GO/PtNPs

G peak corresponds to the E_{2g} phonon vibration in the center of the Brillouin region and is an intrinsic Raman mode of a graphene (Artur et al. 2019; Muniyalakshmi et al. 2020). Partial chemical reduction in GO can bring about structural changes, as evidenced by the shift of the D and G bands to lower wavenumbers and the enhancement of the Raman spectral intensity ratio (I_D/I_G) of the D and G bands (Shu et al. 2015). This may be due to the partial reduction in GO, where a large number of sp^3 hybridized carbon atoms will be partially deoxygenated to re-form new sp^2 hybridized regions. The re-formed sp^2 regions are smaller than those of GO, so that the average size of the sp^2 regions of the reduced graphene becomes smaller with increased number of sp^2 regions. This is reflected in the Raman spectra as an increase in the value of I_D/I_G . The Raman spectra of the PtNPs-GO shows that the characteristic peaks of the D and G bands are at 1336 cm^{-1} and 1593 cm^{-1} , respectively, and the intensity ratio (I_D/I_G) is enhanced (Shu et al., 2015). The peaks can also be seen slightly red-shifted compared with that of pristine GO, and the I_D/I_G ratio increases from 0.89 to



Fig. 1 GO/PtNPs TEM images; A 10 nm, B 5 nm, and C 2 nm

1.09. The slight enhancement of the I_D/I_G ratio suggests that the average size of the sp^2 region of GO decreases in the preparation process of Pt NPs-GO. Therefore, the shifted band and enhanced I_D/I_G indicate that GO was partially reduced during GO/PtNPs preparation.

FT-IR characterization analysis

As shown in Fig. 3, graphene oxide mainly has characteristic peaks at 1053 cm⁻¹, 1227 cm⁻¹, 1616 cm⁻¹, and 1732 cm⁻¹. The C–O–C telescoping vibration peak at 1053 cm⁻¹ may exist, the face-bending vibration of CH may exist at 1227 cm⁻¹, and the peaks at 1616 cm⁻¹ and 1732 cm⁻¹ may have C=O stretching vibration. The disappearance of the characteristic peak of C=O stretching vibration at 1732 cm⁻¹ of GO/PtNPs may be due to the reduction reaction during the synthesis of the composites (Ray et al. 2020). The decrease in the characteristic peak of oxygen-containing functional groups was reported to be due to the partial reduction during the hydrothermal reaction of graphene oxide (Muniyalakshmi et al. 2020).

XRD characterization analysis

For precious metal platinum nanoparticles, XRD is a good means to analyze the crystal structure. The comparison of pristine graphene oxide and GO/PtNPs via XRD in Fig. 4 shows an obvious C (002) peak of graphene oxide at about 10.1°. The enhanced characteristic peak at 23.1° indicates that GO is reduced to a certain extent. Moreover, if GO is completely reduced, there should be a weak and wide peak at 26.6° (Legge et al. 2018; Mitra et al. 2021). However, as shown in Fig. 4, there is no peak at 26.6°, which again indicates that GO is only partially reduced rather than completely reduced. The existence form of GO is an important reason why the composite aqueous solution can maintain good dispersion for a long



Fig. 3 FT-IR of GO and GO/PtNPs



Fig. 4 XRD chromatogram of GO and GO/PtNPs

time. Meanwhile, the three diffraction peaks at 40.2°,47.2° and 67.3° correspond to (111), (200) and (220) of the facecentered cubic lattice of platinum, respectively (Wang et al. 2020; Mitra et al. 2020), which proves that platinum nanoparticles were completely loaded on the surface of graphene oxide.

EDS characterization analysis

EDS analysis of GO/PtNPs in Fig. 5 shows it mainly contains three elements: 1.74% carbon, 97.37% oxygen, and 0.89% platinum, which further indicates that the platinum nanoparticles are immobilized on the surface of the GOs, and the composite material of GO/PtNPs is still rich in oxygen-containing functional groups.

Ultraviolet-visible characterization analysis

The UV–Vis absorption spectra of graphene/platinum nanoparticles and graphene oxide are shown in Fig. 6. Graphene oxide shows a relatively strong characteristic peak at wavelength 231 nm, while graphene oxide/platinum nanoparticles have a strong characteristic peak at





Fig. 6 Ultraviolet–visible spectral characterization of GO and GO/ PtNPs

267 nm in addition to 231 nm, which is due to the reduction in graphene oxide. This indicates that the graphene oxide in graphene/platinum nanoparticles composites is partially reduced.

Optimization of GO/PtNPs preparation conditions

The catalytic activity of the prepared GO/PtNPs complex is directly related to several influencing factors. The experiment investigated the effects of pH value, H₂PtCl₆ concentration, hydrothermal time, and hydrothermal temperature on the peroxidase-like catalytic activity of GO/PtNPs complex during the preparation process. The experimental results are shown in Fig. 7. Figure 7A shows the activity test results of catalysts prepared under different pH values. It can be seen that the catalytic activity of GO/PtNPs increases with the increase in pH value, reaching a maximum when the pH value is 9.5, and decreasing with the increase in pH value starting at pH 9.5. This is due to the fact that the Pt⁰ precursor can be directly reduced to Pt nanoparticles and grown on the graphene surface under alkaline conditions due to the presence of defects and oxygen-containing functional groups on the surface of graphene oxide lamellae during the hydrothermal reaction (Yoo et al. 2009).

Figure 7B shows the activity test results of the catalysts prepared under different concentrations of H_2PtCl_6 . It can be seen that the catalytic activity of GO/PtNPs increases with the increase in H_2PtCl_6 concentration and reaches the maximum when the concentration of H_2PtCl_6 is 0.24 mM. However, the catalytic activity decreases with the increase in H_2PtCl_6 concentration greater than 0.24 mM. This is due to the reduction in Pt^{4+} to Pt^0 during the hydrothermal reduction process and in situ



Fig. 7 Effects of **A** pH value during the preparation of GO/PtNPs at 180 °C, 0.24 mM H_2PtCl_6 , 8 h; **B** H_2PtCl_6 concentration at 180 °C, pH 9.5, 8 h; **C** Hydrothermal reaction time at 180 °C, 0.24 mM H_2PtCl_6 , pH 9.5; and **D** Reaction temperature at 0.24 mM H_2PtCl_6 , pH 9.5, 9 h

growth into platinum nanoclusters (refer TEM images in Figure S1). However, too large a concentration of H_2PtCl_6 can lead to a too large of a particle size of the generated Pt nanoparticles, which reduces the catalyst reactivity (Yuhan et al. 2019).

As shown in Fig. 7C, the catalytic performance of GO/ PtNPs increases from 6 to 9 h and then, decreases with the increase in the reaction time. This shows that the best catalytic performance of GO/ PtNPs was achieved at 9 h of hydrothermal reaction. This is because when the hydrothermal time is too short, Pt^{4+} is not sufficiently reduced to Pt^{0} , and the remaining Pt^{4+} is dispersed in the system and not immobilized on the GO surface (Yoo et al. 2009). When the hydrothermal time is too long, the size of the Pt nanoparticles gradually increases. It was reported that larger size of a nanomaterial reduces the specific surface area and the surface energy generated (Yuhan et al. 2019); thus, the catalytic activity of the composites decreases.

As shown in Fig. 7D, the catalytic activity of GO/PtNPs showed an increasing and then, decreasing trend at a turning point of 180 °C. This is therefore the optimum

hydrothermal synthesis temperature. When the temperature of the hydrothermal reaction is lower, Pt^{4+} has not yet been reduced to Pt^0 . At higher temperatures, the Pt^0 loaded on the surface of graphene oxide increases continuously. Consequently, the spacing between the graphene oxide lamellae is increased, which effectively reduces the possibility of the agglomeration of graphene oxide. This contributes to the increase in the catalytic activity of the material (Yuhan et al. 2019).

Therefore, through the optimization of experimental conditions in the preparation process of GO/PtNPs, the ideal pH value is 9.5, the concentration of H_2PtCl_6 is 0.24 mM, the hydrothermal time is 9 h, and the reaction temperature is 180 °C.

Analysis of catalytic kinetics

The synthesized GO/PtNPs have catalase-like properties. With H_2O_2 and TMB as substrates, the catalytic activity of GO/PtNPs was investigated under the optimal conditions by using the theory and method of enzyme kinetics. In a certain range of substrate concentration, the reaction is typical Michaelis–Menten kinetics as can be seen



Fig. 8 Steady state kinetic measurement and catalytic mechanism of GO/PtNPs (**a**–**d**). **a** Relationship diagram between initial velocity and TMB concentration; **c** Relationship diagram between initial velocity and H_2O_2 concentration; **b**, **d** Catalytic kinetic fitting diagram of GO/PtNPs activity when one substrate (H_2O_2 or TMB) concentration is fixed and the other substrate concentration changes. Reaction condition: **a**, **b** GO/PtNPs 0.047 µg/mL, H_2O_2 0.02 M, TMB 0.001, 0.005, 0.01, 0.02, 0.1, 0.3, 0.5, 1.0, 1.5 mM, pH=5, t=5 min, λ =652 nm (c,d) GO/PtNPs 0.047 µg/mL, H_2O_2 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04 M, TMB 0.02 mM, pH=5, t=5 min, λ =652 nm

in Fig. 8. The kinetic data were obtained by changing the concentration of one substrate and fixing the concentration of another, and applied to the double reciprocal of Michaelis–Menten equation as shown in Eq. 1;

$$\frac{1}{\nu} = \frac{K_m}{V_{\text{max}}} \left(\frac{1}{S} + \frac{1}{K_m}\right) \tag{1}$$

where ν is the initial rate, $V_{\rm max}$ is the maximum reaction rate, [S] is the substrate concentration, and $K_{\rm m}$ is the Michaelis constant (Shi et al. 2011). $K_{\rm m}$ and $V_{\rm max}$ were obtained from Lineweaver–Burk diagram (Table 1). The $K_{\rm m}$ value of GO/PtNPs under H₂O₂ conditions is higher than that of enzymes such as GBR (Ray et al. 2017) (see Table 1), which indicates that the activity of GO/PtNPs under H₂O₂ condition, the relatively small $K_{\rm m}$ value is obtained by changing the concentration of TMB. This indicates that TMB has stronger affinity with GO/PtNPs.

Optimization of test conditions

Composite material concentration

It can be seen from Fig. 9 that with the increase in the concentration of graphene oxide thin/nano-platinum composite, the trend gradually increases at first and then, reaches plateau at 1.5 absorbance. This is because the higher the concentration of GO/PtNPs, the more cata-lase-like catalytic sites in the reaction system. So, it can catalyze more effectively the decomposition of hydrogen peroxide to produce hydroxyl radicals to oxidize TMB into oxTMB, and the more obvious the color change (Liu et al. 2012); that is, the greater the absorbance. However, with the increase in GO/PtNPs dosage, the cost will also increase. Therefore, according to the color development



Fig. 9 Optimization of composite material concentration during color development. Reaction condition: GO/PtNPs (0.047, 0.094, 0.141, 0.187, 0.234, 0.281 μ g/mL), H₂O₂ 0.02 M, TMB 0.02 Mm, pH=5, t=5 min, λ =652 nm

as shown in Figure S2, when the concentration of composite material is 0.05 μ g mL⁻¹, the material cost can be controlled, and the higher absorbance value can reduce the background interference in the detection process. Therefore, the concentration of GO/PtNPs selected for the experiment is 0.05 μ g mL⁻¹ as the detection condition for Ag⁺.

Reaction time

It can be seen from Fig. 10 that the absorbance is proportional to the reaction time. The absorbance reaches plateau after 20 min. The longer the reaction time, the more sufficient GO/PtNPs can catalyze H_2O_2 , and the more hydroxyl radicals generated from decomposition will oxidize TMB into oxTMB (Liu et al. 2012), so the absorbance is also larger. However, the longer the reaction time, the higher the time cost of detecting Ag⁺. Therefore, according to

Table 1 Comparison of apparent Michaelis constant (K_m) and maximum reaction rate (V_{max}) between GO/PtNPs and other catalases

Catalyst	Substance	$V_{\rm max} [10^{-8} { m M s^{-1}}]$	<i>K</i> _m [mM]	References
GO/PtNPs	TMB	16.23	0.041	This study
	H_2O_2	31.25	111.56	
GBR	TMB	0.68	0.83	Ray et al. (2017)
	H ₂ O ₂	3.60	10.98	
CoS-p-rGO	TMB	5.0	0.3380	Borthakur et al. (2017)
	H_2O_2	12.2	0.1114	
Co-ferrocene metal-organic framework	TMB	29.7	27.63	Fang et al. (2020)
	H_2O_2	-	-	
Iridium oxide nanoparticles	TMB	179	19.27	Zhen et al. (2020)
	H ₂ O ₂	-	-	
Fe–N/C single-atom nanozyme	TMB	59.8	0.97	Qc et al. (2020)
	H ₂ O ₂	-	-	
Co-His-GQD-G	TMB	38	0.66	Li et al. (2021)
	H_2O_2	-	-	



Fig. 10 Optimization of reaction time during color development. Reaction condition: GO/PtNPs 0.047 μ g/mL, H₂O₂ 0.02 M, TMB 0.02 Mm, pH=5, t=1, 3, 5, 10, 15, 20, 25, 30 min, λ =652 nm



Fig. 11 Optimization of pH during color development. Reaction condition: GO/PtNPs 0.047 μ g/mL, H₂O₂ 0.02 M, TMB 0.02 Mm, pH=2.2, 3, 4, 5, 6, 7, 8, t=5 min, λ =652 nm

Figure S3, the color development was very obvious at 5 min, so 5 min was selected as the optimum time.

pН

It can be seen from Fig. 11 and Figure S4 that the absorbance increases from pH 2 to pH 5 where the absorbance reaches the maximum value of 0.676. The reason is that GO/PtNPs, as a catalase-like material, is greatly affected by pH as other enzymes. When pH is between 4 and 5, this kind of catalase has the highest catalytic activity (Li et al. 2021; Liu et al. 2012). More hydroxyl radicals are decomposed within this pH, causing stronger oxidation ability to TMB, and thus, increases the absorbance. This is consistent with the results of TMB color conditions reported in the literature (Liu et al. 2012). Therefore, the reaction system with pH 5 was selected as the detection condition of Ag⁺.

Hydrogen peroxide concentration

As shown in Fig. 12, the absorbance values of the system showed a tendency to increase with the increase in hydrogen peroxide concentration before stabilized



Fig. 12 Optimization of H_2O_2 concentration during color development. Reaction condition: GO/PtNPs 0.047 µg/mL, H_2O_2 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04 M, TMB 0.02 Mm, pH=5, t=5 min, $\lambda=652$ nm

beyond 0.035 M. This is mainly due to the increase in H_2O_2 around the catalytic active sites of GO/ PtNPs with the increase in hydrogen peroxide concentration, which decomposes to produce more –OH, and thus, accelerates the color development of TMB (Li et al. 2021; Liu et al. 2012). However, according to the color development shown in Figure S5, the detection can be satisfied when the H_2O_2 concentration is 0.02 M.

TMB concentration

As shown in Fig. 13, the absorbance value keeps on increasing with the increase in TMB concentration. However, at the TMB concentration of 0.02 mM, the absorbance value is 0.485, which can achieve the detection requirements (refer Figure S6). At the same time, this concentration avoids the phenomenon of a high background value caused by the system's too dark in color. Therefore, the TMB concentration in the subsequent experiments was chosen to be 0.02 mM.



Fig. 13 Optimization of TMB concentration during color development. Reaction condition: GO/PtNPs 0.047 μ g/mL, H₂O₂ 0.02 M, TMB 0.001, 0.02, 0.1, 0.3, 0.5, 1.0, 1.5 mM, pH=5, t=5 min, λ =652 nm



nano-platinum peroxidase activity. Reaction condition: GO/PtNPs 0.047 μ g/mL, H₂O₂ 0.02 M, TMB 0.02 Mm, pH=5, t=5 min, λ =652 nm

Ag⁺ ion detection

Specific detection of different metal ions

In order to evaluate the selectivity of Ag⁺ detection based on GO/PtNPs colorimetric sensor, when other conditions remain unchanged, Zn²⁺ Cr⁶⁺ Cu²⁺ Ni²⁺ Al³⁺, Cd²⁺ and Ca^{2+} are selected as interference ions to investigate the specificity of the colorimetric sensing platform. As shown in Fig. 14, the absorbance of the reaction system with interference ions is close to that of the blank group, and there is no obvious inhibition on the properties of GO/PtNPs catalase. However, the absorbance of the reaction system with Ag⁺ decreased significantly, indicating that Ag⁺ significantly inhibited the catalytic ability of GO/PtNPs. This is due to the nonspecific adsorption of Ag⁺ on the surface of GO/PtNPs, which makes the active site on the composite not fully exposed, thus inhibiting the peroxidase-like activity of the composite (Liu et al. 2019). This nonspecific adsorption is that when Ag^+ is added to the solution, it can coordinate with Pt on GO/ PtNPs. Due to the strong coupling effect between Pt and Ag⁺, the composite surface is more conducive to the adsorption and accumulation of Ag⁺, thus reducing the active sites of nano-platinum catalyzing H_2O_2 on the composite (Chang et al. 2016). Therefore, when Ag⁺ appears in the reaction system, it will inhibit the catalysis of GO/PtNPs on H_2O_2 , resulting in a significant reduction in the absorbance of the reaction system.

Actual water sample detection

As shown in Fig. 15A, with the measured concentration of Ag^+ increasing, the color change of the reaction solution gradually weakens. Figure 15B shows the absorbance change curve of the GO/PtNPs-based colorimetric sensing method under different Ag^+ concentration conditions at the wavelength of 652 nm (the characteristic absorption wavelength of oxTMB). It can be seen from the figure that the change of solution absorbance weakens with the increase in Ag⁺ concentration. This is because Ag⁺ will absorb nonspecific on the surface of the composite material, so that the active sites on the composite material cannot be completely exposed, thus inhibiting the peroxidase-like activity of the composite material (Chang et al. 2016). Figure 15C shows the concentration of Ag⁺ (0.5–1000 μ M) and the absorbance of the solution when the system reacts for 5 min. It can be seen that when the concentration of Ag⁺ is 0.5–1000 μ M, it shows a good exponential relationship with the absorbance of the system, and the linear fitting equation from Fig. 15D is shown in Eq. 2;

$$A = -0.1565 \log \left[\text{Ag}^+ \right] - 0.2922 \tag{2}$$

This provides a basis for the quantitative analysis of Ag^+ . The limit of quantification (LOQ) of this sensing method is 0.5 μ M, which is the lowest concentration of the sample that can be detected in the experiment.

In order to explore its reproducibility, Ag⁺ concentration is configured as 0.5, 1, and 10 μ M. The relative standard deviations (RSDs, n-3) of the obtained results are 5.58%, 1.95% and 6.16%, respectively, which proves that the sensing method has good reproducibility. In addition, Ag⁺ samples with different concentrations were prepared and the accuracy of the sensing method was investigated by spiking recovery experiment. Based on the obtained linear fitting equation, the sample Ag⁺ concentration is calculated from the solution absorbance. The calculation results are shown in Table 2. It can be seen that the recovery rate of the method is 96.46-104.57%, within an acceptable range, indicating that the accuracy and precision of this sensing method are good and can be used for the quantitative detection of Ag⁺ in actual water samples.

As shown in Table 3, the detection range of silver ion based on this colorimetric platform is 0.5–1000 μ M. Compared with sensors of the same kind, the detection range is wider and the application conditions are wider. Moreover, the detection limit is 0.5 μ M, which is more sensitive compared with the same kind of colorimetric sensor.

Detection mechanism of Ag⁺ ion

The principle of the colorimetric sensor is based on the redox reaction between the nano-catalytic material and the substance to be tested to generate a chemical signal, which is outputted as an optical signal through the color change of the color-developing substrate, thus realizing the detection process of the target (Chen et al



Fig. 15 A Photographs of color change of solution of detection system at different concentrations of Ag⁺; **B** Colorimetric sensing method based on GO/PtNPs absorbance versus time curve of different concentrations of Ag⁺; **C** The relationship between the absorbance and the concentration of Ag⁺; and **D** Linear fitting curve between absorbance value and—log [Ag⁺]. Reaction condition: GO/PtNPs 0.047 μ g/mL, H₂O₂ 0.02 M, TMB 0.02 Mm, pH=5, t=5 min, λ = 652 nm

2022; Xu et al 2022). The synthesized GO/PtNPs have superior peroxidase-like properties that can catalyze the decomposition of hydrogen peroxide. The hydroxyl radical generated from the decomposition can oxidize the hydrogen peroxide substrate 3,3',5,5'-tetramethylbenzidine (TMB), which can be changed from a colorless substance to a blue product. When the system contains Ag⁺, it mainly reacts with Pt⁰ on the surface of graphene oxide in a redox reaction to produce silver-platinum bimetallic nanoparticles (Ag@PtNPs), resulting in poor affinity with the substrate TMB. This inhibits the catalytic

activity of the composite material, leading to a lighter color and lower absorbance of the system. The higher the concentration of Ag^+ , the lighter the color of the system, and the lower the absorbance value. The qualitative analysis of Ag^+ can be achieved by the naked eye through the change of color. In addition, according to Lambert's Beer's law, the quantitative relationship between the absorbance value and the concentration of Ag^+ can be established, and finally, the quantitative concentration of Ag^+ is achieved. This mechanism of Ag^+ colorimetric sensor is shown in Fig. 16.

Type of water sample	Sample No	Dosage (µM)	Measured quantity (µM)	Recovery rate (%)
Tap water	1	1	1.02±0.02	102.20±1.87
	2	10	10.46±0.48	104.57 ± 4.82
	3	100	101.77±4.31	101.77±4.31
	4	500	493.63±18.82	98.73 ± 3.76
Pond water	1	1	0.99 ± 0.05	99.32 ± 4.58
	2	10	9.90±0.12	98.98 ± 1.19
	3	100	102.27 ± 4.30	102.27 ± 4.30
	4	500	493.70±20.75	98.74 ± 4.15
River water	1	1	0.99 ± 0.04	98.81 ± 3.86
	2	10	9.66±0.24	96.61 ± 2.40
	3	100	103.28±4.37	103.28 ± 4.37
	4	500	482.30±31.21	96.46±6.24

 Table 2
 Detection of Ag⁺ in actual water samples

 Table 3
 Performance comparison of several silver ion sensors

Core materials	Test method	Detection scope (µM)	Detection limit (µM)	References
(E)-1-((pyridin-4-yl)Methylene) Thio- semicarbazide	Colorimetric sensor	2.2	2.2–15	Sahu et al. (2020)
MNTPZ	Colorimetric fluorescence sensor	1.03	1.03–30	Dongare et al. (2020)
HPEI-AuNPs	Colorimetric sensor	10.3	10.3–315	Bian et al. (2020)
Bulk Ion-selective Optodes	Colorimetric sensor	1.92	1.92-500	Phichi et al. (2020)
Silatrane	Colorimetric sensor	0.141	0.141-1	Singh et al. (2019)
GO/PtNPs	Colorimetric sensor	0.5	0.5~1000	This study



Fig. 16 Detection mechanism of Ag⁺ ion colorimetric sensor based on GO/PtNPs

Conclusion

In this paper, GO/PtNPs were synthesized by one-step hydrothermal method, and the visual detection of Ag^+ was realized by using the catalase-like properties of the material and the nonspecific adsorption of Ag^+ on the surface of the composite. The main conclusions are as follows:

- a. GO/PtNPs were prepared by hydrothermal synthesis, and GO/PtNPs were evaluated by TEM, Raman, and XRD characterization. The weak red shift of D band and G band under Raman characterization indicates that graphene oxide was only partially reduced. The characteristic peak of face-centered cubic structure with unique precious metal platinum appeared in the XRD characterization, indicating that nano-platinum was completely loaded on the surface of graphene oxide. The catalytic activity of GO/PtNPs was investigated using H_2O_2 and TMB as substrates by using the theory and method of enzyme kinetics.
- b. By optimizing the synthesis conditions of GO/PtNPs, it was found that the composite with good catalytic performance could be obtained by pH 9.5, H_2PtCl_6 of 0.25 mM, reaction temperature of 180 °C, and reaction time of 9 h. The reaction conditions for the detection of Ag⁺ were explored through single factor experiments. The composite concentration, reaction time and pH of the system in the reaction process were optimized. The final detection condition selects the concentration of GO/PtNPs as 0.005 μ g mL⁻¹,

reaction time of 5 min and system pH of 5 were used as the detection conditions for Ag^+ .

c. Compared with the effect of eight metal ions, this method has good selectivity for Ag^+ . At the same time, Ag^+ in different concentration gradients and Ag^+ in actual water samples of tap water, pond water and river water are detected. The results show that the detection range of this method is 0.5–1000 μ M and the detection limit is 0.5 μ M. The spike-and-recovery rates of tap water, pond water and river water range from 96.61 to 104.57%, and the detection time is 5 min. Compared with sensors of the same kind, the detection range is wider, more sensitive, and the application conditions are wider, thus offering a broader application prospect.

Supplementary Information

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Additional file 1: Fig. S1. Characterization of GO/PtNPs: (A) to (C) chloroplatinic acid concentrations were 0.16, 0.24, and 0.32 mM, respectively. Fig. S2. Pictures for color development in optimization of composite concentration. Fig. S3. Pictures for color development in optimization of reaction time. Fig. S4. Pictures for color development in optimization of pH. Fig. S5. Pictures for color development in optimization of H₂O₂ concentration. Fig. S6. Pictures for color development in optimization of TMB concentration

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Author contributions

YQ is responsible for all research steps, including experimental protocol design, data collection, data analysis, manuscript preparation/revision. IY and RB were responsible for the supervision and revision of the manuscript. WH and LW participated in the collection of partial experimental data, preparation of results and data analysis. YQ wrote the main manuscript text, and all authors participated in the correction and revision of the final version. All authors read and approved the final manuscript.

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Availability of data and materials

Almost all details of experimental data are presented in the article or additional file and more may be available from the corresponding author via a logical request.

Declarations

Ethics approval and consent to participate

The manuscript does not contain clinical or trial studies on patients, humans, or animals.

Competing interests

The authors declare that they have no competing interests.

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