Graphene and graphene-related materials have revolutionized numerous areas of materials science and technology. Their massive technological success is related to their unique structural and chemical properties. Graphene structure and key fundamental properties such as surface area, pore size, and density are examined.

1 Introduction

Graphene has arguably the largest surface area to volume ratio among novel 2D crystalline layered materials. Being spread as an atom-thick layer of hexagonal ring-bound carbon atoms (Figure 1), all atoms in a graphene sheet are surface exposed. This gives graphene a rich array of unique surface physical, chemical, and electronic properties that continue to open doors for new applications in nanotechnology and energy.

2 Surface Area

Surface area impacts every application of graphene and graphene-related materials (such as graphene oxide, graphene-metal oxide composites, heteroatom-doped graphene, and nanostructured photocatalysts, among others). It is largely the exposed surface of these materials that interacts with gases, liquids, solids, electrons, ions, photons, and phonons. Therefore, evaluation of the surface area of graphene materials is a crucial step in understanding and optimizing their performance.

The recommended method to evaluate the surface area of materials is the BET method. This method calculates the BET surface area of graphene from nitrogen or argon sorption isotherms collected at 77 K or 87 K, respectively on suitable equipment [2]. Cryogenic conditions facilitate the formation of an equivalent monolayer of adsorbed gas molecules on the exposed graphene surface. The BET method is able to quantify surfaces inaccessible by other means and is thus recommended by IUPAC for surface area evaluation [2].

Graphene sheets, if fully exposed and reasonably large, have a theoretical surface area of 2,629 m²/g. Surface areas of that magnitude have indeed been reported following, e.g., activation of exfoliated graphene oxide [1]. However, graphene sheets tend to stack one on top of another due to weak, but extensive, van der Waals interactions between their surfaces. Graphene layer stacking reduces their accessible surface area in proportion to their degree of stacking.

3 Pore Size

Pores in graphene or graphene-related materials can include holes within sheets, whose dimensions can be tailored by things such as selective ring removal and nitrogen passivation. It can also include spaces between sheets, with the overall pore dimensions and size distribution being dictated by the degree of stacking, crumpling, or pillaring with additives. A representative example of pore size distribution on a graphene oxide material is shown in Figure 2. In this particular case, chemical activation of an exfoliated graphene oxide material yielded a graphene-derived product with extremely high BET surface area and a broad, roughly bi-model micro- and mesopore size.
distribution [1]. Note that ready access to the ultramicropores below ~0.7 nm was achieved using CO₂ adsorption at 273 K and a full micro-mesopore size distribution was only possible for this sample by combining the pore size distribution from CO₂ (273 K) adsorption with that from the N₂ (77 K) adsorption isotherm, because this material contains pores smaller than can be accessed by N₂ alone.

Pore size distributions were calculated using density functional theory (DFT) methods such as non-local DFT (NL/DFT) and quenched solid DFT (QSDFT, which takes into account the surface heterogeneity of most carbon-based samples). These are the most accurate and recommended methods for pore size distribution calculation [2]. These pore size features have been demonstrated to correlate with the performance of graphene-based materials for a large and increasing number of applications. For example, hierarchical micro-mesopore structures have been shown to enable the retention of high surface area and reactivity in the smaller micropores. In their larger mesopores, faster diffusion and transport of species through the material can reach the reactive sites more efficiently. The gas sorption technique is ideally suited for the characterization of individually or combined micro-mesoporous graphene and graphene-based materials.

4 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 are adequate to assess the differences in chemical and physical characteristics of graphene-related materials.

The density of graphene sheets can increase with increasing stacking order and perfection. Perfectly stacked and aligned graphene sheets have a density close to that of crystalline graphite (2.267 g/cm³). 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. In some cases, pores created during stacking or agglomeration can remain closed to external gases. Closed porosity, in particular, tends to lower measured densities significantly, but can be exposed by, for example, subjecting bulk graphene particles to high energy milling processes. Accordingly, reported densities of graphene-related materials (in the form of powders or films) ranging between ~1.6 – 2.1 g/cm³ are not uncommon.

5 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, and mechanical strain include graphene sheet edges, Stone-Wales defects, heteroatoms, functional groups, impurities, and metal catalysts. Both chemisorption and temperature programming techniques (TPX) can be used to assess the quantity and quality of the more reactive sites on graphenes and graphene-related materials by automated techniques that are readily available using advanced chemisorption instrumentation.

6 Conclusions

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 chemisorption and temperature programming techniques. The techniques described above, utilizing Anton Paar instrumentation, provide useful and precise tools to empower users to push the boundaries of graphene materials research.
7 References
