



High selectivity of colorimetric detection of p-nitrophenol based on Ag nanoclusters

Fei Qu^{a,b,*}, Ping Chen^{a,b}, Shuyun Zhu^{a,b}, Jinmao You^{a,b,c,*}

^a The Key Laboratory of Life-Organic Analysis, Qufu Normal University, Qufu 273165, Shandong, China

^b Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, Qufu Normal University, Qufu 273165, Shandong, China

^c Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining 810001, China

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ABSTRACT

Ag nanoclusters (Ag NCs) templated by hyperbranched polyethyleneimine (PEI) with different terminal groups and molecular weights had been developed as a special optical sensor for detecting p-nitrophenol (p-NP). When adding p-NP into Ag NCs, an obvious color change from pale yellow to deep yellow could be observed by naked eyes, accompanying with an apparent red-shift of absorption peak, and the reason was attributed to the formation of oxygen anion of p-NP based on the transfer of H⁺ from p-NP to amine groups of PEI. The molecular weights of template would greatly affect the sensitivity of p-NP. Ag NCs capped by PEI terminated ethylenediamine (EDA) possessed better sensitivity than other Ag NCs, showing good linear range from 5 to 140 μM with the limit of detection as low as 1.28 μM. Most importantly, this present system displayed high selectivity toward p-NP even in the presence of other nitrophenols and nitrotoluenes. This reliable method had been successfully applied for the detection of p-NP in real water and soil samples.

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1. Introduction

Nitrophenols explosives are organic compounds that contain one or more nitro functional groups (–NO₂), including o-nitrophenol (o-NP), m-nitrophenol (m-NP), p-nitrophenol (p-NP), 2, 6-dinitrophenol (2, 6-DNP), 2, 4, 6-trinitrophenol (TNP) and so on. Among them, 2, 6-DNP and TNP are the main components of explosives in World War I [1]. Although nitrophenol compounds show higher explosive power, they provide lower security than nitrotoluene explosives [2], so at present, they are not the main ingredients in explosives [3]. However, a large number of nitrophenols still have been found in ground water, rivers and soils due to their current applications in dye industrials, pharmaceuticals, and chemical laboratories [4–6]. While because of the nitro and phenol functionalities, they cause strong intense stimulation on the skin and eyes [7,8]. All of these indicate they are harmful to wildlife and humans. In particular, p-NP, a toxic hydrolysis product of the insecticides parathion and paraoxon, has been detected not only in freshwater but also in industrial wastewater and marine environments [9]. It has been proved that p-NP can cause significant damages to biodegradation and the human health including methemoglobinemia and the injuries to the liver and kidney [10]. Therefore, a rapid, sensitive and selective detection of p-NP is highly demanded.

Nowadays, nanomaterials, such as Ag nanoclusters (Ag NCs) [11] and quantum dots (QDs) [12–14], with good chemical stability, biocompatibility, and high quantum yield, have been constructed for analytical detection. However, nanotechnology as optical sensor for measuring p-NP has not been reported, although the most of available nanosensors are used to determinate TNP [11,15–18]. For instance, Min bai's group establishes functionalized β-cysteamine on the surface of fluorescence QDs, which promotes the electron transfer from amine groups to nitro moieties, resulting in fluorescence quenching of QDs by TNP [15]. Normally, electrochemical methods are currently used for the analysis of p-NP [19,20], nevertheless some drawbacks such as long operation time and low anti-interference ability limit the applications.

In this paper, we established a high selectivity of colorimetric sensing platform, which could differentiate p-NP from other nitrophenols based on Ag NCs capped by polyethyleneimine (PEI) terminated enoxylated (EOD), ethylenediamine (EDA) groups and different molecular weights (Mw 600, 10,000, 70,000, and 750,000). Recently, Zhang reported that TNP could quench the fluorescence of PEI-capped Ag NCs via the electron-transfer from electron-rich Ag nucleus to electron-deficient TNP [11]. However, they failed to find special color change of Ag NCs produced by p-NP. In particular, a color change of Ag NCs from pale yellow to deep yellow was observed by naked eyes upon the addition of p-NP in the aqueous phase, and at the same time, the characteristic absorption peak of Ag NCs shifted to long wavelength, so UV–vis measurement was available for selective sensing p-NP with a wide linear range from 5 to 140 μM. As comparison, with addition of other nitrophenols and nitrotoluene compounds, including o-NP, m-

* Corresponding authors at: Qufu Normal University, Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, Qufu, China.

E-mail addresses: qufei3323@163.com (F. Qu), jmyou6304@163.com (J. You).

NP, 2, 6-DNP, TNP, m-nitrotoluene (m-NT), p-nitrotoluene (p-NT), o-nitrotoluene (o-NT), 2, 4-dinitrotoluene (DNT), 2, 4, 6-trinitrotoluene (TNT), there were no apparent peak shift when adding Ag NCs. Besides, this unique sensor could also accurately detect p-NP in the presence of nitrophenols and nitrotoluenes compounds, indicating an excellent capacity of differentiation. With the present sensor, the determination of trace amount of p-NP was realized in real samples, including tap water, river water and soils. The satisfactory recoveries revealed that Ag NCs capped by PEI would be a promising candidate for the environmental monitoring of p-NP.

2. Materials and methods

2.1. Chemicals and reagents

Hyperbranched polyethylenimine (PEI, Mw 600, 10,000, 70,000, 750,000), polyethylenimine branched by EDA, silver nitrate (AgNO_3), formaldehyde (35 wt%), o-nitrophenol (o-NP), m-nitrophenol (m-NP), p-nitrophenol (p-NP), 2,4,6-trinitrophenol (TNP), p-nitrotoluene (p-NT), o-nitrotoluene (o-NT), m-nitrotoluene (m-NT), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). 2,6-dinitrophenol (2, 6-DNP) was supplied by J&K Chemical Reagents Ltd. Polyethylenimine terminated by EOD solution was purchased from Sigma-Aldrich. All chemicals used in this research were of analytical reagent grade. Deionized water (18 M Ω cm) was used in this experiment from a water purification system. All solutions were freshly prepared before use.

2.2. Apparatus

The ultraviolet-visible (UV–vis) absorption spectra were obtained on a Cary 300 Bio UV–vis spectrophotometer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) of Ag NC-PEIs were carried out on a JEM-2100F electron microscope.

2.3. Synthesis of Ag NCs

Typically, the synthesis of PEI stabilized Ag NCs was reported in our previous literature [21]. In this paper, Ag NCs templated by PEI terminated EOD and EDA were synthesized at first time. The synthetic procedure was similar to that reported before and the detailed amounts of AgNO_3 , PEI, and formaldehyde were showed in Table S1. In this assay, Ag NC-PEI 600 was the abbreviation of “Ag NCs templated by PEI with a molecular weight of 600”, and Ag NC-PEI-EOD and Ag NC-PEI-EDA were the

abbreviation of “Ag NCs templated by PEI terminated enoxylated and ethylenediamine groups”.

2.4. Optimization of the sensing system

2.4.1. Concentration of Ag NCs

In this assay, the different concentrations of Ag NCs (0, 3, 5, 7, 9, 10, 12, 15, 17, 19, 25 $\mu\text{L}/\text{mL}$) were added into the p-NP. Subsequently, these mixtures were stirred vigorously for 2 min and equilibrated for 2 min before the UV–vis measurement.

2.4.2. Reaction time

Typically, the mixture of Ag NCs (17 $\mu\text{L}/\text{mL}$) and p-NP (50 μM) were placed different time (2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 min) before measurement.

2.4.3. Ionic strength effect

Firstly, different concentrations of NaNO_3 (0, 0.01, 0.1, 1, 10, 100, 300, 500 mM) were added into the mixture of Ag NCs and p-NP. Subsequently, these mixtures were stirred vigorously for 2 min and equilibrated for 2 min before detection.

2.5. UV–vis detection of p-NP

In a typical experiment, 17 $\mu\text{L}/\text{mL}$ Ag NCs and different concentrations of p-NP (0, 5, 7, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150 μM) were added into ultrapure water. Subsequently, these mixtures were stirred vigorously for 2 min and equilibrated for 2 min before UV–vis measurement. Finally, the absorbance of Ag NCs system in the absence of (A_0) and in the presence of p-NP (A) were recorded at 400 nm, respectively.

2.6. Analysis of real samples

2.6.1. Detection of p-NP in water samples

Typically, the tap water and river water were first treated by ultrafiltration with a 0.45 μm ultrafiltration membrane. Subsequently, 960 μL tap water (or river water) was added. Then, 17 μL Ag NCs and the required amount of p-NP were added to the above solution and the mixture was stirred and incubated for 2 min. Finally, the determination of p-NP in real water samples was analyzed by UV–vis spectrophotometer.

2.6.2. Detection of p-NP in soils

In this assay, approximately 1 g of the removed soil was dissolved in water, and then the solution was centrifuged at 10,000 rpm for 10 min. The supernatant was filtrated through a 0.45 μm ultrafiltration

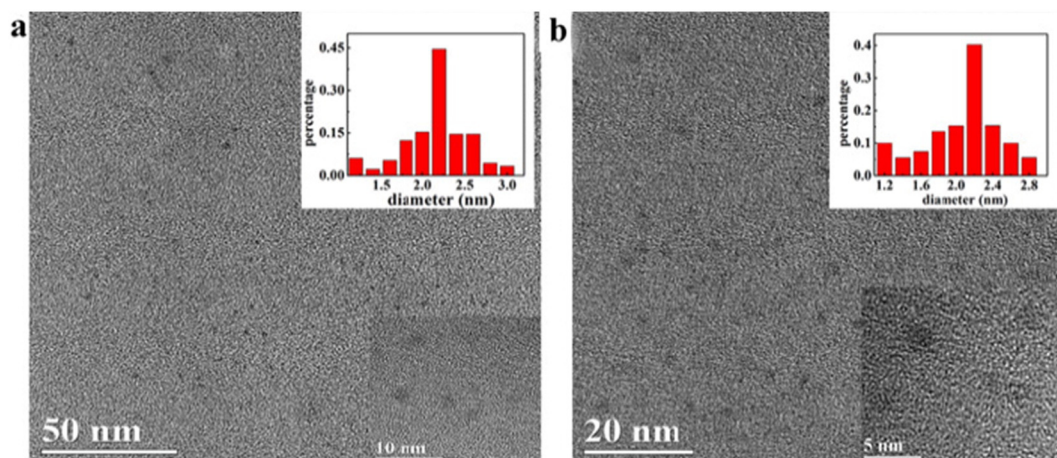


Fig. 1. TEM and HRTEM images of Ag NC-PEI-EOD (a) and Ag NC-PEI-EDA (b).

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