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Lifting the mist of flatland: The recent progress in the characterizations of two-dimensional materials

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ABSTRACT

In the great adventure of two-dimensional (2D) materials, the characterization techniques are the lighthouse to guide the investigators across heavy mist and submerged reef. In this review, we highlight the recent achievements in the characterization of the 2D materials. Firstly, the methods to identify the fundamental properties of the 2D materials are introduced. Then, the specific characterization techniques for analyzing electric, optical and chemical properties are summarized with regards to their corresponding fields of applications. It should also be noted that a big challenge remains in the characterizations of the 2D materials in the hybrid or composite and wide acceptance of the characterization standards need to be established to further promote the industrialization of 2D materials in the near future.

1. The aims of characterization on the big families of two-dimensional (2D) materials

In 1492, Christopher Columbus set his foot on the ground of Guanahani, the first discovered island of the New World. After over five hundred years, one purple flake on a silicon wafer, which was known as graphene later, appeared in Geim and Novoselov's view [1,2]. From then on, a new world of 2D materials was exhibited to the investigators. Before Geim and Novoselov's discovery, 2D compounds were believed to only exist in Shambhala and be thermally unstable according to the Mermin–Wagner theorem [3]. However, once graphene was isolated, people immediately realized that a frontier of 2D materials is waiting to be revealed.

From Guanahani to Cape Horn, it took a European nearly one hundred years. From graphene [1] to phosphorene discovery [4], it only took a decade. 2D materials refer to an infinite sheet strictly in one single layer. Up to now, dozens of two dimensional materials have been labeled on the map [5], and the number is increasing continuously (Fig. 1). According to the element composition, the family of 2D materials can be generally separated into three branches [6]: the first branch involves the elemental 2D materials [7] (e.g., graphene, stanene and black phosphorene) and their isoelectronic compounds (e.g., hexagonal boron nitride [8]); the second branch is the metal chalcogenides [9], including 2D transition metal chalcogenides (e.g. MoS_2 [10]) and main group metal chalcogenides (e.g. InSe [11]); the third branch is the clay-like 2D materials, containing layered silicate [12], layered double hydroxide (e.g., $[Mg^{2+}_{1-x}Al^{3+}_{x}(HO^{-})_2]^{x+}$ $[(NO_3^{-})_x \cdot yH_2O]^{x-}$) [13] and MXene (e.g., Ti_3C_2) [14]; Other branches, such as metal halides (e.g. $CrCl_3$ [15]), metal oxide (e.g. V_2O_5 [16]) are growing. Moreover, based on recent development in chemical total synthesis, the families of 2D covalent organic frameworks (e.g., poly(phenyldiboronic acid) [17], graphitic carbon nitride (g-C_3N_4) [18,19] and metal organic frameworks [20,21] appear on the horizon.

In the early 18th century, John Harrison invented the marine chronometer, a precise and accurate timepiece to determine longitude by means of celestial navigation. Thanks to his invention, being lost in the mist was no longer the major cause of casualties in the Royal Navy. In the progress of mapping the new world of 2D materials, the advanced characterization technologies are always the compass in investigators' hands. In the age of great geographic discovery, the marine chronometer and sextant were used to accurately determine the longitude and horizon coordinates, respectively. Nowadays, diversified characterization techniques are the tools to guide the investigators in the territory of 2D materials. However, there is no one "almighty" characterization technique to give all answers. Therefore, people should now select the proper techniques for their studies based on their different functionalities. Basically for the purposes of characterization of 2D materials one has to answer three questions: "what", "why" and

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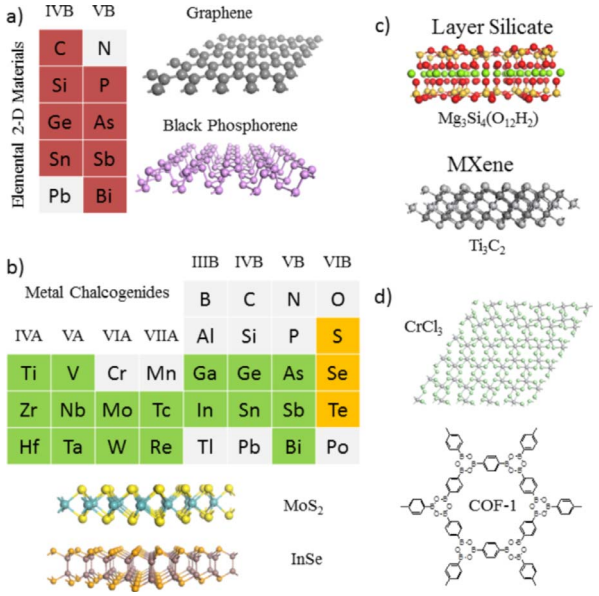

Fig. 1. The families of 2-D Materials: a) elemental 2-D materials; b) metal chalcogenides; c) clay-like 2-D materials; d) other 2-D materials.

"how" which can be can be divided into two groups: the first is to identify the "what" question which refers to the identification of structure parameters of 2D materials;, e.g., the thickness, defects, compositions *etc.*; the second "why" question is to explore the unique properties of 2D materials; the "how" question is to evaluate the performance of 2D materials in practical applications. In this paper, we highlight the characterization based on the above classification. This review firstly concludes the identification technologies for identification, exploration of unique properties and 2D materials, and then we introduce the approaches to evaluate the performance in several practical applications involved in the recent developments of 2D materials, e.g., transistors, nonlinear optics, and electron energy storage devices.

2. Fundamental characterization methods to identify 2D materials

2D materials are specifically defined as an atomically thick infinite sheet in one or few layers. Most unique properties of 2D materials are determined by their chemical structure, so the first aim of the characterization is to identify the structures. Similar to the description of proteins, the structure of 2D materials can also be defined in that there are four levels of 2D materials structure. The primary factor of the structure of 2D materials is the thickness. The properties of 2D materials can be changed even by adding one more layer. For instance, only a single-layer MoS_2 has a direct band gap, showing strong luminescence, while a MoS_2 bilayer is an indirect bandgap semiconductor in contrast, with significantly reduced quantum yield efficiency of luminescence [10]. The secondary structure of 2D materials is the chemical composition, including elemental composition and phase configuration. The group of 2D transition metal dichalcogenides (TMD) is a typical representative exhibiting composition-dependent properties [22]. For example a hexagonal MoS_2 monolayer is a semiconductor, [10] while $NbSe_2$ is a semi-metal [23]; despite having similar compositions the 2H and 1T phase of MoS_2 exhibits semiconducting and metallic behavior, respectively [24]. The tertiary structure of 2D materials is the conformation. For instance, the ripple of graphene will significantly decrease the carrier mobility, [25] while stretching graphene can open its bandgap [26]. In the quaternary structure of 2D materials, interaction with the environment and other dopants shall be considered. For example, Moiré patterns emerge when graphene is placed on boron nitride, [27] and consequently, its superlattice induced band structure exhibits Hofstadter's butterfly spectrum [28].

2.1. Optical light interferometry and ellipsometry

In the initial "magic Scotch tape experiment" on graphene, the first challenge was how to hunt a flake of thin graphene in a time-economic way. The first "Eureka moment" came when Geim et al. pressed their tape with a graphite flake on a SiO_2/Si wafer. They immediately figured out that the interference color was determined by the thickness of graphene on SiO_2/Si [2]. Surprisingly, the first graphene was found under an optical microscope invented over 400 years ago. Owing to the complex refractive index of graphene, the interference color would be determined by the wavelength of incident light and the thickness of SiO_2, besides the thickness of graphene (Fig. 2(a)) [29]. Nowadays the interference color contrast is still the most direct way to search 2D materials having few layers (Fig. 2(b)). The first MoS_2 monolayer [10] and black phosphorene [4] were also found by the interference color contrast method under an optical microscope, a consequence of their universal abundance. However, the residual glue from the tape with a thickness of a few nanometers could mislead the investigators. Consequently, the interference color procedure can only act as a preliminary sorting method for monolayer flacks now. Other characterization techniques shall be used to further confirm the existence of 2D materials.

Ellipsometry was subsequently applied to characterize 2D materials quantitatively by monitoring their effect on the interfacial reflection. If a beam of circularly polarized light was reflected by an anisotropic 2D material, the outgoing light would be changed to elliptically polarized light, because both the amplitude decrease and phase shift perpendicular (*s*-) or parallel (*p*-) to the plane of the 2D material would be

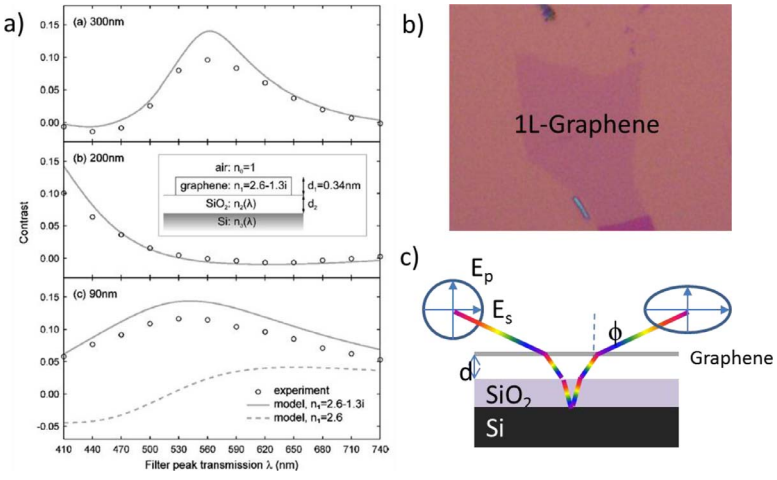

Fig. 2. (a) The contrast of graphene is dependent on the wavelength of incident light and the thickness of SiO_2 substrate. To fit the experimental data, a three layer model, air-graphene-SiO_2 was used; Reprinted with permission from Reference [29] Copyright 2007, AIP Publishing. (b) typical optical image of graphene on 300 nm SiO_2/Si. (c) scheme of the variable angle spectroscopic ellipsometer.