

Supporting Information to

Non-Enzymatic Signal-On Electrochemiluminescence Detection of Organophosphorus Pesticides Based on Tungsten Disulfide Quantum Dots

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1. Absolute photoluminescence quantum yield measurement

Absolute photoluminescence (PL) quantum yield of WS₂ QDs tested using a device using a calibrated integrating sphere system. The setup consists of a 150 W CW Ozone-free xenon arc lamp coupled to a monochromator (Czerny-Turner design with a dual grating turret; plane gratings for accurate focus at all wavelength and minimum stray light), an Integrating Sphere (SC-30), and an Emission Detector (Photomultiplier R928P, spectral coverage 200 nm-900 nm, cooled and stabilized). Determination of absolute PL quantum yield using an integrating sphere device includes the following steps: (1) Under the same measurement conditions (excitation wavelength 360 nm, conventional 10 mm quartz four-way cuvette and room temperature), the transmitted incident radiation power and emission spectra of the sample (WS₂ QDs in DMF solution) and the blank (DMF) were measured, respectively. (2) Select excitation and emission wavelength regions for spectral emission correction and signal integration. (3) The absolute fluorescence quantum yield was calculated from the measured spectrally corrected signals of the sample (WS₂ QDs in DMF solution) and the blank (DMF) according to Eq. S1. Of course, the absolute fluorescence quantum yield is calculated directly by using the software of the Fluoracle.

$$\Phi = \frac{N_{emission}}{N_{absorption}} = \frac{\int \frac{\lambda}{hc} \{I_{em}^{sam}(\lambda) - I_{em}^{ref}(\lambda)\} d\lambda}{\int \frac{\lambda}{hc} \{I_{ex}^{ref}(\lambda) - I_{ex}^{sam}(\lambda)\} d\lambda}$$

(S1)

where $N_{absorption}$ is the number of photons absorbed by a sample and $N_{emission}$ is the number of photons emitted from a sample, “ λ ” is the wavelength, “ h ” is Planck's

constant, “*c*” is the velocity of light, I_{ex}^{sam} and I_{ex}^{ref} are the integrated intensities of the excitation light with and without a sample, respectively I_{em}^{sam} and I_{em}^{ref} are the PL intensities with and without a sample, respectively.

2. Relative ECL efficiency calculation

Relative ECL efficiency (Φ_{ECL} , %) was calculated by comparing the integration of the ECL intensity obtained by the ECL-voltage curve and current (versus time) for WS₂ QDs with that of Ru(bpy)₃Cl₂.¹

$$\Phi_{ECL} = \frac{\left(\frac{\int ECL dt}{\int Current dt} \right)_x}{\left(\frac{\int ECL dt}{\int Current dt} \right)_{st}} \times 100\%$$

(S2)

where “st” represents the Ru(bpy)₃Cl₂ standard and “x” refers to the WS₂ QDs.

3. Experimental section

3.1 Materials and Reagents

WS₂ powder (99.9%), potassium chloride (KCl, 99.5%), potassium dihydrogen phosphate (KH₂PO₄, 99.5%) and dipotassium hydrogen phosphate (K₂HPO₄, 99%) were purchased from Heowns Biochemical Technology Co., Ltd. (Tianjin, China). Dimethylformamide (DMF, 99.5%) was bought from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Potassium persulfate (K₂S₂O₈, 99%) was obtained from Sigma Aldrich (Shanghai, China) and 5,5-dimethyl-1-pyrroline-N-oxide dimethoate (DMPO) and dimethoate were purchased from Aladdin (Shanghai, China).

The naled, malathion, heptachlor and bentazone were bought from Beijing Tanmo Quality Inspection Technology Co., Ltd. (Beijing, China). Methyl parathion was obtained from Macklin Biochemical Co., Ltd. (Shanghai, China) and the permethrin and methomyl were purchased from J&K Chemical Ltd. (Beijing, China). All aqueous solutions were prepared using ultrapure Milli-Q water (18.2 M Ω cm).

3.2 Apparatus and Characterization

The morphology and size of WS₂ QDs were characterized by Field Emission Transmission Electron Microscope (FETEM, JEM-F200, Japan). X-ray photoelectron spectra (XPS) of WS₂ QDs were acquired on an ESCALAB-250Xi spectrometer (ThermoFisher, USA) with Al K α X-ray source (0.43 eV). The X-ray diffraction (XRD) of samples was performed on a MiniFlex600 diffractometer (Rigaku, Japan) with a Cu-K α line excitation source at 60 kV and 80 mA. UV-visible absorption spectroscopy of WS₂ QDs was performed using a UV-3600 plus spectrometer (Shimadzu, Japan). Photoluminescence (PL) measurements of WS₂ QDs were conducted on a FS5 steady-state transient fluorescence spectrometer (Edinburgh, UK) with excitation and emission slit widths set to 4 nm. Absolute PL quantum yield (PLQY) was determined by using a calibrated integrating sphere (SC-30) system of FS5 steady-state transient fluorescence spectrometer. Raman spectroscopy of samples was carried out on a DXR2i laser confocal Raman microscope (ThermoFisher, USA) with a 532 nm laser. The parameters of the Electron Spin Resonance (ESR) instrument (Bruker 5000 spectrometer, Germany) were set as follows: microwave power 10 mW, scan range 200 G, and modulation amplitude 2 G for detection of spin adducts using spin traps DMPO. Sample

solutions were sealed in a glass capillary tube. The tubes were inserted into the ESR cavity and measured at the selected time.

3.3 Electrochemistry and ECL Measurements

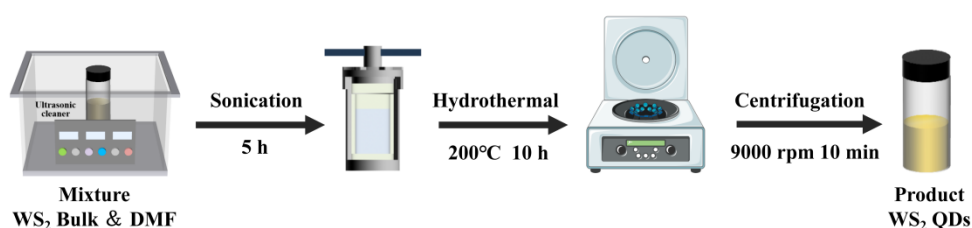
Electrochemistry experiments were conducted using an electrochemical workstation (CHI 760E, Chenhua Instruments, Shanghai, China). Voltammetric ECL curves were acquired on an MPI-E II ECL analyzer (Xi'an Remex Analytical Instrument Co., Ltd., China) with a photomultiplier tube held at 1000 V for the high-voltage supply. Spooling ECL spectra were collected using an Electrogenerated Chemiluminescence Spectrum System (Model ECLS-ML, FORTEC Technology (HK) Co. Ltd., Hong Kong, China) united with a CHI 760E electrochemical workstation. The grating and slit of the spectrograph were set to 50/600 nm and 3 μm , respectively. Before each measurement, the CCD camera (model DU401a-BR-DD) was cooled to -65°C .

A three-electrode system including WS_2 QDs modified-glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode, Ag/AgCl (sat. KCl) and Pt wire as the reference electrode and counter electrode, respectively, were used for electrochemistry and ECL measurements. Before each experiment, the GCE was successively polished using three sized (1 μm , 0.3 μm , and 0.05 μm) Al_2O_3 slurries until a mirror finished. The electrode was then tested in 1 mM potassium ferricyanide solution containing 0.2 M KNO_3 until the potential difference between the anodic peak and corresponding cathodic peak of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ was less than 70 mV. Electrochemistry and ECL measurements were carried out by employing a home-made quartz cell, which was consecutively cleaned in a base bath (5% KOH isopropanol

solution) and an acid bath (5% HCl aqueous solution) for at least 4 h to prevent any contamination. ECL measurements were finally operated by using 0.1 M phosphate buffer solution (PBS, pH = 7.4) containing 0.1 M KCl as the electrolyte. All solutions were purged with N₂ to eliminate dissolved O₂ before each experiment. The high voltage of PMT was set at 1000 V.

3.4 Synthesis of WS₂ QDs

WS₂ QDs were synthesized through a facile top-down method, slightly modified from a reported protocol.² In brief, 50 mg WS₂ powder was first dispersed in a vial by adding 12.5 mL of DMF, the obtained mixture was sonicated for 5 h. After removing the unexfoliated bulk WS₂ precipitation by centrifuging the mixture at 9000 rpm for 20 minutes, the supernatant was then transferred into a 50 mL Teflon-lined autoclave and heated to 200°C for 10 h before it was naturally cooled to room temperature. Finally, the WS₂ QDs solution was separated from the resulting products by centrifugation (9000 rpm for 10 min) to remove the residual WS₂ QDs sediment.



Scheme S1 Synthesis route of WS₂ QDs by ultrasound-hydrothermal-assisted liquid exfoliation method.

3.5 Sample Extraction of Spinach

Firstly, 10 g spinach sample (the spinach was washed with ultrapure water) was ground into vegetable juice. Then, the obtained homogenate of the fresh sample was

added to the mixed solution which consisted of 4.5 mL of PBS (0.1 M, pH = 7.4) and 0.5 mL of acetone. Finally, the mixture was sonicated for 10 min and centrifuged for 10 min at 10000 rpm. The supernatant was 500-fold diluted by PBS and stored at 4°C for further experiments.³

4. Supplementary experimental data

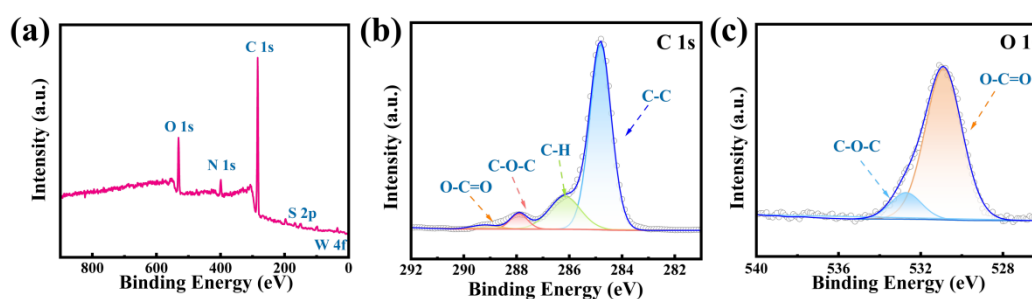


Fig. S1 (a) XPS survey spectrum of as-prepared WS₂ QDs. High-resolution XPS spectra of (b) C 1s, (c) O 1s in as-prepared WS₂ QDs.

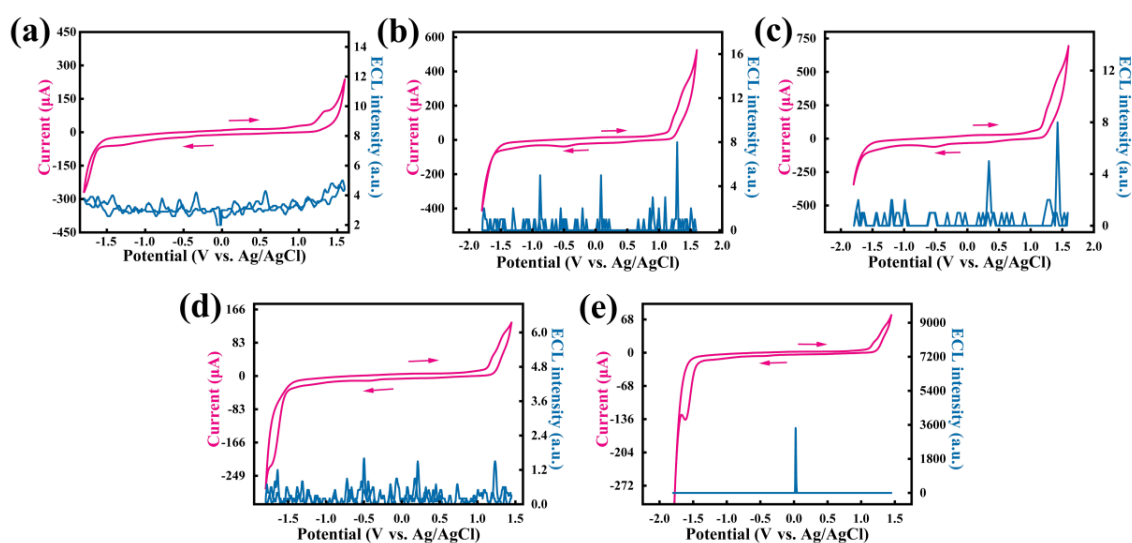


Fig. S2 Cyclic voltammograms and the corresponding ECL-voltage curves of WS₂ QDs modified GCE in the 0.1 M PBS (pH = 7.4) with 0.1 M KCl as the supporting electrolyte at different scan rate: (a) 100 mV/s, (b) 200 mV/s, (c) 400 mV/s, (d) 50 mV/s and (e) 25 mV/s.

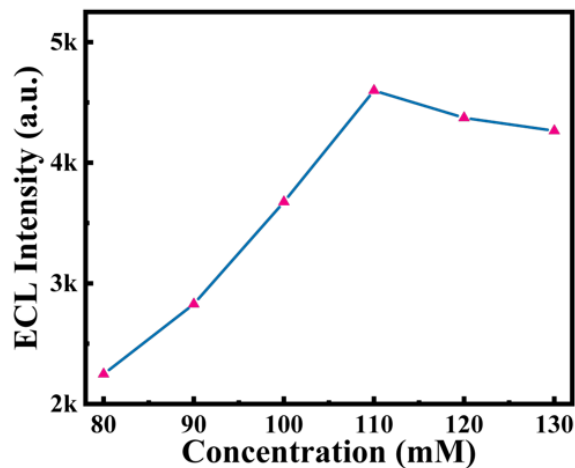


Fig. S3 The ECL intensity of WS₂ QDs modified GCE in the presence of various concentrations of K₂S₂O₈. The electrolyte was 0.1 M PBS (pH = 7.4) with 0.1 M KCl.

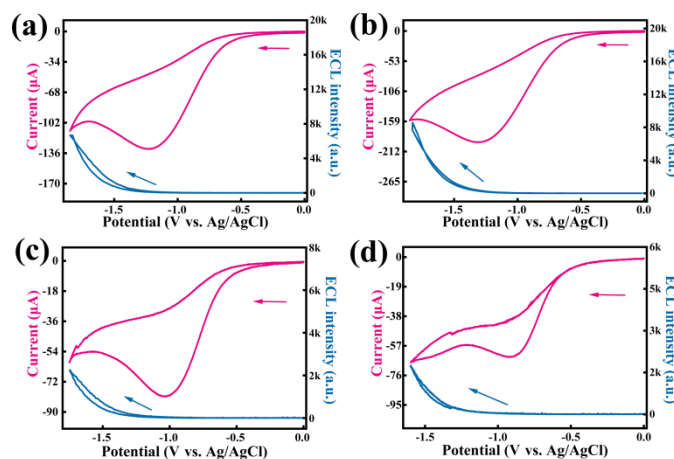


Fig. S4 Cyclic voltammograms and the corresponding ECL-voltage curves for WS₂ QDs modified GCE in the 0.1 M PBS (pH = 7.4) with 0.1 M KCl as the supporting electrolyte in the presence of 110 mM K₂S₂O₈ as the coreactant at different scan rates: (a) 200 mV/s, (b) 400 mV/s, (c) 50 mV/s and (d) 25 mV/s.

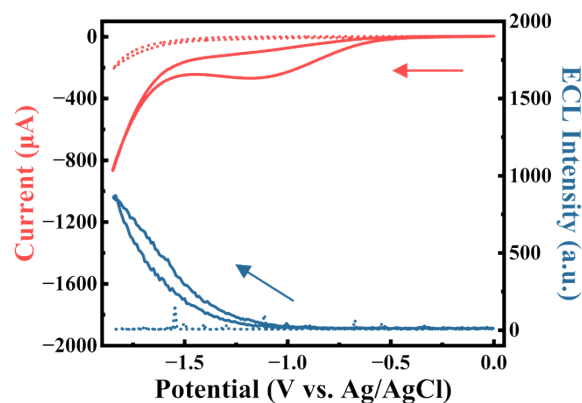


Fig. S5 Cyclic voltammograms (pink) and the corresponding ECL-voltage curves (blue) of the bare GCE in the absence (dashed lines) and presence (solid lines) of 110 mM $K_2S_2O_8$. The supporting electrolyte was 0.1 M PBS (pH = 7.4) containing 0.1 M KCl. Scan rates were all at 0.1 V/s.

Table S1 ECL efficiency (Φ_{ECL}) of WS_2 QDs with 110 mM $K_2S_2O_8$ at different scan rates.

Scan rate (Vs^{-1})	0.1	0.2	0.4	0.05	0.02
Φ_{ECL}	132.42%	155.88%	28.49%	46.23%	29.83%

Table S2 Comparison of the analytical performances with previously reported ECLphores for OPs detection.

ECLphores	Coreactant	OPs	Linear range (pg/mL)	Detection limit (pg/mL)	Ref.
CdTe QDs	Dissolved oxygen	MP	200~10000	6.00	4
			2000~150027		
Luminol	H_2O_2	MP	26~13160	23.69	5
Luminol	MP	MP	10~1000000	3.34	6
Luminol	H_2O_2	MAL	33~16518	52.85	5
$Ru(bpy)_3^{2+}$	TPrA	DM	1146300~91704000	229.26	7
WS_2 QDs	$K_2S_2O_8$	MP	0.33~20	0.15	This work
WS_2 QDs	$K_2S_2O_8$	MAL	25~600	5.58	This work
WS_2 QDs	$K_2S_2O_8$	DM	2.50~80	0.35	This work

5. References

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