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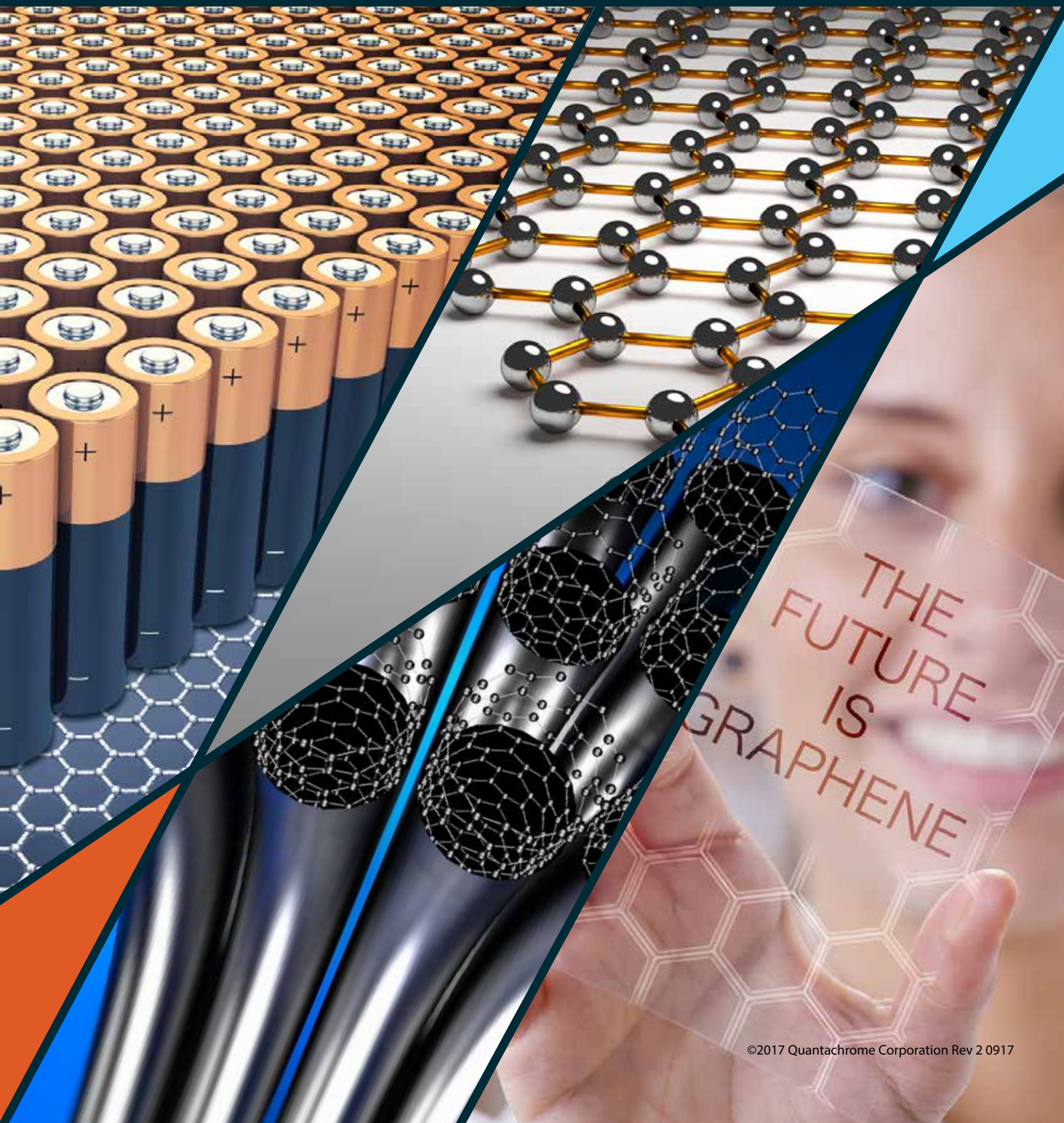
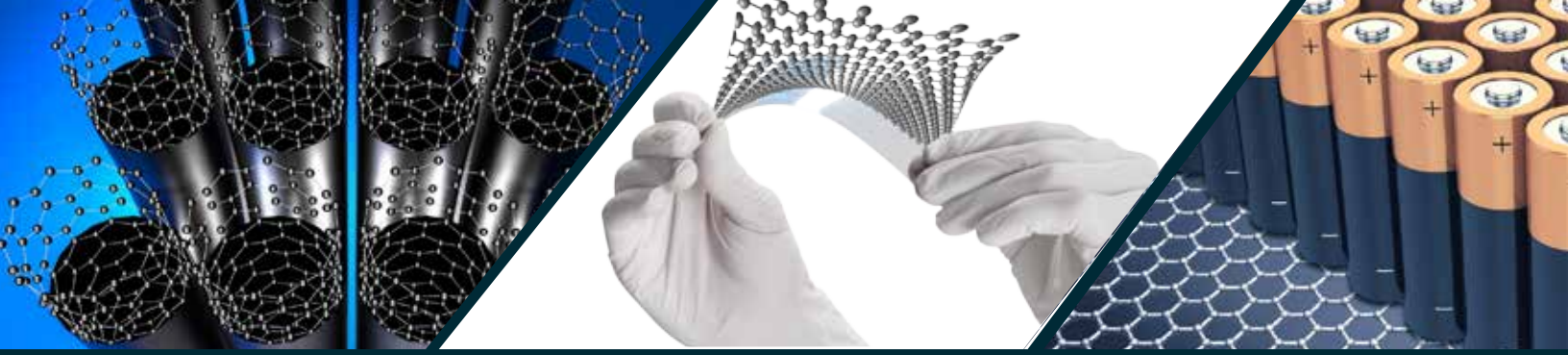
INSTRUMENTS

GRAPHENE

Your Window to the Future

Application Highlight





Graphene and graphene-related materials have, in their relatively short life span, revolutionized many areas of materials science and technology. Their huge technological success is to a large extent related to their unique structure and properties. This Note briefly examines graphene structure and some key fundamental properties that lead graphene, and graphene-related materials, to challenge both fundamental physics and technical frontiers in materials science.

Graphene Surface Area

Surface area impacts every application of graphenes and graphene-related materials (such as graphene oxide, graphene-metal oxide composites, heteroatom-doped graphenes, nanostructured photo-catalysts, etc.). It is largely the exposed surface of these materials that interacts with gases, liquids, solids, electrons, ions, photons and phonons. Therefore, evaluating the surface area of graphene materials (GMs) is a crucial step in understanding and optimizing their performance. Currently the most reliable method to evaluate the surface area of GMs is by the classical BET method. This method derives the BET surface area of GMs from nitrogen sorption isotherms collected at 77K on suitable equipment, such as the **Autosorb-iQ**, the **NOVAtouch**, or the **Quadrasorb evo.**

NOVAtouch

Graphene sheets, if fully exposed and reasonably large, have a theoretical surface area of 2,629 m^2/g. Surface areas of that magnitude have indeed been reported following, e.g., activation of exfoliated graphene oxide. However, graphene sheets tend to stack on top of each other due to weak but extensive van der Waals interactions between their surfaces. Graphene layer stacking reduces their accessible surface area in propotion to their degree of stacking. **Table 1** shows the predictions from a simple scaling law of the form $N = A_t/A_m$, where N is the number of stacked layers, A_t is the theoretical graphene surface area, and A_m is the measured BET surface area, in comparison with N values derived from other techniques.

Commercial Graphene	BET Surface Area [m^2/g]	Number of Stacked Layers, N	
		Reported	Calculated
G1	675	4	4
G2	187	10	14
G3	126	20	21
G4	95	N.R.	27
G5	26	25	100

Table 1.
Comparison of Average Number of Stacked Layers (N) of Commercial Graphene Samples Estimated by Gas Sorption with Reported Values.

Graphene Structure: Graphene has arguably the largest surface area-to-volume ratio among novel 2D crystalline layered materials . Being spread as an atom-thick layer of ring-bound carbon atoms, all atoms in graphene sheets are in fact exposed to its surface. This gives graphene a rich array of unique surface physical, chemical, and electronic properties, which continue to open doors for new applications in nanotechnology and condensed matter physics.

Graphene Pore Sizes

Pores in graphene or graphene-related materials can include holes within sheets, whose dimensions can be tailored by, e.g., selective ring removal and nitrogen passivation, and spaces between sheets, with the overall pore dimensions and size distribution being dictated by the degree of stacking, crumpling, or pillaring with additives. Representative examples of pore size distributions of graphene-based materials measured on an **Autosorb-iQ** are shown in **Figure 1**. In this particular case, chemical activation of an exfoliated graphene oxide material yielded a graphene derived product with 98% sp^2 bonds, extremely high BET surface area, and a bimodal pore size distribution. Note that ready access to the ultramicropores below ~0.7 nm was achieved using CO_2 adsorption at 273 K, in order to avoid the slow diffusion of nitrogen in the smallest nanopores. These pore size features correlate with the performance of graphenes and graphene-based materials for a large an increasing number of applications.

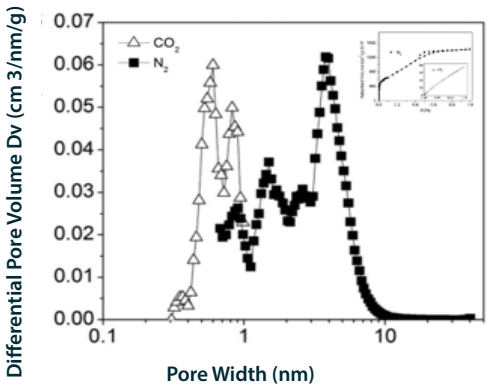


Figure 1 - Graphene GM-PSD.

Autosorb iQ- MP

Graphene Density

Gas pycnometry provides a fast, clean and nondestructive way to assess the density of carbon materials in general. The precision and accuracy of modern gas pycnometers such as the automated **micro-Ultrapyc 1200e** (capable of handling sample volume down to 0.1 cm^3) are adequate to assess the differences in chemical and physical characteristics of graphene-related materials. The density of graphene sheets can increase with increased stacking order and perfection. Perfectly stacked and aligned graphene sheets have a density close to that of crystalline graphite (2.267 g/cm^3). However, heteroatoms, stacking imperfections and defects tend to lower the density to a value that depends on heteroatom nature and content, and on pore characteristics.

Ultrapyc 1200e

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Graphene Reactivity

Although the surfaces of ideal graphene 2D crystals are uniform, real graphene materials are often energetically, chemically and physically heterogeneous. Surface sites that may be more reactive towards adsorption, ion or electron exchange, mechanical strain, etc., include graphene sheet edges, Stone-Wales defects, heteroatoms, functional groups, impurities, metal catalysts, and so on. Both chemisorption and temperature-programming techniques are used to assess the quantity and quality of the more reactive sites on graphenes and graphene-related materials Advanced chemisorption instruments such as the Autosorb-iQ or the **ChemStar** are ideally suited address to these applications.

ChemStar TPx

Concluding Remarks

Graphene and graphene-related materials are currently at the forefront of materials research and technology. The precise evaluation of their structural characteristics is an essential step towards optimizing their performance. Specific properties that affect virtually every application of graphene materials include their specific surface area, pore size distribution, density and reactivity. Graphene surface areas can vary by orders of magnitude depending on their degree of stacking, crumpling, pillaring, and their heteroatom and defect content. Holes and micro-mesopores may be present within and between layers of graphene materials. Densities of bulk graphenes measured by gas pycnometry tend to fall below crystalline densities due in part to some closed or inaccessible pores being present in these materials. Graphene reactivity is related to the nature and concentration of active sites, which can be quantified using modern chemisorption and temperature programming techniques. Much remains to be done to fully exploit and expand the range of applications of graphene materials. The techniques described above provide useful and precise tools to empower users to push the boundaries of graphene materials to ever-increasing levels.

Autosorb IQ-C

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