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A novel electrochemical quercetin sensor based on Pd/MoS_2-ionic liquid functionalized ordered mesoporous carbon

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ABSTRACT

A quercetin (QR) sensor based on Pd/MoS_2-ionic liquid functionalized ordered mesoporous carbon (Pd/MoS_2-IL-OMC) composite is developed. The Pd/MoS_2-IL-OMC composite is prepared by using IL as anchor and OMC as substrate. MoS_2 nanosheets are in situ grown on IL-OMC surface and then Pd nanoparticles are prepared on MoS_2 nanosheets via chemical reduction method. As the nanocomposite combines the high conductivity of IL-OMC and the electrocatalytic activity of Pd nanoparticles and MoS_2, the resulting sensor exhibits good performance towards QR, better than MoS_2-IL-OMC and Pd/IL-OMC nanocomposites modified electrodes. The electrochemical sensor allows for the selective determination of QR, with a detection limit of 8.0 nM (S/N = 3), a linear range of 0.020 μM–10 μM, and a sensitivity of 150.1 μA μM^{-1} cm^{-2}. It also shows good reproducibility and stability, and can be applied to the detection of QR in real samples.

1. Introduction

In last few years, two-dimensional (2D) transition metal dichalcogenide nanomaterials caused much concern because of their intriguing properties. Among them, the graphene-like layered molybdenum disulfide (MoS_2) played an important role in various applications due to its tunable band gap and versatile chemistry [1–4], such as in sensors [5,6], electrode materials [7–9] and catalysts [10]. Although it presented many advantages, the poor conductivity impeded its application in electrochemical analysis. Therefore, many strategies were attempted to overcome the shortcoming, including preparing ultrathin MoS_2 film [11], changing interfacial chemistry [12] and promoting phase transition (from semiconducting 2H phase to metallic 1T phase) [13]. Compared with these methods, incorporating with carbon materials [14] or metal nanoparticles [15] was more easily carried out so that is a better approach to improve its electrochemical property. Among various materials, ordered mesoporous carbon (OMC) and Pd nanoparticles (Pd NPs) were often applied to improve electrochemical performance [16,17]. Generally, OMC was used as support as it has extremely well-ordered pore structure, large pore volume, good conductivity and high surface-to-mass ratio; Pd NPs was selected for the modification of MoS_2 due to its high electrocatalytical activity and antioxidant capacity [15,18]. For examples, Liu's group prepared a MoS_2/OMC composite by hydrothermal method and used it for electrochemical hydrogen evolution; it exhibited excellent catalytic activity and remarkable electrical conductivity [18]. Zhu et al. constructed a Pd-MoS_2 catalyst for the oxygen reduction, which showed high electrocatalytic activity and stability [15]. Recently, ionic liquid (IL) functionalized OMC (IL-OMC) as substrate material was widely applied in electrochemical systems, because IL could improve the electrochemical capability of OMC and introduce charges for binding precursors of nanomaterials [19,20]. Taking into account the advantages of MoS_2, Pd NPs and IL-OMC, their combination was expected to present good electrochemical performance.

Quercetin (QR), one of the most abundant flavonoids, not only widely exists in natural plants, but also has various biological functions, such as antioxidant, anti-inflammatory, antiallergy and anticancer [21]. These efficacies are related to its content and are very beneficial for human's health. Hence, its detection is very important, especially in natural pharmaceutical chemistry, biochemistry and clinical medicine. Compared with HPLC-UV and spectrophotometry for QR determination, electrochemical detection methods get the favour of many researchers as they are low cost, simple, rapid and sensitive [22,23]. For instance, Manokaran and co-workers developed an electrochemical sensor for QR, based on platinum-polydopamine @SiO_2 nanocomposite [24]. Yola et al.

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used p-aminothiophenol functionalized graphene oxide and gold nanoparticles to modify glassy carbon electrode (GCE) for QR determination [25]. These electrochemical approaches displayed some merits, but their sensitivity was not high enough. As far as we know, there is no report about MoS_2 hybrids based sensor for QR.

In this work, an IL-OMC was used as support for MoS_2. The modification of OMC with IL was expected to introduce positive charges that benefited the immobilization of the precursor of MoS_2 on OMC surface. Meanwhile, Pd NPs were efficiently prepared on the surface of MoS_2 via chemical reduction method. Thus, the composite material had large surface, also possessed high electrocatalysis because of the synergistic effect of Pd and MoS_2. The obtained nanocomposite was applied for the construction of QR sensor, and it showed good performance.

2. Experimental

2.1. Reagents and apparatus

The OMC was obtained from Nanjing XF NANO Materials Tech Co., Ltd (Nanjing, China). Na_2PdCl_4 (purity: ≥ 99.95%) was purchased from Energy Chemical (Shanghai, China). Sodium molybdate (Na_2MoO_4•$2H_2O$) and thiourea (NH_2CSNH_2) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The ionic liquid 1-vinyl-3-ethylimidazolium bromide ([VEIM]Br, purity > 99%) was provided by Lanzhou Institute of Chemical Physics (Lanzhou, China) and used as received. QR (purity ≥ 97%) was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). A 0.10 M acetate buffer solution (ABS, pH 5.0) was employed as supporting electrolyte, which was prepared with HAc and NaAc. Other chemicals used were of analytical reagent grade. All solutions were prepared with ultrapure water.

Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry(CV) experiments were performed with a CHI 604D electrochemical workstation (CH Instrument Company, Shanghai, China). A conventional three-electrode system was applied. The working electrode was a modified GCE (diameter: 3 mm), and the auxiliary and reference electrodes were a platinum wire and a saturated calomel electrode (SCE), respectively. The scanning electron microscope (SEM) image was obtained by using field emission SEM (ZEISS, Germany). Transmission electron microscopy (TEM) image was obtained by using a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. X-ray diffraction data (XRD) were recorded with a PANalytical X'Pert Pro diffractometer (Holland) using Cu Kα radiation (40 kV, 40 mA) with a Ni filter. X-ray photoelectron spectroscopy (XPS) was recorded with a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer with Al Kα X-ray radiation for excitation. N_2 sorption analysis was carried out on a Quantachrome Autosorb-iQ gas sorption analyzer. Before gas analysis, the samples were evacuated for 12 h at 120 °C under vacuum.

2.2. Preparation of IL-OMC

The IL-OMC was prepared as follows [20]: 60 mg OMC was dispersed in 10 mL methanol by ultrasonication for 30 min. Then 16 mg IL and 20 mg 2,2′-azobisisobutyronitrile (AIBN) were added to the above dispersion. After ultrasonication for another 30 min, the mixture was transferred to a round-bottomed flask and refluxed at 80 °C for 12 h under vigorous stirring and N_2 protection. The precipitate was collected by centrifugation and washed with acetone and ultrapure water for several times. The product was dried in an oven at 60 °C.

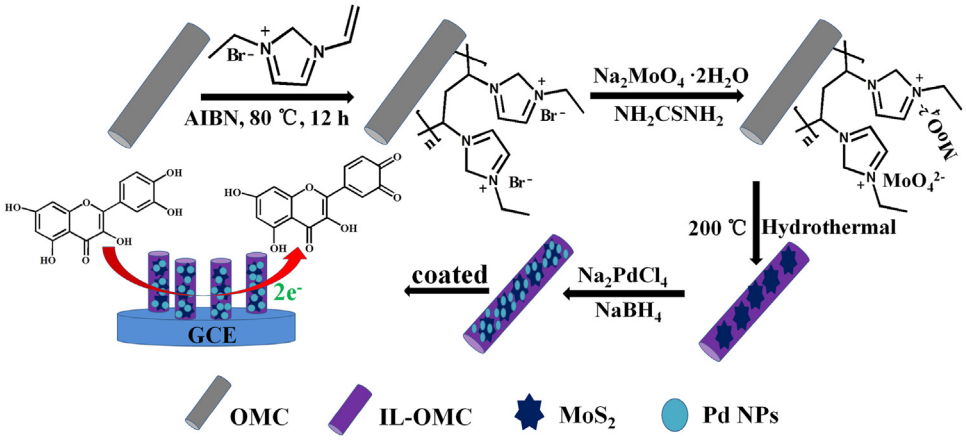
2.3. Synthesis of Pd/MoS_2-IL-OMC

The MoS_2-IL-OMC hybrid was synthesized according to the literature with minor modification [26]. Briefly, 0.5 mmol Na_2MoO_4•$2H_2O$ and 4.5 mmol NH_2CSNH_2 were dissolved in 30 mL IL-OMC suspension (1 mg mL^{-1}) under stirring for 1 h. Then, the resultant solution was transferred into a Teflon-lined stainless steel autoclave and heated at 200 °C for 12 h. The black precipitation was washed with water and ethanol for three times respectively, followed by drying at 60 °C in a vacuum oven overnight to obtain MoS_2-IL-OMC.

In order to load Pd NPs, 15 mg of as-prepared MoS_2-IL-OMC was dispersed into 15 mL ultrapure water by ultrasonication of 1 h, then 1.0 mL 10 mM Na_2PdCl_4 aqueous solution was added. Subsequently, 2.0 mL fresh aqueous solution of $NaBH_4$ (0.10 M) was introduced to reduce Na_2PdCl_4. After stirring for 1 h, the mixture was centrifuged and washed with ultrapure water until pH 7.

2.4. Preparation of modified electrode

Before modification, the bare GCE was polished with alumina slurry (0.05 μm) and then washed thoroughly with ultrapure water, 7 M HNO_3 solution, ethanol, and ultrapure water with the aid of ultrasonication, respectively. Then, 0.5 mg of the as-obtained Pd/MoS_2-IL-OMC was dispersed into 2.0 mL DMF to give homogeneous suspension, and 6.0 μL suspension (0.25 mg ml^{-1}) was dropped onto the surface of cleaned GCE and dried under an infrared lamp. Thus, a Pd/MoS_2-IL-OMC film coated electrode (i.e. Pd/MoS_2-IL-OMC/GCE) was obtained.



Scheme 1. Illustration of the fabrication procedure of Pd/MoS_2-IL-OMC/GCE.