Supporting Information

Hierarchical core-shell structure of 2D VS_2@VC@N-doped carbon sheets decorated by ultrafine Pd nanoparticles: assembled in 3D rosette-like array on carbon fiber microelectrode for electrochemical sensing

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EXPERIMENTAL SECTION

Reagents

CFs (diameter ~10 μm and length 2.5 cm) were purchased from Fuel Cell Earth, USA). Sodium orthovanadate (Na_3VO_4), thioacetamide (C_2H_5NS), potassium tetrachloropalladate (K_2PdCl_4), hydrogen peroxide (H_2O_2), N-formylmethionyl-leucyl-phenyl-alanine (fLMP, ≥99.5%), catalase (come from bovine liver, Lyophilized, ≥3000 units mg^{-1}), uric acid (UA), dopamine hydrochloride (DA, 98%), L-ascorbic acid (AA), tris(hydroxymethyl) aminomethane (Tris, 99.8%), chemotherapeutic agent cisplatin

(DDP) were obtained from Sigma-Aldrich Co., Ltd (USA). Dulbecco's modified eagle's medium (DMEM), fetal bovine serum (FBS), trypsine-EDTA (0.25%) and penicillinstreptomycin were purchased from HyCl one (Waltham, USA). All other chemicals used were of analytical reagent grade. All solutions were prepared using deionized water (resistivity: 18.25 Ω cm^{-1}). For electrochemical experiments and cell testing, 0.1 M phosphate buffer saline (PBS, pH 7.4) solution consisting of KH_2PO_4 and K_2HPO_4 was used as the electrolyte.

Characterizations

SEM and TEM images were obtained on a field-emission SEM instrument (FEI, Nova NanoSEM 450) and TEM instrument (FEI, Tecnai G220). XRD pattern was obtained by diffractometer (X'Pert PRO, Panalytical B.V., Netherlands) using a Cu Kα radiation source (λ=1.5406 Å). XPS was carried out *via* a Kratos-Axis spectrometer with monochromatic Al-Kα (1486.71 eV) X-ray radiation. All the electrochemical experiments were performed with a CHI 660E electrochemical workstation (Shanghai CH Instruments Co., China) using a conventional three-electrode system. The working electrode is the nanohybrid microelectrode, the reference electrode is Ag/AgCl electrode, and the counter electrode is a platinum wire. To examine the cells statues, the fluorescence microscope (Olympus BX41F, Japan) equipped with a DP73 camera was adopted under different light wavelength. The software cellSens standard 1.7 (Olympus, Japan) was taken for gaining images.

Biological Samples

For electrochemical test of live cells, three types of living human breast cells, *i.e.,* human breast epithelial cell HBL-100, and breast cancer cell MCF-7 and MBA-MD-231, were obtained from the American Type Culture Collection (ATCC, Manassas, VA, USA) and used for detecting extracellular release of H_2O_2. The cells were maintained in a culture medium DMEM containing 10% FBS and penicillin (1%), and grown under a humidified atmosphere with 5% CO_2 at 37 ℃ and subcultured every 3 days. After the growth of ~80% confluence, the cells were collected by centrifugation and used for the electrochemical experiments. The clinical specimen of human primary breast tumor was received within

two hours after surgery from a 54-year-old female patient with primary breast cancer at Union Hospital of Huazhong University of Science & Technology (HUST). The surgically resected specimen was a breast cancer tissue enclosed within adipose tissue. By carefully dissecting the adipose tissue, the breast cancer tissue was obtained, which was washed with PBS solution for several times and soaked in PBS solution at 37 ℃ for electrochemical testing.

Electrochemical Analysis of Live Cells and Clinical Cancer Tissue

For real-time tracking H_2O_2 secreted from live cells, the VS_2@VC@NC-PdNPs/CF microelectrode was carefully placed into the testing well containing live cells and located at the edge of the cells. For *in situ* sensitive monitoring of H_2O_2 level in breast cancer tissue, the microelectrode was inserted inside the tissue by a micromanipulator under the microscope. To irritate the live cells to release H_2O_2, 0.05 mM fMLP was added into live cells or a segment of breast cancer tissue by syringe, and the amperometric current density originated from H_2O_2 secreted by live cells was recorded.

Computational Method

All calculations were performed by using DFT integrated in the CASTEP model in Materials Studio of Accelrys Inc. The electron exchange and correlation effects were described by the Perdew-Burker-Ernzerhof (PBE) method along with the generalized gradient approximation (GGA) type exchange correlation function.[1-3] Typically, the wave functions at each k-point were expanded with a plane wave basis set and a kinetic cutoff energy up to 400 eV, the k-point mesh was set to 1 × 1 × 1 and fermi smearing was adopted. The geometries were optimized until the energy was converged to 2×10^{-6} eV/atom while the pseudopotentials and pseudopotential representation was set as ultrasoft and reciprocal space, respectively.

The model of VC, VS_2 and VC-VS_2 were constructed and sealing the rim of all atoms to form the structures. The lattice detail of VC: lengths (Å): a = 2.939592, b = 2.939592, c = 11.200084; The lattice detail of VS_2: lengths (Å): a = 14.368629, b = 5.808105, c = 6.499383; The lattice detail of VC-VS_2 was set as: lengths (Å): a = 14.468745, b = 5.740783, c = 6.58077. In all structural optimization calculations,

the positions of all the atoms were allowed to relax.

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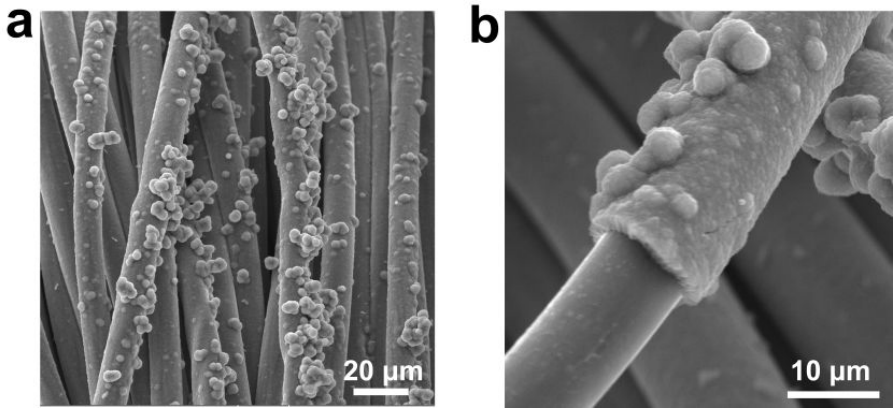

Figure S1 (a) and (b) SEM images of VS_2/CF microelectrode under different magnification. VS_2/CF microelectrode was prepared using VS_2 precursor concentration as low as half of the optimized one.

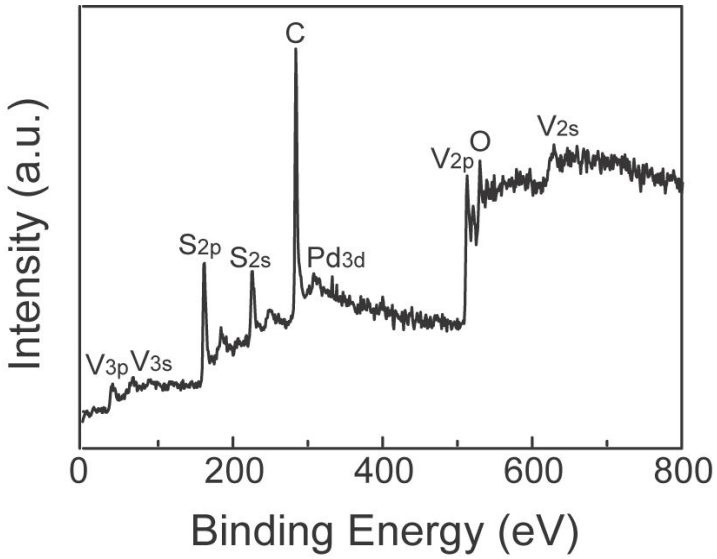

Figure S2 XPS survey spectrum of VS_2@VC@NC-PdNPs/CF.

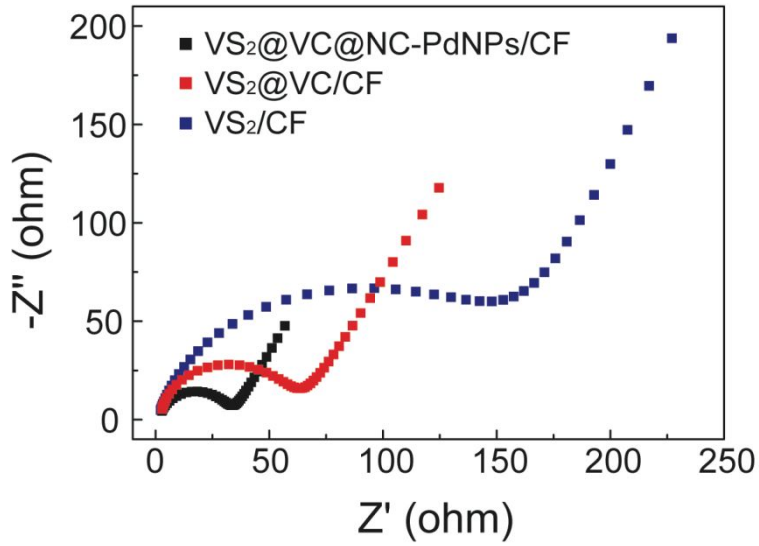

Figure S3 Nyquist plots of VS_2@VC@NC-PdNPs/CF, VS_2@VC@NC/CF and VS_2/CF in 0.1 M KCl solution containing 1.0 mM $K_3Fe(CN)_6$ and 1.0 mM $K_4Fe(CN)_6$.

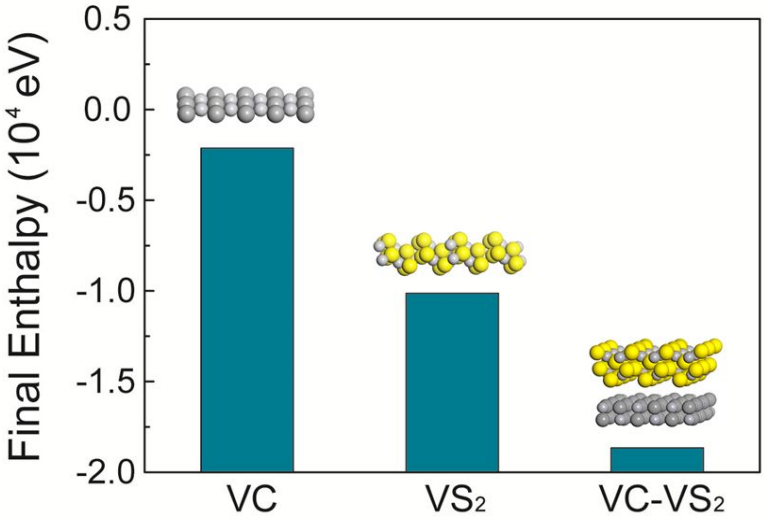

Figure S4 Inset is the total final enthalpy of VC, VS_2 and VC-VS_2 species.

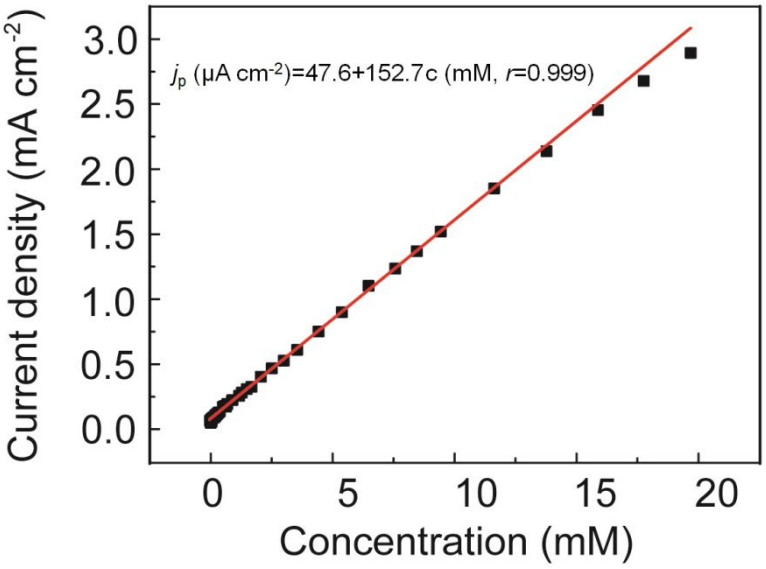

Figure S5 (a) Calibration plot of the amperometric current-time responses of VS_2@VC@NC-PdNPs/CF microelectrode to the successive addition of H_2O_2 with different concentrations from 0.1 μM to 20 mM.

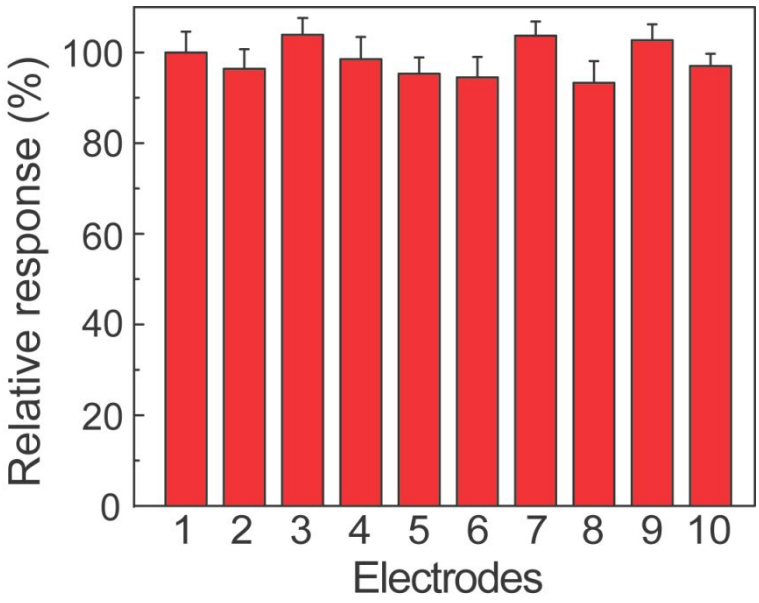

Figure S6 Relative current response of ten different VS_2@VC@NC-PdNPs/CF microelectrodes to 0.1 mM H_2O_2 in 0.1 M PBS solution (pH 7.4).

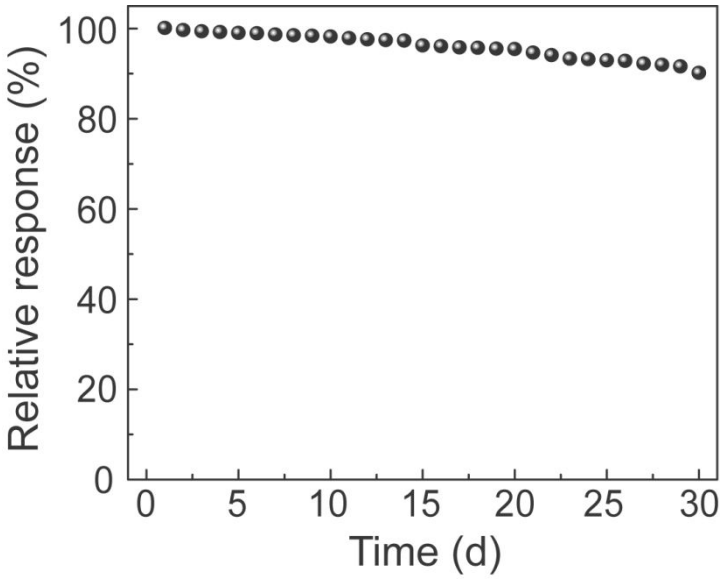

Figure S7 Variation of the relative response current of the VS_2@VC@NC-PdNPs/CF microelectrode to 0.1 mM H_2O_2 in 0.1 M PBS solution (pH 7.4) with time.

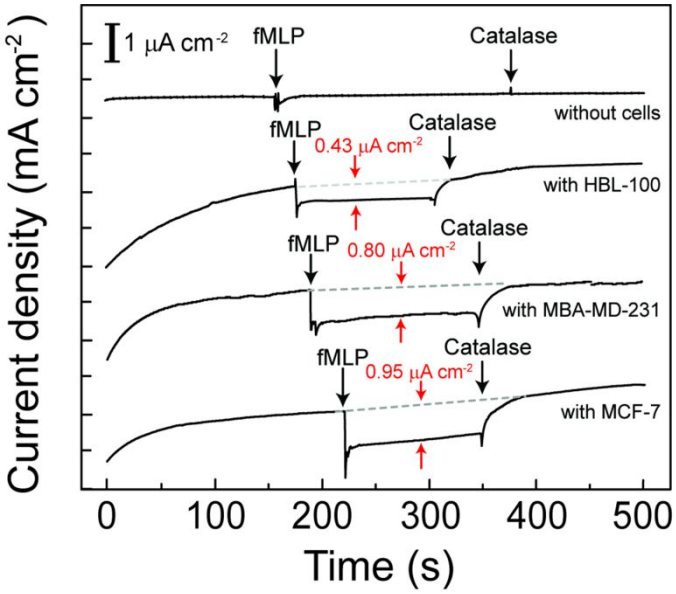

Figure S8 Amperometric responses of VS_2@VC@NC-PdNPs/CF microelectrode to the addition of 0.05 mM fMLP and 500 U/mL catalase in tested well with MCF-7, MDA-MB-231, HBL-100 cells, and without cells.

Table S1 The analytical performances of various nanomaterials based electrochemical sensors for detecting H_2O_2.

Electrode materials	Detection limit (nM)	Linear range (μM)	Sensitivity ($\mu A\ mM^{-1}\ cm^{-2}$)	Ref.
VS_2@VC@NC-PdNPs/CF	50	0.1~17.684	152.7	This work
MNPs@anionicMOFs/ERGO	180	4~11000	80.23	1
Ultrathin concave Ag nanosheets	170	5-6000	320.3	2
Gold nanoparticles decorated MnO_2/graphene-carbon nanotubes	100	0.4~626.8 686~1226	452	3
Ni foam-supported ZnO nanowires and $Co_3O_4/NiCo_2O_4$ double-shelled nanocages	163	0.2~2400	388	4
Co nanoparticles embedded nitrogen-doped mesoporous carbon composites	143	1~30000	234.913	5
AuPd alloy nanoparticles decorated graphene quantum dots assembly	500	1~18440	371	6
Tellurium nanoparticles	28400	100-500	757	7
Silver-iron hierarchical microflowers	100	up to 20000	1.35	8
Pt nanoparticles-carbon quantum dots/ionic liquid functionalized graphene oxide nanocomposites	100	1~900	-	9
Graphene blended with SnO_2 and Pd-Pt nanocages	300	1~300	-	10
Microporous Ni-metal organic framework material-carbon paste electrode	900	4~60000	-	11
Polyoxometalate-based metal–organic	1030	10~50	-	12

framework				
Hollow CuO/PANI fibers	110	5~9255	-	13
Based-stable chromium (III) dicarboxylate metal–organic framework	3520	25~500	-	14
Silica-MnO_2hybrid films electrodeposited on the surface of planar electrodes	15000	25~1000	-	15

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Table S2 Influence of foreign species on the determination of 0.1 mM H_2O_2 in 0.10 M PBS solution containing 0.5 mM interferents by VS_2@VC@NC-PdNPs/CF microelectrode.

foreign species	Change of current response (%)	RSD (%) (*n* =6)
glycine	3.6	3.5
leucine	-3.9	2.6
valine	2.5	4.3
tryptophan	4.6	3.6
phosphotyrosine	-2.7	1.7
glutamine	-3.2	4.2
cysteine	3.8	2.5
adenine	-5.0	3.8
guanine	4.2	2.9
xanthine	3.4	3.1
hypoxanthine	2.7	3.8
glucose	-3.2	2.5
fructose	4.4	4.0
Na^+	-3.8	3.7
K^+	1.7	4.4
Ca^{2+}	2.4	3.5
Mg^{2+}	3.2	2.0
Al^{3+}	-2.8	4.8
Zn^{2+}	4.2	3.5
CO_3^{2-}	3.6	3.4
SO_4^{2-}	-2.1	3.0
PO_4^{3-}	-4.5	2.2
Cl^-	3.5	4.5