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1. Introduction

Surface wetting, capillarity, adhesion, and surface tension-related processes across solid-liquid interfaces have been the focus of extensive theoretical and experimental research in fields such as natural sciences, agriculture, geophysics, technology, water management, biological, and environmental sciences. Intermolecular interactions play a key role in the ability of a liquid to maintain contact with a solid surface, and a balance between cohesive and adhesive forces determines the overall wetting behavior of the system. Some of the wettability applications include superhydrophobic surfaces, dynamics of oil spills, ground water flows, disease transmission, chemical leaching, nanotechnology, and several other real-life applications [1, 2].

The wetting behavior of nanomaterials such as carbon nanotubes (CNT), graphene, graphyne, nanoparticles, and nanoengineered surfaces is an area of intense experimental and theoretical research activity [3–5]. Intermolecular interactions are of crucial importance for controlling nanoscale material behavior in various aspects of nanotechnology, nanodevices, and their applications. Other areas of research include the flow of liquids inside nanochannels, tuning of nanotube forests and arrays for modifying wetting characteristics, development of nanogrippers for manipulating carbon nanotubes for electro-mechanical devices, nanoscale surface treatments for producing hydrophilic or superhydrophobic surfaces [6].

Several advanced optical or microscopic experimental techniques are being used for nanoscale wetting investigations. While the macroscopic contact angle at the solid-liquid interface can be measured using conventional optical techniques, advanced microscopic or indirect techniques are required for micro and nanoscale investigations. It is also a common practice to determine an “effective contact angle” at nanoscale distances due to limited/poor contact at the liquid meniscus, confinement issues, and the influence of long-range forces [7].

A brief overview of measurement techniques is provided next. Surface forces technique determines the influence of separation distance on forces (±10 nN) between two surfaces with the help of capacitive sensors or springs; distances can be controlled down to 0.1 nm with help of piezoelectric positioners. Wilhelmy method measures the force exerted during contact of liquid with a solid specimen for an indirect determination of contact angle [8]. This technique has been used to determine the wetting behavior of nanowires (500 nm dia.) and nanoneedle probes. Widely used sessile drop technique determines contact angle directly from the profile of a liquid drop atop a solid substrate with help of video cameras or telescopic arrangements. This technique can be used to continuously monitor dynamic changes in contact angles as a function of various system variables [9].
Interference microscopy technique computes contact angles (15–30°) from the 3D contours and profiles of liquid droplets by using interference fringe patterns formed at the solid/liquid and liquid/vapor interfacial region [10]. Atomic force microscopy scans the sample surface with a sharp tip to monitor surface topology while maintaining a constant interaction force through feedback loops; a modified nanodispenser tip is used for micro- and nanodroplets [11]. Scanning Polarization Force Microscopy uses electric polarization forces for mapping topography contours for distances in the range 10–20 nm, thereby minimizing the risk of surface contact by probing tip, an aspect especially valuable for soft and liquid specimens [12].

Extensive theoretical research is also being carried out using theoretical modeling, analysis, Monte Carlo, and molecular dynamics computer simulation on a variety of relevant issues. Some of the problems being investigated include the influence of nanoscale confinement on surface tensions, wetting behavior inside small capillaries and nanochannels, effect of line tension, liquid adsorption on capillary walls, and precursor films, the role of nanoscale surface roughness on confinement and wetting among others [13, 14].

In this chapter, a brief overview on the nanoscale wetting behavior of graphene and carbon nanotubes is presented along with factors influencing the wetting phenomena and basic system characteristics of nanomaterials.

2. Graphene

Remarkable technical developments, based on carbon’s ability to bind to itself in a variety of hybridized states, have seen the emergence of synthetic carbons with exotic and exceptional properties, e.g., fullerenes, nanotubes, graphene, graphyne, nanorings, etc. Graphene, the ultimate thin material, is composed of a single sheet of graphite, and is currently one of the most investigated 2D carbon allotrope [15]. Its existence was considered to be purely theoretical for a long time. Single graphene layers were prepared in 2004 by a simple mechanical exfoliation of graphite using a Scotch tape. Graphene is finding extensive applications in nanotechnology, optoelectronics, water desalination, dispersion in polymers, etc. Several of these applications, such as capacitive energy storage and heat transfer coefficient, depend strongly on graphene’s wettability and its surface-based interactions with various liquids [16].

With all its carbon atoms exposed to high levels of surface activity, graphene is a material of choice for interfacial carbon materials, especially for carbon-aqueous liquid interactions. Poor wettability of graphene with water and its hydrophobic nature can limit device contamination during fabrication; however, there are concerns regarding the hydrophilic or hydrophobic nature of graphene and its dependence on operating parameters. The contact angle of graphene with water and aqueous solutions has been found to vary depending upon various conditions, e.g., surface wrinkle morphology, extent of tensile strain, vibrational strain, etc. Other variables include the influence of doping, presence of defects, temperature, and electric field, among others. Graphene monolayer also finds application as an ideal coating material due its wetting transparency [17].

Vertical graphene sheets for applications, such as high-performance super capacitors, are presently being produced using plasma-enhanced chemical vapor deposition technique. During sputtering and deposition process, a number of defects get invariably incorporated in graphene sheets. The density of defects can be controlled through sputtering time. Graphene with low density of defects showed a hydrophobic behavior and poor wettability; significant improvements in the wetting were, however, observed for high defect concentrations [18]. Laser-induced
graphene is produced by irradiating polyimide film with CO\textsubscript{2} laser to burn away all elements except carbon. Operating conditions during their production can impact the chemical composition of the graphene surface affecting its wettability with water; the presence of H\textsubscript{2} gas in the chamber along with limited O and CO contents led to hydrophobic graphene [19].

Graphene, typically a zero-band-gap semiconductor, can be doped as n-type or p-type using sub-surface polyelectrolyte or metals, electrical voltage chemicals, etc., and its wetting properties can be modified with significant changes in contact angles [20]. Doping can modify and regulate the surface electron density of graphene and its interaction with external molecules in the contact region. It may also help to develop a feasible route for tuning the surface wettability of graphene, especially for coating applications. Studies have also been reported on the conversion of its surface wettability from hydrophobic to hydrophilic and vice versa with help of external stimuli [21]. Extensive research is being carried out in this field on several aspects of the wetting behavior of graphene with focus on controlled and reversible tuning.

3. Carbon nanotubes (CNTs)

Carbon nanotubes, seamless rolled-up graphite sheets, are tubular networks of sp\textsuperscript{2}-hybridized carbon atoms; these 2D structures are considered to be one-dimensional due to their high aspect ratio (1–2 nm dia., length in mm) [22]. Produced using techniques such as chemical vapor deposition, graphite evaporation, etc., these can either be single- or multi-walled depending on the production route [23]. Due to several unusual characteristics including nanoscale diameters, non-polar surfaces, CNTs are being investigated for nanoscale water desalination and selective transport in nanochannels. The wetting behavior of CNTs, nanotube forests and arrays, effects of nanoscale confinement, and tunability are areas of intense research [24, 25].

The effect of various conditions on the wetting behavior of CNTs with water has been investigated by several researchers. Key factors were found to be the structure of CNTs, tube’s size, the strength of van der Waals interaction between water and carbon, spontaneous imbition of water in CNTs, surface energies, and temperature [26, 27]. MD simulations on SWCNTs in the temperature range 270–370 K showed an increase in capillary filling and water uptake with increasing temperature. This was attributed to increased wettability and reduced viscosity of water with temperature along with small increases in water imbibition [28].

The wetting behavior inside small capillaries or nanochannels can be very complex depending on intermolecular interactions between the solid and the liquid, van der Waals attraction, surface tension, line tensions along the radius of the nanotubes, tube diameter, etc. [29]. The adsorption of liquid atoms as mono/multilayers on capillary/CNT walls can distort the meniscus profile during the filling of nanochannels and may affect the wetting behavior due to disjoining pressure induced by molecular interactions. Surface roughness can also play an important role during nanoscale confinement, especially when the characteristic variations in surface roughness become comparable to the channel diameters. Surface chemistry is another key factor affecting wettability and flow through nanochannels [30].

A number of investigations have been reported on “nanopumping” to pump liquids through nanotubes based on electrical or mechanical properties of CNTs including studies on the flow of viscous fluids, activation of fluid flow, friction with nanowalls, etc. [31]. The wetting behavior of CNTs has been investigated with a number of polymers, e.g., polyvinylidene fluoride, maleic acid anhydride,
polycaprolactone, polyurethane acrylate, etc. Chemical surface treatments were used to modify the wettability of nanochannels [32]. The wetting of nanotube forests and arrays has been investigated with several liquids including water, glycerol, ethylene glycol, propylene carbonate, olive oil, dimethyl sulfoxide, and nitromethane with contact angles ranging between 60 and 157° [33]. CNT forests have been used to grow hematite nanochain arrays, as filters to capture micro/nanocontaminants in water, and as gas diffusion arrays with contact angles up to 150° [34].

4. Concluding remarks

A number of factors may be used to affect, control, and tune the wettability of nanomaterials. There is immense potential for creating materials with designer characteristics tailored to specific applications. The influence of wetting characteristics, including contact angles, chemical composition of nanosurfaces, and surface roughness on the flow behavior of water, aqueous solutions, and polymers, is being investigated for water filtration, desalination, dispersion in polymers, etc. The contact angle of graphene with water has been found to depend upon doping, concentration of defects, temperature, electric field, surface wrinkle morphology, tensile, and vibrational strains. Nanoscale wetting investigations on materials, e.g., CNTs, graphene, nanochannels, membranes, and nanostructures represent an area of intense theoretical as well as experimental research activity.

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