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Colorimetric determination of o-phenylenediamine in water samples based on the formation of silver nanoparticles as a colorimetric probe

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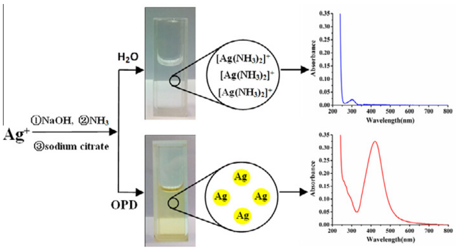
HIGHLIGHTS

- Detection of o-phenylenediamine based on the formation of silver nanoparticles.
- O-phenylenediamine could be monitored by a UV–vis spectrophotometer or the naked eye.
- This method has been applied to determine o-phenylenediamine in water samples.
- Our strategy opens a new avenue for o-phenylenediamine determination.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple, rapid and cost-effective method for visual colorimetric detection of o-phenylenediamine (OPD) based on the formation of silver nanoparticles (AgNPs) has been developed in this paper. Silver ions can be reduced to AgNPs by OPD in a few minutes, causing changes in absorption spectra and color of the reaction system. Therefore, colorimetric detection of OPD could be realized by a UV–vis spectrophotometer or even the naked eye. Results showed that the absorption intensity of AgNPs at 416 nm exhibited a good linear correlation ($R^2 = 0.998$) with OPD concentration in the range from 10^{-6} to 8×10^{-5} mol L^{-1} and the detection limit (3 σ/S) was calculated to be 1.61×10^{-7} mol L^{-1}. Furthermore, as low as 4×10^{-6} mol L^{-1} OPD can be visualized by the naked eye without the requirement of any complicated or expensive instruments. This proposed method has been successfully applied to determine OPD in water samples, and may provide an innovative platform in the development of sensors for guiding environmental monitoring in the future.

Introduction

O-phenylenediamine (OPD), which is known as an important chemical intermediate, is widely used to produce pesticides, medicines, dyes, auxiliaries, photosensitive materials, and has broad market prospects. However, OPD has been found to be a mutagenic substance and be hazardous for human body in the case of ingestion, inhalation, eye contact [1]. Heavy exposure to OPD can damage the respiratory system, digestive system, liver and even lead to cancer. OPD is also regarded as one of the serious environmental pollutants owing to its toxicity and carcinogenicity [2]. The American Conference of Governmental Industrial Hygienists (ACGIH) classified OPD dihydrochloride as a confirmed animal carcinogen with unknown relevance to humans and recommended an occupational exposure limit of 0.1 mg m^{-3} to protect workers

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against blood dyscrasia [3]. OPD is soluble in water, which make it easy to contaminate ground and surface water, and it is of great significance to monitor OPD in drinking and environmental water.

Up to now, several analytical methods have been developed for the determination of OPD including spectrophotometry [4,5], high-performance liquid chromatography (HPLC) [6–8] and capillary electrophoresis (CE) [8,9]. These methods have the advantages of high sensitivity and good selectivity. However, these approaches, which usually require specialized equipments or complicated procedures, are somewhat laborious, time-consuming, expensive, and unsuitable for real-time detection. Therefore, it is highly desirable to develop a new sensitive, fast and practical method for the detection of OPD.

Colorimetric sensors have attracted increasing considerations for their convenience of visual observation and simple operations in recent years [10–12]. Metal nanomaterials such as silver nanoparticles (AgNPs) and Au nanoparticles (AuNPs) have been found wide applications as ideal reporters for colorimetric detection owing to their unique optical and electric properties [13–16]. Taking the advantage of their strong localized surface plasmon resonance (LSPR) absorption with extremely high extinction coefficients, systems based on the formation of metal nanoparticles have been employed for the optical-detection of reducing agents. When gold/silver ions are reduced to AuNPs/AgNPs, solutions show a distinctive color attributed to differences in their size and concentration. Besides, surface plasmon resonance bands of noble-metal nanoparticles are typically located in the visible region and the band is strongly dependent on a nanoparticle's size, shape, composition, crystallinity and interparticle spacing [17]. Therefore, colorimetric sensors can be established relying on the color and UV–vis spectrum response of metal nanoparticles suspension. However, the oxidation of silver ions is weaker than gold ions, and only several substances can reduce silver ions to AgNPs. So the method using silver ions has higher selectivity than that of gold ions. Additionally, Ag nanomaterials are more cost-effective in their preparation compared to Au nanomaterials. The AgNPs-based sensor has been applied to determine many substances such as metal ions [18–21], chiral compounds [22,23], drugs [24–27], pesticide [28,29], small molecular [30–32], and proteins [33,34].

In this paper, a colorimetric sensor for OPD based on its reducing property has been proposed. In the presence of OPD, silver ions can be reduced to AgNPs in a few minutes, accompanied by changes in color and absorption spectra of the reaction system. These changes are proportional to the concentration of OPD. Therefore, OPD can be directly detected by monitoring the color change, scanning UV–vis spectroscopy, or even the naked eye. The proposed method offers many advantages of simplicity, economy, high sensitivity, selectivity and wide linear range. More importantly, our present sensor has been successfully applied to determine OPD in spiked water samples and satisfactory results were obtained. To the best of our knowledge, our strategy is the first example of detecting OPD with visual colorimetric method, and opens a new avenue for OPD determination.

Material and methods

Reagents

OPD ($\geqslant$98.5%), sodium dodecyl sulfate (SDS) and polyvinyl pyrrolidine (PVP) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Silver nitrate ($AgNO_3 \geqslant 99.8\%$) and NaOH were received from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Sodium citrate was obtained from Shanghai Rongrun Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used were of analytical reagent grade and used as received without further purification. Milli-Q-purified distilled water was used throughout the experiments.

Apparatus

TEM analysis was performed on a FEI Tecnai G2 F20 transmission electron microscope (TEM). UV–vis absorption spectra were measured on Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) equipped with 1.0 cm quartz cells. All pH measurements were handled with a pHS-25 digital pH-meter (Shanghai Wei Ye Instrument Factory, China).

Colorimetric detection of OPD

Prior to use, all glassware was soaked in aqua regia (1:3 HNO_3/HCl) and rinsed thoroughly with Milli-Q water and dried in air. 0.5 mL of 15 mmol L^{-1} $AgNO_3$, 0.6 mL of 2 mmol L^{-1} NaOH, 0.25 mL of 0.1 mol L^{-1} NH_3, 0.15 mL of 1% sodium citrate solution and 1 mL of different concentrations of OPD were sequentially added into a 5.0 mL calibrated test tube. Then, the mixture was diluted to 2.7 mL with Milli-Q water and mixed thoroughly to incubate for a certain time. Finally, the reaction solution was transferred into a 1 cm spectrometric cell to record the absorbance. The absorbances were measured at 416 nm (λ_{max} of AgNPs LSPR peak) against a blank solution. It should be noted that the order of addition of reagents is very critical.

Results and discussion

Mechanism of colorimetric detection

Fig. 1 describes the principle of the colorimetric determination of OPD. Obvious color change of the solution can be seen after adding OPD into other reagents. Besides, the absorption of AgNPs was not observed in the presence of OPD alone or other reagents without OPD in the region of 330–700 nm. After the reaction between other reagents and OPD, an absorption peak appeared at about 416 nm, indicating the formation of AgNPs. Based on these phenomenons, a colorimetric method for the determination of OPD could be realized by the naked eye or UV–vis spectroscopy during the formation of AgNPs. Even the presence of trace OPD could result in visual color and absorption spectra changes. The transmission electron microscopy image (Fig. 2) of the reaction system also confirmed the formation of AgNPs. Mechanisms of the formation of AgNPs in the presence of OPD that is based on the similar reaction of resorcinol with silver ions were suggested according to the following equations [35]:

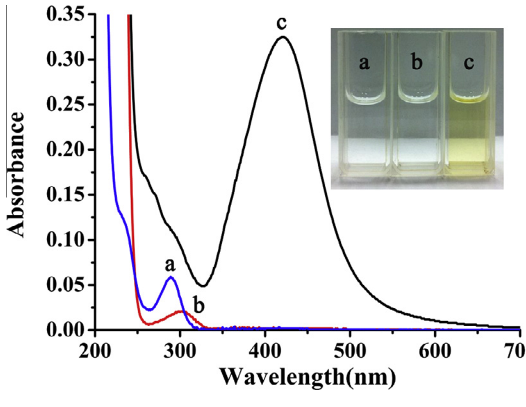

Fig. 1. The absorption spectra and photographs of OPD alone (a), 0.5 mL $AgNO_3$ + 0.6 mL NaOH + 0.25 mL NH_3 + 0.15 mL sodium citrate solution + 1.2 mL H_2O (b), 0.5 mL $AgNO_3$ + 0.6 mL NaOH + 0.25 mL NH_3 + 0.15 mL sodium citrate solution + 1 mL OPD + 0.2 mL H_2O (c). The concentration of OPD is 2×10^{-5} mol L^{-1}.