Surface area measurements of graphene and graphene oxide samples: Dopamine adsorption as a complement or alternative to methylene blue?

Lifu Chen,[a] Christopher Batchelor-McAuley,[a] Bertold Rasche,[a] Colin Johnston,[b] Neil Hindle,[c] and Richard G Compton [a]*

[a] Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK

[b] Department of Materials, Oxford University, Oxford OX5 1PF, UK

[c] Applied Graphene Materials plc, Cleveland TS10 4RF, UK

*To whom correspondence should be addressed

Email: richard.compton@chem.ox.ac.uk

Phone: +44 (0) 1865 275957 Fax: +44 (0) 1865 275410

To be submitted to:

Applied Materials Today

Abstract

The possible use of dopamine, monitored spectroscopically, as a probe molecule for surface area measurements is investigated. Using high surface area carbon materials, including both graphene and graphene oxide (GO), the method is established as a complement or alternative to methylene blue or conventional N_2 (BET) adsorption. The molecular reorientation (flat to vertical) of dopamine on the graphene and GO surface provides a direct indication of the monolayer coverage and the rapid adsorption (within 10 min to saturation) offers high convenience. The smaller dopamine molecule size and less self-repulsion compared to methylene blue can be considered to yield a more closely-packed surface coverage on the materials of interest. Especially for materials with complex morphologies and internal structures, the dopamine adsorption will therefore lead to a more ‘correct’ measurement.

Keywords: Surface area characterisation, Dopamine adsorption, Graphene, Graphene oxide, UV-vis spectroscopy

Graphene and graphene oxide (GO) are the objects of intensive and worldwide studies with numerous applications identified, including batteries, supercapacitors, sensors, catalysts, transistors, photovoltaics, drug delivery, etc., based on their mechanical, electrical and/or catalytic activities.[1-9] Diverse and numerous approaches to their synthesis have been developed prompting an exceptional need for the reliable characterisation of the materials. Not least due to the use of graphene and GO as catalysts, electro-catalysts and catalyst supports, the characterisation of the surface area is desirable and widely undertaken.

Conventionally the measurement of the surface areas of solids in the form of powders, particles or platelets is carried out using gas adsorption isotherm measurements in which the uptake of a gas via adsorption onto the solid is measured as a function of pressure at a constant temperature. For the purpose of inferring surface areas the data is commonly obtained using nitrogen gas, occasionally CO_2, water or argon, and analysed using the BET isotherm dating from 1938.[10] The isotherm essentially allows for the extension of the simple Langmuir isotherm to embrace multi-layer adsorption and for different enthalpies of adsorption of the adsorbate either directly onto the solid (ΔH_1) or onto an already adsorbed molecule (ΔH_2) and takes the form

$$\frac{P}{N_s(P_0 - P)} = \frac{1}{NC} + \frac{C-1}{NC}\frac{P}{P_0}$$

where N_s is the number of molecules adsorbed, N is the total number of sites corresponding to a monolayer, P_0 is the saturation vapour pressure of the adsorbate and

$$C = \exp(\frac{\Delta H_1 - \Delta H_2}{RT})$$

Noting that N or N_s is proportional to the corresponding masses or volumes of gas, plots of $P/V(P_0-P)$ against P/P_0, or their equivalent, allow the determination of C and N. The surface area is related to the latter via $S = N \times A$ where A is the estimated area of one molecule. In modern practice the measurement is automated and carried out routinely.[11] The BET approach is enshrined by the International Organisation for Standardisation (ISO 9277:2010) recommendation on the measurement of disperse solids such as nano-powders and porous solids. The directive stresses that the BET method is only applicable to isotherms of type 2 (disperse, nonporous or macroporous solids) and type 4 (mesoporous solids, pore diameter between 2 nm and 50 nm).[12-14]

The caveats associated with the BET isotherm and especially the fact that many applications of graphene and GO are solution rather than gas phase based, encourage the exploration of complementary solution phase based approaches to the characterisation of the surface area. Probably the best established method is that of the adsorption of the blue dye methylene blue (MB) from water, aqueous or ethanol based solutions onto suspensions of the solid of interest, typically monitored spectroscopically. The amount adsorbed at full uptake is again, in conjunction with an estimated MB molecular area, used to estimate the area of the solid in contact with the solution.

Both the BET and MB methods have been widely studied in the context of graphene and GO characterisation. Generally the surface areas determined by MB adsorption tend to be larger than that reported by BET measurements made on the same sample. Early work[15] contrasted values attained by BET of 600 m^2/g to those from MB adsorption of 1850 m^2/g attributing the discrepancy, at least in part, to the agglomeration of the graphene/GO sheets. Such discrepancies have been repeatedly identified along with various key observations all of which indicate the difficulty of the task. These observations include the recognition of MB dimer and trimer formation,[16] and the contrasting uptake of MB between graphene and GO, which is attributed to functional groups on the latter. Furthermore, increased functionality on

GO has been shown to increase the MB uptake,[17] while aggregation of GO has been emphasised as a further key parameter.[18] In a study[19] of GO yarns a surface area of 4 to 6 times the BET values were measured via MB adsorption and thought to be more reliable partly due to the observation of a type 3 adsorption isotherm in the BET analysis. Comparison of the BET and MB methods in the cases of carbon nanotubes[20] and active carbons[21] is even more complex with porosity and pH effects having marked influences.

In the present paper we explore the use of a possible alternative to MB for surface area measurements via adsorption onto different samples of high surface area carbon materials including both graphene and GO. In particular we note that recent papers[22-24] have shown that dopamine and related quinone type molecules adsorb strongly and quickly onto graphene nanoplatelets and that phase transitions due to molecular reorientation on the surface (flat to vertical) can be observed. The latter can, at least in principle, offer an indication of the realisation of monolayer coverage or otherwise. Moreover, as is shown below, dopamine adsorbs much more rapidly compared to MB offering an improvement on convenience. In the following we compare MB and dopamine adsorption alongside corresponding BET measurements for 5 different high surface area carbon samples.

Of the five high surface area carbons employed in this work, we use three different graphene nanoplatelet samples, one in a powdered state and two dispersed in water. One aqueous based sample is in the form of a suspension of particles and the other is a paste. These three samples are designated as GNP-Powder, GNP-Liquid and GNP-Paste, respectively. GNP-Liquid and GNP-Paste (from Applied Graphene Materials, UK) were produced differently according to the supplier. The GNP-Paste production uses a carbonate template while the GNP-Liquid is formed without a template. The GNP-Powder (STREM Chemicals, USA) is a more conventional graphene nanoplatelet sample and according to the producer is comprised of plates 6-8 nm in thickness and 15 μm wide. Additional to these samples we studied a sample of exfoliated graphite, which has a comparatively low surface area and finally a high surface area graphene oxide (Global Graphene Group, USA).

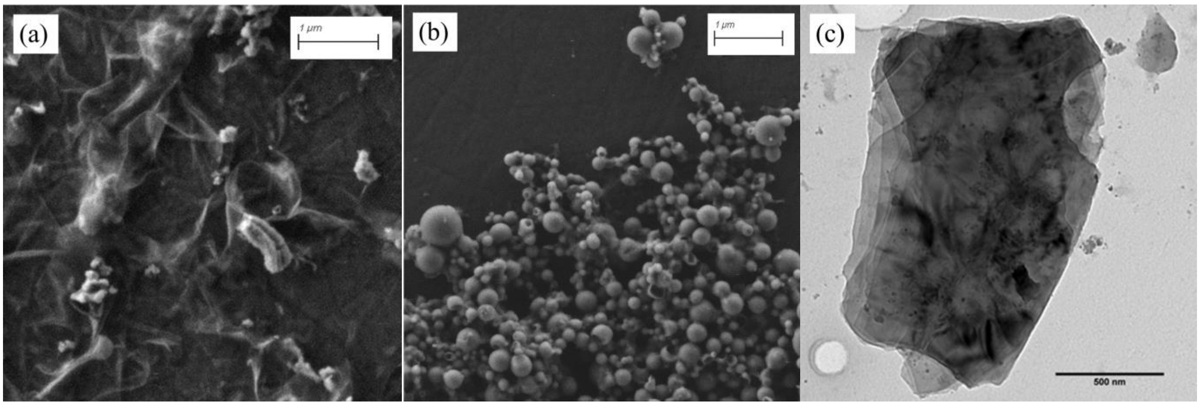

Figure 1. (a) SEM image of GNP-Paste sample, (b) SEM image of GNP-Liquid sample, (c) TEM image of GO sample.

In terms of morphology and crystallinity these samples vary substantially. The scanning and transmission electron microscopy (SEM and TEM) images reveal flakes of varying sizes in case of the GNP-Powder, the exfoliated graphite and the graphene oxide, with the latter showing the thinnest and smallest flakes (Figure 1 (c) and S1, S2 and S5). The X-ray diffraction patterns of these materials show that the GNP-Powder and the exfoliated graphite are relatively crystalline as their diffraction patterns match the one of graphite (Figure S6). Particularly the stacking ((00*l*) diffraction peaks) is well established. Nevertheless, the broadening of the peaks illustrates that the flakes are small and the number of orderly stacked layers is ca. 25 to 30, as estimated from Rietveld fits. In contrast, the much smaller and thinner plates of the GO sample give only an amorphous signal, indicating the effective separation of all layers.

The morphology of the two dispersion samples is markedly different (Figure 1 (a) and (b)). The sample produced with a carbonate template (GNP-Paste) results in a material that is formed of a fused array of graphene based sheets. In contrast, the sample without a template (GNP-Liquid) results in a carbon-black like product. Consistently, the XRD pattern of the

GNP-Paste still shows peaks that can be indexed with graphite, although only the (00*l*) diffraction peaks are visible and even these are very broad. The corresponding Rietveld fit suggests a maximum number of orderly stacked layers between 2 and 7. The GNP-Liquid only yields an amorphous signal.

The measurement of the carbon surface areas using UV-vis spectroscopy is achieved through indirect assessment of the amount of probe molecules that is adsorbed onto the material from a solution of known concentration. Using UV-vis spectroscopy the remaining solution phase concentration of probe molecules (MB or Dopamine) is measured after it has been mixed with the high surface area carbon and the solid has been physically removed via centrifugation. 1 mL of 150 mM dopamine solution was mixed with GNP-Powder or GO and sonicated for different periods to determine the equilibrium time for the full adsorptive uptake. The absorbance of dopamine in aqueous solution reaches a maximum at 279 nm, as depicted in Figure S7, consistent with literature[25]. A linear Beer–Lambert plot with the extinction coefficient (ε) of (0.25 ± 0.004) $M^{-1}\,m^{-1}$ was obtained, as illustrated in Figure S8, correlating the absorption with the dopamine concentration. It is evident that the reduction in magnitude of absorbance peak is related to the adsorption onto carbon materials. Figure 2a plots the amount of dopamine adsorbed by a unit amount (1 mg) of GNP-Powder or GO as a function of adsorption time. The adsorbed amount increases progressively on extending the adsorption time to ca. 10 min and reaches a plateau afterwards, suggesting a maximum uptake of dopamine by both GNP-Powder or GO at this concentration.

Analogous experiments were conducted for MB adsorption onto both GNP-Powder and GO. As shown in Figure S9, the absorbance peak of MB in aqueous solution is at 664 nm in good agreement with literature[18]. The extinction coefficient (ε) of MB is determined as (5.4 ± 0.097) $M^{-1}\,m^{-1}$, as the Beer–Lambert plot illustrated in Figure S10. The adsorbed amount of MB on GNP-Powder or GO was plotted against the adsorption time, as depicted in Figure 2b. To reach the adsorption saturation, GNP-Powder and GO need to be sonicated in MB solution for at least ca. 300 min or 240 min respectively. This is consistent with prior literature[16,26-28], where an overnight (at least 24 hr) stirring was applied to realise maximum adsorption. An additional experiment was conducted where the carbon materials were stirred in the MB solution continuously at 600 rpm without aid of sonication (see Figure S11) and GO requires at least ca. 16 hr adsorption time (18 hr for GNP-Powder) to reach the saturation. In both measurements with or without sonication, it is notable that the adsorbed amount of MB is consistent, suggesting the materials are rigid and their structure and surface areas are not altered by sonication. Moreover, the adsorption time required for saturation of GO is shorter than GNP-Powder suggesting faster adsorption kinetics. This affinity might be tentatively attributed to the abundant oxygen-containing function groups on the GO surface leading to a negatively charged GO surface[29-31] hence causing the enhanced adsorption *via* electrostatic interactions[16,17] with MB as a cationic dye. Comparing the adsorption of dopamine and MB onto graphene and GO materials, dopamine adsorbs *much* more rapidly (10 min to saturation vs. 300 min for MB), resulting from the high solubility of dopamine compared with MB, offering improved convenience.

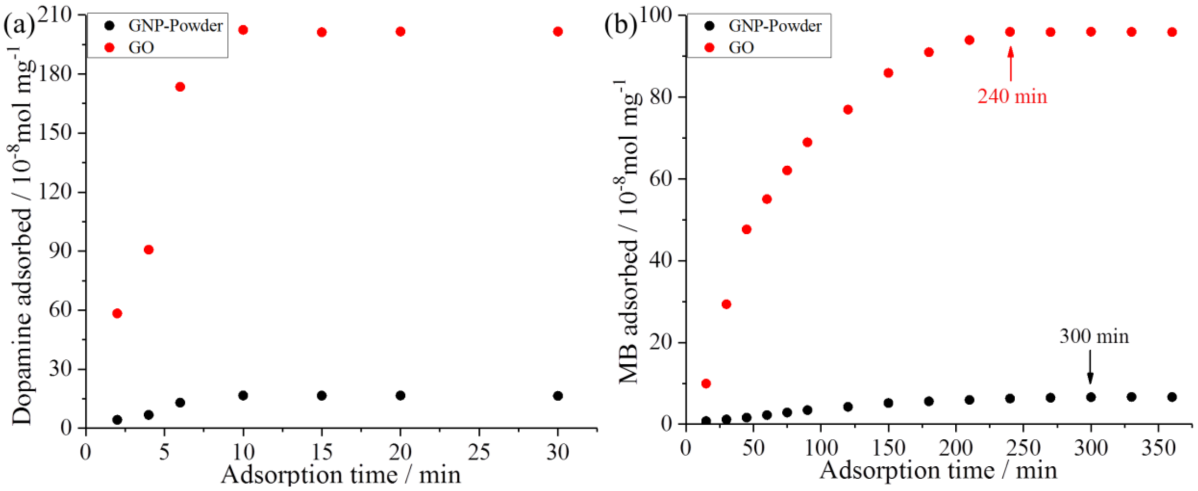

Figure 2. (a) The amount of adsorbed dopamine by GNP-Powder and GO as a function of adsorption time (b) The amount of adsorbed methylene blue by GNP-Powder and GO as a function of adsorption time. Corresponding semi-logarithmic plots are shown in Figure S13 to show the feature for materials with low adsorption capacity.

Having studied the adsorption of dopamine and MB onto GNP-Powder and GO as a function of time, the experiments were then conducted over a wide range of adsorbate concentrations to obtain the corresponding adsorption isotherms. Figure 3a presents the dopamine adsorption isotherms for all five different graphene and GO samples in aqueous solutions. The presence of two expected[22] and distinct plateaux in all five isotherms suggest a flat to vertical concentration driven phase transition[22-24] of dopamine molecules adsorbed on graphene and GO, corresponding to a flat molecular orientation on the adsorbent surface at low concentrations (≤ca.200 mM) and a vertical dopamine orientation at higher concentrations (≥ca.350 mM). This can be confirmed by comparing the ratio of the theoretical estimated dopamine molecule area in the flat orientation to the vertical orientation with the ratio of the dopamine adsorbed amount at second plateau to the first plateau. The theoretical molecule areas of dopamine, as illustrated in Figure S15, are determined by a rectangular box model with all side lengths estimated by trigonometry for bond lengths, bond angles (attained from ChemDraw 15.1) and van de Waals radii of terminating atoms[32]. The molecule area of the flat view and of the vertical view hence are estimated as 6.5×10^{-15} cm^2 and 3.6×10^{-15} cm^2 respectively, consistent with prior reported values[33]. This results in a ratio of flat to vertical molecular areas of 1.80. In the dopamine isotherms, the adsorbed amount of dopamine per unit amount of carbonaceous material reaches the first plateau at adsorbate concentrations close to 200 mM and the second plateau at concentrations close to 400 mM. The ratios of these two limiting uptakes are calculated and tabulated in Table S1 with values ranging from 1.65 to 1.8, very close to the ratio of the molecular areas in the two different orientations. This suggests this concentration driven flat to vertical phase transition occurs on the surfaces of all five graphene/GO materials and provides an indication of the monolayer coverage at low concentrations (≤ca. 200 mM). It is notable that the experimental ratios of the two plateaux are all slightly smaller than the ratio of the theoretical molecule areas, which might be tentatively attributed to the increased self-repulsion among dopamine molecules in the vertical orientation due to the protonated amine group (positively charged) leading to a less close packing on the surface of the adsorbent. Moreover, the GNP-Powder has a known width, thickness and average surface area (297 ± 152 μm^2), as provided by the supplier[34] and confirmed by our previous work[23,24,35,36] spectrophotometrically and electrochemically. The average surface area of each GNP-Powder attained from the dopamine adsorption at the first plateau is 308 ± 28 μm^2, confirming the applicability of dopamine as a probe to determine the surface area of graphene-based materials.

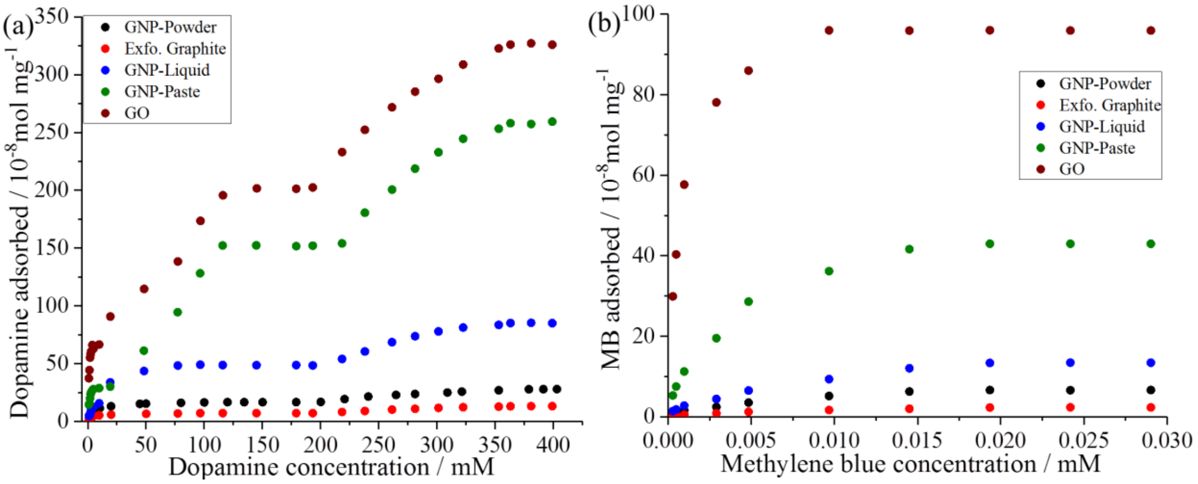

Figure 3. (a) Dopamine adsorption isotherms for five graphene and graphene oxide samples in pH 0 buffer. (b) Methylene blue adsorption isotherms for five graphene and graphene oxide samples in aqueous solution. Corresponding semi-logarithmic plots are shown in Figure S14 to show the feature of isotherms for materials with low adsorption capacity

Analogous adsorption experiments with MB solutions over a wide range of concentrations were then conducted to construct the adsorption isotherms of MB for the five graphene and GO materials. As shown in Figure 3b, the adsorbed amount of MB by four graphene-based materials (GNP-Powder, Exfoliated Graphite, GNP-Liquid and GNP-Paste) reaches a maximum at ca. 0.02 mM whereas for GO the uptake approaches the limiting level at ca. 0.01 mM MB concentration. This suggests the adsorption onto GO is thermodynamically favourable, attributed to the strong affinity between MB molecules and GO, as discussed previously. To examine possible reorientation of MB molecules on the material surfaces, experiments were also conducted at higher concentrations (up to 3.8 mM), as shown in Figure S12. Note that this concentration corresponds to the maximum possible before a significant formation of dimers causes a distorted UV-vis spectrum and a possibly different adsorption manner onto the adsorbent.[18] There is no second plateau in Figure S12 suggesting that no phase transition occurs and that MB adopts a flat orientation on the adsorbent, consistent with literature.

Having studied adsorption isotherms of both dopamine and MB for all five graphene and GO samples, the surface area of each graphene and graphene oxide sample can be probed from the equilibrium uptake of both adsorbates, as given in Table 1 and compared with values obtained from the BET-N_2 technique. The dopamine measurement shows good agreement with BET for the two low surface area samples (GNP-Powder and Exfoliated Graphite). For the other three samples (GNP-Liquid, GNP-Paste and GO), the values obtained from dopamine adsorption are much larger compared to those from BET. The BET method is well-known in the community for its incapability of measuring carbonaceous materials with large surface areas, attributed to the agglomeration state of the dry samples during the measurement[15,37] and extreme weak adsorbate-adsorbent interaction[19]. The former is the main issue for the very thin GO sheets. Moreover, it is also very challenging for the BET technique to measure carbonaceous materials with complex internal structures[19]. Particularly, this might explain the marked discrepancy of the surface area of the GNP-Paste sample measured from BET and dopamine,[38] as the latter has a complex fused sheet like morphology and internal structure (SEM: Figure 1a&S4). Consequently, for the values of the GNP-Liquid, the GNP-Paste and the GO sample, the dopamine measurements can be considered to give a more ‘correct’ indication.

Comparing the values obtained from dopamine and MB adsorption, the GO surface area determined from both methods is remarkably consistent. MB is a cationic dye, which has strong electrostatic interactions with GO attributed to the functional groups as discussed previously. Dopamine is also in cationic form under the experimental conditions employed (pH=0). This consistent behaviour suggests both methods can be used to accurately measure the surface area of GO-based materials, which has abundant functional groups attributing to an enhanced affinity. This result is also consistent with prior literature[15,18,19,37] where MB is used to measure high surface area GO or rGO based materials. To the best of the authors' knowledge, there is no literature reporting using MB as a probe to determine the surface area of graphene-based (not GO) materials. The surface areas of other graphite/graphene samples (GNP-Powder, Exfoliated Graphite, GNP-Liquid and GNP-Paste) measured from dopamine are larger than those from MB. The dopamine might give more 'correct' values for following reasons: first, the monolayer dopamine adsorption has been confirmed via phase transitions of molecular reorientation whereas the MB adsorption on carbonaceous materials is more complicated for reasons such as the concentration-driven MB dimer and trimer formation on the material surface[16]; second, as discussed previously, the surface area of the GNP-Powder is known, as provided by the supplier[34] and further confirmed spectrophotometrically and electrochemically by our previous work[23,24,35,36]. The consistency between this known surface area and the values from BET (for low surface area carbon materials) and dopamine measurements suggests the values from dopamine adsorption are more reliable. Third, it would be more challenging for cationic MB to achieve fully closed packing on the adsorbent if the adsorptive interaction is not strong enough due to self-repulsion, whereas for dopamine, the positive-charged amine group is on side chain possible probably giving less self-repulsion among adsorbed dopamine molecules. The surface areas of the GNP-Liquid and the GNP-Paste samples measured from dopamine and MB adsorption have the largest discrepancy. This might be attributed to large molecular structure of MB causing difficulties in achieving a full surface coverage especially for materials that have complex morphologies and internal structures.

Table 1. Comparison of surface areas obtained by N_2 adsorption (BET), dopamine and MB absorption techniques

	GNP-Powder	Exfo. Graphite	GNP-Liquid	GNP-Paste	GO
BET Surface Area (S_{BET} / m^2/g)	62	25	122	163	500
Dopamine Surface Area (S_{DA} / m^2/g)	64	27	190	596	783
MB Surface Area (S_{MB} / m^2/g)	54	19	109	349	780
S_{BET}/ S_{DA}	0.97	0.93	0.64	0.27	0.64
S_{MB}/ S_{DA}	0.83	0.70	0.57	0.59	1.00

In conclusion it is clear that unambiguous measurement of graphene and graphene oxide surface areas are elusive! However, the use of the dopamine adsorption method as a complement to the BET and MB adsorption measurements may be recommended on the basis that the flat to vertical transition allows confirmation in the attainment of a monolayer coverage. The fact that the measurements are faster than the MB equivalent and that the approach is simple to adopt are further benefits.

Acknowledgements

B.R. acknowledges the financial support from the German Research Foundation (DFG) through the Research Fellowship RA 3120/1-1.

References

1. Pumera, M., Graphene-based nanomaterials for energy storage. *Energy & Environmental Science* **2011,** *4* (3), 668-674.
2. Pumera, M.; Ambrosi, A.; Bonanni, A.; Chng, E. L. K.; Poh, H. L., Graphene for electrochemical sensing and biosensing. *TrAC Trends in Analytical Chemistry* **2010,** *29* (9), 954-965.
3. Ambrosi, A.; Chua, C. K.; Bonanni, A.; Pumera, M., Electrochemistry of Graphene and Related Materials. *Chemical Reviews* **2014,** *114* (14), 7150-7188.
4. Pumera, M., Graphene in biosensing. *Materials Today* **2011,** *14* (7), 308-315.
5. Schwierz, F., Graphene transistors. *Nature Nanotechnology* **2010,** *5*, 487.
6. Raccichini, R.; Varzi, A.; Passerini, S.; Scrosati, B., The role of graphene for electrochemical energy storage. *Nature Materials* **2014,** *14*, 271.
7. Yu, X.; Cheng, H.; Zhang, M.; Zhao, Y.; Qu, L.; Shi, G., Graphene-based smart materials. *Nature Reviews Materials* **2017,** *2*, 17046.
8. El-Kady, M. F.; Shao, Y.; Kaner, R. B., Graphene for batteries, supercapacitors and beyond. *Nature Reviews Materials* **2016,** *1*, 16033.
9. Choi, W.; Lahiri, I.; Seelaboyina, R.; Kang, Y. S., Synthesis of graphene and its applications: a review. *Critical Reviews in Solid State and Materials Sciences* **2010,** *35* (1), 52-71.
10. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society* **1938,** *60* (2), 309-319.
11. Lowell, S.; Shields, J. E., *Powder Surface Area and Porosity*. Springer Science & Business Media: 2013; Vol. 2.
12. Attard, G.; Barnes, C., *Surfaces*. Oxford University Press: 1998; Vol. 59, p 6-9.
13. Standardization, I. O. f., Determination of the Specific Surface Area of Solids by Gas Adsorption - BET Method. *ISO 9277:2010* **2010**.
14. Leofanti, G.; Padovan, M.; Tozzola, G.; Venturelli, B., Surface area and pore texture of catalysts. *Catalysis Today* **1998,** *41* (1-3), 207-219.
15. McAllister, M. J.; Li, J.-L.; Adamson, D. H.; Schniepp, H. C.; Abdala, A. A.; Liu, J.; Herrera-Alonso, M.; Milius, D. L.; Car, R.; Prud'homme, R. K., Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chemistry of Materials* **2007,** *19* (18), 4396-4404.
16. Haubner, K.; Murawski, J.; Olk, P.; Eng, L. M.; Ziegler, C.; Adolphi, B.; Jaehne, E., The route to functional graphene oxide. *ChemPhysChem* **2010,** *11* (10), 2131-2139.
17. Yan, H.; Tao, X.; Yang, Z.; Li, K.; Yang, H.; Li, A.; Cheng, R., Effects of the oxidation degree of graphene oxide on the adsorption of methylene blue. *Journal of Hazardous Materials* **2014,** *268*, 191-198.
18. Montes-Navajas, P.; Asenjo, N. G.; Santamaría, R.; Menendez, R.; Corma, A.; García, H., Surface area measurement of graphene oxide in aqueous solutions. *Langmuir* **2013,** *29* (44), 13443-13448.
19. Aboutalebi, S. H.; Jalili, R.; Esrafilzadeh, D.; Salari, M.; Gholamvand, Z.; Aminorroaya Yamini, S.; Konstantinov, K.; Shepherd, R. L.; Chen, J.; Moulton, S. E., High-performance multifunctional graphene yarns: toward wearable all-carbon energy storage textiles. *ACS Nano* **2014,** *8* (3), 2456-2466.
20. Li, Y.; Du, Q.; Liu, T.; Peng, X.; Wang, J.; Sun, J.; Wang, Y.; Wu, S.; Wang, Z.; Xia, Y., Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. *Chemical Engineering Research and Design* **2013,** *91* (2), 361-368.

21. Wang, S.; Zhu, Z. H.; Coomes, A.; Haghseresht, F.; Lu, G. Q., The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of colloid and interface science* **2005,** *284* (2), 440-446.

22. Chen, L.; Tanner, E. E. L.; Lin, C.; Compton, R. G., Impact electrochemistry reveals that graphene nanoplatelets catalyse the oxidation of dopamine via adsorption. *Chemical Science* **2018,** *9* (1), 152-159.

23. Chen, L.; Li, X.; Tanner, E. E. L.; Compton, R. G., Catechol adsorption on graphene nanoplatelets: isotherm, flat to vertical phase transition and desorption kinetics. *Chemical Science* **2017,** *8* (7), 4771-4778.

24. Chen, L.; Tanner, E. E. L.; Compton, R. G., Adsorption on graphene: flat to edge to end transitions of phenyl hydroquinone. *Physical Chemistry Chemical Physics* **2017,** *19* (27), 17521-17525.

25. Wei, Q.; Zhang, F.; Li, J.; Li, B.; Zhao, C., Oxidant-induced dopamine polymerization for multifunctional coatings. *Polymer Chemistry* **2010,** *1* (9), 1430-1433.

26. El-Kady, M. F.; Strong, V.; Dubin, S.; Kaner, R. B., Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors. *Science (New York, N.Y.)* **2012,** *335* (6074), 1326.

27. Rubino, R. S.; Takeuchi, E. S., The study of irreversible capacity in lithium-ion anodes prepared with thermally oxidized graphite. *Journal of Power Sources* **1999,** *81*, 373-377.

28. Choucair, M.; Thordarson, P.; Stride, J. A., Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nature Nanotechnology* **2009,** *4* (1), 30.

29. Li, D.; Müller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G., Processable aqueous dispersions of graphene nanosheets. *Nature Nanotechnology* **2008,** *3* (2), 101.

30. Li, M.-j.; Liu, C.-m.; Xie, Y.-b.; Cao, H.-b.; Zhao, H.; Zhang, Y., The evolution of surface charge on graphene oxide during the reduction and its application in electroanalysis. *Carbon* **2014,** *66*, 302-311.

31. Si, Y.; Samulski, E. T., Synthesis of Water Soluble Graphene. *Nano letters* **2008,** *8* (6), 1679-1682.

32. Batsanov, S. S., Van der Waals radii of elements. *Inorganic materials* **2001,** *37* (9), 871-885.

33. Soriaga, M. P.; Hubbard, A. T., Determination of the orientation of adsorbed molecules at solid-liquid interfaces by thin-layer electrochemistry: aromatic compounds at platinum electrodes. *Journal of the American Chemical Society* **1982,** *104* (10), 2735-2742.

34. Inc, S. C., Graphene Nanoplatelets. *Strem Product Catalog* **2012**.

35. Poon, J.; Batchelor-McAuley, C.; Tschulik, K.; Compton, R. G., Single graphene nanoplatelets: capacitance, potential of zero charge and diffusion coefficient. *Chemical Science* **2015,** *6* (5), 2869-2876.

36. Wu, H.; Lin, Q.; Batchelor-McAuley, C.; Gonçalves, L. M.; Lima, C. F.; Compton, R. G., Stochastic detection and characterisation of individual ferrocene derivative tagged graphene nanoplatelets. *The Analyst* **2016,** *141* (9), 2696-2703.

37. Schniepp, H. C.; Li, J.-L.; McAllister, M. J.; Sai, H.; Herrera-Alonso, M.; Adamson, D. H.; Prud'homme, R. K.; Car, R.; Saville, D. A.; Aksay, I. A., Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide. *The Journal of Physical Chemistry B* **2006,** *110* (17), 8535-8539.

38. The two measurements are made at very different temperatures namely liquid N_2 and room temperature. Both the surface areas reflect that of a close packed adsorbate layer in each case.