Manganese dioxide-graphene nanocomposite film modified electrode as a sensitive voltammetric sensor of indomethacin detection

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Excess amount of analgesic and anti-inflammatory drug, such as indomethacin, often leads to serious gastrointestinal complications; therefore, amount of such active compound should be regulated in commercial drugs. This study proposes an efficient analytical technique to detect indomethacin selectively. We prepared and investigated electrochemical properties of a manganese dioxide-graphene nanocomposite film modified glassy carbon electrode (MnO_2-Gr/GCE). The behavior of the modified electrode as electrocatalyst towards indomethacin oxidation was also examined. The cyclic voltammetric results reveal that the electrocatalytic activity for the oxidation of indomethacin can significantly be enhanced on the MnO_2-Gr/GCE. Indomethacin exhibited a sensitive anodic peak at about 0.90 V at MnO_2-Gr/GCE. The data obtained from differential pulse voltammetry showed that the anodic peak currents were linearly dependent on the indomethacin concentrations in the range of 1.0×10^{-7} to 2.5×10^{-5} mol/L with a detection limit of 3.2×10^{-8} mol/L ($S/N = 3$). Most importantly, the proposed method shows efficient and selective sensing of indomethacin in commercial pharmaceutical formulations. This is the first report of a voltammetric sensor for indomethacin using MnO_2-Gr/GCE. We believe that this new method can be commercialized for routine applications in laboratories.

Keywords: Manganese dioxide, Graphene, Modified electrode, Indomethacin

Introduction

Indomethacin [1-(4-chloro-benzoyl)-5-methoxy-2-methyl-1H-indole-3-acetic acid] is a non-narcotic analgesic, non-steroidal anti-inflammatory, and antipyretic drug. It is commonly used for treating rheumatoid arthritis. Being a potent inhibitor of cyclooxygenase, it reduces prostaglandin synthesis, and thus alleviates pain and fever. However, analgesic and anti-inflammatory activities often contribute significantly to gastrointestinal complications such as ulcer induction and delayed ulcer healing due to fatal gastrointestinal ulceration and hemorrhage.[1] Therefore, it is necessary to establish sensitive and selective analytical techniques that detect and quantitatively measure drug entities in pharmaceutical and biological samples.

Many analytical methods, such as spectrophotometry,[2,3] fluorimetry,[4] chemiluminescence (CL),[5,6] micellar electrokinetic chromatography (MEKC),[7] high performance liquid chromatography (HPLC),[8–11] LC-MS[12] and enzyme-linked immunosorbent assay (ELISA),[13] are used to detect indomethacin. Although these methods successfully detect indomethacin in pharmaceutical and biological samples, some of them lack sensitivity and involve tedious procedure (time consuming or expensive). Owing to their highly-sensitive, rapid and online detection ability, etc., electrochemical sensors have become increasingly popular for quantitative determination of indomethacin.[14–18]

Inexpensive manganese dioxide (MnO_2), because of its good electrochemical properties and low toxicity, has widely been applied as catalyst,[19] molecular sieve,[20] and electromagnetic material.[21] Nano- and micro-crystals of MnO_2, prepared via controlled synthesis, are known to detect epinephrine,[22] hydrogen peroxide,[23–28] dopamine,[29] catechol,[30,31] theophylline,[32,33] ferulic acid,[34] and heavy metal ions (such as Cr^{3+}, Cd^{2+}, and Pb^{2+}),[35,36] etc. The improvement in electrocatalytic activity of these nano- and micro-structured MnO_2 is related to their shapes. In this connection, graphene (Gr) has attracted tremendous attentions since its first discovery in 2004.[37] Gr exhibits very large 2-D electrical conductivity, large-specific surface area, remarkable mechanical stiffness, and good biocompatibility; hence, it is considered as an ideal material for electrochemical application. Sun et al.[38] used Gr-MnO_2 nanocomposite modified carbon ionic liquid electrode (CILE) to analyze rutin in the commercial drug samples and found that the modification greatly enhanced electrochemical performances of the electrode.[38]

The objective of this study was to design an efficient sensor for detecting indomethacin. We prepared nanostructured MnO_2 using micron-sized commercial electrolytic manganese dioxide (EMD) via a hydrothermal reaction in the presence of sodium dodecylsulphate (SDS). The nanostructured MnO_2 and Gr were brought together with chitosan on the electrode surface to fabricate an effective sensing interface for indomethacin electroanalysis. The ability of MnO_2-Gr/GCE for voltammetric response of indomethacin was evaluated. To the best of our knowledge, this is the first report of voltammetric determination of indomethacin using MnO_2-Gr nanocomposite modified glassy carbon electrode (MnO_2-Gr/GCE). We believe that this new sensor can be used for indomethacin detection in commercial drug samples with satisfactory result.

Experimental

Reagents and Solutions. Indomethacin was purchased from Aladdin-Reagent Company (Shanghai, China). Stock standard solution of indomethacin (0.01 mol/L) was prepared with distilled water and stored at 4 °C. Graphite powder, purchased from Qingdao Hensen Graphite Co., Ltd. (Qingdao, China), was used to prepare graphite oxide following Hummers method.[39] Graphene (Gr) nanosheets were synthesized from graphite oxide via chemical reduction, following a previous report.[40] EMD was kindly gifted by Guangxi Eramet Comilog Chemicals Company Ltd., China. The nanostructured MnO_2 was synthesized from EMD via a hydrothermal reaction in the presence of SDS according to a previous report.[41] Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) with analytical grade.

All solutions were prepared using double distilled water. Phosphate buffer solution (PBS) (0.2 mol/L), used as the supporting electrolyte, was prepared with KH_2PO_4 and Na_2HPO_4. The pH was adjusted with H_3PO_4 and NaOH.

Instruments. The size and morphologies of MnO_2-Gr nanocomposite were characterized by scanning electron microscope (SEM) (ZEISS EVO18, Germany). Atomic force microscopic (AFM) images of nanostructured MnO_2 was acquired using tapping mode at 1024 × 1024 pixel resolution (CSPM5000, Benyuan, China) and analyzed with a CSPM Consol software (Benyuan-CSPM5000, China). The Raman spectra were measured using Renishaw inVia (England). CHI660D electrochemical workstation (Shanghai Chenhua Co., China) was used to detect the electrochemical response of indomethacin to cells. All measurements were carried out in a conventional three-electrode cell consisting of a bare or MnO_2-Gr nanocomposite film modified GCE (Alda Co. Ltd., China, φ = 3 mm) as working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A digital pH meter (Shanghai Leici Instrument Plant, Shanghai, China) model PHS-25 was used to measure the pH of the buffer solutions.

Preparation of the MnO_2-Gr Modified Electrode. To prepare MnO_2-Gr modified electrode, the following procedure was followed: GCE surface was first polished successively with 0.05 μm alumina suspension, homogenous MnO_2-Gr dispersion was obtained by ultrasonic dispersion 1 mg Gr and 1 mg MnO_2 with 1 mL 1% chitosan (Chi) solution, and finally, 5 μL MnO_2-Gr suspension was dropped onto a freshly smoothed GCE surface uniformly; the solvent was then evaporated under an infrared lamp.

Sample Preparation. To analyze the marketed formulation, 12 tablets were accurately weighed and their average weight was determined. The tablets were finely ground to powder, and tablet powder equivalent to three tablets was then dissolved in 25 mL PBS (pH 4.0). After shaking the mixture for 30 min, it was filtered through a 0.45 μm membrane filter paper and washed thoroughly with PBS. All the washings were then combined with the filtrate and made up to 100 mL in a volumetric flask with PBS solvent.

Analytical Procedure. The PBS buffer of pH 4.0 has been proposed as supporting electrolyte for the qualitative detection of indomethacin. Cyclic voltammetric (CV) measurements were performed over a potential range of 0.4–1.2 V at a scan rate of 0.1 V/s. The electrochemical differential pulse voltammetry (DPV) measurements were recorded from 0.4 to 1.0 V with an amplitude of 0.05 V and pulse width as 0.2 s.

Results and Discussion

Characterization of MnO_2-Gr. Figure 1(a) and (b) illustrate SEM images of EMD and the nanostructured MnO_2, respectively. The size of the nanostructured MnO_2 is about 50 nm and is consistent with the earlier report.[41] AFM image (Figure 1(e)) also reveals similar size of MnO_2 (45–50 nm). SEM image of graphene shows transparent and wrinkled sheets (Figure 1(c)), and such sheet structure helps graphene to maintain a high surface area. Figure 1 (d) reveals the morphology of the MnO_2-Gr nanocomposite. In Figure 1(f), Raman spectra from the excitation of 532 nm are shown for graphite and Gr. *G* and *D* peaks are observed at around 1580 and 1345 cm^{-1}, respectively. Compared with graphite, Gr samples had the highest *D*/*G* peak intensity ratio.[42,43]

Electrochemical Behavior of Indomethacin. Figure 2 presents the voltammograms of indomethacin (1.0×10^{-3} mol/L in PBS, pH 7.0) obtained using different electrodes, GCE, MnO_2/GCE, Gr/GCE, and MnO_2-Gr/GCE, respectively. No cathodic peak is seen in the reverse scan, suggesting a totally irreversible electrochemical reaction. The oxidation peak potential of indomethacin is 0.896 V at both Gr/GCE and MnO_2-Gr/GCE and 0.882 V for bare GCE and MnO_2/GCE). The oxidation peak current (Ip) of indomethacin (4.859×10^{-6} A) at MnO_2-Gr/GCE is 3.5 and 3.1 times larger than that measured at the GCE and Gr/GCE, 2.7 times larger than Ip measured at the MnO_2/GCE. The data clearly indicates that nanostructured MnO_2-Gr

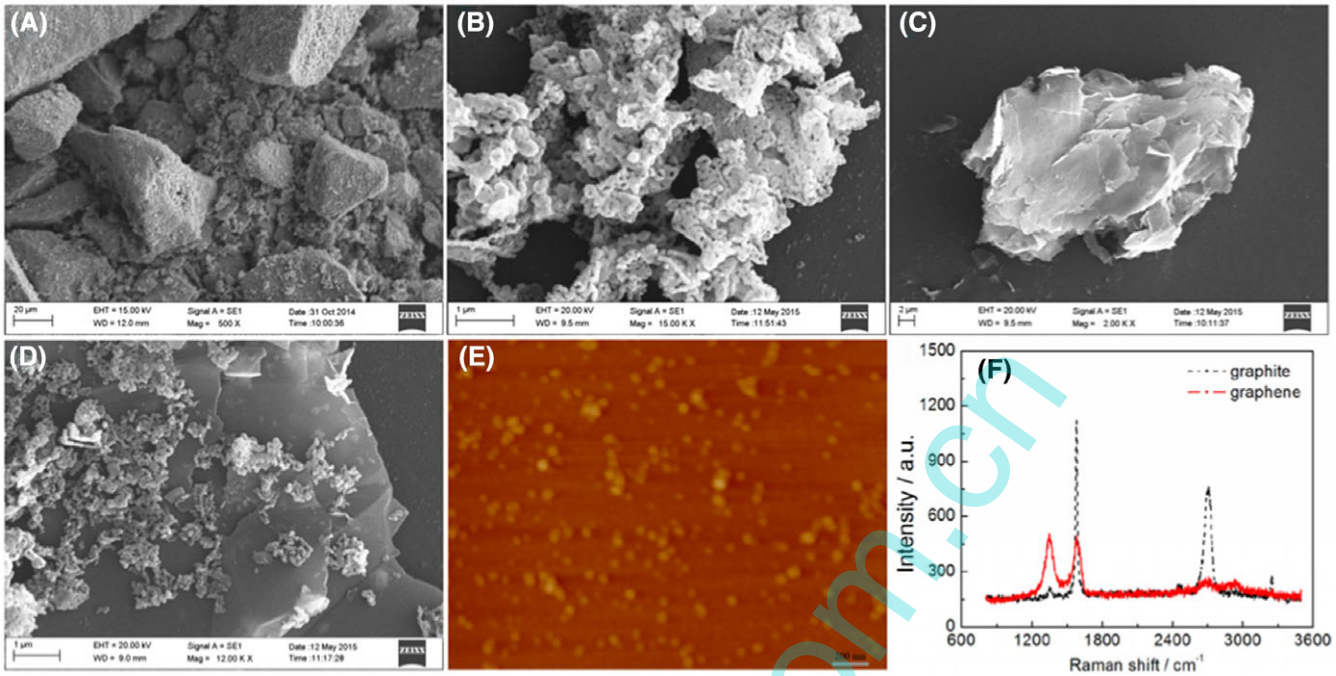


Figure 1. SEM images of EMD (a), MnO_2 (b), Gr (c), and MnO_2-Gr (d). AFM image of MnO_2, (e) and Raman spectroscopy of Gr (f).

composite film improves indomethacin oxidation. These results indicate the presence of MnO_2 nanostructures with high specific surface are in modified electrode provides the platform for indomethacin oxidation with contributing of excess electroactive sites, which enhanced electrocatalytic activity of MnO_2-Gr/GCE. Hence, we selected MnO_2-Gr/GCE for the oxidation of indomethacin.

Effect of pH Value. We investigated the effect of solution pH on the oxidation peak current of indomethacin (1.0×10^{-5} mol/L) at MnO_2-Gr/GCE using cyclic voltammetry in the pH range of 2.0–6.0. As evident from Figure 3, the peak current increases rapidly with increasing pH, and the maximum current response is obtained at pH 4.0. Accordingly, the formal potential shifts towards negative with increase in pH. This result is consistent with a previous study of electrochemical oxidation of indomethacin on iron (III) complexes modified carbon paste electrode, reported by M. Hasanzadeh et al.[15] Hence, we chose pH 4 for the subsequent analytical experiments.

The regression of E_p parameter with respect to pH is defined by the following equation: $E_p(V) = -0.0545$ pH+ 1.1515 ($R = 0.9960$). We calculated the ratio of electron to proton for the oxidation process using the following formula[44]:

$$dE_p/dpH = 2.303mRT/nF$$

where m and n are the numbers of proton electron, respectively. The m/n ratio is 0.94 (approximately equal to 1),

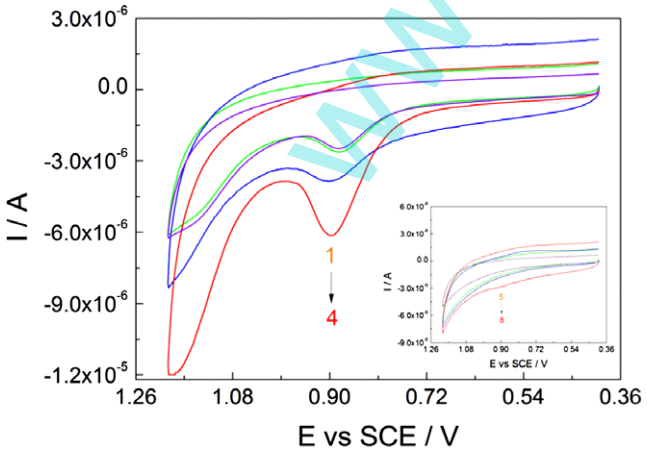


Figure 2. CVs recorded in the presence and absence of 1.0×10^{-3} mol/L indomethacin at bare GCE,[1,5] MnO_2/GCE,[2,6] Gr/GCE,[3,7] and MnO_2-Gr/GCE[4,8] with PBS buffer of pH 7.0; scan rate: 100 mV/s.

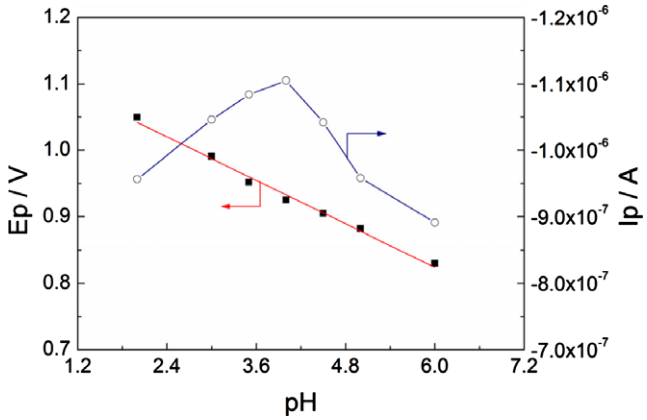


Figure 3. Influence of pH on the oxidation peak current and potential of indomethacin (1.0×10^{-5} mol/L) at the modified electrode.

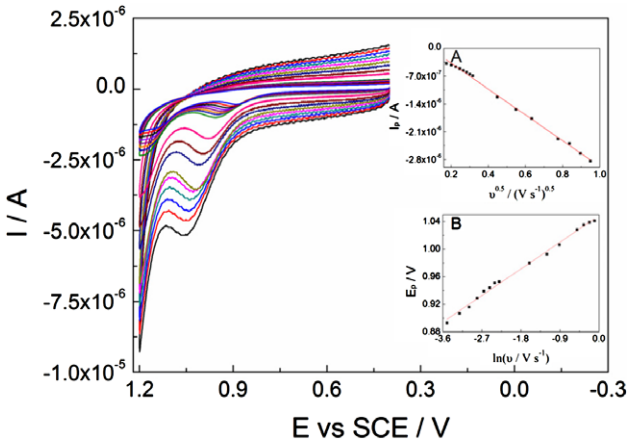


Figure 4. Cyclic voltammograms of indomethacin (1.0×10^{-5} mol/L) in PBS (pH 4.0) at different scan rates (from 1 to 16: 0.03,0.04,0.05,0.06,0.07,0.08,0.09,0.1,0.2,0.3,0.4,0.6,0.7,0.8,0.9 V/s); insert (a) is the *I*p vs. $\upsilon^{0.5}$ plot; insert (b) is the *E*p vs. lnυ plot.

indicating that the number of protons in the processes are equal to the number of the transferred electrons.

Effect of Scan Rate. To understand electrochemical mechanism behind indomethacin oxidation, we examined the effect of scan rate by monitoring the cyclic voltammograms of indomethacin at MnO_2-Gr/GCE. We obtained a linear relationship ($I_p = -3.33 \times 10^{-6}$ $v^{1/2} + 3.03 \times 10^{-7}$) between anodic peak currents and scan rates of indomethacin in the range of 30–900 mV/s with a correlation coefficient of $R = 0.9976$. This result suggests that the oxidation of indomethacin is a diffusion-controlled process.

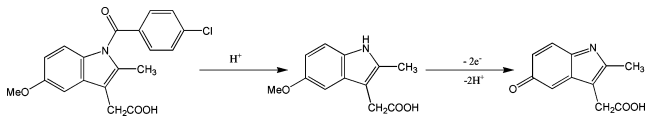
Figure 4 clearly shows that the oxidation peak shifts its peak potential towards more positive values with increasing scan rate. The values of peak potentials are proportional to the logarithm of the scan rate with the correlation coefficient of 0.9964 ($E_p = 0.043$ lnυ + 1.049) (Figure 4, insert B). According to Laviron's theory,[45] the relationship between E_p and the logarithm of the scan rate can be defined by the following equation:

$$E_p = E^{\theta'} + \frac{RT}{(1-\alpha)nF}\ln \nu \qquad (1)$$

where E_p, $E^{\theta'}$, α (alpha), and *n* have their usual meanings. According to Bard and Faulkner,[46] α can be given as

$$\alpha = \frac{47.7}{E_p - E_{p/2}}\text{mV} \qquad (2)$$

here $E_{p/2}$ is the potential when the current is at half the peak value. From this, the value of α was calculated to be 0.691.



Scheme 1. Proposed mechanism behind the electrochemical behavior of indomethacin on the surface of MnO_2-Gr/GCE.

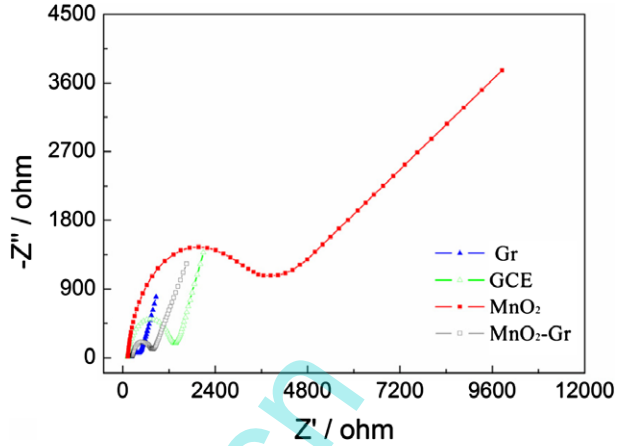


Figure 5. Measured (symbols) EIS of GCE, Gr/GCE, MnO_2/GCE and MnO_2-Gr/GCE in a solution containing $K_3[Fe(CN)_6]$ (1.0×10^{-3} mol/L), $K_4[Fe(CN)_6]$ (1.0×10^{-3} mol/L), and KCl (0.1 mol/L); the corresponding fitted plots (lines) are also shown. Experimental conditions: the applied perturbation amplitude, 0.005 V; init E, 0.236 V, the frequencies swept, 10^5–1 Hz; quiet time, 2 s.

Further, the number of electrons (*n*) transferred in the electro-oxidation of indomethacin was calculated to be 1.93 (approximately equal to 2). The proposed mechanism on the MnO_2-Gr/GCE may be depicted by the following scheme:

As proposed in Scheme 1, this is a two electrons and two protons oxidation process (Scheme 1).

Electrochemical Impedance Spectroscopy of Different Electrodes. The electrochemical impedance spectroscopy (EIS) is an effective technique for investigating chemical transformation and process associated with modified electrode surface. Figure 5 depicts the EIS spectra of the differently modified electrodes. In electrochemical impedance measurement, electron-transfer resistance (Ret) equals to

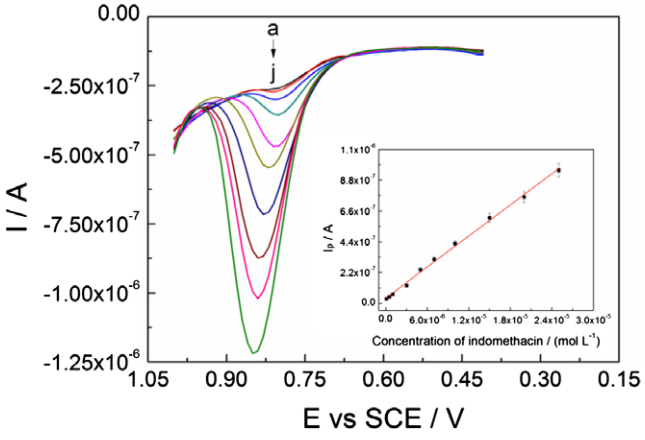


Figure 6. Differential pulse voltammograms of MnO_2-Gr/GCE at different indomethacin concentrations (from a to *j*: 1.0×10^{-7}, 5.0×10^{-7}, 1.0×10^{-6}, 3.0×10^{-6}, 5.0×10^{-6}, 7.0×10^{-6}, 1.0×10^{-5}, 1.5×10^{-5}, 2.0×10^{-5}, 2.5×10^{-5} mol L^{-1}). Insert: calibration curve.

Table 1. Comparison of performance between the fabricated electrode and other electrodes for indomethacin detection.

Electrode	Technique	Linear range (mol L^{-1})	Correlation coefficient	LOD (mol/L)	Ref.
$Ni(OH)_2$-Ni	*i–t*[a]	5×10^{-6}–7.94×10^{-5}	0.9980	1.41×10^{-6}	47
n-GCE[b]	*i–t*	3.84×10^{-4}–1.38×10^{-3}	0.9961	7.49×10^{-5}	48
RB ISE[c]	—	1×10^{-4}–5×10^{-2}	—	3×10^{-5}	49
INDO-TOA ISE[d]	—	1×10^{-5}–1×10^{-2}	—	3.16×10^{-6}	14
Fe(III)-SBMCP[e]	DPV	2.0×10^{-7}–1.5×10^{-4}	0.9995	8.0×10^{-8}	15
GNRs-GO-CNTP/GCE	SWV[f]	2.0×10^{-7}–9.0×10^{-7}, 2.5×10^{-6}–9.15×10^{-5}	—	1.7×10^{-8}	16
MWCNT-IL/CCE	DPV	1.0×10^{-6}–5.0×10^{-5}	—	2.6×10^{-7}	17
MWCNTs-NHNPs-MCM-41/GCE	DPV	8.0×10^{-7}–4.0×10^{-5}, 6.0×10^{-5}–1.6×10^{-4}	0.9965 0.9980	3.1×10^{-7}	18
MnO_2-Gr/GCE	DPV	1.0×10^{-7}–2.5×10^{-5}	0.9989	3.2×10^{-8}	Our work

[a] Amperometric *i–t* curve.
[b] Ni–curcumin-complex-modified GCE.
[c] Indomethacin-selective sensor based on Rhodamine B.
[d] Indomethacin-selective sensor based on tetraoctylammonium 1-(p-chloro-benzoyl)5-methoxy-2-methyl-3-indolylacetate.
[e] FE(III) Schiff base modified carbon paste electrodes.
[f] Square-wave voltammetric sensor.

the diameter of the semicircle part. At the MnO_2/GCE, R_{ct} is 3500 Ω, indicating big electron-transfer resistances. On the other hand, R_{ct} nearly equals to 400 Ω for the Gr/GCE, indicating remarkable increase in the electron-transfer efficiency of Gr modified electrodes. The results also indicate that the composite film consisting of nanostructured MnO_2 and graphene can be employed as a good electron conduction pathway between GCE and electrolyte.

Calibration Curve. Differential pulse voltammetry (DPV), owing to its higher sensitivity than cyclic voltammetry, was employed to measure indomethacin under the optimal conditions. Figure 6 presents the differential pulse voltammograms of indomethacin at different concentrations (pH 4.0). As shown in the inset of Figure 6, we obtained a good linear correlation (I (A) = -3.7×10^{-2} c (mol/L) – 3.7×10^{-8}; R = 0.9986) between the analytical curve and the concentration of indomethacin (1.0×10^{-7} – 2.5×10^{-5} mol/L) was with a detection limit of 3.2×10^{-8} mol/L, calculated from the three-fold background noise. Table 1 presents a comparison of analytical performance between MnO_2-Gr /GCE and other electrodes for indomethacin determination. Compared with the previously reported chemically modified electrodes, the MnO_2-Gr/GCE performed better with wider linear range and lower detection limit (3.2×10^{-8} mol/L), thus offering a promising alternative for determination of indomethacin.

Reproducibility, Stability, and Interferences. To examine the reproducibility of our method, we measured a 1.0×10^{-5} mol/L indomethacin solution using five differently modified electrodes prepared independently. A relative standard deviation (%R.S.D.) of 1.91% for peak current indicates excellent reproducibility of the MnO_2-Gr/GCE modified electrode. Furthermore, we investigated the stability of MnO_2-Gr/GCE and found that it could retain 90.16% of its original response even after storing the electrode at 4 °;C in humid environment for 5 days. Therefore, storage stability is acceptable. In addition, the following substances showed no obvious influence on the oxidation signal of 1.0×10^{-5} mol/L indomethacin (with deviations below 5.0%): (1) 300-fold concentration of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Cl^-, glucose, sucrose, lactose, starch, aminoacetic acid, alanine, and aspartic acid; (2) 100-fold concentration of Al^{3+}, Ni^{2+}, Ba^{2+}, and Co^{2+}; (3) 50-fold concentration of Fe^{3+}, uric acid, Vitamin C, hydroxypropyl cellulose, and sodium dodecyl sulfate; (4) 10-fold concentration of Pb^{2+}, Mn^{2+}, and Fe^{2+}. These results confirm

Table 2. Analysis of pharmaceutical formulations by proposed procedures.

Pharmaceutical formulation[a]	Labeled values (mg/tablet)	Reference procedures[b] (mg/tablet)	Proposed procedures[c] (mg/tablet)	Added (mg/tablet)	Found (mg/tablet)	Recovery (%)
Tablets	25	24.2	24.4 ± 2.6	30.0	54.8	101.3
Capsules	75	74.5	74.9 ± 3.1	30.0	105.1	100.7

[a] Tablets: Batch No. A141203, Expiry date: 06/2017, from Shanxi Yunpeng Pharm. (Linfen, China); Capsules: Batch No. 1150101, Expiry date: 12/2017, from Beijin Honglin Pharm. (Beijin, China)
[b] HPLC method.
[c] Average of five replicate measurements ± SD.

excellent selectivity of MnO_2-Gr/GCE for indomethacin. Therefore, the presence of indomethacin in real samples can be detected using MnO_2-Gr/GCE.

Analytical Application. As a proof of principle, we applied the MnO_2-Gr/GCE to detect indomethacin in two commercial drug samples and compared the results obtained from applying MnO_2-Gr/GCE with a reference procedure using HPLC.[9] Table 2 shows that the two methods agree with each other. The recovery of MnO_2-Gr/GCE is in the range of 100.7–101.3%.

Conclusions

This study focuses on developing an efficient, sensitive analytical technique to determine indomethacin selectively. The MnO_2-Gr nanocomposite, prepared by mixing Gr nanosheets with MnO_2 nanoparticles, was used to modify GCE for sensitive determination of indomethacin. Under optimized conditions, the method showed a linear range of indomethacin detection (1.0×10^{-7} to 2.5×10^{-5} mol/L) with the detection limit of 3.2×10^{-8} mol/L ($S/N = 3$). Furthermore, the proposed method successfully detected indomethacin in commercial drug samples with satisfied recovery of 100.7–101.3%. Therefore, our method has excellent potential to be applied for routine detection of indomethacin in laboratory.

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