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ORIGINAL PAPER

Carbon dots on V_2O_5 nanowires are a viable peroxidase mimic for colorimetric determination of hydrogen peroxide and glucose

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Abstract

A nanocomposite was hydrothermally prepared from C-dots and V_2O_5 nanowires, and characterized by TEM, FTIR and XRD. Due to the synergistic effects between C-dots and V_2O_5 nanowires, the nanocomposite is found to possess peroxidase-mimicking activity. This finding was exploited to design colorimetric methods for determination of H_2O_2 and glucose (via glucose oxidase) by using of 3,3′,5,5′-tetramethylbenzidine (TMB) as the chromogenic substrate. The C-dot/V_2O_5 nanocomposite catalyzes hydrogen peroxide to oxidize TMB and the resultant product, i.e., TMB* produces a blue color in the solution. Also for glucose determination, at first glucose reacts with dissolved oxygen in the presence of glucose oxidase and generates H_2O_2. Then, produced H_2O_2 was monitored by the C-dot/V_2O_5 nanozyme in the presence of TMB. Intensity of the blue color in the solution at wavelength of 650 nm is an indication of H_2O_2 or glucose concentration. The response to H_2O_2 is linear in the 0.5–520 μM concentration ranges, and that for glucose from 0.7 μM to 300 μM.

Keywords Nanozyme · Nanocomposite · Peroxidase · Colorimetric assay · Biomimetic nanomaterials

Introduction

The intrinsic enzyme-like activity of nanoparticles has become a growing area of interest [1–3]. In this way, enzyme mimetic activities of metals [4, 5], metal oxides [6], metal ions [7, 8] and carbon nanostructures [9] have been proved. But because enzymatic reactions happen mainly on the surface of nanozymes [10], nanocomposites as a new generation of nanozymes have been introduced [11–13]. In this way, carbon nanocomposites are the promising ones [9, 14–16]. Carbon nanostructures have large specific surface areas, excellent physical properties and rich surface chemistry [9]. So, presence of carbon nanostructures in nanocomposites enhances their catalytic activity and stability [9]. As a result, C-dots as new kind of carbon nanostructures were used to design the efficient nanocomposites-based nanozymes [17–21]. Pure C-dots catalyze hydrogen peroxide to oxidize 3,3′,5,5′-tetramethylbenzidine (TMB) and hence exhibit high intrinsic peroxidase-like activity [22]. So, the peroxidase like activity of C-dots nanocomposite (hybrid)-based nanozyme were enhanced by using of synergic effect between C-dots and other counterpart in nanocomposites [17, 18, 20].

Different phases of vanadium oxide including VO, VO_2, V_2O_3 and V_2O_5 show outstanding physical and chemical properties [23]. Therefore this kind of materials present fascinating applications in various fields including electrochromic [24] and thermochromic [25] devices, catalysts [26], photocatalysts [27], sensors [28], batteries [29] and etc. Also, enzyme mimetic activity of some forms of vanadium oxide was studied previously. In this way, intrinsic peroxidase-like activity of V_2O_5 nanowires [30], V_2O_3-ordered mesoporous carbon composite [31], VO_2(A) nanoplates [32], VO_2(B) nanobelts [33], VOx nanoflakes [34], V_6O_{13} nanotextiles [35] and V_2O_5-PDA-AuNP [36] was reported. However, there is no report on the enzymatic activity of vanadium oxide nanocomposites especially vanadium oxide/carbon nanocomposite. So, the aim of the present work is synthesis of C-dots/vanadium oxide nanocomposite and evaluation of its horseradish peroxidase-like activity. Also,

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colorimetric determination of H_2O_2 and glucose has been reported as applications.

Experimental

Materials

$VOSO_4.xH_2O$ was purchased from Sigma-Aldrich (http://www.sigmaaldrich.com). Candle soot was obtained from candle combustion. All other chemicals in analytical grade were prepared from Merck (http://www.merckmillipore.com/INTL/en) and used without further purification.

Preparation of C-dots/V_2O_5 nanocomposite

At first, C-dots were prepared as described elsewhere [22]. Then, for synthesis of C-dots/V_2O_5 nanocomposite, 8 mmol $VOSO_4.xH_2O$ and 5 mmol $KBrO_3$ were dissolved in 30 mL 1:2 C-dots and stirred for 30 min at room temperature. Then the solution was placed into a teflon-lined stainless steel autoclave to carry out the reaction at 180 °C for 24 h. After cooling the solution, the precipitate of the nanocomposite was filtered and washed several times with distilled water and ethanol. Finally, dark-yellow nanocomposite was dried overnight in room temperature.

Instrumentation

The morphology and nanostructure of sample were evaluated by transmission electron microscopy (TEM) on a Zeiss, EM10C (accelerating voltage of 80 kV) instrument (www.zeiss.com). X-ray diffraction (XRD) measurements were performed by D8 ADVANCE type (BRUKER-Germany, http://www.bruker.com) with CuKα radiation (λ = 1. 0.1542 nm). The 2θ range was from 15° to 60° in steps of 0.05°. The absorbance of solutions was recorded on a UV-Vis spectrophotometer (Hach DR5000, https://www.hach.com/) with increment of 1 nm at room temperature. The pH of solutions was adjusted by using a Metrohm pH meter (model 780, https://www.metrohm.com/en/).

Tests of peroxidase-like activity

To study the peroxidase-like activity of C-dots/V_2O_5 nanocomposite, a solution contains 0.018 M H_2O_2, 0.036 mg mL^{-1} nanocomposite and 0.065 mg mL^{-1} TMB was prepared. Then, the UV-Vis spectra were recorded in 5 min interval during 30 min. The above experiment was repeated in the same condition for 0.036 mg mL^{-1} V_2O_5 nanowires and 0.06 mL concentrated C-dots.

Determination of H_2O_2 and glucose

For H_2O_2 detection, a series of solution with different concentration of H_2O_2 in the presence of 0.27 mM TMB and 0.036 mg mL^{-1} nanocomposite was prepared. Then UV-Vis spectra of all solutions were recorded after 10 min. This procedure was repeated three times. The calibration plot is drawn by using of the concentration of H_2O_2 and mean corrected absorbance at 650 nm.

Glucose determination was carried out as following: 100 μL of glucose oxidase aqueous solution (1.2 mg mL^{-1}) and different concentration of glucose solution are mixed completely and incubated for 30 min. Then 70 μL of TMB 1.2 mg L^{-1} and 1 mg nanocomposite were added into the previous solution and finally reached to 3 mL with distilled water. The mixed solution was incubated for 10 min and the absorbance was recorded for glucose detection. This procedure was repeated three times to obtain calibration plot.

Results and discussions

Choice of materials

Top-down and bottom-up methods are two types of approaches which were used in C-dots fabrication [37]. Bottom-up method uses small organic molecular precursors while top-down rout is based on cutting small sheets via physical, chemical or electrochemical techniques [37]. In bottom-up approach, usually dialysis bags were needed to separate unreacted species and the synthesis procedure needs more time and cost. But in case of top-down approach, it is just need a centrifuge to separate large unreacted species if the primary reagents were not interfering in the consequent procedure. Here, C-dots were prepared by using of a top-down rout via candle soot [22] to consume time and cost. Also the additional unreacted nitric acid in C-dot solution is useful in the consequent synthesis procedure.

Synthesis of orthorhombic V_2O_5 nanowires has been introduced through a hydrothermal method by using of $VOSO_4$ and $KBrO_3$ as starting materials, previously [38]. So, in the present study, the previously reported reaction for V_2O_5 nanowires preparation was performed in acidic C-dots media, pH ~1. It is worthy to mention that, synthesis of nanocomposite in other pH values of primary solution has not resulted in any precipitate. Because V_2O_5 nanowires were fabricated by this procedure only at pH value range of 1–2 [38].

Characterization of C-dots/V_2O_5 nanocomposite

After nanocomposite preparation, several analytical methods were used to characterize the nanocomposite (Fig. 1 and Fig. S1). The morphology and nanostructure of

nanocomposite were revealed by TEM. The TEM images of fabricated nanocomposite clearly indicate the presence of V_2O_5 nanowires with variable length from 500 nm up to micrometer and width of 20–50 nm (Fig.1a). Also, spherical C-dots with diameter of below 10 nm are arranged on the surface of V_2O_5 nanowire effectively (Fig. 1b). It was reported that V_2O_5 nanowire surface is easily hydroxylated due to the unsaturated V and O atoms at its side faces [30]. Also, on the other hand presence of functional groups such as hydroxyl, carboxyl, and carbonyl groups on C-dots surface provide a center for V_2O_5 formation such as those happened for formation of V_2O_5-anchored carbon nanotubes [39] and V_2O_5 mesoporous carbon [31, 40]. As a result the surface structure of V_2O_5 nanowires enables a good interaction between C-dots and V_2O_5 nanowires. The result of energy-dispersive X-ray (EDX) spectroscopy confirms the presence of V, O and C elements in the nanocomposite. The percentage of C element in the nanocomposite is very low (~ %4.5) (Table S1). Also, XRD analysis was used to investigate the phases of the nanocomposite (Fig. S1b). It seems that presence of C-dots in the synthesis media of V_2O_5 has no effect on crystalline phase of the produced V_2O_5 nanowires because pattern of orthorhombic V_2O_5 in XRD is evident without any changes. For further investigation, FTIR spectrum of C-dots/V_2O_5 nanocomposite was recorded (Fig. S1c). Clearly, the band of V=O stretching was not changed in the nanocomposite, while the changes was occurred in the corresponding wavenumber of V-O-V deformations. These facts show the presence of interaction between C-dots and V_2O_5 through this bond.

The formation mechanism of C-dots/V_2O_5 nanocomposite is probably similar to the formation of Co@C-dots hybrid material [17]. In fact, the surface of C-dots is negatively charged in highly acidic media [18] due to the presence of carboxylic/carbonyl functional groups on it [22]. So, V(IV) cations get attracted to the negative surface of C-dots by electrostatic interactions. Then, the crystal growth for V_2O_5 in the presence of oxidizing agent of $KBrO_3$ was started at 180 °C. In this way, C-dots act as a nucleation seeds.

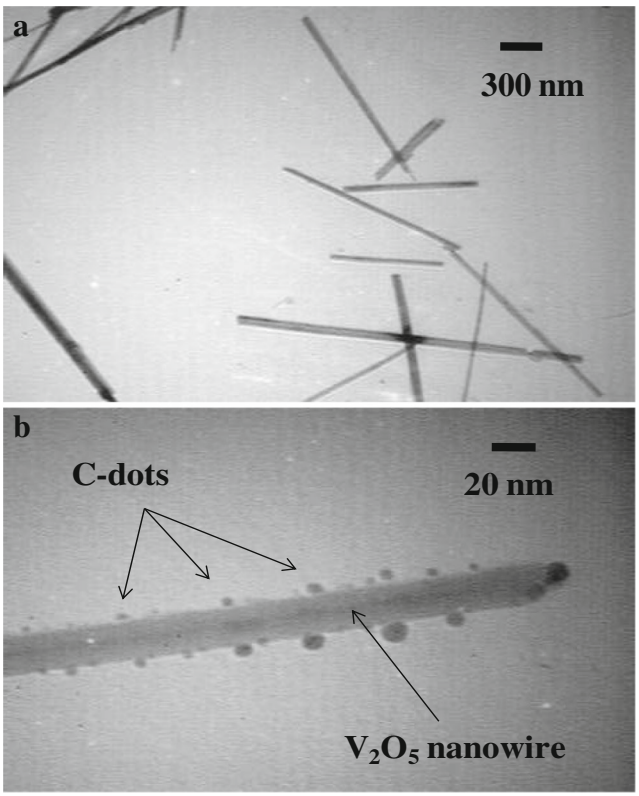

Fig. 1 TEM images of C-dots/V_2O_5 nanocomposite

Peroxidase-like activity of the C-dot/V_2O_5 nanocomposite

Peroxidase enzymes are capable of catalyzing reaction of H_2O_2 with chromogenic substrates such as TMB to produce a blue color (maximum absorbance 650 nm) solution. So, initially peroxidase-like activity of C-dots/V_2O_5 nanocomposite was tested and compared with corresponding activity of C-dots and V_2O_5 nanowires. Figure 2 presents dependency of TMB oxidation activity of C-dots/V_2O_5 nanocomposite on time. Obviously, C-dots/V_2O_5 nanocomposite has an intrinsic peroxidase–like activity towards TMB substrate and more intense blue color was obtained after increasing the time. On the other hand, peroxidase-like activity of C-dots [22] and V_2O_5 nanowires [30] were reported previously. So, the similar reactions were also carried out in the presence of V_2O_5 nanowires and C-dots, separately to compare the activity of three nanozymes to each other (Fig. S2). Clearly, the peroxidase-like activity of C-dots/V_2O_5 nanocomposite is higher than corresponding activity of both single C–dots and V_2O_5 nanowires (Fig. 2). It seems that presence of both nanostructures in

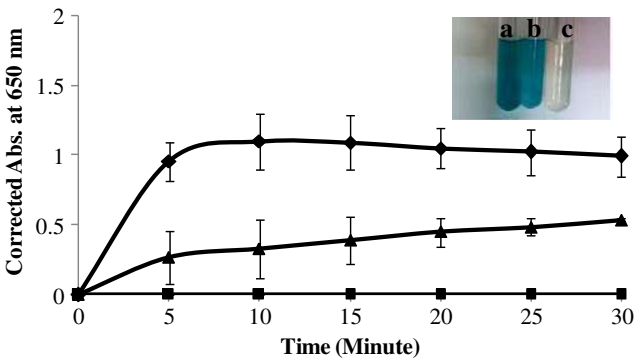

Fig. 2 Dependency of peroxidase-like activity of (■) 60 μL concentrated C-dots, (▲) 200 μL 1 mg mL^{-1} V_2O_5 nanowires and (♦) 200 μL 1 mg mL^{-1} C-dots/V_2O_5 nanocomposite on time in presence of 18 mM H_2O_2 and 0.065 mg mL^{-1} TMB. The error bars represent the standard error derived from three replicate measurements. (Inset: Color changes of (**a**) C-dots/V_2O_5 nanocomposite, (**b**) V_2O_5 nanowires and (c) C-dots after 30 minutes)

the nanocomposite enhances peroxidase-like activity of the resulted nanocomposite.

The peroxidase-like activity of C-dots/V_2O_5 nanocomposite similar to other peroxidase-like nanozyme depends on pH, C-dots/V_2O_5 nanocomposite amount and substrate concentrations (TMB and H_2O_2) (Fig. S3). In short, the maximum catalytic activity of the C-dots/V_2O_5 nanocomposite was obtained at pH 3.0, 0.16 mg mL^{-1} TMB, 0.036 mg mL^{-1} nanocomposite and 340 mM H_2O_2. The result indicates that oxidation of TMB is mediated under acidic conditions. Also, the optimum pH value is in agreement with corresponding results of C-dots, V_2O_5 nanowires and horseradish peroxidase (HRP). Because the maximum peroxidase- like activity of C-dots [22], V_2O_5 nanowires [30, 41] and HRP [42] was recorded at pH of 3.5, 4.0 and 4.0, respectively. Moreover, the results suggest that the C-dots/V_2O_5 nanocomposite required H_2O_2 concentration of about two orders of magnitude higher than HRP to reach the maximum level of peroxidase activity. The obtained value, i.e., 340 mM is near to the corresponding value for C-dots (300 mM) [22]. It seems that the catalytic activity of C-dots/V_2O_5 nanocomposite such as C-dots is more stable at high H_2O_2 concentration rather than that of HRP.

Steady-state kinetic experiments were performed to investigate mechanism of peroxidase-like activity of the C-dots/V_2O_5 nanocomposite. The kinetic data are recorded by changing the H_2O_2 concentration in the presence of constant concentration of TMB. In this way, a typical Michaelis–Menten curve was observed. Then K_m and V_{max} as the Michaelies-Menten constant and the maximal reaction velocity, respectively were obtained by Lineweaver–Burk eq. ($1/v = K_m/(V_{max} \cdot C) + 1/V_{max}$). In this equation, v is the reaction velocity (the reaction rate) and C is the substrate concentration. In this way, K_m and V_{max} were obtained as 53.6 mM and 35.1×10^{-8} M s^{-1}, respectively. A comparison of the kinetic data of C-dots/V_2O_5 nanocomposite and other similar nanozymes is given in Table 1. Obviously, V_{max} of C-dots/V_2O_5 nanocomposite is higher than the corresponding values of HRP [42], C-dots/Fe_3O_4 [20] and GQDs/CuO [43] and very closed to the V_{max} of C-dots.

Stability of C-dots/V_2O_5 nanocomposite was tested by incubating the nanocomposites at different pH values for 1 h. Then the corresponding peroxidase-like activities were recorded (Fig. S4). It was found that the C-dots/V_2O_5 nanocomposite remains stable over a wide range of pH from 2 to 7.

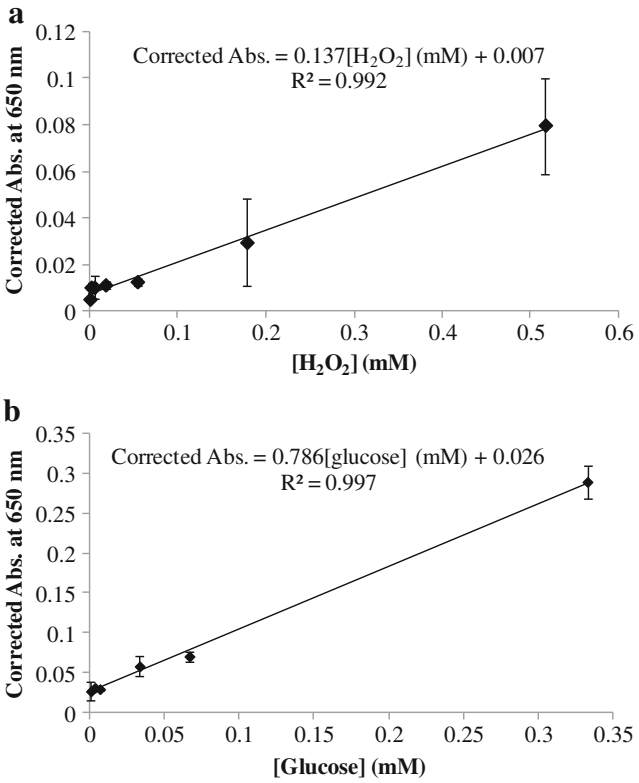

Fig. 3 Calibration plot for (**a**) H_2O_2 and (**b**) glucose at corrected absorbance of 650 nm

Determination of H_2O_2 and glucose by using of C-dots/V_2O_5 nanocomposite

Due to the dependency of catalytic activity of C-dots/V_2O_5 nanocomposite on H_2O_2 concentration, the current system was implemented for determination of hydrogen peroxide. Based on the previous report, the corrected absorbance was obtained by subtracting the absorbance value of 650 from the absorbance value of 750 nm [20]. Figure 3a shows a typical calibration plot for H_2O_2 with regression equation of *Corrected Abs. = 0.137[H_2O_2] (mM) + 0.007* ($R^2 = 0.992$). Limit of detection (LOD) was obtained as the lowest quantity of analyte that can be distinguished from the blank. In this way, H_2O_2 was detected as low as 5.0×10^{-7} M. The obtained LOD is much lower than those of V_2O_5 nanowires [41], V_2O_3-ordered mesoporous carbon composite [40] and C-dots/Pt nanocomposite [44] and very closed to the LOD of C-dots [22] and VS_2 nanosheets [45]. Also, a linear range

Table 1 Comparison of K_m and V_{max} parameters between C-dots/V_2O_5 nanocomposite and other reported nanozymes when H_2O_2 was used as substrate

Catalyst	HRP [42]	C-dots [22]	C-dots/Fe_3O_4 [20]	GQDs/CuO [43]	VO_2(A) [32]	C-dots/V_2O_5
K_m (mM)	3.70	26.77	3.5	0.098	0.165	53.6
V_{max}($10^{-8} \times$ M s^{-1})	8.71	30.61	14.0	3.2	2.4	35.1

Table 2 Analytical performance for H_2O_2 and glucose detection by using of different peroxidase nanozymes

Nanozyme	H_2O_2		Glucose		Ref.
	Linear range (M)	LOD(M)	Linear range (M)	LOD(M)	
V_2O_5	1.0×10^{-6} - 5.0×10^{-4}	1.0×10^{-6}	1.0×10^{-5} - 2.0×10^{-3}	1.0×10^{-5}	[41]
C-dots	1.0×10^{-6} - 1.0×10^{-4}	2.0×10^{-7}	1.0×10^{-6} - 5.0×10^{-4}	4.0×10^{-7}	[22]
V_2O_3-ordered mesoporous carbon composite	5.0×10^{-6} – 2.5×10^{-4}	1.7×10^{-6}	1×10^{-5} – 4×10^{-3}	3.3×10^{-6}	[31]
VO_2(B)	1×10^{-6} – 4×10^{-4}	2.8×10^{-7}	2×10^{-6} –1.2×10^{-4}	6.5×10^{-7}	[48]
C-dots/Pt	2.5×10^{-6} – 1.0×10^{-3}	8.0×10^{-7}	5×10^{-6} – 5×10^{-3}	1.67×10^{-6}	[44]
α-$AgVO_3$ microrods	60×10^{-6} – 200×10^{-6}	2×10^{-6}	–	–	[46]
VS_2 nanosheet	2×10^{-6} – 100×10^{-6}	0.57×10^{-6}	5×10^{-6} – 250×10^{-6}	1.54×10^{-6}	[45]
FeOOH(N)-doped carbon nanosheets	5×10^{-6} – 19×10^{-6}	5×10^{-9}	8×10^{-6} – 0.8×10^{-3}	0.2×10^{-6}	[47]
GQDs/CuO	5.0×10^{-7} – 1.0×10^{-5}	1.7×10^{-7}	2×10^{-6} –2×10^{-4}	5.9×10^{-7}	[43]
C-dots/V_2O_5	5.0×10^{-7} – 5.2×10^{-4}	5.0×10^{-7}	7.0×10^{-7} – 3.0×10^{-4}	7.0×10^{-7}	This study

from 5.0×10^{-7} M to 5.2×10^{-4} M was obtained for H_2O_2. This range is wider than the corresponding linear ranges of C-dots [22], V_2O_5 nanowires [41], C-dots/Pt nanocomposites [44], GQDs/CuO nanocomposites [43], α-$AgVO_3$ microrods [46], VS_2 nanosheets [45] and FeOOH(N)-doped carbon nanosheets [47]. The reusability of C-dots/V_2O_5 nanozyme for H_2O_2 assay was tested for four cycles (Fig. S5). After each cycle, C-dots/V_2O_5 nanocomposite was washed with water and separated by centrifuge. Then, fresh substrates were added and enzymatic activity was explored. It is clear that the activity of nanozyme in the second cycle was decreased to an approximately half with the first cycle. But C-dots/V_2O_5 nanozyme retains the catalytic activity with a little variation (RSD of 18%) in three other cycles. To test the applicability of the assay, human blood serum was tested as real sample. The obtained recoveries were 92.2–106.8% (Table S2).

H_2O_2 is the basic intermediate of glucose detection in glucose oxidase-based assays. Therefore, colorimetric detection of glucose was carried out by using of C-dots/V_2O_5 nanozyme. As presents in Fig. 3b, a satisfied relationship between the corrected absorbance at 650 nm and glucose concentration is observed in the range of 7.0×10^{-7} to 3.0×10^{-4} M with a low LOD of 7.0×10^{-7} M. The linear regression equation is *Corrected Abs. = 0.786[Glucose] (mM) + 0.026* with a correlation coefficient of 0.997. The LOD was improved in comparison with V_2O_5 nanowires [41], V_2O_3-ordered mesoporous carbon composite [40], VS_2 nanosheets [45], C-dots/Pt nanocomposite [44] and GQDs/CuO [43] nanozyme and very closed to the LOD of C-dots [22]. Table 2 summarizes the analytical performance of C-dots/V_2O_5 nanozyme with other nanozymes for H_2O_2 and glucose determinations. By comparing with other nanozymes, it was revealed that this nanozyme has a satisfied linear range and sensitivity. Selectivity of this method for determination of glucose was tested in the presence of 0.1 M maltose, fructose and lactose (Fig. 4). Obviously no significant signals are observed for interferences. Therefore, this biosensing system is highly selective for glucose detection. Also, analysis of glucose in human blood serum was performed as real sample. The original glucose concentration in human serum sample by hospital and current colorimetric method was obtained as 5.55 mM and 4.95 mM, respectively. In this way, the relative deviation for glucose determination is obtained as 10.2%.

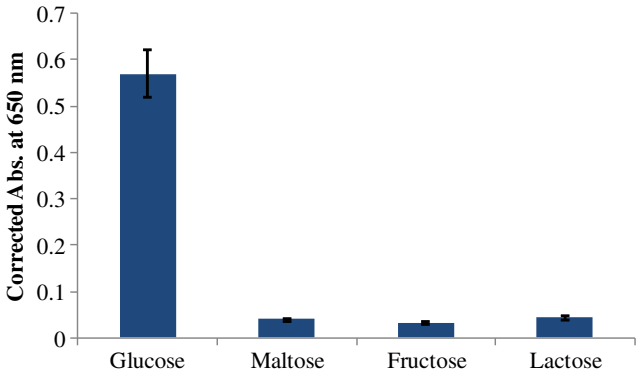

Fig. 4 Selectivity of glucose detection in this system in the presence of 0.1 M glucose and its analogues

Conclusions

In summary, C-dots/V_2O_5 nanocomposite was fabricated successfully by using of a hydrothermal method. In this way, C-dots/V_2O_5 nanocomposite was prepared by in-situ growth of V_2O_5 on the surface of C-dots. This nanocomposite shows highly peroxidase-like activity due to the synergic interaction of C-dots and V_2O_5 nanowires. The maximal reaction velocity of C-dots/V_2O_5 nanocomposite is similar to that of C-dots. Also, colorimetric determination of H_2O_2 and glucose was performed by using of C-dots/V_2O_5 nanocomposite as nanozyme. Thus, the assay was successfully used to quantify H_2O_2 and glucose in human serum samples. Moreover, C-

dots/V_2O_5 nanocomposite is stable over a wide range of pH from 2 to 7. In nutshell, this assay for H_2O_2 and glucose detection is stable, sensitive and selective. The present study is expected to provide new insights into the development of new nanozymes with contribution of vanadium oxides and carbon.

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

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