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Article

Cyclophosphazene Intrinsically Derived Heteroatom (S, N, P, O)-Doped Carbon Nanoplates for Ultrasensitive Monitoring of Dopamine from Chicken Samples

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Supplementary Materials:

1. Experimental Section

1.1 Characterization Analyses

Polymerization was confirmed via Fourier Transform Infrared (FTIR) by using a Bruker Vertex 70 FTIR spectrometer. The morphology of as prepared samples was investigated using Field emission scanning electron microscopy (FE-SEM, S-4800, JEM-6701F). Energy dispersive X-ray spectroscopy (EDX) coupled with FE-SEM was used to determine the elemental percentages. Microstructures of graphitic materials were carried out on FEI Tecnai T-20 TEM. It provides information about the morphology; dimensions and crystallinity as well as defects and crystal orientations. To analyze the crystal structures, a diffractometer (XRD-6000) was used to characterized for powder X-ray diffrac-tion (PXRD) at voltage of 40 kV using monochromated Cu Kα radiation (λ = 1.54 Å, 40 kV, 30 mA) at scan rate of 10° min^{-1}. Raman spectroscopy is a simple but versatile technique used to identify rotational, vibrational, and other lower energy modes in the materials. Using Raman (Renishaw invia microscope), we studied ratio of in-plane vibrations of the sp^2 carbon (G-band) and disorder-induced mode (D-band) at excitation wavelength of 633 nm. The N_2 adsorption-desorption were measured via a Quantachrome Autosorb-1C-VP. Prior to N_2 adsorption-desorption, all the sample were subjected at 200 ˚C under vacuum for 5 hours. Specific surface area was determined via Brunauer−Emme −Teller method. X-rays photoelectron spectroscopy (XPS) is surface sensitive spectroscopic techniques used to measure the chemical states surface compositions, and electronic states. XPS was performed (using K-Alpha, Thermo Fisher Scientific, USA) coupled to an ultrahigh vacuum system equipped with a monochromatic Al Kα (1486.6 eV).

2. Results and discussion

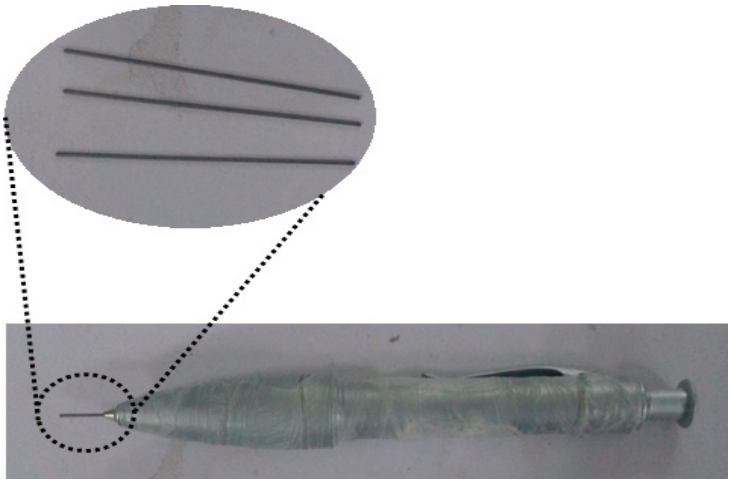

Figure S1. Digital image of LPG system prepared for electrochemical measurements.

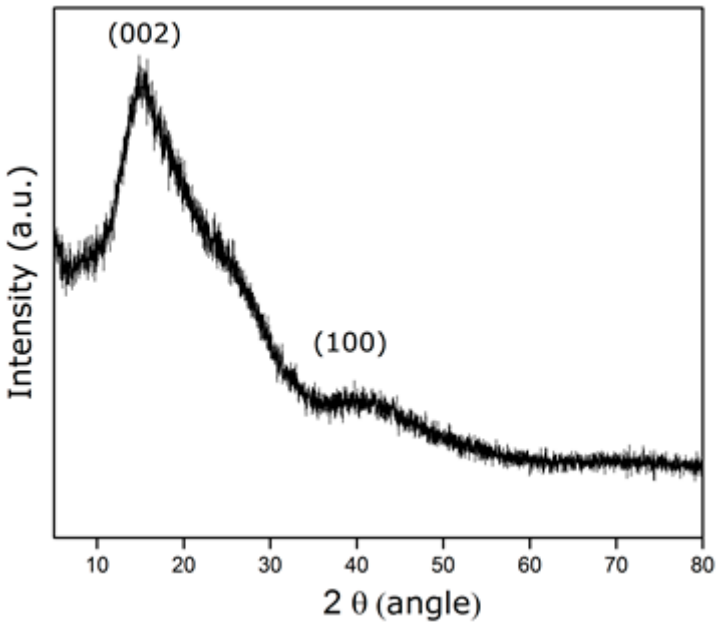

Figure S2. XRD analysis of PCD polymer.

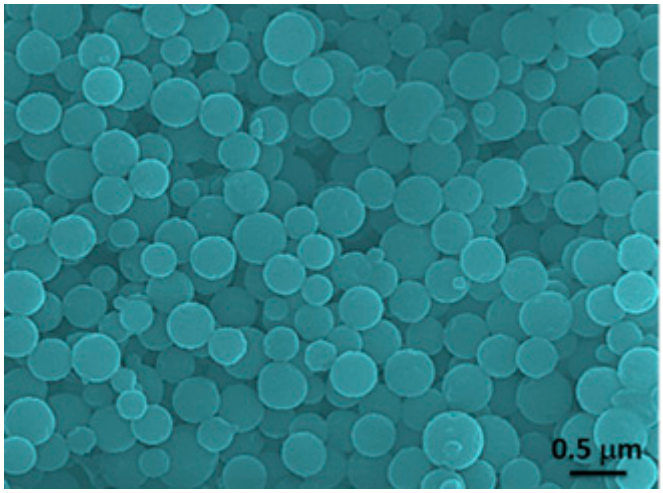

Figure S3. SEM image of PCD polymer revealing sphere like morphology.

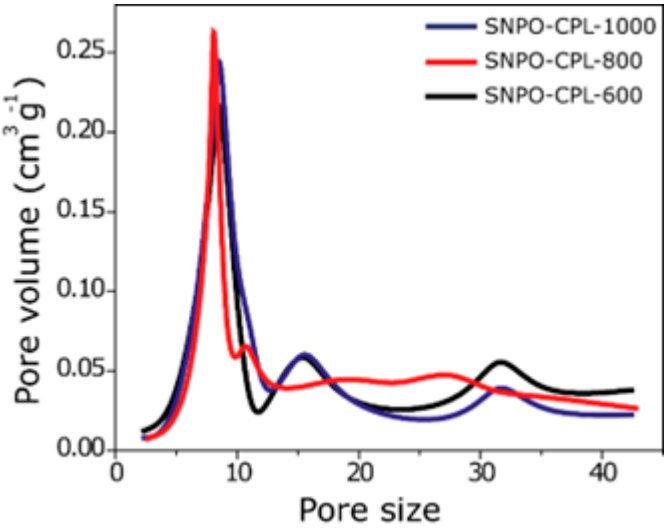

Figure S4. Pore size distribution of all three electrodes.

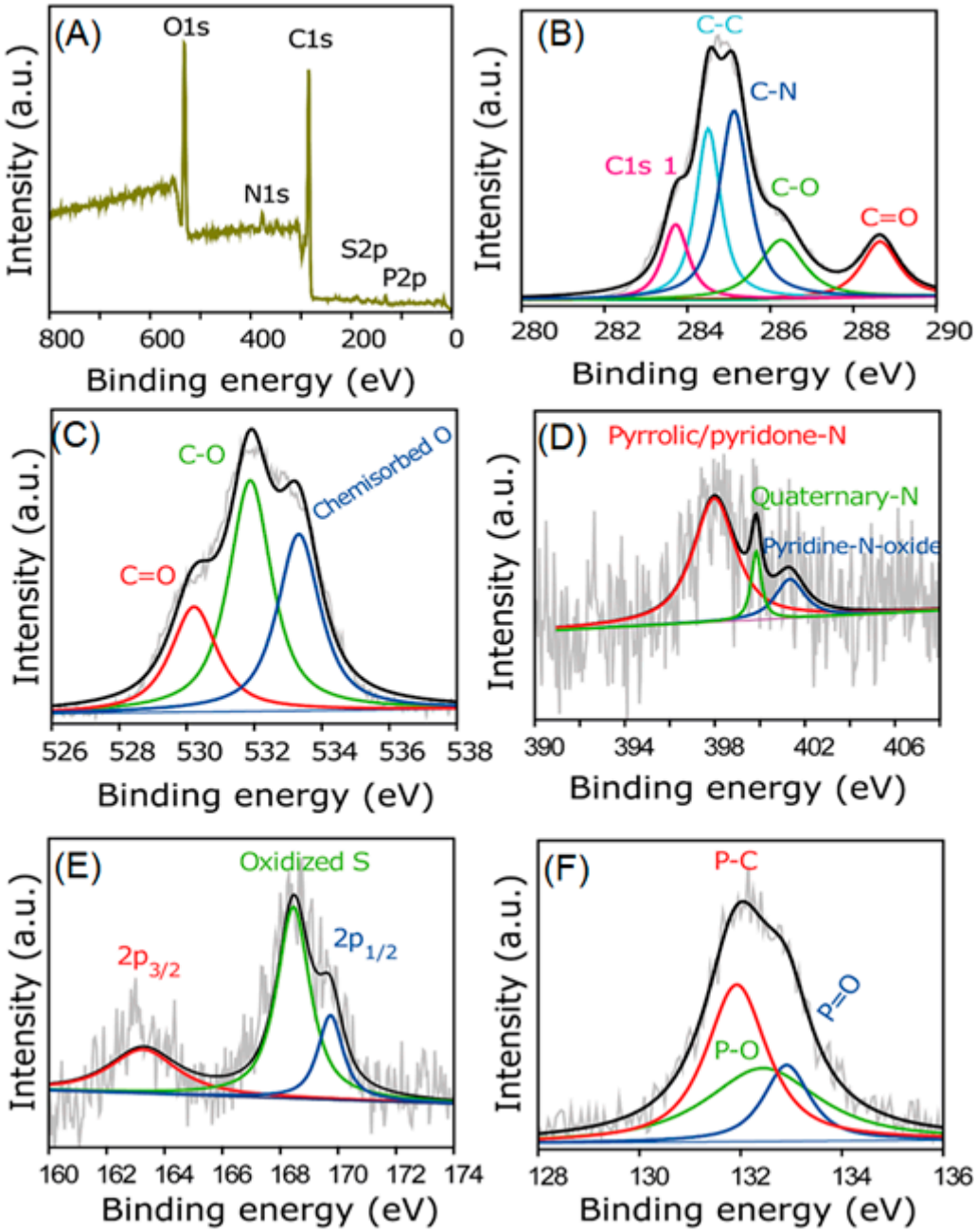

Figure S5. (A) Survey spectrum of SNPO-CPL-800. Deconvoluted high resolution XPS spectrum of C (B), O (C), N (D), S (E) and P (F).

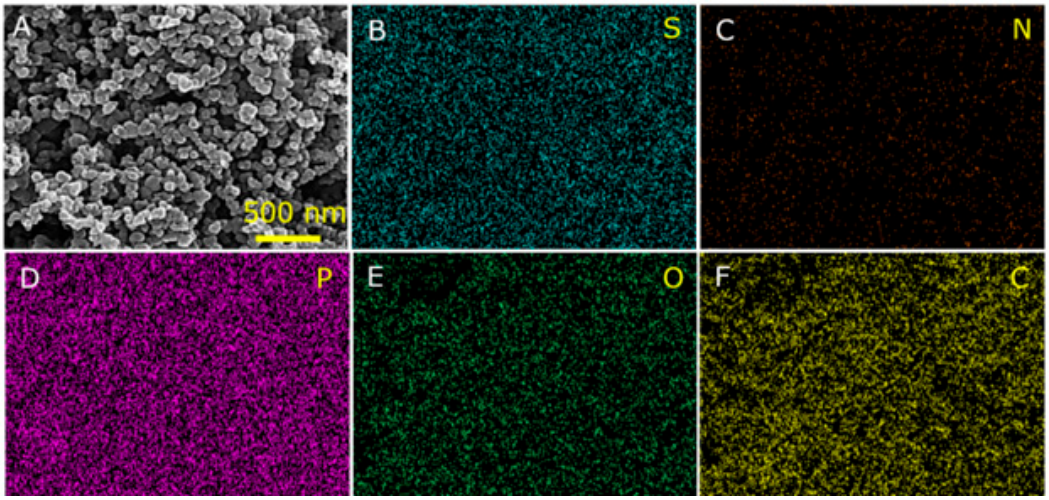

Figure S6. (A) Mapping analysis of SNPO-CPL-800 with homogeneous distribution (A) of S (B), N (C), P (D), O (E) and C (F).

2.1 The Electrochemical Activity of SNPO-CPL-(600, 800 and 1000)

The electrochemical activity of SNPO-CPL-(600, 800 and 1000) modified LPG was assessed through cyclic voltammogram (CV) measurements in 0.1 M PBS electrolyte containing 5 mM $[Fe(CN)_6]$ with in applied potential rang of 0.0 to 0.75 V. A pair of redox peak with varying peak current and potential appeared at the surface of all four electrodes (Figure S7A). However, SNPO-CPL-800 shows high peak current and small peak separation difference compared to SNP-CPL-600 and SNP-CPL-1000. This high sensing efficacy of SNP-CPL-800 could be attributed to efficient charge density at the delocalized surface because of maximum percentage doping of S, N, P, O, and graphitic C.

Additionally, charge transfer capability of the SNPO-CPL-(600, 800 and 1000) were also calculated by impedance spectroscopy (EIS). Figure S7B shows the Nyquist plot of impedance spectrum with two portions; semicircle at high frequency refers the electron transfer resistance (Res) and line part at low frequencies reflects the diffusion process velocity. Results indicate that SNP-CPL-800 have the smallest semicircle diameter compared to others, which indicate high electron transport efficiency of the developed electrode.

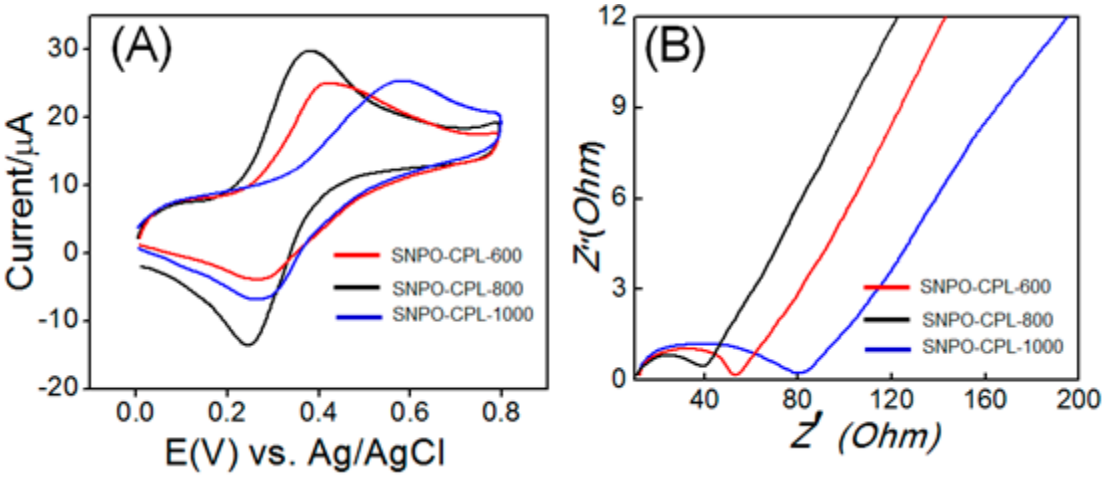

Figure S7. Shows CV (A) and typical -Nyquist impedance spectra (B) for SNPO-CPL-600, SNPO-CPL-800, and SNPO-CPL-1000 in 5 mM [Fe(CN)6] in 0.1 M PBS (pH:7).

Table S1. Atomic percentages of the as synthesized electrocatalysts from XPS analysis.

Catalyst	Atomic % (S)	Atomic % (N)	Atomic % (P)	Atomic % (O)	Atomic % (C)
SNPO-CPL-600	0.63	1.99	1.7	21.89	73.75
SNPO-CPL-800	0.87	2.02	1.87	22.3	72.98
SNPO-CPL-1000	0.00	0.00	0.88	14.24	71.84

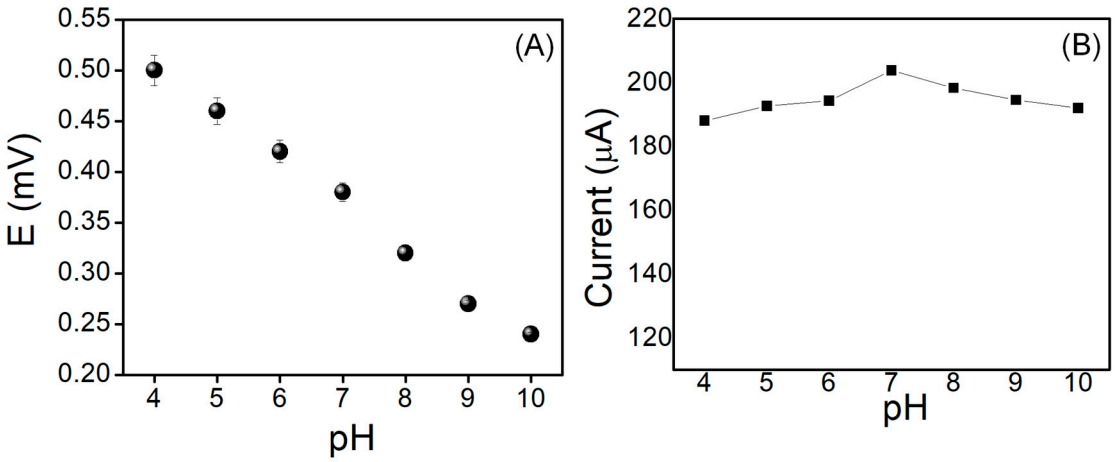

Figure S8. (A) Peak potential versus pH and (B) plot of anodic current versus pH derived from Figure 3B.

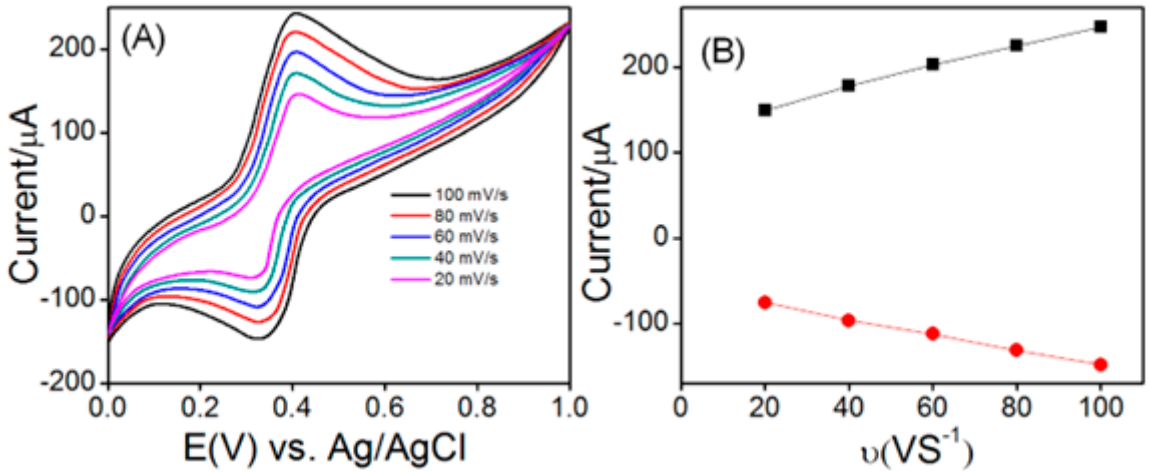

Figure S9. (A) CV of SNPO-CPL-800 with varying scan rate from 20- 100 mV/s. (B) Peak current vs. scan rate derived from figure S9-A.

Table S2. Sensitivity and limit of detection comparison of different carbon-based electrodes for DA.

Electrocatalysts	Sensitivity (μA/mM)	Limit of detection (nM)	References
Carbon nano-rods	5	60	[1]
Graphene oxide nanorib-bons/GCE	2.39	80	[2]
S doped carbon	4.1	3	[3]
N-doped gra-phene	9.87	1	[4]
N Gra-phene/GCE	0.113	250	[5]
N doped gra-phine	2.22	630	[6]
N doped gra-phine	__	930	[7]
N, S doped car-bon	__	0.02	[8]
P doped gra-phene	__	0.36	[9]
N, P doped car-bon	7.94	600	[10]
SNPO-CPL-800	0.38	0.009	This work

Limit of detection calculated by using equation S1.

LOD = F x SD/*b*…….. (S1)

Where

F: Factor of 3.3, SD: Standard deviation of the blank, standard deviation of the ordinate intercept, or residual standard deviation of the linear regression, b: Slope of the regression line

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