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Facile fabrication of tungsten disulfide quantum dots (WS_2 QDs) as effective probes for fluorescence detection of dopamine (DA)

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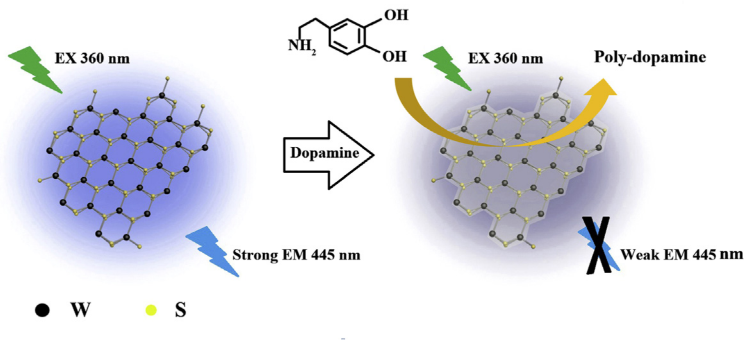
HIGHLIGHTS

- WS_2 QDs are produced using a simple liquid exfoliation of bulk crystals.
- The probe is independent on the pH of solution and hardly interfered by other ions.
- The fluorescent sensor is of very high selectivity for DA detection.

GRAPHICAL ABSTRACT



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ABSTRACT

Through the simple liquid exfoliation method, WS_2 QDs show excellent fluorescent properties. DA could form thin on the surface of WS_2 QDs through the polymerization effect, leading to quenching of fluorescence. The sensing system is highly selective for DA and the limit of detection is 3.3 μM. These results indicate that WS_2 QDs are potentially applicable in optical imaging, catalysis and fluorescence sensing. The strategy might be suitable for the detection of other catecholamine.

1. Introduction

Since the discovery and investigation of graphene, a great deal of attention has been attracted on other two-dimensional (2D) layered materials [1,2], such as boron nitride, black phosphorus and transition metal dichalcogenides (TMDs), due to the semiconducting electronic properties and large surface area [3,4], which are important for sensors, photodetectors, catalysis and energy storage applications [5–8]. As one kind of the typical 2D TMDs, tungsten disulfide (WS_2) is built up of W atoms sandwiched between two sulfur atoms single layers (S-W-S layers) though Van der Waals forces and has shown its potential applications in semiconductor industry for fluorescence sensing, catalysis, and bioimaging [9,10].

Until now, different methods to synthesize WS_2 nanosheets have been reported, including mechanical exfoliation, electrochemical intercalation, and chemical vapor deposition (CVD) [11–14]. However, the obtained WS_2 nanosheets have the deficiencies, such as low quality, insufficient active sites, and containing other heteroatom, which limits the further application [15]. When the size of WS_2 nanosheets are controlled to be less than

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10 nm, zero dimensional WS_2 quantum dots (WS_2 QDs) can be synthesized [16]. Compared with WS_2 nanosheets, WS_2 QDs show unique and outstanding optical properties due to quantum confinement and edge effects. Because of the excellent luminescent property, WS_2 QDs are potentially applicable in optical imaging, catalysis and fluorescence sensing [16–19].

Dopamine (3, 4-dihydroxyphenylethylamine) is one of the important catecholamine neurotransmitter distributed in the central nervous system [20–23]. It also plays key roles in the function of the renal, hormonal, and cardiovascular systems [24–26]. Abnormal release of dopamine causes several incurable diseases, such as Parkinson and Huntington's diseases [27–31]. Besides that, changes in DA concentrations in brain contribute to the decline in neurocognitive functions, including memory, attention, and problem-solving [32,33]. As a result, DA has been given tremendous consideration by neuroscientists and chemists in bio-medical and bio-analytical research and there is a strong need to establish highly sensitive and selective methods for the direct detection of DA.

In the present work, WS_2 QDs produced through a simple liquid exfoliation of bulk crystals are used as the fluorescent probes. In the absence of DA, WS_2 QDs generate a bright fluorescence under the given excitation. When DA is added, DA will snap to the surface of WS_2 QDs and form thin (poly-dopamine) through the self-polymerization effect. Poly-dopamine changes the surface of WS_2 QDs and results in the fluorescence quenching of WS_2 QDs through fluorescence resonance energy transfer (FRET), as shown in Scheme 1. To the best of our knowledge, there has been no report on the use of WS_2 QDs in the fluorescence sensing of DA.

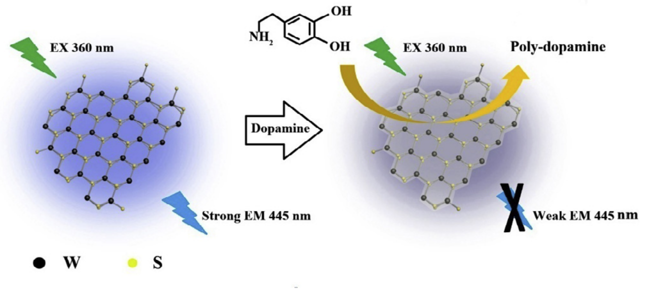
2. Experimental details

2.1. Instrumentation

Transmission electron microscopy (TEM) images are achieved by a JEM-1400 operating at 120 kV. The optical absorption spectra of WS2 QDs is obtained by a UV-3101 scanning spectrophotometer (Shimadzu, Japan) at room temperature. Fluorescence intensity is recorded on the luminescence spectrometer (Fluorolog-3). Fourier transform infrared spectroscopy is achieved by FTIR (Thermo Fisher Nicolet 6700). The X-ray photoelectron spectroscopy (XPS) measurement is carried on PHI Quantera (PHI, Japan), the binding energy is calibrated with C1s = 284.8 eV. Tungsten disulfide (WS_2, 99.8%), 1-Methyl-2-pyrrolidinone (NMP), and Dopamine hydrochloride (DA, 99%) were purchased from Alfa Aesar.

2.2. Synthesis of WS_2 QDs

WS_2 QDs are produced using a simple liquid exfoliation of bulk crystals. Briefly, 50 mg of WS_2 powder (Alfa Aesar) is dispersed in 30 mL NMP (1-Methyl-2-pyrrolidinone) and sonicated for 24 h in ice bath (150 W). After that, the solution is centrifuged for 30 min at 9000 rpm and filtrated to remove large WS2 sheets. Then the suspension is evaporated in order to calculate the concentration of WS_2 QDs and finally re-dissolved in 300 mL deionized water.



Scheme 1. Illustration of the detection of dopamine.

2.3. Assay procedures

Various concentrations of DA solution (2 mL) are mixed with WS_2 QDs (160 μg/mL, 2 mL) together and incubated in oven for 90 min at 60 °C. After the mixture is allowed to cool to room temperature, fluorescence measurements are taken. The fluorescence intensity is recorded at an excitation wavelength of 365 nm and the slits for the emission are set to 5 nm.

3. Results and discussion

3.1. Characterization of WS_2 QDs

PL (photoluminescence) emission spectra of WS_2 QDs is recorded under various excitation. As shown in Fig. 1 (a), the fluorescence peak shifts from 444 to 439 nm with the excitation wavelength ranging from 280 to 310 nm. Then the peak shifts from 439 to 465 nm with the excitation wavelength changes from 320 to 400 nm, illustrating its excitation-dependent fluorescent property. Fig. 1 (b) (3D PL spectra) reveals the trend of the PL intensity at different excitation wavelength. It can be observed that the maximum emission is located at around 445 nm under the excitation wavelength of 360 nm. PL quantum yield of WS_2 QDs and WS_2 QDs-DA (50 μM) are 21.75% and 13.77% using quinine sulphate as a reference at the excitation wavelength of 360 nm. The quantum yield of WS_2 QDs was calculated according to:

$$\frac{Y_x}{Y_s} = \frac{F_x}{F_s} \times \frac{A_s}{A_x} \qquad (1)$$

Where Y is the quantum yield, F is the measured integrated emission intensity, A is the optical density. The subscript "s" refers to quinine sulphate, "x" refers to WS_2 QDs.

XPS characterization is used to determine the chemical states and composition of the WS_2 QDs.

Fig. 1 (c) displays W 4f peaks at 37 eV and 35 eV, corresponding to the W $4f_{5/2}$ and W $4f_{7/2}$ doublet. Meanwhile, the S 2p peak can be deconvoluted into two peaks at around 168.7 eV and 167.8 eV (Fig. 1 (d)), attributing to the coexistence of S $2p_{1/2}$ and S $2p_{3/2}$ orbital. Detailed compositional analysis results reveal that the atomic ratios (W:S) is 1:2.59. These bingding energy values confirm the charge states of W^{4+} and S^{2-} in the WS_2 QDs and this result is consistent with those reported in previous studies [34,35].

The absorption spectrum (Fig. 2 (a)) of WS_2 QDs shows an acromion peak at 300 nm. The spectrum of DA exhibit very weak absorption. WS_2 QDs-DA has an absorption region from 300 to 500 nm. The formation of WS_2 QDs-DA is confirmed by FT-IR spectral analysis (Fig. 2 (b)), ranging from 4000 to 400 cm^{-1}. A broad and strong peak at 3380-2950 cm^{-1} is assigned to O-H and N-H stretching. The DA has characteristic bands at 1610 and 1392 cm^{-1} relating to the aromatic C=C bonds and C=N-C stretching modes, respectively. The peak at 464 cm^{-1} is due to W-S vibration. There are three main absorption peaks of WS_2 QDs-DA different from WS_2 QDs (3156, 1498 and 1189 cm^{-1}). This change may be related to the cover effect of poly-dopamine.

3.2. Detection principle for DA

When DA is added, DA can attach onto the surface of WS_2 QDs