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Adsorption of iodinated methylene blue on the surface of oxidized graphene nanoflakes

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1. Materials and reagents

The synthesis of iodinated methylene blue (MB) was performed using MB (98%), KI (99%, Chimmed, Russia), KIO_3 (99.99%), I_2 (99.99%), HCl water solution («Reachim», Russia), and $AgNO_3$ (99.9%). The melanin used in this study was a commercially available chaga melanin extract with content of basic substance 99.1% (TU 10.89-15-006-2003838090-2022, Perm, Russia). The layered structure of melanin was confirmed by transmission electron microscopy (see manuscript, Figure 1d). The textural characteristics of melanin could not be fully studied due to its decomposition during degassing within sample preparation preceding BET measurements.

2. Synthesis of iodinated methylene blue

Iodination of MB by non-radioactive isotopes was performed the first time. In brief, two methods to obtain the product with quantitative yield were assessed: (1) the oxidation of 0.10 g (0.31 mmol) MB in the 40 mL water solution with 40 mL of 0.0236 M KI and 40 mL of 2.08 M KIO_3 in 10 % HCl solution of at 100 ºC for 1 h in a sealed vial (Figure S1 a) and (2) mechanochemical activation of a solid mixture of 3.20 g (0.01 mol) MB, 2.54 g (0.01 mol) I_2 and 1.70 g (0.01 mol) $AgNO_3$ with trace amounts of acetic acid in an agate mortar during 40 min (Figure S1 b). Product formation was assessed by thin-layer chromatography on Silufol plates ("SORBFIL", PTSKh-AF-V-UF, IMID LLC, Krasnodar, Russia) based on the different R_f values of the MB and I-MB. I-MB was extracted from the reaction mixture with acetonitrile, followed by evaporation of the solvent and isolation of the solid product. Iodinated product was purified by column chromatography. The column was filled with silica gel (particle size is 40-63 μm). The EtOH–$CHCl_3$ (vol. 2:1) eluent was used. According to EDX data, the purified product contained 20.4 wt. % iodine that correspond to monosubstituted derivative. IR spectrum (1202 FTIR spectrometer, Infraspek, Russia), ν, cm^{-1}: 3400 (OH), 3050 (C–H), 2920, 2850 (C–H), 1600, 1630 ($C=N^+$), 1340 (CH_3), 500–530 (C–I).

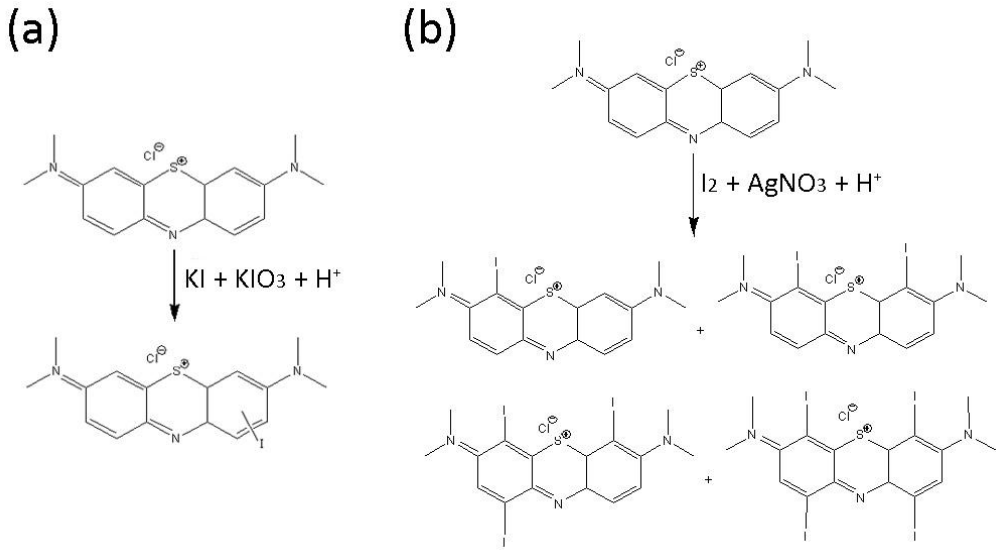


Figure S1 Synthetic route of iodinated MB. Reaction of MB with KI and KIO_3 (a) and mechanochemical activation of MB, I_2 and $AgNO_3$ solid mixture (b).

3. Physico-chemical analysis

The structures of graphene nanoflakes (GNFs) and melanin were investigated by high-resolution transmission electron microscopy (TEM) using a JEOL 2100 F/Cs (Jeol, Tokyo, Japan) microscope operated at 200 kV and equipped with an EEL spectrometer (Gatan, Munich, Germany).

Specific surface area and pore size distribution were determined by applying BET and BJH models[S1] to the low temperature nitrogen adsorption data, obtained with an analyzer Autosorb-1C/QMS (Quantachrome Inc., USA). Samples were degassed at 300 ^{o}C for 3 h prior to adsorption analysis.

Nitrogen adsorption-desorption isotherms of the GNFs at 77 K belong to type IV and had H3 hysteresis loops (Figure S2 a) according to the IUPAC classification.[S1] Mesopore size distribution according to the BJH model is given at Figure S2 b.

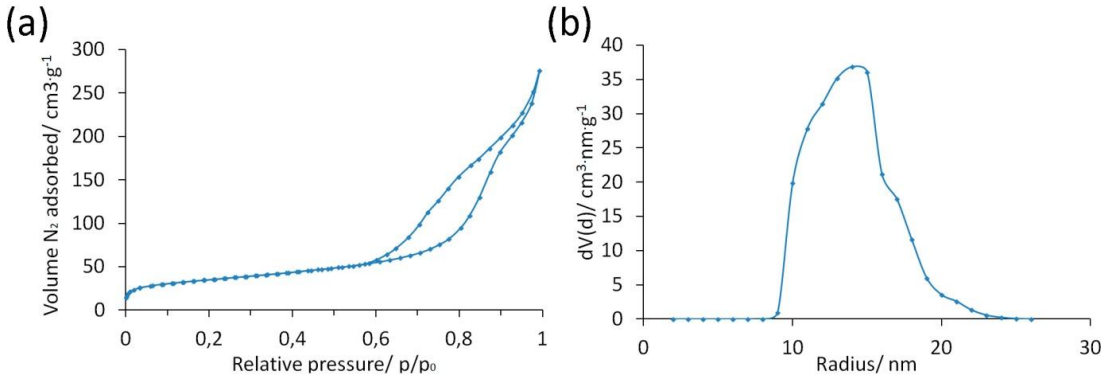


Figure S2 Nitrogen sorption isotherms of the oxidized GNFs (a) and pore volume distribution (b) according to BJH model.

4. Spectrophotometric analysis

The absorption spectra of MB and I-MB solutions were measured using a Jenway 6715 spectrometer. The MB absorption spectrum is shown in Figure S3. It is similar to the previously described absorption spectra for MB and is characterized by two absorption maxima at 613 and 665 nm, which correspond to the dimer and monomer.[S2] The I-MB absorption spectrum was obtained for the first time (Figure S3). In addition to the absorption maxima at 665 and 613 nm, the spectrum has an additional maximum at 443 nm, which can be attributed to the iodinated product and used to determine the concentrations of I-MB.

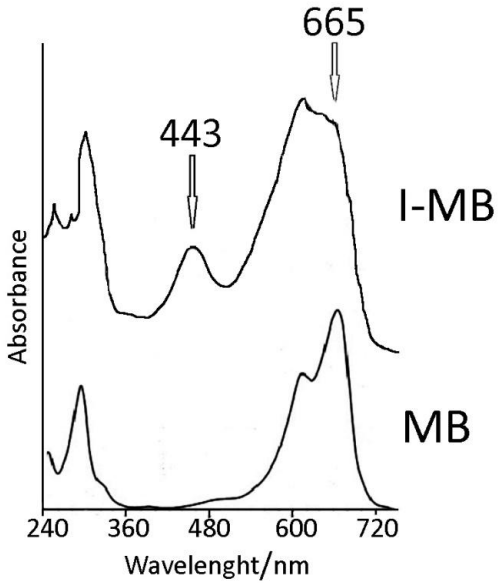


Figure S3 UV–visible spectrum of a water MB and I-MB solutions.

A series of water solutions of MB and I-MB with concentrations of 0, 1.5, 2.5, 5, 7.5, 10 and 15 $mg \cdot L^{-1}$ were prepared to perform the calibrations (Figure S4).

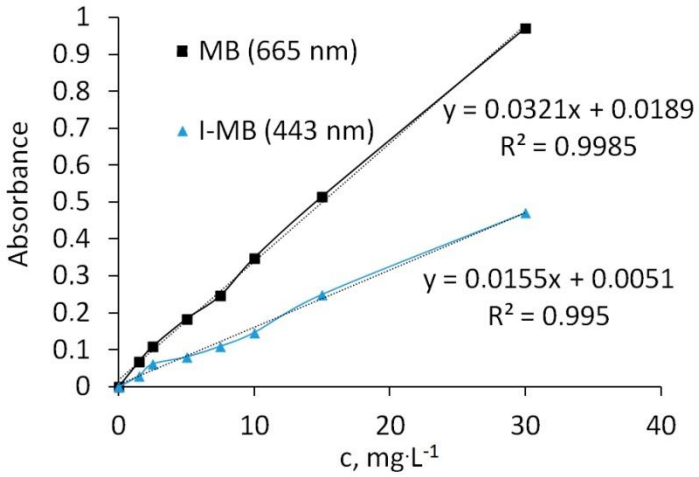


Figure S4 UV–visible spectrum of a water MB and I-MB solutions.

5. Adsorption of MB on the GNFs, N-doped GNFs activated carbon and SiO_2 surfaces

The adsorption of MB was investigated on the surface of GNFs, N-doped GNFs[3], activated carbon (Calgon Carbon, China), and SiO_2 (Xysil200, Henan Xunyu Chemicals CO., Ltd., China) to elucidate the role of adsorbent surface functionalization. According to adsorption isotherms (Figure S5a) and its derivatives in the linear Langmuir (Figure S5b) and Freundlich (Figure S5c) coordinates, MB molecules were adsorbed on the non-functionalized GNFs, activated carbon, and SiO_2 surfaces with the formation of the monolayer (Figure S5, Table S1). The N-doped GNFs have energetically non-uniform surface due to the different types of nitrogen atoms in the carbon sheets forming pyrrole, pyridine-like, NC_4^+ bonds, and surface functional NO_x^- groups.[S3] This explains why the Langmuir model is not suitable for description as in the case of oxidized GNFs. Negative Q_{max} and K_L values indicate a lack of physical meaning. The adsorption parameters of monolayer capacity A_m and the area ω_m occupied by MB in a dense monolayer are presented in Table S2.

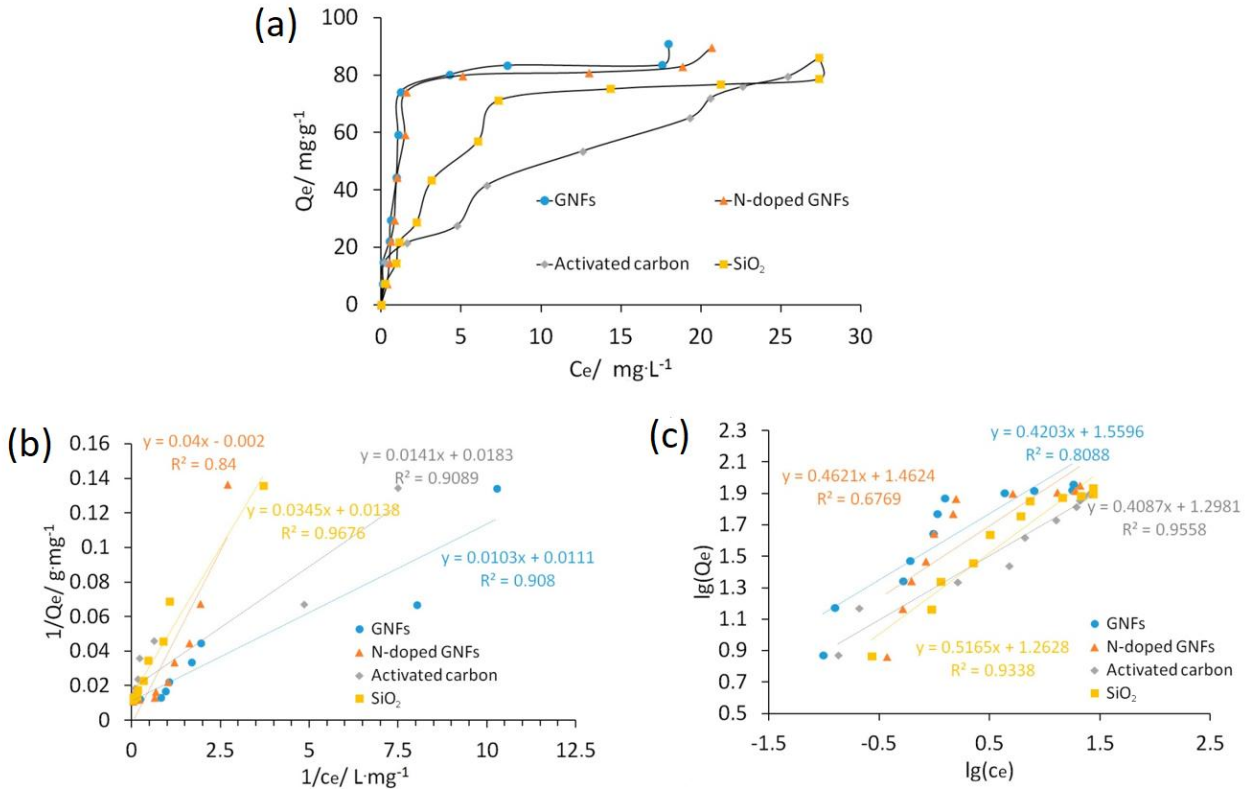


Figure S5 Adsorption isotherm of MB on the GNFs, N-doped GNFs, activated carbon and SiO_2 surface (a) and adsorption isotherms in the liner coordination of Langmuir (b), and Freundlich (c) models. The linear equations and determination coefficient R^2 are shown in the plots.

Table S1 Models, equations and isotherm parameters of MB adsorption on the surface of GNFs, activated carbon and SiO_2.

Model	Equation in the linear coordinate	GNFs	N-doped GNFs	Activated carbon	SiO_2

Langmuir model $Q_e = Q_{max}\frac{K_L c_e}{1+K_L c_e}$	$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}K_L}\frac{1}{c_e}$	$R^2 = 0.908$ $Q_{max} = 90$ $K_L = 1.069$	$R^2 = 0.84$	$R^2 = 0.9089$ $Q_{max} = 55$ $K_L = 1.289$	$R^2 = 0.9676$ $Q_{max} = 72$ $K_L = 0.406$
Freindlich model $Q_e = k\, c_e^{1/n}$	$\ln Q_e = \frac{1}{n}\lg c_e + \lg k$	$R^2 = 0.8088$ $1/n = 0.402$ $k = 36.27$	$R^2 = 0.6769$ $1/n = 0.4621$ $k = 28.98$	$R^2 = 0.9558$ $1/n = 0.4087$ $k = 19.86$	$R^2 = 0.9338$ $1/n = 0.5165$ $k = 18.32$

Q_{max} [mg·g^{-1}] is the theoretical maximum adsorption; K_L [L·mg^{-1}] is Langmuir adsorption constant; n is Freundlich constants; k [mg·g^{-}1 (mg^{-1})] shows the adsorption capacity of the sorbent.

Table S2 Values of maximum adsorption Q_{max}, and monolayer capacity A_m, (μmol·m^2), the area ω_m (nm^2) occupied by MB in a dense monolayer.

Adsorbent	S_{BET}, m^2 g$^{-1.}$	Q_{max},* mg·g^{-1}	A_m, μmol·m^{-2}	ω_m,** nm^2
GNFs	518	90	0.54	3.05
Activated carbon	1516	55	0.11	14.69
SiO_2	198	72	1.14	1.48

* The Q_{max} values correspond to Q_{max} values from Langmuir model (table S1).

** The area ω_m was calculated by the formula $\omega_m = \frac{1}{N_A A_m}$, where N_A is Avogadro's number of 6.022·10^{23} mol^{-1}.

References

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