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ORIGINAL PAPER

Gold nanoparticle-loaded hollow Prussian Blue nanoparticles with peroxidase-like activity for colorimetric determination of L-lactic acid

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Abstract

The intrinsic peroxidase-like activity of hollow Prussian Blue nanoparticle-loaded with gold nanoparticles (Au@HMPB NPs) were applied to oxidize the substrate 3,3′,5,5′-tetramethylbenzidine (TMB) in the presence of H_2O_2 to give a blue-green coloration. The morphology of the Au@HMPB NPs and its peroxidase-mimicking activity was characterized in detail. The catalytic activity follows Michaelis-Menten kinetics and is higher than that of HMPB NPs not loaded with gold nanoparticles. The NPs were employed to detect L-lactic acid colorimetrically (at 450 nm) via detection of H_2O_2 that is generated during enzymatic oxidation by L-lactate oxidase (LOx). The limit of detection is 4.2 μM. The assay was successfully applied to the quantitation of L-lactic acid in spiker human serum samples.

Keywords Tetramethylbenzidine · Human serum sample · Lactate oxidase · Gold nanoparticles

Introduction

The detection of L-lactic acid is of great significance in bioanalytical and clinical fields. L-lactic acid is usually served as indicator for applications such as diagnosing heart disease and neonatology studies [1, 2]. Therefore, the development of low cost methods for L-lactic acid detection with high specificity and high sensitivity are highly required. Different methods for lactic acid detection have been reported [3, 4]. Most of these methods are based on the enzymatic reactions. For example, lactate dehydrogenase (LDH) can catalyze L-lactic acid in the presence of cofactor NAD^+ to generate pyruvic acid (PA) and NADH, which can be detected by absorption or fluorescence spectroscopy [5]. Alternatively, L-lactic acid can be detected by various amperometric biosensors based on the formation of H_2O_2 via the oxidation of L-lactic acid by L-lactate oxidase (LOx) [6]. Besides, enzyme-based colorimetric analysis is of highly competitive, as it can be detected by bare eyes and does not require complex and expensive instruments. In such colorimetric assays, chromogenic substrates were used to react with H_2O_2 in the presence of horseradish peroxidase (HRP) to form colored products [7, 8].

The commonly used chromogenic substrates include 3,3′,5,5′-tetramethylbenzidine (TMB) [9], 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) [10] and o-phenylenediamine (OPD) [11]. Among these substrates, TMB is a better choice since ABTS can be oxidized in the absence of peroxidase using H_2O_2 alone [12]. HRP possess high efficiency and specificity under mild and eco-friendly conditions. However, its inherent defects are also apparent, such as high cost and easy of denaturation under harsh conditions. Thus, it is imperative to develop artificial enzymes to replace HRP.

Nanomaterial based artificial enzymes have aroused the attention of researchers. Since Fe_3O_4 nanoparticles was found to exhibit intrinsic peroxidase-like activity [13], various nanomaterials have been evaluated to possess a peroxidase-like capacity, including Gold NPs [14], Co_3O_4 NPs [15], V_2O_5 nanowires [16], carbon nanomaterials [17] and $ZnFe_2O_4$ NPs [18]. Since these nanomaterials with peroxidase-like activity have the advantages of low cost, ease of preparation and high stability compared to HRP, they can be extensively applied in biosensors and bioassays [19].

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Prussian Blue nanoparticles (PB NPs) possess high peroxidase-like activity, which is widely use in electrochemistry [20, 21]. Little attention has been paid to the peroxidase mimicking behavior of PB NPs for colorimetric biosensing [22]. However, the intrinsic blue color of PB NPs can interfere with the colorimetric detection while the poor dispersibility of PB NPs in aqueous solutions has been reported to inhibit its catalytic activity [23]. To overcome these defects, Wang et al. reported filling of multi-walled carbon nanotubes with PB nanoparticles as peroxidase mimic for colorimetric sensing of H_2O_2 and glucose, which not only improved the color distribution and dispersibility of PB NPs but also enhanced the peroxidase-like activity of PB NPs. [24]

Here, we report on gold nanoparticle-loaded hollow mesoporous Prussian Blue nanoparticles (Au@HMPB NPs) as peroxidase mimic for colorimetric determination of L-lactic acid in serum. The loading of gold nanoparticles onto the surface of PB NPs not only prevented the aggregation of PB nanoparticles, but also enhanced its peroxidase-like activity [25–27]. The detection of L-lactic acid was achieved through the detection of H_2O_2 generated by LOx catalyzed oxidation of L-lactic acid.

Experimental section

Chemical and materials

Unless otherwise stated, the reagents and chemicals used in this study were of analytical grade. Polyvinylpyrrolidone (PVP), potassium ferricyanide ($K_3[Fe(CN)_6]$), L-lactic acid and L-lactate oxidase (LOx) were obtained from Sigma-Aldrich (https://www.sigmaaldrich.com/). 3,3′,5,5′-Tetramethylbenzidine (TMB) were obtained from Heowns Co., Ltd. (Tianjin, China, http://www.heowns.cn/). Gold (III) chloride tetrahydrate ($HAuCl_4{\cdot}4H_2O$) were purchased from Sangon Bitech Co., Ltd. (Shanghai, China, https://www.sangon.com/).

Transmission electron microscope (TEM) images of Au@HMPB were obtained from FEI Tecnai G2 60–300 microscopy (Hillsboro, USA). The optical densities measurements were carried out using a Biotek Model ELx800 Microplate Reader (Shanghai, China).

Synthesis of hollow mesoporous Prussian Blue (HMPB) nanoparticles

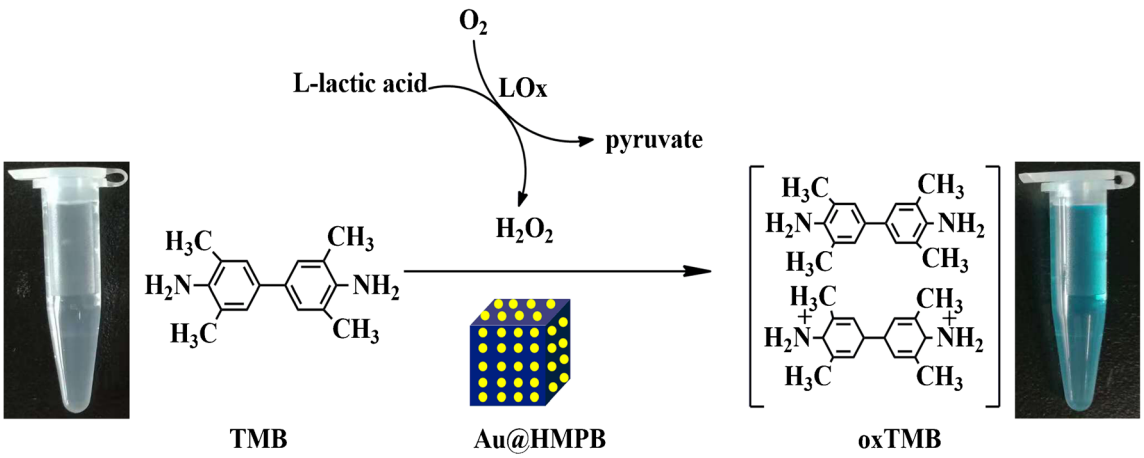
HMPB nanoparticles were prepared according to previous reports with minor revisions [28]. The detailed synthesis procedures are shown in electronic supporting material.

Synthesis of Au@HMPB nanoparticles

Briefly, 5 $mg.mL^{-1}$ HMPB nanoparticles (1 mL) and 0.01% chlorauric acid ($HAuCl_4$) solution (16 mL) were mixed and heated. After boiling, 1% sodium citrate solution (0.34 mL) was quickly added into the above solution under vigorous stirring for 5 min in the dark. The final product was washed and collected by successive centrifugation.

Peroxidase-like activity assays

In a typical assay, the peroxidase-like activity of HMPB NPs and Au@HMPB NPs were carried out at 40 °C in 0.2 M sodium acetate buffer (pH 3.5) in the presence of 800 μM freshly prepared TMB (TMB dissolved in DMSO) and 400 mM H_2O_2. The kinetic analysis with H_2O_2 as the substrate was carried out using standard reaction condition (described above) by varying the concentration of H_2O_2 (0–0.5 M) at a fixed concentration of TMB (800 μM). Similarly, the kinetic analysis with TMB as the substrate was performed using above method by varying the concentration of TMB (0–1 mM) with 400 mM H_2O_2.



Scheme 1 Schematic representation for the detection of L-lactic acid

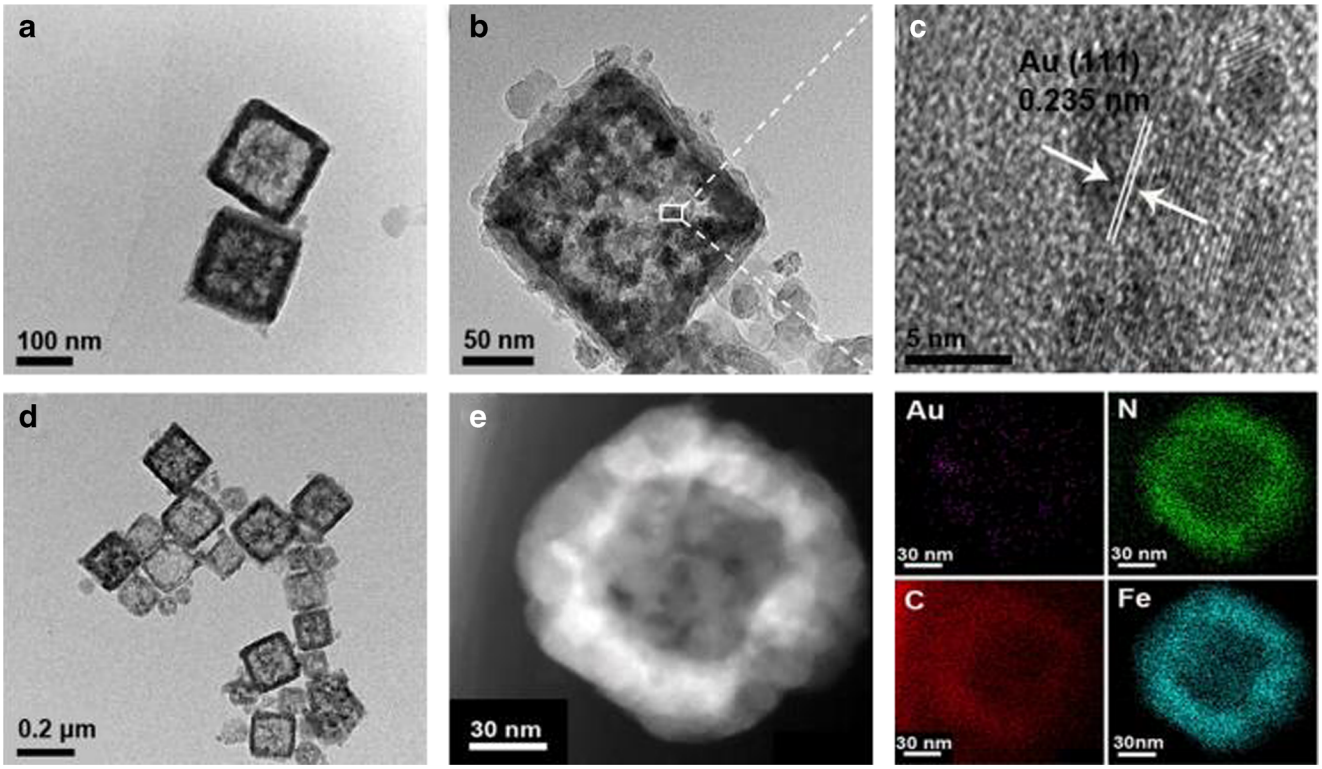


Fig. 1 TEM image of **a** HMPB NPs, **b** Au@HMPB NPs, **c** HRTEM image, **d** dispersed Au@HMPB NPs and **e** elemental mapping images of Au@HMPB NPs (C, N, Fe, Au)

Detection of L-lactic acid by Au@HMPB NPs

50 μL of 0.01 mg.mL^{-1} LOx, 400 μL of L-lactic acid with different concentrations and 50 μL of 200 mM phosphate buffer (pH 7.0) were mixed and incubated at 37 °C for 10 min. Then 90 μL of the above mixture, 100 μL freshly prepared TMB substrate solution (800 μM TMB in 0.2 M acetate buffer, pH 3.5), and 10 μL of the Au@HMPB NPs (0.04 mg.mL^{-1}) were added into the well of 96-well plate and incubated at 40 °C for 1 h in the dark. The color change was visually observed. After adding 4.0 μL of stop solution (2.0 M H_2SO_4), the absorbance was recorded at 450 nm with the ELx800 microplate reader.

Determination of L-lactic acid in serum

For L-lactic acid analysis in serum samples, a standard addition experiment was performed. The serum sample was diluted by phosphate buffer (pH 7.0, 200 mM), spiked with different concentration of L-lactic acid and then analyzed.

Results and discussion

Choice of materials

Gold nanoparticles were loaded onto HMPB to enhance the catalytic activity of HMPB as gold nanoparticles also have peroxidase mimicking behavior. The hollow structure of Au@HMPB NPs can increase surface area that leads to more active sites, which is beneficial for peroxidase-like activity of Au@HMPB NPs.

Synthesis and characterization of Au@HMPB and HMPB nanoparticles

Scheme 1 shows the schematic representation for the detection of L-lactic acid. The HMPB is synthesized by

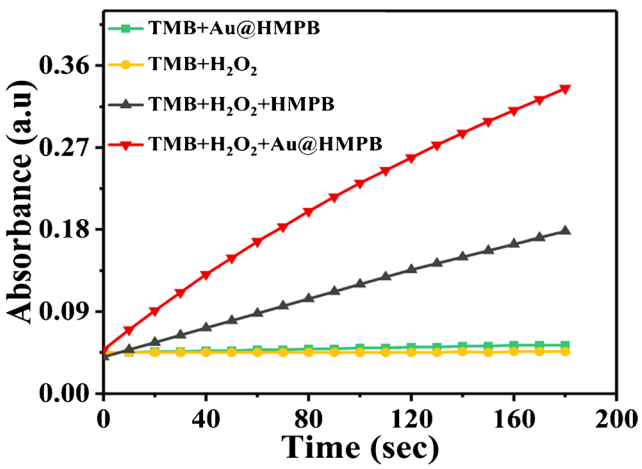


Fig. 2 UV–vis absorption-time curve of the TMB–H_2O_2 system under different conditions

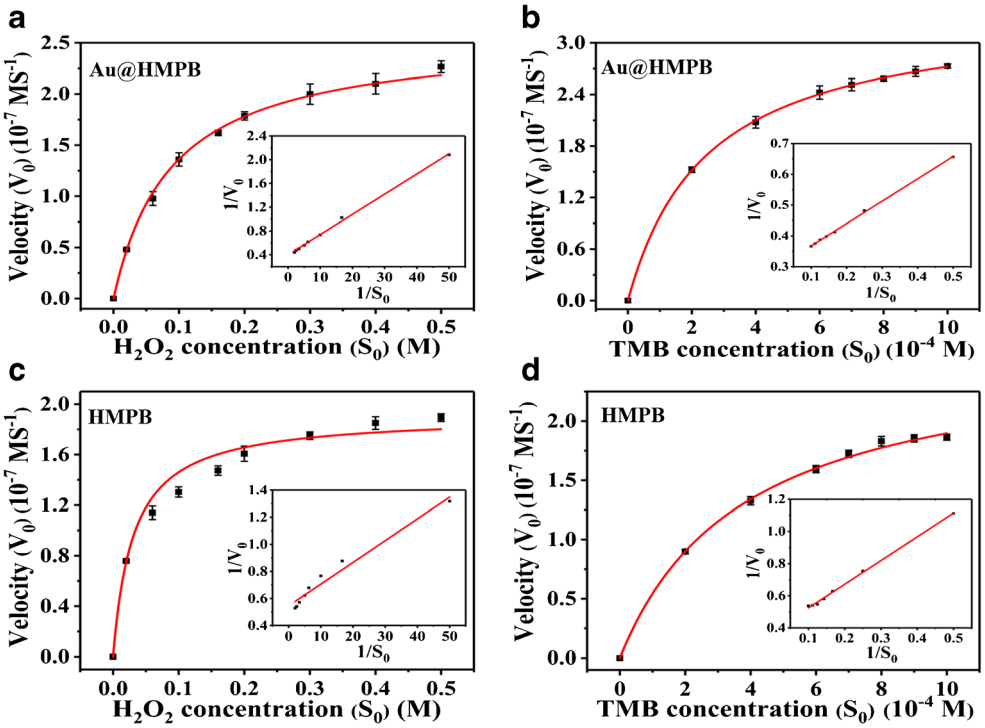


Fig. 3 Steady-state kinetic study using the Michaelis–Menten model and Lineweaver–Burk model (insets) for Au@HMPB and HMPB NPs by **a**, **c** varying the concentration of H_2O_2 with a fixed amount of TMB and **b**, **d** varying the concentration of TMB with a fixed amount of H_2O_2

etching solid PB with acid, and the gold nanoparticles are loaded onto HMPB by reducing $HAuCl_4$ with sodium citrate. The morphology of the Au@HMPB and HMPB nanoparticles were characterized by transmission electron microscope (TEM). As shown in Fig. 1a, the unmodified HMPB possess a hollow and highly porous structure with an average size of 150 nm. The nanoporous shell of the hollow particles resulted in an increase of the surface area, which is beneficial for the following growth of Au nanoparticles. After deposition of Au nanoparticles, Au nanoparticles were distributed on the surface of the nanoparticles (Fig. 1b). In the high-resolution TEM (HRTEM) image (Fig. 1c), the lattice spacing of gold layer was about 0.235 nm, which corresponds to the (111) facets of Au. The gold nanoparticles modified HMPB can be well dispersed into solution (Fig. 1d). Elemental mapping data further proved that Au nanoparticles were well-distributed over the entire HMPB nanoparticles (Fig. 1e).

Table 1 The comparison of the kinetic parameters of HRP, HMPB and Au@HMPB NPs

Materials	Substrate	Km/mM	Vmax/$10^{-6}MS^{-1}$	Temperature
Au@HMPB	TMB	0.25	0.34	
	H_2O_2	88.72	0.25	
HMPB	TMB	0.38	0.26	40 °C
	H_2O_2	30.93	0.19	
HRP	TMB	0.43	0.10	
	H_2O_2	3.70	0.08	

Peroxidase-mimetic activity of Au@HMPB and HMPB NPs

To compare the peroxidase enzyme mimetic activity of HMPB and Au@HMPB NPs, TMB was chosen as the substrate. As shown in Fig. 2, HMPB and Au@HMPB can both catalyze oxidation of TMB in the presence of H_2O_2 to produce the blue color complex, similar to HRP. In the absence of HMPB or Au@HMPB NPs, there was no change in the color of solution, suggesting that the oxidation of TMB would not happen. What's more, it can be seen from the Fig. 2 that the catalytic rate of Au@HMPB NPs is higher than that of HMPB NPs,

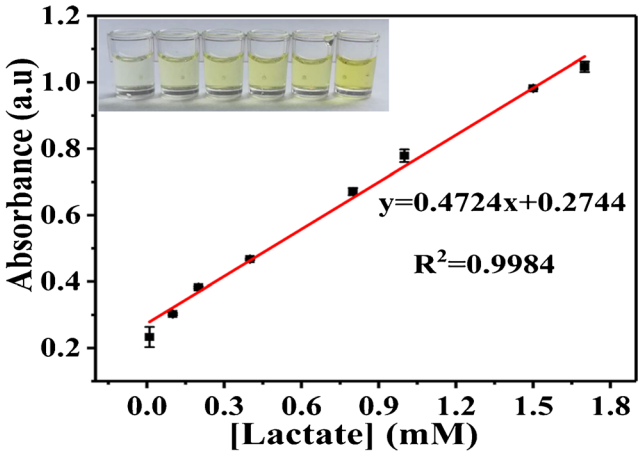


Fig. 4 Linear calibration plot for L-lactic acid assay by the combination of L-lactic acid oxidation catalyzed by LOx and TMB oxidation catalyzed by Au@HMPB NPs. Absorption Data acquired at 450 nm was utilized to draw the calibration curve

Table 2 Compare the performance of the assay for L-lactic acid detection with previous reports

Analytical method	Biosensing materials	Detection limit (μM)	Linear range(μM)	Reference
Electrochemistry	N-CNTs/LOx	4.1	14~3.25 × 10^2	[4]
Fluorimetry	Al-coated nanoprobe/LDH	20	60~1 × 10^3	[32]
Fluorimetry	CuONPs/LDH	0.045	0.8~80	[33]
Chemiluminescent	Luminol/LOx	9.2	50~4 × 10^3	[34]
Colorimetry	Au-Ag/LOx	0.33	0.1~22, 22~220	[35]
Colorimetry	Au@HMPB/LOx	4.2	10~1.7 × 10^3	This work

CNT represents carbon nanotube

suggesting that Au@HMPB NPs exhibit higher peroxidase-like activity. The enhanced catalytic activity is mainly ascribed to the loaded Au nanoparticles.

Optimization of method

The following parameters were optimized: (a) Sample pH value and (b) reaction temperature. Respective data and Figures are given in the Electronic Supporting Material. The following experimental conditions were found to give best results: (a) Best sample pH value of 3.5 and (b) optimal reaction temperature of 40 °C.

Steady-state kinetic analysis of Au@HMPB and HMPB NPs The peroxidase-like activity of Au@HMPB and HMPB NPs were also studied by Michaelis-Menten curves, which were obtained by varying the concentration of H_2O_2 and TMB (Fig. 3). Michaelis–Menten constant (K_m) and maximal velocity (V_{max}), as the crucial enzyme kenetic patameters, can be obtained by fitting the data to Lineweaver-Burk double-reciprocal plot (inset of Fig. 3). K_m is an indicator of enzyme affinity toward its substrates [29]. A high K_m indicates weak affinity, whereas a low value suggests high affinity. The K_m value for Au@HMPB NPs towards TMB is lower than that of HRP and HMPB, suggesting that Au@HMPB NPs have higher affinity with TMB in comparison to HRP and HMPB NPs. Moreover, the K_m value of HMPB NPs is also lower than that of HRP. However, the K_m value of Au@HMPB NPs with H_2O_2 was higher than that for HRP, indicating that a higher H_2O_2 concentration was required to achieve maximal activity for the Au@HMPB NPs (Table 1) [13, 30]. The surface area is closely related to the catalytic active site [31]. Therefore, the hollow and multihole structure of Au@HMPB NPs can expose more active sites that enhanced the peroxidase mimicking behavior. Moreover, Au NPs also has peroxidase-like activities [26], which indicated that the observed enhanced activity of Au@HMPB NPs can be attributed to the synergistic effect between Au NPs and HMPB NPs. A similar phenomenon was also reported for graphene oxide-AuNCs and Au@Ag heterogeneous NRs [25–27].

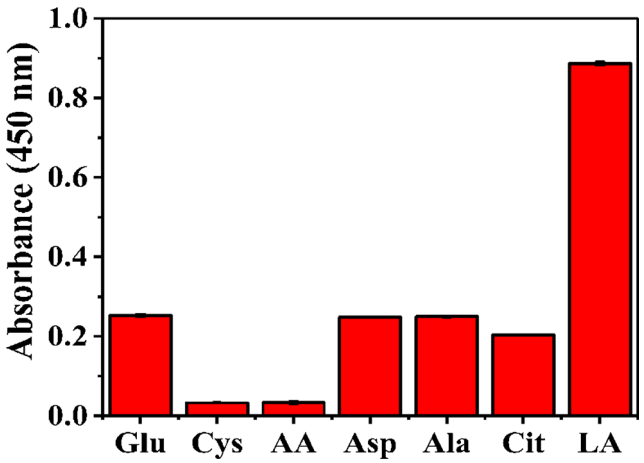


Fig. 5 Selectivity of the L-lactic acid assay. Glucose, L-cysteine ascorbic acid, L-aspartic acid, L-alanine, citric acid and L-lactic acid (each 1 mM) were tested

Analytical application

Reliable and sensitive detection of L-lactic acid is of great importance in biochemistry, clinical diagnostics and food industry. In this assay, LOx catalyzed the L-lactic acid to generate H_2O_2 and pyruvate. Then, H_2O_2 can react with TMB in the presence of Au@HMPB NPs. Therefore, the detection of L-lactic acid can be achieved via detection of enzymatic byproduct, H_2O_2 (Eqs. 1 and 2). As shown in Fig. 4, the colorimetric responses increase linearly with the increasing concentration of L-lactic acid. The linear range for L-lactic acid detection is 10–1700 μM with the linear regression equation of y = 0.4724 x + 0.2744 and correlation coefficient (R^2) of 0.998.The detection limit is calculated to be 4.2 μM based on S/*N* = 3.

Table 3 Analytical results of L-lactic acid deteremination in human serum

L-lactic acid added (mM)	Found(mM)	Recovery(%)	RSD(%)
0.1	0.098	98.0	2.3
0.4	0.411	102.8	1.1
0.8	0.825	103.1	1.0
1	1.03	103.3	2.4
1.7	1.67	98.2	0.34

$$\text{L-lactic acid} + O_2 \xrightarrow{\text{LOx}} H_2O_2 + \text{pyruvate} \quad (1)$$

$$H_2O_2 + \text{TMB} \xrightarrow{\text{Au@HMPB}} H_2O + \text{oxidized TMB} \quad (2)$$

The analytical performance of the assay is compared with previous literaure reports for L-lactic acid detection. Form Table 2, it can be seen the performance of our assay is comparable or better than literature reports.

To investigate the specificity of our assay, a series of controlled experiments were conducted using glucose (Glu), L-cysteine (Cys), ascorbic acid (AA), L-aspartic acid (Aap), L-alanine (Ala) and citric acid (Cit) instead of L-lactic acid. As shown in Fig. 5, no significant signals were observed for the control experiments, suggesting that LOx has high substrate specificity. The result also demonstrated that Au@HMPB NPs as peroxidase mimetics were sensitive and specific enough to detect L-lactic acid.

To evaluate the feasibility of our study for analysis of L-lactic acid in biological samples, a standard addition method was applied to the detection of L-lactic acid in human serum samples. As shown in Table 3, the recoveries of the different concentration of L-lactic acid in serum samples ranging from 98.0% to 103.3% and the relative standard deviation (RSD) was estimated to be <5%. Thus the Au@HMPB NPs were promising as peroxidase mimetics for potential application of L-lactic acid detection clinically.

Conclusions

We demonstrate here that both Au@HMPB and HMPB NPs possess high peroxidase-like activity that can oxidize TMB in the presence of H_2O_2. Moreover, Au@HMPB NPs exhibit higher catalytic activity and higher stability in aqueous solution than HMPB NPs. The enhanced peroxidase-like activity is mainly due to the large surface area and the synergistic effect between Au NPs and HMPB NPs. Taking into accout the above factors, Au@HMPB NPs were chosen to detect L-lactic acid via the detection of H_2O_2 that generated by LOx catalyzed oxidation of L-lactic acid. The synthesized Au@HMPB NPs may find wide applications as peroxidase mimic in different areas. However, the assay was based on detection of absorption intensity of oxidaized TMB product. If the enzyme-mimicking nanomaterials can oxidize substarte to generate fluorescence emission, the detection sensitivity can be significantly enhanced.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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