

Electronic Supplementary Information

Ordered Mesoporous Carbon Covered Carbonized Silk Fabrics for Flexible Electrochemical Dopamine Detection

Experimental

Materials: Phenol, formaldehyde, disodium hydrogen phosphate and sodium dihydrogen phosphate were purchased from Sinopharm Chemicals Reagent Co., Ltd. Dopamine, ascorbic acid, uric acid, glucose, and triblock copolymer F127 were purchased from Sigma-Aldrich Co., Ltd. Silk fabrics were purchased from SAMSILK Co., Ltd. All the reagents (analytical grade) were used as received without further purification. Phosphate buffer solution (PBS, pH = 7.0, 0.1 M) was made from disodium hydrogen phosphate and sodium dihydrogen phosphate. Deionized water was used in all the experiments unless further mentioned.

Synthesis of the flexible OMC/CSF electrodes: First, CSFs were prepared by the carbonization of commercially available nature silk fabrics at 750 °C in nitrogen atmosphere for 2 h. On the other hand, resol-F127 monomicelles were prepared by self-assembly of resol molecules and triblock copolymer Pluronic F127 in weak alkaline aqueous solution. Typically, phenol (0.6 g) was melted at 40 °C and added in the aqueous solution of NaOH (15 mL, 0.1 M) with stirring. The aqueous solution of formaldehyde (2.1 mL, 37 wt%) was then added and the mixture was continuously stirred at 70 °C for 0.5 h to prepare low-molecular-weight phenolic resols. Afterwards, the

aqueous solution of F127 (15 mL, 6 wt%) was added and stirred at 70 °C for another 2 h. After the dilution with water (50 mL), the solution was stirred at 67–70 °C for about 12 h to produce the aqueous solution of resol-F127 monomicelles. To fabricate the OMC/CSF composites, as-prepared resol-F127 monomicelles (7 mL) was diluted with water (30 mL) and then transferred to a Teflon lined autoclave. A piece of CSF (5 cm × 5 cm) was immersed into the solution and kept for 2 h. After that, the autoclave was heated at 130 °C for 20 h. After that, the resulting fabric was washed with water and carbonization at a certain temperature (600, 750 and 900 °C) in nitrogen flow to produce the corresponding OMC/CSF composites.

Structural characterization: The field emission scanning electron microscopy (FE-SEM) were acquired on a Zeiss Ultra Plus field Emission Scanning electron microscope. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2010F (JEOL, Japan) with an accelerating voltage of 200 kV. Fabric for cross-sectional TEM analysis were embedded in epoxide resin and then cut by an ultra-cut microtome with a diamond knife. The obtained slices were supported on a carbon-coated copper grid. The SAXS measurements were performed on the BL16B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The energy of the X-rays was set to 12 keV and the image acquisition time was 30 s. The d spacing values were calculated using the formula $d = 2\pi/q$, where $q = 4\pi(\sin \theta)/\lambda$. The powder-like samples were held in evacuated 1 mm capillaries. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder Diffractometer (Bruker, Germany) using Cu K α radiation (40 kV, 35 mA) at the scan rate of 5° min⁻¹ from 10° to 80° (2 θ). Raman spectra were

recorded on a Senterra R200-L (Bruker Optics, Germany) with the excitation from the 532 nm line of an Ar-ion laser (5 mW). The X-ray photoelectron spectra (XPS) were obtained on ESCALAB 250Xi instrument using a monochromatic Al *Ka* X-ray source.

Electrochemical characterization: All the electrochemical measurements were carried out using a CHI 660E electrochemical workstation in a three-electrode system with PBS (pH = 7.0, 0.1 M) was used as the aqueous electrolyte, platinum wire as the counter electrode, and saturated calomel electrode as the reference electrode. To fabricate the flexible electrodes for DA detection, the OMC/CSFs were connected with copper wire by silver paste and then wrapped by epoxy resin, leaving an active area of 1 cm x 1 cm.

The electrochemical active surface areas (ECSAs) of the flexible OMC/CSFs were obtained according to the double-layer capacitance (C_{dl}) calculated from their cyclic voltammogram (CV) curves. The CV curves were scanned from 10 to 200 mV s^{-1} in the range from 0.10 to 0.20 V vs SCE where no faradaic currents exists. The capacitive currents of $\Delta J (J_{anodic} - J_{cathodic})$ are plotted as a function of the scan rate. The slope of the fitting line is found to be equal-to-twice the double-layer capacitance. The following formula was used to calculate the ECSA:

$$\text{ECSA} = C_{dl}/C_s \quad (\text{Equation S1})$$

For a flat surface, the specific capacitance (C_s) is generally in the range of 20 ~ 60 $\mu\text{F cm}^{-2}$. Therefore, 20 $\mu\text{F cm}^{-2}$ was used here for the calculation of ECSA.¹

The detection limit (LOD) of the OMC/CSF-750 based DA sensor was calculated according to a literature reported equation^{2,3}:

$$\text{LOD} = S/N \times S_b / m \quad (\text{Equation S2})$$

In this equation, S/N is signal-to-noise ratio, S_b refers to the blank standard deviation and m is the slope of calibration curve. Generally, S/N is selected as 3. In the case of the OMC/CSF-750 based DA sensor, S_b is $9.374 \times 10^{-3} \mu\text{A}$, which is the standard deviation of current values within 100 seconds before the injection of DA. According to the linear calibration curve of $i-t$ currents versus the concentration of DA (Figure 5d), m is $0.258 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$. Therefore, the LOD of the OMC/CSF-750 based DA sensor is calculated as $0.11 \mu\text{M}$.

The detection ability of the OMC/CSF-750 based sensor towards DA in real sample was evaluated in human serum (Abbkine Scientific Co., Ltd) using the standard addition method.^{4,5} Typically, human serum was diluted 100 times with PBS buffer solution (pH = 7) and a certain amount of DA was then added to the solution. In order to ascertain the correctness of the results, two types of samples with the DA concentrations of 5 and 10 μM were prepared in this work. During the detection process, different amounts of PBS solutions with the DA concentration of 0.1 M (1, 2 and 4 μL) were added to the sample (20 mL). The current response of the OMC/CSF-750 based DA sensor was recorded when the solution was sufficiently mixed and the test of each sample was repeated for three times. The detection results are summarized in Table S1.

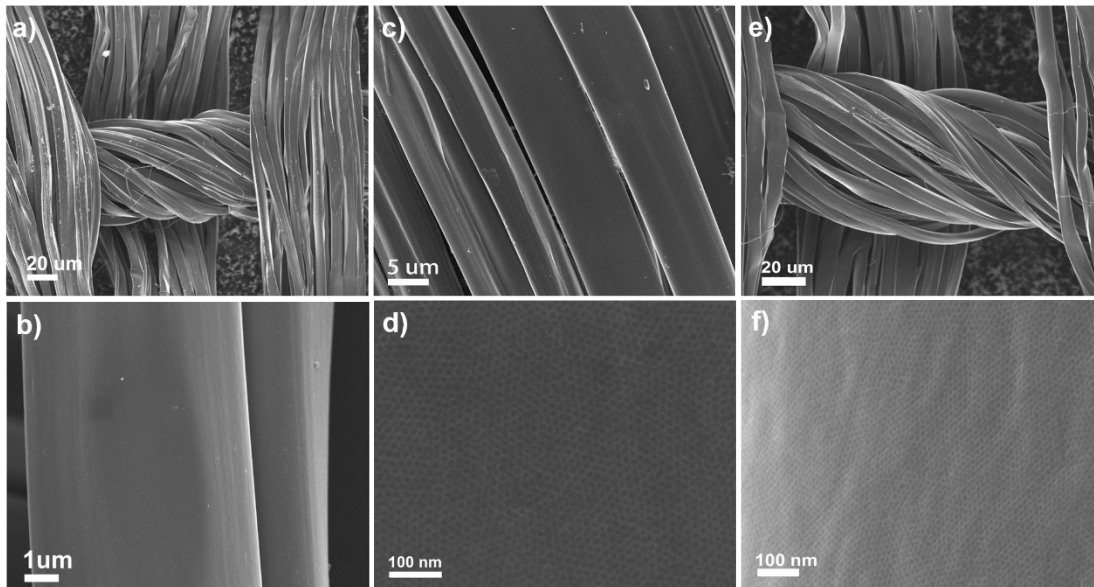


Figure S1. SEM images of a) and b) CSF, c) and d) OMC/CSF-600, e) and f) OMC/CSF-900.

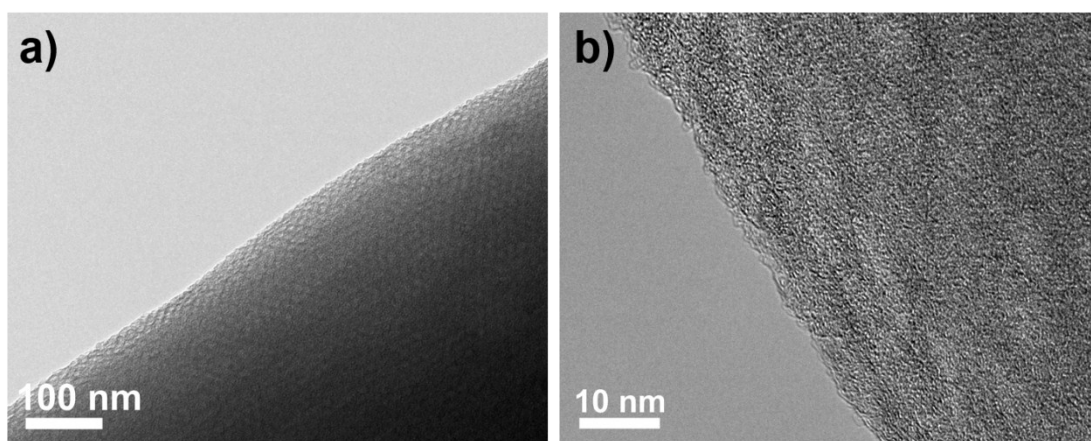
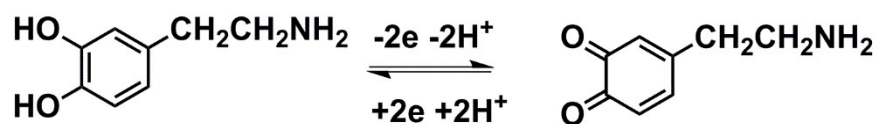


Figure S2. a) TEM and b) high resolution TEM images of OMC/CSF-750.



Scheme S1. The electrochemical reactions of DA on the surfaces of the flexible electrode.

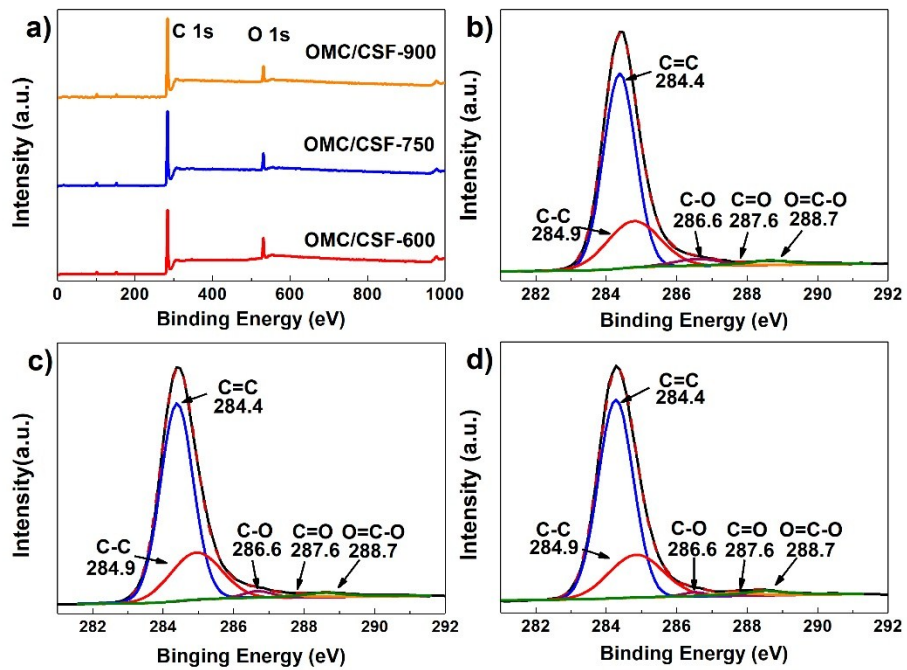


Figure S3. a) XPS spectra of the OMC/CSF electrodes. High resolution C1s spectra of b) OMC/CSF-600, c) OMC/CSF-750, d) OMC/CSF-900.

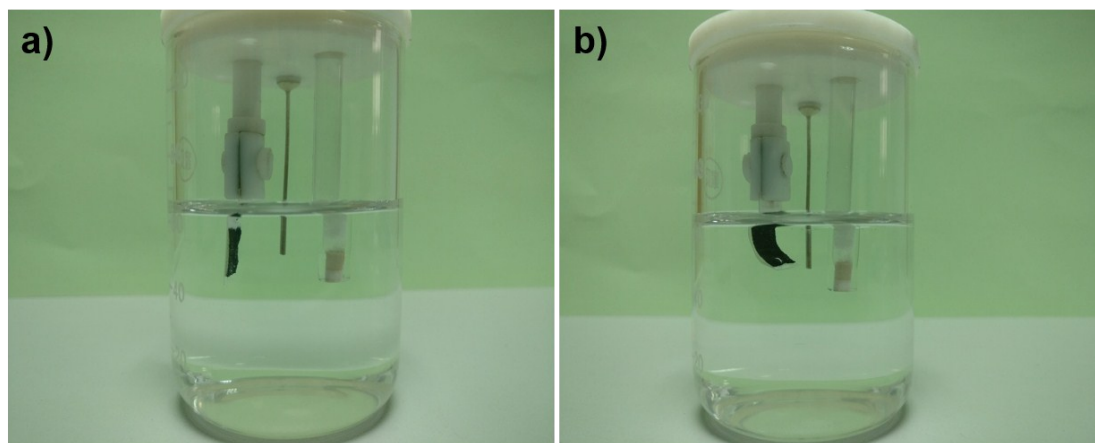


Figure S4. Photos of the OMC/CSF-750 electrode under a) flat and b) slightly bent configuration.

Table S1. The sensing performances of the OMC/CSF-750 based sensor towards DA in human serum

Sample	Original (μM)	Found ^a (μM)	Added DA (μL , 0.1 M)	Found ^b (μM)	Recovery (%)	RSD (%, N=3)
1	5	5.12	0	4.92	0	2.5
			1	9.87	99.0	
			2	15.06	103.8	
			4	24.88	98.2	
2	10	9.84	0	9.99	0	3.2
			1	15.17	103.6	
			2	19.96	95.8	
			4	30.32	103.6	

^aThe DA concentrations obtained from the regression curves;

^bThe DA concentrations obtained from the current response of the DA sensor (Average value from three tests).

Reference

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