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## Colorimetric assay for the detection of dopamine using bismuth ferrite oxide ( $\text{Bi}_2\text{Fe}_4\text{O}_9$ ) nanoparticles as an efficient peroxidase-mimic nanozyme

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1        **Colorimetric assay for the detection of dopamine using**  
2        **bismuth ferrite oxide (Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>) nanoparticles as an**  
3        **efficient peroxidase-mimic nanozyme**

4  
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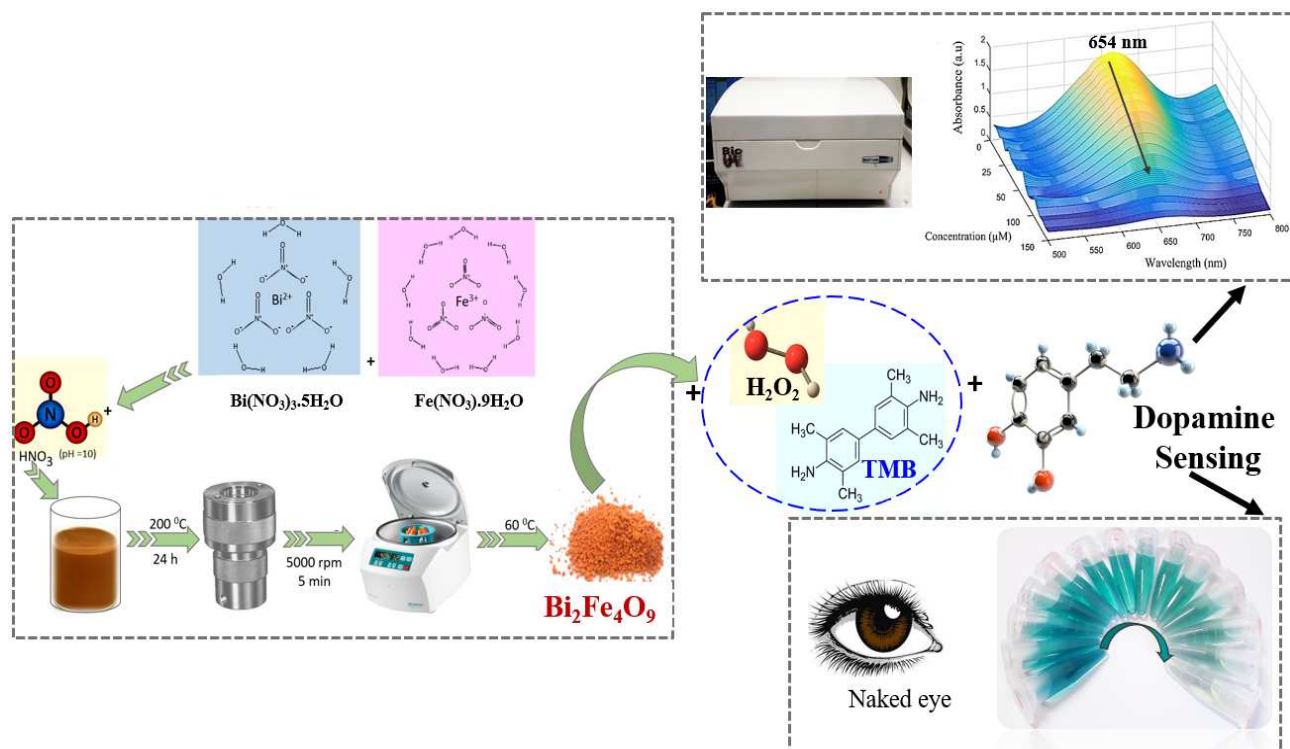
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### 37 Highlights

- 38 ➤  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme as a simple and low-cost colorimetric sensor was developed for easy
- 39 dopamine detection
- 40 ➤ The sensor achieved good performance with a linear range from 0.15 to 50  $\mu\text{M}$  and a
- 41 detection limit of 51 nM
- 42 ➤ The nanozyme was reused up to 4 cycles without a significant decrease in its performance

43

44 **Abstract**

45 This work describes the preparation of ternary bismuth ferrite oxide nanoparticles ( $\text{Bi}_2\text{Fe}_4\text{O}_9$   
46 NPs) with an enzyme mimetic activity for dopamine (DA) qualitative and quantitative  
47 detection.  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs were prepared using a facile, low cost, and one-pot hydrothermal  
48 treatment. The chemical composition, morphology, and optical properties of  $\text{Bi}_2\text{Fe}_4\text{O}_9$   
49 nanozyme were characterized using different techniques such as Fourier-transform infrared  
50 spectra (FTIR), X-ray diffraction pattern (XRD), X-ray photoelectron spectroscopy (XPS),  
51 thermo-gravimetric analysis (TGA), dynamic light scattering (DLS), field-emission scanning  
52 electron microscopy (FESEM) imaging, FESEM-energy dispersive X-ray spectroscopy  
53 (EDS), UV-vis absorption, and fluorescence emission spectroscopy.  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs were  
54 utilized to catalyze the oxidation of a typical chromogenic peroxidase substrate, 3,3',5,5'-  
55 tetramethylbenzidine (TMB), to form the blue-colored oxidized product (oxTMB), in the  
56 presence of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). All reactions occurred in acetate buffer solution (pH  
57 3.5) to generate hydroxyl radicals ( $\cdot\text{OH}$ ) and the kinetics were followed by UV-vis  
58 absorbance at 654 nm. The steady-state kinetic parameters were obtained from the Michaelis-  
59 Menten equation and exhibited a good catalytic efficiency of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs as enzyme  
60 mimetics. Michaelis–Menten constant ( $K_m$ ) values were estimated as 0.07 and 0.73 mM for  
61 TMB and  $\text{H}_2\text{O}_2$ , respectively. The presented method is efficient, rapid, cost-effective, and  
62 sensitive for the colorimetric detection of dopamine with a linear range (LR) from 0.15 to 50  
63  $\mu\text{M}$  and a detection limit (LOD) of 51 nM. The proposed colorimetric sensor was  
64 successfully applied for the detection of different concentrations of dopamine in spiked fetal  
65 bovine serum (FBS) and horse serum (HS) samples. It is anticipated that  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme  
66 holds great potential in biomedical analysis and diagnostic applications of dopamine-related  
67 diseases.

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73 **Keywords:**  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme, 3,3',5,5'-tetramethylbenzidine (TMB), Peroxidase-like  
74 activity, Dopamine, Colorimetric assay.

75

76

77

## 78 **1. Introduction**

79 Dopamine (DA), 4-(2-aminoethyl) benzene-1,2-diol), is a biogenic monoamine and one of  
80 the quite important catecholamine neurotransmitters (NT), which plays significant key roles  
81 in the mammalian central nervous such as memory, learning, cognition, emotions, renal,  
82 hormonal, and cardiovascular systems [1-3]. The abnormal level of dopamine concentration  
83 in the human body can lead to serious neurological syndromes and various diseases like  
84 Alzheimer, Parkinson, Huntington, senile dementia, and Schizophrenia [4-7].

85 Therefore, the measurement of the dopamine level in biological fluids with high accuracy  
86 and sensitivity is an extremely important factor for early diagnosis of diseases and  
87 development of therapeutic approaches [3, 8]. Various analytical strategies have been  
88 developed to detect the DA level, including high-performance liquid chromatography  
89 (HPLC) [9], capillary electrophoresis (CE) [10, 11], field-effect transistor (FET)-based  
90 biosensor [12], fluorometry [13, 14], random lasers (RL) with incoherent feedback [15],  
91 electrochemiluminescence (ECL) [16], and electrochemical methods [17, 18]. However, all  
92 these methods have several constraints; they often require complex and advanced pre-  
93 treatment processes, long analysis times, high-costs, sophisticated instruments, and trained  
94 personnel [4, 8]. In this regard, many studies have been focused on elucidating the  
95 colorimetric assays for dopamine identification, because of their intrinsic advantages of  
96 simple assay design, time-saving, high efficiency, and most importantly, easy visual detection  
97 [3, 4, 7].

98 Traditionally, natural enzymes as biological catalysts have been applied in colorimetric  
99 analysis systems. A common example is the horseradish peroxidase enzyme (HRP). To keep  
100 up with the more efficient performance of natural enzymes, they must be applied under  
101 relatively mild conditions. Natural enzymes feature high substrate-specificity and efficiency.  
102 However, they are limited by some inherent drawbacks such as the high-cost of preparation  
103 and purification, easy denaturation, the extreme sensitivity of catalytic activity towards  
104 environmental changes such as pH or temperature, difficulties in recovery, limited storage,  
105 and availability [19, 20]. As a potential alternative, an emerging group of nanomaterials has  
106 recently been considered. The choice of enzyme-mimics based on nanomaterials rather than  
107 natural enzymes has well-confirmed the rational decision to detect dopamine and conquer  
108 these limitations. The significant properties of nanozymes include a high surface-to-volume  
109 ratio, low-cost, simple preparation, tunable activity, high stability, long-term storage, and

110 easy preparation. As evidenced by the mentioned advantages, nanozymes have been  
111 exploited to further evaluate their analytical performance in bio-nanotechnology [21-23].

112 Yan and colleagues were the first to point out  $\text{Fe}_3\text{O}_4$  NPs as an enzyme-mimic for TMB  
113 substrate [24]. In recent years, ferrite-based enzyme-like nanomaterials have generated  
114 tremendous attention [25-27], because of their potential for various applications such as gas  
115 sensors [28], catalyst for ammonia oxidation [29], photocatalysts for hydrophobic and  
116 organic pollutants degradation [26, 30], removal of heavy metal ions [31], memory devices  
117 [32], data storage [33], and spintronic devices [34]. Lu and colleagues successfully  
118 synthesized and applied  $\text{CuFe}_2\text{O}_4/\text{Cu}_9\text{S}_8/\text{polypyrrole}$  (PPy) ternary nanotubes as a suitable  
119 colorimetric platform for easy detection of dopamine and  $\text{H}_2\text{O}_2$  molecules [35]. Chen et al.  
120 reported that Fe/NC-800 exhibited an enhanced catalytic activity for dopamine sensing [36].  
121 Liu and co-workers reported that  $\text{ZnO}/\text{ZnFe}_2\text{O}_4/\text{graphene foam}$  (ZZFO/GF) is an excellent  
122 colorimetric-catalyst to distinguish hydroquinone (HQ) molecules with the assistance of  $\text{H}_2\text{O}_2$   
123 molecule [37]. Su and co-workers demonstrated the use of the spinel  $\text{ZnFe}_2\text{O}_4$  NP-decorated  
124 ZnO nanofiber as an effective colorimetric platform with a peroxidase-like activity for  
125 glucose detection in urine samples [38]. Hou et al. fabricated  $\text{Fe}_3\text{O}_4@\text{C}@\text{MnO}_2$  composite as  
126 a triple-enzyme mimetic activity to catalyze TMB oxidation reaction and was successfully  
127 applied for dopamine detection [39].

128 In this investigation, we report, for the first time, the application of irregular sheet-like  
129  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanoparticles as one of the Fe-based nanozymes for the colorimetric detection of  
130 nanomolar concentration of dopamine in aqueous media. Fe active sites ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) and the d-  
131 orbitals of  $\text{Fe}^{3+}$  in  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs operate in a Fenton-like reaction to improve the catalytic  
132 oxidization of 3,3',5,5'-tetramethylbenzidine (TMB), a chromogenic substrate, in presence of  
133  $\text{H}_2\text{O}_2$  in acetic acid medium (pH=3.5) to yield a deep-blue product (oxTMB). The  
134 simultaneous existence of large irregular-sheets and Fe, as a transition-metal ion, located at  
135  $\text{FeO}_6$  (octahedral) and  $\text{FeO}_4$  (tetrahedral) in the unit cell of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme, were useful  
136 factors to reduce  $\text{H}_2\text{O}_2$  to  $\cdot\text{OH}$  radical and increase the oxidation of TMB molecules. In  
137 presence of dopamine (DA), as efficient  $\cdot\text{OH}$  radical scavenger, the colorimetric signal of the  
138  $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{H}_2\text{O}_2/\text{TMB}/\text{DA}$  was significantly lower than that of  $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{H}_2\text{O}_2/\text{TMB}$  system,  
139 and the deep-blue color of the ox-TMB was changed to fade-blue color. On the basis of this  
140 quenching behavior, the catalytic activity of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme was exploited to design a  
141 selective and sensitive colorimetric sensor for dopamine concentration determination in fetal  
142 bovine serum (FBS) and horse serum (HS) samples. The results of the study showed that

143 Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs could be developed as a promising group of nanozyme materials for dopamine  
144 diagnostic purposes and biomedical applications.

## 145 **2. Experimental**

### 146 *2.1. Synthesis of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanoparticles*

147 As shown in **Scheme S1**, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs were prepared using the hydrothermal method,  
148 according to a previous procedure with a slight modification [27]. First, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (4.85  
149 g) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (4.04 g) powders were dissolved in 13 mL of deionized water (DIW)  
150 and 2 mL of nitric acid (HNO<sub>3</sub> 65%) at room temperature (RT) to form solution A.  
151 Throughout the process, the above solution was kept under vigorous magnetic stirring for 30  
152 min. Then, 75 mL of potassium hydroxide (KOH, 8 M) as a mineralizer was slowly dropped  
153 into solution A to adjust the pH to 8-9 with rapid stirring. It is worth noticing that a red-  
154 brown suspension of a bismuth-ferrite was formed at room temperature. In hydrothermal  
155 processing, the uniform suspension was transferred into a Teflon-lined autoclave and heated  
156 at 200 °C for 24 h. Then, the autoclave was cooled to room temperature and the formed  
157 precipitate was collected by centrifugation at 5,000 rpm for 5 min and washed at least three  
158 times with deionized water and ethanol (95%) to remove residual ions. Furthermore, the  
159 produced Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> powder was dried in an oven at 60 °C overnight for later use. Ultimately,  
160 the produced Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs were yellow-orange color at room temperature.

161

### 162 *2.2. Peroxidase-like activity of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanoparticles*

163 In a typical assay, different concentrations of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (0-30 µg/mL) were added to 225  
164 µL of TMB (0.3 mM dissolved in ethanol), 225 µL of H<sub>2</sub>O<sub>2</sub> (5 mM) in acetate buffer (pH 3.5,  
165 0.1 M) and the final volume of solution was adjusted to 1.5 mL. The mixture was incubated  
166 for 25 min at 45 °C. All chemical reagents were exactly prepared before every experiment.  
167 UV-vis spectrometry (500 to 800 nm) was used to investigate the absorbance variation at 654  
168 nm due to oxidation of TMB substrate.

169

### 170 *2.3. Steady-state kinetics for the determination $K_m$ and $V_{max}$*

171 The catalytic efficiency and the rate of enzyme reactions of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs can be  
172 determined by the Michaelis–Menten equation. To assess the kinetics parameters, the  
173 utilization of different substrate concentrations (TMB or H<sub>2</sub>O<sub>2</sub>) is an essential factor. Under  
174 the optimized conditions, kinetic experiments were determined by adding various  
175 concentrations of TMB chromogenic substrate (0.01-0.30 mM) at a fixed concentration of

176 H<sub>2</sub>O<sub>2</sub> (5 mM) in the first set of experiments. For the second set of kinetic experiments, the  
177 H<sub>2</sub>O<sub>2</sub> concentration was varied from 0.1 to 5.0 mM while the concentration of TMB substrate  
178 was kept constant (0.3 mM). All experiments were carried out in the acetic acidic buffer (pH  
179 3.5, 0.1 M) and the total volume of the mixture solutions was equal to 1.5 mL. UV-vis  
180 absorbance was recorded within the 500-800 nm range and the obtained V<sub>max</sub>, and K<sub>m</sub> values  
181 were compared with the kinetic parameters of other nanozymes.

182

#### 183 *2.4. Colorimetric assay for the detection of dopamine*

184 To accurately investigate the efficacy of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (120 μL, 8 μg/mL) to detect  
185 dopamine, first, a solution of a fixed concentration of TMB (225 μL, 0.3 mM) and H<sub>2</sub>O<sub>2</sub> (525  
186 μL, 5 mM) in acetate buffer solution (pH=3.5, 0.1 M) was prepared. Afterward, various  
187 dopamine concentrations (0-150 μM) were added to the above solution; the total volume was  
188 1.5 mL. The entire reaction mixture was quickly shaken then incubated at 45 °C for 25 min.  
189 The course of the reaction was monitored using UV-vis spectrometer (500-800 nm). At the  
190 end of incubation, UV-vis absorbance values were recorded at 654 nm and the obtained  
191 maximum absorbance was used to generate the calibration curve and also to determine the  
192 limit of detection of dopamine.

193

#### 194 *2.5. Selectivity and reproducibility of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanoparticles*

195 To evaluate the selectivity of the designed colorimetric assay, various amino acids and  
196 small molecules such as alanine (Ala), cysteine (Cys), arginine (Arg), lysine (Lys),  
197 glutathione (GSH), uric acid (UA), ascorbic acid (AA), lactose (Lac), glucose (Glu), fructose  
198 (Fru), and different ions (K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) were separately added to the mixture  
199 solution of TMB (0.3 mM), H<sub>2</sub>O<sub>2</sub> (5 mM), and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (8 μg/mL) in acetate buffer (pH  
200 3.5, 0.1 M). The concentration of applied interfering components was two times the  
201 concentration of dopamine (100 μM). All the above solutions were incubated for 25 min at  
202 45 °C, and their UV-vis spectra were measured in the 500-800 nm range. The characteristic  
203 reproducibility of the synthesized Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme was examined for four catalytic cycles  
204 of TMB oxidation under the optimized experimental conditions (Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (8 μg/mL), TMB  
205 (0.3 mM), H<sub>2</sub>O<sub>2</sub> (5 mM), acetate buffer (pH 3.5, 0.1 M), T=45 °C, and incubation time=25  
206 min).

207

#### 208 *2.6. Procedure for dopamine detection in real samples*



209 For dopamine analysis in real samples, 1  $\mu$ L of pure fetal bovine serum (FBS) and horse  
210 serum (HS) samples were diluted in phosphate buffer saline (PBS pH 7.4) and then  $\text{Bi}_2\text{Fe}_4\text{O}_9$   
211 nanozyme (8  $\mu\text{g}/\text{mL}$ ),  $\text{H}_2\text{O}_2$  (5 mM), and TMB (0.3 mM) were added. The total volume of  
212 the solution was maintained at 1.5 mL using acetate buffer (pH 3.5, 0.1 M). Afterward,  
213 different concentrations of dopamine (1, 5, and 10  $\mu\text{M}$ ) were introduced into the above  
214 mixture solution and incubated for 25 min at 45  $^\circ\text{C}$ . To detect the presence of dopamine in the  
215 FBS 1 (Sigma-Aldrich), FBS (Fisher Scientific), and HS (Fisher Scientific) samples, the  
216 corresponding changes in the absorbance spectra were monitored by UV-vis spectroscopy  
217 (500-800 nm). All experiments were performed in triplicates.

218

### 219 *2.7. Detection of hydroxyl radicals ( $\cdot\text{OH}$ ) generation in the presence of $\text{Bi}_2\text{Fe}_4\text{O}_9$*

220 In a typical assay, 0.2 mM of terephthalic acid (TA) was dissolved in ethanol. Eight  
221 mixtures were prepared as following: (a)  $\text{H}_2\text{O}_2$  (5 mM) +  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ), (b)  $\text{H}_2\text{O}_2$   
222 (5 mM) +  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ) + dopamine (50  $\mu\text{M}$ ), (c)  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ), (d)  
223  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ) + dopamine (50  $\mu\text{M}$ ), (e)  $\text{H}_2\text{O}_2$  (5 mM), (f)  $\text{H}_2\text{O}_2$  (5 mM) +  
224 dopamine (50  $\mu\text{M}$ ), (g) only TA (15  $\mu\text{l}$ ), and (h) TA (15  $\mu\text{l}$ ) + dopamine (50  $\mu\text{M}$ ) in acetate  
225 buffer (pH 3.5), and all solutions were incubated for 25 min at 45  $^\circ\text{C}$ . The total volume of  
226 eight tubes was filled to 1.5 mL. The change of fluorescence emission spectra ( $\lambda_{\text{ex}}=315$  nm)  
227 was recorded in the 400–550 nm range by utilizing a Safas Xenius XC fluorescence  
228 spectrophotometer.

229 Moreover, to examine the presence of  $\cdot\text{OH}$  radicals as one of the members of reactive  
230 oxygen species (ROS), *tert*-butyl alcohol (TBA) was used as a quencher.  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  
231  $\mu\text{g}/\text{mL}$ ), TMB (0.3 mM),  $\text{H}_2\text{O}_2$  (5 mM), acetate buffer (pH 3.5, 0.1 M), TBA (0.5 mM) were  
232 incubated at 45  $^\circ\text{C}$  for 25 min (total volume of the solution was 1.5 mL). All absorption  
233 spectra of the solutions with or without TBA molecules were recorded at 564 nm.

234

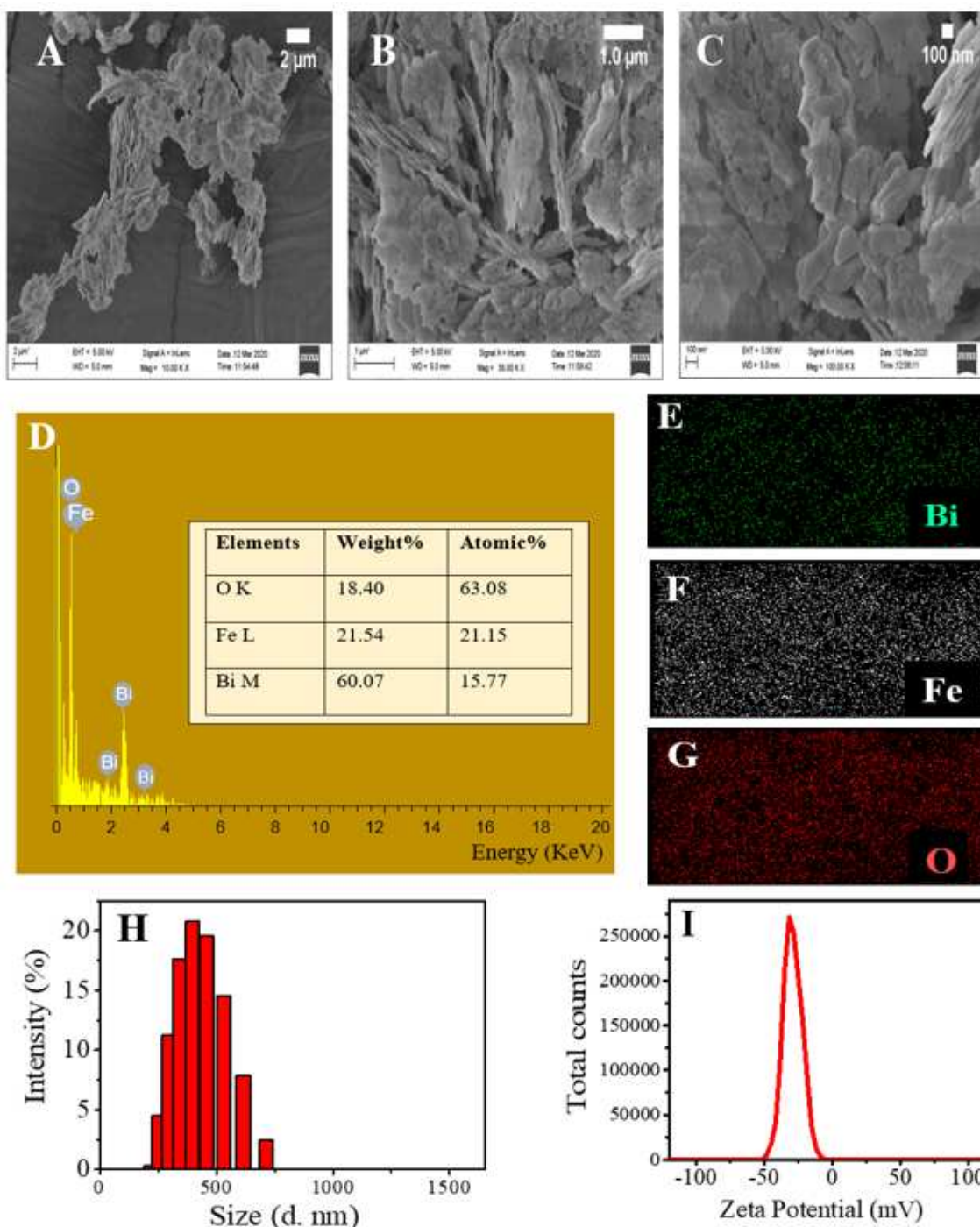
## 235 **3. Results and discussion**

### 236 *3.1. Characterization of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles*

237 As observed in **Fig. 1**, the morphological and chemical composition of the as-prepared  
238  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme were characterized by field emission scanning electron microscopy  
239 (FESEM) imaging and energy-dispersive X-ray (EDX) spectroscopy. The low and high  
240 magnification FESEM micrographs showed that  $\text{Bi}_2\text{Fe}_4\text{O}_9$  consist of an irregularly sheet-like  
241 morphology (**Fig. 1A-C**).

242 The accumulation of initial bismuth and ferrite salts causes the random collision of Bi-Fe-  
243 O elements, which leads to an increase of the irregular sheet growth. The irregular particle  
244 shapes of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  were formed by considering the different growth rates in various  
245 directions. Taken together, the results of elemental distribution mapping and EDX analysis  
246 (**Fig. 1D**) clearly illustrate the presence of Bi, Fe, and O elements, which is in full agreement  
247 with the chemical composition of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs. The atomic percentages of Bi, Fe, and O  
248 elements in the  $\text{Bi}_2\text{Fe}_4\text{O}_9$  sample were equal to 15.77%, 21.15%, and 63.08%, respectively. It  
249 can be noticed that there is a deviation from the stoichiometric composition due to iron  
250 deficiency. As revealed in **Fig. 1E-G**, the elemental mapping of Bi (green), Fe (white), and O  
251 (red) has intelligibly confirmed the uniform distribution of mentioned elements on the surface  
252 of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  enzyme-mimicking nanomaterial [27, 31].

253 The hydrodynamic radius and particle size distributions of the synthesized  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs  
254 were measured by utilizing the dynamic light scattering (DLS) and zeta potential techniques,  
255 respectively (**Fig. 1H and I**). The average hydrodynamic diameter ( $d_{\text{hydr}}$ ) of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs  
256 was  $\sim 396$  nm (3 measurements). In addition, the surface charge of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  was found to be  
257  $-31.62$  mV. Based on these results,  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs with a negative surface charge are expected  
258 to interact electrostatically with the positively charged chromogenic substrate (TMB) and  
259 efficiently catalyze the oxidation of TMB. The positive surface charge of TMB was brought  
260 by the presence of two amine groups [40-42].



261

262 **Fig. 1.** FESEM images at low and high magnifications (A-C), EDX spectrum (D), elemental  
 263 mappings for Bi (E), Fe (F), and O (G), DLS size distribution (H), and zeta potential (I) of  
 264 the as-prepared Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs.

265

266 **Fig. S1** depicts the FTIR spectrum of the Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (700-4000 cm<sup>-1</sup>), which indicates  
 267 the presence of diverse functional groups on the surface of the NPs. The spectrum comprises  
 268 broad and weak absorption bands at 3441 and 1636 cm<sup>-1</sup> related to hydroxyl groups  
 269 stretching and bending vibrations from water molecules or intermolecular hydrogen bonds,

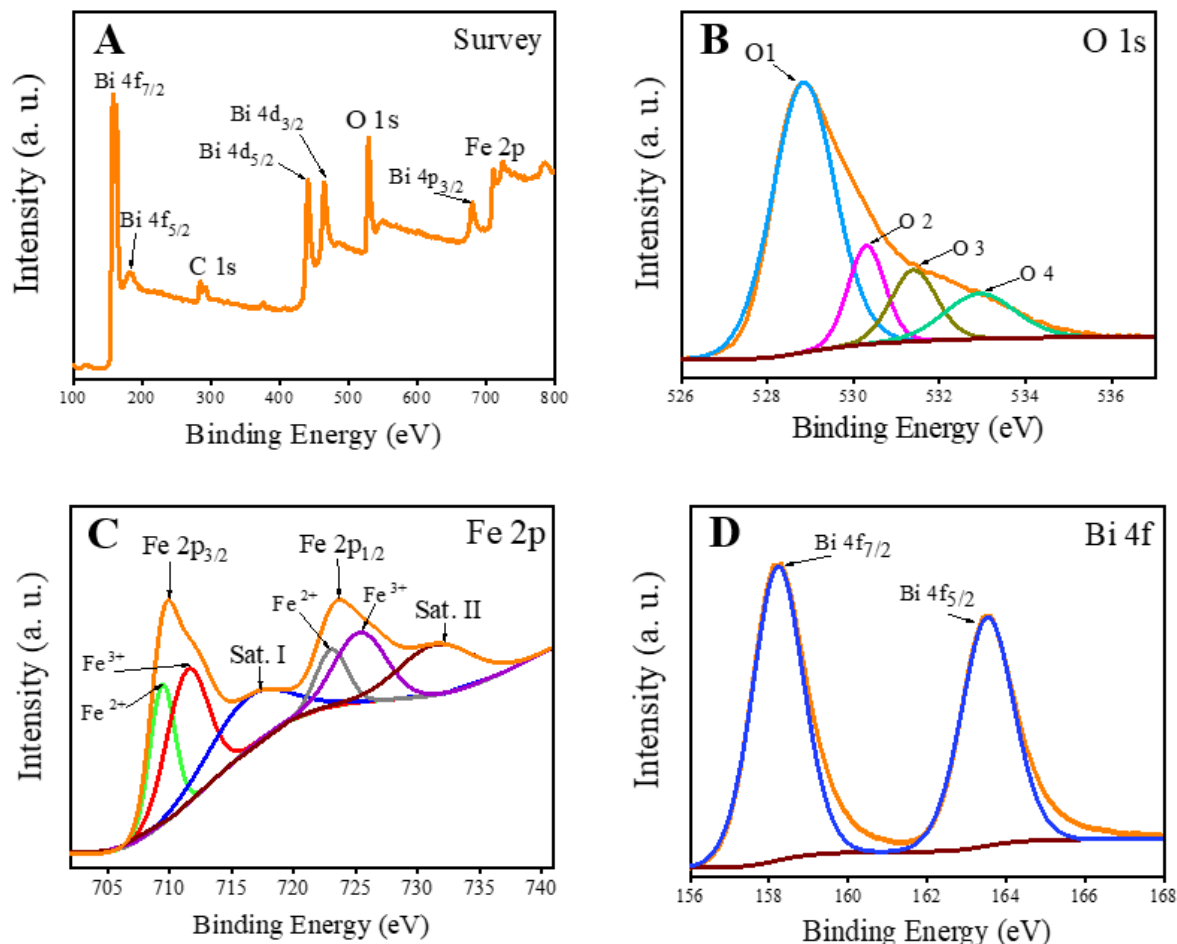
270 respectively. The strong absorption peak at  $1384\text{ cm}^{-1}$  belongs to the residual  $\text{NO}_3^-$  group  
271 incorporated during the preparation of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  sample. Besides, bismuth ferrite is an  
272 isostructural compound and contains tetrahedral  $\text{FeO}_4$ , octahedral  $\text{FeO}_6$ , and octahedral  $\text{BiO}_6$   
273 units. The vibration band at  $808\text{ cm}^{-1}$  is assigned to Fe-O stretching vibrations of  $\text{FeO}_4$  and  
274  $\text{FeO}_6$ , and also Bi-O in the  $\text{BiO}_6$  octahedral pairs [31, 43, 44].

275 The results of the thermogravimetric analysis (TGA) and derivative thermogravimetric  
276 (DTG) of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs in the  $30\text{--}980\text{ }^\circ\text{C}$  temperature range are shown in **Fig. S2**. TGA  
277 analysis of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs demonstrates four clear steps of weight loss: (I)  $50\text{ }^\circ\text{C}$ , (II)  $150\text{ }^\circ\text{C}$ ,  
278 (III)  $220\text{ }^\circ\text{C}$ , (IV)  $657\text{ }^\circ\text{C}$  corresponding to the mass reduction of 0.79%, 0.79%, 0.47% and  
279 5.49%, respectively. The first step belongs to water and residual organic solvent evaporation,  
280 and the second step of the significant mass loss was probably due to the decomposition of the  
281 ternary metal oxide structure of BFO [45]. By increasing the temperature ( $978.5\text{ }^\circ\text{C}$ ), the  
282 TGA curve of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  features an approximate loss of 8.21% of its total mass and 91.79%  
283 of the residual mass was left at the end of heating.

284 X-ray photoelectron spectrometry (XPS) was utilized to examine the elemental  
285 composition and the oxidation states of the as-prepared  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (**Fig. 2A-D**). The XPS  
286 survey spectrum of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs revealed the presence of Bi 4f, Bi 4d, Bi 4p, C 1s, Fe 2p,  
287 and O 1s peaks (**Fig. 2A**). In the survey spectrum of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (**Fig. 2A**), the narrow peak  
288 of C 1s observed at 285 eV is most likely due to surface contamination. On the basis of the  
289 XPS results, the atomic percentages of Bi, Fe, and O elements in  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs were 13.72,  
290 17.62, and 68.66 at.%, respectively. The results reflect Fe deficiency, in accordance with  
291 EDX analysis, even though there was no evidence for the existence of another crystalline  
292 phase (see XRD analysis below).

293 The O 1s wide scan spectrum (**Fig. 2B**) can be fitted with four Gaussian curves at around  
294 528.8 eV (O1), 530.3 eV (O2), 531.4 eV (O3), and 532.9 eV (O4), which are respectively  
295 ascribed to lattice M–O–M bonds, surface lattice oxygen, the presence of oxygen vacancies,  
296 and absorbed  $\text{H}_2\text{O}$  or surface carbonate [27, 46, 47]. As shown in **Fig. 2C**, the wide scan of  
297 Fe 2p XPS profile can be fitted with two components at binding energies of 710.1 and 723.6  
298 eV, that are respectively assigned to Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$ . These binding energies data  
299 confirmed the occurrence of two oxidation states (+2 and +3) in the BFO oxide. The high-  
300 resolution spectrum of Fe  $2p_{3/2}$  can be deconvoluted into two Gaussian peaks at 711.4 and  
301 725.4 eV which belong to the  $\text{Fe}^{3+}$  valence state in the  $\text{Bi}_2\text{Fe}_4\text{O}_9$ . The two peaks at 709.4 and  
302 723.1 eV can be attributed to Fe  $2p_{1/2}$  that correlate with the existence of  $\text{Fe}^{2+}$  ions in Fe-O  
303 bands. Furthermore, the two satellite peaks located at 717.9 eV (Sat. I) and 732.2 eV (Sat. II)

304 both belong to  $\text{Fe}^{3+}$  species in the  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs [27, 47-49]. The Bi 4f XPS plot (**Fig. 2D**)  
 305 can be deconvoluted into two distinct peaks ascribed to Bi 4f<sub>7/2</sub> peak at 158.2 eV and Bi 4f<sub>5/2</sub>  
 306 peak at 164.1 eV. The spin-orbit splitting of Bi 4f (5.90 eV) corresponds to bismuth ion in the  
 307 +3-valence state in the synthesized  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs [26, 27, 50].



308  
 309 **Fig. 2.** (A) XPS survey spectrum, and high-resolution XPS spectra of (B) O 1s, (C) Fe 2p,  
 310 and (D) Bi 4f regions of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs.

311 The phase purity and crystallinity of the as-prepared  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs were analyzed by X-  
 312 ray diffraction (XRD) patterns (**Fig. S3**). The characteristic diffraction peaks located at  $2\theta$   
 313 angles of  $14.78^\circ$ ,  $20.88^\circ$ ,  $22.40^\circ$ ,  $23.88^\circ$ ,  $24.90^\circ$ ,  $25.72^\circ$ ,  $26.88^\circ$ ,  $28.06^\circ$ ,  $28.94^\circ$ ,  $29.72^\circ$ ,  
 314  $30.80^\circ$ ,  $33.58^\circ$ ,  $35.52^\circ$ ,  $36.62^\circ$ ,  $37.54^\circ$ ,  $39.20^\circ$ ,  $44.18^\circ$ ,  $45.40^\circ$ ,  $46.82^\circ$ ,  $48.82^\circ$ ,  $49.50^\circ$ ,  $50.68^\circ$ ,  
 315  $52.04^\circ$ ,  $54.36^\circ$ ,  $55.30^\circ$ ,  $56.54^\circ$ ,  $58.8^\circ$ ,  $61.56^\circ$ ,  $64.68^\circ$ , and  $67.22^\circ$  can be perfectly indexed to  
 316 the orthorhombic  $\text{Bi}_2\text{Fe}_4\text{O}_9$  structure with (001), (020), (200), (120), (210), (021), (201),  
 317 (121), (211), (002), (220), (130), (310), (022), (202), (212), (140), (132), (141), (240), (411),  
 318 (420), (123), (142), (402), (332), (431), (004), (342), and (530), respectively ((JCPDS File  
 319 No. 00-025-0090). The crystalline planes with d-spacing values related to the above crystal

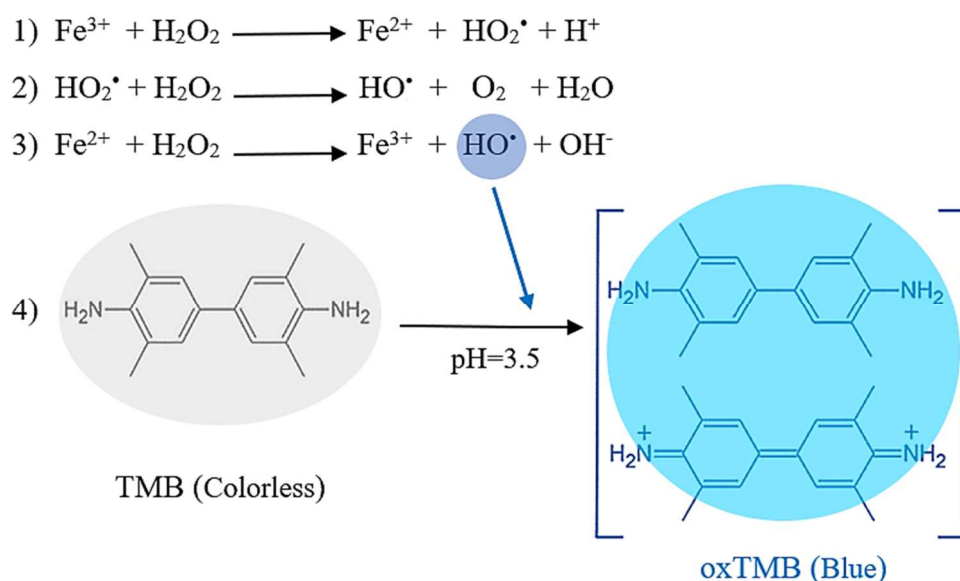
320 planes of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  sample were determined to be 5.99, 4.25, 3.97, 3.72, 3.57, 3.46, 3.32,  
321 3.18, 3.09, 3.00, 2.90, 2.67, 2.52, 2.45, 2.39, 2.30, 2.05, 2.00, 1.93, 1.86, 1.83, 1.80, 1.75,  
322 1.68, 1.65, 1.63, 1.57, 1.51, 1.44, and 1.39 Å, respectively. The sharp diffraction peaks in the  
323 XRD pattern obviously indicate that  $\text{Bi}_2\text{Fe}_4\text{O}_9$  has a well-crystallized structure without the  
324 existence of other impurities [44, 51-53]

325

### 326 *3.2. Peroxidase-like activity of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles*

327 In this catalytic process, the enzyme-mimetic activity of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs was examined for  
328 the oxidation of TMB, as electron-donor species, to ox-TMB in the presence of  $\text{H}_2\text{O}_2$  as  
329 electron-acceptor species. The decomposition of  $\text{H}_2\text{O}_2$  molecules was catalyzed by Fe species  
330 on the surface of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme. Ferrite ions in  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme are located at  $\text{FeO}_6$   
331 octahedral and  $\text{FeO}_4$  tetrahedral in the unit cell. Fe is a useful transition metal ion in Fenton  
332 reactions to reduce  $\text{H}_2\text{O}_2$  to  $\cdot\text{OH}$  radicals. Different oxidation forms of Fe cations like  
333  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and the d-orbitals of  $\text{Fe}^{3+}$  were consecutively produced and used in the suggested  
334 Fenton-reaction cycle. Besides the Fe active-sites, the large irregular sheet area of  $\text{Bi}_2\text{Fe}_4\text{O}_9$   
335 created more reactive sites and enhanced the peroxidase-like activity of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme.  
336 To mimic the Fenton-like reaction, Fe ions and the produced  $\cdot\text{OH}$  radicals played a key role  
337 in oxidizing TMB molecules to the blue-coloured form of TMB semiquinone dimer [43, 44,  
338 47, 54-58].

339 TMB oxidation in presence of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme is believed to occur through a Fenton-  
340 like reaction, as summarized in **Eq. 1-4 (Scheme 1)**. In a weakly acidic medium,  $\text{Bi}_2\text{Fe}_4\text{O}_9$   
341 nanozyme successfully decomposes  $\text{H}_2\text{O}_2$  molecules to hydroxyl radical ( $\cdot\text{OH}$ ), as an  
342 effective intermediate molecule (**Eq. 3**) to carry out the oxidation of TMB molecules in  
343  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9$  system (**Eq. 4**) at room temperature. The oxidized TMB substrate can  
344 be visualized by monitoring the maximum absorbance peak at 654 nm.

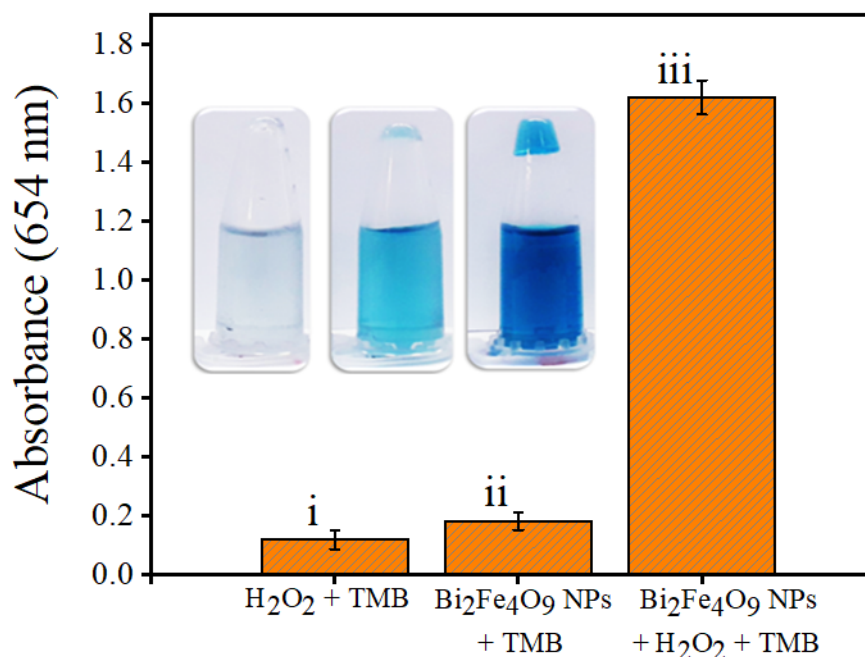


345

346 **Scheme 1.** Schematic illustration of the plausible mechanism of TMB oxidation by  $\text{H}_2\text{O}_2$  in  
 347 the presence of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs.

348

349 Under the reaction conditions, the meaningful effect of the absence and presence of  
 350  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme catalyst and  $\text{H}_2\text{O}_2$  molecule on the catalytic oxidation of TMB substrate  
 351 was investigated and the variation of UV-vis spectra are displayed in **Fig. 3(i-iii)**. Insert in  
 352 **Fig. 3** indicated the recorded photographs of the oxTMB color-change system. The  
 353 experimental systems consisting of only  $\text{H}_2\text{O}_2$  or  $\text{Bi}_2\text{Fe}_4\text{O}_9$  had no obvious effect on the  
 354 oxidation reaction of TMB and the absorbance signal of the solutions was close to the  
 355 background (**Fig. 3i**). Meanwhile, the addition of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  to TMB only slightly increased  
 356 the TMB oxidation (**Fig. 3ii**). After the introduction of both  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{H}_2\text{O}_2$  solutions into  
 357 the fresh TMB reagent, the peroxidase-like activity  $\text{Bi}_2\text{Fe}_4\text{O}_9$  improved and considerably  
 358 decomposed  $\text{H}_2\text{O}_2$  molecules to  $\bullet\text{OH}$  as active intermediates for oxidation of TMB (**Fig. 3iii**).  
 359 In an acidic medium (pH 3.5), the occurrence of the oxidation reaction was confirmed by the  
 360 naked eyes through the color change from the colorless mixtures of  $\text{H}_2\text{O}_2/\text{TMB}$  and  
 361  $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{TMB}$  to the deep-blue color of  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9$ , and also the produced ox-  
 362 TMB recorded a remarkable absorbance at around 654 nm (**Fig. 3**). All of the results  
 363 demonstrated that the presence of both  $\text{Bi}_2\text{Fe}_4\text{O}_9$ , as intrinsic peroxidase-like activity catalyst,  
 364 and  $\text{H}_2\text{O}_2$ , as inherent oxidant, was responsible for the remarkable increase of the oxidation  
 365 rate of TMB substrate.



366

367 **Fig. 3.** Relative UV-vis absorption spectra changes of different solutions containing acetate  
 368 buffer (pH 3.5, 0.1 M) and reaction components recorded after 25 min incubation at T=45 °C.  
 369 Typical photographs of the oxidized TMB (oxTMB) [from left to right: (i) H<sub>2</sub>O<sub>2</sub>+TMB  
 370 without Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (colorless), (ii) TMB+Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> without H<sub>2</sub>O<sub>2</sub> (slightly blue), and (iii)  
 371 TMB+ H<sub>2</sub>O<sub>2</sub>+Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (blue)]. Reaction condition: Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (8 μg/mL), TMB (0.3  
 372 mM), H<sub>2</sub>O<sub>2</sub> (5 mM), T=45 °C (For each solution, n=3).

### 373 3.3. Experimental condition optimization

374 In order to have a better insight into the reaction performance, the enzyme-like catalytic  
 375 reaction was performed under different experimental conditions by varying TMB, H<sub>2</sub>O<sub>2</sub>, and  
 376 Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> concentrations, pH, temperature, and the incubation time of the reaction [24, 59].  
 377 The effects of the different concentrations of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (1-30 μg/mL), TMB (0-0.7 mM),  
 378 and H<sub>2</sub>O<sub>2</sub> (0-8 mM), pH (pH=1-12), incubation time (5-50 min), and temperature (15-60 °C)  
 379 was investigated and clearly depicted in **Fig. S4A-F**. Optimizing the concentrations of  
 380 Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, TMB, and H<sub>2</sub>O<sub>2</sub> molecules were manifested by the maximum value of absorbance  
 381 at 654 nm. As depicted in **Fig. S4A-C**, the optimum absorbance was recorded using 8 μg/mL,  
 382 0.3 mM, and 5 mM of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, TMB, and H<sub>2</sub>O<sub>2</sub> respectively. In this study, the optimum  
 383 concentrations were utilized to carry out the following experiments. The result in **Fig. S4D**  
 384 demonstrated that pH values higher than 3.5 may cause the decomposition of H<sub>2</sub>O<sub>2</sub> substrate  
 385 into H<sub>2</sub>O and O<sub>2</sub> molecules. Consequently, the rate of the formation of •OH radicals was  
 386 decreased, and the distinct blue color-change was obtained only in an acidic condition.  
 387 Therefore, the pH value of 3.5 was selected as the optimum pH that illustrated the blue-dark



388 color solution with the highest absorbance at 654 nm. Another effective factor was the  
389 reaction temperature. In each case, the influence of the temperature on the peroxidase activity  
390 of mimic-catalyst was investigated in a slightly acidic buffer (pH 3.5, 0.1 M). The catalytic  
391 activity of the Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> sharply increased when the temperature was raised from 10 to 45 °C,  
392 and then decreased at temperatures higher than 45 °C. Therefore, the subsequent experiments  
393 were performed at the optimal temperature of 45 °C (**Fig. S4E**). Moreover, incubation time  
394 plays an important role in the decomposition of H<sub>2</sub>O<sub>2</sub> and the accomplishment of the  
395 oxidation reaction for which the selected optimal-time corresponds to 25 min (**Fig. S4F**). As  
396 expected, the mimic-catalytic activity of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> depends on the concentration, pH,  
397 temperature, and reaction-time, similar to other nanozymes reported in the literature.  
398 According to the optimized values, it can be expected that Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme as a metal  
399 oxide-type mimic catalyst can be applied for sensitive and accurate detection of dopamine.

400

#### 401 3.4. Kinetic study of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs and the determination of Michaelis-Menten constants

402 To explore the steady-state kinetic of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> as a peroxidase mimic nanozyme, various  
403 concentrations of H<sub>2</sub>O<sub>2</sub> and TMB as two different substrates were used to determine the  
404 initial rate of H<sub>2</sub>O<sub>2</sub> and TMB in acetate buffer (pH 3.5, 0.1 M) at 45 °C. In order to accurately  
405 calculate the initial velocity rate, the Beer-Lambert Law was applied (**Eq. 5**).

$$406 \quad V = \frac{\Delta c}{\Delta t} = \frac{\frac{\Delta A}{\epsilon b}}{\Delta t}$$

407 (5)

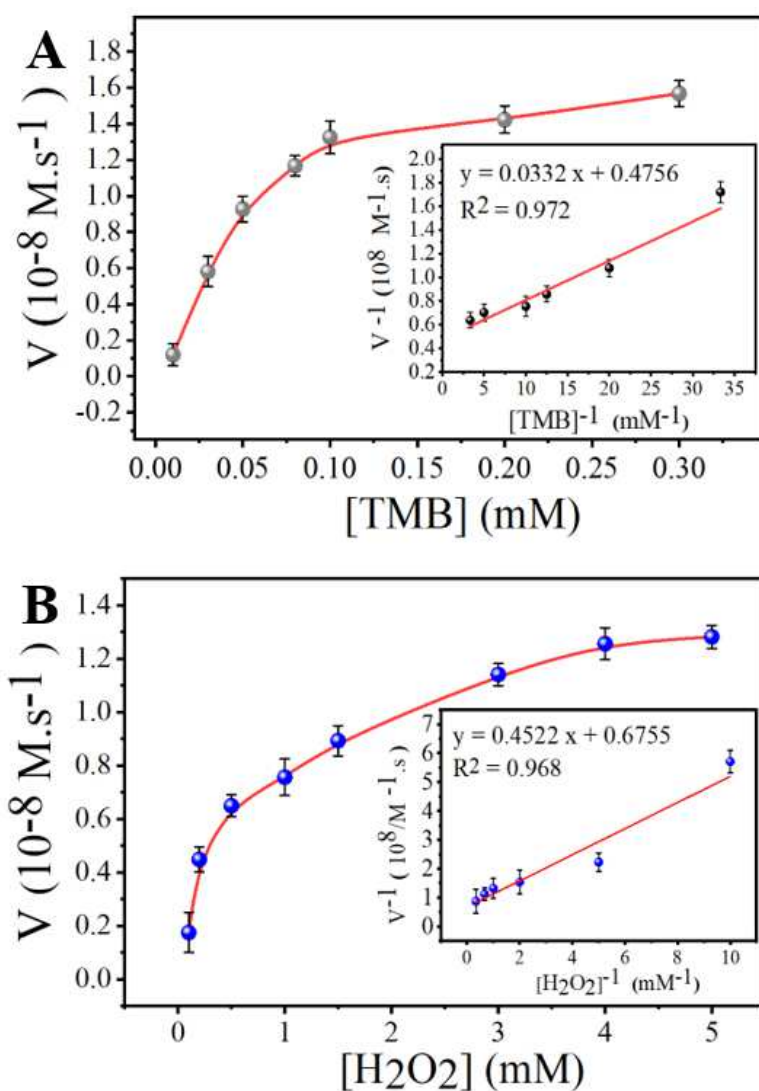
408 where A, b, ε, t and V represent respectively the absorbance at 654 nm, the optical path  
409 length (1 cm), the molar absorptivity coefficient of oxTMB (39000 M<sup>-1</sup>.cm<sup>-1</sup>), the time (min),  
410 and the reaction rate. In the time span of 0-30 min, **Fig S5 (A, B)** depicts the relationship  
411 between the recorded UV-vis absorption spectra at 654 nm with the constant concentration of  
412 one substrate (TMB or H<sub>2</sub>O<sub>2</sub>) and varying the concentration of the other substrate in the  
413 reaction mixture. UV-vis absorption was dramatically increased and then reached a steady-  
414 state level for both TMB (under the constant concentration of H<sub>2</sub>O<sub>2</sub>) and H<sub>2</sub>O<sub>2</sub> (under the  
415 constant concentration of TMB) substrates. And at this investigation time, the Michaelis-  
416 Menten kinetic model fitted well the variation of the absorption process.

417 To determine the kinetic parameters, the Michaelis-Menten model is one of the earliest  
418 descriptions and the best-known models to comprehensively investigate the value of  
419 nanozyme kinetics activity. Michaelis-Menten kinetics of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> peroxidase-mimic

420 catalyst was determined by keeping constant the concentration of TMB or H<sub>2</sub>O<sub>2</sub> as a targeted  
421 substrate and varying the concentration of the other molecule in a time-scan mode,  
422 simultaneously. Kinetic parameters (K<sub>m</sub> and V<sub>max</sub>) were calculated using the Lineweaver–  
423 Burk plots of the double reciprocal of the Michaelis-Menten **Eq. 6**:

$$424 \frac{1}{v} = \frac{1}{[S]} \times \frac{K_m}{V_{max}} + \frac{1}{V_{max}} \quad (6)$$

425 where [S], v, V<sub>max</sub>, and K<sub>m</sub> refer to the substrate concentration, the initial reaction rate, the  
426 maximum reaction rate, and Michaelis-Menten constant, respectively [6, 22, 60]. The steady-  
427 state kinetic measurements were conducted for both TMB and H<sub>2</sub>O<sub>2</sub> as enzyme substrates  
428 (**Fig. 4A-B**). Under the optimized conditions, the Michaelis-Menten curves were generated  
429 for TMB, at different concentrations of TMB (0.01-0.30 mM) and a fixed concentration of  
430 H<sub>2</sub>O<sub>2</sub> (5 mM), **Fig. 4A**, and also for H<sub>2</sub>O<sub>2</sub> at various concentrations of H<sub>2</sub>O<sub>2</sub> (0.1-5 mM) and  
431 a constant concentration of TMB (0.30 mM), **Fig. 4B**. According to the obtained results, the  
432 Michaelis-Menten constant (K<sub>m</sub>) and maximum reaction rate (V<sub>max</sub>) for H<sub>2</sub>O<sub>2</sub>/TMB/Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>  
433 system were calculated and drawn via fitting the data into the Lineweaver Burk double  
434 reciprocal plots (**Fig. 4A and B insets**).



435  
 436 **Fig. 4.** Steady-state kinetic experiments of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs at (A) different concentrations of  
 437 TMB (0.01-0.30 mM) and fixed concentration of  $\text{H}_2\text{O}_2$  (5 mM) substrates, and (B) varying  
 438 concentrations of  $\text{H}_2\text{O}_2$  (0.1-5 mM) and constant concentration of TMB (0.3 mM) substrates.  
 439 Insets: the linear calibration curves for the determination of TMB and  $\text{H}_2\text{O}_2$ . Reaction  
 440 conditions:  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g/mL}$ ), acetate buffer (pH 3.5, 0.1 M),  $T=45^\circ\text{C}$ , and incubation  
 441 time=25 min. UV-vis measurements were repeated three times.

442  
 443 **Table 1** summarizes the obtained enzyme kinetic parameters ( $K_m$  and  $V_{max}$ ) in  
 444 comparison to the horseradish peroxidase (HRP) enzyme and other nanomaterials reported in  
 445 the literature. For TMB and  $\text{H}_2\text{O}_2$  substrates in  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9$  system, the obtained  
 446 constant  $K_m$  and  $V_{max}$  parameters equaled to 0.07 and 0.73 mM, and 2.17 and  $1.56 (\times 10^{-8})$   
 447  $\text{M.s}^{-1}$ , respectively. In this context, the Michaelis-Menten constant ( $K_m$ ) is an effective  
 448 parameter to emphasize the affinity between the  $\text{Bi}_2\text{Fe}_4\text{O}_9$  as an enzyme-like catalytic with

449 peroxidase substrate (TMB or H<sub>2</sub>O<sub>2</sub>). The lower value of K<sub>m</sub> of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> in comparison to  
 450 natural HRP and other nanozyme catalysts refer to its stronger affinity towards both TMB  
 451 and H<sub>2</sub>O<sub>2</sub> substrates. Besides, the lower K<sub>m</sub> value of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs for H<sub>2</sub>O<sub>2</sub> means that the  
 452 higher catalytic response of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs was obtained using a small concentration of H<sub>2</sub>O<sub>2</sub>  
 453 substrate. This means that the decomposition of H<sub>2</sub>O<sub>2</sub> into •OH radical can be accelerated to  
 454 oxidase TMB molecules. According to the obtained K<sub>m</sub> and V<sub>max</sub> constants, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> features  
 455 a good affinity towards TMB and H<sub>2</sub>O<sub>2</sub> for peroxidase-mimic activity.

456

457 **Table 1**

458 Comparison of the steady-state kinetic parameters (Michaelis-Menten constant (K<sub>m</sub>) and  
 459 maximum velocity (V<sub>m</sub>) of H<sub>2</sub>O<sub>2</sub> and TMB substrates with previously reported materials.

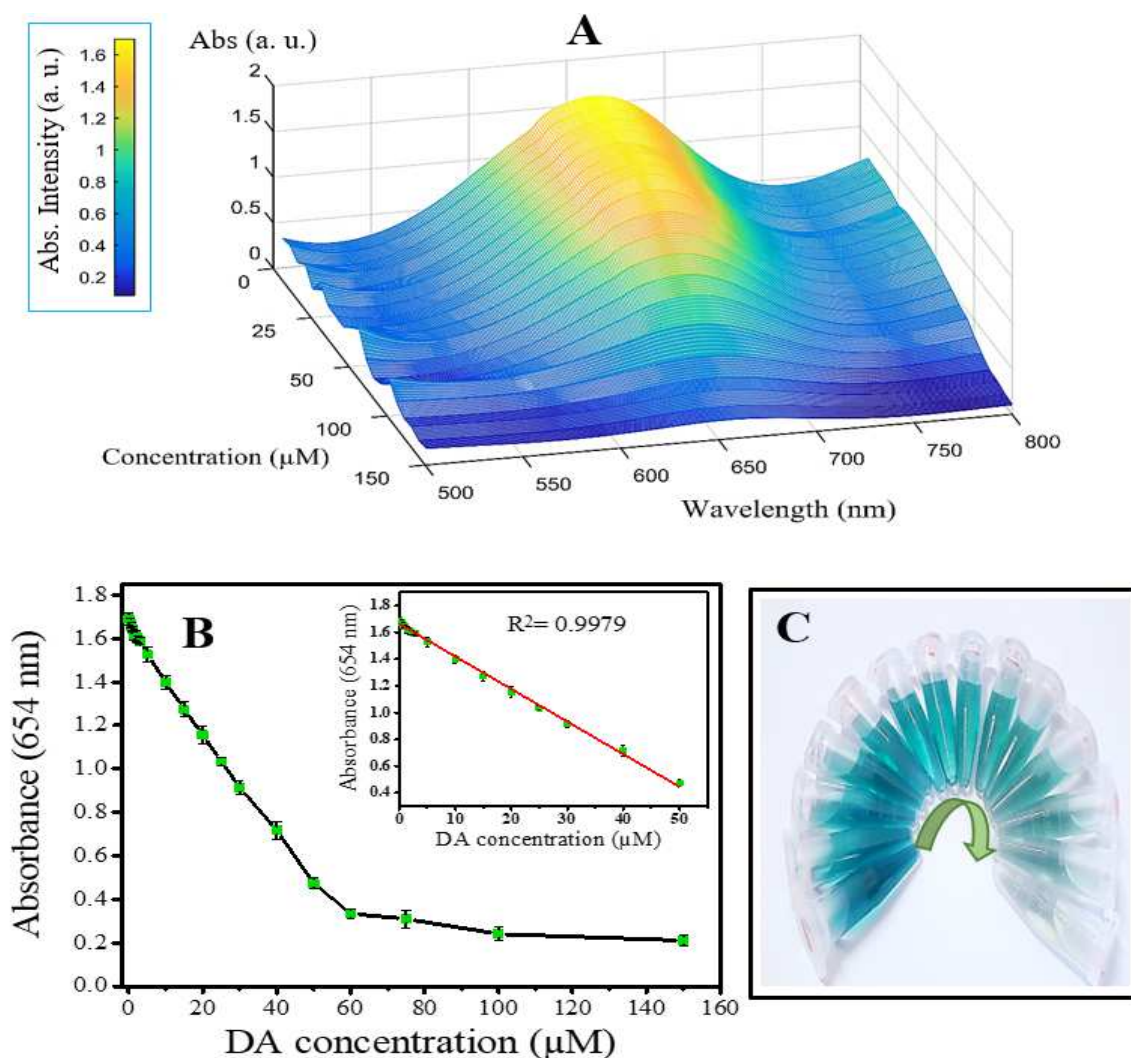
Catalysts	Substrates	K <sub>m</sub> (mM)	V <sub>m</sub> (10 <sup>-8</sup> M.s <sup>-1</sup> )	Ref.
HRP	H <sub>2</sub> O <sub>2</sub>	3.70	8.71	[24]
HRP	TMB	0.43	10.00	[24]
CuFe <sub>2</sub> O <sub>4</sub> /Cu <sub>9</sub> S <sub>8</sub> /PPy	H <sub>2</sub> O <sub>2</sub>	23.83	9.82	[47]
CuFe <sub>2</sub> O <sub>4</sub> /Cu <sub>9</sub> S <sub>8</sub> /PPy	TMB	0.13	6.97	[47]
Co <sub>3</sub> O <sub>4</sub> gilly-flower like	H <sub>2</sub> O <sub>2</sub>	245.00	28.50	[61]
Co <sub>3</sub> O <sub>4</sub> gilly-flower like	TMB	0.12	33.20	[61]
MoS <sub>2</sub> /PPy	H <sub>2</sub> O <sub>2</sub>	12.80	15.10	[62]
MoS <sub>2</sub> /PPy	TMB	0.41	47.40	[62]
Bi <sub>2</sub> Fe <sub>4</sub> O <sub>9</sub>	H <sub>2</sub> O <sub>2</sub>	0.73	1.56	<b>This work</b>
Bi <sub>2</sub> Fe <sub>4</sub> O <sub>9</sub>	TMB	0.07	2.17	<b>This work</b>

460

461 *3.5. Colorimetric sensing of dopamine in the presence of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme*

462 In order to demonstrate the acceptable enzyme-mimetic property of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme,  
 463 the optimized H<sub>2</sub>O<sub>2</sub>/TMB/Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> system was applied as an indirect platform to sense  
 464 dopamine. As displayed in **Fig. 5A-B**, the presence of dopamine molecule with an effective  
 465 inhibiting role, prevents the formation ox-TMB under optimum conditions. A point of fact  
 466 during the increase of dopamine concentration is the gradual vanishing of the dark-blue color  
 467 and the decreased number of ox-TMB molecules (**Fig. 5C**). Therefore, the presence of

468 dopamine effectively prohibited the production of ox-TMB molecules. The color changes of  
469 TMB solutions were easily observable by naked eyes and the variation of the UV-vis spectra  
470 was recorded at 654 nm. This phenomenon clearly indicated the competition between  
471 dopamine and TMB molecules to capture  $\cdot\text{OH}$  generated in the catalytic decomposition of  
472  $\text{H}_2\text{O}_2$  molecules. The notable decrease of accessible  $\cdot\text{OH}$  radicals may be the result of  
473 phenolic ring oxidation in dopamine molecules [1, 60]. Generally, dopamine oxidation was  
474 accelerated using  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme to produce dopamine o-quinone (DOQ). The defined  
475 system outlines a simple colorimetric platform for dopamine sensing that is based on the  
476 oxidation of dopamine by utilizing  $\text{H}_2\text{O}_2$  molecules in presence of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme and  
477 TMB substrate.  
478



479  
480 **Fig. 5.** UV-vis absorption spectra (A) and absorbance at 654 nm (B) of TMB solutions in  
481 presence of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme and various DA concentrations (0-150  $\mu\text{M}$ ). Inset: The linear  
482 calibration curve in the lower concentration range of DA ( $R^2=0.9979$ ). Photographs of the

483 color-changes during TMB oxidation in presence of different dopamine concentrations (C)  
484 (from left to right arrow: increasing the concentration of dopamine). Reaction conditions:  
485 Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (8 μg/mL), TMB (0.3 mM), H<sub>2</sub>O<sub>2</sub> (5 mM), acetate buffer (pH 3.5, 0.1 M),  
486 T=45 °C, and incubation time=25 min. The measurements were performed in triplicates.

487

488 An elevation of dopamine concentration from 0 to 150 μM led to a decrease in  
489 absorbance intensity of ox-TMB at 654 nm. The color tonality faded from deep-blue to  
490 colorless, indicating a decrease in the oxidation rate of TMB oxidation and enhanced  
491 formation of dopamine o-quinone molecule (Fig. 5C). A good linear range of added  
492 dopamine (from 0.15 to 50 μM) to TMB/H<sub>2</sub>O<sub>2</sub>/Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> system was obtained by applying the  
493 equation  $A = -0.024 [\text{dopamine } (\mu\text{M})] + 1.663$  ( $R^2=0.9979$ ). In addition, the limit of detection  
494 (LOD) was determined to be 51 nM at S/N=3, where S and N represent the signal and noise,  
495 respectively.

496 **Table 2** lists the analytical merits of the developed Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme sensor compared  
497 to different nanoparticles using various approaches such as electrochemistry [17, 18],  
498 electrochemiluminescence [16], fluorescence spectroscopy [13], and colorimetric assays [3,  
499 23]. The value of the LOD of our colorimetric-method by using Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme is lower  
500 than previously reported ones. The above results indicate that this designed colorimetric  
501 sensor as a simple, facile, and reproducible assay has a high sensitivity to detect dopamine  
502 molecules.

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**Table 2**

Method	Sensor	Linear range ( $\mu\text{M}$ )	LOD <sup>1</sup> ( $\mu\text{M}$ )	Ref.
Electrochemistry	rGO/TiO <sub>2</sub>	2-60	0.60	[17]
Electrochemistry	CAuNE	1-100	5.83	[18]
ECL <sup>2</sup>	CdSeTe/ZnS QDs	3.75-450	0.10	[16]
Fluorescence	BSA-CuNCs	0.50-50	0.28	[13]
Colorimetric	LaCoO <sub>3</sub>	0.50-20	0.19	[3]
Colorimetric	Co <sub>3</sub> O <sub>4</sub> @NiO	1-1000	1.21	[60]
Colorimetric	CuS/rGO	2-100	0.48	[63]
Colorimetric	Ag NPs	3.20-20	1.20	[64]
Colorimetric	CuFe <sub>2</sub> O <sub>4</sub> /Cu <sub>9</sub> S <sub>8</sub> /PPy	2-20	1.00	[35]
Colorimetric	h-CuS NCs	2-150	1.67	[65]
Colorimetric	NiCo <sub>2</sub> S <sub>4</sub> -rGO	0.50-100	0.42	[23]
Colorimetric	Bi <sub>2</sub> Fe <sub>4</sub> O	0.15-50	0.05	<b>This work</b>

521 Comparison of different analytical methods for quantitative analysis of dopamine.

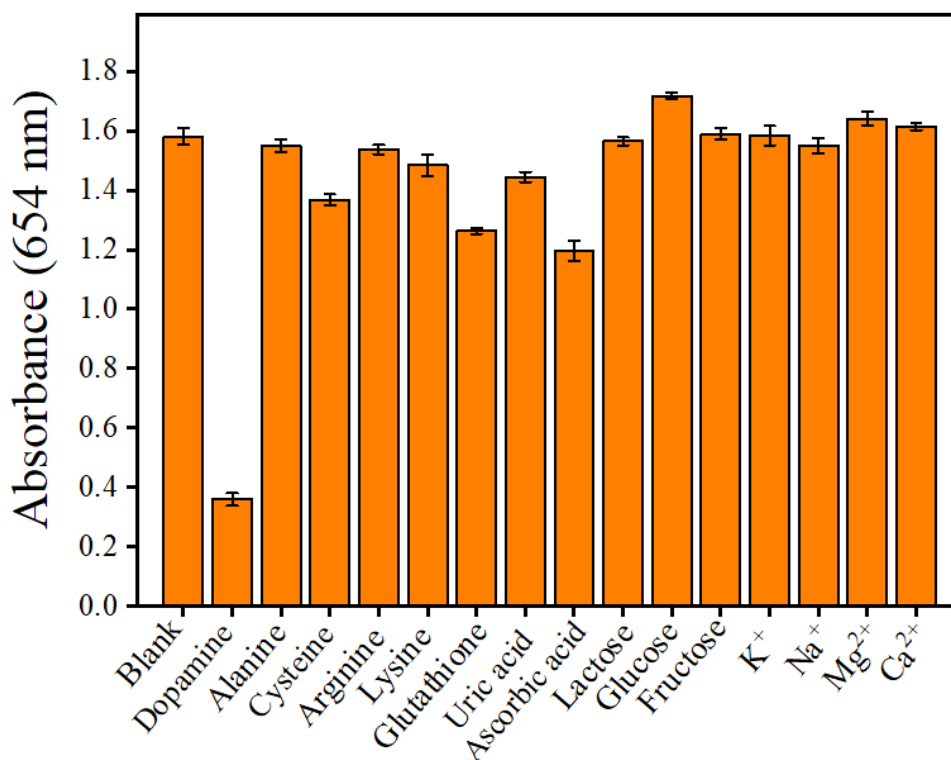
522 <sup>1</sup> Limit of detection (LOD)

523 <sup>2</sup> Electrochemiluminescence (ECL)

524

### 525 3.6. Selectivity of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme-sensor toward dopamine detection

526 Under the optimized conditions, the selectivity of the proposed Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> nanozyme was  
527 investigated in the presence of different molecules such as alanine (Ala), cysteine (Cys),  
528 arginine (Arg), lysine (Lys), glutathione (GSH), uric acid (UA), ascorbic acid (AA), lactose  
529 (Lac), glucose (Glu), fructose (Fru), K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>, with the concentration two  
530 times higher (100  $\mu\text{M}$ ) than the optimized concentration of dopamine. The reduction of UV–  
531 vis absorbance intensity in H<sub>2</sub>O<sub>2</sub>/TMB/Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>/interfering system was compared to control  
532 condition (**Fig. 6**). The excellent inhibition role of dopamine in comparison to other  
533 molecules (at higher concentration) indicates that ox-TMB product could not easily be  
534 generated in the dopamine-containing system.



535

536 **Fig. 6.** Absorption at 654 nm of oxTMB in the presence of different interfering molecules at a  
 537 concentration of 100  $\mu$ M (2 times higher than the concentration of DA); Reaction conditions:  
 538 Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> NPs (8  $\mu$ g/mL), H<sub>2</sub>O<sub>2</sub> (5 mM), TMB (0.3 mM), acetate buffer (0.1 M, pH 3.5),  
 539 T=45  $^{\circ}$ C, and incubation time=25 min. The measurements were performed in triplicates.

540

541 Dopamine is a strong free radical scavenger and has a potent hydrogen-donating activity.  
 542 As presented in **Fig. 6**, the excellent inhibition role of dopamine in comparison to the applied  
 543 interference molecules is obviously reflected from its higher tendency to capture hydroxyl  
 544 radicals ( $\cdot$ OH) in the acidic medium and prohibit the oxidation of TMB molecules. The  
 545 higher quenching ability of dopamine is related to its specific chemical structure. Dopamine  
 546 features several H atoms on its aromatic ring responsible for increasing the electron density,  
 547 mobility, and also the propensity to capture  $\cdot$ OH radicals. During the reaction with the  
 548 reactive oxygen species (ROS) like  $\cdot$ OH radical, dopamine is able to produce several  
 549 derivatives (**Scheme S2 B-D**). As indicated in **Scheme S2**, three initial-hydroxylated  
 550 products of dopamine are generated during the reaction with  $\cdot$ OH radical, namely 2-  
 551 hydroxydopamine (2-OHDA), 5-hydroxydopamine (5-OHDA), and 6-hydroxydopamine (6-  
 552 OHDA). All three ring-monohydroxylated dopamine molecules as reactive species could  
 553 inhibit the oxidation of TMB molecules to oxTMB [1]. Another effective factor of dopamine  
 554 for inhibiting TMB oxidation is associated with the presence of its ethyl-amine group. The



555 amine group in the side chain of the dopamine phenolic ring, as a suitable electron-donor  
556 group, helps to accelerate electron transfer to enhance the interaction among H atoms on  
557 aromatic rings of dopamine with  $\cdot\text{OH}$  radicals. This result means that dopamine has higher  
558 quenching ability of  $\cdot\text{OH}$  radicals compared to ascorbic acid and uric acid [5, 66]. This  
559 oxidation process indicated that the designed colorimetric probe owns a good selectivity and  
560 could play an important role in the low detection of dopamine in aqueous media.

561

### 562 *3.7. Reproducibility of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles*

563 To investigate the nanozyme efficiency, a fresh sample of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ), TMB  
564 (0.3 mM), and  $\text{H}_2\text{O}_2$  (5 mM) in acetate buffer (pH 3.5, 0.1 M) at 45  $^\circ\text{C}$  was slightly shaken  
565 for 25 min. The final volume of the solution was 1.5 mL. For the repeated cycle purpose,  
566  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9$  reaction mixture was centrifuged at 10,000 rpm for 7 min and rinsed  
567 with deionized water at 25  $^\circ\text{C}$  and then the precipitate was added to  $\text{H}_2\text{O}_2/\text{TMB}$  solution  
568 under the obtained optimal conditions. The relative activity versus response cycle is depicted  
569 in **Fig. S6**. The catalytic stability of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  after every catalytic cycle, compared with the  
570 original activity, was slightly reduced. After the fourth independent cycle, the primary  
571 absorbance intensity of the fresh mixture was decreased from 100% to 93%. The result  
572 proved that  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs exhibit a good enzyme-like catalytic activity, stability, and  
573 reproducibility.

574

### 575 *3.8. Detection of dopamine in real samples*

576 To evaluate the practical applicability of the proposed  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs as an efficient  
577 enzyme-like catalyst, we examined dopamine determination in fetal bovine serum (FBS), and  
578 horse serum (HS) samples. It should be noted that FBS and HS samples before adding the  
579 reagents were diluted 1000 times with buffer phosphate saline (PBS 0.1 mM, pH 7.4). Using  
580 the optimized conditions ( $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8 mg/mL),  $\text{H}_2\text{O}_2$  (5 mM), TMB (0.3 mM), pH= 3.5,  
581 incubation time=25 min, and T=45  $^\circ\text{C}$ ), different concentrations of dopamine (1, 5, and 10  
582  $\mu\text{M}$ ) were spiked into diluted FBS 1 (Sigma-Aldrich), FBS 2 (Fisher Scientific), and HS  
583 (Fisher Scientific) solutions.

584 Moreover, the recovery values and the content of dopamine in real samples were  
585 calculated using the obtained calibration curve in **Fig. 5** and the recorded UV-vis absorption  
586 spectra at 654 nm for every real sample (FBS 1, FBS 2, and HS). The result of percentage  
587 recovery ( $[\text{dopamine}]_{\text{found}}/[\text{dopamine}]_{\text{added}} \times 100$ ) and relative standard deviation (RSD %) are  
588 listed in **Table 3**. The relative recoveries of dopamine concentration in FBS (1 and 2) and HS

589 samples were respectively in the ranges of 96.18–118.12% and 97.61–104.92%. It should be  
 590 noted that to reduce the stochastic error effect, UV-vis absorbance values were recorded  
 591 three-times for each experimental condition. The results revealed that this colorimetric  
 592 method, as a feasible and reliable approach, can be applied to determine dopamine in  
 593 different real samples.

594

595 **Table 3**

596 Sensing of DA in fetal bovine serum (FBS 1 and 2), and horse serum (HS) samples (n = 3).

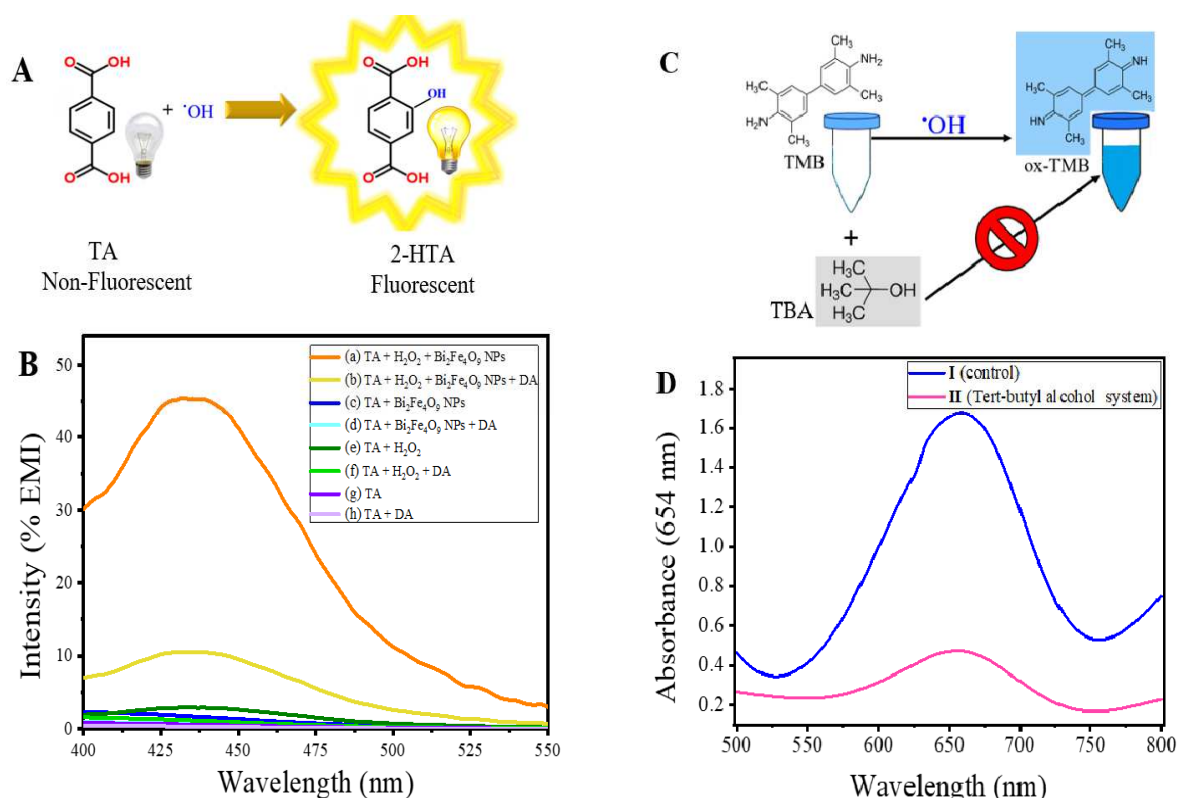
Samples	DA added ( $\mu\text{M}$ )	DA founded ( $\mu\text{M}$ )	Recovery (%)	RSD (%)
FBS 1	1.00	1.02	101.78	0.39
	5.00	5.35	106.95	0.64
	10.00	9.62	96.18	1.76
FBS 2	1.00	1.16	116.22	1.66
	5.00	5.40	108.02	0.39
	10.00	11.81	118.12	3.81
HS	1.00	0.97	97.61	1.42
	5.00	5.10	102.04	0.80
	10.00	10.49	104.92	3.27

597

### 598 3.9. The investigation of the mimic-enzyme catalytic mechanism to produce hydroxyl radicals 599 ( $\cdot\text{OH}$ )

600 To confirm the peroxidase-like mechanism of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs, terephthalic acid (TA)  
 601 molecule was selected as a fluorescence probe. As indicated in **Fig. 7**, TA can react with  $\cdot\text{OH}$   
 602 radicals to yield 2-hydroxyterephthalic acid (HTA) molecule, displaying an intense  
 603 fluorescence signal [6, 67-69]. The general oxidation reaction of the TA molecule is depicted  
 604 in the following **Fig. 7A**. All the solutions (**Fig. 7B**) were prepared in acetate buffer (pH 3.5,  
 605 0.1 M) and the total value was 1.5 mL. As presented in **Fig. 7B (g, e, and c)**, terephthalic acid  
 606 (TA) did not show an obvious emission peak in the absence of  $\text{H}_2\text{O}_2$ , the presence of  $\text{H}_2\text{O}_2$   
 607 alone, and  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs alone. It could be clearly seen, in **Fig. 7B (a)**, that the introduction  
 608 of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme to TA/ $\text{H}_2\text{O}_2$  mixture led to the appearance of fluorescence emission  
 609 with a maximum peak at around 435 nm under optimum experimental conditions, which is a  
 610 strong indication that TA was converted into HTA molecules. The fluorescence curves  
 611 indicated that the formation of HTA molecules was highly related to the presence of both

612  $\text{H}_2\text{O}_2$  substrate and  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme in the reaction mixture ( $\text{H}_2\text{O}_2/\text{Bi}_2\text{Fe}_4\text{O}_9/\text{TA}$ ). In the  
 613 presence of dopamine, the fluorescence intensity of obtained HTA was dramatically  
 614 decreased, which proved the competitive role of dopamine compared to TA for grasping the  
 615 hydroxide radicals (**Fig. 7B (b), orange curve**). The fluorescence intensity related to HTA  
 616 molecules in each of the eight solutions was recorded at 435 nm. The transformation of TA  
 617 into fluorescent (HTA) molecules was accelerated in the presence of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme  
 618 through the decomposition of  $\text{H}_2\text{O}_2$  molecules into hydroxyl radicals ( $\cdot\text{OH}$ ).



620  
 621 **Fig. 7.** (A) The possible mechanism of reaction of terephthalic acid (TA) with hydroxyl  
 622 radicals. (B) Fluorescence spectra using TA as a fluorescent probe ( $\lambda_{ex}=315$  nm), Reaction  
 623 experimental conditions: (a)  $\text{H}_2\text{O}_2$  (5 mM) +  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ), (b)  $\text{H}_2\text{O}_2$  (5 mM) +  
 624  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ) + dopamine (50  $\mu\text{M}$ ), (c)  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ), (d)  $\text{Bi}_2\text{Fe}_4\text{O}_9$   
 625 NPs (8  $\mu\text{g}/\text{mL}$ ) + dopamine (50  $\mu\text{M}$ ), (e)  $\text{H}_2\text{O}_2$  (5 mM), (f)  $\text{H}_2\text{O}_2$  (5 mM) + dopamine (50  
 626  $\mu\text{M}$ ), (g) only TA (0.2 mM), and (h) TA (0.2 mM) + dopamine (50  $\mu\text{M}$ ) in acetate buffer (pH  
 627 3.5, 0.1 M) and all solutions were incubated for 25 min at 45  $^\circ\text{C}$ . (C) The proposed  
 628 mechanism of effect of *tert*-butyl alcohol (TBA) on the peroxidase-mimic catalytic activity of  
 629  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs. (D) UV-vis spectra using TBA as an electron scavenger, Reaction  
 630 experimental conditions:  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs (8  $\mu\text{g}/\text{mL}$ ), TMB (0.3 mM),  $\text{H}_2\text{O}_2$  (5 mM), acetate  
 631 buffer (pH 3.5, 0.1 M), TBA (0.5 mM),  $T=45$   $^\circ\text{C}$ , and incubation time=25 min.

632 In addition, to confirm the role of  $\cdot\text{OH}$  radicals in the reaction mechanism, *tert*-butanol  
633 alcohol (TBA) was used as  $\cdot\text{OH}$  radical scavenger molecule (rate constant =  $6.2 \times 10^8 \text{ dm}^3$   
634  $\text{mol}^{-1} \text{ s}^{-1}$ ). The presence of TBA obviously prevented the oxidation of TMB molecules and  
635 simultaneously produced  $(\cdot(\text{CH}_3)_3\text{O})$  radicals [7, 70]. As mentioned above, TBA can directly  
636 quench reactive oxygen species (ROS) as hydroxyl radicals (**Fig. 7C-D**). The comparison of  
637 the UV-vis absorption spectra of the  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9$  (**Fig. 7D, blue curve**) and  
638  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9/\text{TBA}$  (**Fig. 7D, pink curve**) systems illustrated an obvious absorption  
639 peak in the UV-vis range whose intensity was significantly decreased in the presence of  
640 TBA. These phenomena prove that the hydroxyl radicals play an important role in the  
641 oxidation of TMB substrate and the charge transfer between Fe (II) to Fe (III) ions in the  
642 Fenton-like cycle of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanozyme.

643

#### 644 **4. Conclusion**

645 In summary, dopamine (DA) as a neurotransmitter plays a number of key roles in  
646 humans and animals. Therefore, the control and monitoring of the amount of dopamine is  
647 necessary to prevent disease conditions. In this work, we report, for the first time, a new  
648 colorimetric sensor using  $\text{Bi}_2\text{Fe}_4\text{O}_9$  nanoparticles with peroxidase-mimic catalytic activity.  
649 The metal-based bimetallic  $\text{Bi}_2\text{Fe}_4\text{O}_9$  NPs were prepared by a hydrothermal method that is a  
650 facile and low-cost approach.  $\text{Bi}_2\text{Fe}_4\text{O}_9$  enzyme mimic features high water-solubility and  
651 good stability. On the basis of the outstanding catalytic activity of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  in the presence of  
652 TMB and  $\text{H}_2\text{O}_2$ , a colorimetric sensing platform was developed and exhibited an accurate,  
653 highly sensitive, and selective detection of dopamine at a nanomolar level. This colorimetric  
654 probe achieved a detection limit and linear concentration range of 51 nM and 0.15-50  $\mu\text{M}$  for  
655 dopamine, respectively. The developed sensor outperforms the already reported nanozymes  
656 in literature [3, 35, 63-65]. Under optimized experimental conditions, Michaelis-Menten  
657 kinetics analysis of the oxidation state of TMB substrate, in  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9$  system,  
658 achieved  $V_{\text{max}}$  and  $K_{\text{m}}$  values of  $2.17 \times 10^{-8} \text{ M}\cdot\text{s}^{-1}$  and 0.07 mM, respectively. To gain a better  
659 understanding of the reaction mechanism, we examined the effect of hydroxyl ( $\cdot\text{OH}$ ) radicals  
660 as important reactive oxygen species to oxidase dopamine molecules in the  
661  $\text{H}_2\text{O}_2/\text{TMB}/\text{Bi}_2\text{Fe}_4\text{O}_9/\text{DA}$  colorimetric-system using terephthalic acid (TA) and *tert*-butyl  
662 alcohol (TBA) probes. This spectroscopic method for evaluation of  $\cdot\text{OH}$  radicals is a simple,  
663 inexpensive, and reliable approach. In addition, the potential application of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  as a  
664 peroxidase-mimic catalyst to accurately detect dopamine concentration in fetal bovine serum

665 (FBS) and horse serum (HS) samples was demonstrated. Taken together the results of the  
666 present study highlight the potential application of nanostructured bismuth ferrite ( $\text{Bi}_2\text{Fe}_4\text{O}_9$ )  
667 in the diagnosis of dopamine-related diseases. Future work will introduce the investigation of  
668 dopamine in real samples by using lateral-flow test strips coupled with smartphones. These  
669 studies will open new perspectives for early detection and treatment of different types of drug  
670 addiction and neurological related diseases.

671

#### 672 **CRedit authorship contribution statement**

673 **Mehri Razavi:** Investigation, Methodology, Validation, Visualization, Formal analysis,  
674 Writing-original draft. **Alexandre Barras:** Investigation, Methodology. **Majdid Ifires:**  
675 Resources. **Abir Swaidan:** Resource. **Maryam Khoshkam:** Investigation. **Sabine**  
676 **Szunerits:** Investigation. **Mohsen Kompany-Zareh:** Writing-reviewing and editing. **Rabah**  
677 **Boukherroub:** Supervision, Conceptualization, Writing-review & editing, Funding  
678 acquisition, Project administration.

679

#### 680 **Declaration of Competing Interest**

681 The authors declare that they have no known competing financial interests or personal  
682 relationships that could have appeared to influence the work reported in this paper.

683

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694 **References**

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