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Platinum- polydopamine @SiO_2 nanocomposite modified electrode for the electrochemical determination of quercetin

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ABSTRACT

Quercetin (QR) was electrochemically determined using a platinum-polydopamine coated silica particles modified glassy carbon electrode (Pt-PDA@SiO_2/GCE). Pt-PDA@SiO_2 was prepared by polymerization of dopamine on SiO_2 particles followed by loading of Pt nanoparticle via sodium borohydride ($NaBH_4$) reduction method. The surface morphology of the Pt-PDA@SiO_2 nanoparticles, functional groups of PDA@SiO_2 and crystalline nature of the nanoparticles were characterized by FE-SEM, FTIR and XRD, respectively, The Pt-PDA@SiO_2/GCE modified electrode electro active surface area and conductivity of the modified electrodes were calculated using as Fe^{3+}/Fe^{2+} probe. Quercetin was quantified by Pt-PDA@SiO_2/GCE modified electrode square wave voltammetry (SWV). The Pt-PDA@SiO_2/GCE exhibited good electrocatalytic activity towards the electrochemical oxidation of QR with excellent reproducibility and stability. The modified electrode shows an excellent detection limit and sensitivity of 16 nM (S/N = 3) and 6.47 μA/μM, respectively. The analytical utility of the Pt-PDA@SiO_2/GCE was checked by determining the QR in various real samples such as tea, onion extract, apple juice, human urine and blood plasma.

1. Introduction

Quercetin is one of the flavonoid (3, 3′, 4′, 5, 7, penta hydroxyflavone) whose corresponding chemical structure is shown in Scheme 1, which occurs naturally in plant extract. It has anti-oxidant, antibacterial, anti-inflammatory and antitumor properties [1] and prevents cancer, heart and age related diseases [2]. It also acts as an anti-mutagen which accelerates cell oxidative damage and also protects human colonocyte DNA from oxidative attack *in vitro* [3,4]. Therefore, the determination of QR is very important in human health. After the consumption of flavonoids, QR is rich in urine and blood plasma [5,6].

Quercetin is unstable in the presence of oxygen atmosphere [7] which has radical-scavenging activity and also chelate with transition metal ions forming metal-QR complex. This metal-QR complex has better anti-oxidant and anti-tumor activity than quercetin [8]. QR have five electro-active hydroxyl groups, two hydroxyl groups in catechol ring B, two hydroxyl groups in ring A and one hydroxyl group in pyran ring. The electro-activity of position 3 OH group is high due to electron donating hydroxyl groups at position 5 and 7. The hydroxyl groups in ring B are electron-donating and stabilize active intermediates, and the C-3 hydroxyl group forms intermolecular hydrogen bonds with the oxygen at C-4, also stabilizing active intermediates. [9]

In the oxidation of the catechol ring, 3′, and 4′- dihydroxyl group oxidized at low positive potentials is a two electron two proton reversible reaction. However, depending on the chemical and physical properties of flavonoids, this reaction can become quasi-reversible or irreversible. Hydroxyl group at the 3 position oxidized at middle positive potential region is irreversible reaction, and hydroxyl groups at positions 5 and 7 also oxidized at higher positive potentials is a reversible pH dependent process. [10] The dissociation constant (pK) value of QR was already reported as $pK_1 = 5.9$, $pK_2 = 8.5$ [7], the first dissociation at catechol ring 4′ —OH group and 7 —OH.

There are so many techniques used in QR determination, such as HPLC-UV [11], spectrophotometry [12], capillary electrophoresis [13], liquid chromatography with mass spectrometry [14], and solid phase extraction [15]. These techniques are expensive with less sensitivity; therefore an alternative low-cost and high sensitive technique is desire. Several modified electrodes such as CNTPE-Cu electrode [16], GNs/GCE modified electrode [17], MWCNT/Ch/WGE [18] and AgNPs-AETGO/GCE modified electrode [19] have been proposed for the electrochemical studies of QR.

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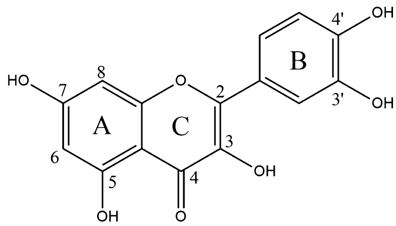

Scheme 1. Chemical structure of quercetin.

Recently silica was used for QR determination due to its high surface area and good biocompatibility properties [20]. Polydopamine on silica nanoparticle (PDA@SiO_2) increases the electro catalytic properties and biocompatibility [21,22]. The Pt nanoparticles have large surface-to-volume ratio, strong adsorption ability, good electrical properties, high surface reaction activity, small particle size and good surface properties. In particular, platinum nanoparticles (PtNPs) have been the subject of intensive research in the design of electrodes [23]. Also, metal nanoparticles incorporated in PDA@SiO_2 exhibits sensitivity and reproducibility, due to its good substrate and synergistic effect of metal nanoparticles with PDA@SiO_2 particles [24].

2. Experimental

2.1. Reagents and Instrumentation

Tetraethoxysilane (TEOS), trioctylamine (TOA), quercetin and chloroplatinic acid were purchased from Sigma Aldrich, USA. Sodium phosphate monobasic and dibasic (Na_2HPO_4 and NaH_2PO_4), acetic acid, and sodium acetate were purchased from Merck. All other reagents and solvents used during the experiment were of an analytical grade.

The FTIR spectra measurements were performed on BRUKER (TENSOR 27). X-Ray diffraction (XRD) pattern were collected

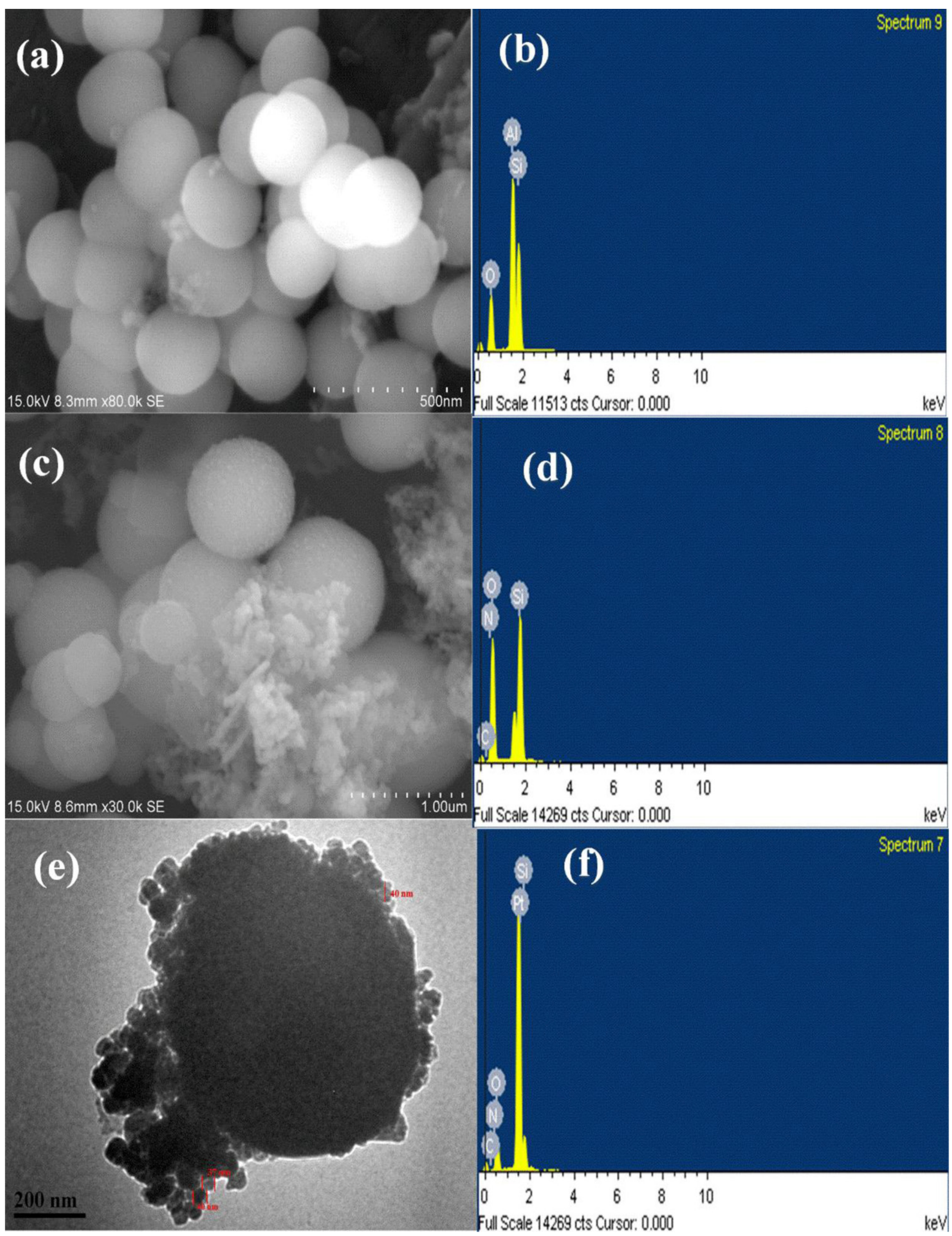

Fig. 1. FESEM image of (a) SiO_2 and (c) PDA@SiO_2, TEM image (d) Pt-PDA@SiO_2 and corresponding EDAX spectra of (b, d and f), respectively.