†Electronic Supplementary Information (ESI†)

Core-Shell TiC/C Quasi-Aligned Nanofiber Arrays on Biomedical Ti6Al4V for Sensitive Electrochemical Biosensing

Liangsheng Hu[a], Kaifu Huo*[a,b], Rongsheng Chen[a], Xuming Zhang[a], Jijiang Fu[a] and Paul K Chu*[b]

[a] *School of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China. E-mail: kfhuo@wust.edu.cn or kaifuhuo@cityu.edu.hk*

[b] *Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China. E-mail: paul.chu@cityu.edu.hk*

Experimental

Fabrication and Characterization of the TiC/C-QANFAs:

Titanium alloy (Ti6Al4V) foils (10 x 10 x 1 mm^3, Goodfellow) were degreased ultrasonically in acetone and ethanol sequentially, followed by polishing in a solution containing H_2O, HF and HNO_3 at a volume ratio of 5:1:4 for 5 min to remove the surface native oxide. After rinsing with double-distilled water and drying under flowing nitrogen, the Ti6Al4V foil was loaded onto a ceramic substrate placed at the center of an alumina tube in a horizontal tube furnace. The reactor was purged with pure argon several times to remove residual oxygen and/or moisture before being heated to 800 °C under Ar. Acetone was subsequently introduced into the chamber together with argon at a flow rate of 150 sccm. The thermal chemical reaction was conducted for 90 min at 800 °C and then the furnace was gradually cooled to room temperature under Ar.

The samples were characterized by XRD (Philips X' Pert Pro), FE-SEM (FEI Nova 400 Nano), TEM and HR-TEM (JEOL JEM-2100), and Raman spectroscopy (Renishaw 2000).

Electrochemical and biosensing evaluation:

The electrochemical measurements were performed in a conventional three-electrode system. The TiC/C-QANFAs grown on the Ti alloy foil were insulated with epoxy resin leaving an open area of 6 x 6 mm^2 as the working electrode. An Ag/AgCl electrode served as the reference electrode and a Pt wire was the counter electrode. A 3 mm diameter GCE was polished with 1, 0.3, and 0.05 μm alumina slurry and then ultrasonically cleaned with ethanol and double-distilled for comparison purposes. All the electrochemical experiments were carried out on a CHI660c potentiostat (CH Instruments Inc. Shanghai, China). The redox system used in the evaluation of ET kinetics consisted of $K_3Fe(CN)_6$ (1 mM) dissolved in a 1 M KCl solution. In the electrocatalytic and biosensing study, the phosphate buffer solution (PBS, 0.1 M) was prepared by dissolving NaH_2PO_4 and Na_2HPO_4 in doubly-distilled water and the pH value was adjusted to 7.4 by adding H_3PO_4 and NaOH.

Simultaneous and selective determination of AA, DA, and UA:

AA, DA, and UA are simultaneously and selectively determined from the mixture by DPV. In each experiment, the concentration of one of the three compounds is changed while the other two are kept constant. The results are shown in Fig. S3a-c. Fig. 3a shows the DPV curves at the TiC/C-QANFAs electrode in a PBS (0.1 M, pH = 7.4) containing 0.1 mM DA, 0.1 mM UA, and different concentrations of AA from 100 to 2500 μM. No obvious change in the DA and UA oxidation currents can be observed when the AA concentration is increased. The AA peak current ($I_{P\text{-}AA}$) increases linearly with the concentration (C_{AA}) and the linear regression equation can be expressed as $I_{P\text{-}AA}(\mu A) = 1.1415+0.0079C_{AA}$ (μM) with a correlation coefficient of 0.9946 (Fig. S3a). Various DA concentrations in the presence of 1 mM AA and 0.1 mM UA in a PBS (0.1M, pH = 7.4) also lead to excellent DPV response. The DA peak current is proportional to the DA concentration in the range of 1-120 μM, whereas the UA and AA peaks remain unchanged (Fig. S3b). The linear regression equation of the peak current versus DA concentration is $I_{P\text{-}DA}(\mu A) = -0.0222 + 0.0692C_{DA}$ (μM) with a correlation coefficient of 0.9994. The influence of AA and DA on the oxidation of UA is also investigated by DPV. No obvious interference can be observed from the DA and AA peak currents when the UA concentration is altered (Fig. S3c). The UA peak current peak current $I_{P\text{-}UA}$ (μA) depends linearly on the UA concentration in the range of 1-120 μM. The resulting equation is $I_{P\text{-}UA}(\mu A) = -0.10638+0.0604C_{UA}$ (μM) and the correlation coefficient is 0.9991. These results clearly demonstrate that the electrochemical oxidation of AA, DA, and UA is independent of each other. The highly sensitive and selective TiC/C-QANFAs electrode offers simultaneous determination of AA, DA, and UA in a mixture.

Keywords: titanium carbide. carbon. nanofiber arrays. dopamine. ascorbic acid. uric acid. electrochemical biosensing.

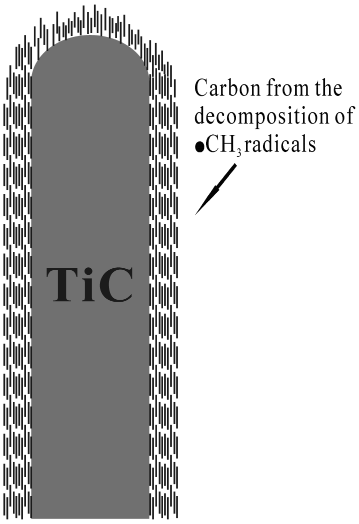

Fig. S1. The schematic illustration of the as-prepared cores-shell nanofiber.

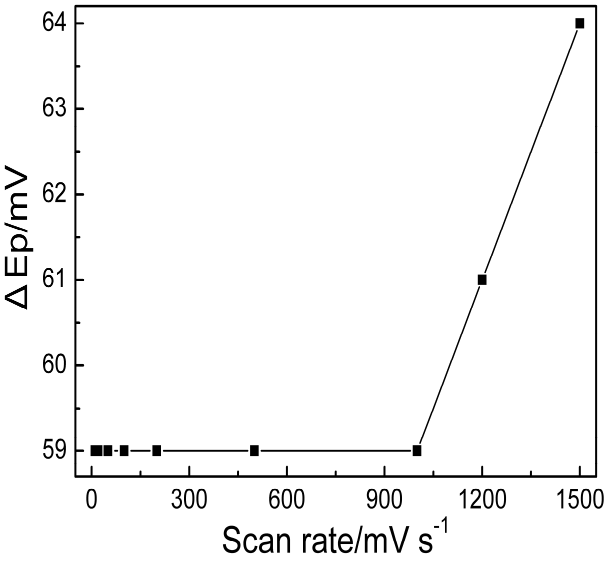

Fig.S2. The plot of ΔE_p vs. scan rates.

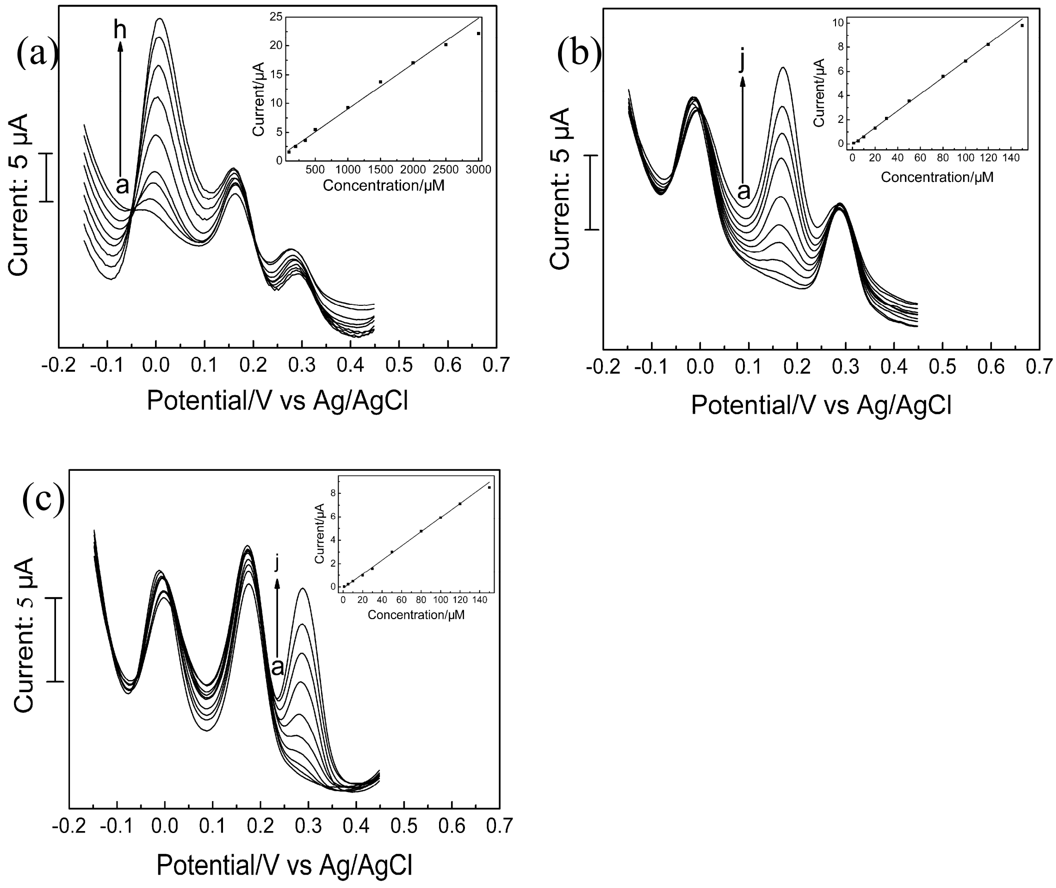

Fig. S3. DPVs at TiC/C-QANFAs electrode in PBS (0.1 M, pH = 7.4): (a) 0.1 mM DA, 0.1 mM UA, and different concentrations of AA (from a to h): 100, 200, 350, 500, 1000, 1500, 2000, 2500 and 3000 μM; (b) 1 mM AA, 0.1 mM UA, and various concentrations of DA (from a to j): 1, 5, 10, 20, 30, 50, 80, 100, 120 and 150 μM, and (c) 1 mM AA, 0.1 mM DA, and different concentrations of UA (from a to j): 1, 5, 10, 20, 30, 50, 80, 100, 120 and 150 μM. The insets are the corresponding calibration curves of the peak currents of AA, DA, and UA. Pulse width = 0.2 s, amplitude = 0.05 V, sample period = 0.0167 s and, pulse period = 0.5 s.

Thermodynamics calculation[S-1] was conducted to study for the formation of TiC under the experimental conditions as following reations:

$Ti + 2Al + 5CO \rightarrow TiO_2 + Al_2O_3 + 5C$ $\Delta_r G_m = -1173.71$ kJ mol^{-1} (Reaction S1)

$3Ti + 2Al + 3CO \rightarrow 3TiC + Al_2O_3$ $\quad \Delta_r G_m = -1306.44\ kJ\ mol^{-1}$ (Reaction S2)

References

S-1. I. Barin and G. Platzki, *Thermochemical data of pure substances*, VCH, New York, 1995.