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APPLICATION PROGRESS OF CARBON-BASED FUNCTIONAL MATERIALS IN THE MARINE FIELD

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Abstract: "Marine Strategy" is an important national development strategy of China. Marine resource development and environmental protection, maritime transportation, seaport and coastal defense construction, marine engineering equipment, and marine exploration equipment all require a large number of new functional materials. Carbon-based materials have shown good application prospects in many scientific and engineering fields. This article systematically reviews the application progress of carbon-based functional materials in the field of marine science, focusing on the applications in environmental emergency materials, anti-corrosion coatings, structural materials, seawater desalination and other fields. It also reviews the emerging applications of carbon-based functional materials in marine energy storage and other fields. Directional applications are prospected.
Keywords: Marine science and technology; Carbon-based materials; Graphene

1 INTRODUCTION

The 21st century is the century of the ocean. Countries around the world have shifted their development strategies from land to ocean, from offshore to far sea, and from shallow sea to deep sea. With the continuous development of marine science and technology, people can understand, utilize and protect the ocean more comprehensively, accurately and deeply. The development of marine science and technology is a systematic project and an integrated intersection of multiple disciplines and fields. The most important and critical technology is the development and breakthrough of materials science, especially marine functions
Material progress [1].
Marine functional materials, broadly speaking, are the general term for materials "taken from the ocean" and "used for the ocean", that is, materials extracted from the ocean and materials used for ocean development and utilization. The proposal of the concept of "marine functional materials" is of great significance to the cross-integration of the two major fields of ocean and materials and the implementation of the national ocean strategy. The development of marine resources, marine engineering equipment, marine transportation, and marine detection equipment all require the support of a large number of new functional materials. Due to the special physical and chemical properties of the ocean, marine functional materials must not only follow the characteristics and laws of material science, but also be closely integrated with the marine environment. Therefore, the development of functional and application-oriented high-performance marine functional materials is crucial to the development of marine science and technology.
Among many functional material systems, carbon-based functional materials, whether traditional carbon-based materials or new carbon-based materials, are widely used because of their unique physical and chemical properties and rich and diverse structural characteristics. Especially in some extreme application conditions, such as the aerospace field, carbon-based materials show advantages that other materials cannot match. Carbon fiber materials have been successfully used in structural materials due to their light weight and high strength; carbon-based composite reinforcement materials have also been successfully used in some extreme environments such as high temperatures [2]. "Going to the sky and going to the sea" has become an important goal for the application of many materials. In addition to important application progress in the aerospace field, carbon-based materials have also begun to emerge in marine science and technology. With the continuous development of marine science and marine technology equipment, carbon-based materials are increasingly appearing in the fields of marine engineering equipment, offshore ships, marine environmental emergency, and anti-corrosion and anti-fouling [3, 4].
Taking the application fields as the line and the functions of carbon-based functional materials as the axis, the author sorted out the application progress of carbon-based functional materials in the field of marine science and technology. In particular, the research on some "new" carbon nanomaterials (graphene, carbon nanotubes) in "emerging" marine fields, such as seawater desalination, heavy anti-corrosion coatings, and marine energy storage, is prospected. As shown in Figure 1.

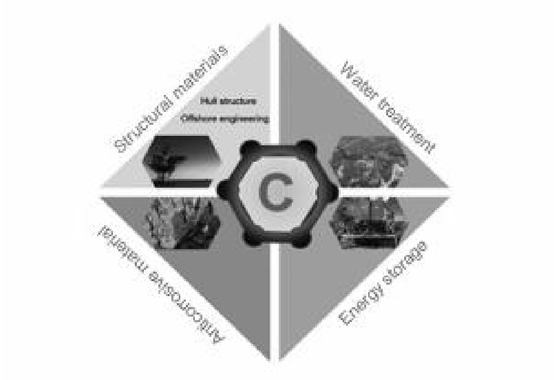

Fig. 1 Schematic diagram of the application of carbon-based materials in marine science

2 MARINE STRUCTURAL MATERIALS

2.1 Ship Structural Materials

Carbon-based materials are widely used in composite reinforcement materials. Carbon fiber reinforced materials formed by composites of carbon fiber and resin, ceramic and other matrices are light in weight and high in strength. Compared with steel ships, the use of carbon fiber reinforced materials to make ship hulls is simple to manufacture, has a small hull weight, and has low fuel consumption. At the same time, carbon fiber composite materials have good fatigue resistance and chemical inertness, and can effectively prevent biological fouling and corrosion. At present, carbon fiber composite materials are being increasingly widely used in the field of military and civilian shipbuilding [5, 6]: (1) Military ships. Carbon fiber composite materials can improve the stealth performance of warships. For example, using carbon fiber composite materials in the hull and mast; applying carbon fiber composite materials in propellers can also reduce vibration and noise, improve detection capabilities, and achieve fast cruising effects. (2) Civilian yachts. It can be used in instrument panels, antennas, rudders, decks, cabins, cables and other structures to improve strength and durability. The "Zhongke-Lianya" yacht is an all-carbon fiber yacht that is 30% lighter than similar yachts, has higher strength, lower fuel consumption, and is faster.

2.2 Offshore Equipment

Environmental effects such as corrosion and high pressure in the ocean place stringent requirements on the strength, fatigue resistance and corrosion resistance of materials. Carbon fiber composite materials are lightweight, corrosion-resistant, and have good mechanical properties, and have good application prospects in offshore engineering equipment. Carbon fiber composite materials have been used in key components such as production well pipes, sucker rods, and oil pipelines on oilfield drilling platforms [7, 8]; carbon fiber composite materials have also been widely used in blades for offshore wind power generation, improving the performance of the blades. The aerodynamic performance makes the fan output power more stable and improves energy efficiency. At the same time, the conductive properties of carbon fiber are used to effectively avoid damage to the blades caused by lightning strikes through special structural design [9]. In addition, carbon fiber composite materials have been used in offshore island and reef buildings, docks, floating platforms, lighthouse towers, submarine pipelines, etc. at home and abroad to replace traditional steel building materials, significantly avoiding the occurrence of corrosion, extending the service life of the platform, and reducing costs. cost.

3 SEAWATER PURIFICATION MATERIALS

3.1 Oil spill Environmental Restoration Materials

With the rapid development of the marine economy, oil spill accidents occur frequently. At the same time, when a cargo ship docks, the discharge of sewage such as ballast water from the ship will also lead to the generation of a large amount of oily wastewater. These spills would wreak havoc on the entire ecological chain, from lowly algae to mammals. Traditional oil spill remediation emergency treatment methods mainly include physical methods and chemical methods. Among them, oil booms, adsorbent materials, mechanical recovery, etc. are physical methods, and methods such as oil spill dispersants and microorganisms are chemical methods. However, traditional treatment methods are less efficient and can easily cause secondary pollution [10, 11]. High-performance adsorbent materials can effectively adsorb marine oil pollution, and adsorbent materials with good regeneration and recycling properties can also effectively reduce environmental treatment costs. However, traditional adsorbent materials also have certain application bottlenecks: poor selectivity, absorbing a large amount of water while absorbing oil, making oil recovery and separation difficult; low oil absorption capacity, slow oil absorption rate, and low efficiency.

Therefore, it is urgent to develop adsorbent materials with high selectivity, large adsorption capacity, fast adsorption kinetics, and recyclability. Superhydrophobic surface, suitable pore structure and good mechanical strength are necessary conditions for ideal adsorption materials. Porous carbon-based materials, due to their abundant
The surface chemistry and porous structure of the
Oil spill environmental restoration materials [12, 13].
Graphene is a single-atom-thick two-dimensional nanomaterial and the basic structural unit for building other two-dimensional carbon-based materials. Graphene-based aerogel is a three-dimensional porous carbon material formed by overlapping graphene sheets. Its developed pore structure, controllable surface chemistry and good mechanical properties make it very potential in oil spill environmental remediation [14-16]. The team of Professor Qu Liangti of Beijing Institute of Technology prepared an ultra-light nitrogen-doped graphene three-dimensional structure and achieved an adsorption performance of 200 to 600 times the self-weight adsorption capacity [17]. The team of Professor Gao Chao of Zhejiang University prepared ultra-light graphene-based carbon aerogels with a porosity of 99.9% and a maximum adsorption capacity of CCl_4 of 913 g/g under vacuum conditions [18]. Professor Qiu Jieshan's team used a microwave-assisted method to prepare super-hydrophobic and super-oleophilic graphene-carbon nanotube hybrid aerogels. Its large pore volume, adjustable pore size and good compressibility endow it with a fast adsorption rate and With large capacity and good recyclability, oil can be quickly recovered through mechanical extrusion (Figure 2a) [19].

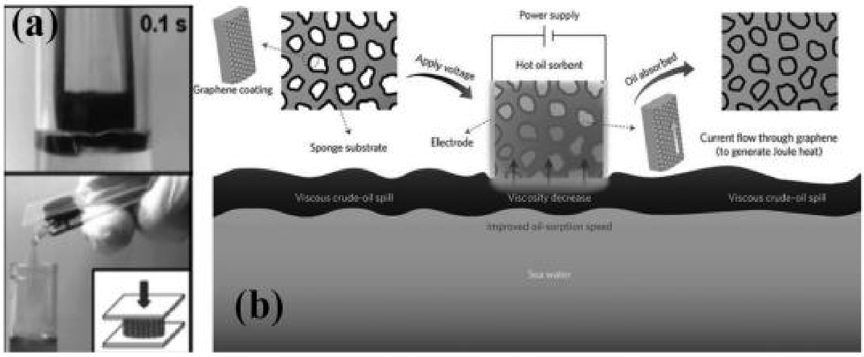

Fig. 2 (a) Graphene airgel adsorption-extrusion recovery experiment [19]; (b) Graphene sponge uses Joule heat to recover high-viscosity oil [20]

Porous carbon materials with good hydrophobic properties have a high adsorption rate for low-viscosity oils, but are often helpless against high-viscosity oils such as crude oil. The team of Professor Yu Shuhong from the University of Science and Technology of China has developed an in-situ heating technology with industrial prospects to achieve rapid adsorption of high-viscosity crude oil (Figure 2b). By evenly coating the surface of a commercial sponge with a graphene coating, it maintains the original porous structure of the sponge and has good conductivity and a hydrophobic surface; applying voltage to the graphene sponge generates Joule heat that can effectively reduce the viscosity of crude oil. Improve the adsorption of high-viscosity crude oil by graphene-modified sponge [20].
Expanded graphite is a new type of loose and porous granular carbon-based material obtained by intercalation, water pouring, drying and high-temperature expansion of natural flake graphite. It not only retains the heat resistance, corrosion resistance, radiation resistance and non-toxicity of natural graphite, but also has the characteristics of adsorption, environmental harmony and biocompatibility that natural graphite does not have, so it is also widely used. Used as oil spill adsorption material [21]. The R&D team of the People's Liberation Army University of Science and Technology tested the adsorption performance of this loose and porous expanded graphite on oil pollution. They heated and expanded the graphite-sulfate interlayer compound to prepare raw materials, and obtained expanded graphite with different structural parameters by controlling the heating temperature. The results show that expanded graphite prepared at 900 ℃ has the best adsorption performance, and the structure of expanded graphite is dominated by large and mesopores, which is suitable for adsorbing oil substances with larger molecules [22]. The R&D team of Xi'an Jiaotong University obtained the optimal conditions for preparing expanded graphite adsorbent by chemical oxidation through orthogonal experiments. They also pointed out that expanded graphite can be regenerated through suction filtration, is reusable, and is adsorbed at the same time. The oil can be recycled [23].
New porous carbon has made great strides in the field of marine oil spill environmental restoration. High-efficiency, low-cost, and recyclable smart repair materials will become an important direction for future development.

3.2 Desalination

The scarcity of freshwater resources is a common challenge facing the world. Therefore, seawater desalination has become a hot research topic around the world and an important direction for the development of marine resources. The promotion of this technology will provide good solutions to water shortage problems such as offshore operations, agricultural irrigation, and drinking water. At present, seawater desalination methods mainly include seawater freezing method, electrodialysis method, distillation method, reverse osmosis method, etc. Currently, the application of reverse osmosis membrane method and flash evaporation method are the mainstream in the market [24-26]. Although reverse osmosis membrane technology is relatively mature, with the continuous development of material science, the research on new seawater desalination membranes has gradually become a hot spot. Ben Corry's research team at the University of Western Australia proposed that carbon nanotube membranes can efficiently purify seawater. If the membrane pore diameter can be reduced to 0.01 nm, the seawater desalination efficiency can be improved hundreds or thousands of times [27]. Rasel Das and his team tested and summarized the desalination efficiency of carbon nanotube membranes with different pore sizes [28].

Professors Nair and Geim of the University of Manchester in the UK have made a series of breakthroughs in graphene-based separation membranes [29-31]. Due to its good hydrophilicity, the traditional graphene oxide membrane cannot filter most water and ions with its interlayer spacing (~1.35 nm). By regulating the different humidity environments of the graphene oxide film, the oxidation can be effectively controlled. The graphene interlayer spacing (0.64 ~ 0.98 nm) can effectively screen ions, and the filtration rate of the resulting graphene oxide film for NaCl can reach 97%. Fang Haiping and his collaborators separated the graphene oxide film from different Precisely controlled interlayer spacing can be obtained after the action of hydrated cations [32]. When the graphene oxide film is combined with an ionic solution with a small hydrated diameter, it can effectively prevent the passage of larger-sized hydrated ions. Therefore, control of cations can be achieved through cation control. Precise control of the interlayer spacing of graphene oxide membranes at the angstrom level achieves the purpose of selective filtration of water molecules and hydrated ions. This research provides theoretical and technical guidance for the interlayer control of graphene oxide, showing its application in seawater desalination, etc. The huge application prospects in the field have also opened up new ideas for the research of other two-dimensional materials in the field of separation membranes.

Graphene-based separation membranes have shown good separation capabilities. While reducing manufacturing costs, further improving separation efficiency and separation throughput is the key to advancing the practical process.

4 ANTI-CORROSION COATING

Marine corrosion not only threatens the safety of offshore engineering equipment, but also causes huge losses to the national economy. The effect of traditional anti-corrosion coatings is not very satisfactory, and a considerable part contains non-environmentally friendly components such as lead, zinc or chromium, and is expensive. Therefore, people need new anti-corrosion coatings that are more environmentally friendly, economical and efficient to reduce the possibility of corrosion. Heavy-duty anti-corrosion coating refers to a type of anti-corrosion coating that can be used in relatively harsh corrosive environments compared to conventional anti-corrosion coatings, and can achieve a longer protection period than conventional anti-corrosion coatings. In the marine environment, the role of heavy-duty anti-corrosion coatings is even more prominent. Port buildings and containers in ports and ocean transportation require the application of a large number of heavy-duty anti-corrosion coatings; offshore oil production platforms must not only consider the maintenance difficulties of underwater corrosion, but also prevent atmospheric and salt spray corrosion and the corrosion characteristics of the "splash zone", which requires coatings The requirements are more stringent; wind power generation also has extremely stringent requirements for heavy-duty anti-corrosion coatings, which must not only prevent corrosion, but also have good resistance to sea wind impact and anti-icing properties [33].

Graphene has a good effect in blocking contact between metal and the outside world due to its good barrier properties and chemical stability. The Ningbo Institute of the Chinese Academy of Sciences has made a series of progress in the research of graphene heavy-duty anti-corrosion coatings and has entered the large-scale demonstration stage. The products have been used in large-scale application demonstrations in large-scale power transmission rail structures, petrochemical equipment and other fields.

While graphene heavy-duty anti-corrosion coatings are showing great potential, research on their anti-corrosion mechanisms and failure analysis are equally crucial. Recently, Professor Huang Jiaxing of Northwestern University published a review article detailing the mechanism and strategy of graphene anti-corrosion from the perspective of electrochemical mechanism. That is to say, a graphene coating with a complete structure has good barrier and anti-corrosion effects. When cracks appear in the coating, the potential of graphene becomes more negative, which will accelerate the corrosion rate of the exposed area and reduce the strength of the matrix. In future applications, they proposed to construct graphene-polymer composite coatings, construct components with anode protection such as graphene-zinc, and construct self-healing graphene, which can further improve the performance of anti-corrosion coatings [34] (Figure 3).

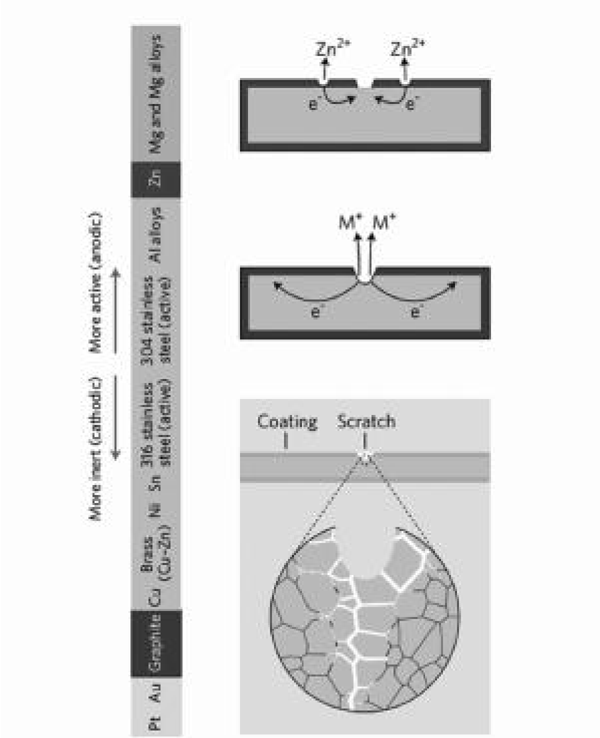

Fig. 3 Schematic diagram of the working mechanism of anti-corrosion coating [34]

Although the application of graphene heavy anti-corrosion coatings has made some progress, its mechanism still needs to be further explored and clarified to better screen and regulate the coating components according to the corrosive environment and maximize the performance advantages of the coating.

5 OCEAN ENERGY STORAGE

Electrochemical energy storage devices have been widely used as large-scale energy storage or power devices in electric vehicles, smart grids and other fields, and their applications in "heaven and sea" have also attracted much attention. Ocean navigation and ocean development have increasingly higher requirements for power devices, and high-performance energy storage devices are crucial to offshore operations. In a deep-sea environment of 10,000 meters, the energy storage device used must have very high pressure resistance and safety to ensure the safety of the entire equipment to the greatest extent. At the same time, it can withstand the corrosion of the complex seawater environment and have good low-temperature resistance; especially In extreme environments such as the deep sea where photoelectric conversion is impossible, solid-state energy storage devices with high energy density, long life and high safety are needed [35, 36].

In 2017, the solid-state lithium battery (Qingneng I) developed by the Qingdao Institute of Bioenergy and Processes, Chinese Academy of Sciences, went out to sea with the deep submersible of the Institute of Deep Sea Science, Chinese Academy of Sciences, and conducted a full-ocean depth demonstration application in the Mariana Trench. This is China's first Independently developed high-energy-density, high-performance all-solid-state lithium batteries that can be used in deep submersibles. They can still charge and discharge safely and stably under the 10,000-meter-deep sea. At the same time, with the development of equipment integration, the volumetric energy density of power devices has received more and more attention. Therefore, the development of new energy storage devices with high volumetric energy density, good cycle stability and high safety is essential for ensuring ocean exploration, transportation and Some special applications are of great significance. Carbon-based nanomaterials have been widely used in components such as electrode materials, conductive frameworks, and buffer materials. The densified construction of carbon-based materials is an important prerequisite for achieving "smaller" energy storage devices. Yang Quanhong's research group at Tianjin University used the interfacial assembly of graphene and the regulation of the solvent removal mechanism to obtain a three-dimensional graphene assembly with ultra-high density, and combined it with sulfur, polyaniline, ruthenium dioxide, tin oxide and other materials Compounding, by regulating the pore structure of the material, achieves a balance between electron transmission and ion transport, greatly improving the volume capacity performance of the material without loss of mass capacity, and obtaining a series of high volume energy density through device integration. Energy storage devices, such as supercapacitors, lithium-sulfur batteries, lithium-ion batteries, etc. [37-42]. These high volumetric energy density electrochemical energy storage devices will play an important role in ocean exploration.

6 OUTLOOK-CARBON-BASED MATERIALS BRING NEW DIRECTIONS FOR THE DEVELOPMENT OF MARINE SCIENCE

With the gradual upgrading of the country's "marine strategy" and "marine security", the exploration and development of marine resources has become more and more important, and the development of sea-related equipment has become imminent. The progress of marine science and technology depends largely on the development of advanced materials. The emergence of new marine materials will surely provide new impetus for the development of marine science and technology. The continuous emergence of the carbon-based material family, from graphite, diamond, carbon nanotubes, fullerene to graphene, as well as new allotropes such as graphyne, has provided many opportunities for the advancement of materials science and has also brought about downstream applications. With the advent of new power, especially in extreme application environments, carbon-based materials have shown very excellent properties and completed the task of "reaching the sky and exploring the sea" that many materials cannot achieve. Today, with the rapid development of marine science, especially the urgent need for deep-sea exploration, carbon-based materials have emerged in the fields of anti-corrosion, structural materials, seawater desalination and other fields. Although there are still many problems that need to be optimized and solved, their application prospects are huge.

In the future development of marine science, carbon-based materials will play an increasingly important role as they do in aerospace. The development of new materials and new processes will bring revolutionary changes to new marine materials: (1) High-strength, high-chemical-stability carbon-based materials and composite reinforced materials will become important choices for marine engineering materials and aircraft structure materials. Achieve the goal of "light weight and durability"; (2) Seawater resource utilization and environmental restoration. The emergence of new carbon-based separation membranes will further improve seawater desalination efficiency and solve the problem of water shortage; carbon-based environmental restoration materials will also further promote the development of the marine environment restoration industry; (3) Graphene-based anti-corrosion coatings will greatly improve offshore engineering equipment and offshore buildings, reduce maintenance costs, and significantly extend the service life and economic benefits; (4) The application of new energy storage devices will upgrade the service life and safety of current ocean exploration equipment and navigation aids, and improve the “exploration capabilities, and apply advanced energy storage technology to satellites, ships, autonomous underwater vehicles (AUV), remotely operated vehicles (ROV), and manned submarines (Human occupied vehicle, HOV), deep-sea landing detection, buoys and tides and other new energy storage; (5) Develop advanced gas purification materials based on carbon-based materials for air pollution in small confined spaces such as ships, and cooperate with gas Treatment system to achieve efficient air purification and waste recycling.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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