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## Morphology–dependent electrochemical sensing properties of manganese dioxide–graphene oxide hybrid for guaiacol and vanillin



## Tian Gan\*, Zhaoxia Shi, Yaping Deng, Junyong Sun, Haibo Wang

College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, PR China

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## ABSTRACT

Various morphologies of manganese dioxide (MnO<sub>2</sub>) electrocatalysts, including nanoflowers, nanorods, nanotubes, nanoplates, nanowires and microspheres were prepared via facile hydrothermal synthesis and precipitation methods. By simply grinding with graphene oxide (GO), MnO<sub>2</sub> could be readily dissolved in water with high solubility and stability. The structures and electrochemical performances of these as–prepared MnO<sub>2</sub>–GO hybrids were fully characterized by various techniques, and the properties were found to be strongly dependent on morphology. As sensing materials for the simultaneous determination of guaiacol and vanillin for the first time, the nanoflowers–like MnO<sub>2</sub>, coupled with GO, exhibited relatively high sensitivity. The enhanced electrocatalytic activity was ascribed to the high purity, good crystallinity, and unique porous microstructure, which were favorable for transfer of electrons. These results may provide valuable insights for the development of nanostructured modified electrodes for next–generation high–performance electrochemical sensors.

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#### 1. Introduction

Guaiacol and vanillin are two kinds of phenolic compounds that widely distribute in various plants and also be found in common foods and plant origin [1], which definitely have positive effect on human health because of their anti-allergic, anti-artherogenic, anti-inflammatory, antioxidant, antimutagens and antimicrobial activity [2,3]. In some cases, they are essential for the overall food flavour perception, but they become undesirable when their concentration exceed certain limits, leading to typical phenolic off-flavour [4]. More than that, if large amounts of these flavor enhancers are ingested, they cause headaches, nausea and vomiting, and can affect liver and kidney functions [5]. Consequently, it is important to determine the contents of guaiacol and vanillin in foods. A number of commonly used analytical methods are available for qualitative and quantitative determination of guaiacol and vanillin such as spectrophotometry [6], liquid chromatography [7], capillary electrophoresis [8] and gas chromatography-mass spectroscopy [9]. However, these methods require time-consuming sample preparation, expensive and unportable equipment, and a skilled person to operate [10]. Nevertheless, the electrochemical sensors have advantages such as low-cost instrumentation, fast analysis, and improved sensitivity.

http://dx.doi.org/10.1016/j.electacta.2014.09.116 0013-4686/© 2014 Elsevier Ltd. All rights reserved. Therefore, there is an interest in developing a simple, sensitive and rapid method such as electrochemical sensor for the determination of guaiacol and vanillin. Up to our knowledge, there is no report about the simultaneous determination of guaiacol and vanillin using electrochemical techniques.

Manganese dioxide (MnO<sub>2</sub>) is one of the most important functional metal oxides not only due to its good electrochemical properties, low toxicity, low cost, relative abundance but also for its wide applications. In the past few decades, with the advances of nanoscience, the controlled synthesis of MnO<sub>2</sub> nano-and microcrystals with desired shapes had fuelled fundamental studies, due to their morphology had an important impact on the surface area, active site and ion kinetics of materials, which could effectively influence its electrochemical performance [11]. Therefore, it is necessary to investigate the morphology-depending electrochemical performance of various MnO2 nanostructures. Until now, several types of morphologies have been made available through studies including porous [12], rod [13], tube [14], plate [15], wire [16], and sphere [17] MnO<sub>2</sub>. These studies show that nanostructured MnO<sub>2</sub> leads to the improvement of its electrochemical capacity [11]. However, the poor electrical conductivity and dispersibility of MnO<sub>2</sub> have limited its applications in electrochemical sensing.

It is well known that graphene oxide (GO), the derivant of graphene, not only acts as a support for nanocrystals but also as a conductive material for electron transfer in composite catalyst systems [18,19]. In fact, with a large number of hydrophilic

<sup>\*</sup> Corresponding author. Tel.: +86-376-6390702; fax: +86-376-6390597. *E-mail address:* gantianxynu@163.com (T. Gan).



Fig. 1. SEM images of MnO<sub>2</sub> with nanoflowers (a,b), nanorods (c), nanotubes (d), nanoplates (e), nanowires (f) and microspheres (g,h) morphology.

oxygen–containing functional groups on a hydrophobic basal plane, GO also behaves as an amphiphilic macromolecule [20]. With such structural features, GO can be utilized as a special kind of surfactant to enhance the dispersion of  $MnO_2$  in water.

Hereby, MnO<sub>2</sub> catalysts with different morphologies including nanoflowers, nanorods, nanotubes, nanoplates, nanowires and microspheres were prepared by facile hydrothermal synthesis and precipitation methods and then loaded on GO layers. The electrochemical activities of guaiacol and vanillin on MnO2-GO nanocomposites modified electrode were tested in this study. The reasons for different electrocatalytic activities of MnO<sub>2</sub> correlated with different morphologies and for largely improved electrocatalytic activity of MnO<sub>2</sub>-GO were explored. The following electrochemical experiment showed that the MnO<sub>2</sub> with nanoflowers morphology had the most sensitive determination signals for the simultaneous determination of guaiacol and vanillin, which could be attributed to the big surface area and high active sites of MnO<sub>2</sub> nanoflowers. Therefore, a novel and highly sensitive electrochemical method for simultaneous determination of guaiacol and vanillin was proposed.

### 2. Experimental

#### 2.1. Chemicals and apparatus

Mn(NO<sub>3</sub>)<sub>2</sub>, KMnO<sub>4</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O, Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, MnSO<sub>4</sub>, P123, sodium dodecylbenzenesulfonate (SDBS), urea, oxone monopersulfate compound, AgNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, P<sub>2</sub>O<sub>5</sub> and graphite powder were purchased from Aldrich Chemicals with analytical purity. All chemicals were used as received without further purification. The water used was re–distilled.

Electrochemical measurements were performed on a CHI 660 E electrochemical workstation (CH Instruments Inc. Shanghai). A conventional three–electrode system, consisting of a MnO<sub>2</sub>–GO modified glassy carbon electrode (GCE), a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed. Field emission scanning electron microscopy (SEM) was conducted with a Hitachi S–4800 microscope (Japan). Field emission transmission electron microscopy (TEM) images were measured using a Tecnai G220 S–Twin microscope (FEI Company, Netherlands).

Raman spectra were recorded using a micro–Raman spectrometer (Witech CRM200, the excitation wavelength at 532 nm). Fourier transform infrared spectroscopy (FTIR) was measured on a Bruker–Tensor 27 IR spectrophotometer. Powder X–ray diffraction (XRD) analyses were carried out with a Bruker D8 Advance X–ray diffractometer with Cu–K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 1.5406 Å). The Brunauer–Emmett–Teller (BET) surface area (S<sub>BET</sub>) of the MnO<sub>2</sub> was analyzed by nitrogen adsorption at 77 K in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (U.S.A.). All the samples were degassed at

150 °C prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure ( $P/P_0$ ) range of 0.05–0.3. An adsorption isotherm was used to determine the pore size distribution by the Barret–Joyner–Halenda (BJH) method, assuming a cylindrical pore model. The nitrogen adsorption volume at the relative pressure ( $P/P_0$ ) of 0.990 was used to determine the pore volume (PV) and average pore size (APS). The number of surface catalytic active sites per unit surface area ( $N_s$ ) was quantified by methanol chemisorption in a Cahn TGA microbalance (Model TG– 131) coupled with a PC for temperature and weight monitoring [21]. The MnO<sub>2</sub> based catalysts were exposed to a mixture of 2000 ppm of methanol vapor in He at 100 °C that generated a stable monolayer of surface methoxy species. The amount of adsorbed surface methoxy species was determined gravimetrically.

#### 2.2. Synthesis of manganese dioxide-graphene oxide

## 2.2.1. Manganese dioxide nanoflowers

In a typical procedure [12], 20 mL water containing 0.396 g of  $Mn(NO_3)_2 \cdot 6H_2O$  and 0.1 g of triblock copolymer P123 was slowly added dropwise into 20 mL of 0.1 M KMnO<sub>4</sub> with vigorous stirring at 100 °C. After that, the precipitate was quickly collected by filtration, washed with water and absolute ethanol for six cycles, and finally dried at 60 °C for 6 h.

#### 2.2.2. Manganese dioxide nanorods

0.1 M MnSO<sub>4</sub> and 0.1 M KMnO<sub>4</sub> were firstly dissolved in 30 mL water [13]. To this 1 mL of  $H_2SO_4$  (60% concentration) was added under vigorous stirring conditions for 30 min. The prepared solution was transferred to a 100 mL Teflon–coated container and autoclaved at 150 °C for 30 min. The resultant solution was centrifuged for 30 min at 8000 rpm and the obtained precipitate was thoroughly washed using water and dried at 60 °C for 6 h.

#### 2.2.3. Manganese dioxide nanotubes

Table 1

 $MnO_2$  nanotubes were prepared by a hydrothermal method [14]. 0.45 g of KMnO<sub>4</sub> and 1.0 mL of concentrated hydrochloric acid were added to 40 mL of water and kept stirring for 20 min. Then the

The specific areas and pore characteristics of the MnO<sub>2</sub> with different morphologies

Samples	$S_{BET} \left(m^2 g^{-1}\right)$	APS (nm)	$PV (cm^3 g^{-1})$
MnO <sub>2</sub> nanoflowers	207	3.4	0.51
MnO <sub>2</sub> nanorods	179	3.6	0.50
MnO <sub>2</sub> nanotubes	122	7.1	0.32
MnO <sub>2</sub> nanoplates	94	4.8	0.17
MnO <sub>2</sub> nanowires	87	11.5	0.13
MnO <sub>2</sub> microspheres	86	27.7	0.11



**Fig. 2**. (A): DPVs of 1.0 μM guaiacol and vanillin on GCE modified by GO–MnO<sub>2</sub> nanocomposites with different morphologies in pH 1.81 B–R buffer. Accumulation time = 2 min, amplitude = 50 mV, pulse width = 0.2 s, pulse period = 0.5 s. (B): Oxidation peak current change of guaiacol and vanillin on different GCE surfaces.

mixture was transferred to a 50 mL Teflon–lined autoclave. Then the autoclave was kept at 110 °C for 10 h. After cooling down to room temperature, the brown precipitation was collected by centrifugation at 8000 rpm for 10 min. The product was washed with water and ethanol for six cycles and then dried at 60 °C for 10 h.

### 2.2.4. Manganese dioxide nanoplates

In order to prepare  $MnCO_3$  precursor [15], 2 mmol  $MnCl_2 \cdot 4H_2O$  and 3 mmol urea were added into 45 mL of 3 mmol SDBS water solution sequentially under stirring. After another 30 min, the solution was transferred into a 50 mL Teflon–lined autoclave and kept at 110 °C for 12 h. The autoclave was cooled naturally to room temperature. The precipitates were centrifuged, washed with water and ethanol for six cycles and dried at 60 °C for 10 h. Finally, the  $MnCO_3$  was calcined at 400 °C for 4 h to obtain  $MnO_2$  nanoplates.

#### 2.2.5. Manganese dioxide nanowires

 $MnO_2$  nanowires were synthesized according to the report [16]. 0.008 mol  $MnSO_4$ ·H<sub>2</sub>O and an equal amount of  $(NH_4)_2S_2O_8$  were put into 35 mL water at room temperature to form a homogeneous solution, which was then transferred into a Teflon–lined autoclave and maintained at  $120 \,^{\circ}$ C for 12 h. After the reaction was completed, the resulting black solid product was filtered, washed with water and dried at  $120 \,^{\circ}$ C for 3 h.

### 2.2.6. Manganese dioxide microspheres

 $MnO_2$  microspheres were synthesized through catalytic oxidation method [17]. 2 g  $Mn(CH_3COO)_2 \cdot 4H_2O$ , 15 g oxone monopersulfate compound and 5 mL AgNO<sub>3</sub> solution (0.06 M) were mixed together in 200 mL of water under room temperature. Then, 10 mL concentrated sulfuric acid was added into the solution. After the homogenous solution stood for 36 h, the resulting black precipitate was washed with water for six times and then dried at 105 °C for 24 h.

#### 2.2.7. Manganese dioxide-GO

GO was synthesized according to a modified Hummer's method mainly including two approaches [22]. The first process was the preoxidation of graphite using thermic concentrated  $H_2SO_4$ ,  $K_2S_2O_8$ , and  $P_2O_5$ . The second one was the further oxidation of the preoxidized graphite with iced concentrated  $H_2SO_4$  and KMnO<sub>4</sub>. Followed by washing with 10% HCl solution and water, GO could be obtained after being dried.



Fig. 3. TEM images of GO (a), MF (b,c) and MFG (d,e,f).



Fig. 4. Raman spectra (A), FTIR spectra (B) and XRD pattern (C) of MFG.

 $MnO_2$  with different morphologies were respectively mixed with GO with a mass ratio of 1:5 in an agate mortar and ground for 2 h by hand with no others to add, producing a dark brown  $MnO_2$ –GO colloidal powder with uniform color that was readily dissolved in water by vigorously ultrasonic treatment to produce  $2 \text{ mg mL}^{-1}$  suspension. No filtration or washing was needed in the whole process.

#### 2.3. Electrode preparation

A GCE (diameter of 3 mm) was firstly polished with 0.05  $\mu$ m alumina slurry on silk, and then washed with ethanol/water (1:1, V/V) and water in an ultrasonic bath, each for 1 min. 10.0  $\mu$ L of the obtained MnO<sub>2</sub>–GO colloid solution was coated onto the surface of GCE and allowed to dry under an infrared lamp in the air.

## 2.4. Analytical procedure

Unless otherwise stated, a Britton–Robinson (B–R) buffer of pH 1.81 was used as the supporting electrolyte for electrochemical measurements. After 5 mL of pH 1.81 B–R buffer was placed in the electrochemical cell, the required volume of guaiacol and vanillin standard solution was added by a micropipette. Finally, the differential pulse voltammograms were recorded after 2 min of accumulation at 0.1 V. The oxidation peak currents at 0.68 V and 0.86 V were measured for guaiacol and vanillin, respectively.

#### 3. Results and discussion

## 3.1. Morphology–dependent electrochemical activity of manganese dioxide–graphene oxide

SEM images of the samples reflect the idea about the morphology of samples. Fig. 1 shows clear images of  $MnO_2$  with

different morphologies. The well-shaped morphologies indicate that MnO<sub>2</sub> nanoflowers, nanorods, nanotubes, nanoplates, nanowires and microspheres are successfully prepared. Image a confirms the large-scale production of flower shaped nanostructures, which are composed of interconnected nanoflakes, showing a porous nature. The pore size between the sheets is observed in a wide range of 6-32 nm (b). The thickness of the nanoflakes is found to be about 6 nm. These indicate that specific surface area of the nanoflowers should be great. SEM result in image c reveals that the nanorods-shaped structure of MnO<sub>2</sub> is uniform, which has a diameter of 15-34 nm and a length of 80-210 nm. The tubes-like MnO<sub>2</sub> is synthesized successfully and shown in image d. The obtained MnO<sub>2</sub> nanotubes have smooth surfaces with an outer diameter of about 90 nm. Fig. 1e shows the typical morphology of MnO<sub>2</sub> nanoplates. Hexagonal plates with somewhat smooth surface and lots of fragments can be seen from the image. In detail, the average thickness and diameter of the nanopaltes are  $\sim$ 200 nm and  $\sim$ 4  $\mu$ m, respectively. Furthermore, the building nanoplates are randomly inclined or perpendicular to the substrate. By contrast, the nanowire size of MnO<sub>2</sub> in image f is about 200 nm thick and about 9 µm long. Fig. 1g indicates that the hierarchically assembled MnO<sub>2</sub> spheres are multi-scale organized nanoarchitecture. The diameter of the MnO<sub>2</sub> spheres ranges from  $2 \,\mu m$  to  $3 \,\mu m$ , indicating the microstructure of the synthesized material. The high-resolution SEM image in Fig. 1h shows that the prepared MnO<sub>2</sub> sphere possesses dense nanostructure on its surface, constructing a hierarchical dandelion-like structure.

Furthermore, the BET surface area, pore volume and average pore size of MnO<sub>2</sub> catalysts were also investigated and summarized in Table 1. It is found that the MnO<sub>2</sub> nanoflowers show the highest surface area which is decreased by changing morphology to nanorods. The surface area of MnO<sub>2</sub> nanorods is higher than that of MnO<sub>2</sub> with other morphologies. The data in Table 1 also suggest



**Fig. 5.** (A): DPVs of 1.0 μM guaiacol and vanillin on GCE (a), GO/GCE (b), MF/GCE (c) and MFG/GCE (d). Curve e corresponds to DPV curve of MFG/GCE in pH 1.81 B–R buffer. Other conditions are as in Fig. 2. (B): Nyquist diagram (Z'' vs. Z') for the EIS measurements in the presence of 5 mM K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> (1:1) in 0.1 M KCl at different electrodes.



Fig. 6. The cyclic voltammograms of 50.0  $\mu$ M guaiacol (A) and vanillin (B) on MFG/GCE in pH 1.81 B–R buffer at scan rates from 50 to 300 mV s<sup>-1</sup>. Inset: the effects of scan rate on oxidation peak current (a,b) and peak potential (a',b') of guaiacol and vanillin, respectively.

the pore diameters of all the catalysts were between 3.4 nm and 27.7 nm. The strategic configuration of the nanoflowers–type MnO<sub>2</sub> is reckoned to achieve a high electrochemical performance.

For comparison purposes, MnO<sub>2</sub> with different morphologies and GO nanocomposites were used to the simultaneous determination of 1.0 µM guaiacol and vanillin in pH 1.81 B-R buffer through differential pulse voltammetry (DPV) technique, and the results were presented in Fig. 2A. The increased oxidation peak heights in the DPVs denote increased electrocatalytic activity. On the GCE modified with GO and microspheres, nanowires, nanoplates or nanotubes-like MnO2, a very small oxidation peak belonging to guaiacol and an evident oxidation peak attributing to vanillin can be observed, indicating the electron transfer rate of guaiacol is very slow on MnO<sub>2</sub> with these shapes. However, two oxidation peaks of guaiacol and vanillin are independent and evident on MnO<sub>2</sub> nanorods-GO modified electrode, indicative of high selectivity. The highest electrocatalytic activity in this series of nanocomposites is observed using MnO<sub>2</sub> nanoflowers-GO modified electrode. The sharp anodic current peaks appear at 0.68 V and 0.86 V for guaiacol and vanillin, respectively. The oxidation current change of guaiacol and vanillin on different GCE surfaces is shown in Fig. 2B. Hence, there is a strong evidence that the electrochemical sensing properties of GO-MnO<sub>2</sub> samples can be tailored by their morphologies. From SEM images d-g in Fig. 1, it can be seen that lots of amorphous impurities and fragments present among MnO<sub>2</sub> crystals, in contrast, regular nanoflowers and nanorods provide high purity, good crystallinity, which are favorable for reducing the probability of the recombination of electrons and thus reduce the chemical energy barrier. Additionally, the nanoflowers-like MnO<sub>2</sub> in Fig. 1a shows good dispersity and no obvious agglomeration is observed, plus the significantly



Scheme 1. Oxidation mechanism of guaiacol and vanillin on MFG/GCE.

rough surfaces and abundant pores, the specific surface area of nanoflowers–like MnO<sub>2</sub> increases dramatically, as Table 1 indicates. It is well known that large specific surface areas provide more active sites and absorbed more analytes. Moreover, these pores also allow the electrons to transit inside their interior pore channels, which would improve electrocatalytic activity [23]. Take the selectivity and sensitivity for the simultaneous determination of guaiacol and vanillin into consideration, MnO<sub>2</sub> nanoflowers and MnO<sub>2</sub> nanoflowers–GO hybrid, which are respectively defined as MF and MFG for simplification, were selected as sensing materials in the following work.

# 3.2. Characterization of manganese dioxide nanoflowers-graphene oxide nanocomposite

The structural information of MFG was further confirmed through TEM. As expected, the lamellate and nanosheets GO is successful prepared (Fig. 3a). Fig. 3b shows the 3D hierarchical structure of the MF nanostructures. It can be seen that MF nanostructures is made up of many thin nanosheets, and a large amount of irregular pores are randomly distributed in the nanosheets of MF. According to TEM images of d and e in Fig. 3, the crystals of MF are covered and wrapped by ultrathin GO layers, which may expose hydrophilic groups outside and enhance the dispersion of MF in water. Furthermore, a high–resolution TEM image (Fig. 3c) recorded from a free nanosheet of MF gives clear lattice fringes arise from MnO<sub>2</sub> crystallites, which is different from the image in Fig. 3f, because the fuzzy contrast which appears on the outer surface of MnO<sub>2</sub> crystallites originates from the amorphous GO.

Since Raman spectroscopy is a useful technique for distinguishing the order and crystalline structures of GO layers and oxidebased materials, we studied the Raman spectra of different samples, as shown in Fig. 4A. At 200–800 cm<sup>-1</sup> regions, the spectra show Raman vibrations of MF. The band around 642 cm<sup>-1</sup> can be attributed to the symmetric stretching vibration (Mn-O) of the  $MnO_6$  groups, while the peak at  $572 \text{ cm}^{-1}$  can be due to the Mn–O stretching in the basal plane of the  $MnO_6$  sheet [24]. So the MF may be birnessite [25]. The well-known Raman peaks for GO structures are D and G bands at around 1350 and 1585 cm<sup>-1</sup> corresponding to the presence of defects/disorders and well-defined sp<sup>2</sup> graphitized structure [26], respectively. So, greater  $I_D/I_C$  peak intensity ratio indicates higher defects and disorders in hexagonal carbon-type structure of graphene. The  $I_D/I_G$  ratio for GO does not change after the loading of MF crystals, confirming the attachment of MF nanostructures on GO sheets with almost no disorders and defects, this is an advantage for the MFG in charge for electrons transportation [27]. However, the weakened bands attributing to MF on MFG may be ascribed to the low density of MF with the introduction of GO.

## Table 2

Number of surface active sites of MF and MFG in different electrolytes and with different mass ratios

	Samples	$N_{ m s}~(\mu { m mol}{ m m}^{-2})$
MF	pH 1.81 B-R buffer	3.8
	pH 1.81 B–R buffer (mass ratio 1:5)	7.0
	pH 7.00 B–R buffer (mass ratio 1:5)	4.4
	pH 11.92 B–R buffer (mass ratio 1:5)	3.2
MFG	Mass ratio 1:7 (pH 1.81 B–R buffer)	3.2
	Mass ratio 1:6 (pH 1.81 B–R buffer)	4.7
	Mass ratio 1:5 (pH 1.81 B–R buffer)	7.0
	Mass ratio 1:4 (pH 1.81 B-R buffer)	6.4
	Mass ratio 1:3 (pH 1.81 B-R buffer)	6.2

The FTIR spectra of GO and MFG samples are shown in Fig. 4B. The spectra of GO confirms the presence of C–O–H ( $\nu_{O-H}$  at 3407 cm<sup>-1</sup>), COOH ( $\nu_{C=O}$  at 1721 and 1407 cm<sup>-1</sup>) and C–O–C ( $\nu_{C-O}$  at 1225 cm<sup>-1</sup>). The band at 1628 cm<sup>-1</sup> is due to the deformation of the O–H bond in water. The peaks locate at 1056 and 1096 cm<sup>-1</sup> are due to C–O (*i.e.*, hydroxyl, ether) stretching vibrations [28]. In the case of MFG, the main characteristic peaks of GO still remain and a new peak appears at 520 cm<sup>-1</sup>, which arises from the stretching vibration of the Mn–O bonds [29].

XRD pattern of the resulting MFG is shown in Fig. 4C. The diffraction peak at around  $2\theta = 10^{\circ}$ , corresponding to the (001) reflection of GO, which overlaps with the (001) basal reflection of MF. The diffraction peak at  $2\theta = 24^{\circ}$  is resulted from (002) basal reflection of MF, while two other peaks are indexed as the (20*l*/11*l*) and (02*l*/31*l*) diffraction bands, respectively [30]. The strategic configuration of the MF is reckoned to achieve a high electrochemical performance.

# 3.3. Enhancement effect of manganese dioxide nanoflowers-graphene oxide hybrid

In order to understand the enhanced electrocatalytic activity of MFG hybrid, the DPV behaviors of a mixture of  $1.0 \mu$ M guaiacol and vanillin at different electrodes were compared in pH 1.81 B–R buffer. As shown in Fig. 5A, at bare GCE (curve a), two small anodic peaks are obtained with a potential difference of about 120 mV. After modification of the GCE by GO, the peak potential shifts negatively but only one anodic peak is observed (curve b), the peak potentials of guaiacol and vanillin are indistinguishable, indicating poor selectivity and sensitivity. In contrast, two oxidation peaks corresponding to guaiacol and vanillin are observed on MF modified GCE (curve c). The oxidation peak currents on MF/GCE are obvious but weaker and wider, the sensitivity is poor for further

determination. However, the peak currents at the MFG/GCE (curve d) are remarkably enhanced. Noteworthy is the biggest potential difference (*i.e.* 180 mV) on MFG/GCE, rendering this particular composite is more selective for the simultaneous determination of guaiacol and vanillin. Besides, the DPV curve of MFG/GCE in pH 1.81 B–R buffer is featureless, showing the attribution of the two oxidation peaks to guaiacol and vanillin, respectively.

Electrochemical impedance spectroscopy (EIS) has been employed to study the interfacial properties of the modified electrodes. Nyquist plots were obtained for bare GCE, GO/GCE, MF/GCE and MFG/GCE in the frequency range from 1 to 10<sup>5</sup> Hz and represented in Fig. 5B. The impedance spectra were recorded using a redox couple of  $5 \text{ mM K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  (1:1) in 0.1 M KCl as an electrochemical probe. The information regarding electron transfer kinetics and diffusion characteristics can be obtained from the shape of the impedance spectrum. The semicircle portion and linear portion of the impedance spectra respectively correspond to the electron transfer limiting and diffusion limiting electrochemical processes, respectively. And the charge transfer resistance  $(R_{ct})$ refers to the semicircle diameter [31]. A semicircle of about 3110 ohm in diameter for bare GCE indicates a slow electron transfer process. After modification of MF or GO on GCE surface, the semicircle diameter decreases to 1167 and 1050 ohm, respectively. The remarkable decrease of semicircle diameter (i.e., 311 ohm) can be obtained on MFG/GCE because lots of active sites occurred, suggesting that a significant acceleration of the Fe  $(CN)_6^{3-/4-}$  redox reaction occurred on the surface of MFG film modified GCE. The results prove that the MFG nanocomposite on the GCE surface can reduce the electron transfer resistance to the flow of electrons, confirming the results obtained from Fig. 5A.

#### 3.4. Reaction mechanism of guaiacol and vanillin

The oxidation peak currents of 50.0  $\mu$ M guaiacol and vanillin on the MFG film modified electrode were also examined when changing the scan rate in the range of 50–300 mV s<sup>-1</sup> using cyclic voltammetry (CV) technique (Fig. 6). The results show that the oxidation peak currents ( $I_p$ ,  $\mu$ A) of guaiacol and vanillin linearly increase with scan rate ( $\nu$ , mV s<sup>-1</sup>) according to the regression equations:  $I_p$  = 3.976 + 0.136  $\nu$  (r<sup>2</sup> = 0.996) (inset a of Fig. 6A) and  $I_p$  = -6.933 + 1.370  $\nu$  (r<sup>2</sup> = 0.998) (inset b of Fig. 6B), indicating adsorption–controlled electrode processes of guaiacol and vanillin on MFG/GCE. Meanwhile, the oxidation peak potentials ( $E_p$ , V) of guaiacol and vanillin positively shift with scan rate (inset a' of Fig. 6A and inset b' of Fig. 6B), and the relationship between  $E_p$  and  $\nu$  is in accordance with the following equation [32]:



**Fig. 7.** DPVs at MFG/GCE in (A) 1.0  $\mu$ M vanillin and different concentrations of guaiacol: 0.03, 0.05, 0.08, 0.1, 0.3, 0.5, 0.8 and 1.0  $\mu$ M, and (B) 1.0  $\mu$ M guaiacol and different concentrations of vanillin: 0.03, 0.1, 0.3, 0.5, 0.8, 1.0, 3.0, 5.0, and 8.0  $\mu$ M. The insets show the calibration plots of guaiacol and vanillin versus peak current. Other conditions are as in Fig. 2.

#### Table 3

Comparison of the analytical performances of this work with the reports

Modified electrode	Linear range ( $\mu$ mol dm <sup>-3</sup> )		Detection limit ( $\mu$ mol dm <sup>-3</sup> )		Ref.
	Guaiacol	Vanillin	Guaiacol	Vanillin	
Laccase/screen printed electrode	0.1~500		0.05		[33]
PEI/Au/laccase/GCE	0.79~170		0.03		[34]
laccase or tyrosinase/GCE	1~10		0.11		[35]
Reduced graphene oxide/GCE	0.5~500		0.2		[36]
AuPd-graphene/GCE		0.1~7.0 and 10~40		0.02	[37]
Boron-doped diamond electrode		3.3~98		0.16	[38]
Au–Ag/GCE		0.2~50		0.04	[39]
Arginine/graphene/GCE		2~100		0.332	[40]
MFG/GCE	0.03~30	0.03~8	0.0013	0.0015	This work

$$E_{\rm p} = E^{0\prime} + \frac{RT}{\alpha nF} \ln \frac{RTk^0}{\alpha nF} + \frac{RT}{\alpha nF} \ln \nu \tag{1}$$

where  $k^0$  is the standard rate constant of the surface reaction,  $E^{0'}$  is the formal potential,  $\alpha$  is transfer coefficient of the oxidation of guaiacol and vanillin, and other symbols have their usual meanings. According to Eq. (1), the plot of  $E_p$  vs.  $\ln \nu$  has a good linear relationship, from which  $\alpha n$  can be determined from the slop (*i.e.*, 0.0285 for guaiacol and 0.0215 for vanillin). Assuming  $\alpha = 0.5$ , the value of  $n \approx 2$  is calculated for guaiacol and vanillin. Therefore, both of the oxidation of guaiacol and vanillin are two– electron reaction, as demonstrated in Scheme 1.

#### 3.5. Simultaneous determination of guaiacol and vanillin

The conditions of the electrolyte, such as types of electrolyte and solution pH, are major factors that affect the response of guaiacol and vanillin on the MFG/GCE. Therefore, the electrochemical responses of  $1.0 \,\mu$ M guaiacol and vanillin at the MFG/GCE in different supporting electrolytes such as  $0.2 \,\text{M PBS}$  (pH 5.8–8.0),  $0.2 \,\text{M}$  sodium acetate–acetic acid buffer (pH 2.6–5.8), boric acid–borax buffer (pH 7.4–9.0), B–R buffer (1.81–11.92) and 0.1 M NaOH, HCl,  $H_2SO_4$ , HClO<sub>4</sub> solution were examined by CV. It is found that the oxidation peaks of guaiacol and vanillin are distinguishable in B–R buffer, and the biggest peak currents for them can be obtained when the pH value is 1.81. So pH 1.81 B–R buffer is chosen as the electrolyte for the electrochemical oxidation of guaiacol and vanillin.

Next, the effect of the mass ratio between MF and GO on the determination of guaiacol and vanillin was studied. It is found that the MFG is difficult to fully disperse in water when the mass ratio of MF vs. GO exceeds 1:3, which may be caused by the weak solubility of MF in water. So the mass ratios between MF and GO including 1:7, 1:6, 1:5, 1:4 and 1:3 were investigated, and the highest peak could be obtained when the mass ratio is 1:5. As discussed before, the MF has definitely catalytic effect on the oxidation of guaiacol and vanillin, and GO acts as the support and electron transfer media, so both of them are indispensable. Here, MF was mixed with GO according to the mass ratio of 1:5 for better determination sensitivity.

In order to further testify the catalytic activity of MFG in different electrolytes and with different mass ratios, a methanol chemisorption technique was conducted to estimate the number of surface catalytic active sites per unit surface area ( $N_s$ ) (Table 2). The



Fig. 8. Differential pulse voltammograms at MFG/GCE in food sample (black curves), food sample with first standard addition (red curves) and food sample with second standard addition (blue curves). Other conditions are as in Fig. 2.

active surface site density of MF is found to have an increase from 3.8  $\mu$ mol m<sup>-2</sup> to 7.0  $\mu$ mol m<sup>-2</sup> after combining with GO, further indicating the contribution of GO in this electrochemical system. And the N<sub>s</sub> value is the biggest for MFG with mass ratio of 1:5 under acidic environment, which is in well accordance with the above discussion about the effects of electrolyte and mass ratio on determination sensitivity of guaiacol and vanillin.

The influence of amount of MFG suspension on the oxidation peak current of guaiacol and vanillin was investigated. When gradually improving the volume of MFG suspension from 0 to 10  $\mu$ L, the oxidation peak currents of guaiacol and vanillin greatly increase. During this period, the accumulation efficiency of MFG/GCE obviously enhances, resulting in remarkable oxidation peak current enhancement of guaiacol and vanillin. However, the oxidation peak currents decrease slightly with further improving the amount of MFG suspension up to 15  $\mu$ L, maybe due to the blocking of too thick film for electrons transfer. In order to shorten the time of solvent evaporation and to achieve high sensitivity, 10  $\mu$ L MFG suspension is used to modify the GCE surface.

For further improving the sensitivity, accumulation was employed when detecting guaiacol and vanillin. It is found that the oxidation signals of guaiacol and vanillin obviously increase with positive shift of accumulation potential from-0.3 to 0.1 V. As further moving the accumulation potential to 0.5 V, the oxidation peak currents of guaiacol and vanillin decrease. To achieve high sensitivity and excellent oxidation shape, the accumulation was performed at 0.1 V. The influences of accumulation time on the oxidation signals of guaiacol and vanillin were further studied. When improving the accumulation time form 0 to 2 min, the oxidation peak currents of guaiacol and vanillin on MFG film modified GCE greatly enhance. The remarkable signal enhancement indicates that accumulation is feasible to improve the detection sensitivity. Longer accumulation time than 2 min does not enhance the oxidation peak currents of guaiacol and vanillin obviously, suggesting that the amount of guaiacol and vanillin tend to a limiting value. Considering sensitivity and efficiency, 2-min accumulation is employed.

In this work, we found that the MFG modified GCE was unqualified for the successive measurements because the oxidation peak currents of guaiacol and vanillin decreased continuously. Thus, it was just employed for the single measurement. The reproducibility between multiple MFG/GCEs was then tested by parallel determination of the oxidation peak currents of 1.0  $\mu$ M guaiacol and vanillin. The relative standard deviation (RSD) is 3.2% and 3.7% for ten MFG/GCEs, respectively, indicative of excellent fabrication reproducibility and detection precision.

The potential interferences for the detection of guaiacol and vanillin were studied. Under the optimized conditions, the oxidation peak currents of guaiacol and vanillin were individually measured in the presence of different concentrations of interferents and the peak current change was then checked. No influence on the detection of  $1.0 \,\mu$ M guaiacol and vanillin is found after the addition of 2000–fold concentration of NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup>,

Na<sup>+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>; 1500–fold concentration of Cu<sup>2+</sup>; 2000–fold concentration of citric acid, sucrose, glucose, tartaric acid; 1000–fold concentration of glycine; 100–fold concentration of uric acid; 80–fold concentration of dopamine, L–dopa, and 50–fold concentration of ascorbic acid (peak current change <8%).

For simultaneous and quantitative determination of guaiacol and vanillin, DPV curves at different concentrations of guaiacol were recorded in Fig. 7A, where vanillin concentration was kept at  $1.0 \mu$ M. The inset shows that the peak current varies linearly with guaiacol concentration between 0.03 and  $1 \mu M$  with  $r^2 = 0.995$ . Importantly, the anodic peak current of vanillin is almost uninfluenced by the increase of guaiacol concentration, suggesting that oxidations of guaiacol and vanillin at the MFG/GCE are independent of each other. With the DPV technique the detection limit of guaiacol is 1.3 nM in the presence of  $1.0 \mu M$  vanillin interference (S/N = 3). Fig. 7B presents DPV responses at different concentrations of vanillin while guaiacol is kept constant at 1.0 µM. Similar to the scenario in Fig. 7A, the anodic peak current of guaiacol stays almost constant as vanillin concentration is increased gradually, further confirming that this modified electrode can be employed for simultaneous determination of guaiacol and vanillin. The inset in Fig. 7B illustrates that the peak current increases linearly with vanillin concentration between 0.03 and  $8 \,\mu\text{M}$  with  $r^2 = 0.995$ . In the presence of guaiacol, the low limit is 1.5 nM for vanillin (S/N=3). Although a number of guaiacol or vanillin sensing composites have been reported in recent years [33–40], it is significant that MFG used in our study can realize the direct determination of guaiacol without the help of expensive enzyme, so it is more stable under robust sampling conditions, and the lowest detection limits for guaiacol and vanillin were achieved compared with the reported electrochemical methods (Table 3). Moreover, this is the first report for the simultaneous determination of guaiacol and vanillin using electrochemical method as far as our knowledge.

#### 3.6. Practical application

The MFG modified GCE was used in several food samples including biscuit, jelly, chocolate and juice to evaluate its practical application. The samples were purchased from local market. Thereinto, the juice sample was used directly, but biscuit, jelly and chocolate samples were used after pretreatment. For biscuit and chocolate samples, 10 g of each was ground to powder in an agate mortar, respectively, and then stirred with 15 mL absolute ethanol for 30 min. For jelly sample, 4g of it was dissolved into 10 mL mixture of pH 1.81 B-R buffer and 1% ethanol, which was shook vigorously for 10 min. The filtrates of these three solutions were collected after vacuum filtered and diluted in 50 mL volumetric flasks using water, respectively. Upon addition of 100 µL sample solution into 5.0 mL pH 1.81 B-R buffer, the DPV curves were recorded from 0.3 to 1.1 V after 2 -min accumulation at 0.1 V (black curves in Fig. 8), it can be seen that there is only one oxidation peak attributing to vanillin in biscuit and chocolate samples, indicating

Table 4

Detection and recovery of guaiacol and vanillin in biscuit, jelly, chocolate and juice samples

Sample		Detection	Detection		Recovery test		
		This method (nmol dm <sup>-3</sup> )	RSD (%)	Spiked (nmol dm <sup>-3</sup> )	Found (nmol dm <sup>-3</sup> )	Recovery (%)	
Biscuit	guaiacol	_	_	100.0	91.64	91.64	
	vanillin	38.0	3.8	100.0	102.3	102.3	
Jelly	guaiacol	12.0	3.9	200.0	189.6	94.80	
	vanillin	122	2.6	200.0	197.4	98.97	
chocolate	guaiacol	_	_	300.0	277.8	92.55	
	vanillin	85.0	4.2	300.0	285.9	95.26	
Juice	guaiacol	32.5	1.2	200.0	207.6	103.8	
	vanillin	_	-	200.0	195.7	97.83	

the existence of individual vanillin in these two food samples. However, guaiacol and vanillin coexist in jelly sample because two oxidation peaks locating at about 0.66V and 0.86V appear. Regarding to the juice sample, there are two peaks at the potential of 0.69 V and 0.97 V, which correspond to the respective oxidation of guaiacol and certain interferent in complicated real sample. Each sample is determined by three times, and the RSD is lower than 4.5%, revealing good precision. The contents of guaiacol and vanillin are obtained by the standard addition method (red curves in Fig. 8), and the results are listed in Table 4. In addition, the recovery of guaiacol and vanillin standard is performed to testify the accuracy of this method. In order to achieve this, different guaiacol and vanillin standard solutions are further added into these four samples, respectively, as shown in blue curves in Fig. 8. The value of recovery ranges from 91.64% to 103.8%, suggesting that this method is effective and reliable.

#### 4. Conclusion

In this work, the effect of GO–MnO<sub>2</sub> morphologies on electrochemical sensing properties was systematically investigated. Nanoflowers, nanorods, nanotubes, nanoplates, nanowires and microspheres–like MnO<sub>2</sub> with a controllable structure and uniform size were successfully synthesized via facile hydrothermal synthesis and precipitation methods. When they were loaded on GO layers and then used as sensing materials for the simultaneous determination of guaiacol and vanillin, the MnO<sub>2</sub> with morphology of porous nanoflowers showed relatively high sensitivity. The excellent electrocatalytic activity was likely related to the novel MnO<sub>2</sub> nanostructures with high purity, good crystallinity and plenty of pores, which made them promising candidates for application as sensing materials in next–generation high–performance electrochemical sensors.

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