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A novel electro analytical nanosensor based on graphene oxide/silver nanoparticles for simultaneous determination of quercetin and morin

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ABSTRACT

In this report, silver nanoparticles (AgNPs) with the mean diameters of 10-30 nm were self-assembled onto the surfaces of 2-aminoethanethiol (2-AET) functionalized graphene oxide (AETGO) sheets. The graphene oxide (GO) and AgNPs-AETGO nanocomposites were characterized by a transmission electron microscope (TEM), x-ray photoelectron spectroscopy (XPS), reflection–absorption infrared spectroscopy (RAIRS) and the x-ray diffraction (XRD). The simultaneous determination of quercetin (QR) and morin (MR) has been performed on glassy carbon electrode (GCE) modified with AgNPs-AETGO (AgNPs-AETGO/GCE). QR presented an oxidation step at Ea of 200 mV and reduction step at Ec of 150 mV and RT presented an oxidation step at Ea of 600 mV at AgNPs-AETGO/GCE by cyclic voltammetry (CV). The linearity ranges and the detection limits of QR and MR were 1.0 × 10-8 - 5.0 × 10-6 M and 3.3 × 10-9 M, respectively. The AgNPs-AETGO/GCE was also applied to real samples for the simultaneous determination of QR and MR. Thus the developed method can be adopted as an alternative to the published chromatographic, spectrophotometric and electroanalytical methods for simultaneous determination of QR and MR.

1. Introduction

MR and QR (Scheme 1) are isomeric antioxidant flavonols [1] widely distributed in fruits and vegetables as well as in many chinese herbs. It has been reported that MR has numerous many pharmacologic effects such as preventing coronary artery disease, inhibiting proliferation of tumors [2,3] and protecting human erythrocytes, ventricular myocytes and saphenous vein endothelial cells [4] as well as free radical scavenging activity [5]. QR is a potential drug because it has a variety of beneficial pharmacologic effects. It has been found to inhibit the growth of cancer cells in vitro [6] and to reduce tumor development in experimental animals [7]. The contents of QR and MR of foodstuffs are a range of 2–250 mg/kg wet weight in fruits, 0–100 mg/kg in vegetables (onions being especially rich: 200–600 mg/kg), 4–16 mg/L in red wine, 10–25 mg/L in tea and 3–13 mg/L in fruit juices [8,9].

Because MR and QR have beneficial activities, the determination of QR and MR has been interesting research area in last decade. Several methods have been developed for the determination of QR or/and MR including chromatography [10], spectrophotometry [11], capillary electrophoresis [12] and spectrofluorimetry [13]. The methods may provide high selectivity, but also leads to some disadvantages such as operational complexity, time and reagent consumption, high cost, etc. Because QR and MR are electrochemically active, electrochemical methods with their advantages of higher sensitivity, low cost and less interferences are preferable. Especially, the electrochemical methods based on various nanocomposite have been developed in order to increase the sensitivity and selectivity [14–31]. Among nanocomposites, graphene/graphene oxide has been especially considered a "rising star" carbon material because of its superior mechanical strength [32–35], low density and high heat conductance [36,37]. Many applications have been developed based on graphene-polymer composites [38–40], batteries [41], fuel cells [42–45], drug delivery and biosensors [46–50]. In addition, many reports have been reported about nanostructured materials which have chemical, optical, adsorption and electronic properties [51–53]. Metallic nanoparticles, especially noble metal nanoparticles, usually exhibit high electrocatalytic activities towards the target compounds. Among all the nanomaterials, AgNPs exhibited catalytic activity for the reduction of H_2O_2 [54,55]. Welch et al. proved that the reduction of H_2O_2 was facilitated by the modification of the GCE with AgNPs [54]. Isse et al. reported silver nanoclusters deposited on glassy carbon from $CH_3CN + 0.1$ M $LiCO_4$ plating solutions containing 1-2 mM $AgClO_4$. The Ag-modified electrode was used in preparative scale electrocatalytic reduction of benzyl chloride in

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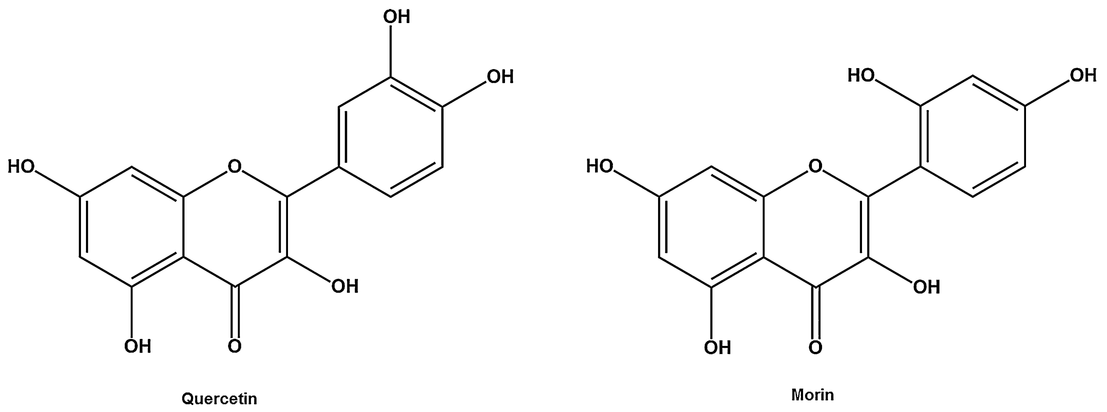

Scheme 1. The chemical structures of QR and MR.

different experimental conditions [56]. Bellomunno et al. studied electrochemical activity of four model organic bromides by nine cathodes of widely different affinity for halide anions (Pt, Zn, Hg, Sn, Bi, Pb, Au, Cu, Ag) [57]. In addition, Xu et al. prepared carbon black supported ultra-high loading silver nanoparticle catalyst and exhibited higher electrocatalytic activity for oxygen reduction reaction in alkaline medium [58]. In addition, AgNPs can improve the stability of sensor and electron transfer rate of electrochemical reactions [59,60].

The aim of this report is to prepare silver nanoparticle/graphene oxide composite and develop a new square wave voltammetry (SWV) method for the simultaneous determination of QR and MR. In literature, there is no report about simultaneous determination of QR and MR which is performed by AgNPs-AETGO/GCE. In addition, the developed SWV method based on this nanocomposite shows high sensitivity and high selectivity for determination of QR and MR in grape wine. In addition, the performance of the nanocomposite has also been compared with those reported in the literatures. AgNPs-AETGO/GCE shows lower LOD with perfect selectivity for simultaneous determination of QR and MR. Moreover, reproducibility and stability properties of proposed electrode are evaluated.

2. Experimental

2.1. Materials

QR and MR were bought from Fargem Company (Düzce, Turkey) and used as received. The stock solutions of QR and MR (1.0 mM) were prepared by dissolving it in 5 mL ethanol and then diluting it with ultra pure quality water to 25 mL. The working solutions were prepared by diluting the stock solution with 0.10 M acetate buffer (pH 5.0). Graphite powder, 2-aminoethanethiol (2-AET), silver nitrate ($AgNO_3$), 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC), HPLC grade acetonitrile (MeCN), ethanol, isopropyl alcohol (IPA), hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4) and activated carbon were purchased from Sigma–Aldrich (USA). Potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide (P_2O_5), acetic acid and sodium acetate were bought from Merck (Germany). All chemicals were reagent grade quality and were used as received. The preparation of the aqueous solutions was carried out using ultra pure quality water with a resistance of 18.3 MΩ cm (Human Power 1$^+$ Scholar purification system).

2.2. Instrumentation

All electrochemical experiments were performed using C3 cell stand and IVIUM work-station (U.S).

The infrared spectra of the composites were recorded with Bruker Tensor 27 FT-IR DTGS detector by using a Ge total reflection accessory (GATR; 65^0 incident angle relative to surface normal, Harrick Scientific).

A Rikagu Miniflex X-ray diffractometer using mono-chromatic CuKα radiation operating at a voltage of 30 kV and current of 15 mA was used for X-ray diffraction measurement of the samples. A scanning speed of $2^0 2\theta$/min and a step size of 0.02^0 were used to examine the samples in the range of 5–75$^0 2\theta$.

TEM measurements were performed on a JEOL 2100 HRTEM instrument (JEOL Ltd., Tokyo, Japan) to examine the morphology of AgNPs and GO.

XPS analysis was performed on a PHI 5000 Versa Probe (Φ ULVAC-PHI, Inc., Japan/USA) model X-ray photoelectron spectrometer instrument with monochromatized Al Kα radiation (1486.6 eV) as an X-ray anode operated at 50 W. The pressure inside the analyzer was maintained at 10^{-7} Pa. The sample for XPS measurement was prepared on a clean glass slide by placing one drop of the nanostructure, and then allowing it to air dry.

2.3. Cleaning procedure for the glassy carbon electrode surface

GCE was cleaned and prepared by polishing it to a mirror-like finish with fine wet emery paper (grain size 4000). The electrodes were polished successively in 0.1 μm and 0.05 μm alumina slurries (Baikowski Int. Corp., U.S) on microcloth pads (Buehler, Lake Bluff, IL, U.S). The electrodes were sonicated first in ultra pure water two times and in 50:50 (v/v) IPA + MeCN solution purified over activated carbon. After removal of trace alumina from the surface by rinsing with water and a brief cleaning in an ultrasonic bath (Bandelin RK 100, Germany) with water and then with IPA + MeCN mixture purified over the activated carbon, they were rinsed with MeCN to remove any physisorbed or unreacted materials from the electrode surface.

2.4. Preparation of AgNPs

The silver colloids were synthesized according to the following procedure [61]. Ag^+ was reduced by β-cyclodekstrin in aqueous solution. The solution was heated until the color of solution turned pale yellow. The pale yellow color indicates the formation of AgNPs.

2.5. Preparation of GO

GO was synthesized by a modified Hummers method [62–64]. A mixture containing 25 mL of H_2SO_4 (98%) with 5 g of $K_2S_2O_8$, 5 g of P_2O_5 and 5 g of graphite was placed in a flask and was kept at 80 °C for six hours. The mixture was cooled to 20 °C and diluted with 1 L