Electronic Supporting Information (ESI):

Surfactant exfoliated 2D hexagonal Boron Nitride (2D-hBN) explored as a potential electrochemical sensor for Dopamine: surfactants significantly influence sensor capabilities

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Experimental details

SPEs: Fabrication and electrochemical properties

The screen-printed graphite electrodes (SPEs) utilised throughout this work consist of a graphite working electrode, a graphite counter electrode and an Ag/AgCl reference electrode. The SPEs, which have a 3.1 mm diameter working electrode, were fabricated in-house with appropriate stencil designs using a microDEK 1760RS screen-printing machine (DEK, Weymouth, UK). This SPE design has been previously reported.\textsuperscript{1-3} For the case of each fabricated electrode, first a graphite ink formulation (Product Code: C2000802P2; Gwent Electronic Materials Ltd, UK), which is utilised for the efficient connection of all three electrodes and as the ink material for both the working and counter electrodes, was screen-printed onto a polyester (Autostat, 250 µm thickness) flexible film. After curing the screen-printed graphite layer in a fan oven at 60°C for 30 minutes, an Ag/AgCl pseudo reference electrode was included by screen-printing Ag/AgCl paste (Product Code: C2030812P3; Gwent Electronic Materials Ltd, UK) onto the polyester substrates, which was subsequently cured once more in a fan oven at 60°C for 30 minutes. Finally, a dielectric paste (Product Code: D2070423D5; Gwent Electronic Materials Ltd, UK) was then screen-printed onto the polyester substrate to cover the connections and define the area of the active electrodes, including that of the working electrode (3.1 mm diameter). After curing at 60°C for 30 minutes, the SPEs are ready to be used. For experimental continuity, the SPE’s on-board Ag/AgCl reference and carbon counter electrodes were removed prior to use within this work. These components were replaced with external SCE reference and Pt counter electrodes respectively. Note that the physicochemical characterisation of the fabricated SPEs has previously been reported, including SEM/EDX, XPS and Raman Spectroscopy analysis.\textsuperscript{3-4}

The SPEs have been electrochemically characterised previously and exhibit a heterogeneous electron transfer rate constant, $k_{\text{eff}}^a$, of ca. $1.08 \times 10^{-3}$ cm s\(^{-1}\) using 1 mM hexaammineruthenium (III) chloride/0.1 M KCl.\textsuperscript{5} The reproducibility and repeatability of the fabricated batches of electrodes were explored through comparison of cyclic voltammetric responses using 1 mM Ru(NH\(_3\))\(_6^{2+/3+}\) in 0.1 M KCl supporting electrolyte.
Exfoliation/synthesis of 2D-hBN

The 2D-hBN utilised throughout this work was synthesised via a surfactant based liquid exfoliation, sonication and centrifugation methodology. Liquid exfoliation was performed by adding bulk h-BN powder into an aqueous solution of sodium cholate hydrate (SC: concentration, 6 g/L) contained within a 100 mL beaker. The resulting dispersion of bulk h-BN comprised a concentration of 30 g L\(^{-1}\). This dispersion was then sonicated in a sonication bath (Ultrawave, UK) (60 % amplitude) for 1 hour, prior to a centrifugation step that was performed at 5000 rpm for 90 minutes. Following centrifugation, the corresponding supernatant was discarded and the resulting sediment was re-agitated/dispersed into aqueous SC (2 g/L, 100 mL). Next, the said re-agitated sediment underwent sonication in a sonication bath (Ultrawave, UK) (60 % amplitude) for a further 5 hours. Upon completion of the sonication treatment, the solution was separated into 20 mL aliquots before each sample was centrifuged at 2000 rpm for 90 mins (separately). The sediment from this process contained un-exfoliated h-BN and was consequently discarded, with the remaining supernatant being subjected to a further centrifugation period at 5000 rpm for 90 minutes. Finally, the forthcoming supernatant was removed and found to contain the 2D-hBN nanosheets that are utilised herein.

Physicochemical Characterisation Equipment Details

Transmission electron microscopy (TEM) images were obtained using a 200 kV primary beam under conventional bright-field conditions. The surfactant-exfoliated 2D-hBN sample was dispersed onto a holey-carbon film supported on a 300 mesh Cu TEM grid. Scanning electron microscopy (SEM) images and surface element analysis were obtained using a JEOL JSM-5600LV model equipped with an energy-dispersive X-ray (EDX) microanalysis package. An Agilent 8453 UV-visible Spectroscopy System (equipped with a tungsten lamp assembly, G1315A, 8453 for absorption between 250 nm and 1500 nm and a deuterium lamp, 2140-0605 for absorption between 200 nm and 400 nm) was used to obtain the absorption spectroscopy. The absorption spectra was analysed using the UV-Visible ChemStation software. For Raman spectroscopy and x-ray diffraction (XRD) analysis, the surfactant exfoliated 2D-hBN solution was drop-casted onto a supporting silicon wafer and dried in air. Raman spectroscopy was performed using a ‘Renishaw InVia’ spectrometer with a confocal microscope (×50 objective) spectrometer with an argon laser (514.3 nm excitation) at a very low laser power
level (0.8 mW) to avoid any heating effects. Spectra were recorded using a 10 second exposure time for 3 accumulations. The XRD was performed using a “X’pert powder PANalytical model” with a copper source of $K_\alpha$ radiation of 1.54 Å and $K_\beta$ radiation of 1.39 Å, using a thin sheet of nickel with an absorption edge of 1.49 Å to absorb $K_\beta$ radiation.

X-ray photoelectron spectroscopy (XPS) was used to analyse the 2D materials. Such analysis was conducted upon a thin layer of surfactant-exfoliated 2D-hBN, dried from a sodium cholate suspension onto a Si(111) wafer fragment. The Si(111) wafer was sputter cleaned (prior to 2D-hBN deposition) using argon ions, in-situ, within the vacuum of the XPS instrument to remove surface contaminants, thus allowing for the layer composition of surfactant-exfoliated 2D-hBN to be calculated. XPS data were acquired using a bespoke ultra-high vacuum system fitted with a Specs GmbH Focus 500 monochromated Al $K\alpha$ X-ray source, Specs GmbH PHOIBOS 150 mm mean radius hemispherical analyser with 9-channeltron detection, and a Specs GmbH FG20 charge neutralising electron gun. Survey spectra were acquired over the binding energy range 1100 – 0 eV using a pass energy of 50 eV and high resolution scans were made over the C 1s and O 1s lines using a pass energy of 20 eV. Under these conditions the full width at half maximum of the Ag 3d$_{5/2}$ reference line is $ca.$ 0.7 eV. In each case, the analysis was an area-average over a region approximately 1.4 mm in diameter on the sample surface, using the 7 mm diameter aperture and lens magnification of $\times$5. The energy scale of the instrument is calibrated according to ISO standard 15472, and the intensity scale is calibrated using an in-house method traceable to the UK National Physical Laboratory. Data were quantified using Scofield photoelectric cross sections corrected for the energy dependencies of the electron attenuation lengths and the instrument transmission. Data interpretation was carried out using CasaXPS software.

**Physicochemical Characterisation**

TEM, SEM, XRD, XPS, EDX, UV-visible spectroscopy and Raman spectroscopy were utilised to provide a comprehensive physicochemical characterisation of the surfactant exfoliated 2D-hBN. TEM images are depicted in ESI Figure 1 and indicate that the surfactant exfoliated 2D-hBN platelets have an average particle size (lateral) of $ca.$ 200 nm, which is in agreement to an independent literature report utilising an equivalent fabrication methodology. It is also clear from the TEM images that the surfactant exfoliated 2D-hBN exists in few layers. Complementary to the TEMs, ESI Figures 2B and 2C depict SEM images of surfactant exfoliated 2D-hBN and illustrate
how the 2D material rests upon the surface of a SPE. To investigate the layer thickness of surfactant exfoliated 2D-hBN in solution, the UV-visible absorption spectrum methodology was employed (see Experimental section for full details of the optical band gap calculation). This investigation allows for the optical energy band gap of surfactant exfoliated 2D-hBN to be calculated, which corresponds to the number of layers of 2D-hBN in solution. ESI Figure 1C illustrates the surfactant exfoliated 2D-hBN exhibits an absorption peak at 203 nm which agrees well with previous literature. A plot of $\varepsilon^{1/2}/\lambda$ vs. $1/\lambda$ can be constructed (inset ESI Figure 1C), allowing for a straight line at the absorption range to intersect the x-axis, (defined as $1/\lambda_g$) where $\lambda_g$ is the gap wavelength. Thus, the calculated gap wavelength ($\lambda_g$) relates to 221.2 nm, with a corresponding optical band gap of 5.61 eV indicating that 2–4 layer 2D-hBN is present in solution. This is also in good agreement with previous literature utilising the same fabrication methodology. It has previously been reported an optical band gap of 6 eV corresponds to monolayer 2D-hBN, whereas a band gap of 5.2 – 5.4 eV relates to bulk h-BN present in solution. Considering deposition of our nanomaterial onto a surface, ESI Figure 1D shows a typical Raman spectra of the surfactant exfoliated 2D-hBN, which gives rise to a characteristic Raman peak at 1366 cm$^{-1}$. The Raman peak is due to the $E_{2g}$ phonon mode and agrees well with prior literature reporting the fabrication of 2D-hBN. Full width at half maximum (FWHM) peak analysis of the Raman spectra (ESI Figure 1D) exhibits a value that corresponds to 12.1 cm$^{-1}$, which upon comparison to a recent report by Tran et al. indicates that few to multilayer surfactant exfoliated 2D-hBN is present. Due to overlapping signals occurring between surfactant exfoliated 2D-hBN and carbon (graphite), Raman spectra is not easily de-convoluted/observed for 2D-hBN when one material is deposited upon the other and therefore we cannot perform Raman mapping to determine the surface coverage of our supporting electrodes. Moreover, it is not feasible to refer to surfactant exfoliated 2D-hBN modified graphite electrodes in terms of the number of layers immobilised upon the electrode surface in question, but rather the mass of 2D-hBN immobilised. Resultantly, coverage studies were performed to ensure full coverage of surfactant exfoliated 2D-hBN upon the electrode surface, a parameter often overlooked in the literature. What is clear however, is that the surface deposited material remains of the same quality (2–4 layers, as shown through Raman) as when it exists suspended in solution (as shown though UV analysis).

XPS was performed and the resultant spectra (see ESI Figure 4) showed the presence of a single component at 191.1 eV in the B 1s spectrum, with the N 1s spectrum exhibiting a main peak
at 398.7 eV; both are in good agreement to previous literature. The stoichiometry of 1:1 for B:N is noted and the binding energies for the B 1s and N 1s photoelectron peaks agree well with the expected values for 2D-hBN. ESI Table 1 exhibits the full surface composition obtained from the XPS analysis of the dried surfactant exfoliated 2D-hBN layer (when supported on Si(111)). The C and O present are a result of residuals from the sodium cholate surfactant used to disperse the 2D-hBN. The presence of a C-O component in the C 1s spectrum confirmed this, with the Na attributed to the sodium of the cholate structure (ESI Figure 4A). Finally, ESI Figure 4D depicts the XRD spectra obtained for the surfactant exfoliated 2D-hBN. XRD indicates that the surfactant exfoliated 2D-hBN crystals are oriented in the (002) plane, with a characteristic peak observed at 26.7°, which is in agreement with previous literature.

The combined surface and physicochemical analysis presented above indicates that our fabricated material comprises high quality and high purity surfactant (sodium cholate) exfoliated 2D-hBN nanosheets; the surfactant serves to stop coagulation and leaves 2D-hBN sheets as few layer (2–4) 2D-hBN, which is maintained upon deposition onto supporting surfaces. We now explore this material’s electrocatalytic properties/potential towards the electrochemical oxidation/detection of DA and consider the implications of the surfactant’s presence towards the observed electrochemistry.
ESI Scheme 1
A schematic representation of the surfactant encapsulated 2D-hBN.

Surfactant encapsulation

2D-hBN sheet/layer

Sodium cholate
**ESI Figure 1**

Typical TEM images of surfactant exfoliated 2D-hBN after deposition onto a holey carbon film supported upon a Cu TEM grid (A), and at a higher magnification (B). Scale bars are 100 nm (A) and 200 nm (B). (C) depicts a UV-visible absorption spectra of 2D-hBN nanosheets, where the inset shows the corresponding plot of $\varepsilon^{1/2}/\lambda$ vs. $1/\lambda$. Typical Raman spectra (D) obtained for surfactant exfoliated 2D-hBN when immobilised upon a supporting silicon wafer.
ESI Figure 2

Typical SEM images of an unmodified SPE (A) and a 300ng surfactant exfoliated 2D-hBN modified SPE (B) and further magnified (C). The surfactant exfoliated 2D-hBN platelets are evident as small, disc-like shapes, approximately 200 nm in size.
**ESI Figure 3**

SEM image (A) of surfactant exfoliated 2D-hBN immobilised on a SPE along with EDS elemental analysis highlighting the underlying SPE carbon support (B, in green), boron (C, in red) and nitrogen (D, in purple) coverage of image A respectively.
ESI Figure 4

XPS survey spectrum for a sample of the surfactant exfoliated 2D-hBN following deposition onto a Si(111) wafer (A). Curve fitted XPS spectra of the B atom is shown in (B) and spectra (C) is that of the N atom. (D) depicts XRD spectra of the surfactant-exfoliated 2D-hBN deposited onto a glass slide between 20 and 45°, exhibiting a characteristic peak at 26.7°. Note that the baseline is such given that the support substrate was glass but still clearly shows the identifiable peak.
ESI Table 1
A summary depicting analysis of XPS spectra concerning the composition of a surfactant exfoliated 2D-hBN layer dried onto a Si(111) wafer. Note that the analysis includes data from the 2D-hBN and the sodium cholate residue.

<table>
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<tr>
<th>Element</th>
<th>Atom %</th>
<th>Layer composition</th>
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<tbody>
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<td>O 1s</td>
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<tr>
<td>C 1s</td>
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<td>N 1s</td>
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ESI Figure 5

Analysis of the cyclic voltammograms of 7.5 – 300 ng surfactant exfoliated 2D-hBN and (separately) 2 – 80 µg sodium cholate modified SPEs is presented in the form of plot (A), illustrating the oxidation potential of DA (circle), AA (inverted triangle) and UA (square) vs. mass of surfactant exfoliated 2D-hBN immobilised (red) and equivalently oxidation potential of DA (circle), AA (inverted triangle) and UA (square) vs. mass of sodium cholate immobilised (blue). Plot (B) depicts the peak current of DA (circle), AA (inverted triangle) and UA (square) vs. mass of surfactant exfoliated 2D-hBN immobilised (red) and equivalently peak current of DA (circle), AA (inverted triangle) and UA (square) vs. mass sodium cholate immobilised (blue). In plots A and B, the black circle, inverted triangle and square represent the unmodified SPE towards DA, AA and UA oxidation respectively. Scan rate: 100 mV s\(^{-1}\) (vs. SCE). Each data point (A and B) is the average and standard deviation (\(N = 3\)).
### ESI Table 2
Tabulated data shown from ESI Figure 5.

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<th>Material</th>
<th>Mass (ng)</th>
<th>Oxidation potential DA (V)</th>
<th>Oxidation potential AA (V)</th>
<th>Oxidation potential UA (V)</th>
<th>Oxidation Current DA (µA)</th>
<th>Oxidation Current AA (µA)</th>
<th>Oxidation Current UA (µA)</th>
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<th>Material</th>
<th>Mass (µg)</th>
<th>Oxidation potential DA (V)</th>
<th>Oxidation potential AA (V)</th>
<th>Oxidation potential UA (V)</th>
<th>Oxidation Current DA (µA)</th>
<th>Oxidation Current AA (µA)</th>
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ESI Figure 6

Typical DPVs (A) for the simultaneous detection of DA and AA utilising unmodified/bare SPEs by adding aliquots of DA at concentrations in the range of 3 – 75 µM into a 0.1 mM AA solution (pH 7.4 PBS); the dashed line represents the 0.1 mM AA scan in the absence of DA. (B) illustrates typical DPVs for the simultaneous detection of DA and UA utilising unmodified SPEs by adding aliquots of DA at concentrations in the range of 3 – 75 µM into a 0.1 mM UA solution (pH 7.4 PBS); the dashed line represents 0.1 mM UA scan in the absence of DA. Conditions as follows: $E$-pulse, 20 mV; $t$-pulse, 200 ms; equivalent scan rate, 10 mV s$^{-1}$; (vs. SCE).
ESI Figure 7

DPVs obtained utilising (A), 40 µg sodium cholate modified SPEs by adding aliquots of DA at concentrations in the range of 3 – 75 µM into a 0.1 mM AA solution (pH 7.4 PBS); the dashed line represents 0.1 mM AA scan in the absence of DA. Analytical curves (B) obtained utilising unmodified and sodium cholate modified SPEs of masses ranging from 2 – 80 µg corresponding to the anodic peak current for the oxidation of DA over the concentration range. Conditions as follows: $E$-pulse, 20 mV; $t$-pulse, 200 ms; equivalent scan rate, 10 mV s$^{-1}$; (vs. SCE). Each data point (B) is the average and standard deviation ($N = 3$).
ESI Figure 8

DPVs obtained utilising (A), 150 ng surfactant exfoliated modified SPEs by adding aliquots of DA at concentrations in the range of 3 – 75 µM into a 0.1 mM UA solution (pH 7.4 PBS); the dashed line represents 0.1 mM UA. Analytical curves (B) obtained utilising unmodified and surfactant exfoliated 2D-hBN modified SPEs of masses ranging from 7.5 – 300 ng corresponding to the anodic peak current for the oxidation of DA over the concentration range. (C) analytical curves obtained utilising unmodified and surfactant exfoliated 2D-hBN modified SPEs of masses ranging from 7.5 – 300 ng corresponding to the anodic peak current for the oxidation of UA over the concentration range. Conditions as follows: $E$-pulse, 20 mV; $t$-pulse, 200 ms; equivalent scan rate, 10 mV s$^{-1}$; (vs. SCE). Each data point (B and C) is the average and standard deviation ($N = 3$).
ESI Figure 9

DPVs obtained utilising (A), 40 µg sodium cholate modified SPEs by adding aliquots of DA at concentrations in the range of 3 – 75 µM into a 0.1 mM UA solution (pH 7.4 PBS); the dashed line represents 0.1 mM UA. Analytical curves (B) obtained utilising unmodified and sodium cholate modified SPEs of masses ranging from 2 – 80 µg corresponding to the anodic peak current for the oxidation of DA over the concentration range. (C) analytical curves obtained utilising unmodified and sodium cholate modified SPEs of masses ranging from 2 – 80 µg corresponding to the anodic peak current for the oxidation of UA over the concentration range. Conditions as follows: \( E \)-pulse, 20 mV; \( t \)-pulse, 200 ms; equivalent scan rate, 10 mV s\(^{-1}\); (vs. SCE). Each data point (B and C) is the average and standard deviation \((N = 3)\).
References