Layered Nanomaterials-A Review

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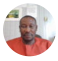

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LAYERED NANOMATERIALS - A REVIEW

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Abstract

Layered materials can become a myriad source of two-dimensional crystals if the layers can be separated from each other, for example via exfoliation. Potential applications for single layer materials range from energy storage, electronics and mechanical reinforcement of plastics, to life-saving applications such as drug delivery, medical imaging and clean-up of toxic materials in the environment. Layered nanomaterials can be found naturally and can also be synthesized in the laboratory in order to suite certain specific applications. We describe here key layered materials including some naturally occurring (graphite, graphene, clays, layered hydroxides (LDHs)) and others that have been synthesize through chemical combination of some atomic species such as boron nitride (BN), transition metal oxides (TMOs), LDHs, and transition metal dichalcogenides (TDMs), along with a discussion of their properties and potential applications.

***Keywords**: Nanomaterials; Clays; Graphite; Graphene; TMOs LDHs TDMs.*

Introduction

The emergence of newer technologies induces great excitements and at the same time concerns be it in the academia, policy-making, businesses, investments, ethicism, journalism, futurism, the general public and many more. Nanoscience currently, is certainly a flashpoint for irrational exuberance and fears. In terms of definition, there is always a knowledge gap associated with the early stages of any new technology; and nanotechnology and nanomaterials science are no exception. Research Scientists and Engineers are still learning about nanoscience and its applications. In the meantime, hope and hype naturally and irresistibly fill this vacuum of knowledge. In nanomaterials science and nanotechnology, we find an entire range of speculative possibilities, from limitless life to the end of days. Depending on which school of thought, this field could help solve the world's energy and hunger issues. Or help us easily ride into orbit on a space elevator or evolve into cybernetic beings. Or, alternatively by manipulating the basic building blocks of nature – nanomaterials may scorch the earth and fulfil a prophecy of Armageddon. We may finally cause our own undoing by unleashing a powerful technology that we do not yet fully understand and thus may not be able to control. Most of these visions are based on fertile imagination and creative speculation rather than the real nanoscience research underway in laboratories.

So what are nanomaterials? Will nanomaterials bring a new era for humanity or its reckless demise? Or perhaps neither of these: nanomaterials could be much talk about nothing, with some mundane and humdrum products it has enabled today such as longer lasting tennis balls and stain resistant pants. Maybe most likely is a gradual change and incorporation of nanomaterials, improving pre-existing products by extending the life of telephone batteries or improving their screens, toughening car paint or making windows 'anti-fog', or changing chemical production processes so they need less energy and produce less toxic by-products.

Frankly speaking none of us know the exact answer, despite a continuous flood of predictions. But what we do know is that nanotechnology and nanomaterials are starting to enter the marketplace, and on-going research is exploring both the potential for risk such as environmental and health harms, as well as potential for innovation from "self-healing" concrete to flexible smart phones. It is becoming clear that nanomaterials science has the potential to profoundly change the world, even if the most visible of today's products are perhaps more focussed on "high-tech" marketing than real product innovation. Understanding what nanomaterials are and why they matter is the first step in a roadmap towards our future: it is the next generation for industries, financial markets, research labs, headlines, and our everyday lives. This article seeks to demystify the speculation surrounding this modern area of materials and engineering with an informed and balanced look at one part of this puzzle - layered nanomaterials.

To this end, a discussion is presented on the need for nanomaterials, the various forms of layered nanomaterials; the structure of carbon nanomaterials; clay and other layered materials; and specific applications of this new class of nanomaterials.

The Need for Nanomaterials

Looking at the envisaged applications there is a common need to work with nanostructured materials. In recent times, nanostructural science and technology has become one of the most interesting, diverse and fast growing research areas in materials science and engineering. Some emerging multidisciplinary fields of applications have appeared in nanoelectronics, nanostructured sensors (nano-nose) and nanostructured solar cells.

A clear classification and discussion on the use of nanomaterials can be found in the pioneering work of Gleiter and co-workers (Gleiter, 1989). The main idea behind the nanoscience is to control and/or engineer the structural, physical, chemical or biological properties of materials on the nanometer (atomic) scale. It is worth stating that, in some cases the properties of these materials can be very different (most often superior) in comparison to the macroscale (bulk) properties of the same material. Most of the properties of say, a homogeneous bulk spherical solid material with macroscopic dimensions are related to its crystal structure and chemical composition. The surface atoms of this bulk material comprise a negligible proportion of the total number of its constituent atoms and hence play a negligible role in the observed (bulk) properties of the material. However, that surface atoms may play a predominant role in properties involving exchanges at the interface between the material and the surrounding medium such as crystal growth, chemical reactivity and thermal conductivity.

When the size of the particles is reduced to the nanometric scale, the proportion of atoms located at a surface area is considerably high in relation to the total volume of atoms in the material. This has a strong effect on the materials properties. For instance, at 5nm (ca. 8000 atoms) the proportion of surface atoms is estimated to be about 20 % whilst at 2nm (ca. 500 atoms), it stands at 50%. Assuming that the particles are spherical in shape, then the surface area to volume ratio can be given as $S/V = 3/r$ where r is the radius of the particle. Decreasing the particle radius increases the surface area to volume ratio. For instance, a 1 cm^3 of 1 nm sized particles would have an active surface area of about 100 m^2 Ichinose, Ozaki & Kashu, (1988). From Maxwell (1904), it is known that the effective thermal conductivity of suspensions containing spherical particles increases with the volume fraction of the solid particles. Since heat transfer takes place at the surface of the particles, it is preferable to use particles with a large surface area to volume ratio. Thus, if nanometer-sized particles could be suspended in traditional heat transfer fluids, a new class of engineered fluids with high thermal conductivity, called “nanofluids” Choi, (1995); Eastman, Choi, Li, Yu, & Thompson. (2001), and highly sensitive gas sensors such as the nano-nose could be fabricated.

Because of the extremely small size of the grains (domains) of nanomaterials, a large fraction of the atoms in these materials is located at the grain boundaries which impede movement of dislocations, thereby allowing the material to exhibit a superior physical, mechanical, magnetic, electronic and biometric properties in comparison with coarse-grained/bulk (>1 µm) materials. This phenomenon is attributed to the fact that the grain boundary energy of nanocrystalline powders is larger than the grain boundary energy of fully equilibrated grain boundary Johnson, (1988). Furthermore, these materials show increased strength, high hardness, extremely high diffusion rates, and consequently reduced sintering times for powder compaction.

The synthesis of nanomaterials and the creation of nanostructures are achieved mainly through two complementary approaches identified as top-down and bottom-up (see figure 1).

The top-down approach involves whittling down the size of materials from the bulk (macroscopic) to the nanometer scale. This approach generally relies on physical processes, or a combination of physical and/or chemical, electrical or thermal processes for their production. Usually the top-down approach is cost-effective but the control over the produced material is poor.

The bottom-up approach, on the contrary, involves assembling atom-by-atom, or molecule-by molecule into structures on the nanometer scale with properties varying according to the number of constituent entities/grain size. Building the system atom by atom or molecule by molecule guarantees the best control over all particles in the system. Colloidal dispersions such as microemulsions are a good example of the bottom-up concept of nanomaterials synthesis.

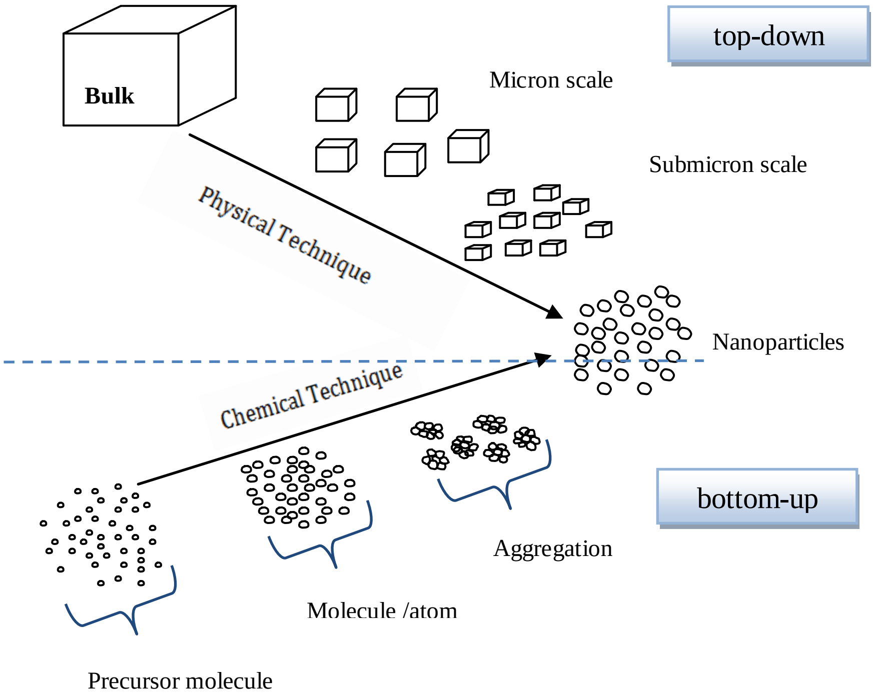


Figure 1. The two complementary approaches to nanoparticles synthesis.

Layered Nanomaterials

Most common materials are three-dimensional; the atoms that make up their structure are arranged in regular, crystalline patterns, filling space like a stack of oranges at a market stall. However there also exist a class of materials where the atoms are arranged in flat layers, which are then stacked on top of each other like sheets of paper in a pile. Until recently it was thought that these layers could not be separated out from each other, and it is only in the last ten years that there has been an explosion of interest and new techniques developed to separate out individual two-dimensional layers of material. A common route to production of layered nanomaterials is called *exfoliation*, where the individual layers in a bulk material are separated out, either chemically, or for example through mechanical abrasion. Another more recent route is direct chemical growth of individual layers, for example graphene sheets can be grown by the chemical vapour deposition technique (CVD) on the surface of a metals catalyst (e.g, copper) by heating at high temperatures (≈600ºC-1200ºC) and passing a carbon containing gas such as methane over the copper.

This class of materials represents a diverse and largely untapped source of two-dimensional (2D) systems with exotic electronic properties and high specific surface areas that is important for sensing, catalysis, and energy storage applications Coleman et al. (2011). The most common naturally occurring layered materials are graphite, graphene, clays and layered hydroxides (LDHs). However, other forms of layered compounds such as transition metal dichalcogenides (TMDs), transition metal oxides (TMOs), and other 2D compounds such as BN, Bi_2Te_3, and Bi_2Se_3. LDHs have also been synthesized, with several hundred layered materials now identified in nature. Some of the basic host lattice dimensionalities of materials are schematically shown in figure 2.

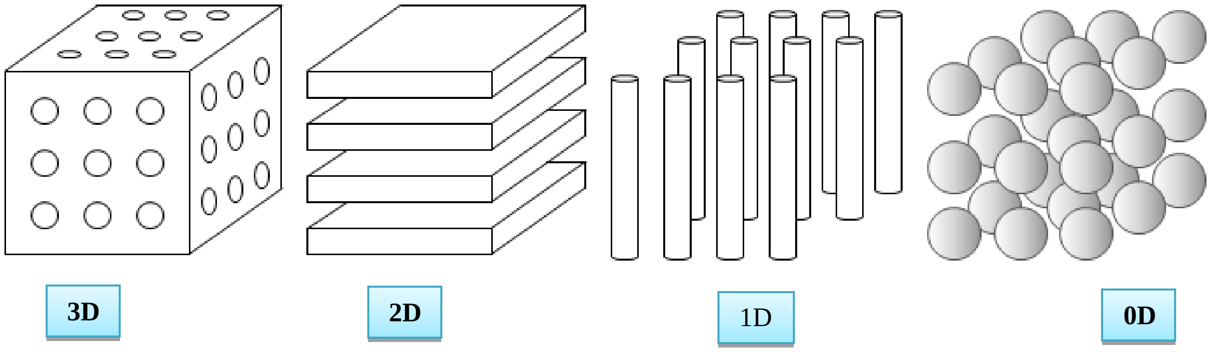
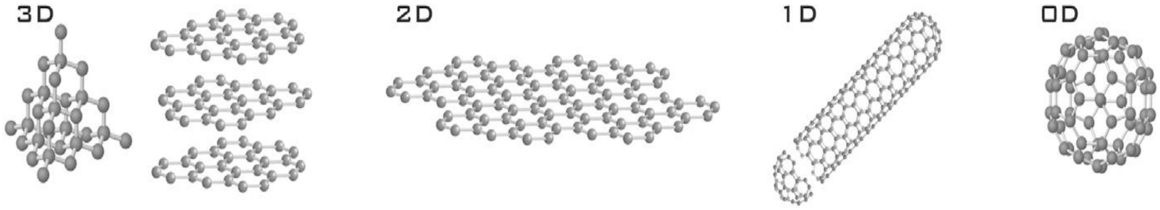


Figure 2. The basic host lattice dimensionalities; 3D (crystals), 2D (layers), 1D (rods, tubes, chains) and 0D (separate molecules) (O'Hare, 1996)

Layered Carbon Nanomaterials

Carbon is a very versatile material which exists in nature in different structural forms. It is the third most abundant element in the universe after hydrogen and helium. On the periodic table, it is classified in group IV together with silicon, germanium, tin and lead. Most of these elements exist in tetrahedral (sp^3) bonding, that is, each carbon atom in a crystal has four neighbouring atoms surrounding it in a pyramid arrangement. In the case of carbon, this material is diamond. Carbon is the only member of this group that can also take other different configurations such as a plane hexagonal (sp^2) (with three neighbours arranged in hexagons - graphite) or linear (sp) configurations (carbynes) depending on the atom or compound in bonding with it.

The extraordinary properties of carbon nanomaterials can be traced from the hybridization of carbon; electrons in the innermost shell of carbon atoms make up an electron 'core' adequately enclosed to allow the outer electrons to mix with other atoms to form linear or one-dimensional (1D), plane or two-dimensional (2D) and tetrahedral or three-dimensional (3D) materials (see figure 2 & 3). Here the two most common layered carbon materials (graphite and graphene) are discussed.



); Graphene

Graphite allotrope was discovered around 1987 by Abraham Gottlob Werner. He named it allotrope from the Greek word *graphein*, meaning to 'write' or to 'draw'. It is known to be the most thermally stable form of carbon in standard conditions. Graphite can be classified into both natural and synthetic categories. Various graphites within the same classification vary considerably in crystallinity; hence, natural graphite is further sub-divided into flake (crystalline), vein (lump) and microcrystalline (amorphous) graphite. These different types of natural graphite are each constituted from different ores Boucher, (1985) but flake graphite is the form commonly found in nature.

This naturally occurring *crystalline flake graphite* occurs as isolated, flat plate-like particles with hexagonal edges if unbroken; when broken, the edges can be irregular or angular. They are generally classified by flake size with diameters ranging from 50 to 800 μm and thicknesses from 1 to 150 μm. Crystalline flakes are obtainable in metamorphosed coal beds and silica-rich quartzites. Due to the high degree of crystalline perfection of their structure, their density, electrical conductivity and thermal conductivity values are close to the theoretical maximum. Flake graphite exhibits excellent compacting properties and has a high carbon content of 90–95% Shibata, (2008). Furthermore, it can be purified by hydrofluoric and hydrochloric acid treatment, following extraction using similar or the same solvents. The final stage of purification is heat treatment to 1500 ^{o}C under vacuum or, alternatively, by flowing chlorine at 3000^{o}C Ragan & Marsh, (1983).

Vein graphite, also known as lump graphite, occurs in filling fissures (cracks in rocks), and in veins in metamorphic or igneous (formed from molten magma or lava) rocks. This form of graphite has various forms and dimensions from fine powder to lumps of 10 cm in size. The structure is highly crystalline, which provides the material with excellent electrical conductivity. Vein graphite has the highest degree of cohesiveness of all natural graphite, Kelly & Gittus, (1981).

Microcrystalline graphite (commercially called amorphous graphite) is also a coal or soot with no defined crystal structure. It occurs in metamorphic anthracite coal beds or in carbonaceous sedimentary rocks in the form of extremely fine crystalline grains. Its graphite content ranges from 25 to 85%, depending on geological conditions. However, it is a form of natural graphite with a high degree of graphitisation and microcrystals oriented in different directions. The high degree of graphitisation of amorphous graphite led to the accidental discovery of synthetic graphite by Edward Goodrich Acheson Tamashausky, (2006). He discovered synthetic graphite while manufacturing silicon carbide. Essentially, there are two forms of synthetic graphite, which are produced differently. The first form is electro-graphite, which has high carbon content and is produced from petroleum coke calcined at 1300ºC. It is then crushed and the blended particles are mixed with binder pitch and extruded to get a green artefact, which is then graphitised at 2800°C, in an electric furnace.

The other form is produced from heating petroleum pitch calcined at 2800ºC; the resulting synthetic graphite has low density, high porosity and high resistance. However, thermal heating under pressure of materials produced through chemical vapour deposition (CVD) yields synthetic graphite known as highly oriented pyrolytic graphite (HOPG) Synthetic graphites are polycrystalline materials with variable degrees of crystallite perfection, crystallite dimensions and preferred orientation. They also vary with regard to properties such as electrical resistivity, porosity and optical texture (*Ragan & Marsh, (1983*). Graphite products can be moulded into diverse shapes and sizes based on their application.

Graphite has a layered structure in which the atoms are arranged in a hexagonal pattern within each layer, each atom having three neighbours. The layers are stacked in an 'AB sequence', i.e. half the carbon atoms have carbon atoms directly above and below them in the neighbouring sheets, half have 'holes' above and below them. This results in a hexagonal unit cell with dimensions (a = 2.46 Å, c = 6.71 Å) Chung, (2002); Telling and Heggie, (2003); Charlier, Gonze, and Michenaud, (1994). Bernal was the first to propose the hexagonal structure of graphite. Bernal, (1924) (see figure 4).

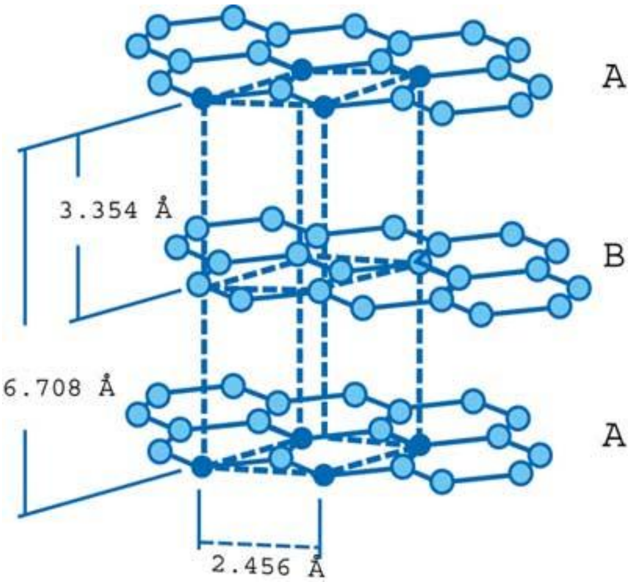


Figure 4. Crystal structure of graphite (Chung, 2002). The primitive unit cell is hexagonal with dimensions (a = 2.46 Å and c = 6.71 Å). The in-plane bond length is 1.42 Å. There are four atoms per unit cells labelled as A and B.

Graphite is also known to exhibit both rhombohedral and hexagonal crystal stacking structures, as shown in figure 5. The stacking sequence of the hexagonal crystal structure (-ABAB-) repeats with the second layer and is known to be thermodynamically stable and predominantly found in synthetic graphite. On the other hand, the rhombohedral arrangement is such that the first and the third layers counterbalance each other, resulting in -ABCABC- stacking.

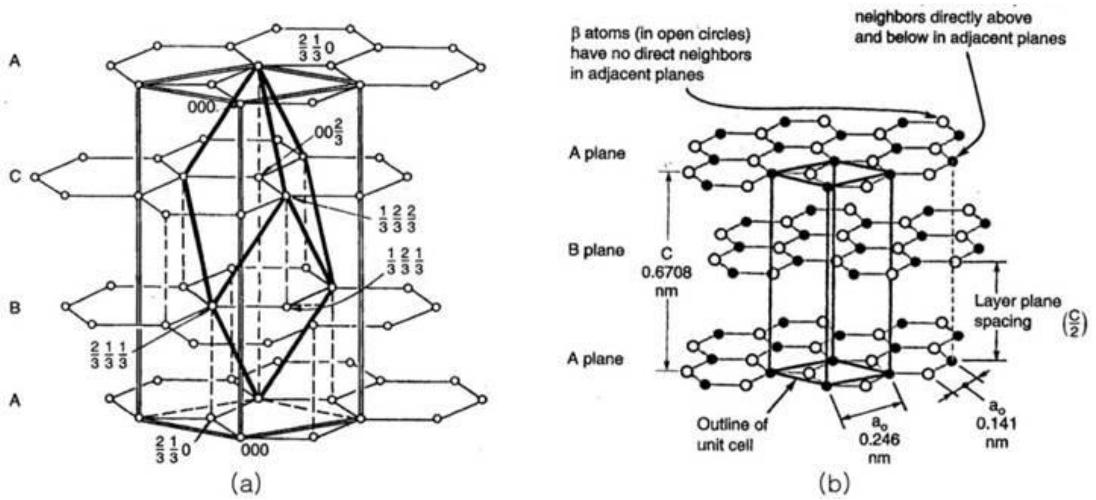


Figure 5: (a) Rhombohedral and (b) hexagonal crystal structure of graphite showing the stacking arrangement of the layers.

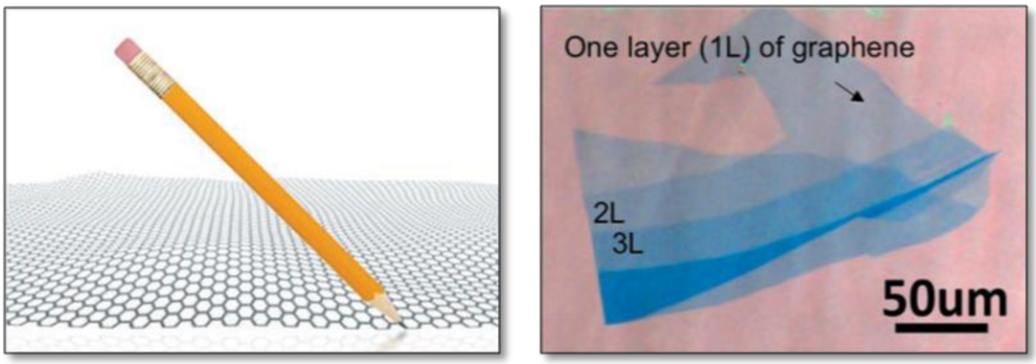
Natural graphite mostly contains both structures. Each stacking form has a distinct influence on the resulting properties of the graphite specimen. Since rhombohedral stacking is not thermodynamically stable, it can revert to hexagonal stacking with heat treatment to temperatures above 1600ºC, Ewels, Telling, El-Barbary & Heggie, (2003). For this reason natural graphite is purified to equivalent higher temperatures before its applications. Graphite composites have recently become of great interest due to their potential in technological applications.

The unique properties of graphite result from two different types of bonds in the structure, as a result of sp^2 bonding*:* directional σ bonds between carbon neighbours and π bonding spread out above and below the carbon sheet. In contrast the sp^3 hybridization consisting only of 4 bonds is the bonding associated with diamond crystals, Charlier, Gonze & Michenaud, (1994). The bonds that exist between carbon atoms in the same layer are covalent, however the inter-layer interactions have been a subject of debate amongst the science fraternity with some authors suggesting a van der Waals type of interaction between the layers and others suggesting a mixture of Van der Waals and weak electrostatic interatomic interaction. The graphene planes are separated by a distance of 3.35 Å.

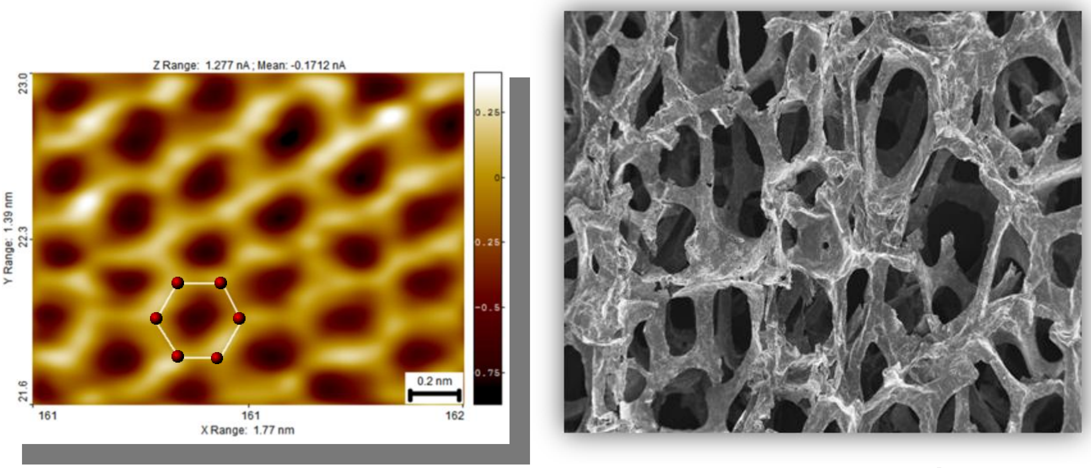
Due to the weak interplanar interactions, the carbon layers can slide over each other making it useful as a lubricant or in pencils. Graphite has many applications including as a moderator in nuclear reactors to control thermodynamic reaction process Ewels et al, (2003), and as a refractory material in furnaces.

Graphene

The term graphene was first used in 1987 according to Mouras et al, (1987) to describe single layers of graphite. While the concept of a single layer has existed for a long while, it was only in 2004 that an experimental way was found to remove layers of graphene from graphite and deposited on a silica substrate Novoselov et al, (2004). According to the Mermin–Wagner theorem Mermin, (1968), "long-wavelength fluctuations destroy the long-range order of 2D crystals", and this was thought to preclude the existence of individual "free-standing" atomic layers. These fluctuations can, however, be suppressed by anharmonic coupling between bending and stretching modes or the presence of a substrate, meaning that an isolated 2D membrane can exist but will exhibit strong height fluctuations Fasolino, Los & Katsnelson, (2007). Graphene is only one atom thick, the thinnest material imagineable. It has a number of remarkable properties, notably there is a peculiar behaviour of the charge carriers in these ultra-thin sheets which has resulted into worldwide research in this material. In graphene, electrons move with such an ease and possess a vanishing mass and have an intrinsic degree of freedom known as helicity, Özyilmaz, (2010). The mechanical exfoliation of graphene and its visualization from optical microscopy (exfoliated graphene on Si/SiO_2 substrate), scanning tunnelling microscopy and scanning electron microscopy view point are shown in figure 6.



(a) (b)



(c) (d)

Figure 6. (a) Technique for making graphene a pencil (graphite) leaving a trace of graphite on a paper. (b) Optical microscopy image of mechanically exfoliated few layer graphene flakes on SiO_2 substrate. (Taken from Özyilmaz, (2010), (c) STM Atomic resolution image of the graphene honeycomb lattice and (d) SEM image of 3D graphene foam network.

Due to easy manufacturing procedure and affordance of this material, it is envisioned for many potential applications covering a wide range of fields such as, graphene field effect transistor in gigahertz (microchip) and terahertz range which is ideal for the identification of hidden weapons, bio-sensors, touch screens and solar cell application. Also, the mechanical properties of graphene have open up many exciting studies in composites and force sensing and detection. It is almost transparent and yet conducts electricity, making it a possible candidate for the surface of touch-screen displays, with the added advantage that it is flexible.

Clay Materials

Generally the term clay implies a natural earthy, fine-grained material which develops plasticity when mixed with water. Their chemical structure is normally a mix of different metals such as aluminium with materials such as silicon, as well as high concentrations of oxygen. Clays are often layer materials and the clay sheets and interlayer space have width in the nanometre scale. They are naturally occurring and individual clay layers can separate from the bulk material and roll up, forming clay 'nanoscrolls' like rolled paper. These are abundant in river clay, for example, and are a good example of a naturally occurring nanomaterial. The most abundantly occurring cationic clay minerals have alumino-silicate sheets which are negatively charged containing variable amounts of iron, magnesium, alkali metals and alkaline earths. The sheets are then held together via species or atoms that must obviously carry a positive charge.

Clay also contains varying percentages of clay-grade materials and varying relative amounts of nonclay-mineral and clay mineral components. There is not any known clay which does not contain nonclay-mineral material coarser than the clay-grade even though the amount in that produced by clays from hydrothermal processes is much smaller (less than 5%), Grim, (1968). Many materials have been labelled as clays although the clay-grade and clay mineral component make up considerably less than half of the total rock. On a whole, fine-grained materials have been called clay so long as they have distinct plasticity and insufficient amounts of coarser materials to warrant the appellations of silt or sand.

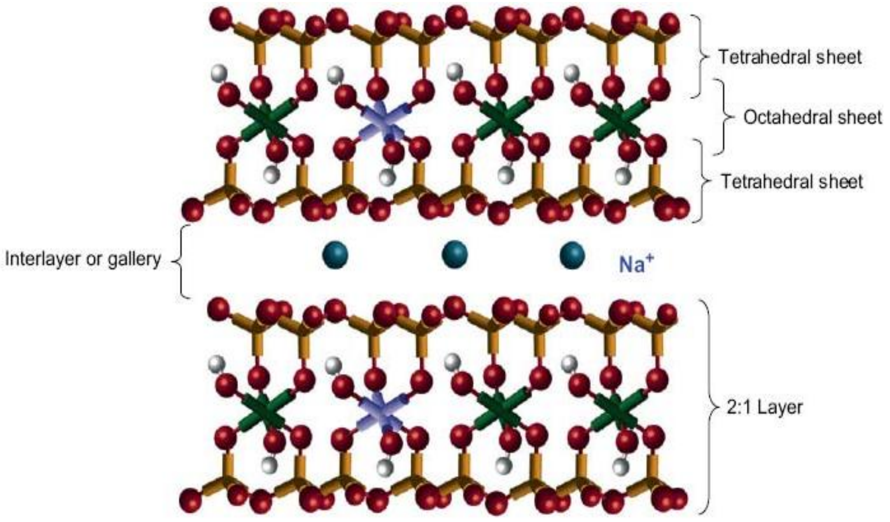


Figure 7. Example of a layered clay structure (Montmorillonite) Chen et al., (2008)

Metal oxides normally consist of metal cations surrounded by oxygen in either tetrahedral or octahedral arrangements. As in all Phyllosilicates, clay minerals are identified by two dimensional sheets of corner sharing SiO_4 tetrahedral and or AlO_4 octahedral. The sheet units are chemically composed of $(Al,Si)_3O_4$. Each silica tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedral, forming a hexagonal array in two-dimensions. The fourth vertex is not shared with another tetrahedron and all of the tetrahedral "point" in the same direction; i.e. all of the unshared vertices are on the same side of the sheet.

Clays can be categorised depending on how tetrahedral and octahedral sheets are arranged into layers. If there is only one tetrahedral and one octahedral group in each layer, the clay is known as 1:1 clay. The alternate form, 2:1 clay, contains two tetrahedral sheets with the unshared vertex of each pointing towards each other and forming each side of the octahedral sheet. An interaction between the tetrahedral and octahedral sheets requires that the tetrahedral sheet becomes corrugated or twisted; causing ditrigonal distortion to the hexagonal array, and the octahedral sheet is flattened. This minimizes the overall bond-valence distortions of the crystallites. Clays such as vermiculate, chlorite, smectite, illite, halloysite, mixed layered minerals, allophone, attapulgite-palygorskite-sepioli and kaolinite, have been classified (see table 1).

Montmorillonite and hectorites clays, structure shown in figure 5 above, are commonly employed in polymer/clay nanocomposites due to their swelling properties which results from their ability to hold water and other organic molecules between the silicate layers, high aspect ratio, high cation exchange capacities and large surface area Chen et al, (2008). They belong to the groups containing either dioctahedral or trioctahedral (two or three aluminium-centred octahedron in the unit cell respectively) and they have the chemical formulae; $Al_2Si_4O_{10}(OH)_{2\cdot y}H_2O$ and $Mg_3Si_4O_{10}(OH)_2.yH_2O$ respectively Chen et al, (2008). Sometimes, Al^{3+} cations in montmorillone is substituted by Mg^{2+} and likewise some Mg^{2+} cations in hectorite are substituted by Li^+. This substitution usually causes charge defects and is balanced by external cations present in the galleries such as Na^+ resulting in chemical formulae; $Mx/nn^+.yH_2O[Al_{4.0}\text{-}xMgx(Si_{8.0})O_{20}(OH)_4]$ and $Mx/nn^+.yH_2O[Mg_{6\cdot 0}\text{-}_xLi_x(Si_{8.0})\,O_{20}(OH,F)_4]$ Chen et al, (2008).

Table 1. Classifications of different clay types Paul & Robenson,(2008).

Structure type	**Group**	**Mineral examples**	**Ideal Composition**	**Basal Spacing (Ȧ)**
2:1 (TOT)	Smectite	Montmorillonite	$[(Al_{3.5\text{-}2.8}Mg_{0.5\text{-}0.2})(Si_8)O_{20}(OH)_4]Ex_{0.5\text{-}1.2}$	12.4-17
		Hectorite	$[(Mg_{5.5\text{-}4.8})Li_{0.5\text{-}1.2})O_{20}(OH)_4]Ex_{0.5\text{-}1.2}$	
		Saponite	$[(Mg_6)(Si_{7.5\text{-}6.8})Al_{0.5\text{-}1.5})O_{20}(OH)_4]Ex_{0.5\text{-}1.2}$	
2:1 (TOT)	Illite	Illite	$[Al_4)(Si_{7.5\text{-}6.5})Al_{0.5\text{-}1.5})O_{20}(OH)_4]K_{0.5\text{-}1.5}$	10
2:1 (TOT)	Vermiculite	Vermiculite	$[Al_4)(Si_{6.8\text{-}6.2}Al_{1.2\text{-}1.8})O_{20}(OH)_4]Ex_{1.2\text{-}1.8}$	9.3-14
1:1 (TO)	Kaolin-Serpentine	Kaolinite, dickite, nacrite	$Al_4Si_4O_{10}(OH)_8$	7.14

Other forms of Layered Nano Materials

Although, graphene, graphite and clays are probably the most well-known layered materials, other layered materials have been synthesized through chemical combination of single atoms which have proven to be equally important. Other layered materials such as transition metal dichalcogenides (TMDs), transition metal oxides (TMOs), and other 2D compounds such as BN, Bi_2Te_3, Bi_2Se_3 and layered double hydroxides (LDHs) have been synthesized in the laboratory or can be found in nature Coleman et al. (2011). Nonetheless, the development of these materials have been hampered by the lack of a simple method to exfoliate them to give single or few-layer flakes in large quantities. The transition metal dichalcogenides (TMDs) is made up of hexagonal layers of metal atoms (M) sandwiched between two layers of chalcogen atom (X) with a resulting stoichiometry MX_2. Similar to graphene and graphite, chemical bonds within these trilayer sheets is strong and covalent, while adjacent sheets then stack through weak van de Waals interactions to form a 3D crystal. TMDs occur in more than 40 different types Marseglia, (1983), Wilson, and Yoffe, (1969), depending on the combination of chalcogen (S, Se, or Te) and transition metal Yoffe, (1969). Depending on the coordination and oxidation state of the metal atoms, TMDs can be metallic, semimetallic, or semiconducting Marseglia, (1983); Wilson and Yoffe (1969); for example, WS_2 is a semiconductor, whereas $NbSe_2$ is a metal Wilson and Yoffe (1969). In addition, superconductivity Gamble and Silbernagel, (1975) and charge-density wave effects Clerc et al., (2007) have been observed in some TMDs. It is only last year or two years ago that a method has been found to separate individual layers out of these materials and therefore we are only at the very beginning to understand these and find out what their properties are.

Hexagonal boron nitride (h-BN) is another layered material with structure similar to graphite made up of hexagonal ring layers separated by 3.33 Å in which every boron atom is connected to three nitrogen atoms and vice versa; the B–N distance is 1.44 Å Torrones et al., (2001). Between the layers, every Boron interacts with a nitrogen atom through electrostatic interaction and Van der Waals forces. This versatility makes these types of materials extremely useful for electronic applications (see Fig. 6).

However, like graphene Geim, (2009), layered materials must be exfoliated to fulfil their full potential. For example, films of exfoliated Bi_2Te_3 should display enhanced thermoelectric efficiency by suppression of thermal conductivity Poudel et al., (2008). Exfoliation of 2D topological insulators such as Bi_2Te_3 and Bi_2Se_3 would reduce residual bulk conductance, highlighting surface effects. In addition, we can expect changes in electronic properties as the number of layers is reduced; for instance, the indirect band gap of bulk MoS_2 becomes direct in few-layer flakes Splendiani et al., (2010). Although exfoliation can be achieved mechanically on a small scale Novoselov et al., 2005; Ayari et al, (2007), liquid-phase exfoliation methods are required for many applications Ruoff, (2008).

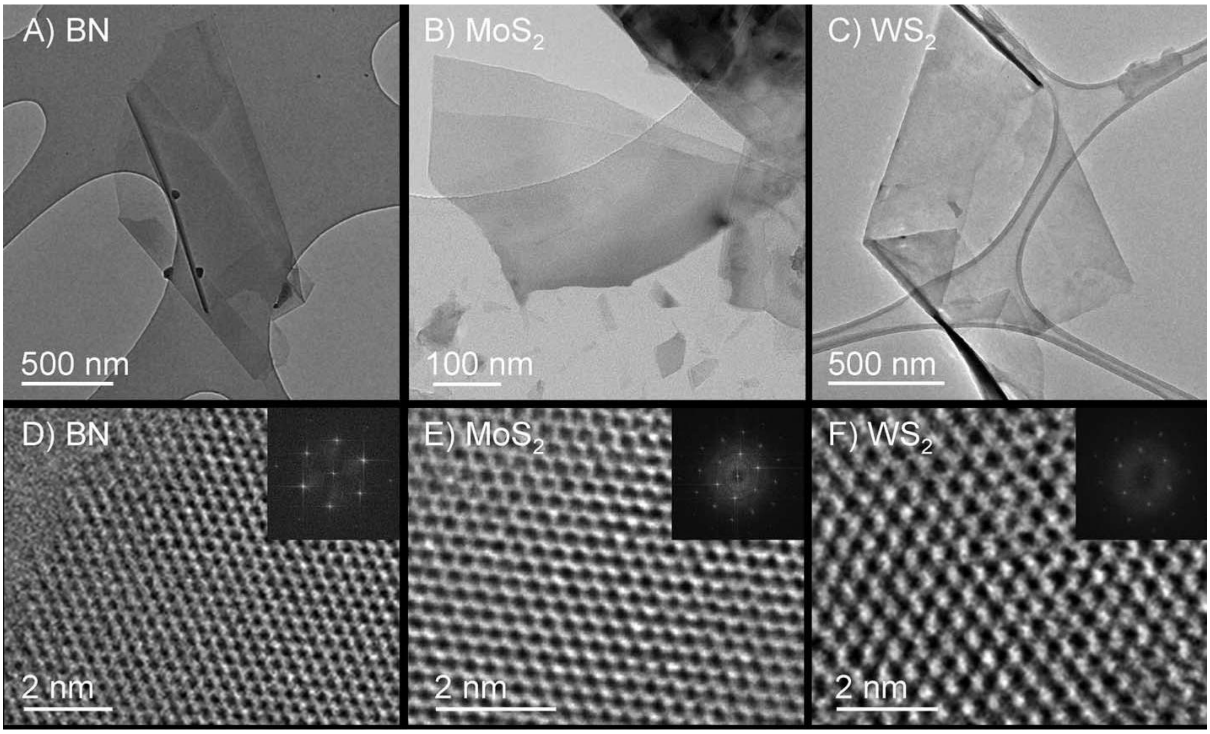


Figure 8.TEM of nanosheets. (A to C) Low-resolution TEM images of flakes of BN, MoS$_2$, and WS$_2$, respectively. (D to F) High-resolution TEM images of BN, MoS$_2$ and WS$_2$ monolayers Coleman et al. (2011).

LDHs, also known as hydrotalcite-like materials or anionic clays, can be found in nature as minerals and readily synthesized in the laboratory (structure shown in Fig.7). They can be formed naturally, from the weathering of basalts or precipitation in saline water sources Zhao et al (2002). All LDH minerals found in nature and synthesized in the laboratory have a structure similar to that of hydrotalcite or its hexagonal analogue, manasseite, and the majority obey the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{II} represents a divalent metal cation, M^{III} a trivalent metal cation, and A^{n}– an anion. But the LDHs are not limited to divalent and trivalent metal cations, also monovalent M^{I} and tetravalent M^{IV} (such as Ti^{IV}, Si^{IV}) cations Cavani et al., (1991). Structurally, LDHs consist of cationic brucite-like layers and interlayer anions as well as water molecules. The commonly used method to synthesize LDHs in the laboratory is coprecipitation at varied or constant pH, followed by aging at a certain temperature Khan and O'Hare, (2002). Furthermore, the as-prepared LDH materials in aqueous suspension are severely aggregated to sizes of between 1–10 μm Zhao et al, (2002), comparable with the cell size (10–100 μm). Therefore, it is necessary to disperse the aggregates into individual LDH nanocrystallites in a stable suspension for applications such as cellular drug or gene delivery.

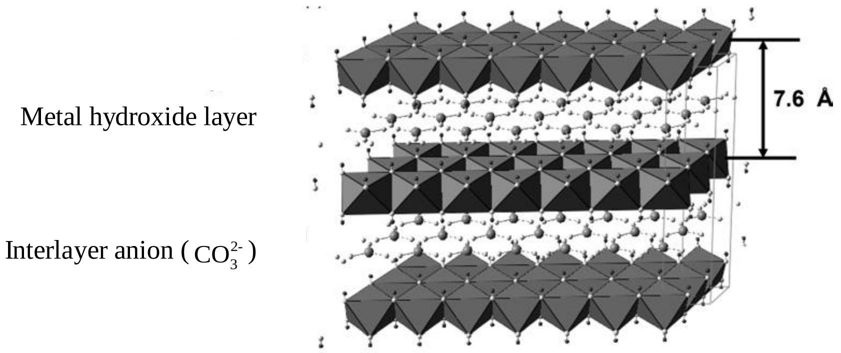


Figure 9. Schematic structures of anionic layered metal hydroxide: layered double hydroxides. Jae-Min et al. (2008).

Potential Applications of Layered Nano Materials

Layered materials have not only proven to be of technological importance in a variety of industrial and medical applications including catalysis, molecular separations, and drug delivery, however, they are critical to a number of environmental issues involving the fate of contaminants and ground water quality Braterman et al., (2004); Sposito (1984). Of most technological significance is the ability of many of these layered materials to intercalate neutral molecules or charged chemical species into their interlayers. From the intercalation of inorganic metal cations to large organic polymers, from the sequestering of metal pollutants and radionuclide contaminants to biomolecules for drug delivery, layered materials present a versatile class of phases for a wide set of applications. These two-dimensional layered materials systems are also important for microelectronics, various types of hypersensitive sensors and energy storage. Considering the flexible interlayer space, layered nanomaterials can accommodate various sized molecules such as proteins, deoxyribonucleotides, viruses, pesticides, etc.

Furthermore, the bio-compatibility and low toxicity of certain layered nanomaterials enables their ecological and biological applications. The intercalated biomolecules or bio-functional molecules can be protected from external harsh conditions such as physical, chemical and biological attack. The guest molecules can then be intentionally de-intercalated by chemical treatment like anion exchange reaction in the presence of various electrolytes or in modified pH conditions. Aside this, layered materials that have been synthesize through combinations of other compounds can be used as topological insulators and thermoelectric materials Coleman et al. (2011).

The applications of LDHs have been a subject of many reviews in recent times which cover a wide-range of fields such as catalysis, separation science, polymer additives, biological storage and delivery, as well as electrochemistry and photochemistry Desigaux et al., (2006). The properties of these LDHs can be tuneable by varying the M^{2+}/M^{3+} layer composition and the interlayer anion. The materials are easily synthesised at low cost making them attractive candidates for industrial applications.

Conclusions

We have shown some important areas in which layered nanomaterials can be applied. Furthermore, it has been shown that layered materials which can be found in nature (graphite, clays, LDHs) have found many applications such as electronics, drug delivery and composites. Other forms of layered materials have been synthesized in the laboratory (BN, TMOs, LDHs, TDMs) are equally significant as in the areas of electronics, control of toxic materials in the environments. To render these layered materials useful for any application it is of critical importance to exfoliate group of materials which are normally characterized by weak interlayer interactions.

Finally we note that once it is possible to separate out individual layers of these materials, in principle they could be recombined in different combinations, for example placing insulating individual BN layers between conducting graphene sheets. This possibility to mix layers of different materials in different ratios and combinations opens up a truly exciting new field of custom-designed multi-layered materials, whose properties are designed and tuned depending on requirements. The field of layered materials is one of great importance and large scale research efforts round the world. We are just at the beginning of understanding the possibilities and potential of these two dimensional structures.

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