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Nanocarbon and nanodiamond for high performance phenolics sensing

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Phenolic compounds are pollutants of major concern, and effective monitoring is essential to reduce exposure. Electrochemical sensors offer rapid and accurate detection of phenols but suffer from two main shortcomings preventing their widespread use: electrode fouling and signal interference from co-existing isomers. Here we demonstrate a potential solution based on environmentally friendly and biocompatible carbon nanomaterials to detect monophenols (phenol and cresol) and biphenols (hydroquinone and catechol). Electrode fouling is tackled in two ways: by introducing electrochemically resistant nanodiamond electrodes and by developing single-use nanocarbon electrodes. We provide a comprehensive analysis of the electrochemical performance of three distinct carbon materials (graphene, nanodiamond and nanocarbon). Nanocarbon exhibits the lowest detection limit below 10^{-8} M, and one order of magnitude higher sensitivity than the other carbon nanomaterials. We detect co-existing phenol isomers with nanocarbon electrodes and apply it in river water and green tea samples, which may pave the way towards low-cost industrial scale monitoring of phenolic compounds.

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Phenolic compounds, a class of chemicals containing one or more hydroxyl groups attached to an aromatic ring, are ubiquitous in the environment. They occur naturally in plants and form an essential part of the human diet including wine and fruits¹. Also of artificial origin, these compounds are used in the manufacturing industry and are found in wastewaters, exhaust gases and as by-products of chemical engineering processes^{2,3}. Their occurrence in waterbodies is undesirable, as they can cause severe adverse effects on animals and humans above a specific dose, resulting in severe kidney, liver and cardiovascular diseases^{4,5}. At least 11 phenolic compounds are listed by the US Environmental Protection Agency and the European Union as priority pollutants^{6,7}. Rapid and accurate monitoring of phenolic compounds in solution would be beneficial to quantifying and reducing the exposure to these contaminants⁸.

Detection of phenolic compounds is possible employing chromatography⁹, spectrophotometry¹⁰ and capillary electrophoresis¹¹, reaching detection limits in the micromolar range. Using the redox reaction of hydroxyl groups on the aromatic ring, electrochemical methods have complemented the previous schemes, offering a quick, reliable and low-cost assay of phenolic compounds in the aqueous phase^{12,13}. Biphenols, like hydroquinone (HQ) and 1,2-dihydroxybenzene (catechol), can be directly oxidised at electrodes at low over-potential¹³. However, monophenol detection requires the use of enzymes, such as tyrosinase, lactase and polyphenol oxidase^{8,14}. These enzymes oxidise monophenols into o-biphenols which are subsequently oxidised to o-quinones, thereby facilitating their detection.

Electrochemical detection of phenolic compounds faces two challenges that hinder their use at industrial scales: First, reaction by-products lead to fouling of electrodes, which limits their accuracy and lifespan. Secondly, similar chemical structures of co-existing phenol isomers, such as HQ and catechol, result in overlapping redox peaks that makes simultaneous detection of these species challenging.

We show that carbon materials can offer solutions to these challenges. They are abundant, highly biocompatible and more

importantly, span a wide range of physical and chemical properties, which highly depend on the carbon-carbon molecular orbital hybridisation^{15,16}. Carbon electrode materials have impacted a range of disciplines from electrochemical sensing^{17,18}, to energy storage and conversion^{15,19}. Graphene-like carbon materials have been intensively studied as electrochemical sensors for phenolic compound detection. Notable examples are graphene and carbon nanotubes^{20–22}. However diamond-like materials and amorphous carbon²³, which interact with phenols differently due to their molecular bonding, have been largely overlooked.

In this work, we demonstrate that both nanodiamond and amorphous nanocarbon offer a facile solution to the aforementioned challenges due to their consistently high sensitivities, prevention from passivation and fouling and superior biocompatibility to enzyme modification^{24–26}. We provide a comprehensive analysis of their electrochemical performance and compare them to graphene-modified electrodes for detection of mono and biphenols. The wide range of electrochemical methods, including voltammetry and amperometry allow the comparison of three distinct carbon materials systematically and provide sensing performance benchmarks. Further, we demonstrate the simultaneous detection of co-existing phenolic isomers using nanocarbon electrodes, and apply these methods to detect phenolics in real Thames river water samples and green tea.

Results

Electrochemical characterisation of carbon electrodes. In this study we selected three types of carbon materials based on their carbon-carbon hybridisation, i.e. graphene (mainly sp^2), amorphous carbon (a mixture of sp^2 and sp^3) and boron-doped nanodiamond (mainly sp^3)^{24–26}. Conversion into carbon nanoparticles was achieved by microbead-assisted ultrasonic disintegration (Fig. 1a, b), yielding particle sizes of 4 to 8 nm, as measured by dynamic light scattering. These particles were drop-coated onto glassy carbon electrodes (GCE) (Fig. 1c) and were used to detect biphenols (Fig. 1d) and monophenols with the addition of the enzyme tyrosinase (Fig. 1e).

Fig. 1 Scheme of electrode preparation for phenolic compound detection. **a** Microbead-assisted ultrasonic disintegration of carbon materials suspended in water for 12 h. **b** Carbon nanomaterials after ultrasonication (size 4–8 nm). **c** Drop-coating of resulting suspension of nanocarbon onto a polished glassy carbon electrode (GCE). **d** Direct use of a modified electrode for biphenol detection, e.g. hydroquinone oxidises to quinone. **e** Additional modification of electrode with the enzyme tyrosinase for monophenol detection, e.g. phenol is first converted into hydroquinone by the enzyme (cartoon adapted from PDB ID: 3NM8³⁸) and then oxidises into quinone at the electrode

Fig. 2 Electrochemical characterisation with cyclic voltammetry of modified carbon electrodes. **a** Cyclic voltammograms (CV) of modified carbon electrodes in 0.1 M phosphate buffer and 0.2 mM HQ: glassy carbon electrode (GCE) in black, nanodiamond-GCE in orange, graphene-GCE in blue and nanocarbon-GCE in red dashed lines. Nanocarbon-GCE exhibited eight times higher current density than GCE; **b** magnified CV from **a** of GCE, nanodiamond and graphene-modified GCE. **c** CV of nanocarbon-GCE at increasing scan rates immersed in the same solution as **a**. The inset figure shows a linear relationship between the peak current and the scan rate (from 20 to 200 mV s^{-1}), indicative of adsorption of HQ at the surface; **d** CV in 0.1 M phosphate buffer after exposing nanocarbon-GCE to a solution of 2 mM HQ for the increasing dipping times. **e** The plot indicates peak currents achieved in **d** at shown dipping times; **f** CV in 0.2 mM cresol of modified GCE with nanocarbon-GCE without tyrosinase (red), tyr-GCE without nanocarbon (blue) and tyr-nanocarbon-GCE (black). A significant redox peak was only observed for tyr-nanocarbon-GCE (black)

We first characterised the modified carbon electrodes by cyclic voltammetry, i.e. graphene-GCE, nanodiamond-GCE and nanocarbon-GCE. Experiments were performed in 0.1 M phosphate buffer and 0.2 mM HQ. The cyclic voltammograms (CV) in Fig. 2a showed that nanocarbon-GCE exhibited eight times higher current density than GCE. CVs were obtained at nanocarbon-GCE with increasing scan rates (Fig. 2c), showing a linear relationship between peak current and scan rate. This linearity indicates that the main contribution to the measured current is coming from adsorbed HQ at the surface, rather than by diffusion from the bulk²⁷. To test the adsorption of HQ at nanocarbon-GCE, we dipped the electrode into 2 mM HQ for periods up to 600 s and then performed CV in 0.1 M phosphate buffer (Fig. 2d). The observed cumulative redox peaks after successive dipping in HQ confirm that the species adsorbs at the electrode surface. Analogous experiments were carried out at GCE, nanodiamond-GCE and graphene-GCE. For these cases, the peak current was found to depend linearly on the square root of the scan rate (Supplementary Figure 1), indicative of a diffusion-controlled process, as described by the Cottrell equation²⁷.

Nanocarbon-modified electrodes showed enzyme biocompatibility. The detection of phenol was facilitated by the presence of the enzyme tyrosinase, which converted monophenol molecules into biphenol (Fig. 1e). We performed CV in cresol solutions and observed redox peaks when nanocarbon-GCE was modified with tyrosinase. However, in the absence of either nanocarbon or tyrosinase, no significant peak was detected (Fig. 2f). Enzyme modification was also possible for graphene-GCE (Supplementary Figure 2a), while nanodiamond-GCE did not show similar

properties (Supplementary Figure 2b), which we attribute to its sp^3 hybridisation.

To understand the high peak current observed at nanocarbon-GCE (Fig. 2a), we calculated the heterogeneous rate constant of hydroquinone using the Laviron equation^{28–30}. This equation relates the heterogeneous rate constant k with the variations of the peak potentials as a function of the scan rate (full calculations are given in Supplementary Figure 3). We report a transfer coefficient and number of transferred electrons of $\alpha = 0.46$ and $n = 1.7$, in agreement with previous results^{31–34}. Using these parameters in the Laviron equation yields a rate constant of $k = 2.06 \text{ cm s}^{-1}$, which is significantly higher than the value at graphene/chitosan-GCE (0.0147 cm s^{-1})³¹, CILE (0.0629 cm s^{-1})³³ and carbon fibres (0.0219 cm s^{-1} in water and 0.167 cm s^{-1} in 1 M H_2SO_4)³⁴.

Electrochemical sensing of phenolic compounds. It is possible to detect biphenols (HQ and catechol) directly at carbon electrodes. Here we test the performance of GCE, nanodiamond-GCE, graphene-GCE and nanocarbon-GCE as biphenols sensors by three electrochemical methods: cyclic voltammetry (CV), square-wave voltammetry (SWV) and amperometry. Figure 3 shows representative results obtained using nanocarbon-GCE for HQ detection. When the HQ concentration raised, the corresponding peak current of the redox reaction scaled linearly, as measured both in CV (Fig. 3a and Supplementary Figure 4a) and SWV (Fig. 3b and Supplementary Figure 4b). To detect low concentrations of HQ at nanocarbon-GCE, we performed amperometry by successive additions of HQ, which resulted in

Fig. 3 HQ detection at nanocarbon-modified electrode. **a** CV at increasing concentration of HQ as indicated. **b** Square-wave voltammetric measurement of HQ at increasing concentrations, as indicated. **c** Amperometric detection of successive addition of HQ at indicated concentrations with applied potential of +0.2 V. Plot shows the first 600 s of the full experiment in the inset figure. **d** Results from amperometric experiments for four carbon-modified electrodes, i.e. GCE, nanodiamond-GCE, graphene-GCE and nanocarbon-GCE. The plot shows the current increase against added HQ concentration. Nanocarbon-GCE exhibits highest sensitivity, as indicated by the slope

sharp current jumps (Fig. 3c). Current jumps of 15 ± 1 nA were measured for additions of 0.2 μM of HQ. Analogous experiments using nanodiamond-GCE, together with GCE and graphene-GCE as comparison were carried out (Supplementary Figure 5). Measured current changes as a function of HQ concentrations are plotted in Fig. 3d for four electrodes. The sensitivity of each electrode is given by the slope of linear fits in Fig. 3d, among which nanocarbon-GCE stands out as the electrode with the highest sensitivity. Similar measurements for detection of catechol are given in Supplementary Figure 6.

Monophenols (phenol and cresol) were detected after additional modification of nanocarbon-GCE with the enzyme tyrosinase following the scheme in Fig. 1e. At 0 V we measured current jumps by successive addition of phenol (Fig. 4a, b) and cresol (Fig. 4c, d). The detection limits of four phenolic compounds for all measured carbon electrodes, together with previously reported ones are listed in Table 1. Among them, nanocarbon-GCE exhibited the lowest detection limit, reaching values below 100 nM.

Low surface fouling at nanodiamond-glassy carbon electrodes.

Fouling of electrodes is a problem for phenolic sensors³⁵. The by-products from phenolic compound oxidation react with the electrode, thereby inactivating it. It is well-known that boron-doped diamond benefits from high chemical resistance²². To test whether nanodiamond-GCE resists fouling when used to detect phenolics, we performed cyclic voltammetry in HQ for consecutive cycles. After ten scan cycles (Fig. 5a in red) the voltammogram did not change significantly. In contrast, a dramatic drop of redox peak current was observed at a graphene electrode

(Fig. 5b) indicating surface fouling. This comparison shows the excellent inertness of nanodiamond against phenolic compounds. We observed that peak currents at nanodiamond-GCE scale linearly with HQ concentration up to 100 μM (Fig. 5c). This shows that nanodiamond-GCE have a wider detection range. In comparison, graphene-GCE depart from linearity at concentrations above 10 μM (Fig. 5d), as well as nanocarbon-GCE (Supplementary Figure 4). We attribute fouling of graphene and nanocarbon electrodes to their sp^2 carbon-carbon hybridisation, which facilitates the adsorption and reaction of phenolics oxidation by-products.

Simultaneous detection of phenolics.

In addition to electrode fouling, interference from co-existing isomers disrupts the electrochemical signal due to their similar chemical structure and overlapping redox peaks. Here we used nanocarbon-GCE to resolve the peaks from HQ and catechol, two common phenolic contaminants that coexist in environmental waters¹³. We performed a series of experiments via SWV (Fig. 6). First, we added equal amounts of HQ and catechol successively, reaching equal final concentrations. We observed that two distinguishable oxidation peaks increased simultaneously with a significant separation of about 56 mV. When the catechol concentration was successively increased, but not HQ, only the catechol peak exhibited higher peak currents (Fig. 6b). Similarly, when catechol levels remained constant, but HQ was added, only the HQ peak showed an increment in current (Fig. 6c). Plotting peak currents against final concentrations of each species yielded a linear relationship shown in Fig. 6d. The achieved detection limits are below

Fig. 4 Amperometric detection of monophenols with nanocarbon-GCE. **a** Current change upon addition of phenol at nanocarbon-GCE modified with tyrosinase with applied potential of 0 V. **b** Current jumps as a function of phenol concentration extracted from amperogram a). **c** Analogous amperogram performed with addition of cresol. **d** Current jumps as a function of cresol concentration extracted from amperogram c)

Table 1 Detection limits of phenolic compounds

Sensors	HQ (μM)	Catechol (μM)	Phenol (μM)	Cresol (μM)
GCE	1.75	1.2	—	—
Nanodiamond-GCE	0.43	0.12	—	—
Graphene-GCE	0.17	0.10	0.14	0.2
Nanocarbon-GCE	0.11	0.023	0.04	0.025
GCE	3.9 ³⁵	7.33 ³⁵		
Graphene-polyoxometalate	0.09 ³⁹	0.05 ³⁹		
Co(OH) ₂	0.5 ⁴⁰			
Montmorillonite	0.57 ⁴¹			
PDDA-G/GCE	0.25 ⁴²			
Graphene-chitosan	0.75 ³¹			
tyr/MWCNTs	0.2 ⁴³	0.2 ^{43, 44}	1.1 ⁴⁴	2.0 ⁴⁴
tyr/Ti			0.13 ¹⁴	0.14 ¹⁴
tyr/Ag-BDD			0.1 ⁴⁵	0.2 ⁴⁵
tyr/CaCO ₃			0.0062 ⁴⁶	0.0054 ⁴⁶

List of measured (in bold) and reported detection limits of phenolic compounds at various modified electrodes. HQ and catechol were measured at potential of 0.2 V (vs. Ag/AgCl) and phenol and cresol at 0 V (vs. Ag/AgCl).

GCE glassy carbon electrode, tyr tyrosinase, BDD boron-doped nanodiamond, MWCNT multiwalled carbon nanotube, HRP horseradish peroxidase

0.02 μM. A comparison with other reported sensors is listed in Table 2.

Nanocarbon as reproducible single-use electrodes. We tested the suitability of nanocarbon as a single-use disposable electrode by performing voltammetry at increasing concentrations of catechol (Fig. 7a) and HQ (Fig. 7b). Each cycle was performed at a freshly prepared nanocarbon-GCE and discarded afterwards. When plotting peak currents against concentrations a

linear relationship was measured (slope 1.88 ± 0.03 A/M and, $R^2 = 99.7\%$), indicative of an accurate and highly reproducible approach.

We used single-use nanocarbon-GCE to detect HQ and catechol in Thames river water samples. Known concentrations of HQ and catechol were added to river water samples (Fig. 8a in red) and SWV was used at nanocarbon-GCE to measure their concentration (Fig. 8a in blue). Found concentrations were extrapolated using the linear relationship shown in Fig. 7. Each measurement was repeated ten times. The average recovery rate

Fig. 5 Resistance to electrode fouling of nanodiamond. **a** Plot shows first scan cycle at nanodiamond-GCE in 0.2 mM HQ (black) and after 10 scan cycles (red). **b** Analogous experiment as **a** performed with a graphene-GCE for comparison. **c** Peak currents at nanodiamond-GCE plotted against HQ concentration. **d** Results for an analogous experiment with a graphene-GCE

Fig. 6 Simultaneous detection of HQ and catechol at nanocarbon-GCE. **a** Square-wave voltammogram in 0.1 M phosphate buffer and successive addition of equal amounts of HQ and catechol reaching indicated final concentrations; **b** only addition of catechol from 8 to 13 μM while maintaining a fixed concentration of HQ (8 μM). **c** only addition of HQ from 8 to 13 μM while maintaining a fixed concentration of catechol (13 μM). **d** Plot of peak currents against concentration of HQ (black) and catechol (red), demonstrating the simultaneous detection of both species. The data points are extracted from **a–c** as indicated

was 102% for HQ and 101% for catechol. This experiment demonstrates that nanocarbon-GCE can be successfully applied in river water samples, without significant interference from additional co-existing compounds.

It is known that green tea contains high levels of various phenolic compounds, giving it its antioxidant properties¹. We applied nanocarbon-GCE to detect HQ and catechol levels in green tea. We first performed SWV in PBS buffer (Fig. 8b, in black). We then boiled green tea in PBS buffer following the protocol in Methods section. The resulting peaks are shown in Fig. 8b (in blue). To test whether these peaks corresponded to HQ and catechol, we added equal amounts of each and obtained peaks at similar potentials (Fig. 8b in red). As shown in Fig. 6d, we assume a linear relationship between phenolic compound concentration and its detected peak current in this concentration range. Therefore, we extrapolated the HQ and catechol levels in the green tea sample to be $48 \mu\text{M g}^{-1}$ and $64 \mu\text{M g}^{-1}$, respectively, which is of the same magnitude as reported in the literature^{36,37}.

Discussion

To tackle the challenges for the large-scale use of electrochemical sensors of phenolic compounds, we developed two promising electrodes based on carbon nanomaterials, i.e. nanodiamond electrode and nanocarbon electrode. On the one hand,

nanodiamond, with its unique carbon bonding hybridisation, exhibited excellent resistance to fouling, which led to a wider detection range and longer lifetime, compared with graphene-modified electrodes.

On the other hand, we converted the abundant, cheap and biodegradable amorphous carbon into 5 nm size nanocarbon material by bead-assisted ultrasonication disintegration. Biphenols (HQ and catechol) adsorbed strongly onto the surface of nanocarbon-modified electrodes and exhibited redox peak currents one order of magnitude higher than other carbon nanomaterials. We also demonstrated that this nanocarbon material is biocompatible with the enzyme tyrosinase, thereby enabling the detection of monophenols (phenol and cresol). The high sensitivity and low detection limits make nanocarbon materials very efficient sensors to detect phenolic compounds. The strong adsorption properties also enables nanocarbon electrodes to resolve the signal from co-existing isomers (HQ and catechol), therefore making it an attractive option for simultaneous detection of phenolic compounds.

The protocol to prepare this nanocarbon electrode is easy to operate, safe, stable and highly reproducible, which facilitates the development of single-use disposable sensors using this material. We tested the single-use nanocarbon electrodes in real samples, i.e. river water and green tea, and accurately detected levels of HQ and catechol. This successful measurement in real contexts with a facile and biodegradable system paves the way for low-cost industrial scale monitoring of phenolic compounds.

Table 2 List of measured and reported simultaneous detection limits of hydroquinone (HQ) and catechol at modified electrodes

Sensors	Detection limit HQ/ catechol (μM)	Reference
Nanocarbon-GCE	0.018/0.015	This work
Polymer + graphene	0.2/0.25	42
Graphitised mesoporous	0.91/1.31	36
Graphene + cobalt hexacyanoferrate	0.2/0.21	47
MWNTs/Co(II)TPP/GCE	0.8/0.5	48
Electrospun carbon nanofiber	0.2/0.4	49
Au + carbon fibres	0.36/0.86	50
Graphene-chitosan composite film	0.75	31
Zn/Al-GCE	1.2/9.0	51
MWNTs	0.6	52
Activated GCE	0.16/0.11	53

Methods

Materials and reagents. The commercial Monarch 430 amorphous carbon (Cabot Corporation, CB M 430) was purchased from James M Brown Ltd (Staffordshire, UK). Graphene nano-platelets of $3 \mu\text{m}$ diameter and less than 10 nm thickness were acquired from Angstrom materials. The nanodiamond powder (ND-105/G4) was purchased from Yorkshire Bioscience Ltd. Other chemicals were obtained from Sigma-Aldrich unless otherwise stated.

Preparation of modified electrodes by microbead-assisted ultrasonic disintegration

Glassy carbon electrodes were cleaned before use by polishing with alumina powder, which was then removed by ultrasonication in water for 3 min. A total of 5 g milling beads were mixed with 1 mg powder of carbon nanomaterials and 5 mL Milli-Q water. The mixture was sonicated for 12 h, and then centrifuged ($3 \times 5 \text{ min}$, 10,000 rpm). Ten microlitre carbon materials suspensions were drop-coated onto a glassy carbon electrode with a surface area of 0.0707 cm^2 , and subsequently dried in the fume hood. Tyrosinase-modified electrodes used to detect phenol and cresol were prepared by dropping $10 \mu\text{L}$ 1 mg mL^{-1} tyrosinase solution onto the electrode surface and dried for 1 h (Tyr/nanocarbon-GCE). The protocol is illustrated in Fig. 1.

Fig. 7 Detection of HQ and catechol with single-use nanocarbon electrode. Square-wave voltammograms in 0.1 M phosphate buffer and increasing concentrations of catechol (a) and increasing concentrations of HQ (b). Each cycle has been performed at a freshly prepared nanocarbon-GCE. Inset plots show the peak current against concentration of each species

Fig. 8 Phenolic compound detection in river water and green tea using a nanocarbon-GCE. **a** Detection of phenolic compounds in Thames river water after addition of known concentrations of HQ and catechol (in red). SWV method was used at nanocarbon-GCE and measured concentrations (in blue) were extrapolated using the linear relationship shown in Fig. 7. Each measurement was repeated ten times (error bars indicate standard deviations). **b** Voltammograms in 0.1 M phosphate buffer (background signal in black), green tea sample (blue) and after addition of 10 μM HQ and catechol to the green tea sample (red)

Electrochemical measurements. Electrochemical measurements were performed at room temperature ($20 \pm 2^\circ\text{C}$) with $\mu\text{-AUTOLAB III}$ potentiostat (Eco-Chemie, Netherlands), running GPES software (Version 4.9). A three-electrode system was used consisting of a working electrode, a Pt wire as counter electrode and an Ag/AgCl reference electrode. Electrochemical experiments were carried out in 0.1 M phosphate buffer solution (pH 7.4) at room temperature. All solutions and subsequent dilutions were prepared with Milli-Q water ($> 18\text{ M}\Omega\text{ cm}$). The SWV used frequency of 10 Hz, sensitivity of 1 mV and amplitude of 10 mV.

Size characterisation by dynamic light scattering. Dynamic light scattering (Viscotek, Malvern) was used to measure the hydrodynamic diameter of the carbon nanomaterials. The average size of graphene was about 80 nm initially and it reduced to 56 nm after sonication. Nanocarbon powder had initial sizes of 50–70 nm and decreased to 5–8 nm after sonication. The size of nanodiamonds was measured to be 4–5 nm.

River water and tea sample preparation. A total of 0.1 M phosphate buffer was prepared using river water collected from the Thames River (Oxford). Tea samples were prepared by adding 2.5 g green tea (Twinings) into 50 mL 80°C Milli-Q water for 5 min. Tea leaves were then removed and the sample was filtered using a 11 μm pore-size filter (Whatman, Grade 1).

Data and code availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

L.J. performed the experiments. L.J. and I.S. analysed the results. I.S. wrote the manuscript with the support from L.J. L.J., I.S. and J.F. discussed the results and commented on the final manuscript.

Additional information

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