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Artificial Enzymes

Nanocomposite Incorporating V_2O_5 Nanowires and Gold Nanoparticles for Mimicking an Enzyme Cascade Reaction and Its Application in the Detection of Biomolecules

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Abstract: Artificial enzyme mimics are a current research interest, and many nanomaterials have been found to display enzyme-mimicking activity. However, to the best of our knowledge, there have not hitherto been any reports on the use of pure nanomaterials to construct a system capable of mimicking an enzyme cascade reaction. Herein, we describe the construction of a novel nanocomposite consisting of V_2O_5 nanowires and gold nanoparticles (AuNPs) through a simple and facile chemical method, in which V_2O_5 and AuNPs possess intrinsic peroxidase and glucose oxidase (GOx)-like activity, respectively. Results suggest that this material can mimic the enzyme cascade reaction of horseradish peroxidase (HRP) and GOx. Based on this mechanism, a direct and selective colorimetric method for the detection of glucose has been successfully designed. Because single-strand and double-strand DNA (ssDNA and dsDNA) have different deactivating effects on the GOx-like activity of AuNPs, the sensing of target complementary DNA can also be realized and disease-associated single-nucleotide polymorphism of DNA can be easily distinguished. Our study opens a new avenue for the use of nanomaterials in enzyme mimetics, and holds promise for the further exploration of nanomaterials in creating alternative catalytic systems to natural enzymes.

Introduction

Developing artificial enzymes has received great interest recently owing to the advantages that they offer over natural enzymes in practical applications, such as the low cost of their preparation and purification, superior operational stability, and high stability to environmental conditions.[1] The emergence and recent advances of nanoscience and nanotechnology have opened new opportunities for the design and construction of enzyme mimics.[2] The exciting first report of intrinsic horseradish peroxidase (HRP)-like activity of inert ferromagnetic nanoparticles aroused great attention for further innovative research on nanomaterials in the enzyme mimetic field.[3] Thereafter, more nanomaterial-based peroxidase mimics emerged in succession, showing that graphene oxide,[4] carbon nanotubes,[5] carbon dots,[6] nanoceria,[7] gold nanoparticles (AuNPs),[8] and V_2O_5 nanowires[9] may also be potential substitutes for natural enzymes. Although these enzyme mimics showed promising potential in biomedical applications and environmental detection,[4–9] engineering these synthetic nanocomponents into organized functional systems mimicking complex natural enzyme systems, especially for enzyme-catalyzed cascade reactions, still remains a major challenge in this field.[10]

Recently, AuNPs have been found to be capable of catalytically oxidizing glucose to produce gluconates in a "green" manner. This transformation resembles that performed by the natural enzyme glucose oxidase (GOx), which catalyzes the oxidation of glucose with the co-substrate oxygen (O_2) to produce gluconate and H_2O_2.[8b] V_2O_5 nanowires exhibit an intrinsic HRP-like activity towards classical peroxidase substrates such as 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) in the presence of H_2O_2.[9a] These V_2O_5 nanowires show an optimum reactivity at pH 4.0 and their catalytic activity is dependent on their concentration. Herein, we report the construction of a novel nanocomposite with dual enzyme-mimetic activities by combining V_2O_5 nanowires and AuNPs. On the basis of the unique and attractive properties of these components, this system could be applied as a robust nanoreactor for mimicking an enzyme cascade reaction without the need for the natural enzymes. Furthermore, the system can not only be used for the detection of glucose, but can also serve as a nanoprobe for colorimetric sensing of target DNA with high sensitivity and selectivity.

Results and Discussion

The preparation of the nanocomposite and the enzyme-mimetic catalytic cascade reaction are illustrated in Scheme 1. V_2O_5

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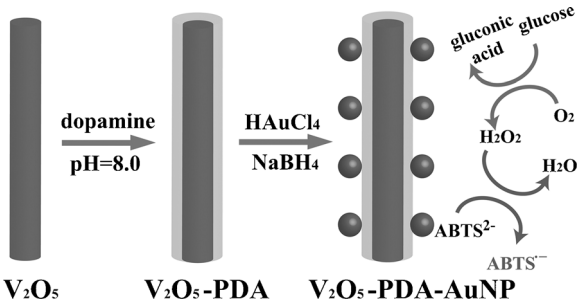


Scheme 1. Schematic representation of the preparation of V_2O_5-PDA-AuNP composite material and its mimicking of an enzyme cascade reaction process.

nanowires were prepared by a hydrothermal method as described elsewhere.[9a] A V_2O_5-polydopamine (PDA) composite could be readily synthesized because dopamine (DA) can self-polymerize at alkaline pH values and spontaneously deposit uniform polydopamine films on the surfaces of V_2O_5 nanowires.[11] The thickness of such a uniform coating can be precisely controlled by adjusting the DA concentration. The formation of the PDA layer is of critical importance for the synthesis of the composite material. On the one hand, PDA contains plenty of functional groups that provide abundant heterogeneous nucleation and anchor sites for AuNPs and can facilitate the formation of uniform and ultrafine AuNPs. On the other hand, the PDA layer serves to protect the structure of the V_2O_5 nanowires from damage by the strong reducing agent $NaBH_4$ used in the synthesis of AuNPs. Thus, AuNPs were synthesized by $NaBH_4$ reduction using PDA as a template. The steps of the procedure are described in the Experimental Section. The morphologies and compositions of these materials were fully characterized and analyzed by TEM, SEM, UV/Vis, FTIR, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) measurements.[12]

The morphologies of the three kinds of V_2O_5 materials were firstly characterized by TEM and SEM measurements. Figure 1 and Figure S1 in the Supporting Information show typical TEM and SEM images, respectively. The freshly synthesized V_2O_5 nanowires were of various sizes of up to several μm in length and several tens of nm in width.[9a] A typical image of V_2O_5-PDA shows that it has a distinctly rougher surface than that of the V_2O_5 nanowires, confirming that PDA was coated on the surface of the V_2O_5. An SEM image (Figure S1 B) revealed that the V_2O_5-PDA nanowires were much shorter than those of pure V_2O_5, typically several hundreds of nm in length, because ultrasonication broke up the long V_2O_5 nanowires. The smaller size favored dispersion of the V_2O_5 in aqueous solution. As shown in Figure 1 C, D, typical TEM images of the V_2O_5-PDA-AuNP composite revealed that isolated, homogeneous, and ultrafine spherical AuNPs with a mean size of about 4.5 nm were extensively decorated on the V_2O_5-PDA surface. SEM images (Figures S1 C and S1 D) showed the V_2O_5-PDA-AuNP composite to be well-dispersed with no aggregation, and that AuNPs were densely assembled on the surfaces of all of the nanowires.

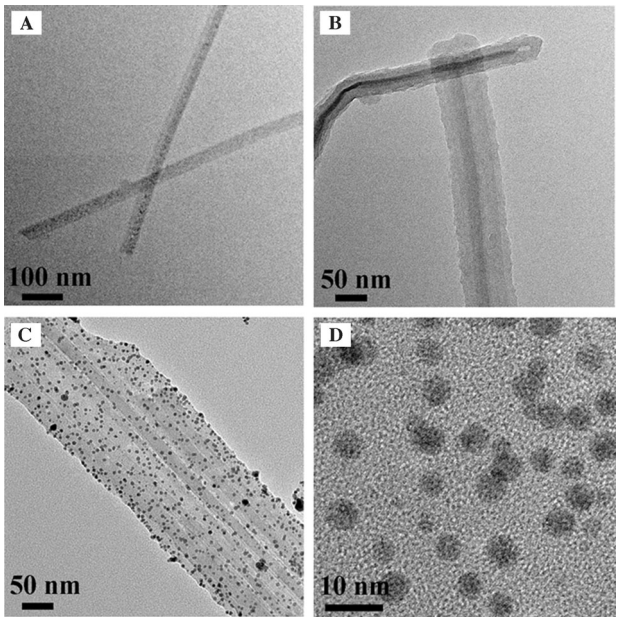


Figure 1. TEM images of (A) V_2O_5 nanowires, (B) V_2O_5-PDA, (C) V_2O_5-PDA-AuNP composite, and (D) AuNPs on the surface of V_2O_5-PDA.

When the V_2O_5 nanowires were dispersed in water, a clear, light-yellow, homogeneous suspension was obtained that showed no obvious absorbance peak in the UV/Vis range (Figure 2 A). After coating with PDA, the suspension obtained was brown in color, indicating stronger absorption over the UV/Vis range than that of the V_2O_5 nanowires. The peak at 280 nm may be ascribed to the absorption of PDA. The UV/Vis spectrum of V_2O_5-PDA-AuNP features an obvious peak at 520 nm, which indicates the presence of AuNPs, and is similar to the peak seen for AuNPs of size about 5 nm alone.[13] FTIR spectra (Figure 2 B) were used to identify the functional groups present on V_2O_5-PDA, and the observed peaks at 1502 and 1616 cm^{-1} are consistent with the indole or indoline structures proposed previously.[14] The broad and intense peak centered at 3159 cm^{-1} and the band at 1286 cm^{-1}, which relate to C–OH stretching and –OH bending vibrations, imply the presence of a large number of residual hydroxyl groups.[14] The TGA curve indicated about 30 wt% PDA on the surface of the V_2O_5 nanowires, which was lost at about 330 °C (Figure 2 C).

XPS analysis confirmed that the V_2O_5 nanowires contained 31.2% V and 68.8% O (Figure 3 A). Figure 3 C shows the core-level binding energies for the V 2p peaks. The binding energies for vanadium $2p_{3/2}$ and $2p_{1/2}$ observed at 517.2 and 524.5 eV, respectively, are in good agreement with those of V^{5+} in V_2O_5 (Figure 3 C).[15] The corresponding O 1s spectrum is shown in Figure 3 D; the O 1s spectrum is broad and asymmetric and can be deconvoluted into two peaks, indicating the presence of two different oxygen species. The peaks at binding energies of 530 and 531.5 eV can be attributed to O 1s of V_2O_5 and OH, respectively.[15] The formation of V_2O_5-PDA was further confirmed by XPS. As shown in Figure 3 B, peaks corresponding to carbon, oxygen, and nitrogen were seen. Only a small amount of vanadium was also observed, indicating the formation of a near-complete PDA coating on the V_2O_5 nanowires.

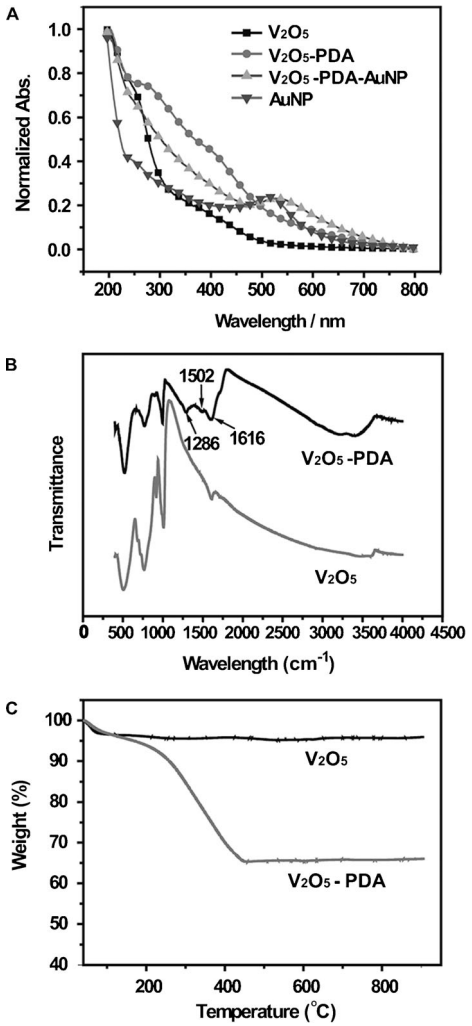


Figure 2. (A) UV/Vis spectra of V_2O_5, V_2O_5-PDA, V_2O_5-PDA-AuNP, and 5 nm AuNPs alone; (B) FTIR spectra of V_2O_5 and V_2O_5-PDA; (C) TGA curves of V_2O_5 and V_2O_5-PDA.

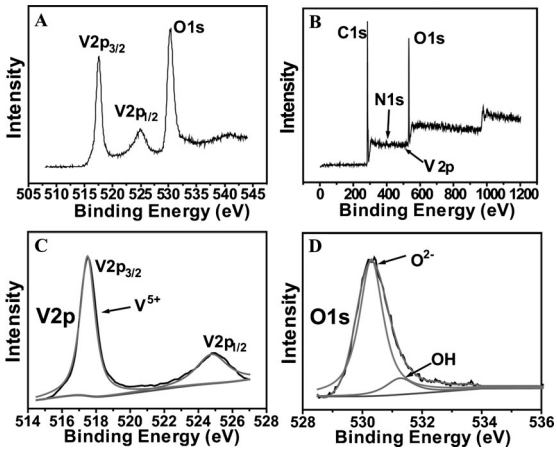


Figure 3. XPS spectra of (A) V_2O_5 showing V and O peaks and (B) V_2O_5-PDA showing C, N, O, and V peaks; (C) V2p and (D) O1s spectra of the V_2O_5 nanowires.

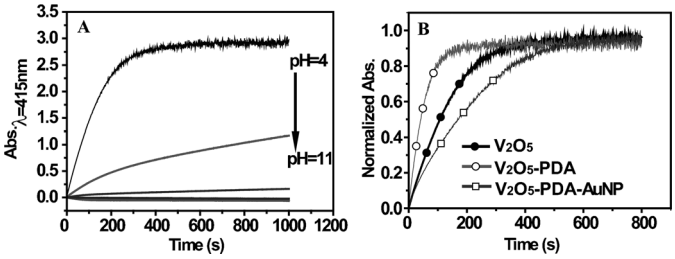


Figure 4. (A) The intrinsic peroxidase-like activity of V_2O_5 in 10 mM NaOAc buffer of different pH values. (B) The intrinsic peroxidase-like activities of V_2O_5, V_2O_5-PDA, and V_2O_5-PDA-AuNP in pH 4.0, 10 mM NaOAc buffer.

As reported previously, V_2O_5 nanowires are capable of catalyzing typical peroxidase reactions, using peroxidase substrates such as ABTS in the presence of H_2O_2 to generate a green-colored product.[9a] Initially, we evaluated the catalytic activity of V_2O_5 nanowires at different pH values. Reactions were carried out by incubating 0.02 mg mL^{-1} V_2O_5 nanowires with the substrate ABTS (0.68 mM) and H_2O_2 (1 mM) at room temperature in 10 mM NaOAc buffer of different pH values. As shown in Figure 4A, V_2O_5 nanowires display their strongest intrinsic peroxidase-like activity towards ABTS at pH 4.0. Under the same conditions (Figure 4B), V_2O_5-PDA showed better activity than V_2O_5 nanowires owing to its good dispersion in aqueous solution. The slightly slower catalytic rate seen with V_2O_5-PDA-AuNP may be due to partial blocking of the active sites of the V_2O_5 nanowires by the attached AuNPs.

As AuNPs exhibit GOx-like activity at pH 7.0 whereas V_2O_5 nanowires show their strongest intrinsic HRP-like activity towards ABTS at pH 4.0, mimicking of the enzyme cascade reaction by the V_2O_5-PDA-AuNP composite material was performed in two steps. 1) V_2O_5-PDA-AuNP was incubated for 30 min with ABTS and glucose in pH 7.0 NaOAc buffer (10 mM). In this process, the AuNPs mimicked GOx in catalyzing the oxidation of glucose to gluconic acid. In the meantime, the substrate oxygen was converted into H_2O_2. 2) The mixture was then adjusted to pH 4.0 by adding pH 4.0 NaOAc buffer (100 mM), whereupon H_2O_2 was reduced by the V_2O_5 nanowires, mimicking peroxidase in the presence of ABTS as co-substrate at pH 4.0 and producing a green color.[4] The detailed procedure is described in the Experimental Section. According to this principle, we designed a colorimetric method for the detection of glucose using V_2O_5-PDA-AuNP for the enzyme-mimicking cascade reaction. Figure 5A shows the time-dependent absorbance changes at 415 nm versus the concentration of glucose. The absorbance at 400 nm gradually increased with increasing concentration of glucose, indicating that the addition of glucose was effective in accelerating the enzyme cascade reaction. As shown in Figure 5B, a good linear correlation ($R^2 = 0.99$) was observed over the concentration range 0–10 μM and a detection limit of 0.5 μM was obtained based on a 3δ/slope. The demonstrated sensing system thus proved to be highly selective for glucose. The glucose analogues fructose, lactose, and maltose were selected for control experiments.[4] The selectivity is shown in Figure S2A in the Supporting Information. Evidently, the absorbance hardly increased for these three ana-

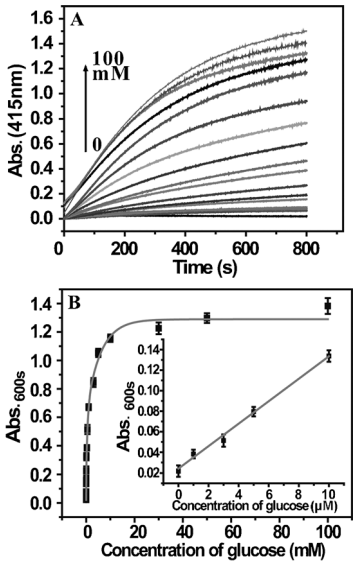


Figure 5. (A) The time-dependent absorbance changes at 415 nm using V_2O_5-PDA-AuNP as an artificial enzyme in the presence of different concentrations of glucose first in pH 7.0 NaOAc buffer (10 mM), incubated for 30 min at room temperature, and then adjusting to pH 4.0 by adding pH 4.0 NaOAc buffer (100 mM). (B) The relationship between absorbance at 600 s (Abs_{600s}) and concentration of glucose from 0 to 100 mM. The inset shows a linear region versus the concentration of glucose from 0 to 10 μM.

logues, and the signal remained as low as the background. Glucose concentrations in diluted blood and apple juice could also be determined by this method (Figure S2 B). According to the calibration curve, the glucose concentration in the blood sample was 4.36 mM, within the range of 3–8 mM for healthy persons.

It has been reported previously that the GOx-like activity of AuNPs is extremely sensitive to surface passivation.[16] As shown in Scheme 2, single-strand DNA (ssDNA) strongly binds to AuNPs, leading to effective suppression of their catalytic activity, whereas double-strand DNA (dsDNA) binds only weakly to AuNPs and thus only slightly perturbs their catalytic activity.[17] By taking advantage of this unique feature, we explored the practicality of using our platform for the colorimetric sensing of target DNA. We first attempted to investigate the influence of ssDNA on the catalytic activity of V_2O_5-PDA-AuNP nanocomposites. V_2O_5-PDA-AuNP was first mixed with ssDNA and then deployed for the cascade reaction as above. As shown in Figure S2, the color change was found to be gradually attenuated as the concentration of ssDNA was increased, suggesting effective suppression of the cascade reaction by ssDNA as a result of its strong adsorption on the surface of AuNPs. When the concentration of ssDNA was increased to 10 μM, the catalytic activity was completely suppressed. Therefore, we chose 10 μM ssDNA, 50 mM glucose, and 0.5 mM ABTS as the optimal conditions for complementary DNA (C-DNA) detection.

Under the above-mentioned conditions, we evaluated the capability of this enzyme-mimicking cascade reaction for the quantitative detection of C-DNA. As shown in Figure 6 A, the absorbance at 415 nm gradually increased with increasing concentration of C-DNA, indicating that the formation of duplex DNA could make ssDNA dissociate from the surface of the AuNPs, thereby restoring their activity. Figure 6 B shows a plot of Abs_{600s} versus concentration of C-DNA from 0 to 200 μM. A good linear correlation ($R^2 = 0.99$) is observed over the concentration range 0–0.10 μM and a detection limit of 2.3 nM was determined based on a 3δ/slope.

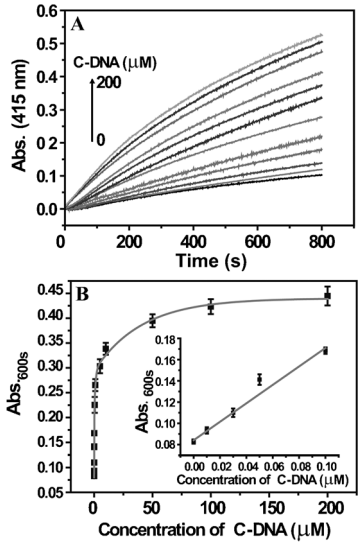
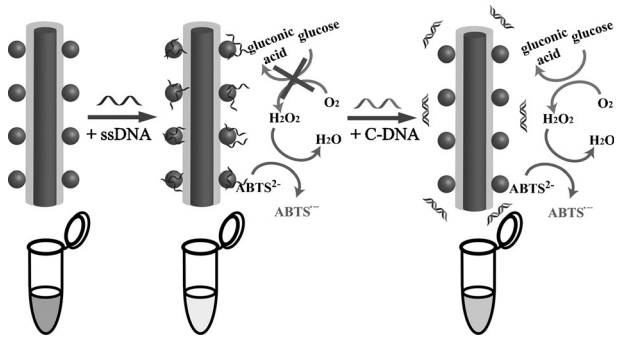


Figure 6. (A) The time-dependent absorbance changes at 415 nm using V_2O_5-PDA-AuNP as an artificial enzyme in the presence of different concentrations of C-DNA (ssDNA: 10 μM, glucose: 50 mM, ABTS: 0.5 mM). (B) The relationship between absorbance at 600 s (Abs_{600s}) and concentration of C-DNA from 0 to 200 μM. The inset shows a linear region versus the concentration of C-DNA from 0 to 0.10 μM.



Scheme 2. Illustration of the GOx-like catalytic activity of AuNPs regulated by DNA hybridization, resulting in suppression and restoration of mimicking of the enzyme cascade reaction by the V_2O_5-PDA-AuNP composite material. This mechanism underpins the colorimetric sensing of target DNA.

In a control experiment, we challenged AuNPs with a mixture of ssDNA and a non-cognate DNA dT_{22}. As shown in Figure 7 A, the absorption intensity was even lower than that with ssDNA alone, suggesting that the sequence-specific formation of duplex DNA was critical for regulating the catalysis of AuNPs. Indeed, the additional non-cognate dT_{22} increased the coverage of DNA on the surface of the AuNPs, resulting in further

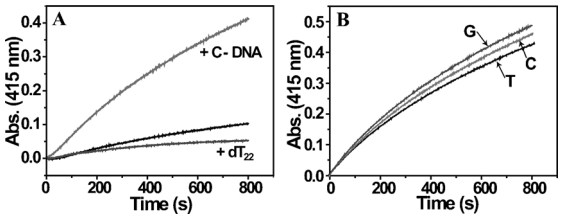


Figure 7. (A) The time-dependent absorbance changes at 415 nm using V_2O_5-PDA-AuNP as an artificial enzyme in the presence of 50 μM C-DNA and 50 μM dT_{22} (ssDNA: 10 μM, glucose: 50 mM, ABTS: 0.5 mM). (B) SNP detection in the presence of 200 μM C-DNA with "A" mutated to either T, C, or G.

deactivation of the catalysis. We then evaluated the selectivity of this system for disease-associated single-nucleotide polymorphism (SNP) of DNA by testing its response to 200 μM C-DNA with "A" mutated to either T, C, or G (Figure 7B).[5] A difference in signal could be discerned, thus indicating that this method is sensitive and could detect SNP in DNA.

Conclusion

We have developed a facile method for fabricating V_2O_5-PDA-AuNP nanocomposite with dual enzyme-mimetic activities. The intrinsic HRP-like activity and GOx-like activity of the hybrid material allowed the system to serve as a robust nanoreactor for mimicking the complexities and functions of an enzymatic cascade system. By taking advantage of these unique features, this system has been further applied as a robust nanoprobe for the detection of glucose as well as for the colorimetric sensing of target DNA with high sensitivity and selectivity. Our work is expected to provide new insights into the development of enzyme mimics with versatile functionalities and reactivities, a field that holds great promise, with potential applications in biocatalysis, bioassays, nano-biomedicine, and nanotechnology.

Experimental Section

Chemicals and materials

Vanadium(IV) oxosulfate and potassium bromate were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) diammonium salt was purchased from Sigma–Aldrich (St. Louis, MO, USA). H_2O_2 was obtained from Beijing Chemicals Inc. (Beijing, China). Tetrachloroauric acid ($HAuCl_4 \cdot 3H_2O$), sodium borohydride ($NaBH_4$), dopamine, and glucose were purchased from Alfa Aesar (USA). All of these reagents were used as received without further purification. Nanopure water (18.2 MΩ; Millipore Co., USA) was used in all experiments.

DNA oligomers were purchased from Sangon (Shanghai, China) and used without further purification. Concentrations of these oligomers were determined by measuring the absorbance at 260 nm. Extinction coefficients were estimated by the nearest-neighbor method using mononucleotide and dinucleotide values. DNA sequences were as follows:

ssDNA: TTT TTT CTT CTT CTC CTC CTT T; C-DNA: AAA GGA GGA GAA GAA GAA GAA AAA A; control DNA: dT_{22}; single-base mutated DNA: 1) AAA GGA GGA G***T***A GAA GAA GAA AAA A; 2) AAA GGA GGA G***C***A GAA GAA GAA AAA A; 3) AAA GGA GGA G***G***A GAA GAA GAA AAA A.

Instrumentation

UV/Vis spectra were recorded on a Jasco-V550 UV/Vis spectrophotometer. Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 FTIR spectrometer. Samples were prepared in pellets using spectroscopic grade KBr. Thermogravimetric analysis (TGA) was performed on a Rigaku Standard type analyzer at a heating rate of 10 °C min^{-1} from room temperature to 900 °C. Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 instrument (Japan). Transmission electron microscopy (TEM) experiments were performed using a Philips Tecnai G2 20 S-TWIN microscope operating at 200 kV. XPS measurements were performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with $Al_{K\alpha}$ radiation as the X-ray source for excitation.

Synthesis of V_2O_5 nanowires

V_2O_5 nanowires were prepared by a hydrothermal method as described elsewhere.[9a] Briefly, for the synthesis of V_2O_5 nanowires, water-soluble vanadium(IV) oxosulfate ($VOSO_4$) was oxidized with potassium bromate ($KBrO_3$) by stirring for 30 min at room temperature. After lowering the pH using nitric acid, the reaction mixture was kept at 180 °C for 24 h. After cooling to room temperature and extensive washing, the dark-yellow precipitate was dried in an oven at 80 °C overnight.

Synthesis of V_2O_5-PDA composite

V_2O_5 nanowires (20 mg) and dopamine (DA; 2 mg) were added to 10 mM Tris-HCl buffer (pH 8.0). The mixture was ultrasonicated for 2 h and then centrifuged. The collected solid was washed several times with doubly-distilled water.

Synthesis of V_2O_5-PDA-AuNP composite

V_2O_5-PDA (5 mg) was dispersed in H_2O (20 mL) with the aid of ultrasonication. A 1 mM aqueous solution of $HAuCl_4$ (50 μL) was then added, ultrasonication was continued for 5 min, freshly prepared $NaBH_4$ solution (20 μL; 5 mg/200 μL H_2O) was added, and the mixture was further ultrasonicated for 10 min at room temperature. It was then centrifuged and the collected solid was washed several times with doubly-distilled water and then dissolved in H_2O (5 mL) to obtain a 1 mg mL^{-1} aqueous solution of V_2O_5-PDA-AuNP composite material.

Detection of glucose

V_2O_5-PDA-AuNP was first mixed with different concentrations of glucose in pH 7.0 NaOAc buffer (10 mM) and incubated for 30 min (V_2O_5-PDA-AuNP: 20 μg mL^{-1}, glucose: 50 mM, ABTS: 0.5 mM) at room temperature. The mixtures were then adjusted to pH 4.0 by adding pH 4.0 NaOAc buffer (100 mM). The time-dependent absorbance changes at 415 nm were monitored by UV/Vis spectrophotometry.

Detection of DNA

First, the influence of ssDNA on the enzyme cascade reaction was studied. Different concentrations of ssDNA were added to solutions

(containing V_2O_5-PDA-AuNP: 20 μg mL^{-1}, glucose: 50 mM, ABTS: 0.5 mM) in pH 7.0 NaOAc buffer (10 mM) and incubated for 30 min at room temperature. The mixtures were then adjusted to pH 4.0 by adding pH 4.0 NaOAc buffer (100 mM). The time-dependent absorbance changes at 415 nm were monitored by UV/Vis spectrophotometry.

For DNA detection, different concentrations of C-DNA were added to solutions (containing V_2O_5-PDA-AuNP: 20 μg mL^{-1}, ssDNA: 10 μM, glucose: 50 mM, ABTS: 0.5 mM) in pH 7.0 NaOAc buffer (10 mM) and incubated for 30 min at room temperature. The mixtures were then adjusted to pH 4.0 by adding pH 4.0 NaOAc buffer (100 mM). The time-dependent absorbance changes at 415 nm were monitored by UV/Vis spectrophotometry. Control experiments and SNP detection were carried out using dT_{22} and single-base mutated DNA, respectively, instead of C-DNA under the same conditions.

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Keywords: cascade reaction · detection · DNA recognition · enzyme mimicking · gold nanoparticle · sensors · V_2O_5 nanowire

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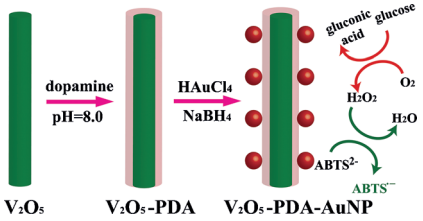
FULL PAPER

Towards artificial enzymes: A novel nanocomposite consisting of V_2O_5 nanowires and Au nanoparticles (NPs) has been constructed and used for an enzyme-mimicking cascade reaction, whereby V_2O_5 and AuNPs display intrinsic peroxidase and glucose oxidase-like activity, respectively (see scheme; PDA = polydopamine, ABTS = 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid). This system can be used for the detection of glucose and as a nanoprobe for colorimetric sensing of target DNA with high sensitivity and selectivity.



Artificial Enzymes

*K. Qu, P. Shi, J. Ren, X. Qu**

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Nanocomposite Incorporating V_2O_5 Nanowires and Gold Nanoparticles for Mimicking an Enzyme Cascade Reaction and Its Application in the Detection of Biomolecules