Supporting Information to

Rapid and Sensitive Determination of Doxorubicin in Human Whole Blood by Vertically-Ordered Mesoporous Silica Film Modified Electrochemically Pretreated Glassy Carbon Electrodes

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Table of Content

S1. Characterization of the p-GCE

S1.1 Contact angle

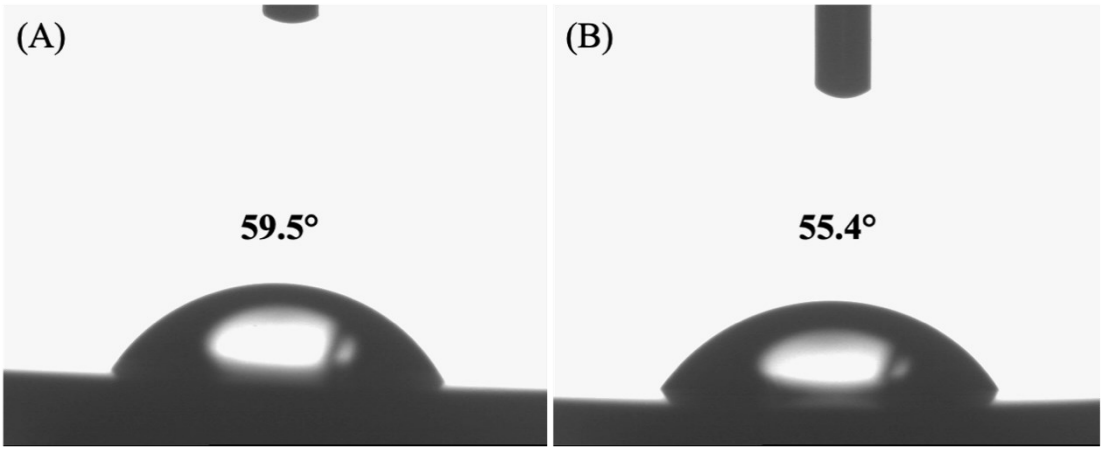

Figure S1 Contact angle images of the bare p-GCE (A) and VMSF/p-GCE (B).

S1.2 XPS

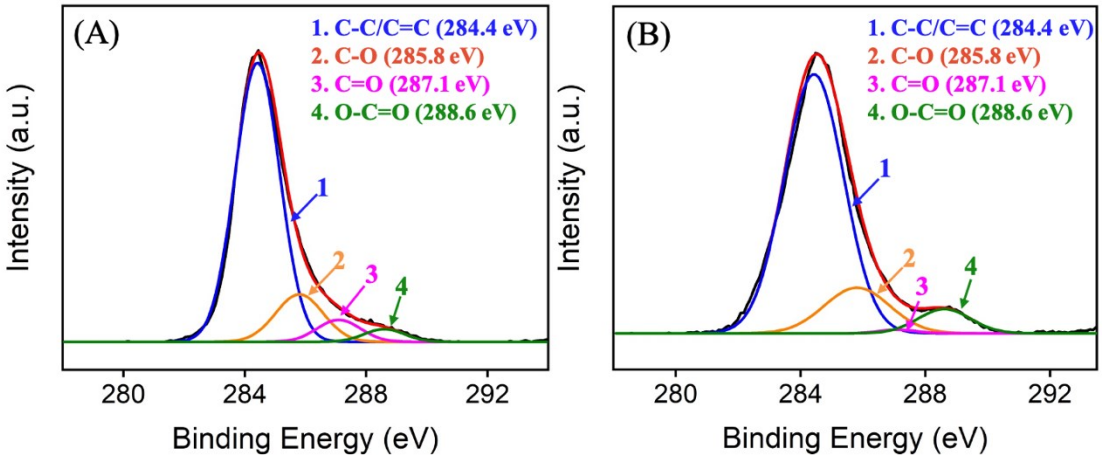

Figure S2 High-resolution XPS spectra for C1s of GCE (A) and p-GCE (B).

S2. Characterizations of the VMSF/p-GCE

S2.1 SEM

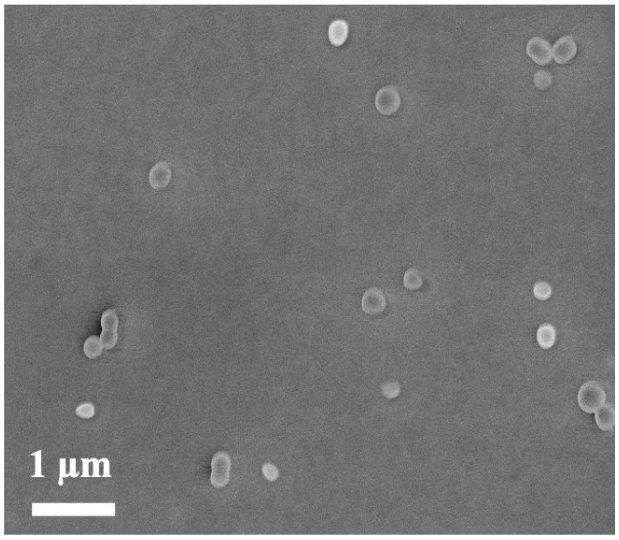

Figure S3 SEM of the VMSF/p-GCE.

S2.2 Electrochemistry

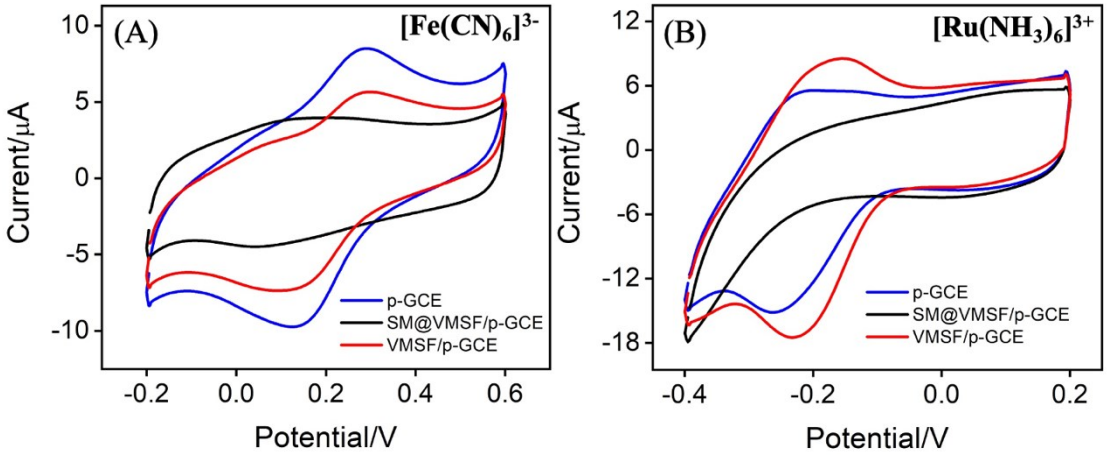

Figure S4 CV curves obtained from p-GCE, SM@VMSF/p-GCE and VMSF/p-GCE electrodes in (A) $[Fe(CN)_6]^{3-}$ and (B) $[Ru(NH_3)_6]^{3+}$ solution. The supporting electrolyte was 0.05 M KHP and the scan rate was 50 mV/s.

S3. Study of memory effect

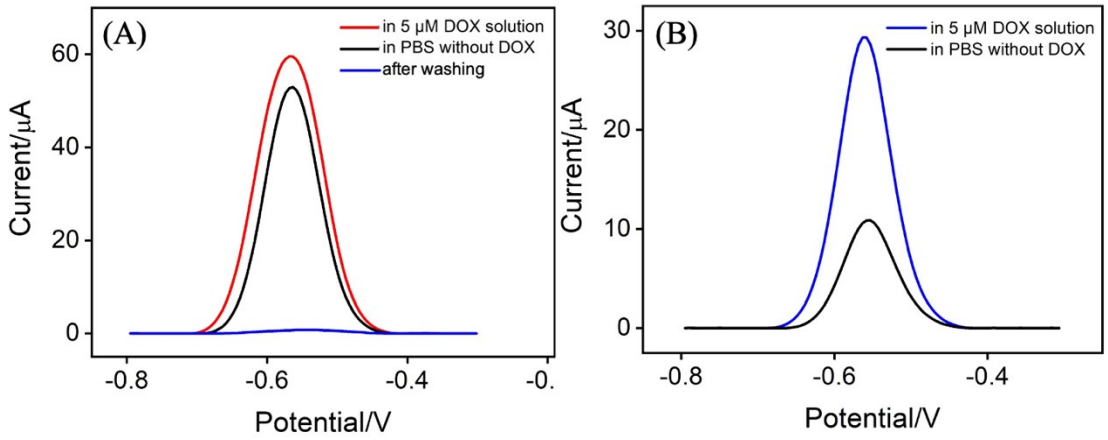

Figure S5 DPVs of the VMSF/p-GCE (A) and p-GCE (B) in 0.1 M PBS solution (pH 6.0) containing 5 μM DOX and their DPV responses in 0.1 M PBS solution (pH 6.0) after DOX measurement. After washing in (A) means the used VMSF/p-GCE was immersed into 0.1 M HCl-ethanol solution under stirring for 2 min.

S4. Optimized conditions for DOX detection

S4.1 pH of supporting electrolyte

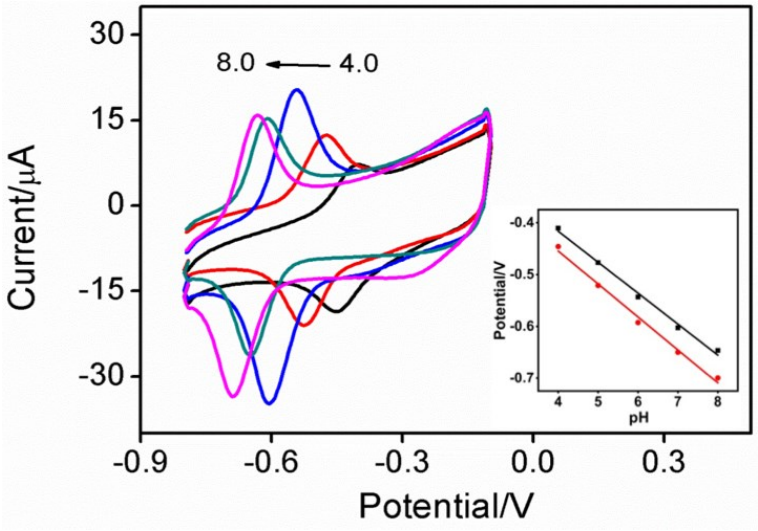

Figure S6 CVs of the VMSF/p-GCE in 0.1 M PBS solution containing 10 μM DOX at different pH values. Inset shows the dependence of cathodic peak potential (E_{pc}) and anodic peak potential (E_{pa}) on the pH value.

S4.2 Preconcentration time

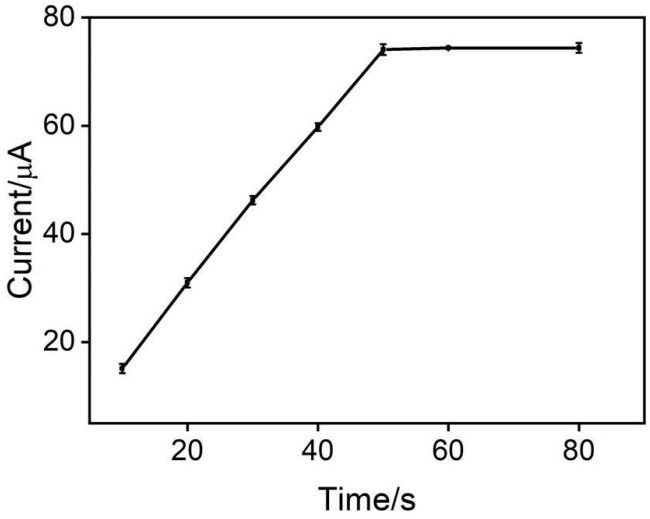

Figure S7 Influence of the stirring time on the current response in 0.1 M PBS solution (pH 6.0) containing 10 μM DOX. The error bars represent the standard deviation of three measurements.

S5. DPVs of DOX in PBS

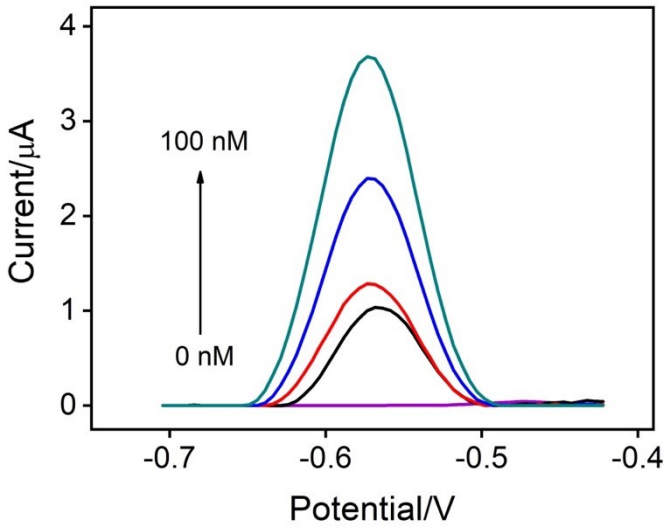

Figure S8 DPV curves of VMSF/p-GCE in 0.1 M PBS solution (pH 6.0) containing DOX ranging from 0 nM to 100 nM. The concentration of DOX were 0 nM, 0.5 nM, 10 nM, 50 nM and 100 nM.

S6. DPVs of DOX in human whole blood

S6.1 bare GCE

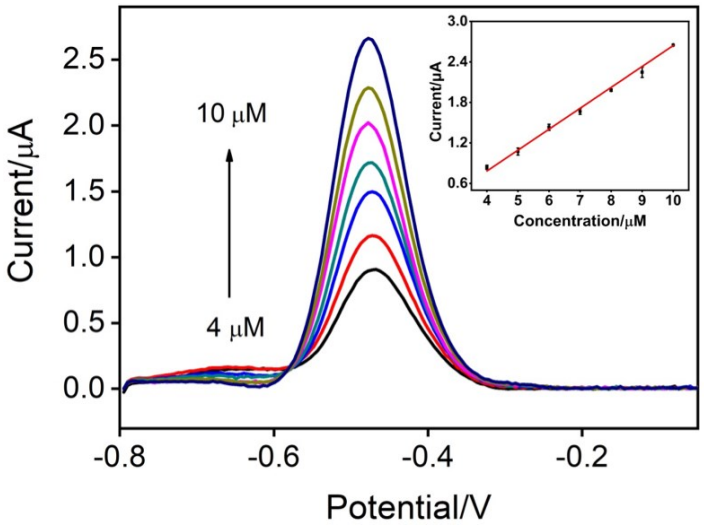

Figure S9 DPV curves of bare GCE in 50-times diluted human whole blood sample containing various concentrations of DOX ranging from 4 μM to 10 μM. The inset is the calibration curve and the error bars represent the standard deviation of three measurements.

S6.2 p-GCE

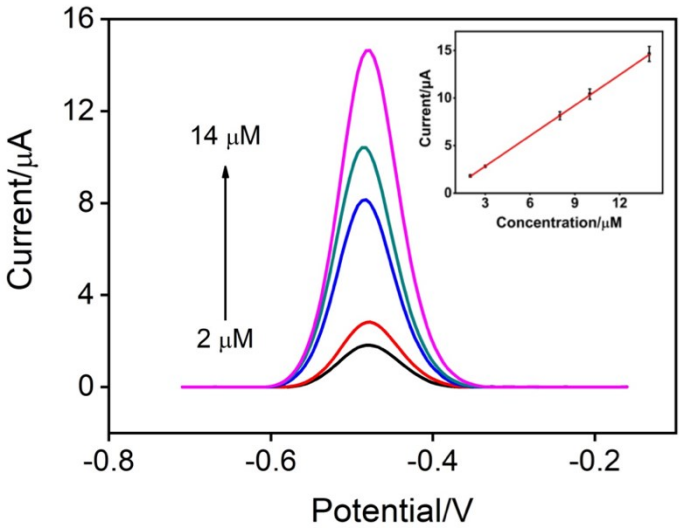

Figure S10 DPV curves of p-GCE in 50-times diluted human whole blood sample containing various concentrations of DOX ranging from 2 μM to 14 μM. The inset is the calibration curve and the error bars represent the standard deviation of three measurements.

S6.3 Comparison of various electrodes for electrochemical detection of DOX

Table S1. Comparison of various electrodes for electrochemical detection of DOX in human whole blood.

Electrode	Range (μM)	Sensitivity (μA/μM)	LOD (nM)	R
VMSF/p-GCE	0.0005–2 2–20	20.32 2.696	0.3	0.9910 0.9996
p-GCE	2–14	1.067	400	0.9994
bare GCE	4–10	0.3097	500	0.9973