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Histidine-mediated tunable peroxidase-like activity of nanosized Pd for photometric sensing of Ag^+

Wenchi Zhang[a], Xiangheng Niu[a,*], Suci Meng[a], Xin Li[a], Yanfang He[a], Jianming Pan[a], Fengxian Qiu[a,*], Hongli Zhao[b], Minbo Lan[b,*]

[a] Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China
[b] Shanghai Key Laboratory of Functional Materials Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

In this work, we proposed a new and facile strategy for the high-performance colorimetric detection of Ag^+ based on the tunable peroxidase-like activity of Pd nanoparticles (NPs) mediated by histidine (His). Bare Pd NPs possess intrinsic catalytic ability to trigger the oxidation of colorless 3,3′,5,5′-tetramethylbenzidine (TMB) to blue TMBox in the presence of H_2O_2. After being decorated by His, the formed His-Pd nanozyme exhibits significantly improved mimetic activity due to its favorable physicochemical characteristics including smaller size, interactions between Pd and His, and better hydrophilicity, and such that an enhanced TMB color reaction is observed. When Ag^+ exists, it is able to despoil the His modifier from the His-Pd surface via the specific interaction between Ag^+ and His, resulting in the bald Pd again with weak activity. With this principle, highly sensitive determination of Ag^+ in a linear scope of 30–300 nM was achieved with a limit of detection down to 4.7 nM. In addition, the colorimetric sensor based on the tunable enzymatic activity of nanosized Pd adjusted by His could provide excellent selectivity for Ag^+ sensing against common interferents. Reliability of the strategy for practical detection of Ag^+ was also demonstrated.

1. Introduction

In recent years, nanosized materials with enzyme-like activity (nanozymes) have been attracting increasing interest due to their advantages of low cost, easy mass-production, good stability against denaturing, and long-term storage [1–7]. These merits endow them with promising applications in a series of fields, especially in chemo- and biosensing [8–18]. However, in comparison with natural bio-enzymes and organic catalysts, the activities of most current nanozymes are still lower, which inevitably affects their wider applications. To address this deficiency, one has developed several strategies to improve the catalytic properties of nanozymes, including controlling size [19,20], tuning morphology [21,22], screening composition [23], forming hybrids [24,25], optimizing crystal facet [26], and modifying surface [16,27–31]. Among these strategies, surface modification is especially attractive. Coatings on the surface of nanozymes are able to not only stabilize their nanosized structures but also provide potential functional groups for further bioconjugation. More importantly, appropriate surface modification can tune the catalytic activities and efficiencies of nanozymes via changing electronic structure, adjusting surface acidity, blocking surface access, promoting product desorption, and so on [31].

Up to now, a number of substances, including inorganic ions (F^- [32], I^- [16], Hg^{2+} [12,33], PO_4^{3-} [34], S^{2-} [35], et al.), small molecules (DNA [27,29], amino acids [36], et al.), and macromolecules (PEG [19], proteins [37], et al.), have been employed to improve the enzymatic characteristics of nanozymes. Among these modifiers, amino acids are drawing increasing attention because of their excellent biocompatibility and low cost. More importantly, using amino acids to modify the surface of nanozymes can mimic the natural bio-enzymes (in which active sites are usually surrounded by amino acids) better [36]. In addition, from the analytical chemistry point of view, amino acids are easy to interact with other species such as metal ions. Thus, selective detection of metal ions may be achieved in the amino acid-containing system.

Inspired by the above considerations, here we reported the visual sensing of Ag^+ in aqueous phase based on the tunable peroxidase-like activity of nanosized Pd mediated by histidine (His). Ag and its compounds have been widely used in the electrical, photography, and pharmaceutical industries. Moreover, its compounds play an essential role in various medical applications including anti-bacteria, implanted

* Corresponding authors.
E-mail addresses: niuxiangheng@126.com (X. Niu), fxqiu@ujs.edu.cn (F. Qiu), minbolan@ecust.edu.cn (M. Lan).

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prostheses, and water disinfection [38]. These widespread applications have resulted in the increased Ag level in environment. Besides, Ag accumulated in human body can lead to the well-known argyria. Therefore, it is of great importance to explore methods to effectively monitor the species in various environmental and biological samples. In this work, His was employed to modify the surface of Pd nanoparticles (NPs), and significantly improved activity to trigger the color reaction of 3,3′,5,5′-tetramethylbenzidine (TMB) in the presence of H_2O_2 was observed in the formed His-Pd compared with bare Pd. When Ag^+ was added, it despoiled the His modifier from the His-Pd surface via the specific interaction between Ag^+ and His, resulting in the bare Pd again with weak activity. With this principle, a new and facile colorimetric assay was developed for the highly sensitive and selective determination of Ag^+. In comparison with conventional methods such as atomic absorption spectrometry [39], inductively coupled plasma-atomic emission spectrometry [40], and voltammetry [41], the sensor developed has the unique advantage of portable monitoring with no need of sophisticate equipments, which makes it possible for in-field analysis.

2. Experimental

2.1. Chemicals

$PdCl_2$ was provided by Shanghai Aladdin Biochemical Technology Co., Ltd. $NaBH_4$, L-glutamine (Glu), L-phenylalanine (Phe), L-tyrosine (Tyr), L-histidine (His), $AgNO_3$, sodium acetate (NaAc), acetic acid (HAc), 3,3′,5,5′-tetramethylbenzidine (TMB), and H_2O_2 were purchased from Sinopharm Chemical Regent Co., Ltd. All other chemicals were of analytical grade and utilized without further purification. Deionized water was used throughout the study.

2.2. Synthesis of His-Pd

The His-Pd nanozyme was synthesized using a one-pot wet-chemical method. Briefly, 5 mL of 50 mM $PdCl_2$ solution and 10 mL of 0.1 M His solution were first mixed together with a mild stir for 1 h at room temperature; then 15 mL of 0.1 M $NaBH_4$ solution was quickly added into the mixture for reaction for 12 h; the formed solid product was rinsed with ethanol and deionized water alternately for several times, and the material was collected by centrifugation and freeze drying for 48 h, thus the His-Pd nanozyme was obtained. To investigate the effects of different amino acids on the peroxidase-like activity of nanosized Pd, another three amino acid-decorated nanozymes (Glu-Pd, Phe-Pd, and Tyr-Pd) were also prepared using the same method. For comparison, the bare Pd counterpart was also obtained with no amino acid added into the synthetic system, as illustrated in Scheme S1 (Supporting information).

2.3. Characterizations

X-ray diffraction (XRD) patterns were obtained on a 6100Lab diffractometer (Shimadzu) with a Cu Kα radiation. Fourier transform infrared spectra (FT-IR) were detected by a Nicolet Nexus 470 instrument (USA Nicolet Co., Ltd.). Transmission electron microscopy (TEM) measurements were carried out on a JEM-2100F microscope (JEOL) with an accelerating voltage of 100 kV. Zeta potentials of samples in 0.2 M NaAc-HAc buffer (pH 4) were performed on a Nano ZS90 instrument (UK Malvern Co., Ltd.). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB-MKII spectrometer (Thermo-Fisher Scientific Co., Ltd.) with an Al Kα radiation as the excitation source. Water contact angles of samples were obtained at room temperature using a KSV CM200 instrument (Finland Attention Co., Ltd.) combined with a high speed camera.

2.4. Colorimetric measurements

The peroxidase-like activities of the synthesized materials were investigated by the catalytic oxidation of TMB in the presence of H_2O_2. All the reactions were monitored by a Cary 8454 ultraviolet-visible (UV–vis) spectrometer (Agilent Technologies Co., Ltd.). A 5 mM TMB stock solution was prepared with ethanol for use. H_2O_2 stock solutions with various concentrations were daily prepared. 0.2 M NaAc-HAc solutions with different pH values (adjusted by diluted HCl or NaOH) were prepared as the incubation buffer. Typically, the colorimetric measurements were performed in a 5 mL cylinder with 3 mL NaAc-HAc buffer (0.2 M, pH 4.0) consisting of 5.55 μg/mL nanozyme, 0.327 M H_2O_2, and 0.167 mM TMB. The time-dependent absorbance changes were recorded with a 30 s interval. The steady-state kinetic measurements were carried out by recording the absorbance at 652 nm at a 5 s interval within 1 min. The apparent kinetic parameters were calculated based on the equation $v = V_{max} \times [S]/(K_m + [S])$, where v is the initial velocity, V_{max} is the maximum reaction velocity, $[S]$ is the substrate (H_2O_2 or TMB) concentration, and K_m is the Michaelis-Menten constant.

For the detection of Ag^+, the target with various concentrations was mixed with the His-Pd peroxidase mimic in 0.2 M NaAc-HAc solution (pH 4.0) for 10 min. Then, 50 μL of 9.8 M H_2O_2 and 50 μL of 5 mM TMB were added into the mixture. After reaction for 15 min, the solution was ready for colorimetric measurements.

3. Results and discussion

3.1. Synthesis and characterization of His-Pd

In the present study, the His-Pd material was prepared by a commonly used reduction approach in aqueous phase at room temperature. As illustrated in Scheme S1 (Supporting information), $PdCl_2$ and $NaBH_4$ are employed as the Pd precursor and the reductant, respectively. His is added into the synthetic system to obtain the His-Pd nanozyme. For comparison, the bare Pd counterpart was also synthesized under identical conditions with no His added.

First, the synthesized materials were characterized by several means. Fig. 1(A) compares the XRS patterns of His-Pd and bare Pd. The bare Pd provides three remarkable diffraction signals at $2\theta = 40.12°$, 46.66° and 68.12°, which should be attributed to the (111), (200) and (220) planes of the face-centered cubic structure of Pd (JCPDS No. 46-1043). These peaks are well defined with narrow full width at half maximum (FWHM) and high intensity, indicative of a good crystallinity of the bare Pd. With regard to His-Pd, three recognizable peaks of Pd located at the same places are also observed. Due to the modification of His on the Pd surface, these diffraction signals turn to be less remarkable, providing wider FWHM and lower intensity. In the FT-IR spectra (B), the bare Pd exhibits no unique absorption signal. In comparison with bare Pd, the His-Pd material provides several notable peaks: the significantly enhanced broad peak in the wavenumber window of 3150–3700 cm^{-1} is ascribed to the −OH group and the $-NH_2$ group in His, the C—H stretching vibration offers the absorption peaks at around 2900 cm^{-1}, the increased signal at ~1650 cm^{-1} is due to the −COOH group in His, and in the 800–1400 cm^{-1} wavenumber range the His-Pd mimic also provides corresponding absorption signals. The FT-IR result clearly demonstrates that His has been successfully modified onto the Pd surface via the one-pot wet-chemical method.

Furthermore, the morphology of the synthesized His-Pd was observed by TEM. As shown in (C), irregular particles with a large size (> 10 nm) are obtained for bare Pd. The His-Pd material also exhibits a shape of NPs (D), while these particles have a smaller size (~4.4 nm). Both Pd and His-Pd NPs show a certain agglomeration, while no precipitate of these particles is found in aqueous solution with aging time. Zeta potential measurements indicate that, in comparison with the bare Pd (with a Zeta potential of 10.2 mV), the modification of His onto the Pd surface (with a Zeta potential of 11.5 mV) increases its dispersibility