Influence of VO$_2$ Nanoparticle Morphology on the Colorimetric Assay of H$_2$O$_2$ and Glucose

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Abstract: Nanozyme-based colorimetric sensors have received considerable attention due to their unique properties. The size, shape, and surface chemistry of these nanozymes could dramatically influence their sensing behaviors. Herein, a comparative study of VO$_2$ nanoparticles with different morphologies (nanofibers, nanosheets, and nanorods) was conducted and applied to the sensitive colorimetric detection of H$_2$O$_2$ and glucose. The peroxidase-like activities and mechanisms of VO$_2$ nanoparticles were analyzed. Among the VO$_2$ nanoparticles, VO$_2$ nanofibers exhibited the best peroxidase-like activity. Finally, a comparative quantitative detections of H$_2$O$_2$ and glucose were done on fiber, sheet, and rod nanoparticles. Under the optimal reaction conditions, the lower limit of detection (LOD) of the VO$_2$ nanofibers, nanosheets, and nanorods for H$_2$O$_2$ are found to be 0.018, 0.266, and 0.41 mM, respectively. The VO$_2$ nanofibers, nanosheets, and nanorods show the linear response for H$_2$O$_2$ from 0.025–10, 0.488–62.5, and 0.488–15.625 mM, respectively. The lower limit of detection (LOD) of the VO$_2$ nanofibers, nanosheets, and nanorods for glucose are found to be 0.009, 0.348, and 0.437 mM, respectively. The VO$_2$ nanofibers, nanosheets, and nanorods show the linear response for glucose from 0.01–10, 0.625–15, and 0.625–10 mM, respectively. The proposed work will contribute to the nanozyme-based colorimetric assay.

Keywords: VO$_2$ nanoparticles; morphology; nanozyme; colorimetric sensor

1. Introduction

Natural enzymes with great catalytic capacity and high substrate specificity have attracted much research interest in the fields of medicine, biology, and food industry. Despite these broad developments, natural enzymes often have inherent drawbacks, such as high preparation and purification costs, low operational stability, sensitivity of catalytic activity to environmental conditions, and difficulty of recovery. These shortcomings are limited to its practical application [1]. Artificial mimic enzymes have the characteristics of high catalytic efficiency, stability, economy, and large-scale preparation which has been rapidly developed in the fields of medicine, chemical industry, food, agriculture, environmental science, and analytical chemistry [2]. Among the various artificial mimic enzymes, nanozymes as the new-generation enzyme-mimetic have attracted considerable interest since the ferroferric oxide nanomaterial has the catalytic properties similar to horseradish peroxidase (HRP) [3]. Many nanoparticles have been studied as enzyme mimetics, including ferromagnetic NPs [3–11], cerium oxide NP [12–14], metal NPs [15–23], carbon-based nanomaterials [24–28], V$_2$O$_5$ nanowires [29,30], and perovskite oxide [31,32].

Vanadium dioxide (VO$_2$) have received considerable attention for their redox activity and layered structures, which can serve as very good intercalation materials and smart sensors [33]. The VO$_2$ exists in multiple morphologies, such as fibers, nanorods, nanosheets, spheres, and hollow spheres [34,35]. The shape of the nanoparticle has attracted growing interest due to its effect on the
catalytic, optical, electronic, and magnetic properties [9,36–41]. For example, one-dimensional (1D) nanostructures—such as nanotubes, nanorods, and nanowires—exhibit higher activity and durability, compared with zero-dimensional (0D) nanostructures, due to possessing fewer lattice boundaries, fewer defect sites, and longer segments of surface crystalline planes [36]. Therefore, we focused on the effect of different morphology on the catalytic activities of VO2 nanoparticles in order to obtain more information for their potential applications in biosensor and biocatalysts.

Herein, different morphologies VO2 nanoparticles—including fibers, sheets, and rods—were synthesized. The catalysis activities and kinetic mechanic of various VO2 nanoparticles were investigated upon the reaction of hydrogen peroxide with its reducing substrates 3,3′,5,5′-tetramethybenzidine (TMB). The hydrogen peroxide and glucose colorimetric sensors were developed based on VO2 nanoparticles with different shapes. In this colorimetric assay, different analytical parameters—such as concentrations of nanoparticles, buffer solution, and pH of the analyte medium—were determined. Under optimal reaction conditions, the detection system of fiber-like VO2 nanoparticles shows the most sensitive response to H2O2 and glucose than the other two VO2 nanoparticles.

2. Results and Discussions

2.1. Characterization of VO2 Nanoparticles

The structural characterizations of the VO2 nanoparticles were done by transmission electron microscopy (TEM) and X-ray powder Diffraction (XRD). TEM images indicate the VO2 nanoparticles of different morphology, fibers, rods, and sheets (Figure 1). The formation of VO2 nanoparticles is confirmed from the X-ray diffraction pattern (Figure 2). The VO2 nanoparticles with fiber, sheet, and rod shapes have the same crystal structures as those reported in the literature [34,35], and are monoclinic VO2 (Joint Committee on Powder Diffraction Standards card No. 31-1438 and No. 65-7960: see Figure 2).

![Figure 1. TEM images of VO2 nanoparticles. (a) VO2 nanofibers (b) VO2 nanosheets (c) VO2 nanorods.](image)

![Figure 2. XRD patterns of VO2 nanoparticles. (A) VO2 nanofiber; (B) VO2 nanosheets; (C) VO2 nanorods.](image)
2.2. Principle

In pH 4 citrate buffer solution at room temperature, VO2 nanoparticles with different morphologies catalyzed the oxidation of a peroxidase substrate 3,3′,5,5′-tetramethylbenzidine (TMB) in the presence of H2O2 to obtain the TMB oxidized product with blue color. As shown in Figure 3, when various VO2 nanoparticles were added into the TMB/H2O2 solution, the strong absorption peaks were obtained at 656 nm. However, there were no strong absorption peaks when the solution did not contain H2O2 or VO2 nanoparticles. The absorbance becomes stronger due to more TMB being oxidized with the increasing of the concentration of H2O2. The absorbance also showed a linear trend depending on the concentration of H2O2.

![UV-Visible absorption spectra and color changes of different reaction systems.](image)

**Figure 3.** UV-Visible absorption spectra (a) and color changes (b) of different reaction systems. ((A) TMB + H2O2, (B) TMB + VO2 nanorod, (C) TMB + VO2 nanosheet, (D) TMB + VO2 nanofiber, (E) TMB + VO2 nanorod + H2O2, (F) TMB + VO2 nanosheet + H2O2, (G) TMB + VO2 nanofiber + H2O2).

2.3. Effect of pH

The effect of pH value (pH 3.0–8.0) on absorption value with TMB was investigated in the citrate buffer system, as shown in Figure 4. Each of the VO2 nanofibers, nanosheets, and nanorods of the system reached their maximum peaks when the pH value was 4.0. Therefore, pH 4.0 was selected to detect H2O2 and glucose with various VO2 nanoparticles.

![The effect of pH on absorption value with TMB and color changes.](image)

**Figure 4.** The effect of pH on absorption value with TMB and color changes. (a) VO2 nanofibers; (b) VO2 nanosheets; (c) VO2 nanorods. The error bars represent the standard deviation of three measurements.

2.4. Effect of Buffers

The effect of buffers on absorption value of TMB oxide product was examined. The time response curves of TMB with H2O2 catalyzed by VO2 with different morphologies, in pH 4.0, 0.2 M acetate, phosphate, and citrate buffers. The results were shown in Figure 5. Up to 300 s, the VO2 nanoparticles were more active in the citrate buffer solution. Thus, the citrate buffer solution (pH = 4.0, 0.2 M), was chosen as the optimal reaction solution for the H2O2 and glucose colorimetric assay.
The effect of VO2 nanofibers, nanosheets, and nanorods with TMB as the substrate was apparently lower than VO2 nanofibers, with the concentration of VO2 nanofibers, nanosheets, and nanorods with TMB were 0.518, 0.111, and 0.801 mM, respectively. The Vmax of VO2 nanofibers, nanosheets, and nanorods with H2O2 were 1.043, 2.924, and 6.469 mM. The KM values shows that VO2 nanosheets with TMB as the substrate was apparently lower than VO2 nanofibers, VO2 nanosheets, and nanorods with H2O2 were 4.66 × 10−4, 9.73 × 10−4, and 3.99 × 10−5 M, respectively. The KM of VO2 nanoparticles were determined in detail. As shown in Figure 7, the typical Michaelis-Menten curve were obtained for VO2 nanozymes. Michaelis-Menten constant (KM) and maximum initial velocity (Vmax) were known from Michaelis-Menten curve use a Lineweaver-Burk plot. A comparison of the kinetic parameters of VO2 nanoparticles were determined in detail. As shown in Figure 6, the absorption values at OD656nm of TMB oxide product increased gradually with the concentration of VO2 nanoparticles. The system reached its maximum absorption value when the concentrations of VO2 nanofibers, nanosheets, and nanorods were 10, 10, and 2 mM, respectively. The results show that the catalytic activity of VO2 nanofibers is stronger than the other two, shown in the Figure 6.

2.5. Effect of VO2 Nanoparticle Morphologies and Concentrations

As shown in Figure 6, the absorption values at OD656nm of TMB oxide product increased gradually with the concentration of VO2 nanoparticles. The system reached its maximum absorption value when the concentrations of VO2 nanofibers, nanosheets, and nanorods were 10, 10, and 2 mM, respectively. The results show that the catalytic activity of VO2 nanofibers is stronger than the other two, shown in the Figure 6.

2.6. Steady-State Kinetic Assay

For further understanding the influence of particle morphology on the catalytic mechanism of VO2 nanoparticles, the steady-state kinetic assay for VO2 nanoparticles were determined in detail. As shown in Figure 7, the typical Michaelis-Menten curve were obtained for VO2 nanozymes. Michaelis-Menten constant (KM) and maximum initial velocity (Vmax) were known from Michaelis-Menten curve use a Lineweaver-Burk plot. A comparison of the kinetic parameters of VO2 nanozymes, V2O5 nanozymes, Fe3O4 magnetic nanoparticle (MNP5), and HRP was given in Table 1. The KM of VO2 nanofibers, nanosheets, and nanorods with TMB were 0.518, 0.111, and 0.801 mM, respectively. The Vmax of VO2 nanofibers, nanosheets, and nanorods with TMB were 9.3 × 10−5, 1.68 × 10−4, and 3.99 × 10−4 M·s−1, respectively. The KM of VO2 nanofibers, nanosheets, and nanorods with H2O2 were 1.043, 2.924,
and 6.469 mM. The $V_{\text{max}}$ of VO$_2$ nanofibers, nanosheets, and nanorods with H$_2$O$_2$ were $4.66 \times 10^{-4}$, $9.73 \times 10^{-4}$, and $1.46 \times 10^{-3}$ M·s$^{-1}$, respectively. The $K_M$ values shows that VO$_2$ nanosheets with TMB as the substrate was apparently lower than VO$_2$ nanofibers, VO$_2$ nanorods, V$_2$O$_5$ nanozymes, Fe$_3$O$_4$ MNPS, and HRP. It shows that the VO$_2$ nanosheets have a higher affinity to TMB compared with VO$_2$ nanofibers, VO$_2$ nanorods, Fe$_3$O$_4$ MNPS, and HRP. Which means that a lower TMB concentration was required to reach the maximal activity for VO$_2$ nanosheets. The apparent $K_M$ values of VO$_2$ nanofibers with H$_2$O$_2$ as the substrate was apparently lower than VO$_2$ nanorods, VO$_2$ nanosheets, Fe$_3$O$_4$ MNPS, and HRP. It shows that the VO$_2$ nanofibers have a higher affinity for H$_2$O$_2$ compared with VO$_2$ nanosheets, VO$_2$ nanorods, Fe$_3$O$_4$ MNPS, and HRP. That means a lower H$_2$O$_2$ concentration was required to reach the maximal activity for VO$_2$ nanofibers.

Figure 7. The steady-state kinetic assay and catalytic mechanism of VO$_2$ nanofibers (a,b); VO$_2$ nanosheets (c,d); and VO$_2$ nanorods (e,f) as peroxidase mimics. Conditions: pH, 4.0 (0.2 M citrate buffer); temperature, 25 °C; incubation time, 5 min.
Table 1. Comparison of the $K_M$ and $V_{\text{max}}$ of VO$_2$ nanozymes, V$_2$O$_5$ nanozymes, Fe$_3$O$_4$ MNPs, and HRP, respectively.

| Nanozymes     | Substrate | $K_M$ (mM) | $V_{\text{max}}$ (M·S$^{-1}$) |
|---------------|-----------|------------|-------------------------------|
| VO$_2$ nanofibers | TMB     | 0.518      | $9.3 \times 10^{-5}$           |
| VO$_2$ nanofibers | H$_2$O$_2$ | 1.043      | $4.66 \times 10^{-4}$          |
| VO$_2$ nanosheets | TMB     | 0.111      | $1.68 \times 10^{-4}$          |
| VO$_2$ nanosheets | H$_2$O$_2$ | 2.924      | $9.73 \times 10^{-4}$          |
| VO$_2$ nanorods | TMB     | 0.801      | $3.99 \times 10^{-4}$          |
| VO$_2$ nanorods | H$_2$O$_2$ | 6.469      | $1.46 \times 10^{-3}$          |
| V$_2$O$_5$ nanozymes | TMB     | 0.738      | $1.85 \times 10^{-5}$          |
| V$_2$O$_5$ nanozymes | H$_2$O$_2$ | 0.232      | $1.29 \times 10^{-5}$          |
| Fe$_3$O$_4$ MNPS | TMB     | 0.434      | $1.00 \times 10^{-8}$          |
| Fe$_3$O$_4$ MNPS | H$_2$O$_2$ | 154        | $9.78 \times 10^{-8}$          |
| HRP           | TMB     | 0.434      | $1.24 \times 10^{-8}$          |
| HRP           | H$_2$O$_2$ | 3.70       | $2.46 \times 10^{-8}$          |

2.7. Calibration Curve for H$_2$O$_2$ and Glucose Detection

Under the optimal conditions (pH 4.0 citrate buffer, the concentrations of VO$_2$ nanofibers, nanosheets and nanorods were 2, 10, and 10 mM, respectively) the calibration curves of H$_2$O$_2$ were obtained with VO$_2$ nanoparticles different morphologies (Figure 8). The correlation between the absorbance values and H$_2$O$_2$ concentration are linear over the range of 0–100 mM (nanofibers), 0–500 mM (nanosheets) and 0–500 mM (nanorods) with correlation coefficients 0.99981, 0.99364, and 0.99222, respectively. The lower limit of detection (LOD) of the VO$_2$ nanofibers, nanosheets, and nanorods for H$_2$O$_2$ are found to be 0.018, 0.266, and 0.41 mM, respectively.

![Figure 8](image-url)

**Figure 8.** A dose-response curve depending of the absorbance at 656 nm in the presence of different concentrations of H$_2$O$_2$. (a) VO$_2$ nanofibers; (b) VO$_2$ nanosheets; (c) VO$_2$ nanorods. Error bars represent the standard deviation of three measurements. Conditions: pH 4.0 (0.2 M citrate buffer); temperature, 25 °C; incubation time, 5 min.

As glucose oxidase (GOx) can catalyze the oxidation of glucose and produce H$_2$O$_2$, the absorption value with TMB was changing by H$_2$O$_2$ in presence of VO$_2$ nanoparticles. Because the GOx would be denatured in pH 4.0 buffer, the glucose detection was produced in two steps: first, H$_2$O$_2$ was induced by GOx oxidation of glucose and then the reaction solutions were detected by TMB/different VO$_2$ nanoparticles system. As shown in Figure 9, the absorption increases gradually with the increasing of glucose concentration. The correlation between the absorbance at 656 nm and glucose concentration are linear over the range of 0–30 mM (nanofibers), 0–40 mM (nanosheets) and 0–40 mM (nanorods) with the correlation coefficient of 0.988557, 0.98919, and 0.99502, respectively. The lower limit of detection (LOD) of the VO$_2$ nanofibers, nanosheets, and nanorods for glucose are found to be 0.009, 0.348, and 0.437 mM, respectively.

The VO$_2$ nanofibers showed the highest peroxidase activity in the H$_2$O$_2$ and glucose colorimetric assay, followed by VO$_2$ nanosheets, and finally VO$_2$ nanorods. Additionally, it was reported that
the specific surface area of VO$_2$ nanoparticles greatly influences their catalytic activities. The specific surface area of VO$_2$ nanofibers (185 to 122 m$^2$ g$^{-1}$) [34] is also much larger than that of other VO$_2$ micro/nanoparticles, such as hollow microspheres (22.3 m$^2$ g$^{-1}$), nanowires (12.3 m$^2$ g$^{-1}$) [42], nanobelts (18.6 m$^2$ g$^{-1}$) [43], nanorods (42 m$^2$ g$^{-1}$) [44], VO$_2$ mesocrystals (28.4 m$^2$ g$^{-1}$) [45], mesoporous VO$_2$ nanowires (46.7 m$^2$ g$^{-1}$) [46], and 3D GO-VO$_2$ nanosheet flowers (71.6 m$^2$ g$^{-1}$) [47]. Therefore, the VO$_2$ nanofibers demonstrated the most sensitive response during the H$_2$O$_2$ and glucose sensing. By comparing with other nanozymes to further understanding the catalytic activity of VO$_2$ nanozymes as peroxidase mimetics, as shown in Table 2, the VO$_2$ nanofibers have a wider linear range.

![Figure 9](image_url)

**Figure 9.** A dose-response curve depending of the absorbance at 656 nm in the presence of different concentrations of glucose. (a) VO$_2$ nanofibers; (b) VO$_2$ nanosheets; (c) VO$_2$ nanorods, in which error bars represent the standard deviation of three measurements. Conditions: pH, 4.0 (0.2 M citrate buffer); temperature, 25 °C; incubation time, 5 min.

**Table 2.** Comparison of different nanozymes for the detection of H$_2$O$_2$.

| Nanozymes        | Linear Range | Limit of Detection | Reference |
|------------------|--------------|--------------------|-----------|
| Fe$_3$O$_4$ MNPs | 1–100 μM     | 0.5 μM             | [48]      |
| HRP              | 1–60 μM      | 1 μM               | [49]      |
| Pt-DNA complexes | 0.979–17.6 mM| 0.392 mM           | [50]      |
| V$_2$O$_5$ nanozymes | 1–500 μM | 1 μM               | [30]      |
| VO$_2$ nanofibers | 0.025–10 mM  | 0.018 mM           | This work |
| VO$_2$ nanosheets | 0.488–62.5 mM| 0.266 mM           | This work |
| VO$_2$ nanorods  | 0.488–15.6 mM| 0.41 mM            | This work |

3. Materials and Methods

3.1. Chemicals and Materials

All the chemicals used were of analysis grade without further purification. 3,3',5,5'-Tetramethylbenzidine (TMB) was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Glucose oxidase (GOx) was obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). V$_2$O$_5$, oxalic acid, methanol, glucose, hydrogen peroxide (H$_2$O$_2$, 30%), etc., were purchased from Beijing Chemical Works (Beijing, China). The water used in the experiments was purified.

3.2. Synthesis of VO$_2$ Nanoparticles

The synthesis of VO$_2$ nanofiber contains two steps: synthesis of VO$_2$ hollow sphere and the supernatant collecting and drying. According to the literature procedure [35] synthesis of VO$_2$ hollow sphere, with minor adjustment. Briefly, V$_2$O$_5$ and oxalic acid (the ratio of molar is 1:3) were first dissolved in 7 mL distilled water and stirred for 10 min at room temperature. Then the 23 mL methanol was added in the solution and stirred for another 10 min. The mix solution was transferred to a Teflon-lined autoclave with stainless steel, and heated at 200 °C for 24 h. The sample was cooled down naturally. The black precipitates were filtered off and washed with distilled water and ethanol, and then dried at 80 °C overnight, and finally the VO$_2$ hollow spheres were dissolved, the supernatant...
was collected and dried. Similar procedures were adopted to prepare nanorods and nanosheets: when the water content is 10 mL, the product is nanorods, and when the solution is completely water, the product is just nanosheets (with water and methanol measures maintained at 30 mL).

3.3. Physical Characterization

The morphology and size of the VO$_2$ nanoparticles were acquired using a transmission electron microscopy (TEM) by JEM-1011 transmission electron microscopy (JEOL, Tokyo, Japan) with a working voltage at 100 kV. The X-ray powder diffraction method was carried out in a D/max-α power diffractometer (Rigaku, Tokyo, Japan) using Cu-Kα monochromatic radiation ($\lambda = 1.5418$ Å).

3.4. H$_2$O$_2$ Detection Using VO$_2$ Nanoparticles as Peroxidase Mimetics

To discover the peroxidase-like character of VO$_2$ nanoparticles, the experiments were performed as follows: 60 µL VO$_2$ nanoparticles solution (the concentrations of nanofibers, nanosheets, and nanorods are 2, 10, and 10 mM, respectively) in a reaction volume of 2400 µL citrate buffer solution (pH = 4.0) and 480 µL TMB solution (1.5 mM in ethanol), followed by the addition of 60 µL H$_2$O$_2$ (30%). The mixed solution was reacted for 5 min at room temperature. Then used for the UV-Vis spectrophotometer (Metash Instruments Inc., Shanghai, China) record the spectra at 656 nm for TMB.

To investigate the influence of buffer solution on the VO$_2$ nanoparticle characteristics, the pH—ranging from 3.0 to 8.0 of the buffer solution—was examined, under conditions identical to these used above.

To investigate the influence of different reaction buffers on the VO$_2$ nanoparticles characteristics, catalytic reactions incubated in difference buffer solution—including citrate, phosphate, and acetate—were examined, under conditions identical to these used in above. For a blank, only substrate solution was used. All experiments were conducted at room temperature (25 °C).

3.5. Glucose Detection Using VO$_2$ Nanoparticles

Glucose detection was examined as follows: (a) 200 µL of GOx (1 mg/mL) and 200 µL of glucose of different concentrations in 400 µL of phosphate buffered saline (PBS, pH = 7.0) were incubated at 37 °C for 60 min; (b) 400 µL of TMB (1.5 mM in ethanol) and 50 µL of VO$_2$ nanoparticles solution (the concentrations of nanofibers, nanosheets, and nanorods are 2, 10, and 10 mM, respectively) in 1750 µL of citrate buffer solution (pH = 4.0) were added into the above glucose reaction solution; (c) The mixed solutions with different concentrations of glucose were incubated for 5 min; (d) the UV-Vis spectrophotometer was used to record the spectra.

4. Conclusions

VO$_2$ nanoparticles with different structures—nanofibers, nanosheets, and nanorods—have been successfully fabricated and show peroxidase-like activities. The catalytic behaviors of VO$_2$ nanoparticles show Michaelis-Menten kinetics and good affinity to both H$_2$O$_2$ and TMB. The VO$_2$ nanoparticle-based colorimetric assay provides fast, sensitive, and low-cost H$_2$O$_2$ and glucose sensors. Compared with VO$_2$ nanorods and VO$_2$ nanosheets, the VO$_2$ nanofibers demonstrated the most sensitive response during the H$_2$O$_2$ and glucose sensing. This investigation is significant for vanadium-based nanozyme application in biosensor and biocatalysis.

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