# Supporting information

## A novel electrochemical sensor based on $P_2W_{15}V_3$@CNTs composite for the sensitive determination of baicalin

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### 1.1 *Materials and Reagents*

All chemicals and reagents were commercially obtained and used without further purification. Carbon nanotubes (CNTs, ≥99% purity) with inner diameter 5-8 nm, outer diameter 10-15 nm, length 2-8 μm, and resistivity 1700 μΩ·m were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Methyl parathion (99.8% purity) was purchased from TMRM Quality Inspection Technology Co., Ltd. Baicalin (99.8% purity) was purchased from Yuanye Bio-Technology Co. Ltd. Nafion (5 wt%) was offered by Sigma-Aldrich (Shanghai, China). The following chemicals were procured from aladdin Biochemical Technology Co., Ltd. (Shanghai, China): Zinc chloride ($ZnCl_2$, ≥98.0%), potassium chloride (KCl,, ≥99%), ferric chloride ($FeCl_3$, ≥99.0%), glucose (≥99.8%), citric acid (≥99.5%), ascorbic acid (≥99.7%), urea (≥99.0%), potassium ferrocyanide trihydrate ($K_4[Fe(CN)_6]$, ≥99.5%), potassium ferricyanide ($K_3[Fe(CN)_6]$, 99.5%). Phosphate buffer solution (PBS, pH = 7.0) was prepared using $NaH_2PO_4·2H_2O$ and $Na_2HPO_4·2H_2O$. The pH value of PBS was adjusted with 0.1 mol/L $H_3PO_4$ and 0.1 mol/L NaOH solution. Ultrapure water was used for the preparation of all solutions.

### 1.2 *Physical measurements*

Infrared (IR) spectra were acquired with an Nicolet iS50 FT/IR spectrometer employing KBr pellets in the region of 400-4000$cm^{-1}$. X-ray diffraction (XRD)

patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer, using Cu-Kα radiation ($\lambda$ = 1.54 nm) and 2θ ranging from 5 to 90°. X-ray photoelectron spectra (XPS) were collected with a ESCALAB 250Xi microscope (Thermo, USA). The samples' morphology was examined using transmission electron microscopy (TEM, Tecnai F20, USA). The energy dispersive spectroscopy (EDS) was analysed on a field emission scanning electron microscope (Bruker XFlash 6T-30). The Raman spectra were recorded on a microscopic Raman spectrometer (Horiba HR Evolution, France) with a 633 nm laser source.

**1.3** ***Electrochemical methods***

Electrochemical experiments were performed on a CHI-660E electrochemical workstation (Chenhua Instrument, Shanghai, China) equipped with a standard three-electrode system consist of a bare glassy carbon electrode (GCE) or modified GCE as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode as the reference electrode. CV curves of desired Bn concentration were recorded in 0.1 mol·$L^{-1}$ phosphate-buffered solution (PBS, pH 7.0) over a potential range from -0.3 to 0.6 V, with a scan rate of 100 mV·$s^{-1}$. EIS measurements were carried out in a 5 mM $[Fe(CN)_6]^{3-/4-}$ solution with 0.1 M KCl as the supporting electrolyte, under the following parameters: frequency range of 10 Hz to 1000 kHz, AC amplitude of 5.0 mV, and a constant overpotential of 150 mV. Electrochemical detection of Bn was achieved using adsorptive stripping voltammetry, which included two sequential steps: (I) Enrichment step: The working electrode was immersed in 5 mL of Bn solution in 0.1 mol $L^{-1}$ PBS (pH 7.0) and maintained at +0.15 V for 480s at room temperature to facilitate static adsorption of Bn. (II) Detection step: DPV measurements were conducted within a potential range of -0.2 to 0.4 V using optimized parameters: pulse amplitude = 0.05 V, pulse width = 0.05 s, pulse period = 0.5 s, and quiet time = 2 s.

**1.4** ***Real sample pretreatment***

Add 1.0257 g of Scutellaria baicalensis to 50 mL of ethanol-water (3:7, v/v) mixed solvent, reflux extract at 80°C for 3 hours, filter, and collect the filtrate for later

use. Detection was performed using the standard addition method: 20 μL of the sample filtrate was added to PBS buffer (pH 7.0), followed by the addition of Bn standard solutions (0, 2.6, 4.5, and 6.8 μM), and the volume was adjusted to 10 mL. Immerse the $P_2W_{15}V_3$@CNTs/GCE electrode in the solution for 8 minutes to enrich it, then measure using DPV, with three parallel measurements for each concentration.