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Optical and electrical properties and applications of two-dimensional carbon-based nanomaterials

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Abstract. As an emerging material, two-dimensional (2D) carbon-based nanomaterials have unique optical and electrical properties due to their unique atomic layer structure. On the one hand, due to their high transmittance, high carrier mobility, controllable Fermi level, and wide spectral light saturation absorption characteristics, they can be applied in new-generation solar cells, organic light-emitting diodes, touch screens, and fiber optic devices. On the other hand, due to their unique nanostructure, they have high specific surface area, low diffusion distance, high conductivity, and ion conductivity. They can serve as substrates and work together with other materials as electrode materials for future fuel cells and lithium-ion batteries and have significant advantages in fields such as sensors. This article mainly summarizes the impact of two-dimensional carbon-based nanomaterials represented by graphene, Mxene, and 2D covalent organic frameworks (COFs) on their optical and electrical properties, and summarizes the latest practical applications and research progress of these nanomaterials in the field of optics and electronics. In addition, a corresponding summary and outlook have been made on the problems that need to be solved in future applications of 2D carbon-based nanomaterials.

Keywords: 2D carbon nanomaterials, Functionalization, Graphene, MXenes, 2D-COFs

1. Introduction

Since 2004, single-atom layer graphene has been prepared by mechanical exfoliation method by Geim and Novoselov from the University of Manchester in the UK [1]. Due to the unique atomic layer structure of graphene and its related two-dimensional carbon nanomaterials with similar structures, it has become a research hotspot in various fields. two-dimensional carbon nanomaterials have extremely high specific surface area, excellent planar mechanical properties, and unique optical and electrical properties, thanks to their unique two-dimensional carbon atomic layer structure. It has important application potential in various electronic, optoelectronic, and electrochemical devices including solar cells, field effect transistors (FETs), light emitting diodes (LEDs), sensors, lithium-ion batteries, fuel cells, etc. In addition, two-dimensional carbon nanomaterials can also be functionalized to derive more new functions. At present, the functionalization modification methods for two-dimensional carbon nanomaterials include heteroatom doping, surface oxidation or grafting, coating and composite, and polymer or metal-organic framework carbonization [2]. The functionalized two-dimensional carbon nanomaterials can maintain their original physical and chemical properties as much as possible while adding other functions to meet practical needs.

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Currently, in practical applications, two-dimensional carbon-based nanomaterials stand out among nanomaterials due to their high specific surface area, high transmittance, and easily modified two-dimensional planar structure. In terms of optical applications, such as the high transmittance, high conductivity, and even flexible transparent electrodes required for solar cells, the use of two-dimensional carbon nanomaterials can effectively meet these requirements. In terms of electrical applications, such as high energy density cathodes and anodes required for lithium batteries or fuel cells, the two-dimensional structure of two-dimensional carbon nanomaterials can better accommodate adsorbed ions to meet energy storage needs. This article elaborates on the nanostructures and optical and electrical properties of two-dimensional carbon-based nanomaterials such as graphene and its functionalized products. It summarizes the representative preparation methods and applications of the products in the optical and electrical fields of two-dimensional carbon-based nanomaterials, and prospects for the future performance in corresponding fields.

2. Representative 2D carbon-based nanomaterials

2.1. Graphene

Graphene refers to a two-dimensional carbon nanomaterial with a honeycomb-like structure arranged in regular hexagonal order, formed by the tightly connected carbon atoms of sp^2 orbital hybridization [3]. The adjacent carbon atoms are connected by carbon-carbon single bonds with a bond angle of 120°, resulting in a hexagonal structure with good mechanical properties in the plane direction. For the unhybridized P orbitals of the carbon atoms that make up graphene, they are parallel and overlap on the plane, forming delocalized large π bonds perpendicular to the graphene plane, thus graphene has good conductivity. Due to its unique nanostructure, graphene has many excellent properties. Optical performance: The single-layer atomic arrangement structure of graphene gives it good transparency, with a visible light transmittance of up to 98.5% [4]. And its good mechanical properties in the plane direction make it suitable for flexible optical devices. Electrical performance: Graphene has large delocalized π bonds both in the same layer and between layers, resulting in a large number of freely movable electrons in the plane direction of graphene. This gives graphene a relatively high conductivity, and its carrier mobility can reach 15000 cm ²/ (V s) at room temperature [5].

2.2. MXenes

In 2011, Gogotsi's team successfully produced a compound Ti_3C_2 for MXenes, and papers on the physicochemical properties and applications of MXenes emerged like mushrooms after a rain [6]. MXenes are a type of two-dimensional layered transition metal carbides, nitrides, and carbonitrides, which can be formally divided into two categories. One type of structural formula is $M_{n+1}X_n$, and the other type is $M_{n+1}X_nT_x$. M refers to early transition metal elements (such as Sc, Ti, V, Cr, etc.) in the third to sixth subgroups of the periodic table, X refers to carbon, nitrogen, or carbon and nitrogen, and T refers to surface terminal functional groups such as hydroxyl, oxygen, fluorine, or chlorine, n=1,2,3,4.

In terms of electrical properties, due to the fact that the main charge carriers in MXenes are electrons when oxygen and water molecules in the air are adsorbed into MXenes thin sheets, their conductivity decreases. This is irreversible because MXenes flakes are oxidized in air. Although it is not conducive to electrochemical performance, it can be used to construct $Ti_3C_2T_x$ -TiO_2 heterojunctions [7]. When MXenes are stacked layer by layer with other substances to form a composite, they have a large interlayer spacing, good conductivity, fast diffusion performance of ions and molecules, and a considerable electron density near the Fermi level. Therefore, they have great potential for application in the fields of batteries and supercapacitors [8].

In terms of optical properties, most MXenes are unable to generate photo-generated carriers due to their metallic properties but can be combined with other materials to construct Schottky/p-n/p-p heterojunctions to promote the separation of photo-generated carriers and serve as co-catalysts for photocatalytic reactions. Some functionalized titanium carbide nanosheets, due to their excellent absorption properties in the near-infrared region, can be used as photothermal agents to combat cancer

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cells [9]. Nb_2C nanosheets have extremely high photothermal conversion efficiency and high photothermal stability, showcasing the promising prospects of MXenes in photothermal therapy [10].

2.3. 2D-COFs

COFs are a new type of crystalline organic porous polymers composed of light elements such as C, H, O, and B connected by strong covalent bonds. They utilize dynamic covalent chemistry (DCC) polymerization reactions to arrange structural units in an orderly manner at the atomic scale, thereby forming periodic network framework structures. According to the types of covalent bonds formed by condensation reactions, COFs can be divided into boric acids, triazines, imines, phenylhydrazones, ketones/enamines, polyimides, phthalocyanines, and porphyrins.

In terms of electrical properties, due to the periodic arrangement of 2D-COFs, they may have considerable conductivity and photoconductivity. Through the superposition of π orbitals within the layer, significant electronic coupling can occur between π orbitals, effectively promoting the conduction of charge carriers in their π channels.

In terms of optical properties, phthalocyanine compounds have strong absorption in visible light and are excellent optoelectronic materials. Jiang's team synthesized two materials using the organic compound pyrene as the substrate, namely PPY-COF and TP-COF [11], which have certain fluorescence properties, among which PPY-COF can generate photocurrent.

3. Applications of 2D carbon-based nanomaterials

3.1. Graphene

3.1.1. Solar cells. As a device that can convert light energy into electricity, solar cells play an extremely important role in the field of green energy. At present, graphene is mainly used in two categories in the field of solar cells, i.e.: organic solar cells and dye-sensitized solar cells. The former requires highly transparent electrodes, with indium tin oxide (ITO) and F-doped tin oxide (FTO) being the most commonly used electrode materials. Park et al. prepared graphene-based flexible polymer solar cells based on anode and cathode by heat treatment of the MoO_3 electron barrier layer and direct deposition of the ZnO electron transport layer on graphene [12]. The energy conversion efficiency reached 6.1% and 7.1%, respectively. As a new type of inexpensive thin film solar cell, the introduction of platinum-free counter electrodes is currently a hot research topic due to the difficulty in getting rid of the dependence on precious metal platinum as the counter electrode material. Sudhakar et al. used conductive polymer complex poly (3,4-ethylene dioxythiophene): polystyrene sulfonate (PEDOT:PSS) composites containing nanoporous reduced graphene oxide on the surface of FTO conductive glass as counter electrodes to prepare dye-sensitized solar cells [13]. The light conversion efficiency of the battery was 9.57%, while the FTO conductive glass surface coated with platinum as the counter electrode prepared under the same conditions had a light conversion efficiency of 9.64%, and their performance was basically equivalent. This composite has great potential as a platinum-free counter electrode material in dye-sensitized solar cells.

3.1.2. Touch screens. At present, the main material for touch screens is ITO, but it requires the use of relatively scarce indium resources. Currently, ITO films have the disadvantages of brittleness and poor heat dissipation. Sukang Bae et al. used chemical vapor deposition and stacked layer by layer to obtain a doped four-layer graphene film [14]. The film had a surface resistivity of 30 Ω/square and a transmittance of 90%, which was superior to commercial transparent electrodes. It was successfully applied to touch screens.

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3.2. MXenes

3.2.1. Photocatalysts. Most of the research on the application of MXenes in the field of photocatalysis has focused on meeting the requirements of photocatalytic applications by utilizing the surface terminal groups of MXenes (such as -F, =O, -OH groups) or as co-catalysts. The most active co-catalyst for hydrogen evolution, Pt, is expensive and extremely scarce, limiting the commercialization of photocatalysts. Therefore, finding an inexpensive and highly active co-catalyst to replace Pt is of great significance for achieving large-scale production of solar hydrogen. Ran et al. utilized modern theoretical tools to design and synthesize a novel MXenes material Ti_3C_2 nanoparticles [15], which were used as highly active catalysts. A high melting point CdS/Ti_3C_2 composite photocatalyst was prepared by hydrothermal treatment using - O/- OH termination instead of -F termination on Ti_3C_2, and coupling the pre-treated Ti_3C_2 with CdS. This photocatalyst composite not only has extremely high visible light catalytic activity [14342 μmol/(h g)] but has a significant quantum efficiency (40.1% at 420 nm), making it an excellent non-precious metal sulfide photocatalyst.

3.2.2. Supercapacitors. Supercapacitors have high power density, can transfer stored energy in a short period of time, and can be used for a long time. However, due to the high cost of its materials, the main problem that needs to be overcome is the synthesis of efficient and stable electrode materials. Jiang et al. used titanium carbide MXenes ($Ti_3C_2T_x$) to study the characteristics of negative potential operation in acidic electrolytes and combined it with a ruthenium oxide (RuO_2) positive electrode to design a fully pseudocapacitive asymmetric device [16]. After 20000 charging and discharging cycles, the capacitance retention rate was 86%. These results indicate that in asymmetric electrochemical capacitors, pseudo-capacitive MXenes negative electrodes can improve energy density.

3.3. 2D-COFs

3.3.1. Photocatalysis. As a sustainable clean energy source, hydrogen has always been considered the best alternative to traditional fossil fuels. Using light energy to drive water decomposition to produce hydrogen is a simple and economical way to obtain hydrogen. Lotsch et al. applied COFs for the first time in photocatalytic hydrogen evolution by condensing 2,4,6-tris (4-formylphenyl) -1,3,5-triazine (TFPT) with 2,5-diethoxy-phenyl benzoyl hydrazine (DETH) to form a hydrazone linked COF (TFPT COF) with photocatalytic activity [17], using triethanolamine (TEOA) as a sacrificial reagent and Pt as a cocatalyst and visible light ($\lambda >$ Under irradiation conditions of 420 nm), the hydrogen evolution rate of this COF is 1970 μmol $g^{-1}h^{-1}$, while the apparent quantum efficiency at 400 nm is 2.2%. The flatness, crystallinity, specific surface area, and hydrophilicity of the building blocks of materials can all affect the photocatalytic hydrogen evolution rate. Currently, designing and constructing COFs with photocatalytic activity at the molecular level is the mainstream approach to improving the performance of photocatalytic hydrogen evolution.

3.3.2. Photosensitive materials. COFs extend the π conjugated system to the entire two-dimensional structure, expanding the delocalized range of π electrons and suppressing π-π interactions between conjugated units. Therefore, COFs have high electron mobility and excellent photoconductivity. N. Huang et al. obtained the photosensitive intelligent composite material photo-responsive 2D-COF (Ph-An-COF) for the first time, which can control its gas adsorption, molecular storage, sensing, semiconductor, and other properties by external stimuli by changing the lighting and heat treatment conditions [18]. The interlayer [4π+4π] cycloaddition of anthracene units stacked in π- columns produces a concave-convex polygonal skeleton, which undergoes a reversible transformation under light and is accompanied by a significant property transformation.

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4. Conclusion

As an excellent new type of material, two-dimensional carbon-based nanomaterials have excellent planar mechanical properties, high specific surface area, and optical and electrical properties due to their unique single atomic layer structure. In addition, functionalization and modification can also be applied by introducing other functional groups or doped atoms into two-dimensional carbon nanomaterials, enabling them to have more diverse functions to meet application needs. However, it is not easy to achieve ideal functionalization and modification of two-dimensional carbon-based nanomaterials. How to determine the reaction mechanism, whether the functionalized products can be easily prepared, and how to maintain the physicochemical properties of the products are currently several difficulties in research and applications. However, it is undeniable that the diverse application scenarios of two-dimensional carbon nanomaterials have significant research and application potential. It is believed that two-dimensional carbon nanomaterials will be an indispensable direction in research and application in various fields in the future.

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