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Two-dimensional crystals-based heterostructures: materials with tailored properties

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Abstract
Graphene is just one example of a large class of two-dimensional crystals. These crystals can either be extracted from layered three-dimensional materials or grown artificially by several different methods. Furthermore, they present physical properties that are unique because of the low dimensionality and their special crystal structure. They have potential for semiconducting behavior, magnetism, superconductivity, and even more complex many-body phenomena. Two-dimensional crystals can also be assembled in three-dimensional heterostructures that do not exist in nature and have tailored properties, opening an entirely new chapter in condensed matter research.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Technological progress is determined, to a great extent, by the developments in materials science. The most surprising breakthroughs are attained when a new type of material, with unusual dimensionality and complexity, is created. Some of the most famous examples are the conducting polymers, heavy-fermion magnets, high temperature superconducting cuprates, carbon nanotubes, graphene, topological insulators, iron superconductors, just to name a few. One of the ultimate goals of modern materials science is to develop novel complex architectures and structures with tailored and emergent properties. These properties are not necessarily easy to predict due to the structural and electronic complexity involved. Hence, beyond new technologies, new materials create new challenges in condensed matter research.

The current progress in two-dimensional (2D) crystal isolation [1] and growth [2] can lead to a new paradigm of 'complex materials on demand' by first identifying and constructing the key building blocks and then combining them into complex architectures. This approach consists of three strategies: creation of various 2D materials by micro-mechanical exfoliation and/or growth; modification of electronic, structural, optical and chemical properties of such materials by strain engineering, chemical functionalization or other means; and development of novel 3D materials by controlled multi-stacking of such 2D platforms. The number of different structures that one can obtain based on these strategies is practically unlimited and their physical properties are hard to predict *a priori*. Nevertheless, by understanding the properties of the 2D components, one should be able to create materials that have interesting structural, electronic, optical, mechanical and other properties.

Moreover, these strategies also open doors for a multitude of applications, since it becomes possible to create artificial materials which would combine several unique properties that will allow their use in novel multi-tasking (mechanical, optical and electronic) applications, as, for instance, 'smart' composites and coatings for flexible electronic and photovoltaics or photonic devices for integrated optoelectronic circuits. One can identify already several key areas where this kind of approach can have a strong

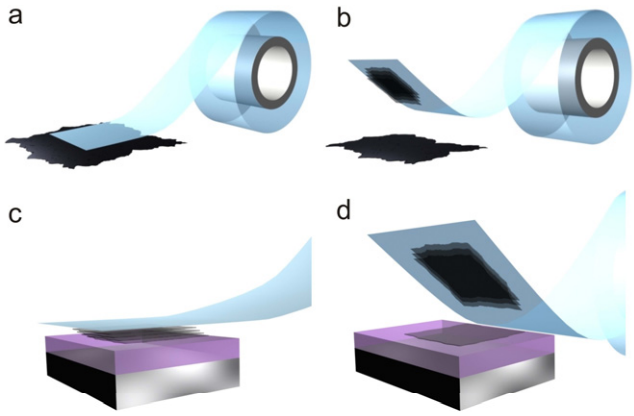

Figure 1. Micromechanical exfoliation of 2D crystals. (a) Adhesive tape is pressed against a 2D crystal so that the top few layers are attached to the tape (b). (c) The tape with crystals of layered material is pressed against a surface of choice. (d) Upon peeling off, the bottom layer is left on the substrate.

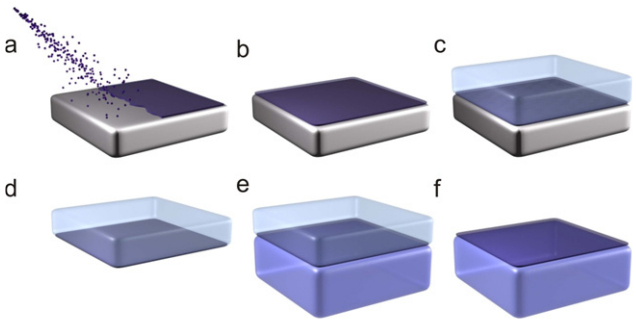

Figure 2. Transfer of chemical vapor deposition (CVD) grown 2D crystals. (a), (b) 2D crystals are grown by CVD on a surface of a metal. (c) A sacrificial layer is deposited on top of the 2D crystal. (d) The metal is etched away, leaving 2D crystal stuck on the sacrificial layer. (e) The sacrificial layer, together with the 2D crystal is transferred onto the substrate of choice. (f) The sacrificial layer is removed.

impact: (i) 'smart' ultra-strong nano-composite materials; (ii) electro-mechanical devices for ultra-fast electronics; (iii) materials with predetermined band-gap and work functions for next generation photovoltaic (solar-cells) applications; (iv) atomically thin film transistors for photonic applications.

The real advantage of this approach is that one is able to create materials that can perform several functions (mechanical, electronic, and optical) simultaneously. Such materials (let alone devices based on them) are not available yet. However, as the functionality of modern portable electronic equipment grows exponentially, we already see a huge demand for such multi-functional, multi-task, materials.

2. 2D crystals

Since graphene was isolated for the first time [3] several ways of synthesizing this material have been introduced. This includes mechanical exfoliation (see figure 1) [1, 3] epitaxial growing on the surface of silicon carbide [4], epitaxial growth on metal surfaces [5], chemical exfoliation [6], etc. Depending on the particular application, one or another method can/should be used. There are also a number of ways to modify the properties of graphene obtained by various methods. The most common ones are the introduction of mechanical strain (of various configurations) and chemical modification. The latter also leads to the production of other 2D materials. Simply using graphene as a scaffolding, one can attach various chemical species to it and end up with a new 2D atomic crystal.

In general, all the methods of graphene production known to us could be also applied to the production of other 2D crystals. Thus, mechanical exfoliation of other layered materials has already been demonstrated [1] as well as epitaxial growth on the surface of a metal [7] or chemical exfoliation [8] (figure 2). This gives us huge opportunities in terms of a variety of different properties covered by those materials.

It seems clear that graphene is going to play an important role in a series of technological applications, from transparent conducting electrodes [9] to high speed electronics [10]. The major reason why it took only five years for the transition from the laboratory bench-top to industrial production is because graphene offers really unique properties of which the most striking is the 2D nature [11]. Many applications, already in place, have been waiting for a material like this for years. Hence, when graphene became available, a whole community of scientists and technologists reacted immediately. There have been significant efforts to improve the existing processes and procedures and develop novel methods of graphene production, as well as investigate other 2D materials which might be similarly successful in the future. One emerging example is boron-nitride (BN), which is sometimes called 'insulating graphite' and it might be in use everywhere where graphene's high conductivity is a disadvantage (ultra-thin, high quality, insulating layers for nano-electronics, non-conductive, ultra-strong, composite materials). However, there is a huge class of 2D materials, including exotic types such as MoS_2, $NbSe_2$, Bi_2Te_3, that can be either isolated by micro-mechanical or chemical exfoliation or epitaxial growth (figure 3).

The capability of growing different families of 2D crystals artificially will enhance tremendously the 'library' of materials that one can obtain and will also allow the exploration of the unusual physics that occurs in 2D. Unlike the case of 1D materials, such as conducting polymers (such as polyacetylene) and carbon nanotubes, where phase space strongly constraints electron–electron interactions, and ordinary 3D solids, where interactions are essentially suppressed, 2D crystals are characterized by strong quantum fluctuations and an enhanced phase space for interactions, making the physics in this dimensionality very special.

3. 2D-based, 3D materials

Composite materials are omnipresent in technology and many existing applications rely on light, conductive (or insulating), and strong composites. The performance of such materials is, however, fundamentally limited by the interaction between the filler and the matrix. Hence, out of a great number of possible combinations, only a few really work. Moreover, having a

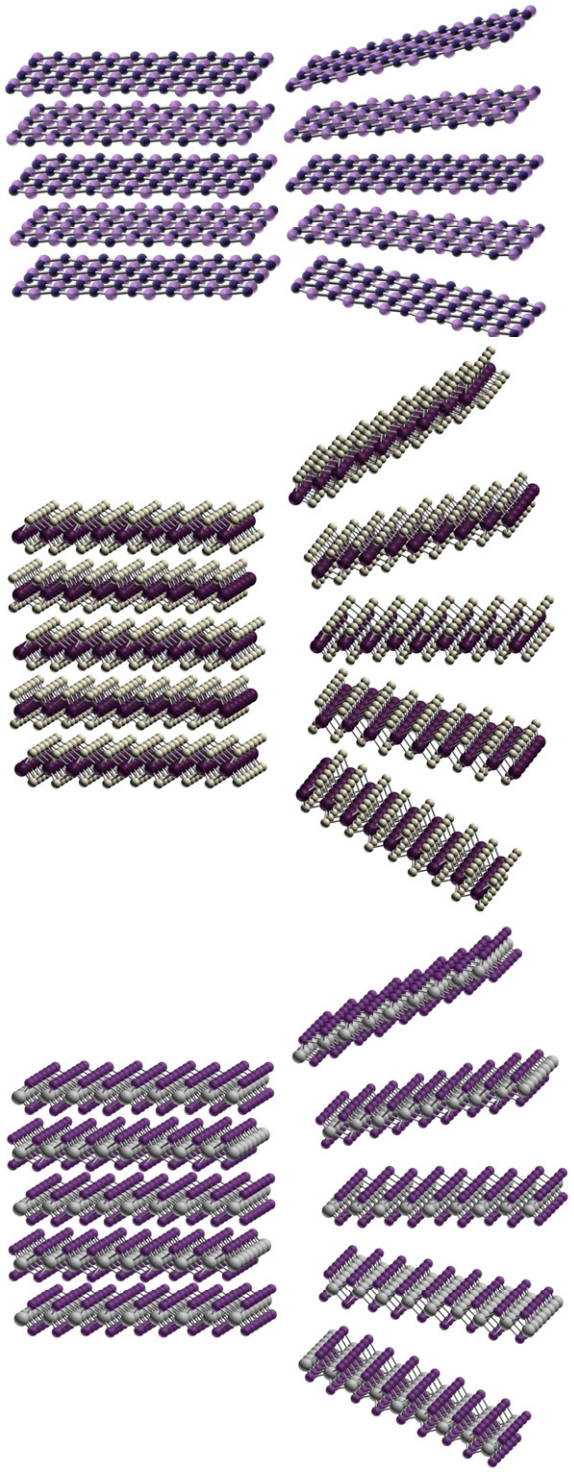

Figure 3. Exfoliating other 2D crystals: BN (top panel), MoS_2 (middle panel) and $NbSe_2$ (bottom panel).

complex structure, such materials are subject to unpredictable failure. It has been recently demonstrated that graphene can improve mechanical, chemical and electrical properties of composite materials dramatically. Graphene is the strongest material known to us [12], but also it is truly 2D (so it cannot be cleaved further and has the ultimate aspect ratio). Moreover, one can produce graphene of suitable dimensions and in large quantities very cheaply. Thus, one can improve the quality of such composite materials by fine-tuning the interaction with the matrix (via controlled chemistry on

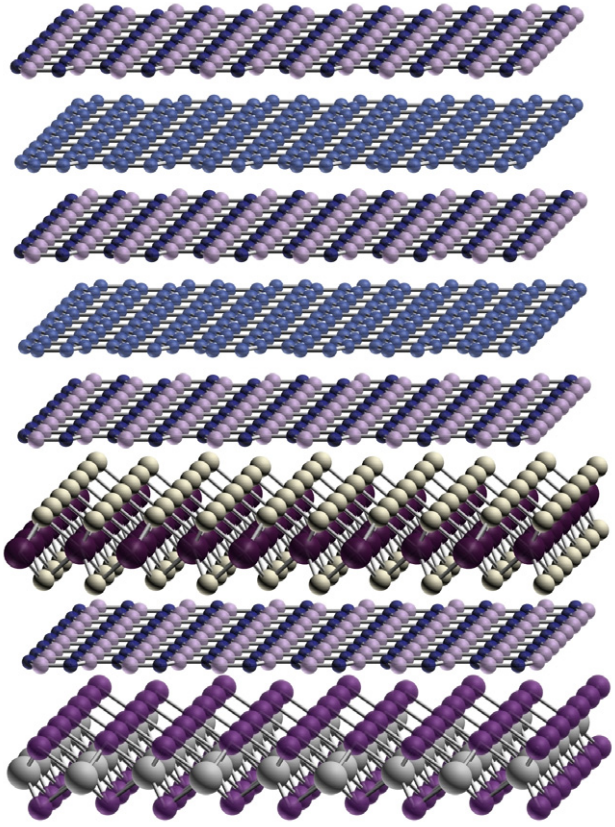

Figure 4. Hypothetical example of a 2D-crystals based heterostructure.

graphene surface, for instance, it was shown that hydrophobic graphene can be turned hydrophilic by hydrogenation [13]), but also adding additional functionalities, such as the ability to monitor stress distributions, the control of optical gaps, and electrical conductivity. One can apply a similar strategy to other 2D materials to produce high-performance composites with a wide range of functionalities and physical behavior (figure 4).

Micro-mechanical cleavage and artificial growth can be used to obtain other 2D materials (graphene, BN, MoS_2, Bi_2Te_3, etc) to be used as fillers in composite materials. Using materials other than graphene allows one to expand the complexity of such composites. One can make them optically active in various parts of the optical spectra by using chemically modified graphene or materials with various band-gaps. By creating semiconductor–metal and/or semiconducting–semimetal interfaces, either in the form of dispersed heterojunctions or layered junctions, efficient light collection and charge transfer across the interface can be achieved—giving rise to the photovoltaic effect. Previous work has explored, for instance, electrostatically stacked TiO_2-graphene layers [14], where functional segregation of exciton generation and charge transport can be separated.

It has also been shown that graphene's Raman spectrum is extremely sensitive to applied strain and that strain transfer between the matrix and graphene is very efficient [15]. This property can be used to create composite materials where accumulated stress could be monitored by contactless, non-invasive, optical methods. Such techniques can be of crucial importance in certain areas of engineering where catastrophic material failure is a major issue and where

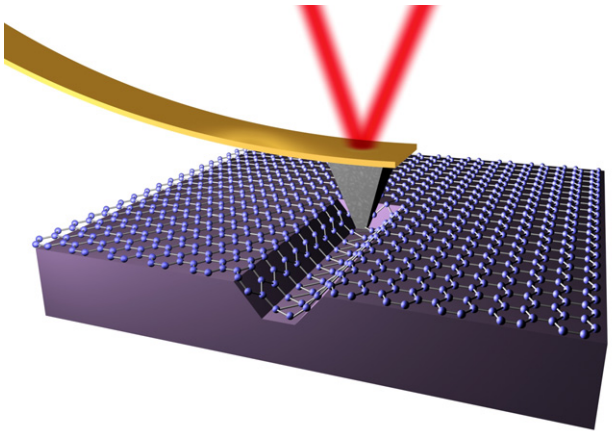

Figure 5. Introducing local strain in graphene by an atomic force microscopy cantilever.

permanent monitoring of the performance of a material is crucial (such as avionics, electrical grids, medicine, etc).

4. Strain engineering or 'straintronics'

One of the pillars of solid state physics is that the band structure of 3D materials is set by their geometry and chemistry. Although this concept is the force behind modern electronics and technology, it also has its limitations: it is very difficult to modify and manipulate (to create a new functionality one has to create a new crystal); the structure might not be stable (for instance, one can have electron migration) or can be strongly modified by external, environmental, conditions (such as radiation damage); the same chemistry that is used to achieve the desired electronic structure (for instance, by doping) might cause detrimental effects on other parameters (such as the decrease of the mobility due to scattering by dopants). In contrast, 2D materials open a new avenue for control of electronic properties. It has been demonstrated that the electronic structure of 2D materials can be considerably modified by strain, shear and bending [16]. Moreover, one gets much better control of those parameters in 2D as compared to 3D systems (for instance, graphene can be stretched up to 20% without structural failure) (figure 5).

Uniaxial and biaxial strain, applied along different crystallographic directions, can reversibly tune graphene from metallic to insulating [17, 18] or significantly change the band structure. Furthermore, usually the two valleys are affected differently by strain, which gives us a mechanism to differentiate between the valleys and effectively leads to valleytronics. Just as spin can be used for spintronics where the electron spin is manipulated by external magnetic fields, valleytronics uses the orbital degree of freedom (the valley index) as a new quantum number that can be manipulated externally. Band structure is also strongly influenced by stacking. A well-known example is graphite, depending on the stacking order (Bernal versus rhombohedral versus hexagonal versus turbostratic) its electronic properties can be rather different [19]. Furthermore, intercalation of layers of different atoms can completely change the electronic states. For instance, graphite intercalated with alkali metals becomes superconducting [20]. By introducing different 2D materials, with different properties, into a 3D matrix, one is able to modify the final electronic properties.

A completely new field of exploration is the study of multi-stacked materials under strain. Given that the elastic properties of the 2D layers can be rather different because of the atomic bonding (say, graphene in comparison to BN), the final elastic properties of the 3D super-structure can be engineered as well. The electronic properties of such engineered 3D structures will also be affected by strain leading to new possibilities in terms of electronic functionalities. Even in the simplest case of stacking—bilayer graphene—the electronic structure depends crucially on the stacking order. A small uniaxial strain or a minute shift between the layers would immediately lead to strong changes in the electronic structure.

By arranging different 2D materials into stacks it should be possible to achieve new, composite, materials with novel electronic, mechanical and optical properties. The typical mechanisms for the modification of the electronic bands in such stacks are based on changing the symmetry of the structure and opening gaps in the electronic spectrum.

5. Optically active materials

It has been demonstrated that, due to the long mean-free path and high Fermi velocity, graphene can serve as an excellent light-to-current converter with quantum efficiency reaching close to 100% [21]. Its use for solar-cell applications is however limited, due to the low absorption of graphene (hence, the total efficiency is low) and difficulties with creation of p–n junctions (necessary for electron–holes separation) in 2D materials. Nevertheless, the efficiency of these devices can be greatly enhanced by exploring different geometries, for instance the vertical geometry, where the electron–hole pair is separated between two neighboring layers (figure 6).

The strategy would be to separate electron and hole pairs into the neighboring layers of multi-layer structures. This can be achieved either by applying an external electric field or by selective doping of the two layers (one n-type, another p-type). Selective doping can be implemented either during growth by substitutional doping or by doping with adatoms. It has been shown that strain generates scalar potential [22], which leads to the formation of local p–n junctions. It is possible to use this concept to create an array of p–n junctions. One can use stacks of various 2D crystals (either the same materials with different doping or completely different materials) to form multi-layers. One can also use layers of insulating material (such as BN) to separate the conductive layers for more efficient electron–hole separation (to create weak tunneling barriers).

It has been demonstrated that graphene absorbs only 2.3% of light in the wide range of visible spectra [23]. This number is even lower for chemically modified graphene and for some other 2D materials. Combined with the excellent conductivity properties, these materials are extremely promising for transparent conductive coating applications. One can use local chemical modification to define conductive and non-conductive areas to create atomically thin film transistors.

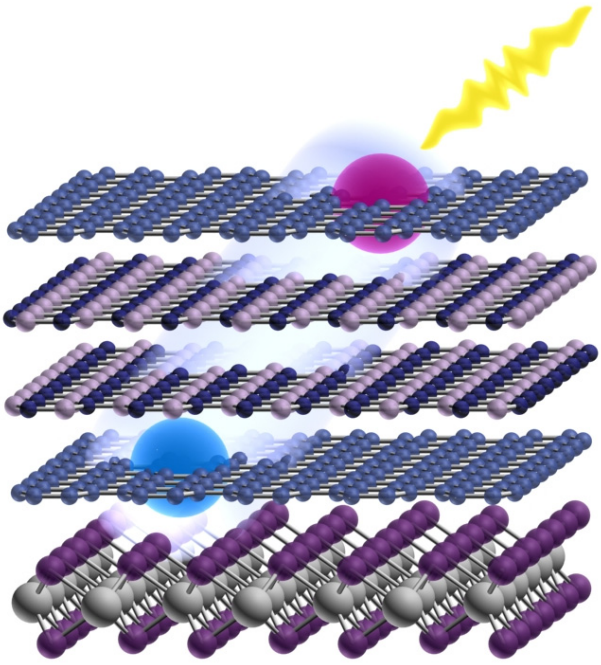

Figure 6. Optically active material. Two graphene layers are separated by several layers of BN, which serve as a tunneling barrier. One of the graphene layers is in close proximity to a layer of $NbSe_2$, and gets doped due to the difference between the work-functions of $NbSe_2$ and graphene. Such doping creates a built-in electric field between the two graphene layers. Such a field separates an electron–hole pair which is created by an incoming photon, resulting in photocurrent.

Another large application for 2D materials is coating. The high quality of 2D crystals one can obtain make them perfect gas barriers. Even a single layer of graphene is impermeable for most gases [24]. Furthermore, such a coating can be created by CVD growth directly on an arbitrary shaped surface—acting as a protective barrier. Another promising application in coating technology is in transparent conductive films. Two types of approaches can be used to create transparent conductive coating: chemical exfoliation and epitaxial growth of graphene and other conductive materials. Uniaxial strain breaks the symmetry of the lattice and produces rotation of the planes of polarization. This effect is enhanced in an applied magnetic field. Application of strain allows the production of tunable polarizers in a broad band of optical frequencies. One can use chemical modification to define conductive and non-conductive areas for atomically thin film transistors.

6. Conclusions

We have learned in the last few years that 2D crystals can be obtained by several methods such as exfoliation, molecular bean epitaxy and chemical vapor deposition. We also know that the physical and chemical properties of these 2D crystals can be modified by chemical or molecular doping, by application of strain, shear or pressure, and by intercalation with different types of atoms and molecules. We can now create a new class of 2D artificial materials that do not exist in nature and whose properties we can control and explore.

It is not hard to imagine that we can take all these 2D crystals and pile them into 3D structures. Given that each one of these 2D crystals can have different physical properties we can imagine creating a library of 2D crystals and using those to make new 3D artificial structures with unique properties. The outcome of such a scheme would be a large portfolio of new materials with different functionalities. In this way, we could develop a 'materials-on-demand' strategy for novel complex architectures and structures with precisely tailored properties for emerging technological applications.

The most important lesson from the graphene story is probably this one: there is a universe of 2D crystals out there just waiting to be studied. Each one of them has its own beauty and purpose. Paraphrasing Isaac Newton we can say that we are still in the infancy of a broad field and diverting ourselves with graphene, a material that looks more interesting than ordinary, whilst a great field of 2D crystals lays undiscovered before us.

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