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Full Length Article

Single-layer MnO_2 nanosheets for sensitive and selective detection of glutathione by a colorimetric method

Weihua Di*, Xiang Zhang, Weiping Qin*

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

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ABSTRACT

The rapid, sensitive and selective detection of glutathione (GSH) is of great importance in the biological systems. In this work, a template-free and one-step method was used to synthesize the single-layer MnO_2 nanosheets via a redox reaction. The resulting product was characterized by XRD, TEM, FTIR, XPS and UV–vis absorption. The addition of GSH results in the change of solution color depth owing to the occurrence of a redox reaction between MnO_2 and GSH, enabling colorimetric detection of GSH. At a pH of 3.6, the proposed sensor gives a linear calibration over a GSH concentration range of 10–100 μM, with a rapid response of less than 2 min and a low detection limit of 0.5 μM. The relative standard deviation for seven repeated determinations of GSH is lower than 5.6%. Furthermore, the chemical response of the synthesized MnO_2 nanosheets toward GSH is selective. Owing to the advantages with good water solubility, rapid response, high sensitivity, good biocompatibility and operation simplicity, this two-dimensional MnO_2-based sensing material might be potential for detecting GSH in biological applications.

1. Introduction

Glutathione (GSH) is the most abundant cellular biothiols and essential endogenous antioxidants. It plays a central role in cellular defense against toxins and free radicals [1,2]. Abnormal levels of GSH have been implicated with the development of many kinds of diseases. For example, GSH deficiency can lead to various diseases such as leukocyte loss, cancer, AIDS and neurodegenerative disease [3–6]. Therefore, the rapid, convenient, sensitive and selective detection of GSH is of great importance in clinical diagnosis [4–7].

Nanomaterials are potential candidates for analyte detection, because their reduced size leads to an exceptionally high surface area and tunable surface chemistry, and thus creates a remarkable increase in sensor sensitivity towards change in its surrounding chemical environment [8,9]. Nanosheets are a class of two-dimensional (2D) nanomaterials with high specific surface area, characterized by a thickness of nanometers and lateral dimensions of sub-micrometers to micrometers. Recently, the emerging (2D) nanomaterials (e.g., graphene, MoS_2, WS_2, etc.) have attracted wide attention due to their unique physicochemical properties, and found the potential applications in a variety of areas including electrics, energy storage, catalysis, and biology [10–16]. Particularly, for single-layer 2D nanomaterials, an intense interest has been focused to develop the intelligent sensing nanosystems that can interact with various biomolecules and respond rapidly with their electrical, optical or magnetic properties for biodetection [17–22].

Manganese dioxide (MnO_2) is a well-known functional transition metal oxide. Owing to its unique physicochemical properties, and environmental and biological compatibility, MnO_2 has attracted wide research interest and found diverse potential applications including cell batteries [23,24], catalyst [25–28], sensing [29,30], and biological uses in the magnetic resonance imaging and drug delivery [31,32].

In this work, we used a template-free and one-step method to synthesize single-layer MnO_2 nanosheets via a redox reaction between $KMnO_4$ and sodium dodecyl sulfate. The synthesized MnO_2 nanosheets can be dispersed in the water to form the stable brown colloidal solution with an intense absorption in the UV–vis region centered at 375 nm. The addition of GSH to MnO_2 solution at an acidic pH condition led to a quick transformation of the solution color from brown to colorlessness due to the reduction of MnO_2 to Mn(II) by GSH, which enabled the colorimetric determination of GSH.

* Corresponding authors.
E-mail addresses: whdi@jlu.edu.cn (W. Di), wpqin@jlu.edu.cn (W. Qin).

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2. Experimental

2.1. Chemicals

Analytical grade $KMnO_4$, sodium dodecyl sulfate (SDS), concentrated sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), citric acid and sodium citrate were obtained from Beijing Chemicals Reagents. GSH, glucose, fructose, uric acid, cysteine (Cys) and 1,4-dithiothreitol (DTT) were purchased from Sigma-Aldrich Co. (Shanghai, China). MiliQ water was used throughout. All other chemical reagents were of analytical reagent grade. The citrate buffer was prepared by mixing an approximate ratio of citric acid and sodium citrate solutions.

2.2. Synthesis of single-layer MnO_2 nanosheets

Single-layer MnO_2 nanosheets were synthesized following a typical process as below [33]. 32 mL of SDS solution (0.1 M) and 1.6 mL of H_2SO_4 solution (0.1 M) were added into 283.2 mL distilled water and heated at 95 °C for 15 min first. 3.2 mL of $KMnO_4$ solution (0.05 M) was added into the above solution quickly to start the reaction and the reaction mixture was maintained at 95 °C for 60 min. In this process, the initial $KMnO_4$ solution with purplish red color was gradually transformed to the dark brown colloidal suspension. The resulting suspensions were centrifuged, and the precipitates were thoroughly washed with ethanol for 3 times and subsequently dried in air at 50 °C for various analyses. The purified MnO_2 was dispersed in citrate buffer to form a colloidal suspension for analyte detection.

2.3. GSH detection

In a typical process of GSH detection, 50 μL of GSH solution with a given concentration was added into 2 mL of citrate buffer containing MnO_2 (0.05 mM). The above mixed solution was reacted with a slight shaking for 3 min. Then, the supernatant was immediately moved to a quartz cuvette for UV–vis absorption measurement. To establish the relationship between the absorbance of the solution and GSH concentration, GSH concentration was changed, but other reaction conditions keep the same according to the above experiment procedure.

2.4. Characterizations

The X-ray powder diffraction (XRD) data were collected on an X'Pert MPD Philips diffractometer (CuKα X-radiation at 40 kV and 50 mA) with a scanning step of 0.02°. The transmission electron microscopy (TEM) observations were carried out using a JEOL 2200FS microscope. Samples for TEM investigations were prepared by first dispersing the particles in ethanol under assistance of ultrasonification and then dropping one drop of the suspension on a copper TEM grid coated with a holey carbon film. Fourier transform infrared (FT-IR) spectra (Mattson 5000) of the samples were measured in the range of 4000–450 cm^{-1} in transmission mode. The pellets were prepared by adding 0.8 mg of the sample powder to 80 mg of KBr. The powders were mixed homogeneously and compressed at a pressure of 10 kPa to form transparent pellets. X-ray photoelectron spectroscopy (XPS) analysis was performed using a PHI Quantera SXM (ULVAC-PHI) device operating at a pressure of 10^{-8} Torr. The photoelectron emission spectra were recorded using a monochromatic Al Kα source (100 W). The angle between the x-ray direction and the emitted electron direction was 45°. The UV–vis absorbance measurements were carried out using a Schimadzu UV-2550 scanning spectrophotometer with a scan rate of 240 nm min^{-1}. For the measurement of the absorbance evolution with time after adding a given concentration of GSH, an immediate measurement was carried out, and a fast scan rate of 1200 nm min^{-1} was used.

3. Results and discussion

3.1. Synthesis and characterization of single-layer MnO_2 nanosheets

A template-free and one-step method was used to synthesize the single-layer MnO_2 nanosheets via a redox reaction between $KMnO_4$ and sodium dodecyl sulfate (SDS). The crystal structure of the synthesized product was characterized by XRD. The XRD profile shown in Fig. 1(a) exhibited four characteristic peaks at 2 theta = 12.1°, 24.2°, 36.7°, 66°, indicating a typical lamellar structure. All the diffraction peaks can be well indexed to δ-MnO_2 phase (JCPDS No. 18-0802). Fig. 1(b) shows a TEM image of representative areas of the as-synthesized product. The sample was typically composed of ultrathin and transparent lamellar structure with ample graphene-like wrinkles and folds, displaying a typical 2D morphology of MnO_2 nanosheets [33]. The perceived average lateral dimension of the nanosheets is estimated to be ~200 nm. The thickness of nanosheets was characterized to be smaller than 1 nm, confirming the formation of single-layer MnO_2 nanosheets.

The FT-IR spectrum (Fig. 1(c)) provides further insight into the structure and surface state of synthesized MnO_2. The peaks at 518, 473 cm^{-1} are assigned to the characteristic absorption of the Mn–O stretching vibration of octahedral [MnO_6] framework [34,35]. Two intense bands at 3420 and 1625 cm^{-1} are attributed to the physically adsorbed water and the interlayer water in the MnO_2 nanosheets [34]. The low intensity of peaks in the 2922–2995 cm^{-1} region are assignable to the asymmetric and symmetric $-CH_2$ and $-CH_3$ stretching due to the use of SDS in the synthesis [36].

XPS was used to make a qualitative analysis of chemical valence and binding of the element for the synthesized MnO_2. Two characteristic peaks centered at 642.2 and 654.1 eV were observed, corresponding to Mn $2p_{3/2}$ and Mn $2p_{1/2}$ of MnO_2, respectively (Fig. 1(d)) [34,37]. The spin-energy separation of ~11.9 eV is also consistent with those previous reports by other research groups [34,38]. No additional signals attributed to Mn_2O_3 and $KMnO_4$ were found in the XPS spectrum, indicating the generation of pure MnO_2. The XPS spectrum of oxygen shows two peaks centered at 529.8 and 532.7 eV (Fig. 1(e)), which are assigned to the lattice oxygen of [MnO_6] octahedra and the oxygen in the interlayer H_2O or H_3O^+, in good agreement with the FTIR result [34].

The UV–vis absorption spectrum (Fig. 1(f)) of the synthesized MnO_2 solution exhibits a broad absorption band around ~375 nm, which is attributed to the d–d transition of Mn(IV) in the octahedral [MnO_6] unit. The wavelength and intensity of the absorbance are in line with the previous findings of single-layer MnO_2 nanosheets by other groups [39–41]. The colloidal suspension of single-layer MnO_2 nanosheets shows good stability and remains stable at 4 °C in the dark for more than 15 days without any precipitates.

3.2. Redox reaction between MnO_2 and GSH

In our preliminary experiment, it is interesting to find that, the addition of GSH to MnO_2 solution caused the MnO_2 solution to fade. Correspondingly, the UV–vis absorbance of the MnO_2 solution decreased due to the reaction of MnO_2 with GSH. Moreover, the reactivity of MnO_2 with GSH depended strongly on the solution pH values. To demonstrate the effect of solution pH on the reactivity of MnO_2 with GSH, the experiments were conducted as below. The equivalent quantities of MnO_2 were dispersed in 5 mL citrate buffer with different pH values ranging from 3.8 to 5.6 and MiliQ water with pH 7.4, respectively. Then, 50 μL of GSH solution