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Sandwich nanohybrid of single-walled carbon nanohorns- TiO₂-porphyrin for electrocatalysis and amperometric biosensing toward chloramphenicol

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Experimental

Materials. Hydroxyferritoporphyrin (hematin, 98%) and chloramphenicol (99%) were purchased from Alfa Aesar China Ltd. (China). Single-walled carbon nanohorns (SWNHs) were kindly provided from Professor Sumio Iijima leading carbon nanotube project in Japan Science and Technology Agency. TiO₂ nanopowder (anatase, <25 nm, 99.7%) was purchased from Aldrich (USA). All other chemicals were of analytical grade. Aqueous solutions were prepared with twice-distilled water. 0.1 M phosphate buffer solution (PBS) was always employed as supporting electrolyte deaerated with high purity nitrogen. The pH value of PBS was 7.0 except those indicated.

Apparatus. X-ray photoelectron spectroscopic (XPS) measurements were performed with an ESCALAB 250 spectrometer (Thermo-VG Scientific, USA) with ultra-high vacuum generators. Transmission electron micrographs (TEM) were obtained using a JEM-2100 TEM (JEOL, Japan). Fourier-transform infrared spectra (FTIR) were obtained on a NEXUS 870 FTIR instrument (Nicolet, USA). Resonance

Raman spectra were recorded on a Renishaw-inVia Raman microscope (Renishaw, United Kingdom). Electrochemical impedance spectroscopic (EIS) measurements were carried out on a PGSTAT30/FRA2 system (Autolab, Netherlands) in 0.1 M KCl solution containing 5 mM $K_3[Fe(CN)_6]$ /5 mM $K_4[Fe(CN)_6]$. The impedance spectra were recorded in the frequency range of 10^{-2} – 10^5 Hz. The amplitude of the applied sine wave potential in each case was 5 mV. Cyclic voltammetric experiments were performed on a CHI 610C electrochemical workstation (CH Instruments Inc., USA), and amperometric experiments were performed on a CHI 812B electrochemical workstation (CH Instruments Inc., USA). All experiments were carried out at room temperature using a conventional three-electrode system with a modified glassy carbon electrode (GCE) as working, a platinum wire as auxiliary and a saturated calomel electrode as reference electrodes.

Preparation of SWNHs-TiO₂-porphyrin and modified GCEs. SWNHs were dispersed in 30% HNO₃ and then refluxed for 24 h at 140 °C to obtain carboxylic group functionalized SWNHs. The resulting suspension was centrifuged, and the sediment was washed with twice-distilled water until the pH reached 6.0. The oxidized SWNHs were dispersed in twice-distilled water to form a stable suspension with concentration of 2 mg mL⁻¹. Hydroxyferritoporphyrin was dissolved in 5 mL dimethyl sulphoxide (DMSO) to get a DMSO solution of 20 mM porphyrin. 100 mg TiO₂ nanoparticles were ultrasonically dispersed in 5 mL twice-distilled water to get a suspension of 20 mg mL⁻¹ TiO₂. Then, 5 mL DMSO solution of 20 mM porphyrin was added into 5 mL suspension of 20 mg mL⁻¹ TiO₂ with the aid of ultrasonic agitation to obtain a suspension of TiO₂-porphyrin, following with discarding the upper solution to remove free porphyrin. Further, 2 mL suspension of 2 mg mL⁻¹ SWNHs was added into 2 mL suspension of 10 mg mL⁻¹ TiO₂-porphyrin with the aid of ultrasonic agitation to produce a suspension of SWNHs-TiO₂-porphyrin. After discarding the upper solution, the resulting sediment was dispersed in water to obtain SWNHs-TiO₂-porphyrin suspension with concentration of 6 mg mL⁻¹.

The GCEs (3 mm in diameter) were polished to a mirror finish with 1.0 and 0.05 μm alumina slurry on chamois leathers, and then washed ultrasonically in absolute ethanol and twice-distilled water for two minutes respectively, dried at room temperature. Then 10 μL suspension of 6 mg mL⁻¹ SWNHs-TiO₂-

porphyrin was dropped on the GCE and dried at room temperature to obtain the SWNHs-TiO₂-porphyrin modified electrode. Similarly, TiO₂-porphyrin, SWNHs-TiO₂ and the modified GCEs were prepared in the absence of SWNHs and porphyrin, respectively.

O1s X-ray photoelectron spectra of porphyrin and SWNHs

The XPS characterization was performed to analyze the composition of porphyrin and SWNHs. The O1s XPS spectrum of porphyrin consists of two peaks assigned to carbon-oxygen double bonding (C=O, 532.3 eV) and single bonding (C-O, 533.7 eV) (Fig. S1a). These peaks could be produced by the oxidation treatment of SWNHs (C=O at 532.0 eV and C-O at 533.6 eV) (Fig. S1b).

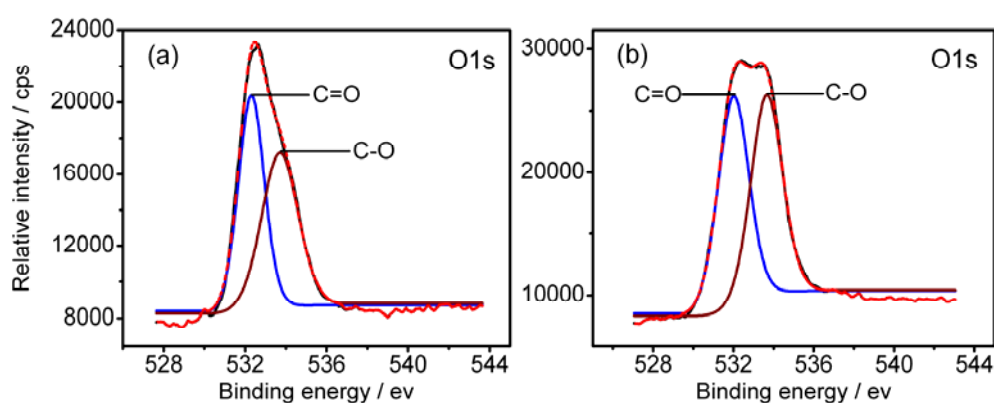


Fig. S1. O1s XPS spectra of porphyrin (a) and SWNHs (b).

FTIR spectra

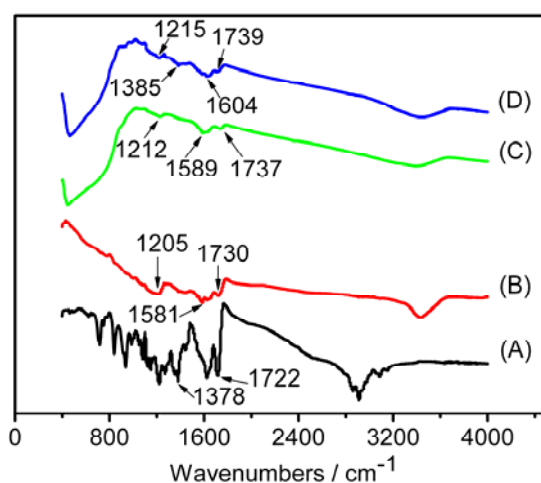


Fig. S2 FTIR spectra of porphyrin (A), SWNHs (B), SWNHs-TiO₂ (C), and SWNHs-TiO₂-porphyrin (D).

Raman spectra

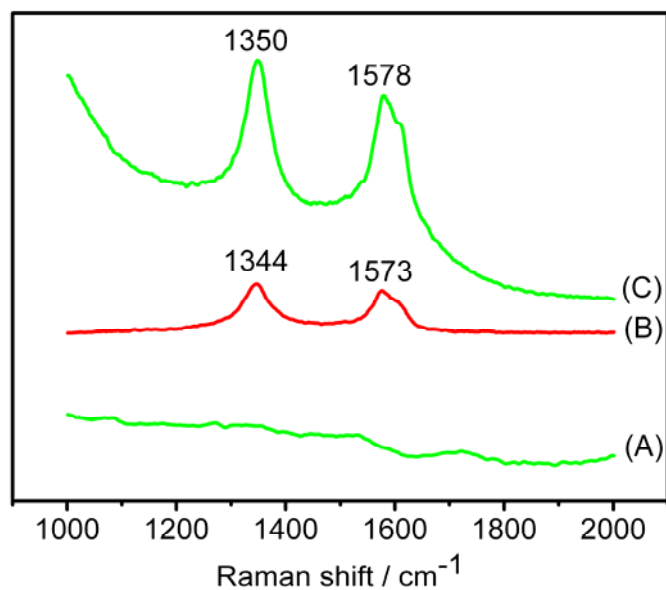


Fig. S3 Raman spectra of TiO₂ (A), SWNHs (B), and SWNHs-TiO₂ (C).

TEM characterization

The formation of SWNHs-TiO₂-porphyrin was further examined by transmission electron micrographs (TEM). The TEM images of SWNHs and SWNHs-TiO₂-porphyrin films demonstrated that TiO₂ stacked on the surface of SWNHs and the original dahlia-flower-like morphology of the SWNH aggregates was still sustained (Fig. S4). The average diameter of the flower like-hybrid material was estimated to be around 80 nm.

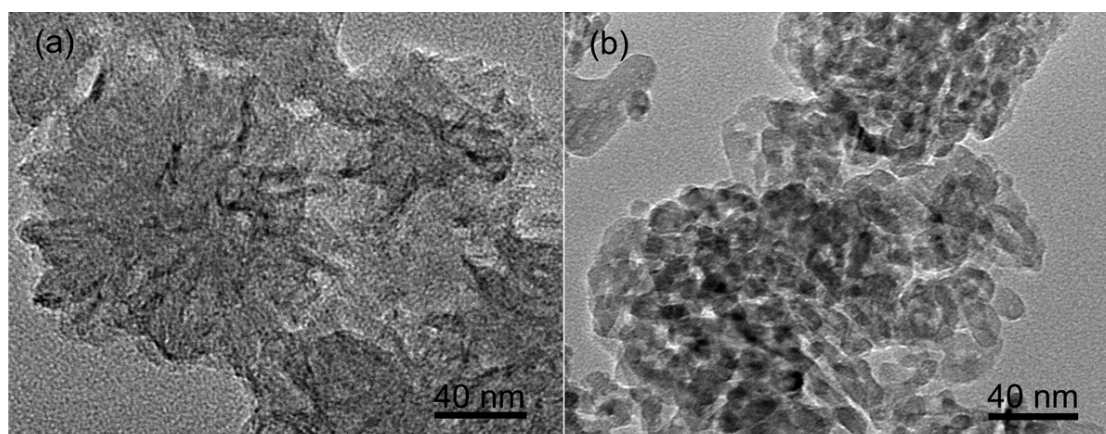


Fig. S4 TEM of SWNHs (a) and SWNHs-TiO₂-porphyrin (b).

Electrochemical behaviors of SWNHs-TiO₂-porphyrin modified GCE

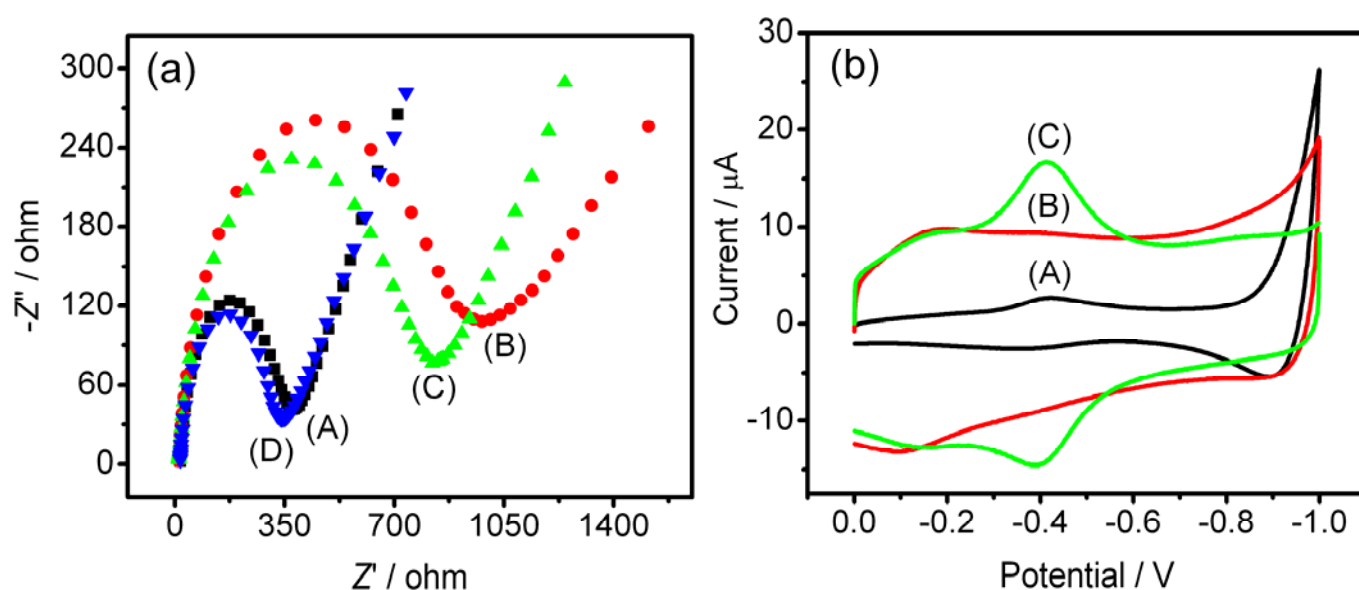


Fig. S5 Electrochemical impedance spectra of bare (A), porphyrin (B), TiO₂-porphyrin (C), SWNHs-TiO₂-porphyrin (D) modified GCEs in 0.1 M KCl solution containing 5 mM K₃[Fe(CN)₆]/5 mM K₄[Fe(CN)₆] (a) and cyclic voltammograms of TiO₂-porphyrin (A), SWNHs-TiO₂ (B), SWNHs-TiO₂-porphyrin (C) modified GCEs in 0.1 M pH 7.0 PBS at 100 mV s⁻¹ (b).

The reduction and oxidation peak currents of SWNHs-TiO₂-porphyrin modified GCE increased linearly with the scan rate in the range of 40–500 mV s⁻¹ (Fig. S6), while the difference of redox peak potentials showed slight increase, indicating a surface controlled electrode process. The redox peak potentials of porphyrin in the film showed strong dependence on the pH value of the external solution. With the increasing pH from 5 to 9, the formal potential, midpoint of reduction and oxidation potentials, exhibited a linear relationship with a slope of -48.9 mV pH^{-1} .

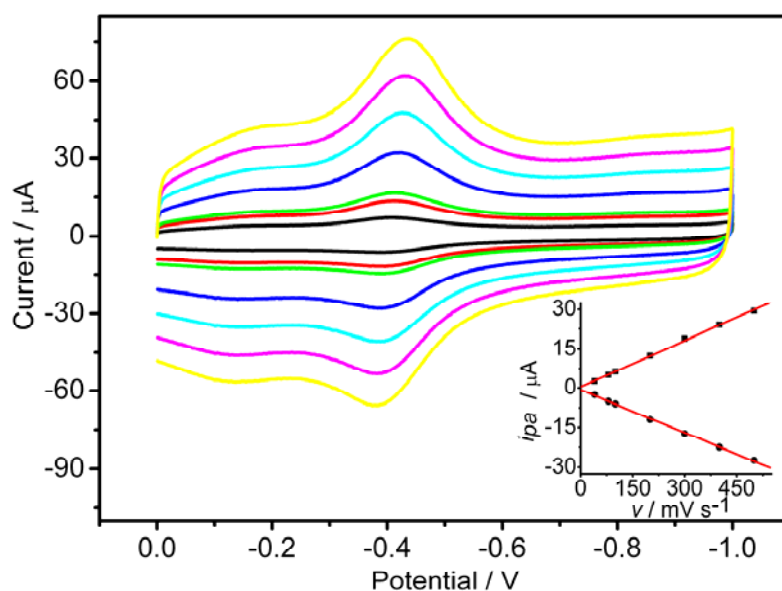


Fig. S6 Cyclic voltammograms of SWNHs-TiO₂-porphyrin modified GCE at 40, 80, 100, 200, 300, 400 and 500 mV s⁻¹ (from inner to outer) in 0.1 M pH 7.0 PBS. Inset: plots of oxidation and reduction peak currents vs. v .

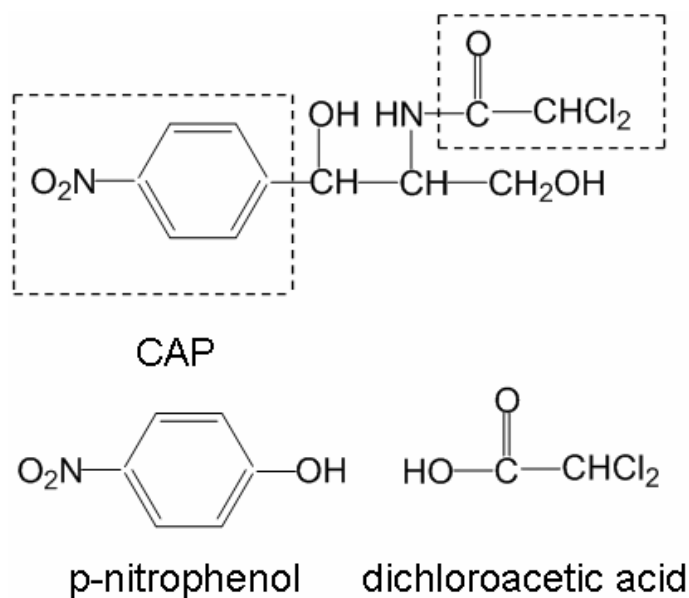


Fig. S7 Chemical structures of CAP, p-nitrophenol and dichloroacetic acid.

Effects of SWNHs and TiO₂ contents for preparation of SWNHs-TiO₂-porphyrin on electrocatalytic peak current

In Fig. S8(a), with the increasing SWNHs content the electrocatalytic current increased and then trended to a constant value, which was attributed to the excellent electric conductivity of SWNHs for accelerating the electron transfer between porphyrin and GCE and the electrocatalysis toward reduction of CAP. The saturation of SWNHs in the nanohybrid resulted in the plateau. Thus 1 mg mL⁻¹ SWNHs was chosen for the preparation of SWNHs-TiO₂-porphyrin nanohybrid.

TiO₂ content was also an important parameter for obtaining an optimal electrocatalytic response. As shown in Fig. S8(b), with the increasing TiO₂ content, the electrocatalytic current of CAP increased and reached a maximum value at 5 mg mL⁻¹. However, when the TiO₂ content was more than 10 mg mL⁻¹, the electrocatalytic current decreased because excessive TiO₂ nanoparticles slowed down the electron transfer in the electrocatalytic process. This work used 5 mg mL⁻¹ TiO₂ for the preparation of the nanohybrid.

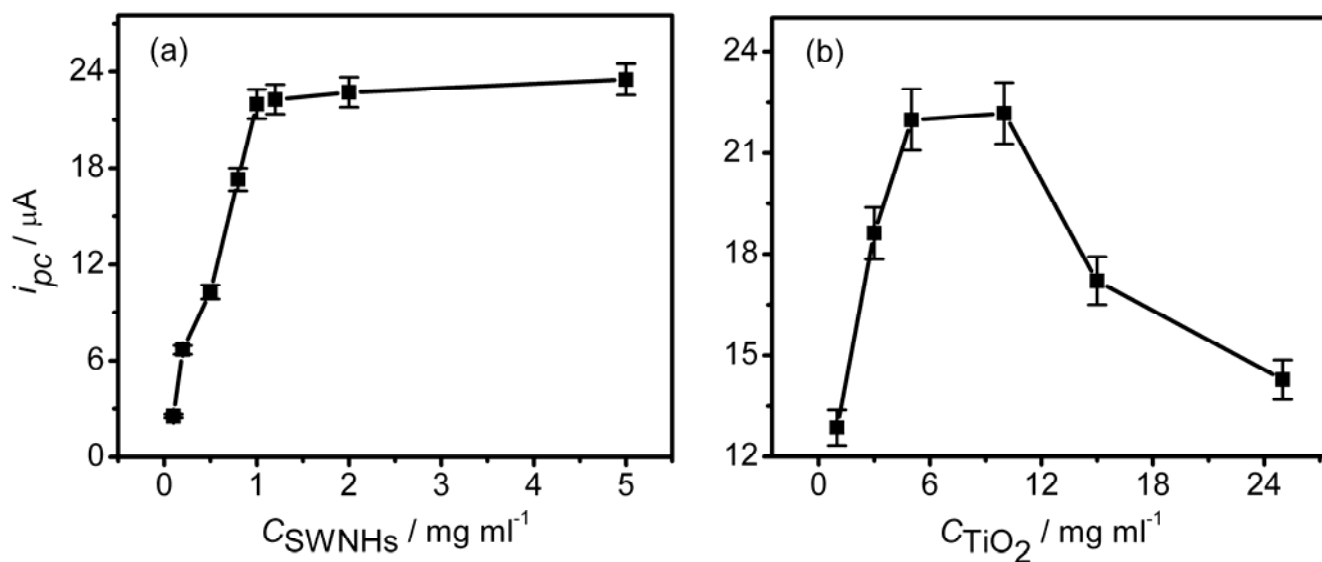


Fig. S8 Effects of SWNHs (a) and TiO₂ (b) for preparation of SWNHs-TiO₂-porphyrin nanohybrid on electrocatalytic peak current in 0.1 M PBS containing 100 μM CAP at 100 mV s⁻¹.

Amperometric response to CAP

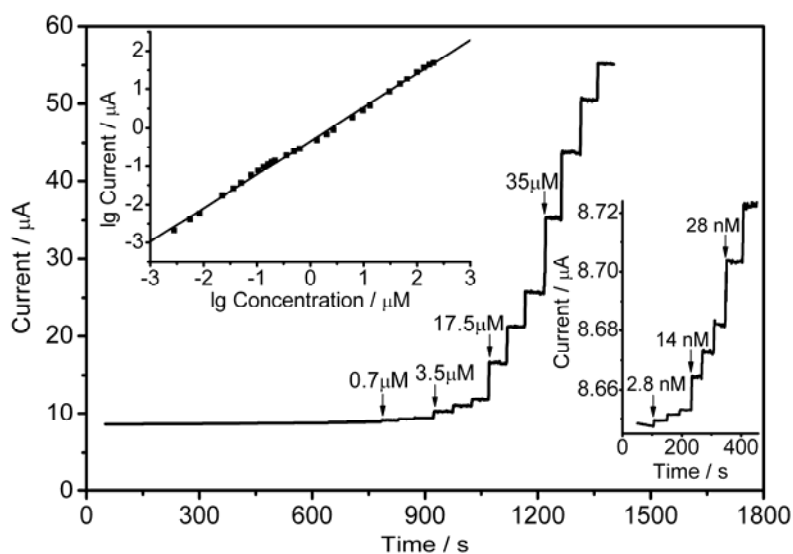


Fig. S9 Successive amperometric response of SWNHs-TiO₂-porphyrin modified GCE to CAP in 0.1 M pH 7.0 PBS at -0.56 V. Upper inset: calibration curve; lower inset: amplified response.

Stability of the sensor upon consecutive cyclic voltammetric sweep

In 0.1 M pH 7.0 PBS containing 50 µM CAP, the cyclic voltammogram of the sensor for consecutive fifty scans between 0 and -1.0 V showed acceptable stability of the sensor. The response of CAP at the fiftieth scan remained 94.1% of its initial response (Fig. S10).

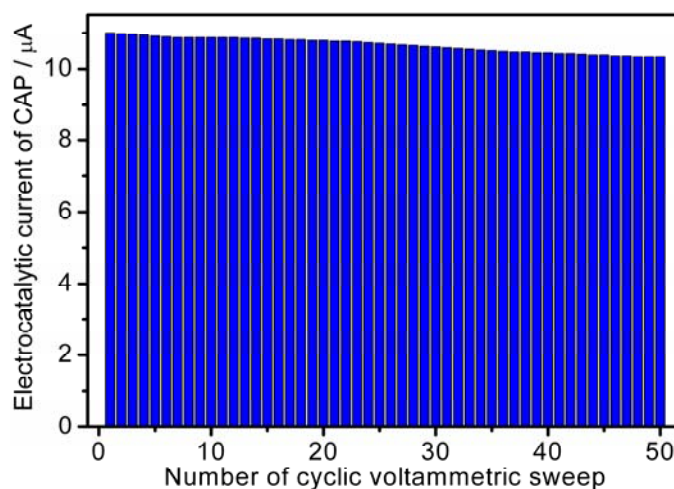


Fig. S10 Dependence of electrocatalytic peak current of 50 µM CAP at SWNHs-TiO₂-porphyrin modified GCE in 0.1 M pH 7.0 PBS on the number of cyclic voltammetric sweep at 100 mV s⁻¹.