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# NiFe<sub>2</sub>O<sub>4</sub> nanoparticles decorated with MWCNTs as a selective and sensitive electrochemical sensor for the determination of epinephrine using differential pulse voltammetry†

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A glassy carbon electrode was modified with nickel-ferrite magnetic nanoparticles and decorated with multiwall carbon nanotubes (NiFe<sub>2</sub>O<sub>4</sub>-MWCNTs). Differential pulse voltammetry was then used to investigate the electrochemical behavior of epinephrine at the surface of the modified electrode. The properties of the nanocomposite were also characterized using different techniques. The electrode showed an excellent synergic effect on epinephrine oxidation. At the optimum pH level, the electrode's response in 0.1 mol L<sup>-1</sup> phosphate solution was proportional to the concentration of epinephrine in the range of 0.9–800.0 μmol L<sup>-1</sup> with a detection limit of 0.09 μmol L<sup>-1</sup>. The effects of different potentially interfering substances on the epinephrine signal were also studied. Finally, the sensor was evaluated with respect to its reproducibility and stability. It was found that the modified electrode had a good sensitivity, selectivity, and reproducibility for the determination of epinephrine in real samples.

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## 1. Introduction

Nanoparticles coming in different sizes, shapes, and compositions are nowadays revolutionizing the field of bioanalytical measurement. Nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>), with an inverse spinel structure, shows ferrimagnetism that originates from the magnetic moment of anti-parallel spins between Fe(III) ions at tetrahedral sites and Ni(II) ions at octahedral sites.<sup>1</sup> Y. L. Liu *et al.*<sup>2</sup> reported a hydrogen sulfide sensor based on NiFe<sub>2</sub>O<sub>4</sub> nanopowder doped with noble metals. L. Yang *et al.*<sup>3</sup> prepared NiFe<sub>2</sub>O<sub>4</sub> by inverse titrating chemical co-precipitation and studied the electrical and gas-sensing characteristics of the material using several gases such as hydrogen. L. Luo *et al.*<sup>4</sup> reported a glucose biosensor based on NiFe<sub>2</sub>O<sub>4</sub> nanoparticles and chitosan.

Carbon nanotubes (CNTs) have received increasing attention due to their unique mechanical, chemical, and electrical properties such as high electrical conductivity and high surface area-to-mass ratio.<sup>5–9</sup> Numerous applications of CNTs-modified sensors have been used in electrochemical sensors.<sup>10–17</sup> Decoration of CNTs films with spinel ferrite nanoparticles with the chemical formula MFe<sub>2</sub>O<sub>4</sub> (M = Mn, Co, Ni, Mg, or Zn)<sup>18–20</sup> improves the electrochemical properties of the nanocomposite to create high performance electrochemical sensors.<sup>2–5</sup>

Epinephrine (known as adrenaline) is one of the most important catecholamine neurotransmitter for message transfer in the mammalian central nervous system, and it is released by the adrenal gland under conditions of low blood sugar levels or in reaction to psychological stresses.<sup>21–23</sup> It has important functions in the regulation of physiological processes in living systems, treatment of myocardial infarction, bronchial asthma, hypertension, and cardiac surgery.<sup>24</sup> The quantitative determination of epinephrine is, therefore, important not only in nerve physiologic functions but also for diagnostic and control in clinical medicine.<sup>24</sup>

Several methods for the determination of epinephrine have been reported, including high performance liquid chromatography (HPLC),<sup>25,26</sup> HPLC-mass spectrometry,<sup>27</sup> fluorimetry,<sup>28</sup> HPLC-optical fiber biosensor,<sup>29</sup> capillary electrophoresis,<sup>30,31</sup> flow injection,<sup>32,33</sup> HPLC with fluorimetric detection,<sup>34</sup> chemiluminescence,<sup>35,36</sup> spectrophotometry<sup>37,38</sup> and electrochemical methods.<sup>39–46</sup> Electrochemical techniques are suitable for the detection of epinephrine due to their sensitivity, rapidity, accuracy, and low cost. For these reasons, different modified electrodes have been introduced for the detection of epinephrine, including gold electrode,<sup>42</sup> ionic liquid-modified carbon nanotubes paste electrode,<sup>43</sup> MnO<sub>2</sub>-Nafion-modified glassy carbon electrode,<sup>44</sup> glassy carbon electrode modified with carbon fiber ultra microelectrode,<sup>45</sup> and graphene/gold nanocomposite modified-glassy carbon electrode.<sup>46</sup>

Nanoparticles based on transition metals oxides<sup>44</sup> and/or spinel ferrite nanoparticles with a chemical formula of MFe<sub>2</sub>O<sub>4</sub> are good candidates<sup>20</sup> to develop electrochemical sensors for the

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