Preparation of carbon/transition metal dichalcogenide hybrids for water-related applications

Chen, Bo

2016

Chen, B. (2016). Preparation of carbon/transition metal dichalcogenide hybrids for water-related applications. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69291>

<https://doi.org/10.32657/10356/69291>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**PREPARATION OF CARBON/TRANSITION METAL
DICALCOGENIDE HYBRIDS
FOR WATER-RELATED APPLICATIONS**

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**Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute**

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DICHALCOGENIDE HYBRIDS
FOR WATER-RELATED APPLICATIONS**

CHEN BO

**Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute**

A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

17-Aug-2016

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Abstract

Carbon-based heterostructures have received extensive research interest owing to their unique physical and chemical properties, and various important applications, such as water remediation, water splitting and sensing. Recently, it was found that the physical and chemical properties of carbon-based materials can be greatly tuned by surface modification/combination with other materials (such as transition metal dichalcogenides (TMDs)) or tuning of its inner structures. Therefore, it is of great importance to develop new methods/strategies for the preparation of carbon-based functional hybrids with controlled inner structures. To realize this objective, the following research works have been conducted.

Firstly, a kapok-derived carbon aerogel (KCA) with high hydrophobicity, high sorption capacity, and good recyclability has been prepared using the low-cost kapok as the raw material via a facile pyrolyzation method. The KCA can absorb various organic solvents up to 160 times of its own weight. It is worth to point out that both distillation and squeezing are applicable for recycling KCA, because of its good thermal stability and mechanical properties. Moreover, the abundant natural source and easy fabrication method make the KCA very cost-effective and beneficial for large-scale production. Therefore, our KCA could be a highly promising sorbent for low-cost and highly efficient removal of pollutants from water. Remarkably, the KCA can also be used as three-dimensional (3D) substrate for loading photocatalysts (such as MoS_2). The as-obtained KCA/ MoS_2 shows good sorption and photocatalytic degradation properties.

Secondly, a graphene/ MoS_2 aerogel (GMA) has been synthesized via a modified hydrothermal method followed by a typical freeze-drying process to maintain the porous structures. The as-obtained GMA shows good removal efficiency towards several categories of contaminants. Importantly, the GMA can absorb mercury ions up to 1245 mg g^{-1} , which is one of the highest values so far. Furthermore, the GMA also shows good sorption ability towards organic dyes (such as methyl orange (MO) and methylene blue (MB)). The sorption mechanism has been also investigated and deduced to be a synergetic effect of electrostatic interaction and surface area.

Thirdly, a facile and general strategy for the preparation of TMD/CNT-based flexible fiber has been demonstrated. It is noteworthy that the as-prepared hybrid fibers retain good

mechanical strength and exhibit remarkable catalytic performance towards electrocatalytic water splitting. The extremely low onset potential (about 0 to -15 mV) and Tafel slope (30 to 36 mV per decade), excellent long-term stability both in acid and basic environment, as well as high flexibility and mechanical stress, enable these fibers to be one of the most promising hydrogen evolution reaction (HER) catalysts in the future. Importantly, our strategy is applicable for the preparation of various hybrid fibers, thus showing great potentials for developing multi-functional materials for a wide range of applications, such as catalysis, sensing, and energy storage.

Acknowledgements

First of all, I would like to show my deepest appreciation to my main supervisor, Professor Zhang Hua, for his careful guidance and constant support in the past 4 years, as well as his efforts towards the completion of my Ph.D. thesis. I also would like to give the heartfelt thanks to my former main supervisor, Professor Huang ling, my co-supervisor, Associate Professor Lim Teik Thye, and my mentor, Associate Professor Richard David Webster, for their patience, encouragement, and help throughout my research work. I am really grateful to ECMG, NEWRI and IGS for financial support for my Ph.D. study.

Secondly, I also want to express my warmest gratitude to Dr. Du Yaping, Dr. Yin Zongyou, Dr. Wu Xuejun, Dr. Tan Chaoliang, Mr. Ma Qinglang, Dr. Sun Gengzhi, Dr. Cao Xiehong, Dr. Bi Hengchang, Dr. Li Bing, for their meaningful suggestions on my research. Special thanks are dedicated to Dr. Melinda Sindoro, Miss Chen Ye, Miss Cheng Hongfei, Miss Wang Jie, and Mr. Huang Jingtao, for their kind help on revision of my thesis.

Thirdly, I would like to thank all my group members and friends: Dr. Huang Xiao, Dr. Zhang Zhicheng, Dr. Han Shikui, Dr. Fan Zhanxi, Dr. Lu Qipeng, Dr. Yu Yifu, Dr. Zhao Meiting, Dr. Luo Zhimin, Dr. Ping Jianfeng, Dr. Wang Yixian, Dr. Yang Nailiang, Dr. He Qiyuan, Dr. Pei Wenbo, Dr. Peng Yongwu, Dr. Qi Xiaoying, Dr. Zeng Zhiyuan, Dr. Hong Xun, Dr. Liu Juqing, Dr. Li Hai, Dr. Zheng Bing, Dr. Wu Jumiati, Dr. Liu Zhengdong, Dr. Xu Huan, Dr. Zhao Wei, Mr. Chen Junze, Miss He Xinyan, Mr. Zhang Xiao, Mr. Yang Jian, Miss. Huang Ying, Mr. Lai Zhuangchai, Miss Zhang Ying, Mr. Nam Gwang-Hyeon, Mr. Hu Zhongting, Mr. Ma Chongbo, Mr. Toh Zhiwei, and all other colleagues. I really spent happy time together with them in lab.

Last but not the least, I am deeply grateful to my devoted wife, Ms. Guo Can, for her encouragement, selfless love, and continuous support in the last few years. I would also extend my sincere thanks to my parents, Mr. Chen Xianghui and Ms. Wang Yunxia, for giving me life and raising me up. This thesis is dedicated to you.

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Abbreviations

1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
AC	Activated Carbon
AFM	Atomic Force Microscopy
CCA	Cotton-Derived Carbon Aerogel
CDI	Capacitive Deionization
CE	Counter Electrode
CMB	Carbon Microbelt
CNF	Carbon Nanofiber
CNT	Carbon Nanotube
CR	Congo Red
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
ECF	Elastic Carbon Foam
EDS	Energy Dispersive X-ray Spectroscopy
FFT	Fast Fourier Transformation
FTIR	Fourier Transform Infrared
GMA	Graphene/MoS ₂ Aerogel
GO	Graphene Oxide
HAADF	High-Angle Annual Dark-Field
HER	Hydrogen Evolution Reaction
HRTEM	High Resolution Transmission Electron Microscopy
HTC	Hydrothermal Carbonization
KCA	Kapok-Derived Carbon Aerogel

LIB	Li Ion Battery
LSV	Linear Sweep Voltammetry
MB	Methylene Blue
MO	Methyl Orange
NMP	N-methyl-pyrrolidone
PAA	Polyacrylic Acid
PEC	Photoelectrochemical Cell
PTFE	Polytetrafluoroethylene
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
RE	Reference Electrode
rGO	Reduced Graphene Oxide
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SGH	Self-Assembled Graphene Hydrogel
STEM	Scanning Transmission Electron Microscopy
TCF	Twisted Carbon Fiber
TC	Tetracycline Antibiotic
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TMD	Transition Metal Dichalcogenide
UFA	Ultra-Flyweight Aerogels
UV	Ultraviolet
WE	Working Electrode
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy

Chapter 1 Introduction

1.1 Hypothesis/Problem Statement

Carbon-based three-dimensional (3D) architectures have attracted considerable attention in the past two decades due to their emerging properties, such as huge surface area, interconnected porous structures, and macroscopic bulky shape, which enable them to be one of the most outstanding and promising materials for water treatment. Promising recent studies shown that 3D carbons, particularly those made of graphene and carbon nanotube (CNT), have excellent performance in removal of pollutants out of waste water. Nevertheless, the practical applications of CNT- and graphene-based 3D structures, especially for water treatment, are limited by their high cost and complicated synthesis procedures. Hence, moving forward, the research goal on alternative water treatment is always to prepare highly efficient sorbents of low cost. Biomass materials are some of the most promising precursors, being low cost, eco-friendly, and naturally exist in great abundant. In previous system, our group have developed a facile method to fabricate 3D carbon aerogel from raw cotton. To the best of our knowledge, there are several natural cellulosic products, such as kapok, milkweed, and flax which are similar to cotton and also can be the source for carbon aerogel. The hypothesis here is that the structure and component of biomass-based raw materials may have great impact on the sorption performance of final products. Thus, high efficiency carbon-based 3D sorbents may be made from raw materials with hollow structure and higher surface area.

Even though carbon-based 3D porous networks have superior sorption ability in water remediation, most of the architectures are compatible only with one category of contaminants. Thus, most porous architectures may not be sufficient to treat industrial waste water which always contains many different types of pollutants (*e.g.* dyes, heavy metal ions, oils, and other organic compounds). Hence, it is logical to explore process to modify the surface of 3D carbon with other functional materials in order to change the surface properties. The hybrids are expected to exhibit enhanced sorption capacity for absorbing different types of water pollutants.

Carbon-based heterostructures are also suitable for water splitting. Multi-walled CNT (MWCNT) sheets, which can be continuously drawn out from vertically aligned arrays of

MWCNT, are novel structure with considerable interest. For example, the unique features of free-standing MWCNT sheets, such as excellent mechanical properties, high electrical conductivity, as well as good flexibility, enable these materials to be widely used as substrate for functional materials in various applications, including supercapacitors, lithium-ion batteries, and memory devices. Moreover, MWCNT sheets can be spun into hybrid fibers upon mixing the material with other functional materials. The hypothesis here is that MWCNT sheets might be able to combine with transition metal dichalcogenide (TMD) materials to form flexible hybrid fibers and water splitting performance of TMD materials might be beneficial from the incorporation with MWCNT sheets to overcome the poor conductivity of TMD materials along the lamellae structure as well as to prevent them from aggregation.

1.2 Objectives and Scope

Based on the hypotheses proposed above, my objectives and scope are listed below.

First, carbon aerogel with 3D architecture was fabricated using low-cost kapok hollow fibers as raw material *via* a facile pyrolysis method. The as-obtained kapok-derived carbon aerogel (KCA) was characterized by FTIR, SEM, TGA, and EDS. The sorption performances of KCA toward various oil and organic solvents were also explored. Moreover, the as-prepared KCA can be used as 3D substrate for loading photocatalysts (such as MoS₂). Further, the potential applications of the hybrid for water remediation were explored.

Second, a simple hydrothermal method was used for in-situ modification of MoS₂ on the surface of 3D graphene aerogel. The effect of precursor concentration on the morphology of hybrid graphene/MoS₂ aerogels (GMAs) was also explored. The as-prepared GMAs were characterized by TEM, STEM, XPS, FTIR, SEM, and EDS. The potential application of the as-obtained GMA as multi-functional sorbent for removal of different types of pollutants, such as dyes, heavy metal ions, oils, and other organics from waste water were explored.

Last, several MWCNT/TMD-based flexible sheets were produced via a facile and general drop-casting strategy. These sheets were further transformed to flexible and weavable hybrid fibers. The resultant hybrid fibers were characterized by TEM, XPS, SEM, EDS, and Raman spectroscopy. The potential applications of the as-obtained flexible fibers as working electrode for electrocatalytic water splitting were also explored.

1.3 Dissertation Overview

The thesis addresses multiple problems in 2D ultrathin materials and 3D hybrid porous structures. The themes of this thesis are organized into separate chapters according to the material used and the technique developed. Particular attentions are made to elaborate the following points in their respective chapters: how to synthesize novel carbon-based 3D architectures from biomass; how to coat ultrathin 2D metal chalcogenide nanomaterials on the surface of 3D carbon; how to assemble of 2D nanosheets to 3D hybrid heterostructures *via* one-pot reaction; how to prepare flexible MWCNT/TMD hybrid fibers with good mechanical properties; how to use powerful techniques to characterize the as-obtained novel Carbon/TMD hybrid materials; demonstrating the potential of these hybrid materials for water-related applications like water remediation and water-splitting.

Chapter 1 provides a rationale for the research along with outlining the goals of each project and their respective scopes.

Chapter 2 gives the big picture on the current research progress. The literature included reviews on water treatment technologies and general sorbents for removal of pollutants, preparation of carbon-based 3D architectures for water remediation, as well as carbon/TMD hybrid materials for water remediation and water splitting.

Chapter 3 discusses the rational for methods/materials selection, the synthesis to obtain the hybrid materials, the characterization techniques employed, and the potential applications for carbon/TMD hybrid materials.

Chapter 4 elaborates the synthesis as well as the characterization of KCAs and KCA/MoS₂ which were then utilized for absorptive and photocatalytic removal of pollutants from water.

Chapter 5 elaborates the synthesis and characterization of 3D GMAs with bulky form and interconnected porous heterostructures along with demonstrating the enhanced sorption performance towards different categories of contaminants.

Chapter 6 elaborates the preparation of a series of CNT/TMD hybrid fibers, and the utilization of as-obtained fibers as the working electrode for electrochemical water splitting.

Chapter 7 concludes the whole thesis and elaborates the reconnaissance of the overall studies which could be conducted in the near future.

1.4 Findings and Outcomes/Originality

From the abovementioned projects, I have learned a lot about the synthetic skills. These, combined with the selection of outstanding research projects, culminate in several novel structures and synthetic strategies as listed:

1. Highly hydrophilic KCA with high sorption capacity and good recyclability, fabricated from low-cost biomass (*i.e.* kapok) as raw material. The KCA can absorb various chemicals with a weight of 80-160 times of its own weight. Both mechanical squeezing and distillation are suitable for recycling the absorbed pollutants from KCA because of its mechanical properties and good thermal stability. Last but not the least, KCA can also be used as 3D substrate for loading photocatalysts (such as MoS₂). The as-obtained KCA/MoS₂ shows good sorption and photocatalytic degradation properties.
2. GMA with 3D architecture can simply be synthesized by the hydrothermal method followed by a typical freeze-drying process to maintain the porous structures. The as-obtained GMAs show good removal property towards multi-pollutants (such as positive charged ions and organic dye). More importantly, the GMA can absorb mercury ions up to 1245 mg g⁻¹, recording the highest values so far.
3. A facile and general strategy is developed to prepare several CNT/TMD-based flexible and weavable fiber devices. The as-obtained fibers retain good mechanical strength while maintaining guest functionality and exhibiting remarkable electrocatalytic performance towards water splitting, comparable to the commercial Pt/C. The resulting fibers exhibit extremely low onset potential and Tafel slope as well as excellent long-term stability both in acid and basic environments.

Chapter 2 Literature Review

2.1 Water Remediation and Conventional Sorbent Materials

Undoubtedly, we are now facing the challenge of fresh water shortage, threatening the health and live of people worldwide.^[1] Although water covers 70% of the earth surface, fresh water – one that is potable - only accounts for about 0.14% of the total volume.^[2] This problem is worsen by the increasing demand of clean water due to the growing population. According to scientific prediction, water scarcity would trouble one third of the world population by 2030.^[3] Furthermore, water pollution resulting from improper discharge of domestic, agricultural, and industrial effluents has severely aggravated the situation. Recent United Nations (UN) report mentioned that about 300-500 million tons of waste water containing toxic ions, dyes, and other harmful organics are discharged into the environment every year.^[4] In addition, the increasing number of anthropogenic marine disasters, including frequent oil spills during transportation and drilling, could exert a catastrophic impact on marine livings. For instance, in 2006, a massive oil spill took place at the Prudhoe Bay, which brought fatal and lasting damage to more than 8300 living species in the habitat.^[5]

2.1.1 General Water Purification Technologies

To address urgent issue of clean water shortage, one of the most effective ways is through water purification. Over the last several decades, technologies have been developed to deal with water purification in pursue of higher efficiency, minimal environmental impact, and lower cost, various novel materials, and innovative.^[1] To date, different methods, such as sorption, electrolysis, ion exchange have been utilized to purify polluted water. Among these methods, sorption has some outstanding advantages, like fast performance, cost-effectiveness, eco-friendliness, thus it has been extensively studied and used for water remediation.

2.1.2 Materials for Pollutant Sorption

In recent decades, extensive research work has been conducted to develop multifunctional materials that can effectively remove contaminants from waste water.^[6-10] Various sorbents with porous structures have been used to purify waste water, such as activated carbon

(AC),^[11, 12] metal oxides,^[13-15] minerals,^[16, 17] expanded graphite,^[18] as well as agriculture wastes^[19-23]. Broadly, these sorbents can be classified into four categories: mineral products, synthetic organic products, natural fiber products, and carbonaceous materials.^[24, 25]

2.1.2.1 Mineral Products

Examples of mineral products include zeolites, silica aerogel, organophilic clays, and expanded perlites. The following sections will mainly focus on zeolites and silica aerogel.

Zeolite

Zeolite is an important category of sorbents which has hydrophobic nature and microporous structures. It has been broadly used as an alternate of AC to absorb organic pollutants.^[26-28] Naturally occurring zeolite is formed via mixing and fusing certain amount of feldspar and soda ash clay. Later on, synthetic zeolites were prepared by mixing and fusing sodium silicate, bauxite, and caustic soda. Interestingly, some synthetic zeolites have large surface area ($700 \text{ m}^2/\text{g}$). These distinguish them from naturally occurring zeolites that show very small apparent surface area. Zeolites are inflammable and remain stable under higher temperature ($1300 \text{ }^\circ\text{C}$).^[29] However, their applications are restricted by the low sorption capacity.

Silica Aerogel

Silica aerogel is a nanoporous material prepared from sol-gel process followed by supercritical drying. Advantages of this type of material include large specific surface area (more than $1000 \text{ m}^2/\text{g}$), high porosity, low density, and small thermal conductivity.^[30, 31] However, the aerogel structure will collapse after absorbing certain amount of water, which is the major obstacle to its commercialization. Commonly used materials for supercritical drying are CO_2 and alcohol. Comparing these two, CO_2 is relatively safer and more economical, because of its chemical inertness, low critical temperature, as well as non-flammable and non-explosive properties. However, the aerogels prepared by CO_2 supercritical drying always show higher hydrophobicity. Therefore, quite a lot of research work has been done to improve the hydrophilicity of silica aerogel.^[30-34]

Apart from the aforementioned materials, expander perlite and clay minerals have also been used as sorbents for water treatment. For instance, Teas *et al.*^[24] reported that the oil sorption

capacity of expended perlite was comparable to that of synthetic organic sorbents. In another study, organophilic clay was used for the removal of grease and emulsified oil.^[35]

2.1.2.2 Synthetic Organic Products

Synthetic organic products, such as polypropylene, have several outstanding properties including hydrophobicity and oleophilicity. For instance, Jarre and co-workers prepared the ultra-light polyurethane foams which can absorb oil up to 100 times of its own weight after chemical modification.^[36] More recently, Teas and his co-workers demonstrated that the treated polypropylene showed higher sorption capacity compared with expanded perlite and cellulosic fiber.

In the last decade, tremendous attention has been given to conjugated microporous polymers which have extremely high surface area, particular microporosity, good stability and, hence, show promising in the sorption of organics. Recently, Li and co-workers^[37] successfully prepared super-oleophilic and super-hydrophobic porous sponges which are coated with conjugated microporous polymer (so-called conjugated microporous polymer-1 and conjugated microporous polymer-2). In the sorption of polar and nonpolar organic solvents as well as oils (Figure 2.1), these sponges exhibited excellent recyclability, good selectivity, and fast sorption kinetics. The inset of Figure 2.1 is optical microscopy image of the conjugated microporous polymer-1 treated sponge with corresponding camera image in its lower right corner.

Figure 2.1 Sorption efficiency of the conjugated microporous polymer-1 and conjugated microporous polymer-2 treated sponges for various organic solvents and oils. Reproduced with permission.^[37] Copyright 2011, Royal Society of Chemistry.

Although these synthetic organic products have exhibited attractive advantages, their disadvantages are also obvious. For one, they are of higher cost than that of natural fibrous products and commercial mineral products. For another, they have very low degradation rate, resulting in concomitant environmental problems.^[24, 25, 38]

2.1.2.3 Natural Fiber Products

Unlike the mineral, natural fibrous sorbents are obtained from animals and plants. So far, most common natural sorbents include rice straw, cotton, corn stalk, milkweed floss, peat moss wood fibers, wool, and kapok.^[25, 39] without further treatment, these sorbents have been used in various forms, such as filter, pads, boom, sheets, and fiber assemblies.^[40-43] These natural sorbents have lower density than most mineral sorbents whilst also cost effective and environmentally friendly.^[44, 45] Among these fibrous sorbents, kapok is one of the most outstanding ones. Studies have demonstrated that the oil sorption efficiency of the kapok with hollow structures is significantly higher than that of commercial polypropylene fiber.^[25, 46, 47] Moreover, the absorbed oil can be regenerated and the sorbents do not show obvious loss in sorption capacity after several cycles.^[25, 48]

2.1.2.4 Carbonaceous Materials

Carbon-based sorbents, a special class of materials which have been studied more widely and deeply, are highlighted as follows.

Activated Carbon

The most widely used sorbent for removing pollutants from waste water is AC. AC has good sorption efficiency towards a host of materials such as metals, dyes, phenols, organic compounds, and several bio-organisms. However, its high cost and inefficient regeneration limit its widespread use.

To reduce the cost of AC, a common way is to use waste materials from industry or agriculture to prepare it. An interesting example is the utilization of waste newspapers. Shimada and co-workers^[49] obtained AC via carbonizing the mixture of used newspaper and certain amount of phenol resin in N₂ gas at 800 °C. Prior to the carbonization, waste newspaper was heated at 150 °C for 10 min. The as-prepared AC exhibited high surface area (about 1000 m²/g), which leads to high sorption capacity, as evidenced by high methylene blue (326 mg/g) and iodine (1310 mg/g) loading number.

Exfoliated Graphite

Exfoliated graphite is one of the most excellent oil sorbents with high buoyancy.^[50, 51] It can absorb heavy oil with a high sorption capacity up to 80 g/g, which is much higher than lots of the above-mentioned natural fiber sorbents and synthetic organic products.^[50-55] Meanwhile, just by simple compression, 80% of the absorbed heavy oil can be recovered. However, the exfoliation of graphite still remains a challenge. Hence, developing effective and practical techniques to manipulate it is needed.

2.2 Carbon-Based 3D Macroscopic Architectures for Water Remediation

The unique physical and chemical properties of carbon-based materials make them very popular in the recent years. They show excellent physical, chemical, and thermal stability under extreme conditions (*e.g.* strong acid/basic environments and high temperature) which can ensure their fantastic performance over long-term in the practical water treatment. It is important to note that carbonaceous materials are generally harmless to the environment. The research interest in carbonaceous materials is further triggered by the discovery of graphene

and carbon nanotubes (CNTs). Generally, the unassembled CNTs and graphene are small in size, making it difficult to completely collect and recycle them after usage and may bring about secondary environment pollutions. In contrast, it is easier to collect and recycle the carbon-based materials which have macroscopically bulky shape without leading to additional contamination. In recent years, carbon-based three-dimensional (3D) architectures have attracted huge interest and become quite promising for water purification, owing to their superior properties, such as interconnected porous structures, huge surface, and macroscopic bulky shape.^[56-60]

In the following sections, discussions will be focused on the recent development in the design, fabrication, and application of carbon-based 3D macroscopic architectures for water remediation, such as foams, aerogels, hydrogels, *etc.* In particular, carbon-based 3D architectures prepared from CNTs, graphene, biomass, and synthetic polymers are elaborated. Their preparation methods and applications in water remediation, including removal of oils/organic solvents, metal ions, and dyes are discussed.

2.2.1 Raw Materials for Carbon-Based 3D Macroscopic Architectures

Carbon-based 3D macroscopic materials can be divided into four categories based on the components and sources: CNT-based, graphene-based, biomass-derived, and synthetic polymer-derived, as shown in Figure 2.2.

Figure 2.2 Four categories of raw materials used for carbon-based 3D macroscopic architectures.

2.2.1.1 *CNT-Based 3D Macroscopic Architectures*

Since the first report of CNT in 1991, extensive research efforts have been devoted into carbonaceous materials.^[61] Consequently, tremendous patents and papers have reported the preparation, characteristics, and applications of CNTs as well as their derivatives. The great interest in studying CNTs is attributed to their various unique characteristics. For example, they can act as building blocks of macroscopic monolithic 3D architectures, as well as functional materials in devices. CNT-based 3D materials show high conductivity, low density, tuneable hydrophobicity, and low defect concentration which enable them to be very promising in a lot of applications, especially environmental remediation and clean energy.

2.2.1.2 *Graphene-Based 3D Macroscopic Architectures*

Apart from CNTs, tremendous attention has been given to graphene as well as its derivatives since 2004.^[62-78] Inspiringly, within the last few years, great efforts have been taken to prepare 3D macroscopic architecture/aerogels through the self-assembly of graphene and/or

reduced graphene oxide (rGO) nanosheets. It has been proved that construction of graphene-based macroscopic 3D architectures plays an important role in further optimizing the properties of two-dimensional (2D) graphene for real applications, including sensors,^[79] supercapacitors,^[80-83] lithium-ion batteries,^[84, 85] sorbents,^[86] vibration damping,^[87] capacitive deionization,^[88] microbial fuel cell,^[89] catalysis,^[90] *etc.*^[91-94]

Demonstrations showed that unaffiliated graphene nanosheets and their derivatives perform well in absorbing poisonous metal ions, oils, dyes and other organic contaminants from waste water.^[95-99] However, they are difficult to be recycled and reused, leading to secondary pollution. Recent research shows that 3D macroscopic architectures constructed from the assembly of graphene-based sheets can exhibit improved performance for specific application or have promising potentials in some new applications.^[91]

2.2.1.3 Biomass-Derived 3D Macroscopic Architectures

The practical applications of CNT- and graphene-based 3D structures, especially for water treatment, have been limited by their high cost and complicated synthesis procedure in spite of their various advantages described before. Hence, moving forward, the research goal on alternative water treatment is always to prepare highly efficient sorbents with low cost. One of the most promising precursors for producing carbon-based materials is biomass materials, which have characteristics, such as low cost, eco-friendliness, and great abundance in nature. Until now, various sustainable natural products with low cost, or agriculture and industry wastes have been explored as carbon source, such as maize cob, steel plant slag, peat, or wood shaving.^[21] Unfortunately, a majority of biomass-derived carbon materials have the drawbacks of poor hydrophobicity, high density, low efficiency, poor decomposability and recyclability.

2.2.1.4 Synthetic Polymer-Derived 3D Macroscopic Architectures

Synthetic polymeric/organic gels have also been used to fabricate carbon-based aerogels. Typically, monomers were first polymerized via sol-gel process, forming polymeric gel. Then, freeze-drying or supercritical drying was conducted to remove the solvent from the obtained organic gel, resulting in polymeric aerogel. Subsequently, the as-prepared polymeric aerogel was carbonized to obtain carbon-based aerogel. The carbonization process was performed in an inert gas through pyrolysis, similar to the process of using mass to prepare carbon aerogels. Moreover, micro-sized pores can be created via an additional activation

process which can increase the total specific surface area (SSA). Initially, resorcinol and formaldehyde were used to prepare the polymer-derived carbon aerogels.^[75, 100] Later, carbon aerogels with different properties were also prepared using many other organic monomers. For example, the expensive resorcinol was partially replaced by gallic acid which could stimulate a self-catalyzed polymerization.^[101] After pyrolysis, the internal structure of the resulted 3D carbon aerogel consists of monomodal mesopores and it is superimposed with micropores after the activation by CO₂.

2.2.2 Synthetic Methods for Carbon-Based 3D Macroscopic Architectures

2.2.2.1 Assembly in Solutions

By dispersing CNT in aqueous or organic solutions which contain surfactants or polymers, CNT organogels or hydrogels can be formed, respectively. The solvent in the resulted wet gels was then removed using freeze-drying or supercritical drying without collapsing the entire structure. This step led to the formation of the monolithic and bulky CNT aerogels which have porous structure. For instance, Bryning *et al.* prepared a CNT hydrogel by dispersing CNTs into the aqueous solution of sodium dodecylbenzene sulfonate, then, the subsequent supercritical drying or freeze-drying resulted in CNT aerogel.^[102] This aerogel has a porous internal structure formed by interconnecting of individual CNTs, while its macroscopic shape is cylinder (Figure 2.3a). However, the as-prepared CNT aerogel showed poor mechanical strength. To improve this shortcoming, poly(vinyl alcohol) (PVA) was added into the macroscopic network to reinforce the structure, after which the as-obtained hybrid aerogel could bear a load as high as 8000 times of its weight, demonstrating an extremely high specific mechanical strength.

Figure 2.3 (a) Images of CNT aerogels. Upper left: Pristine CNT aerogel in black colour (left) and PVA-reinforced hybrid aerogel in grey colour (right). Lower left: SEM image showing the PVA-reinforced hybrid aerogel. Right: PVA-reinforced aerogels lifting up a 100 g weight. Reproduced with permission.^[102] Copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA. (b) Left: digital photos showing a PSS-G/PVA aerogel in a syringe. Right: SEM image exhibiting the layered structure with inter-layer crosslinks in lamellar arrangement. Reproduced with permission.^[103] Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA. (c) Schematics showing the preparation process of self-assembled hydrogel (SH) derived from GO/DNA composite. (d) Digital images showing the process of self-healing. The as-prepared SH showed in (c) was cut into three small blocks. By putting the freshly formed surfaces in close contact with each other and after 90 °C heating for 3 min in air, these three blocks adhered to each other. Reproduced with permission.^[104] Copyright 2010, American Chemical Society.

In 2009, a graphene-polymer hybrid aerogel which has high-order 3D architectures was successfully fabricated by Mann and co-workers (Figure 2.3b).^[103] After that, many 3D macroporous structures based on graphene were reported. For instance, Shi *et al.* fabricated a hybrid 3D architecture having good mechanical properties and self-healing ability, prepared by the self-assembly of 3D GO/DNA hydrogel (Figure 2.3c,d).^[104] Wang and co-workers also developed a metal-assisted method to prepare graphene-derived 3D macroporous architectures via self-assembly. The as-prepared samples have a compressive strength of 0.042 MPa and compression modulus of about 0.26 MPa.^[105]

Moreover, GO and graphene can be coated onto other 3D architectures to modify the surface, owing to their good flexibility. For instance, a super-hydrophobic and super-oleophilic sponge was prepared *via* a facile method based on dip coating.^[106] This novel sponge was fabricated by modifying the surface of a super-hydrophilic material (*e.g.* commercial melamine sponges) with graphene (Figure 2.4a-c). It is worth noting that the sponge changed from super-hydrophilic to super-hydrophobic after its surface was covered by graphene nanosheets (Figure 2.4d-f). The resulted graphene-coated sponge exhibited high sorption capacity, excellent recyclability, and good selectivity towards oils as well as organic solvents.

Figure 2.4 (a-c) Typical SEM images showing (a) the original melamine sponge, (b) the graphene coated sponge, and (c) the graphene-PDMS co-modified sponge. Insets are the respective high-magnification SEM images. (d) After dispersing water and oil droplets on the sponge surface shown in (c). The inset shows that the surface is super-hydrophobic with a relatively high water contact angle (162°). (e) Digital photos showing the original sponge (white) placed in water while the graphene-modified sponge (black) floating on the surface of water. Inset shows the graphene-modified sponge is partially immersed into water by applying a force. Reproduced with permission.^[106] Copyright 2012, Royal Society of Chemistry.

2.2.2.2 Hydrothermal Method

Another effective way that has been broadly used to fabricate 3D carbon networks from carbonaceous precursors is hydrothermal method. For example, self-assembled graphene hydrogel (SGH) in a cylindrical shape was prepared by Shi *et al.* through a one-step hydrothermal method (Figure 2.5).^[107] The SGH was obtained from GO aquatic solution without any other reagents and it has an interconnected macroporous structure (Figure 2.5c). More importantly, SGH has good mechanical properties (Figure 2.5b) with a relatively high compression modulus (around 470 kPa) which is much higher than that of hydrogels generated from other precursors. By controlling reaction time and/or GO concentration, microstructures and properties of the SGH can be well tuned.

Figure 2.5 (a) Digital image showing the homogeneous GO aqueous dispersion with a GO concentration of 2 mg/mL (left), and the product of the GO solution after 12-hour hydrothermal reduction (right). (b) Left: a SGH is held by a tweezers. Right: SGHs hold a 100g weight. (c) Typical SEM image showing the internal microstructure of SGH. Reproduced with permission.^[107] Copyright 2010, American Chemical Society.

A commonly used approach to prepare carbonaceous materials in autoclave is called hydrothermal carbonization (HTC).^[57, 58] Recently, Yu *et al.* utilized the HTC method to fabricate hydrogels and aerogels based on carbon nanofiber (CNF). Using tellurium nanowires (TeNWs) as template, glucose first underwent HTC treatment; then, the TeNWs core was etched away; last, freeze-drying was utilized to remove the solvent.^[60] Eventually CNF aerogel with interconnected internal structure was obtained (Figure 2.6a). By controlling the reaction time and glucose concentration, the thickness of HTC carbon could be tuned. It is worth noting that the CNF aerogel can be synthesized in a large scale of 12 L (Figure 2.6b). However, like other HTC carbon, the CNF aerogel is hydrophilic because there are plenty of oxygen-containing groups on its surface. Surface modification with PDMS

made the CNF aerogel become hydrophobic, hence the obtained aerogel could absorb various kinds of organics up to 15 times of its own weight (Figure 2.6c). Later on, another study demonstrated the oil sorption of CNF aerogels at extreme high (164.7 °C) and low temperatures (-103.2 °C). Moreover, GO nanosheets can also be reduced and assembled into 3D graphene aerogel via similar hydrothermal methods.^[108] interestingly, in a recent study, watermelon was used as raw material to produce sponge-like carbon-based hydrogel and aerogel through simple hydrothermal treatment.^[109]

Figure 2.6 (a) Schematics illustrating the synthetic steps of preparing preparation CNF aerogel. (b) Photograph showing a monolithic wet gel. (c) Water contact angle measurement indicating that the obtained CNF aerogel is super-hydrophilic (left), while the silicone-coated aerogel is super-hydrophobic (right). Reproduced with permission.^[60] Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA.

2.2.2.3 Chemical Vapor Deposition Methods

Beside the liquid-phase techniques, the commonly used gas-phase method for preparing carbon aerogel is chemical vapor deposition (CVD).^[6, 110, 111] For example, using CH₄ as carbon source, a composite nanosponge was fabricated by growing CNTs on surface of expanded vermiculites (EV).^[112] EV is highly hydrophilic in nature and changes into highly hydrophobic after the growth of CNTs, due to the super-hydrophobic nature of CNTs. Consequently, the oil uptake capability was increased while the water uptake capability was reduced. Although it was demonstrated that the as-obtained CNT hybrid “sponge” could be

applied as sorbent to absorb oil from oil/water mixtures selectively, the low oil sorption capacity (below 4 g/g) and water-absorbing nature still hinder its practical applications. Gui *et al.* fabricated a series of 3D architectures utilizing their sponge-like CNT aerogels which were directly synthesized through CVD method.^[6, 113-115] Ferrocene acted as catalyst and 1, 2-dichlorobenzene provided carbon source. It is believed that these two compounds promoted random growth and non-directional stacking of CNT fibers, resulting in the formation of isotropic CNT network (Figure 2.7a). The isotropic arrangement of CNT fibers is believed to be responsible for the excellent flexibility and deformability of the CNT sponge. The CNT sponge could be deformed into any kind of shape and compressed to a large extent in liquids without obvious collapse (Figure 2.7b).

Figure 2.7 (a) Porous, light, and flexible CNT sponges. Upper left: a digital image shows that a CNT sponge is bent, indicating its flexibility. Upper right: schematics illustrating the internal microstructure of the CNT sponge, which is composed of randomly arranged CNTs. Lower right: SEM images shows the cross-section of the sponge, revealing a porous structure and overlapped CNTs. (b) Loading and unloading curves of the CNT sponge immersed in ethanol, demonstrating a full recovery. Two cycles were tested (red and black lines). Upper inset illustrates the compression process, in which ethanol was squeezed out. Lower inset illustrates the unloading process, in which ethanol was absorbed into the sponge and the sponges recovered to original volume rapidly. Reproduced with permission.^[6] Copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA.

2.2.2.4 Pyrolyzation

Apart from the above-mentioned strategies, another commonly applied approach to produce 3D carbon architectures is pyrolyzation. The carbon-rich precursors used in pyrolyzation typically are synthetic polymers and biomass. In 1990s, the pioneer work of Wierik *et al.* reported the fabrication of starch-derived aerogels through the thermal treatment of starch.^[58]

A typical example of carbon aerogel derived from biomass is named starbon, a commercial starch-derived product.^[57] Even much earlier, carbon-based aerogels derived from synthetic polymeric gels had been reported.

A big advantage of pyrolyzation is its simplicity which makes it highly effective in converting biomass sponge into carbon aerogel and cellulosic fibers into carbon fibers^[116]. For example, Wu *et al.* reported that flexible, light-weight, and anti-fire CNF aerogels could be produced from bacterial cellulose.^[69] In a typical preparation process, an aerogel was first fabricated from bacterial cellulose by freeze-drying; then, the aerogel underwent high-temperature pyrolysis in an inert atmosphere, generating a porous carbon aerogel with interconnected structure, ultralow density, and good fire-resistance. Notably, the CNF aerogel shows good recyclability, excellent selectivity in the sorption of various organics up to 310 times of its own weight.

Similarly, carbon aerogels can also be prepared from polyurethane (PU)-based commercial sponges. Specially, through direct pyrolysis of commercial PU sponge grafted with metal acrylate, ultra-light Fe₂O₃/C composite foams with ultralow density (below 5 mg cm⁻³) were prepared (Figure 2.8a).^[117] The as-obtained hybrid aerogels consist of interconnected hollow nanotubes (Figure 2.8c), forming a 3D continuous architecture (Figure 2.8b). After further modification with methytrichlorosilane, the hybrid aerogels show a high oil sorption capability up to 100 times of its own weight. Moreover, due to the presence of Fe₂O₃, the Fe₂O₃/C foam can be manipulated by magnetic bar (Figure 2.8d) to facilitate the collection and recycling ease of the foams.

In conclusion, various methods have been developed to construct carbon-based 3D porous architectures. It is noteworthy that for solution-based techniques (such as self-assembly and hydrothermal method), the final products' porosity, pore size, and density can be easily tuned by changing the reactants, additives and reaction temperatures. More importantly, to avoid collapse of the as-obtained porous 3D structures, freeze-drying or supercritical-drying is highly required for the drying process. However, there are some drawbacks of the solution-based techniques, such as high cost, time consuming. Other than solution-based methods, CVD is another important bottom-up approach to prepare 3D carbon architectures. This method can generate structures that have lower defect density and can be used as electrodes for highly efficient removal of various heavy metal ions from waste water which is attributed to the high temperature and catalysts used during the deposition. However, CVD is costly and

involves complex procedures, like the cumbersome post-treatment for the catalyst removal, thus it is not suitable for massive production of carbon-based 3D architectures. Compared with the solution-based techniques and CVD method, pyrolyzation is more cost-effective and much simpler, but it is more difficult to tune the structures of the products because the obtained structure is highly dependent on the original structure of raw material. In future, it seems that more efforts should be taken to develop highly efficient and cost effective methods that are suitable for large-scale production of 3D carbon architectures.

Figure 2.8 (a) Schematics illustrate the fabrication process of the ultra-light magnetic foam from polyurethane sponge grafted with polyacrylic acid (PAA). (b,c) The framework of the foam, *i.e.* the polyurethane sponge, consists of 3D interconnected microtubes with wall thickness in nanoscale. (d) A digital image shows that the ultra-light Fe₂O₃/C foam is attracted by a magnet bar. Reproduced with permission.^[117] Copyright 2013, Royal Society of Chemistry.

2.2.3 Applications for Water Treatment

2.2.3.1 Removal of Oils and Organic Solvents

Massive oil spill accidents during shipping and drilling bring fatal damage to marine species and the ecological impact would last for a long time. Shortage of high quality drinking water has become a serious global issue, which is further aggravated by contamination of rivers by toxic substances, such as organic solvents. Therefore, from the point of view of both environment and industry, it is highly desired to develop products for removal of spilled oil and organics from waste water with low cost and high efficiency. Traditional ways include skimming, suction and combustion, which have some inevitable drawbacks. For example, skimming and suction give extremely low efficiency and requires high operation cost, while

combustion generates secondary pollution and results in a waste of precious oil resources. Another current solution, *i.e.* chemical degradation, also suffers from some problems, such as low efficiency, high cost, possible toxicity, and difficulty to retrieve and reuse. Compared with all the above-mentioned methods, sorbents based on carbon-based 3D networks have proved to be highly promising for removing oil/organic solvents from waste water.

As a typical example, CNT sponge can selectively absorb oils which are floating on water surface. Before sorption, the sponge is in a compact form; upon contacting with organic solvents, it swells instantaneously. Interestingly, owing to its hydrophobic and oleophilic properties, it can drift on water surface and move towards the remaining oil, which is so-called “floating-and cleaning” capability and is of particular use in oil spill clean-up (Figure 2.9). The CNT sponge can absorb various oils and organic solvents up to 180 times of its own weight, demonstrating its high sorption capability. Later on, the same authors reported that the absorbed oil or solvents could be easily removed by mechanical compression or direct burning in air. Notably, the regeneration process does not destroy the sponge structure.^[114] After 1000 recycling cycles of compression and distillation, the sorption capacity of the sponge could retain up to 76% of the initial value^[115] and the capacity remains almost unchanged after 10 cycles of burning.^[114]

Figure 2.9 Digital images showing the sorption of Large-area oil by a CNT sponge. Upper image: before the sorption and oil was dyed in blue. Lower image: after the sorption and oil was completely absorbed. Insets are the corresponding CNT sponge. Reproduced with permission.^[6] Copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA.

Polymers and CNTs can also be used to fabricate hybrid porous networks through various techniques. For example, CNTs can be coated onto the porous PDMS scaffold via direct physical absorbing,^[24] and the electrospun polyvinylpyrrolidone (PVP) fibers are also used as support for physical cohering of CNT clusters.^[118] Generally, the mechanical robustness of porous CNT networks is improved by polymers, but their sorption capacity for oils and organic solvents is compromised.

To date, despite promising results that have been reported on CNTs, the commercial applications of CNT-based aerogels in water remediation are still hindered by their high synthesis cost. Hence, only when the fabrication cost of massive production can be lowered to a level comparable to commercial sorbents, like polypropylene (PP), can the widespread application of CNT-based aerogels be realized. Among various CNT based aerogels, those produced by CVD technique show better performance. Nevertheless, their application is limited because CVD technique is difficult to be scaled. Reviewing the recent results and development, some low-cost novel carbon materials have been successfully developed for water treatment, especially those derived from waste, so CNT-based sponges might not be favoured for large-scale industrial application.

Compared to CNTs, graphene oxide (GO) is more cost-effective as a carbon source for preparing 3D carbon network. Ruoff and co-workers reported a shape-moldable and macroporous spongy graphene (SG), which has a specific surface area of about $432 \text{ m}^2 \text{ g}^{-1}$ (Figure 2.10a-c). They systematically demonstrated that SG is a promising sorbent with good recyclability. SG can absorb not only petroleum products and fats, but also organic solvents such as chloroform (Figure 2.10d). Its sorption capacity toward chloroform can be up to 86 times of its own weight, which is tens of times higher than that of commercial sorbents, such as PP. Interestingly, SG can be easily regenerated by distillation, and the oil/organic sorption capacity decreased negligibly after 10 cycles (Figure 2.10e).^[108]

Figure 2.10 (a) A SG (0.32 g) is able to absorb 16.1 g dodecane, demonstrating high oil sorption capacity. (b) Upper image: a water droplet stands on the SG surface, proving the hydrophobicity. Lower image: the SG is wetted by dodecane, proving the oleophilicity. (c) A SEM image showing the porous internal structure of the SG, where pores are in fusiform shape. (d) A histogram showing the sorption efficiency of SG. (e) A diagram showing the recyclability of SG, where the absorbate is toluene and the regeneration is via heating at 105 °C. Reproduced with permission.^[108] Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA.

However, most graphene-based 3D networks are relatively fragile, so they can be easily crushed under compressive or shear stress. Recently, all-carbon ultra-flyweight aerogels (UFAs) (Figure 2.11a) were reported by Gao and co-workers, which showed improved mechanical property.^[119] Through the freeze-drying of mixed aqueous solution of CNTs and GO nanosheets, aerogels were obtained, which were further treated by hydrazine vapor to reduce GO nanosheets into rGO. The synergistic effect between CNT “ribs” and rGO walls (Figure 2.11b,c) endows the all-carbon UFAs with several unique properties such as super-recyclable compressibility, super-hydrophobicity, and low density (less than 1 mg cm⁻³). In addition, the obtained aerogel has an ultra-high sorption capacity for various organics and oils (about 200 to 900 times of its weight), owing to its high porosity (99.9%). Such capacities are

highest among all of the reported data. CNTs are believed to play an import role, not only acting as the “reinforcing steel bar” to enhance the mechanical properties but also making the material surface becoming hydrophobic. However, again, the high cost and complex procedures of CNT preparation hamper their large-scale production for real applications. Hence, finding cost-effective materials as reinforcing component of 3D graphene framework is highly required.

Recently, cost-effective precursors like raw cotton have also been used as carbon source to prepare carbon aerogels.^[120] In contrast to the expensive CNT- and graphene-based aerogels, the raw cotton-derived aerogel, which is twisted carbon fiber (TCF) aerogel (Figure 2.12a,b), is more cost-effective because the precursor is much cheaper. The TFC aerogel has good mechanical property because of the twisted structures. It was shown that heptane dyed with Sudan red 5B floating on water surface can be absorbed completely within 40 s, while chloroform dyed with Sudan red 5B at the bottom of water can be totally absorbed within 5s (Figure 2.12c). The TCF aerogel also has very high sorption capacity which can be up to about 190 times of its weight. The sorption efficiency of TCF aerogel is much higher than that of raw cotton. Moreover, the TCF aerogel can remove various oils and organics from waste water with excellent recyclability. Its high sorption capacity was retained after 5 cycles of regeneration by using burning, squeezing or distillation methods to get rid of the absorbed liquids (Figure 2.12f,g).

It is noted that the recyclability of the sorbents and the recoverability of pollutants are key criteria for oil clean-up applications. To date, squeezing, distillation, and combustion are three of the most widely methods for recycling. For those non-flammable and precious pollutants, squeezing and distillation are good choices to be applied instead of solvent extraction which is complicated, incomplete, and more expensive. Combustion in air is quite simple, however, it may lead to potential emission of secondary pollution. Thus, it is quite promising to utilize the heat generalized during the combustion process.

Figure 2.11 (a) A piece of foxtail lifting up a 100 cm³ UFA cylinder. (b,c) Typical SEM images showing the macroporous architecture of the UFA. (d) Schematics illustrating the movement of a single CNT/rGO hybrid cell wall in response to the compression and release. (e) A graph plotting the correlation between the sorption capability of the UFA and the density of the absorbates. Reproduced with permission.^[119] Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 2.12 (a,b) SEM images showing the microstructure of the TCF aerogel, which consist of randomly arranged carbon fibers. (c) Digital images showing the process of TCF absorbing chloroform. (d) FTIR spectrum of raw cotton. Inset showing a raw cotton ball. (e) FTIR spectrum of TCF aerogel. Inset showing a TCF aerogel ball. (f,g) Recyclability performances of TCF aerogels. Inserts showing the regeneration processes. Reproduced with permission.^[120] Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA.

In another interesting example, waste paper was used as precursor to fabricate carbon microbelt (CMB) aerogel, which showed good ability of selective sorption (Figure 2.13).^[121] The CMB aerogel could efficiently absorb petroleum products, fats and organic solvents including chloroform (up to 188 times of its own weight). Moreover, after being regenerated by distillation for many times, the CMB aerogel did not show obvious decrease in sorption capacity. It is worth noting that the raw material is waste paper; a sustainable and very cheap material. In alignment to low cost idea, the obtained CMB aerogel is a very promising candidate for massive production in practical applications. In addition of the above examples, a few other biomass materials, including kapok,^[75] winter melon,^[122] watermelon^[109] have been used as precursors to prepare carbon aerogels. In conclusion, biomass-derived aerogel is believed to be a new class of economical and promising sorbents for water treatment.

Figure 2.13 (a) CMB aerogel was prepared in 4 steps: 1: making pulp by immersion and agitation; 2: obtaining pulp fiber aerogel via freeze drying; 3: generating CMB aerogel through pyrolysis. (b) Photograph shows a pulp fiber aerogel after absorbing a water droplet dyed with MB, where a blue stain was left on the aerogel. (c) Image showing a droplet of water standing on a black CMB aerogel ball. (d,e) Graphs plotting the recyclability tests of CMB aerogels. Reproduced with permission.^[121] Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA.

Another widely used parent network for carbonization is melamine-based polymer foam because of its abundance and low cost.^[123-125] For example, elastic carbon aerogel, derived from commercially available melamine sponge (Figure 2.14a-d), could absorb different organic solvents with a high capacity up to 410 times of its own weight, owing to its super-hydrophobicity.^[123] Additionally, due to the high nitrogen content in melamine, carbon aerogel that is rich in nitrogen could be generated through pyrolysis of the synthetic melamine-based polymer foam.^[125] Nitrogen doping can enable the carbon aerogel to have

excellent fire-resistance (Figure 2.14e). Therefore, both mechanical compressing and direct burning can be used as simple methods to regenerate the melamine-derived carbon aerogels.

Figure 2.14 Digital images showing the (a) melamine foam (b) elastic carbon foam (ECF). (c) Schematic illustrating the ECF network. (d) SEM image showing the microstructure of ECF. Inset showing the cross-section of a fiber. (e) Digital images showing ECF aerogel immersed in ethanol (1), burning of ECF aerogel after absorbing ethanol (2), the ECF aerogel after burning (3). (f) Digital images showing the process of ECF aerogel absorbing benzene (dyed in orange) from water surface. (g) Digital images showing ECF aerogel immersed in water and oil. Inset showing a droplet of water standing on the surface of ECF. Reproduced with permission.^[123] Copyright 2013, Royal Society of Chemistry.

Generally, it is easy to control and tune the microstructure of the synthetic polymer-derived carbon aerogels because there is a wide range of choices for the monomers and the polymerization conditions can be well controlled. As a result, this type of aerogels has well-developed network with high porosity and hierarchical structure. This beneficial structure ensures both high SSA and fast mass transfer for liquid sorption within meso- and macropores and it also could significantly increase the efficiency of electrosorption and gas phase sorption.^[101, 126, 127] However, such benefit is not obvious in the clean-up of oil and organic solvent. The complicated synthesis process of polymer-based 3D architectures can be effectively simplified by using commercial polymer sponges as template or precursors, hence, reducing the fabrication cost. However, the variability of designing and controlling the aerogel structure is limited due to the constraint of the parent forms. Table 2.1 summarizes various sorbents for removal of oils and organics for comparison purpose.

Table 2.1 Comparison of various materials for removal of organics and oils.

	Carbon Source/ Building Block	Synthetic Method	Absorbate	Density (mg cm^{-3})	Sorption capacity (g g^{-1})	Contact Angle	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Porosity	Cost	Ref.
1	Carbon nanotube (CNT)	CVD	Pump oil, Chloroform, Ethylene glycol, <i>etc.</i>	5-10	80-180	156°	300-400	>99%	High	[6]
2	Graphene oxide (GO)	Hydrothermal	Cyclohexane, Toluene, Vegetable oil, <i>etc.</i>	—	10-30	—	—	—	Medium	[86]
3	GO	Thermal steaming	Petroleum, Toluene, <i>etc.</i>	30	5-40	—	—	—	Medium	[128]
4	GO	Hydrothermal	Diesel oil, Ethanol, Chloroform, <i>etc.</i>	—	75-154	—	399	—	Medium	[97]
5	GO	Assembly based on other 3D architectures	Pump oil, Toluene, Chloroform, <i>etc.</i>	11.3	60-165	132°	—	—	Medium	[106]
6	GO and CNT	CVD	Pump oil	6.92	80-140	152.3°	—	—	High	[129]
7	GO and CNT	Assembly in Solution	Motor oil, Phenoxin, Chloroform, <i>etc.</i>	0.16-0.45	215-913	132.9°	272	99.9%	High	[119]
8	GO and CNT	Assembly in Solution	Vegetable oil, Gasoline, Toluene, <i>etc.</i>		21-35	108.3°-147.6°	315	—	High	[130]
9	Biomass: Winter Melon	Hydrothermal and Pyrolyzation	Pump oil, Toluene, Chloroform, <i>etc.</i>	48	16-50	135°	—	>97.5%	Medium	[122]
10	Biomass: Cellulose	Hydrothermal	Vegetable oil, Phenoxin, Cyclohexane, <i>etc.</i>	3.3	40-115	155°-161°	300	>99%	High	[60]
11	Biomass: Glucose	Hydrothermal and Pyrolyzation	Pump oil, Chloroform, Phenoxin, <i>etc.</i>	10	51-139	135.8°	547	>99%	Medium	[131]
12	Waste Paper (Biomass: Cellulose)	Pyrolyzation	Pump oil, Chloroform, Toluene, <i>etc.</i>	5.8	56-188	—	178	—	Medium	[121]
13	Biomass: Raw Cotton	Pyrolyzation	Pump oil, Toluene, Chloroform, <i>etc.</i>	12	50-192	—	—	—	Low	[120]

14	Biomass: Bacterial Cellulose	Hydrothermal and Pyrolyzation	Gasoline, Phenoxin, Chloroform, <i>etc.</i>	4-6	106-312	113.5°- 128.6°	—	99.7 %	Medium ^[69]
15	Synthetic Polymer: Melamine Formaldehyde	Hydrothermal	Pump oil, Chloroform, Toluene, <i>etc.</i>	24-95	5.0-12.5	97.4°- 127.2°	12.51	87.7%	Medium ^[125]
16	Synthetic Polymer	Hydrothermal and Pyrolyzation	Pump oil, Toluene, Phenoxin, <i>etc.</i>	15-19	23-48	137- 143°	1354	—	High ^[127]
17	Conjugated Microporous Polymers	Polymerization	Pump oil, Chloroform, Toluene, <i>etc.</i>	30	20-53	—	1701	97%	Medium ^[132]
18	Synthetic Polymer: Poly(melamine formaldehyde)	Pyrolyzation	Vegetable oil, Chloroform, Toluene, <i>etc.</i>	8-9.5	71-158	145.4°	—	—	Low ^[124]

2.2.3.2 Removal of Ions

Another type of major water contaminants is metal ions, such as mercury, lead, cadmium, chromium, and arsenic ions. Only a few types of ions are essential elements for human body when presented in little amount, such as copper and iron ions while most of heavy metal ions are poisonous to human and can cause a series of health-related problems, ranging from headache, lung scarring, anaemia, and neurotic disorder to cancer and even death. In natural environment, heavy metal ions maybe existed in soils, rocks and groundwater, and some natural processes such as corrosion and leaching which can results in the leakage of heavy metal ions into the aqueous system. However, the heavy metal pollution has been significantly aggravated by human activities. The toxic ion concentrations of the untreated effluent discharges from various industries, such as chemical manufacturing, electroplating, mining, and battery disposal may far exceed the regulated acceptable level. Therefore, developing materials and technologies to effectively remove the excess ions is highly desired. To remove heavy metal ions from waste water, various techniques have been adopted such as sorption, precipitation, and membrane filtration. Among them, it is believed that sorption with 3D carbon architectures is potentially the most promising because of its convenience, environmental friendliness, and high energy efficiency. Thus, much research focus has been given to this method.

It has been proven that carbon-based 3D architectures are very effective and efficient in removing metal ions from aqueous system through surface complexation or electrostatic attraction. The micropores in the 3D networks result in high surface area for binding while the macropores serve as the fast diffusion paths facilitating sorption as well as desorption. Therefore, the hierarchical structures of 3D carbon networks significantly benefit the sorption of ions.

GO derived aerogels are generated from assembling of 2D nanosheets which results in high surface area and abundant functional groups serving as the binding sites.^[86, 96, 97, 133-137] For example, GO aerogel fabricated via the unidirectional freeze-drying method could remove Cu^{2+} ions from aqueous solution.^[133] This study indicated that the pH of the solution could strongly affect sorption. When pH was increased from 2 to 6, the removal efficiency greatly increased from 32.3% to 96.8%. This strong pH dependency indicates the sorption mechanism is ion exchange. The aerogel surface is negatively charged, so, Cu^{2+} ion competes with H_3O^+ in electrostatic sorption onto the surface. To increase the metal ion removal capability, composite aerogels were also prepared by hybridizing GO with other materials. For example, a composite aerogel, prepared from hybridizing GO with chitosan, showed an increased Pb^{2+} sorption capacity up to 99 mg g^{-1} ,^[134, 136] Pd^{2+} ion up to 217 mg g^{-1} , and Au^{2+} ion up to 1077 mg g^{-1} .^[137] Similarly, Cong *et al.* fabricated a multifunctional FeOOH/graphene aerogel with maximum Cr^{6+} and Pb^{2+} sorption capacities of 139.2 mg g^{-1} and 373.8 mg g^{-1} , respectively.^[86] The synergistic effect of surface complexation and electrostatic interaction accounts for the sorption process.

Graphene and pyrolysis-derived carbon networks showed lower sorption capability than GO, probably because there are less sorption sites on the, relatively hydrophobic surface.^[138-144] For example, carbon aerogel generated from pyrolysis of formaldehyde-resorcinol polymeric hydrogel showed very low Cu^{2+} and Cd^{2+} sorption capacity, only 8.5 and 14.2 mg g^{-1} , respectively. To better understand the Cd^{2+} ion sorption of one commercial cellulose-based carbon aerogel, Goel *et al.* performed a detailed study.^[139] Their study suggested the Cd^{2+} ion sorption onto the carbon aerogel depended on temperature, sorbent concentration and pH of the solution, and the maximum sorption capacity was 15.53 mg g^{-1} . The sorption performance can be increased by proper surface modification. For example, carbon xerogel derived from formaldehyde –resorcinol could be doped with nitrogen during pyrolysis in the ammonia gas.^[140] The resulted N-doped carbon xerogel showed an improved hydrophilicity and

sorption capacity towards Cu^{2+} and Pb^{2+} ions, about 19.05 mg g^{-1} and 51.8 mg g^{-1} , respectively.

Similar to non-GO based carbon networks, pristine graphene has no functional groups to interact with heavy metal ions. However, the pristine graphene has much higher conductivity than GO, which make it a promising electrode material to remove ions through electrosorption in capacitive deionization (CDI) process.^[145] For example, 3D graphene networks fabricated through CVD technique exhibited an extremely high deionization ability towards many heavy metal ions such as Ni^{2+} ion ($1,683 \text{ mg g}^{-1}$), Cu^{2+} ion (1683 mg g^{-1}), Pb^{2+} ion (882 mg g^{-1}), and Cd^{2+} ion (434 mg g^{-1}).^[96]

2.2.3.3 Removal of Dyes

Dye is harmful to human and is one of the most commonly pollutants found in the industrial waste water. Similar to the sorption of ions, GO can efficiently remove dye from water, because of the high density of sorption sites on the GO nanosheets. In most case, different from GO, graphene shows low sorption efficiency in absorbing organic dyes. Recently, rGO aerogels with different properties have been reported, which is achieved by hybridizing with other particles or doped with heteroatoms. For example, by adding thiourea into the GO dispersion, Cheng and his co-workers successfully fabricated nitrogen and sulphur doped 3D rGO sponge through the similar hydrothermal and freeze-drying process.^[97] Under high-temperature condition, the thiourea decomposed into ammonia and hydrogen sulfide, which reacted with rGO nanosheets to form amino and sulfonic acid functional groups attached on rGO. On one hand, negative electrostatic potential was introduced into the aerogel by these N- and S-containing functional groups, which made the aerogel suitable for absorbing organic dyes with positive charges, such as methylene blue (up to 70 mg g^{-1}). On the other hand, the large surface area of aerogel enabled efficient sorption of other types of organic dyes and oil-phase solvents. Table 2.2 summarizes the properties of various sorbents for the removal of heavy ions and organic dyes.

Figure 2.15 (a) Digital images showing GS cut in various shapes. (b) Digital images showing the loading and unloading process of GS using a 500g weight. (c) Digital images showing the typical process of a GS absorbing and desorbing RhB. (d) Stress-strain curve of a GS under compression. (e) Plot of the amount of absorbed RhB in terms of sorption time. (f) Plot of Zeta potential. GS1, GS2 and GS3 denoted three different kinds of GSs with different thiourea content. Reproduced with permission.^[97] Copyright 2012, Royal Society of Chemistry.

Table 2.2 Comparison of various sorbents for heavy metal ions and organic dyes.

	Carbon Source/ Building Block	Synthetic Method	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Absorbate	Sorption Capacity (mg g^{-1}) and condition	Removal Efficiency (%)	Cost	Ref.
1	GO	Assembly in Solution	—	Cu^{2+}	Up to 30, 40 °C	10.5	high	[133]
2	GO	Assembly in Solution	—	Pb^{2+}	Up to 99, Room Temperature (RT)	—	low	[136]
3	GO	Hydrothermal	399	Rhodamine B	Up to 72.5, RT	—	high	[97]
4	GO and Synthetic Polymer	Assembly in Solution	476	Amaranth, etc.	Up to 800, RT	—	high	[146]

5	GO and Oxides	Assembly in Solution	—	Pb ²⁺ and Cr ⁶⁺	Up to 378.8, RT, pH=3	60	high	[86]
6	Graphene	CVD	560	Cu ²⁺ , <i>etc.</i>	Up to 3820, RT, pH=2, Electrical Sorption Capacities	—	high	[96]
7	Synthetic Polymer	Sol-gel Polymerization	700	Pb ²⁺ , <i>etc.</i>	Up to 34.96, 70 °C, pH=7	90	low	[138, 139, 143]
8	Synthetic Polymer	Pyrolyzation	570	Cu ²⁺ and Cd ²⁺	Up to 14.2, RT	—	low	[146]

Carbon-based 3D architectures have different sorption performance towards water-insoluble and water-soluble compounds, due to different sorption mechanisms. Generally, for the sorption of oils and most organic solvents, the sorption capacity of sorbents is highly dependent on their density, porosity and surface area. Meanwhile, the hydrophobicity, measured by contact angle, determines the selectivity of materials towards organic solvents and oils. As for the sorption of water-soluble ions and dyes, the sorption capacity and rate of the sorbents depend on the density of surface functional groups that interact with the contaminants, and the driving force between sorbents and absorbates.

2.3 TMD-Based Materials: Preparation and Application

2.3.1 TMD-Based Materials

2D transition metal dichalcogenides (TMDs) are a class of layered semiconductors with general chemical formula of MX₂, where M represents a transition metal atom including Mo, Ti, Ta while X symbolizes chalcogen atom such as S, Se, or Te (Figure 2.16a,b).^[147] Typically, one M-atom layer is sandwiched between two X-atom layers. For example, based on both theoretical simulation and experimental observation, the thickness of MoS₂ monolayer is found to be 6.5 Å (Figure 2.16c). For other TMDs, the thickness is slightly different because of the differences in crystal structure and atom size.

Over the last few decades, TMD-based materials have received increasing attention due to their unique chemical and physical properties. Thus, as one of the emerging materials, various novel TMD-based structures have been prepared for applications in numerous fields.^[147] In this section of literature review, recent progress on the preparation of TMDs and their derivative materials (especially carbon/TMD nanomaterials) and their applications in water remediation and water splitting is summarized.

Figure 2.16 (a) The typical periodic table highlights the transition metals (Mo, Ti, W, *etc.*) and the chalcogen elements (S, Se, and Te) that predominantly crystallize in layered structure. (b) c-Axis and sectional view of a single-layer TMD sheet with trigonal prismatic coordination. (c) 3D representation of MoS₂ layered structure with interlayer distance of 6.5 Å. Reproduced with permission.^[147] Copyright 2013, Nature Publishing Group.

2.3.2 TMD and Derivative Materials for Water Remediation

2.3.2.1 TMD and Derivative Materials for Pollutant Sorption

A wide range of materials, including CNTs, AC, mesoporous silica materials, polymer resin, biomass ashes, clay minerals, and sludge have been investigated for the sorption and removal of pollutants such as tetracycline antibiotics (TGA), attracting increasing worldwide attention. In contrast to the aforementioned materials, graphene-like TMD materials are deemed as alternative sorbent for TCs removal due to their special layered structures and large surface areas.^[148] Furthermore, combining porosity with ultra-thin layered structures, TMDs are more suitable for removal of pollutants. In 2013, Chao *et al.*^[149] studied the

performance of ultra-thin MoS₂ nanosheets for removal of doxycycline (DC), one of the most commonly used TCs. The as-obtained ultra-thin MoS₂ nanosheets with average thickness of 4-5 nm (8-12 layers) present a significantly higher capability for sorption of DC than the commercial MoS₂ within the whole pH range studied.^[149]

Recently, Tang *et al.* synthesized 3D flower-like MoSe₂ microspheres from selenium powder and sodium molybdate via a more facile hydrothermal approach.^[150] As indicated in Figure 2.17a, the as-obtained MoSe₂ microspheres also contain nanosheets of ~20 nm in thickness. Clear lattice fringes with 0.28 nm lattice spacing can be observed in these MoSe₂ microspheres (Figure 2.17b), indicating the existence of the (100) plane of the hexagonal MoSe₂ phase. Meanwhile, the 0.65 nm interlayer spacing supports the feature of the layered structure. The time profile of MO sorption at various concentrations in the presence of 20 mg MoSe₂ is presented in Figure 2.17c, from which it can be seen that the sorption rate is extremely high in the first 20 min and then slowly plateau as the absorbed amount reached its equilibrium.^[150] In sum, TMD nanomaterials with novel hierarchical structures have provided an attractive approach for waste water treatment.

In addition, TMD/magnetic nanomaterial hybrids are becoming increasingly appealing since the super-paramagnetic particles can be employed to separate the structure from the remaining aqueous media under an external magnetic field.^[151-153] In 2015, Song and co-workers prepared super-paramagnetic MoS₂/Fe₃O₄ nanocomposites with a facile hydrothermal method.^[154] The as-prepared products were easily separated from suspension under an external magnetic field (Figure 2.17d) showed ease of usage for water treatment. As indicated by the sorption isotherm results, the sorption capacity for CR can reach up to 71 mg/g, while the time it takes to reach sorption equilibrium is just two minutes. After then, the CR solution will turn from red to colorless (right-down inset of Figure 2.17d). Moreover, MoS₂/Fe₃O₄ nanocomposites exhibit high selectivity for CR compared to RhB, MG, MB, and EY. The time profile of removal percentage also indicates that a very short period, *e.g.* 2 minutes, is sufficient to reach sorption equilibrium of MoS₂/Fe₃O₄ nanocomposites.^[154]

Figure 2.17 SEM (a) and HRTEM (b) images of MoSe₂ flower-like microspheres. Inset of (b): crystal structure of MoSe₂. (c) Time profiles of MoSe₂ for removal of MO with different initial concentrations. Reproduced with permission.^[150] Copyright 2016, Elsevier. (d) Magnetic hysteresis loops of pure Fe₃O₄ nanoparticles and MoS₂/Fe₃O₄ hybrid under room temperature. Reproduced with permission.^[154] Copyright 2015, Elsevier.

2.3.2.2 TMD and Derivative Materials for Pollutant Photodegradation

Solar energy conversion has aroused widespread interest in materials such as TiO₂ and ZnO in the UV spectral range as well as WO₃, CdS, Bi₂WO₆, and graphene-based hybrid semiconductors in the visible range.^[155] Considering that UV/visible light-active photocatalysts utilize no more than 50% of the solar light, near-infrared light (NIR)-active photocatalysts that can take advantage of over half of the solar energy are more attractive. However, not so many NIR light-active semiconductors are available because of the narrow band gap semiconductors that can absorb NIR light are considered to be lacking in photocatalytic activity, converting the NIR solar energy into heat instead. Very recently, a new mechanism about photocatalytic water splitting reactions under NIR light was proposed

based on the design of a nano-heterojunction with appropriate band position which enabled the band gap restriction of the photocatalyst to be tuned. For example, C. Pak *et al.*^[156] constructed Au-tipped PbSe/CdSe/CdS heterostructures with the band structure configuration designed to be highly efficient in NIR-induced degradation of MB despite their complex structure as well as the limited NIR spectral range. In fact, not all of the materials with narrow band gaps are NIR-active photocatalysts. For instance, black hydrogenated TiO₂ nanocrystals exhibit only 1% enhancement of photocatalytic performance under NIR light. From the understanding, the construction of novel NIR photocatalysts with not only narrow band gaps but also high efficiency in NIR sorption is fundamental for practical applications and deeper understanding of photocatalytic mechanism. WS₂, as one ideal example, has attracted huge attention.^[157] WS₂ is a graphite-like layered semiconductor with narrow band gaps (1.35 eV) which can confer a wide light sorption region. Note that, 2015 is the first time that Liu and co-workers^[158] have successfully designed and constructed a novel NIR light-active photocatalyst based on WS₂ nanosheets (Figure 2.18a), having valuable full solar spectrum sorption. The as-obtained WS₂ nanosheets showed excellent photodegradation performances towards both MO and RhB under irradiation of UV, visible, and NIR light sources. Figure 2.18b shows the full-spectra photocatalytic activity of WS₂ nanosheets. It is noted that when irradiated under UV light for 100 min, MO could be fully decomposed while the degradation rates were 90% and 80% under 300-min visible light and NIR light irradiations, respectively. The aforementioned results indicate that WS₂ nanosheets possess wonderful NIR light-active photocatalytic ability in degradation of MO. Figure 2.18c provides another evidence for the sorption-degradation-release processes in photocatalytic reaction with the FTIR spectra of the MO powder. The peaks at 1605 and 1120 cm⁻¹ indicate the existence of MO after the sorption process without light irradiation. However, all the peaks attributed to MO disappeared following irradiation.^[159] As shown in Figure 2.18d, 60% of the RhB was degraded after five hours of NIR light irradiation, further suggesting the good NIR-active photocatalytic capacity of WS₂ nanosheets. In extrapolation, WS₂ nanosheets can be a promising alternative for other commercial photocatalysts towards degradation of organics.^[158]

Figure 2.18 (a) TEM image of WS₂ nanosheets. Inset of (a): XRD pattern of as-obtained WS₂ and the corresponding standard PDF card. (b) Catalytic photodegradation of MO solution under irradiation of different light sources (UV, visible, and NIR light) with as-obtained WS₂ nanosheets. (c) FTIR spectra of the MO, WS₂ nanosheets after absorbing MO and after photocatalytic degradation. (d) Typical UV-vis sorption spectra of RhB under NIR light irradiation in the presence of WS₂ nanosheets. Reproduced with permission.^[158] Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA.

2.3.3 TMD/Carbon Hybrid Materials for Water Splitting

2.3.3.1 TMD/Carbon Hybrid Electrocatalysts for Water Splitting

At present, hydrogen (H₂) is one of the clean and renewable energy sources that has aroused global interest due to the limitations of traditional fossil fuels. In general, H₂ can be split from water using Pt as working electrode.^[160] Succinctly, the most effective HER electrocatalyst, Pt-based, are also highly expensive. So, developing abundantly available and active HER electrocatalysts at lower costs is greatly desirable. Electrocatalytic HERs based on TMDs or TMD-based hybrids are quite promising due to the high efficiency of these catalysts.^[161-163] Typically, MoS₂, exposing large numbers of active sulfur edges, is one of the most studied TMD-based catalysts for HER. Currently, a wide range of MoS₂-based composites have been prepared, including MoS₂/Au,^[164] MoS₂/AC,^[165] MoS₂/carbon paper,^[166] MoS₂/graphite^[167],

with overpotentials and Tafel slopes ranges from 0.1 to 0.4 V and 55 to 120 mV/decade, respectively. Over the last decade, Dai and co-workers have designed and constructed a series of nanostructures based on TMD materials. In 2011, for the first time, they managed to prepare MoS₂/rGO nanocomposites (Figure 2.19a-d) and found that these composites possessed impressive HER electrocatalytic activity (Figure 2.19e-g) with not only low overpotential (~ 0.1 V) but also small Tafel slope (41 mV/decade).^[168] The obtained MoS₂/rGO showed extremely better catalytic performance than MoS₂ nanoflowers (MoS₂NFs) and rGO.

Figure 2.19 Schematic illustration of the preparation of MoS₂/rGO hybrid nanosheets (a) and free MoS₂NFs (c). Typical SEM and TEM images of the MoS₂/rGO hybrid nanosheets (b) and free MoS₂NFs (d). Polarization curves (e) and corresponding Tafel plots (f) of several catalysts including as-obtained MoS₂/rGO hybrid nanosheets. (g) Polarization curves of as-obtained MoS₂/rGO hybrid nanosheets before and after 1000 cycles. Reproduced with permission.^[168] Copyright 2011, American Chemical Society.

Moreover, Manish's group^[169] reported the synthesis of WS₂/rGO hybrid nanosheets via a scalable and facile hydrothermal method (Figure 2.20a) and further investigated their implementation as efficient catalysts for HER. Almost at the same time, Zhang and co-workers reported a one-pot solvothermal method for coating MoS₂NFs on rGO paper. The as-obtained MoS₂NF/rGO paper was applied as a freestanding and flexible working electrode

for HER, where the Tafel slope was found to be ~ 95 mV/decade with overpotential as low as -0.19 V (Figure 2.20b-d).^[170]

Figure 2.20 (a) Schematic illustration of the preparation of WS₂/rGO hybrid sheets with the corresponding typical SEM image. Reproduced with permission.^[169] Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA. Side view (b) and top view (c) of a MoS₂/rGO hybrid sheet. (d) XPS spectra of MoS₂ NFs and bulk MoS₂. (e) Polarization curves of several catalysts including as-obtained free-standing MoS₂/rGO hybrid sheet. Reproduced with permission.^[170] Copyright 2014, Royal Society of Chemistry.

2.3.3.2 TMD/Carbon Hybrid Photocatalysts for Water Splitting

Apart from outstanding electrocatalytic efficiency, TMD-based materials also have exciting photocatalytic properties for HERs which is the focus in the last few decades.^[171] For example, MoS₂ with truncated triangular single-layer morphology possesses a large quantity of exposed Mo edges^[164, 172] and shows impressive performances for photocatalytic H₂ production. Furthermore, hydrogen evolution efficiency can be greatly enhanced by combining nanosized MoS₂ with several carbon sources, such as graphene^[168] and CNTs^[171], because the good conductivity of carbon materials can facilitate an efficient electron transfer. Moreover, incorporating of MoS₂ with N-doped graphene which possesses higher electron donating ability can lead to a better catalytic activity. For instance, MoS₂ combined with high concentration nitrogen (ca. 15 wt%) doped rGO shows impressive HER activity, which results from the generation of a *p-n* junction between *n*-type N-doped rGO and *p*-type MoS₂ (Figure 2.21).^[173] Herein, N-doped rGO are able to not only extend the lifetime of the singly excited EY but also collect and transfer the photogenerated electrons to MoS₂ while N-doped graphene can be strongly coupled with MoS₂ and to transport electrons to MoS₂ more effectively.^[173] With that taken into consideration, during the photocatalytic processes, the electrons were transferred from photogenerated species EY⁻ (EY represents Eosin) to MoS₂ instead of generated directly on MoS₂. The HER performances followed the trend of NEG-MoS₂>EG-MoS₂>MoS₂.^[174]

Wu and co-workers^[175] reported that 5-20nm sized *p*-type MoS₂ nanoparticles could be deposited on the *n*-type N-doped rGO (*n*-rGO) nanosheets, forming hierarchical *p-n* junctions. The *p*-MoS₂/*n*-rGO hybrid showed outstanding catalytic activity towards HER within a large wavelength range (from NIR to UV light). The measurements of photoelectrochemical cell (PEC) indicated that the charge generation was enhanced significantly due to the synergetic effects between the *p*-MoS₂/*n*-rGO junction, which in the meanwhile suppressed the recombination of charge. These two points are responsible for great enhancement of photocatalytic HER.^[175]

Figure 2.21 (a) Schematic illustration of the photocatalytic processes of as-obtained *p*-MoS₂/*n*-rGO heterostructures under light irradiation. (b) Mott-Schottky plots of *p*-MoS₂/*n*-rGO nanosheets under different conditions (with/without light irradiation). (c) Polarization curves of several catalysts including as-obtained *p*-MoS₂/*n*-rGO nanosheets. (d) Photocatalytic hydrogen evolution performances of *p*-MoS₂/*n*-rGO, MoS₂/rGO and pure MoS₂. Reproduced with permission.^[175] Copyright 2013, American Chemical Society.

Recently, Ye and co-workers^[176] reported the preparation of a hybrid nanomaterial consisting of nanocrystalline CdS grown on MoS₂/graphene and its application as a noble-metal-free along with visible light-active catalyst for solar hydrogen generation. The optimized MoS₂/G-CdS nanohybrid (molar ratio of graphene to MoS₂ is 2 to 1 and total wt% of co-catalyst (MoS₂/graphene) is 2.0%) showed the highest photocatalytic HER performance. The photocatalytic HER activity of the as-obtained MoS₂/G-CdS hybrids were investigated and compared in lactic acid solution (H₂ evolution rate: 1.8 mmol/h) and Na₂SO₃-Na₂S solution (H₂ evolution rate: 1.2 mmol/h). Notably, the performance of the noble-metal-free MoS₂/G-CdS nanohybrid in lactic acid solution was even better than that of Pt/CdS. The relative possible mechanism has been systematically studied both from experimental and theoretical sides. As claimed by the authors, the as-obtained MoS₂/G-CdS hybrid would be one of the most promising photocatalysts with low cost and high efficiency for photocatalytic HERs (

Figure 2.22).^[176]

Figure 2.22 (a) HRTEM image of $MoS_2/G-CdS$ hybrid nanosheets. (b) Schematic illustration of photocatalytic reactions under visible light. Photocatalytic hydrogen evolution rate (c), time-dependent hydrogen evolution amount (d) and cycling behaviour (e) of several photocatalysts including as-obtained $MoS_2/G-CdS$ hybrid nanosheets. (f) Schematic illustration of coordination conditions of S-atom in MoS_2 (left) and (e) the co-catalytic

hydrogen evolution mechanism of as-obtained material in acid solution. Reproduced with permission.^[176] Copyright 2014, American Chemical Society.

Chapter 3 Experimental Details

3.1 Chemicals and Materials

Potassium tetrachloroplatinate(II) (K_2PtCl_4 , 99.99%), sodium citrate tribasic dehydrate (99.0%), dimethylformamide (DMF, 99.8%, anhydrous), Ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$, 99.97%), hydriodic acid (HI, $\geq 57\%$), hydrochloric acid (HCl, 97%), hydrogen peroxide (H_2O_2 , 30%), , potassium permanganate ($KMnO_4$, $\geq 99\%$), sulfuric acid (H_2SO_4 , 98%), sodium nitrate ($NaNO_3$, $\geq 99\%$), tri-octylphosphine (TOP, technical grade, 90%), and Pt on charcoal (10%) was bought from Sigma-Aldrich (Steinem, Germany). Ethanol (C_2H_5O , $\geq 99.9\%$) was bought from Merck (Darmstadt, Germany). Natural graphite was bought from Graftech International (Rochester, MI, USA). Bulk MoS_2 was bought from Rose Mill (West Hartford, USA). Lithium foil and copper foil used in the lithium ion battery were bought from ACME Research Support Pte Ltd. (Bukit Batok Street, Singapore). Electrolyte for lithium ion battery was bought from Charslton Technologies Pte Ltd. (International Business Park, Singapore). All the chemicals were directly used as received without any purification unless otherwise noted. Deionized (DI) water (18.2 M Ω) used in all experiments was produced by Milli-Q System (Millipore, Billerica, MA).

3.2 Preparation of Kapok-Derived Carbon Aerogel (KCA)-Based Materials

3.2.1 Preparation of KCA

The raw kapok was separated into appropriate size and then rinsed by DI water for several times, and then dried in vacuum drying box at 60 °C. The as-dried kapok balls were heated to different temperature (400-800 °C) with Ar as inner gas and then kept at corresponding temperature for 10 min to 2 h, in order to complete pyrolyzation and finally got the carbon aerogels.

3.2.2 Preparation of KCA/ MoS_2

The MoS_2 loaded on KCA, referred to as KCA/ MoS_2 , was prepared using a modified solvothermal method. In a typical experiment, 26 mg of $(NH_4)_2MoS_4$ was dissolved in 10 ml

of DMF and stirred for 20 min at 60 °C. 10 ml of DMF was then added to the solution, which was then transferred to a 50 ml Teflon-lined autoclave. The KCA was placed in the autoclave and the autoclave was then placed in an oven at 200 °C for 24 hrs. The resultant product was rinsed for five times with methanol and dried at 50 °C in vacuum oven for 12 hrs.

3.2.3 Sorption Capacity Measurements for Oils and Organics

The KCA was put into different organic solvents and oils for a specific amount of time to allow the aerogel fully absorbed. The sorption time is species dependent. The sorption capacity was calculated by

$$q = (m_f - m_i) / m_i.$$

q (g g^{-1}) is the sorption capacity expressed in mass of absorbates absorbed per unit mass of KCA. The mass of KCA before and after sorption are m_i (g) and m_f (g), respectively.

3.3 Preparations of Graphene/MoS₂ Aerogels

3.3.1 Preparation of GO

GO was produced according to the literature method so-called Hummers method.^[108] In typically, graphite powders (4 g), sodium nitrate (2 g) and sulfuric acid (92 mL, 98 wt%) were mixed and added to a flask (volume: 500 ml). followed by adding the flask into an ice bath. To prevent the temperature over 20 °C, the flask was then transferred into an ice bath, and potassium permanganate (12 g) was added slowly to the solution. After then, the flask temperature was increased to about 35 °C and kept for 12-24 hrs. Followed by adding deionized water (184 mL) into the mixture. The suspension was heated to about 98 °C and kept for 15- 30 min to increase the oxidation degree of the GO product. After mixing with distilled water (560 mL), the brown suspension was further treated with 12 mL hydrogen peroxide (30%). Finally, the mixture was separated by filtration or centrifugation and washed several times by diluted hydrochloric acid (5 v%) and deionized water and dried at 40 °C in the vacuum oven for 48 hrs.

3.3.2 Preparation of Graphene/MoS₂ Aerogels

Specifically, for the preparation of GMA-1, 10 ml GO solution (2.5 mg ml⁻¹) was mixed with 15 mg thioacetamide (C₂H₅NS) and 30 mg sodium molybdate dehydrate (Na₂MoO₄). After each addition, the whole suspension was sonicated for 10 min and placed into polytetrafluoroethylene (PTFE)-lined autoclave. Then the autoclave was heated to 200 °C and kept at that temperature for 24 hrs. After naturally cooling down to room temperature, the black mixture was transferred into a centrifuge tube to soak in DI water for at least 24 hrs. The whole system was then frozen by liquid nitrogen and freeze-dried for 48 hrs to form porous aerogel structure. For GMA-2 to 4, all experimental steps were the same as those of GMA-1, except for the amount of C₂H₅NS and Na₂MoO₄. For GMA-2, 60 mg C₂H₅NS and 30 mg Na₂MoO₄ were used. For GMA-3, 90 mg C₂H₅NS and 45 mg Na₂MoO₄ were used. For GMA-4, 120 mg C₂H₅NS and 60 mg Na₂MoO₄ were used.

3.3.3 Sorption Capacity Measurements for Oils and Organics

The as-obtained GMAs were immersed into the oils and organic solvents until the aerogels were fulfilled with organics and then picked out for weight measurements. It is noted that these measurements should be done in a short time in order to avoid the absorbed organic solvents from evaporating. The weight of GMAs before and after sorption tests was recorded for counting the gain of weight.

3.3.4 Sorption Capacity Measurements for Organic Dyes and Heavy Metal Ions

Specific amount of different dye powders, such as methyl orange (MO), methylene blue (MB), rhodamine B (RhB), rose bengal (RB) and acridine orange (AO) and salt of heavy metals (PbCl₂ and HgCl₂) were dissolved in DI water to a specific concentration. A piece of GMA was submerged into the solution for 24 hours in order for fully sorption. The sorption capacity was calculated by

$$Q = (C_i - C_f)V/W.$$

Q (mg g⁻¹) stands for the sorption capacity, defined as the mass of contaminants absorbed per unit mass of sorbent. C_i and C_f (mg L⁻¹) are the contaminant concentrations before and after sorption, respectively. V (L) stands for the total volume of the solution and W (g) is the sorbent mass. The dye concentrations in the solution were measured with a UV-vis

spectrophotometer (Shimadzu UV-2501PC), and that of heavy metal ion solutions were measured with ICP-OES. For desorption of dyes, the fully absorbed GMAs were immersed into pure ethanol, after which the ethanol gradually stained by the dyes. The GMAs were washed with ethanol several times until the ethanol remained colourless.

3.4 Preparation of CNT/TMD Fibers

3.4.1 Exfoliation of Transition-Metal Dichalcogenides (TMDs)

The single- or few-layered TMD (*e.g.* MoS₂, MoSe₂ and MoS_xSe_{2-x}) nanosheets were prepared using the lithium intercalation method developed by our group.^[177, 178] Briefly, lithium intercalation process was performed in an electrochemical test cell with Li foil as anode. The electrolyte was prepared by dissolving 1 M LiPF₆ in a 1:1 (volume) mixture of ethyl carbonate and dimethyl carbonate. A mixed slurry of MoS₂ powder, acetylene black and PVDF binder in mass ratio of 8:1:1 was dispersed in N-methylpyrrolidone and used as cathode material, where The resultant mixture was uniformly pasted on a copper foil and dried in vacuum oven at room temperature for 12 hours. The lithium intercalation process was carried out in a Neware battery test system, where the intercalation was then carried out at a discharge current density of 0.05 mA. The resultant Li-intercalated MoS₂) was washed with acetone to eliminate any residual LiPF₆ and then ultra-sonicated for exfoliation.

3.4.2 Growth of Pt Nanoparticles on TMD Nanosheets

The growth of Pt nanoparticles on TMD nanosheets was carried out by a photochemical reduction method.^[179, 180] Typically, 4 mL MoS₂ solution (0.8 mg) was added into 16 mL aqueous solution in a 20 ml glass vial, which contains pre-dissolved 0.3 mM trisodium citrate and 0.2 mM potassium tetrachloroplatinate. After that, the mixed solution was irradiated under a 150 W halogen lamp (Fiber-Lite MI-150) with 80% of its maximum intensity for 2 hrs. The ice bath was used to cool the glass vial and prevent the light-induced overheating. After the photochemical reduction reaction was over, the solution was centrifuged at 6500 rpm for 15 min and washed with deionized water for 3 times. Finally, the hybrid nanomaterial was re-dispersed in DMF at a concentration of 2 mg mL⁻¹ and was thoroughly ultra-sonicated before use.

3.4.3 Fabrication of Fibers and Fiber-Based Electrodes

The multi-walled carbon nanotube (MWCNT) array was grown by vertically aligning them via chemical vapor deposition (CVD) in a quartz tube furnace following our previously work.^[181, 182] The MWCNT sheet with an areal density of around $2.12 \mu\text{g cm}^{-2}$ (single layer) was pulled out from the array.^[183] Four layers of the sheets with length of ~ 8.5 cm and width of ~ 1.5 mm) were then stacked on each other and laid on a polytetrafluoroethylene (PTFE) substrate. Active nanomaterials (MoS_2 etc.) dispersed in DMF (2 mg mL^{-1}) were then added onto the stacked MWCNT sheet by drop by drop. The loading amount (weight percentage) of active material in each fiber was calculated as follows, loading amount = $W_g/(W_g+W_h)$, where W_g and W_h represent weight of guest material (TMDs) and weight of host material (MWCNT), respectively. The resultant hybrid sheet was then dried in fume hood, and then carefully peeled off from the PTFE substrate. To obtain the hybrid fiber, one end of the hybrid sheet was pasted on the scotch tape, while the other side was twisted by an electric motor, which rotates at a speed of 200 rpm for 2 min. The fiber electrodes were fabricated by mounting the as-prepared hybrid fiber (~ 1 cm) onto a glass substrate.^[184] A Cu wire was connected to one end of the fiber using Ag paste which was subsequently insulated by silicon rubber.

3.4.4 Electrocatalytic Measurements for HER

The electrochemical measurements were obtained by by an Autolab electrochemical workstation (PGSTAT302N, Metrohm Autolab, Switzerland). Linear sweep voltammetry (LSV) was carried out in 0.5 M H_2SO_4 or 1 M KOH (deaerated by N_2) at a scan rate of 2 mVs^{-1} . Pt wire was used as the counter electrode, Ag/AgCl electrode (3 M KCl) was used as the reference electrode, and the as-obtained fiber electrode was used as the working electrode. All the measured potentials were calculated towards stadard values versus the reversible hydrogen electrode (RHE). Cyclic voltammetry (CV) was conducted by using the same three-electrode setup with a scan rate of 100 mVs^{-1} at room temperature.

3.5 Characterizations and Analysis

3.5.1 Scanning Electron Microscopy (SEM)

SEM was carried out using a JSM-7600F field-emission SEM (FESEM) operated at 5 kV. The corresponding energy dispersive X-ray spectroscopy (EDS) data was collected at 20 kV.

3.5.2 Transmission Electron Microscopy (TEM)

High-resolution TEM (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were collected using a JEM 2100F transmission electron microscope operated at an accelerating voltage of 200 kV. The TEM sample was prepared by dropping about 5 μL sample solution on copper grid (200 mesh) with full carbon/lacey carbon-coating and then drying at ambient condition.

3.5.3 X-ray Photoelectron Spectroscopy (XPS)

The XPS data was collected on either a Theta Probe electron spectrometer (ESCA-Lab-200i-XL, Thermo Scientific) or an AXIS ultra-spectrometer (Kratos). The XPS sample was prepared by drying the droplets of sample solutions on Si/SiO_x substrates at ambient conditions.

3.5.4 X-ray Diffraction (XRD)

The XRD pattern was collected on a Shimadzu thin film XRD-6000 X-ray diffractometer with Cu K α X-ray source. The XRD sample was prepared by drying concentrated sample drops on a glass substrate at ambient conditions.

3.5.5 Atomic Force Microscopy (AFM)

The AFM image was acquired with a scanning line of 512 and a scanning frequency of 1 Hz on a Dimension 3100 AFM (Veeco, USA), NSCRIPTOR system using a Si tip (spring constant: 42 N m⁻¹; resonance frequency: 320 kHz).

3.5.6 Raman

Raman spectra were taken using a WITec CRM200 confocal Raman microscopy at room temperature with an excitation line of 488 nm (WITec Instruments Corp, Germany). The spectrometer was pre-calibrated using Raman band of Si at 520 cm⁻¹ as the reference.

3.5.7 Others

Fourier transform infrared (FTIR) spectra were carried out by a Perkin Elmer Frontier FTIR spectrophotometer. Thermogravimetric analysis (TGA) was recorded under N₂ gas (temperature range: 50-800 °C with a ramping rate of 10 °C min⁻¹). Ion concentrations were

investigated by an inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer). UV-vis spectra were carried out by a Shimadzu UV-2550 spectrometer.

Chapter 4 Kapok-Derived Carbon Aerogel and its Derivate for Water Remediation

4.1 Introduction

There are many natural based products that can be used as biodegradable sorbents for water treatment. Yet, since most of them are not super- hydrophobic, they always absorb water instead of oil. Several ways of modification have been reported to render cellulosic sorbents hydrophobic. Among these, one of the most practical ways is changing the surface nature of cellulosic materials by annealing or carbonization. For example, raw cotton has been exploited as carbon source for fabrication of carbon aerogel by our group recently.^[185] The as-prepared cotton-derived carbon aerogel (CCA) showed excellent properties for oil and organic solvent sorption. To the best of our knowledge, there are several natural cellulosic products, such as kapok, milkweed, and flax which are similar to cotton and also can be the source for carbon aerogel. Notably, kapok has hollow structures. If this structure does not collapse after heat treatment, the sorption efficiency may be better than that of cotton. In this work, the modification of kapok was investigated in order to find out the optimum conditions to prepared kapok-derived carbon aerogel (KCA) and then to apply the as-obtained materials as sorbents for water treatment.

4.2 Synthesis and Characterization of KCA

Kapok fiber, similar to cotton fiber, is one of the lightest fibrous materials obtained from nature products. Kapok trees are wildy grown in the south Asia (Figure 4.1).

Figure 4.1 (a) Raw kapok fibers. (b) Kapok tree, bud, and fruit.

Several pieces of raw kapok, after purification, were pyrolyzed in argon gas at different temperatures (400-800 °C) with varied time duration (10 minutes to 2 hours), resulted in the generation of black and lightweight KCA product. Figure 4.2a,c show the typical scanning electron microscopy (SEM) images of raw kapok. As shown in the low-magnification SEM image, raw kapok has an internal microstructure consisted of porous, interconnected, and well-organized 3D network, formed by long fibers. Most of the fibers have a length up to several centimetres or longer (Figure 4.2a). The “fibers” with a diameter around 33 μm in kapok are actually hollow, as indicated by the high magnification SEM images (Figure 4.2c). As seen from the cross section of a kapok fiber, the external and internal radius of fiber is about 16.5 and 14.5 μm , respectively. This result indicates that the wall thickness of kapok fiber is about 2 μm and more than 70% volume of the kapok fiber is lumen.^[186] After pyrolysis, as shown in insets of Figure 4.2a,b, respectively, the diameter of raw kapok dropped almost 50% (from 3.2 cm to 1.6 cm). As a result, the volume of KCA is only ~25% of that of the raw kapok. After the annealing treatment, the hollow structure of fibers in KCA (Figure 4.2d) is similar to the kapok. However, the diameter of fibers in KCA decreased to 15-20 μm (Figure 4.2d).

Figure 4.2 (a) SEM image of raw kapok. Inset of a: photograph of a raw kapok ball. (b) SEM image of KCA. Inset of b: photograph of a KCA ball. (c,d) large magnification SEM images of kapok before and after thermal treatment.

It is noteworthy that the as-obtained KCA has much lower density (10 mg cm^{-3}) compared to that of raw kapok (100 mg cm^{-3}). However, the mechanical property of KCA is much better than that of kapok. As shown in Figure 4.3, a piece of kapok with a diameter of 3.0 cm and height of 3.0 cm was significantly compressed under the loading of a 15.3 g glass bottle (Figure 4.3b), while a KCA block with a diameter of 1.4 cm and height of 1.5 cm can give better support for the same bottle (Figure 4.3d).

Figure 4.3 Photographs of raw kapok (a,b) and KCA (c,d) before and after loading a bottle.

In addition, the wettability can be changed dramatically from hydrophilic, for raw kapok, to highly hydrophobic, for KCA. When a water droplet landed on the surface of KCA, it attached on the aerogel surface for more than one hour (Figure 4.4a). Further, we can investigate the combined effect of pressure and hydrophobicity by immersing the KCA into water using a tweezer. On the boundary between water and KCA, a uniform mirror-reflection can be discerned (Figure 4.4b), confirming the high hydrophobicity of the as-obtained KCA.^[33] This reflection results from trapped air on the KCA surface which hamper the penetration of water into the hollow structure.

Figure 4.4 (a) KCA with a water droplet on the top. (b) A mirror-reflection occurred after inserting a piece of KCA into DI water.

As shown in Figure 4.5, fourier transform infrared spectroscopy (FTIR) further proved the change of wettability. From the FTIR spectrum of kapok, there are several oxygen-related hydrophilic functional groups, for example, -OH , C-O and C=O , (Figure 4.5a), proving that kapok is hydrophilic. The characteristic peaks appear at 1034.47 cm^{-1} , 1238.98 cm^{-1} , and 1732.96 cm^{-1} are attributable to C-O , epoxy C-O , carboxy C-O , and C=O groups, respectively.^[187] In contrast, after annealing at high temperature, these peaks corresponding to these hydrophilic functional groups remarkably decrease. It is noted that after only 10-minute annealing at $400\text{ }^{\circ}\text{C}$, the peaks nearly all disappear. While, after annealing at $800\text{ }^{\circ}\text{C}$ for 2 hours, no obvious peak is observed, indicating that hydrophobic KCA is resulted.

Figure 4.5 FTIR spectra of (a) raw kapok and (b-e) KCAs. Inset: a typical cellobiose unit of cellulose.

The element analysis results are listed in Figure 4.6 and Table 1. Note that the weight percentage of C increases significantly from 45.93% for raw kapok to 85.98% for KCA annealed under 800 °C for 2 hours. While, weight percentages of O and H both decreased under all annealing conditions. This is because of the decomposition of the corresponding functional groups.

Figure 4.6 Element analysis of kapok and KCAs.

Figure 4.7a shows the typical TGA analysis result of kapok. The first main mass loss is about 5% at around 100 °C, which is due to the removal of the absorbed water. The second main mass loss is about 75% at 300-400 °C, which is due to removal of –OH group *etc.*, consistent with FTIR results. After the temperature further increased from 400 to 800 °C, the mass loss is negligible. The typical SEM images of kapok before (Figure 4.7b) and after annealing (Figure 4.7c,d) show that no obvious structural changes occurred during the annealing processes.

Table 4.1 Elements analysis of kapok and KCAs.

Element wt%	Raw Kapok	KCA 400 °C 10 min	KCA 400°C 2 h	KCA 600 °C 10 min	KCA 800 °C 10 min	KCA 800 °C 2 h
C	45.93	73.75	75.36	83.53	85.4	85.98
H	6.36	3.87	3.9	2.44	1.15	1.16
O	42.71	14.45	11.75	5.26	4.21	3.52

Figure 4.7 (a) TGA analysis of kapok. SEM images of kapok (b) and KCAs prepared under different conditions: 400 °C for 10 minutes (c), 800 °C for 10 minutes (d).

4.3 Water Remediation Performances of KCA

As such, the KCA is an ideal candidate for absorbing contaminants such as oils and organic solvent, owing to its 3D porous structure and surface hydrophobicity. The sorption is demonstrated in a series of photos in Figure 4.8. Once the KCA was in contact with cyclohexane (dyed with Sudan red 5B), it quickly absorbed the cyclohexane within 20 seconds; time reference here depends on the volume of the cyclohexane and KCA. After absorbing the cyclohexane, the KCA still floats near the water surface due to its low density and hydrophobic nature. The preferred location of KCA offers a facile and useful approach for removing spilled oil – usually located on top of water layer - and other low-density leaked chemicals.

Figure 4.8 The process of the KCA absorbing cyclohexane (floating on water surface and dyed with Sudan red 5B). Pictures were taken at an interval of 5 s. The cyclohexane was entirely absorbed within 20 s.

Moreover, the as-obtained KCA also can selectively absorb heavy organics under water whilst still maintaining oil selectivity and showing no sign of water sorption. As shown in Figure 4.9, chloroform at the bottom of water, dyed with Sudan red 5B, was entirely absorbed within 3 seconds.

Figure 4.9 The process of the thermally treated kapok aerogel absorbing chloroform (at the bottom of water). The chloroform was totally removed within 3 s.

Quantitatively, the sorption capability can be compared through a variable called sorption capacity, hereby defined as weight gain (wt%). A series of organic liquids that are common contaminants in both industry and daily life (fats, vegetable oil, and ketones) were tested in these series of experiments. The sorption capacities of some common organics such as alcohol, toluene, and acetone were also evaluated. The KCA shows a quite high sorption capacity towards all of the aforementioned organics.

KCA can absorb the organic solvents at up to 160 times of its weight (Figure 4.10). In particular, KCA can absorb vegetable oil, hexane, toluene, DMF, and acetone at rate of 160x, 80x, 115x, 108x, and 96x respectively. In general, the capacity of absorbers depends on their surface area and porosity. There are two main sorption mechanisms for KCA during the liquid sorption: surface sorption where the organic liquids are coating on the fiber and uptake by the inter-fiber capillaries.^[27] It is believed that the latter makes greater contribution to a high sorption capacity.

Figure 4.10 Sorption capacity of KCA with error bar.

The sorption capacity of the KCA is much higher than that of other sorbents, such as polymers (from 5 to 25 times),^[10] nanowire-based membrane (from 4 to 20 times),^[35] wool-based nonwoven (from 9 to 15 times),^[34] exfoliated magnetic graphite (from 30 to 50 times),^[36] rGO sponge (from 20 to 86 times),^[4] and boron doped CNT sponge (from 25 to 125 times).^[37] To the best of our knowledge, the KCA still shows a relatively lower capacity compared to UFA frameworks,^[38] CNF aerogel,^[12] and graphene foam with nitrogen doping.^[23] However, the real application of graphene is difficult to be realised, because the fabrication process is complicated, costly, and produces considerable amount of waste. Even compared with the relatively low-cost CNF aerogel, the cost of our KCA is still much lower. It is noteworthy that the starting material of KCA, raw kapok, is economic and environmental-friendly since raw kapok is one of the main agricultural products in our life. Moreover, KCA shows a sorption capacity even better than previously reported CCA from our group (Figure 4.11). Therefore, our KCA is economical and has a bright prospect in the sorption of pollutants.

Figure 4.11 Sorption ability comparisons between CCA and KCA.

Table 4.2 Comparison of various materials for removal of organics and oils.

	Sorbent materials	Sorbed substances	Sorption capacity (g g ⁻¹)	Cost	Ref
1	Wool-based nonwoven	diesel, crude oil, SN 150	9-15	low	[34]
2	Polymers	oils and organic solvents	5-25	medium	[10]
3	Nanowire membrane	oils and organic solvents	4-20	low	[35]
4	Magnetic exfoliated graphite	oils	30-50	high	[36]
5	rGO sponge	oils and organic solvents	20-86	high	[4]
6	Boron doped CNT sponge	organic solvents	25-125	high	[37]
7	Carbon nanotube sponges	oils and organic solvents	80-180	high	[6]
8	Nitrogen doped graphene foam	oils and organic solvents	200-600	high	[23]
9	UFAs	oils and organic solvents	215-913	high	[38]
10	Our KCA	oils and organic solvents	80-160	quite low	This work

In practical applications, the recoverability of pollutants is also one of the most key factors for the clean-up of oil/chemicals since the pollutants are either toxic substances (*e.g.* toluene) to be disposed properly or precious resources (*e.g.* crude oil) to recover. Figure 4.12 illustrates the regeneration of the KCA and the recycle of pollutant, *e.g.* ethanol (boiling point 78.4 °C). Ethanol absorbed by KCA can be removed by distillation whilst maintaining the size, shape, and inherent 3D porous structure of the aerogel even after distillation. After absorbing ethanol, the KCA was heated to 80 °C to vaporize ethanol. This process was repeated 6 times followed by the regeneration of KCA to check the subsequent cycle's feasibility and completeness of recycling organics from KCA. As shown in Figure 4.12, after each cycle the residual ethanol in the KCA is less than 5% weight of the absorbed ethanol, indicating the highly stable recycling performance. No obvious change in the sorption ability of KCA was observed after 6 cycles of testing. No mechanical damage to the KCA was observed after the whole recyclability test. In addition, for those nonflammable and precious pollutants, squeezing is a good choice. KCA is not fragile, thus mechanical recovery is a viable method. Here, it is important to note that the strain induced by squeezing should not be higher than 70% in order to retain the sorption stability of KCA; otherwise, the long fibers might be broken into short pieces and can be detrimental to its mechanical properties. To achieve a more complete recycle of the pollutants, the two methods mentioned above can be also combined to use. Compared with other sorbents, KCA possesses some outstanding

features, such as large-scale synthesis, low cost, facile preparation, biodegradability, good sorption capacity, and good recyclability.

Figure 4.12 Recyclability test of KCA using ethanol as the absorbate.

Moreover, it has been demonstrated that MoS_2 can be uniformly coated on the surface of KCA, as shown in Figure 4.13. The typical SEM images (Figure 4.13b-d) show that the coating of MoS_2 on KCA is quite uniform. The nanosheets will increase the surface area of KCA meanwhile introduce more functionalities.

The EDS analysis of as-obtained hybrid aerogel is shown in Figure 4.14, the atomic ratio of Mo and S is 2.04, indicating the formation of MoS_2 on the surface of KCA.

Figure 4.13 (a-d) SEM images of KCA/MoS₂ hybrid fibers.

Figure 4.14 EDS analysis of KCA/MoS₂ hybrid fibers.

As a proof-of-concept application, the as-obtained KCA/MoS₂ and CCA/MoS₂ were used as catalysts for photocatalytic degradation of MB (Figure 4.15). The preliminary results show that both KCA/MoS₂ and CCA/MoS₂ show good sorption and photocatalytic degradation properties. We will further investigate this property in the future.

Figure 4.15 Comparison of photocatalytic degradation and sorption ability between CCA/MoS₂ and KCA/MoS₂: (a,c) Sorption without light for 25 hours. (b,d) Sorption without light for 24 hours, after then with 1 hour visible light irradiation.

4.4 Conclusions

In conclusion, KCA with superhydrophobicity, high sorption capacity, and good recyclability has been fabricated using low-cost and from eco-friendly raw material via a facile method. The KCA can absorb various chemicals with a weight of 80-160 times of its own weight. Both, distillation and squeezing, are suitable for recycling the absorbed pollutants from KCA because of its good mechanical properties and thermal stability. Importantly, the easy fabrication method and abundant natural source make the KCA very cost-effective and beneficial for industrial-scaled real production. Therefore, our KCA is indeed a highly promising absorber for low-cost and efficient removal of pollutants from water. Last but not the least, KCA can also be used as 3D substrate for loading photocatalysts (such as MoS₂), the as-obtained KCA/MoS₂ show good sorption and photocatalytic degradation properties.

Chapter 5 Graphene/MoS₂ Aerogel for Water Remediation

5.1 Introduction

In the last decades, the superior sorption abilities of carbon-based 3D porous networks have received huge attentions in the field of water remediation. Most of the reported architectures are only used to absorb one category of contaminants. However, in real application, waste water always contains many different types of pollutants, such as dyes, heavy metal ions, oils, and other organics. Since current porous architectures may not be sufficient to treat industrial waste water in a simple manner, it is of great importance to develop a novel technology that able to absorb different types of water pollutants.

Herein, several graphene/MoS₂ aerogels (GMAs) with porous architecture and bulky shape have been prepared using graphene oxide (GO) as carbon source via a facile hydrothermal method. The as-obtained GMAs have shown good sorption performances for several contaminants (especially heavy metal ions) in waste water. Moreover, after structural modifications, the as-obtained multifunctional carbon/TMD hybrids show good removal performances towards both dyes and organic compounds.

5.2 Synthesis and Characterization of GO Nanosheets

GO nanosheets were prepared by a modified Hummer method.^[108] As shown in Figure 5.1a, GO nanosheets could be well dispersed in DI water, forming brown aqueous suspension. Figure 5.1b reveals the representative AFM height image obtained from a GO nanosheet. As measured by AFM, the typical thickness of the as-obtained GO is about 1.0 nm (Figure 5.1c), in agreement with the reported value of single-layer GO.^[188] Moreover, it is obvious that the size of the as-prepared GO nanosheets is in the order of micrometres.

Figure 5.1 (a) Photograph of a bottle of GO aqueous solution (about 1.0 mg ml⁻¹). Representative AFM height image (b) and corresponding section line analysis (c) of a GO nanosheet.

5.3 Synthesis and Characterization of GMA

Assembly of GO nanosheets into a 3D bulky form is not a new story. However, there are only few reports about the preparation of graphene/TMD-based aerogels. We developed a new system in which GMA could be prepared via a simple one-step hydrothermal method, detail description is as followed: Specifically, for the preparation of GMA-1, 10 ml GO solution (2.5 mg ml⁻¹) was mixed with thioacetamide (C₂H₅NS) and sodium molybdate dehydrate (Na₂MoO₄). After stirring for half an hour, the mixture was transferred into a 25 ml polytetrafluoroethylene (PTFE)-lined inner vessel. The reactor was then sealed and put into a dry oven at 200 °C for 24 hours. The final product is cylinder-like sponge. After freeze-drying step, the as-prepared aerogel exhibited spongy and dark-colored appearance (inset of Figure 5.2a). The morphology of GMA was investigated by scanning electron microscope as illustrated in Figure 5.2. It can be clearly observed that the as-prepared GMA still maintains a highly interconnected porous network after being coated with MoS₂ (Figure 5.2a). Moreover, the nanosheets have lots of wrinkles, as shown in high magnification SEM image (Figure 5.2b).

The as-obtained nanosheets are quite thin, similar to that of pure rGO nanosheets. The high transparency of these nanosheets is comparable with the carbon film in the typical transmission electron microscopy (TEM) image (Figure 5.3a), indicating the ultra-thin nature of the as-obtained hybrid sheets.

Figure 5.2 (a,b) SEM images of GMA under different magnifications; inset of (a) is a digital image of GMA

The typical high-resolution TEM (HRTEM) image of as-obtained rGO/MoS₂ nanosheet is shown in Figure 5.3b. The clear lattice spacing of 0.64 nm corresponds to the (002) planes of MoS₂. The typical high-angle annular dark-field (HAADF) scanning TEM image and the corresponding EDS mapping images of the as-obtained rGO/MoS₂ nanosheet are shown in Figure 5.3c, revealing the uniform distribution of Mo and S on the rGO nanosheets.

Figure 5.3 (a) Low-magnification TEM image, (b) HRTEM image, and (c) corresponding EDS elemental mapping analysis of Mo, S and C in GMA structure.

The electron binding energy of GMA-1 was analysed by X-ray photoelectron spectroscopy (XPS), as seen in Figure 5.4. The XPS survey spectrum (Figure 5.4a) contains several sharp peaks that suggest the presence of elements Mo, S, and C. In Figure 5.4b, it is clear that electron at C 1s level can be observed from the 2 peaks. The main one at around 284.6 eV matches the C-C bonds of rGO nanosheets while the lower peak at 286.0 eV corresponds to C-O bond. In addition, the chemical states of Mo and S in GMA-1 were also investigated, as shown in Figure 5.4c,d. The peaks of Mo 3d_{3/2} and Mo 3d_{5/2} were located at 232.1 and 228.8 eV, respectively, revealing a characteristic of Mo⁴⁺ in MoS₂ (Figure 5.4c). The peaks at 161.7 and 162.8 eV in S 2p spectra separated by a spin-orbit splitting of 1.1 eV were attributed to the S²⁻ of MoS₂ (Figure 5.4b). All the aforementioned results confirm the formation of uniform and ultra-thin MoS₂ coating on the surface of rGO nanosheets.

Figure 5.4 Electronic binding energy of GMA by XPS analysis.

5.4 Water Remediation Performances of GMA

As a proof-of-concept application, the as-obtained GMA-1 was used to absorb several pollutants from waste water (Figure 5.5). The sorption capacities of GMA, compared with those of pure graphene aerogel (PGA), show quite different trends for different categories of contaminants. It is noted that GMA-1 shows superior sorption capacities towards both Hg^{2+} (719 mg g^{-1}) and Pb^{2+} (449 mg g^{-1}), while the sorption capacities of PGA are only 155 and 72 mg g^{-1} for Hg^{2+} and Pb^{2+} , respectively. However, PGA shows better sorption capacities towards chloroform (86 g g^{-1}) and ethanol (53 g g^{-1}) while there is about 25% decrease for GMA-1. Furthermore, for absorbing negatively charged methyl orange (MO), GMA is better than PGA. On the contrary, for positively charged methylene blue (MB), GMA is worse than

PGA. It is believed that after being coated with MoS₂, the surface properties drastically change and, hence, dramatically affect the sorption performances.

Figure 5.5 The comparisons between PGA and GMA for removal of heavy metal ions (a,b), organics (c,d), and organic dyes (e,f).

The recyclability test of GMA was also investigated with distillation method. As shown in Figure 5.6, after each cycle the residual ethanol in the GMA is less than 5% weight of the absorbed ethanol, indicating the highly stable recycling performance. No obvious change in the sorption ability of GMA was observed after 7 cycles of testing.

Figure 5.6 Recyclability test of GMA-1 using ethanol as the absorbate.

5.5 Investigation of Possible Sorption Mechanism

To better understand the sorption performance and to deduce the possible sorption mechanism, a series of GMAs with different loading amount of MoS₂ (referred as GMA-1, GMA-2, GMA-3 and GMA-4, where, the wt% of MoS₂ increases from GMA-1 to GMA-4, see the Experimental Section for details) were prepared. As shown in Figure 5.7, the morphology is distinguishably different. Moreover, the high-magnification SEM images (insets of Figure 5.7) show that the twisting degree of hybrid sheets increases from GMA-1 to GMA-4. This is because the presence of higher ion concentration of precursor induced much stronger electrostatic interaction, resulting in the distortion of the electrostatic repulsion between individual GO sheets.

Furthermore, the zeta potentials of GMAs were measured under the sample pH. It is obvious that the surfaces of the GMAs were charged negatively and the surface potential became much more negative as the amount of MoS₂ precursors increased from GMA-1 to GMA-4 (Figure 5.8).

Figure 5.7 SEM images of GMAs with increasing loading amount of MoS₂: GMA-1 (a) < GMA-2 (b) < GMA-3 (c) < GMA-4 (d). Insets are corresponding high-magnification SEM images.

Notably, as shown in Figure 5.9, the 24-hour sorption capacities for Hg²⁺ are 719, 876, 930, and 970 mg g⁻¹ from GMA-1 to GMA-4, respectively; the corresponding 4 day-sorption capacities for Hg²⁺ are 897, 1015, 1188, and 1245 mg g⁻¹, respectively. These results suggest that the electrostatic interactions together with the high surface area are the dominant sorption mechanisms for organic dyes and heavy metal ions.

The quantitative sorption capacities of GMA-1, GMA-2, GMA-3 and GMA-4 were studied over ethanol and heptane, which are two common organic solvents in the chemical industries. It is found that the sorption capacities of GMA-1 are significantly higher than those of GMA-2, GMA-3 and GMA-4. Thus, it seems coating of MoS₂ does not have positive effect on the sorption of organic solvents. This may be due to that the density of GMA is increased with the loading amount of MoS₂, while the surface area is decreased.

Figure 5.8 Zeta potentials of GMAs.

Figure 5.9 The sorption performance of GMAs for 24-hour and 4-day sorption of Hg²⁺.

5.6 Conclusion

In conclusion, herein we demonstrate that 3D GMA can be simply synthesized by the hydrothermal method followed by a typical freeze-drying process to maintain the porous structures. The as-obtained GMAs show multi-pollutant removal property. More importantly, the GMA can absorb mercury ions up to 1245 mg g⁻¹, which is one of the highest values so

far. Furthermore, GMAs also show good sorption ability towards several other contaminants, such as MO, MB and so on. The sorption mechanism is deduced to be a combination effect of electrostatic interaction and high surface area. All in all, GMA is a promising multifunctional sorbent with high efficiency.

Chapter 6 CNT/MoS₂ Fibers for Water Splitting

6.1 Introduction

Two-dimensional (2D) layer-structured transition-metal dichalcogenides (TMDs) have attracted intensive attentions in the last few years due to their outstanding electronic, optical, and mechanical properties.^[147, 189-191] Tremendous efforts have been devoted to the preparation of functional TMD-based materials as well as their applications in various fields, such as supercapacitors, piezoelectric device, homogeneous phototransistors, bio-probes, field-effect transistors, lithium-ion batteries, gas sensors, photocatalysts, memory devices, and templates for epitaxial growth of hetero-nanostructures.^[121, 192-205] Particularly, TMD-based materials, especially MoS₂ and its derivatives, have been demonstrated to be one of the most efficient and abundant electrocatalysts for sustainable hydrogen production.^[23, 206-208] Based on the theoretical and experimental results, reducing the dimension of TMD structures to the nanoscale is one of the best strategies to largely expose the edge sites for enhancing activity.^[125, 164, 209, 210] In addition, it is also very effective to further improve the hydrogen evolution reaction (HER) performance by epitaxial growth of uniform-sized metal nanoparticles with highly active facets on the surface of TMD nanostructures.^[179, 180] Nevertheless, these 2D layered nanomaterials may easily restack owing to their interlayer van der Waals attractions and high surface energy, leading to the loss of active edge sites, which then greatly limits their further applications.^[211] Another drawback is the poor electrical conductivity of TMDs across their layers which restricts efficient electron transfer as well as the related electrochemical kinetics.^[212, 213] Thereby, integration of ultra-thin TMD nanosheets with electrically conductive carbon materials (graphene and carbon nanotube (CNT)) has been a promising strategy to overcome the former weakness.^[168, 214] Moreover, current substrate to evaluate HER performance, glassy carbon electrode (GCE), has weak interaction with the catalyst which cause the sample to peel off from the substrate and to lose its HER performance. In some cases, binder might be used to enhance the adherence and increase the stability of materials but it normally reduces the electrochemical activity. Furthermore, GCE is rigid. Its applications have been limited by the inability to integrate it into flexible devices. Thus, flexible, binder-free and freestanding host materials with favourable mechanical strength and high conductivity that can enhance the electrocatalytic performance of TMDs are highly desirable.

In recent years, multi-walled CNT (MWCNT) sheets (also referred as MWCNT aerogels), which can be continuously drawn out from vertically aligned arrays of MWCNT, are receiving considerable interest.^[215] The unique features of free-standing MWCNT sheets, such as excellent mechanical properties, high electrical conductivity, as well as good flexibility, enable these materials to be widely used as substrate for functional materials in various applications, such as supercapacitors, lithium-ion batteries, and memory devices.^[216] Moreover, MWCNT sheets can be spun into fibers together with several functional materials.^[217] Thus, HER performance of TMD materials can be beneficial from the incorporation with MWCNT sheets to overcome the poor conductivity of TMD materials along the lamella structure as well as to prevent them from aggregation. However, it is still a big challenge to spin high concentration of conventionally-unspinnable TMD materials into fibers with a low concentration of host materials (*e.g.* MWCNT).

Here, we report a general strategy for the fabrication of binder-free and flexible hybrid fibers from based on MWCNT and TMD-based materials (*e.g.* MoS₂, MoS_xSe_{2-x}, MoSe₂ and Pt-TMD hybrids). Significantly, for the first time, we are able to take the advantage of a small percentage (10 wt%) of MWCNT host in the sheet to obtain flexible, wearable, durable, functional TMD/MWCNT-based single fibers containing high percentage (90 wt%) of active materials. More importantly, MWCNTs not only serve as a host for the formation of binder-free hybrid fiber but also assure charge transfer during the electrochemical reactions due to their high conductivity. Remarkably, the as-prepared Pt-MoS₂/MWCNT fiber, used as electrodes for HER, showed superior electrocatalytic performance in both acidic and basic environments. Both prolonged cycling and continuous operation at constant voltage were carried out to demonstrate the long-term stability of the catalyst. More importantly, the obtained fibers can not only be used as the single electrode for HER but also be woven into textile as flexible electrode, showing a steady hydrogen evolution activity in water splitting.

6.2 Synthesis and Characterization of CNT/MoS₂ fibers

In this work, monolayer TMD nanosheets were prepared by referring the lithium-intercalation method reported by our group.^[177, 178] The growth of Pt nanoparticles on TMD nanosheets was carried out by a photochemical reduction method.^[179, 180] Transmission electron microscopy (TEM) image, selected area electron diffraction (SAED) pattern, high-resolution TEM (HRTEM) image, energy dispersive spectroscopy (EDS) spectrum, high-angle annular dark-field scanning TEM (HAADF-STEM) image, and the corresponding EDS element

mapping images of the obtained Pt-MoS₂ nanosheet are shown in Figure 6.1 and Figure 6.2, revealing the uniform decoration of Pt nanoparticles on the single-layer MoS₂ nanosheet.

Figure 6.1 TEM image (a), SAED pattern (b), HRTEM image (c), EDS spectrum (d) of the obtained Pt-MoS₂ nanosheet.

Figure 6.2 HAADF-STEM image (a) and the corresponding elements EDS mapping images (b-d) of the obtained Pt-MoS₂ nanosheet.

The fabrication process of hybrid fibers is schematically shown in Figure 6.3a. The fabrication procedures are developed based on the method developed by our group^[218] using slight modifications on the parameters to optimize the condition (see the Experimental Section for more details). Briefly, four layers of MWCNT sheet (width of ~1.5 mm and length of ~8.5 cm) fabricated by from vertically aligned MWCNT array,^[181, 182] were piled and placed on a polytetrafluoroethylene (PTFE) substrate (Step 1, Figure 6.3a).^[183] TMD-based materials (MoS₂ *etc.*) were dispersed in DMF (2 mg mL⁻¹) and drop casted onto the stacked MWCNT sheets with a pipette along the planar direction of MWCNT sheet (Step 2, Figure 6.3a). The loading amount of each material was fixed at 90 wt% unless otherwise noted. The resultant hybrid sheet was dried in fume hood and peeled off from the PTFE substrate. Scotch tape was applied to fix one end of the hybrid sheet on a holder, while the other end was attached to an electric motor, which rotated at a speed of 200 rpm for 2 min to twist the sheet into the hybrid fiber (Step 3, Figure 6.3a). Figure 6.3b shows the corresponding photographs of the fabrication processes for hybrid fibers.

Figure 6.3 Schematic illustration (a) and photographs (b) of the fabrication process of hybrid fibers.

Figure 6.4a shows the typical scanning electron microscope (SEM) images of a Pt-MoS₂/MWCNT hybrid fiber. The high-magnification SEM image (inset of Figure 6.4a) indicates that several nanosheets are immobilized onto the MWCNT framework. The incorporation of Pt-MoS₂ nanosheets in the resultant Pt-MoS₂/MWCNT hybrid fiber was confirmed by the Pt and Mo (S) peak signals at 2.0 and 2.3 keV in the EDS spectrum (Figure 6.4b). As a comparison, EDS was also performed on MoS₂/MWCNT hybrid fiber (Figure 6.5). The EDS mapping images of the Pt-MoS₂/MWCNT hybrid fiber, as shown in Figure

6.4c-f, further prove the successful incorporation and well distribution of Pt-MoS₂ in the hybrid fiber. Raman spectra of the pristine MWCNT fiber, MoS₂/MWCNT fiber, Pt-MoS₂/MWCNT fiber and MoS₂ nanosheets are shown in Figure 6.6. The three characteristic peaks located at about 1352, 1590 and 2704 cm⁻¹ arise from the D, G and 2D bands of MWCNT, respectively, which represents the disordered C atoms in the hexagonal graphitic network and the in-plane vibrational mode of *sp*²-bonded C atoms.^[219-222] Another two Raman peaks located at about 381 and 406 cm⁻¹ are attributed to the typical Raman active in plane E_{2g}^1 phonon mode and out-of-plane A_{1g} vibration phonon mode of MoS₂, respectively,^[223, 224] implying the presence of MoS₂ in the hybrid fiber.

Figure 6.4 (a) SEM images of a Pt-MoS₂/MWCNT fiber. Inset of (a) is the corresponding high-magnification SEM image. EDS spectrum (b) and the corresponding EDS element mapping images (c-f).

Figure 6.5 Low-magnification (a) and high-magnification (b) Scanning electron microscope (SEM) images, EDS spectrum (c) and the corresponding EDS element mapping images (d-f) of a MoS₂/MWCNT fiber.

Figure 6.6 Raman spectra of the bare MWCNT fiber, MoS₂/MWCNT fiber, Pt-MoS₂/MWCNT fiber and MoS₂ nanosheets under different grating: (a) 1800 g/mm and (b) 600 g/mm. The spectrometer was calibrated using Raman band of Si at 520 cm⁻¹ as the reference.

6.3 HER Performances of Various Hybrid Fibers

As proof of concept, the as-obtained fibers were used as electrode for HER. For easy handling, the fiber electrodes were fabricated by mounting the as-prepared hybrid fiber (~1 cm) onto a glass substrate.^[184] A Cu wire was connected to one end of the fiber using silver paste, which was subsequently insulated by silicon rubber (Figure 6.7a,b).

Figure 6.7 (a) Photograph of a fiber-based electrode on a glass slide. (b) Schematic illustration of a standard three-electrode setup for HER measurements using a Pt-MoS₂/MWCNT fiber electrode, a Pt wire and a standard 3 M KCl Ag/AgCl electrode as the working electrode (WE), the counter electrode (CE) and the reference electrode (RE), respectively. e⁻ represents electron. Polarization curves (c) and the corresponding Tafel plots (d) of MWCNT fiber, MoS₂/MWCNT fiber and Pt-MoS₂/MWCNT fiber at 2 mV s⁻¹ in 0.5 M H₂SO₄. The dashed lines in (d) shows the linear regions applied to estimate the Tafel slopes. (e) The polarization curves before and after 6000 cycles of cyclic voltammetry sweeps from -0.45 to 0.2 V (vs. RHE) at a scan rate of 100 mV s⁻¹ in 0.5 M H₂SO₄. Negligible HER current loss was observed. (f) Time-dependent long-term current density curves under a static overpotential of 100 mV in 0.5 M H₂SO₄. Inset of (f): enlargement of a serrate area shows the alternate typical processes of bubble accumulation and release.

The electrocatalytic HER performance of the as-prepared fibers was investigated by using standard three-electrode system at ambient conditions, as illustrated in Figure 6.7b. The polarization curves and Tafel plots of fiber-based electrodes in acid environment were obtained by conducting a LSV from -0.45 to 0.2 V (*vs* RHE) at a scan rate of 2 mV s⁻¹ in 0.5 M H₂SO₄. The linear regions of the Tafel curves were fitted to the typical Tafel equation, $\eta = b \log j + a$, where η , b and j are the overpotential, Tafel slope and the current density, respectively.^[168, 208, 225] Compared with the pure MWCNT fiber electrode, the MoS₂/MWCNT fiber exhibited excellent electrochemical catalytic activity for HER. As shown in Figure 6.7c, at overpotential of 300 mV, the current density of MoS₂/MWCNT fiber was about 13.0 mA cm⁻², which was about two orders of magnitude larger than that of pure MWCNT fiber. Moreover, the as-obtained MoS₂/MWCNT fiber exhibited a much lower onset potential of -170 mV, estimated from the inflexion point in the Tafel plot (Figure 6.8a). In addition, we also investigated several other Pt-MoS₂/MWCNT fibers with different loading amount of active material. The Pt-MoS₂/MWCNT fiber with Pt-MoS₂ loading amount of 90 wt% exhibits optimal performance (Figure 6.9). More importantly, Pt-MoS₂/MWCNT fiber exhibits superior catalytic activity with an onset potential of about 15 mV in acidic electrolyte (Figure 6.8b). To reach current densities of 10 and 30 mA cm⁻², the Pt-MoS₂/MWCNT electrocatalyst needs overpotentials of only 37 and 69 mV, respectively. Tafel plots in Figure 6.7d show a small Tafel slope of 30 mV per decade for Pt-MoS₂/MWCNT fiber, similar to that of commercialized Pt/C catalyst (28-31 mV per decade). Normally, a smaller Tafel slope suggests a faster HER increment with increasing potential.^[164, 226] The Tafel plots in Figure 6.7d indicate that the kinetics of the electrochemical hydrogen evolution on Pt-MoS₂/MWCNT fiber (30 mV/dec) is much faster than the pure MWCNT fiber (184 mV/dec) and MoS₂/MWCNT fiber (118 mV/dec). By extrapolating the features in the Tafel plot, the exchange current density of Pt-MoS₂/MWCNT, MoS₂/MWCNT and bare MWCNT can be calculated as 0.4554, 0.0413 and 0.0005 mA cm⁻², respectively, which are well in line with the results of LSV and Tafel slopes (Table 6.1).

Figure 6.8 Tafel plots of MoS₂/MWCNT fiber (a) and Pt-MoS₂/MWCNT fiber (b) in 0.5 M H₂SO₄ in the region of low current densities. The onset overpotential is determined by the potential when the plot starts to deviate from the linear region as indicated by the arrow.

Figure 6.9 Polarization curves of various Pt-MoS₂/MWCNT fibers with different loading amount (wt%) of Pt-MoS₂ at a scan rate of 2 mVs⁻¹ in 0.5 M H₂SO₄.

Table 6.1 Summary of HER activities of various fiber electrodes.

Material	Electrolyte	Onset potential (mV)	Potential at $j = 10 \text{ mA cm}^{-2}$ (mV)	Potential at $j = 30 \text{ mA cm}^{-2}$ (mV)	Tafel slope (mV per decade)	Tafel per region (mV)	Exchange current density (mA cm^{-2})
MWCNT fiber	0.5 M H ₂ SO ₄	-250	—	—	184	250-330	0.0005
MoS ₂ /MWCNT fiber	0.5 M H ₂ SO ₄	-170	-283	-372	118	170-280	0.0413
Pt-MoS ₂ /MWCNT fiber	0.5 M H ₂ SO ₄	-20	-37	-69	30	20-35	0.4554
Pt-MoS ₂ /MWCNT fiber	1 M KOH	0	-23	-74	36	0-15	3.1622

Long-term stability is one of the most important criteria to evaluate the performance of electrocatalyst. To probe the stability of the Pt-MoS₂/MWCNT fiber, long-term cycling tests were conducted from -0.45 to 0.2 V (vs. reversible hydrogen electrode (RHE)) at a scan rate of 100 mV s⁻¹ for 6000 cycles. It is noteworthy that the activity degradation after 6000 cycles is negligible (Figure 6.7e), indicating the excellent durability of Pt-MoS₂/MWCNT catalyst in an acidic environment. Moreover, the stability of the hybrid product is also investigated by long-term electrolysis at constant potentials in Figure 6.7f and Figure 6.10a. In fact, the current density of Pt-MoS₂/MWCNT fiber remains almost unchanged in 0.5 M H₂SO₄ for more than 10000 s under an overpotential of 100 mV, which is consistent with above results. The inset in Figure 6.7f clearly indicates the typical alternate processes of bubble accumulation and bubble release. The stability of Pt-MoS₂/MWCNT fiber electrode under a lower overpotential (50 mV) and a higher overpotential (150 mV) were also investigated (Figure 6.10a). Notably, the fiber electrode shows extremely good durability under all the above conditions. The current density exhibits only a slight decrease, which might be due to the remaining hydrogen bubbles or the consumption of H⁺ that hindered the electrocatalytic reaction.

Figure 6.10 Time-dependent current density curves of a Pt-MoS₂/MWCNT fiber electrode under different static overpotentials (50, 100 and 150 mV) in 0.5 M H₂SO₄ (a) and 1 M KOH (b).

The electrocatalytic performance of Pt-MoS₂/MWCNT in basic solution was also investigated. Figure 6.11 shows the electrocatalytic properties of the Pt-MoS₂/MWCNT fiber in basic condition. Surprisingly, Pt-MoS₂/MWCNT fiber possesses excellent catalytic activity with an onset potential of nearly 0 mV in basic electrolyte (inset of Figure 6.11a). The corresponding Tafel slope is about 36 mV per decade, even lower than that of Pt/C in the same condition and suggesting that the hybrid fiber has superior properties. It is noteworthy

that the current density of Pt-MoS₂/MWCNT fiber generally remains stable in 1 M KOH for more than 10000 s (Figure 6.11b and Figure 6.10b). Due to the unique structure and synergetic effect between MWCNTs and Pt-MoS₂ nanosheets, the HER performance of our Pt-MoS₂/MWCNT fiber can be compared favourably with many other representative catalysts (Table 6.2).

Figure 6.11 (a) Polarization curve of a Pt-MoS₂/MWCNT fiber at 2 mV s⁻¹ in 1 M KOH. Inset of (a) is the corresponding Tafel plot. (b) Time-dependent long-term current density trends under a static overpotential of 100 mV in 1 M KOH. Inset of (b) shows the typical bubble accumulation and release processes.

Table 6.2 Comparison the present obtained TMD/MWCNT fiber and other previously reported catalysts for HER performance.

Catalyst	Onset Potential (mV)	Overpotential (mV) at 10 mA cm ⁻²	Tafel Slope (mV/dec)	Ref.
Pt-TMD/MWCNT Fiber	-15	37	30	Present Work
MoS ₂ /MWCNT	-90	185	44.6	[227]
Defect-Rich MoS ₂ Nanosheets	-120	200	50	[209]
Vertically MoS ₂ Aligned Layers	-200	>400	75	[228]
MoS ₂	-150	187	43	[212]
2H MoS ₂ Nanosheets	-250	300	75-85	[229]
Amorphous MoS ₂ Film	-100	210	40	[230]

Four possible reasons were responsible for the good electrocatalytic performance of our hybrid fiber-based flexible electrodes. First, the well-aligned MWCNT network not only serve as the host for the formation of binder-free hybrid fiber but also assures fast charge

transport during the HER process due to their high conductivity. Second, MWCNT-based framework wrapped and supported the active materials, thus, preventing the latter materials from peeling off which are beneficial to the structural stability of the electrodes. Third, the active materials were well dispersed on the surface of MWCNT sheets which were integrated to a scroll structure during the spinning process, thus, preventing the structure aggregation of TMD nanosheets as well as exposing more active edge sites. Lastly, the 2D TMD nanosheets provide high interfacial contact area with the electrolyte due to their large specific surface area for charge transfers in a 3D matrix, thus, facilitating the ionic interchange as well as efficient charge transfer at the catalyst surface.^[179, 231] Meanwhile, the epitaxially-grown Pt nanoparticles with uniform size of 1-3 nm expose large amount of highly active facets (*e.g.* Pt (110), Pt (311)), which contribute effectively to the electrocatalytic HER current.^[232, 233] Nevertheless, it is necessary to carry out more investigations to reveal the detailed mechanism involved.

Apart from good conductivity, the obtained hybrid fibers possess several fantastic properties such as good mechanical strength, high flexibility and weavability which are important for future smart textiles.^[234] Significantly, the as-prepared hybrid fibers could be integrated into structural textiles and intelligent clothing, thus, providing advantages over many other bulk or power composites. When ten TMD fibers were woven into a white textile (Figure 6.12a), the obtained sheet is highly flexible and can be bended (Figure 6.12b,c). When used for electrocatalytic water splitting, one end of the hybrid fiber/textile sheet was painted with sliver paste and then the sheet was applied as a working electrode for HER. The electrolysis process was performed at a fixed potential of 100 mV *vs.* RHE with significant H₂ evolution in 0.5 M H₂SO₄ for more than 30000 s. As shown in Figure 6.12d, the textile electrode exhibits well stability under the continuous operation. During the HER test, H₂ bubbles continuously evolved on the surface of hybrid fibers (inset of Figure 6.12d), suggesting that the hydrogen production on the flexible textile was violent.

Figure 6.12 (a-c) Photographs of a white textile with 10 woven fibers (pointed by a black arrow). The obtained fabric is weavable (a,b) and can be bended (c). (d) Time-dependent long-term current density curve under a static overpotential of 100 mV in 0.5 M H₂SO₄. Inset of (d) is a photograph shows the generation of H₂ bubbles (pointed by red arrows) on the surface of textile electrode.

More importantly, this synergistic strategy can also be applied to other materials. For example, by employing the similar protocol, several other TMD nanosheets (*e.g.* MoS_xSe_{2-x}, MoSe₂, TiS₂ and their hybrids) were successfully used to fabricate TMD/MWCNT hybrid fibers (Figure 6.13-16), exhibiting the outstanding HER performance (Figure 6.17).

Figure 6.13 Low-magnification SEM image (a), EDS element mapping images (b-f).

Figure 6.14 High-magnification SEM image (a) and the corresponding EDS spectrum (b) of a Pt-MoS_xSe_{2-x}/MWCNT fiber.

Figure 6.15 SEM image (a), EDS spectrum (b) and the corresponding EDS element mapping images (c-f) of a Pt-MoSe₂/MWCNT fiber.

Figure 6.16 SEM image (a), EDS spectrum (b) and the corresponding EDS element mapping images (c-f) of a Pt- TiS₂/MWCNT fiber.

Figure 6.17 Polarization curves of a Pt-MoS_xSe_{2-x}/MWCNT fiber before and after continuous potential sweeps at a scan rate of 100 mVs⁻¹ in 0.5 M H₂SO₄. Negligible HER current loss was observed after 1000 cycles of cyclic voltammetry sweeps from -0.45 to 0.2 V vs RHE.

6.4 Conclusions

In summary, we developed a facile and general strategy to use small amount (10 wt%) of MWCNT host sheet to prepare several TMD/MWCNT-based flexible and weavable fiber devices. The as-obtained fibers retain good mechanical strength while maintaining guest functionality and exhibiting remarkable electrocatalytic performance towards water splitting, comparable to the commercial Pt/C. The extremely low onset potential (about 0 to -15 mV) and Tafel slope (30 to 36 mV per decade), excellent long-term stability both in acid and basic environment, as well as high flexibility and mechanical stress, enable these fibers to be one of the most promising HER catalysts in the future. Moreover, our strategy is applicable for the preparation of various hybrid fibers, thus showing great potentials for developing high-performance, multi-functional hybrid materials for various applications, such as catalysis, sensing, and energy storage.

Chapter 7 General Discussion and Future Work

7.1 General Discussion

In this thesis, I focus on the preparation of novel carbon-based three-dimensional (3D) architectures made from biomass, the coating of ultrathin two-dimensional (2D) metal chalcogenide nanomaterials on the surface of 3D carbon, the assembly of 2D nanosheets to 3D hybrid heterostructures, and the preparation of flexible carbon/ transition metal dichalcogenide (TMD) hybrid fibers. At the same time, I also explore on the water-related application for the as-prepared carbon/TMD hybrids, specifically towards water remediation and water splitting.

To summarize, I have prepared two types of carbonaceous materials for water treatment. The first one is kapok-derived carbon aerogels (KCAs), prepared by facile pyrolyzation of low-cost kapok. The resulted KCA is highly hydrophobic, allowing selective sorption towards various organic solvents in the waste water. In addition, KCA also shows remarkable sorption capability with capacity up to 160 times of its own weight. Moreover, the good thermal stability of KCA makes it suitable for recycling by distillation. In short, our KCA shows great potential for highly efficient removal of pollutants from water. Notably, after loading photocatalysts (such as MoS_2), the as-obtained KCA/ MoS_2 exhibits photocatalytic degradation property in addition of good sorption performance.

The second material is made of graphene/ MoS_2 aerogels (GMAs). The porous structures are fabricated by hydrothermal reaction followed by freeze-drying. The as-obtained GMAs can effectively remove several categories of contaminants from water, such as metal ions and organic dyes. It is worthwhile to note that its sorption capability towards mercury (1245 mg g^{-1}) is the highest value recorded thus far. Mechanistic insight proved that the strong electrostatic interaction and high surface area are the sorption driving force.

A promising catalyst for water splitting, CNT/TMD-based flexible fiber, was also developed via a general strategy. This hybrid fiber exhibits remarkable catalytic performance towards electrocatalytic hydrogen evolution reaction (HER). Its onset potential (about 0 to -15 mV) and Tafel slope (30 to 36 mV per decade) are extremely low. In addition, it also shows good flexibility, high mechanical strength, and excellent long-term stability both in acidic and

basic environment. Remarkably, this strategy is applicable in the preparation of various other hybrid fibers, rendering it useful for various other applications (*e.g.* catalysis, sensing, and energy storage).

7.2 Reconnaissance Work not Included in Main Chapters

Several promising results were achieved through the works described in this thesis and, still, there are many more opportunities to explore in this interesting field. Based on the recent works discussed in this thesis, I will give general discussion for the promising direction of the future works.

Previous studies have demonstrated that kapok could be pyrolyzed to form carbon material with 3D architecture. The as-obtained KCA exhibited excellent sorption performance for oils and organic solvents. Immobilizing suitable photocatalyst on the surface of sorbent can be one of the most promising ways to enhance the water remediation performance of sorbents. Several benefits can be achieved by such hybrid materials. First, the photocatalyst could continually degrade the absorbed organics, overcoming the sorption limit of the pure carbon frameworks. Second, due to the bulky nature of the KCA, the immobilized photocatalysts can be easily recycled. Preliminary results have proven that after coating with MoS₂ nanosheets on the surface of KCA, the as-obtained materials showed enhanced removal efficiency. Thus, further optimization of the experimental conditions is essential to prepare hybrid materials with better performance. In addition, I recommend exploring possible strategies to uniformly coat other excellent photocatalysts (*e.g.* TiO₂) on the surface of KCA and GMA for potential water remediation applications.

Second, GMAs have been proved to be excellent sorbent for adsorptive water remediation. Since the chemical and physical properties of GMAs are directly correlated to their morphology, improving the current TMD coating methods can yield well-organized hybrids. As per various theories, we can expect the 3D graphene/TMD hybrids to have great potential as key active materials in sensors, photocatalysts, electrocatalysts, supercapacitors, lithium ion batteries, and other new fields. Hence, exploration may go beyond the cross fertilization between potential applications in the aforementioned fields.

Third, the CNT/TMD fibers prepared *via* drop-casting method exhibited relatively good electrocatalytic HER activities. Integration between ultra-thin 2D nanosheets and conductive

carbon materials (*e.g.* graphene and CNTs) will be a promising strategy to overcome the weaknesses of 2D TMDs. Thus, it is highly recommended to coat the CNT fiber with TMD or other functional materials *via* more controllable solution-based methods, such as solvothermal reaction and electro-deposition. Oxygen evolution reaction (OER) is another critical half-reaction for water splitting. OER is kinetically sluggish and typically requires suitable catalyst to speed up the process. Since this critical field is still plagued by obscure mechanism that determined results in practical applications, it is recommended to explore the OER performance of CNT/TMD based fibers to further determine the relationship between the electrochemical performance of hybrid fibrous electrodes and deformation degree. To add, the obtained fibers are functional beyond their function as the single electrode but also to be woven into textile as flexible electrode.

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