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Reduced graphene oxide supported raspberry-like $SrWO_4$ for sensitive detection of catechol in green tea and drinking water samples

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ABSTRACT

The raspberry-like strontium tungstate microspheres supported on reduced graphene oxide nanosheets (rGOSs@$SrWO_4$) were prepared by a hydrothermal method and it was applied to the electrocatalytic sensing of catechol. The as-prepared rGOSs@$SrWO_4$ composite was characterized by XRD, Raman, FESEM, EDX, EIS, and voltammetric techniques. Morphology studies reveal the uniform wrapping of raspberry-like $SrWO_4$ microstructure by thin sheets of rGOSs and the composite possesses large surface area and abundant catalytic active sites. The rGOSs@$SrWO_4$ composite modified screen-printed multi-conventional electrode (SPME) was fabricated which was found to exhibit extraordinary electrocatalytic activity and excellent selectivity towards the detection of catechol. The rGOSs@$SrWO_4$/SPME displayed a linear range of 0.034–672.64 µM and detection limit of 7.34 nM using differential pulse voltammetry as signal read-out. Furthermore, the electrode was durable, reproducible and repeatable. The practical utility of the method was demonstrated in green tea and drinking water samples.

1. Introduction

Catechol (1, 2-hydroxybenzene) is a basic isomer of benzenediol, which is naturally distributed ubiquitously in plants. It has primary role in biological and industrial production activities, such as fur dyes, lubricating oils, photographic rubbers, and pharmaceuticals [1,2]. However, catechol is less degradable and toxic to the water and environmental resources [3]. As the human population increases, the need for the production of more industrial products, such as pesticides, cosmetics, medicines, tanning removers, flavoring agents, photography chemicals is increases. As a result, industrial sewages are constantly released that contaminates water resources such as, rivers, ponds, lakes, and oceans [4]. Because catechol is more attractive to the researchers to detect catechol even in low concentration and at the same time catechol to be detected in a reliable, simple and rapid manner [5,6]. Various methods are already in practice, such as capillary zone electrophoresis [7], synchronous fluorescence [8], chemiluminescence [9], high-performance liquid chromatography [10], and electrochemical methods [6,11] . Compared with traditional analytical methods, electrochemical technique is cheap, robust, rapid, high sensitive, and selective [12–14].

Recently, increasing interest has been focused on the development of catechol sensors based on metal oxide electrode modifiers [15–17]. In recent years, metal tungstate (MWO_4, M: Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} etc.) have attracted much attention due to their interesting structural and chemical properties. They have promising applications in optics and photocatalysis. On the other hand, carbonaceous materials have high conductivity, unique mechanical, excellent flexibility, good corrosion resistance and high surface area and hence they are good support materials for metal tungstates [18–20]. Yet, mostly applied materials in electrochemical applications are graphite, porous carbon, n-doped graphene, and activated carbon [21–23]. In recent years, many of transition metal oxides/hydroxides/sulfides supported on carbonaceous materials were developed for electrochemical sensing applications [24–28]. Specially, graphene supported $SrWO_4$ attracted considerable attention in many fields because $SrWO_4$ materials are low-cost, highly stable, and holding excellent electrocatalytic property for several important reactions [29].

Here, we have synthesized strontium tungstate ($SrWO_4$) microspheres enveloped reduced graphene oxide nanosheets (rGOSs) via

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hydrothermal approach. The resulting composite holds excellent conductivity and very good intrinsic electrocatalytic properties. Besides, an electrochemical response for catechol at rGOSs@$SrWO_4$ shows reliable sensitivity and selectivity. The practical feasibility of the method was acquired in green tea and drinking water samples using rGOSs@$SrWO_4$ composite modified screen-printed multi-conventional electrode (SPME).

2. Experimental section

2.1. Reagents, materials and instruments

Graphite (powder, < 20 µm), $Na_2WO_4.2H_2O$, $Sr(NO_3)_3$, catechol, folic acid and all other reagents including solvents were purchased from Sigma-Aldrich and used as received. Sodium dihydrogen phosphate and disodium hydrogen phosphate were used to prepare pH. Electrochemical studies were performed in a SPME three-electrode system, which contains printed carbon as a working electrode (area 0.071 cm^2), silver as a reference electrode and printed carbon as a counter electrode. The SPME were purchased from Zensor R&D Co., Ltd., Taipei, Taiwan.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed using CHI 1205A and CHI 900 electrochemical workstations (CH Instruments, Inc., U.S.A), respectively. All the electrochemical experiments are conducted at ambient conditions. Surface morphological studies were carried out using field emission scanning electron microscope (FESEM) (H-7600, Hitachi-Japan). X-ray diffraction (XRD) studies were performed in a XPERT-PRO (PANalytical B.V., The Netherlands) diffractometer using Cu Kα radiation ($k = 1.54$ Å). Raman spectra have been acquired by Micro-Raman spectrometer (RENISHAW in via system, U.K) by a 514.4 nm He/Ne laser. Energy-dispersive X-ray (EDX) spectra was recorded using Horiba Emax x-act (sensor + 24 V = 16 W, resolution at 5.9 keV = 129 eV) and EIM6ex Zahner (Kronach, Germany) was used for electrochemical impedance spectroscopy (EIS) studies.

2.2. Preparation of GOSs and synthesis of rGOSs@$SrWO_4$ composite

1 g of graphite oxide was synthesized by modified Hummer's method [30]. It was exfoliated in water through ultrasonication for 2 h to get graphene oxide nanosheets (GOSs). Then, the GOSs solution was subjected to centrifugation for 30 min at 4000 rpm to remove any unexfoliated graphite oxide. Thereafter, 5 mM of $Sr(NO_3)_2$ and 5 mM of Na_2WO_4 were added to a 25 mL of as-prepared GOSs solution and stirred for 5 min. Further, 1 mM folic acid was added, and the pH of the whole mixture was adjusted to pH 7.0 by slowly adding 0.1 M NaOH. The whole mixture was transferred into a 50 mL Teflon-lined autoclave and hydrothermally treated at 180 °C for 24 h. A white precipitate was obtained which was separated, washed (water and ethanol) and freeze-dried to yield powder of rGOSs@$SrWO_4$ composite.

2.3. Fabrication of rGOSs@$SrWO_4$ composite modified electrode

The rGOSs@$SrWO_4$ composite (1 mg mL^{-1}) was redispersed in water/ethanol (1:2; v/v) mixture through ultrasonication for 10 min. 8 µL dispersion of rGOSs@$SrWO_4$ was drop-casted at the working electrode surface of SPME using micropipette, and dried at ambient conditions. The amount of rGOSs@$SrWO_4$ covered on the work electrode surface was 8 µg and the covering area was 0.071 cm^2. Moreover, GOSs modified SPME was also prepared under same conditions for control experiments (Fig. 1).

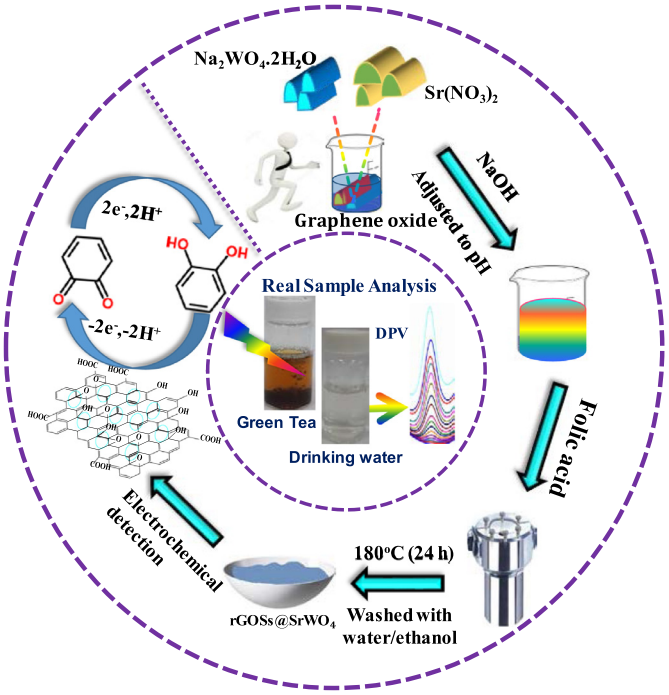

Fig. 1. Schematic representation for the hydrothermal synthesis of rGOSs@$SrWO_4$ and its electrochemical application to determining of catechol in green tea and water samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussions

3.1. Physicochemical properties of rGOSs@$SrWO_4$

The XRD patterns of GOSs and rGOSs@$SrWO_4$ composite are shown in Fig. 2A. The XRD curve of GOSs displays a characteristic sharp peak at 2θ of 11.5° that can be correlated to the (001) planes of GOSs [31]. Interestingly, the XRD pattern of rGOSs@SrWO4 displays several additional diffraction peaks at 16.11°, 26.92°, 30.01°, 32.10°, 37.42°, 43.90°, 45.96°, 48.12°, 52.28°, 55.98°, 57.33°, 59.92°, 62.54°, 67.46°, 69.92°, 72.14°, 75.08°, 77.81°, and 79.50° that are indexed to (101), (112), (004), (200), (211), (213), (204), (220), (116), (312), (224), (215), (008), (323), (400), (208, 316), (332), (404), and (420) planes. These planes are matched with the crystal facets of $SrWO_4$ having tetragonal phase crystalline (D_4h) structure (JCPDS no.08–0490) [32]. Besides, the peak at 11.5° observed for GOSs was shifted to the expected 2θ angle of 24.85° (002), which is due to the reduction of GO to rGOSs [33].

Next, the composite was further examined by Raman spectroscopy as shown in (Fig. 2B). Both GOSs and rGOSs@$SrWO_4$ exhibit the characteristic D (related to defects in graphitic lattice) and G bands (originates from the stretching of in-plane sp^2 atoms) at 1328 and 1609 cm^{-1}, respectively [34]. The D to G band intensity ratio (I_D/I_G) was 0.933. In addition, to D and G bands, the Raman spectrum of rGOSs@$SrWO_4$ displays additional peaks, which are explained as follows. The bands at 50–150 cm^{-1} are assigned to SrO_8 polyhedra structure. The first Raman active mode B_g at 78 cm^{-1} correspond to the symmetric bending vibration of O-Sr-O, then the second active mode E_g at 99 cm^{-1} is linked to free motion of SrO_8 polyhedra structure, and the third active band E_g at 136 cm^{-1} is ascribed to symmetric stretching of O-Sr-O bond. The bands located above 150 cm^{-1} are characteristic of the WO_4 tetrahedron structure, those at 195 cm^{-1} are free rotation A_g mode. The bands A_g/B_g located at 300–400 cm^{-1} are respectively, asymmetric and symmetric bending of the E_g/B_g bands at 790–850 cm^{-1} are

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