WS2-Based Nanomaterials Employed for Photocatalytic Water Treatment

Subjects: Materials Science, Composites | Nanoscience & Nanotechnology
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Water pollution is one of the most serious environmental issues globally due to its harmful consequences on the ecosystem and public health. Various technologies have been developed for water treatment such as photocatalysis, which has recently drawn scientists' attention. Photocatalytic techniques using semiconductors have shown an efficient removal of various water contaminants during water treatment as well as cost effectivity and low energy consumption. Tungsten disulfide (WS_2) is among the promising Transition Metal Dichalcogenides (TMDs) photocatalysts, as it has an exceptional nanostructure and special properties including high surface area and high carrier mobility. It is usually synthesized via hydrothermal technique, chemical vapor deposition (CVD), and liquid-phase exfoliation (LPE) to obtain a wide variety of nanostructures such as nanosheets and nanorods. Most common examples of water pollutants that can be removed efficiently by WS_2-based nanomaterials through semiconductor photocatalytic techniques are organic contaminants, pharmaceuticals, heavy metals, and infectious microorganisms.

Keywords: photocatalysis ; tungsten disulfide ; water treatment ; heterostructure ; nanomaterials

1. Introduction

Currently, the world is suffering from great water concerns including waterborne infections and the lack of clean water supply due to the enormous development of the industry. Today's most serious environmental aspect is water, and it is predicted to be the reason for wars in the future. Among the top priorities for the long-term economic situation are providing access to safe and valid drinking water. Chemicals such as dyes, pesticides, and pharmaceuticals as well as heavy metals and pathogenic microorganisms are among the most common pollutants that create significant threats to the natural environments and human health. This leads scientists to continuously investigate efficient water treatment technologies. Water treatment using photocatalysts can solve the problem of freshwater shortage taking place in many countries worldwide in recent decades [1][2][3][4].

Photocatalysis is the process that converts the energy of photons into chemical energy via semiconductors [5]. Photocatalytic systems have been widely used as a fascinating era in environment remediation and water cleaning, which is attributed to their effectiveness in removing contaminants [6]. The semiconductor photocatalytic technique is being studied and invested as a promising tool for water purification, as it is sustainable, has high efficiency and consumes low energy [7]. Moreover, it is considered cost-effective, environmentally friendly, and produces almost no by-products [8]. This technique implements light to degrade the pollutants into less harmful molecules [9]. Photocatalysis is considered an effective photochemical advanced oxidation process (AOP), as it is capable of degrading contaminants in gaseous and liquid mediums, as well as killing pathogenic microorganisms by using the naturally existing solar energy as a renewable light source, which makes the process sustainable and eco-friendly [10][11]. Photocatalysis produces the hydroxyl radical ($^{\bullet}OH$) with oxidizing power of 2.80 V, which is considered relatively high [6].

Two-dimensional (2D) nanostructured materials are extensively used in water treatment for the removal of organic substances, pharmaceuticals, and heavy metal ions from water. These materials have a large surface area prepared out of layered structured materials that are strongly bonded within planes and weekly bonded between nanolayers via van der Waal forces. Generally, several approaches can be used to enhance the efficiency of photocatalytic 2D materials including doping and forming heterojunctions [12].

Recently, transition metal dichalcogenides (TMDs) are considered among the promising photocatalysts because of their tunable bandgaps, enhanced catalytic properties, ultra-thin thickness, and 2D structure [13]. Moreover, this type of nanomaterial is known for its excellent photocatalytic and electronic performances because it shows good stability, excellent carrier mobility, increased surface area, and controllable interfaces [14]. TMDs are known as 2D-layered materials in the form of (X-M-X), where M represents the transition metal sandwiched between two X, which represents the chalcogen. The thickness of each layer of TMDs is around 6–7 Å [15]. The transition-metal sulfide material is not active [16]. However, when the size is nano-scaled, the properties are significantly influenced. There is a diversity in the properties of bulk TMDs where they can be insulators such as HfS_2, semimetals such as WTe_2, metals such as NbS_2, and semiconductors such as WS_2. When these materials are exfoliated into few layers, they preserve their properties in addition to new characteristics generated by the confinement effect [17][18]. TMDs can exploit sunlight as an energy source for the removal of the bad chemicals present in water because of the significant photocatalytic potential of their nanostructure. Recent studies on TMDs show that the photocatalysts that are based on TMDs can be useful in a wider range of applications compared to other traditional photocatalysts, including TiO_2 and ZnO, which are active only under the UV light region, whereas TMDs can react to visible light as well [19].

Tungsten disulfide (WS_2) is a TMD that consists of S-W-S planes bound to each other via van der Waals interactions. The first forms of WS_2 were described in 1992 as inorganic polyhedral, cylinders, and fullerene-like (IF) nanomaterials [20]. WS_2 can be implemented in plenty of applications including photodetectors, solar cells, batteries, etc. The bandgap of the semi-conductive version ranges from 1.3 to 2.1 eV depending on the number of layers. WS_2 is a promising photocatalyst due to its direct bandgap transition, large spin-orbit coupling, and strong quantum confinement effect [21]. Exfoliating the bulk WS_2 to nanosheets can control its bandgap from indirect to direct type [22].

2. WS_2 as a Photocatalyst

2.1. Structure

WS_2 is found in two different phases, which are prismatic trigonal 2H phase and octahedral 1T phase, and each phase has different properties, where 2H-WS_2 is semiconducting, and 1T-WS_2 exhibits metallic properties. Both phases can be transformed into one another under certain conditions [23][24][25]. The bulk hexagonal WS_2 (2H-WS_2) shows an indirect band gap, whereas it exhibits an indirect-to-direct band gap transition when it is a monolayer [26][27]. The lattice parameters *a* and *c* for 2H-WS_2 are 3.155 Å and 12.349 Å, respectively, and the internal coordinate *z* that determines the interlayer sulfur plane distance for bulk 2H-WS_2 is 1.573 Å [28][29].

2.2. Properties

Among the 2D materials, WS_2 is more abundant in the crust of Earth, has less toxicity, and is cheaper compared to other TMDs. Moreover, it is special for its extraordinary properties including high surface area, favorable electrochemical activity, photocatalytic and electronic efficiency, high carrier mobility, biocompatibility, and its tunable bandgap. In addition, WS_2 is commonly used as a light-absorbing material due to its broad absorption spectrum, which makes it an efficient photocatalytic material. However, WS_2 shows some limitations for some photocatalytic applications, as the band edge potential of its conduction band minimum does not match the potential requirements for photocatalytic water splitting for instance [30]. WS_2 can show a low indirect band gap (less than 1.5 eV) and a higher direct bandgap (larger than 2 eV) depending on the synthesis technique used [31][32][33]. This relatively narrow band gap increases the light absorption region to 910 nm, which enables it to undergo the redox chemistry required for degradation of organic pollutants [34].

2.3. Synthesis

Various methods have been employed for the WS_2 synthesis, among them are the mechanical activation method, sol-gel method, thermal evaporation technique, liquid-phase exfoliation method, hydrothermal method, and chemical deposition techniques. In addition, WS_2 can be synthesized with a wide range of morphologies including nanosheets, nanofibers, and nanorods [20].

The hydrothermal route is among the promising techniques, as it is a simple process, yields a highly pure product, and is environmentally friendly. Cao, Liu, Hussain, and others succeeded in synthesizing different nanostructures of WS_2 with various morphologies including nanorods, nanofibers, nanoparticles, and nanosheets via a hydrothermal route with the addition of the surfactants polyethylene glycol (PEG) and cetyltrimethylammonium ammonium bromide (CTAB). The surfactants were found to affect the fabrication of different morphologies of WS_2 nanostructures [35].

3. Photocatalytic Water Treatment Using WS_2 and Heterostructures

When different semiconductors having different energy gaps are coupled to form heterostructures, this will result in controlling the recombination process of the photogenerated charge carriers, improving the photocatalytic activity, reducing the bandgap, and moving the optical response to be in the visible light region to enable the investment of the solar energy. Forming a well-matched conduction band and valence band levels leads to a dimensional separation between the photogenerated electrons and holes [36]. The construction of heterojunctions is among the most common methods for photocatalysts fabrication and modification because it provides high activity and visible light response [37]. When using WS_2 as a cocatalyst, semiconductor–semiconductor, or metal-semiconductor, heterojunctions will be constructed, which will result in creating more interfaces [38]. As a result, the charge separation and migration can be improved, and hence, the photoactivity will be enhanced [39].

3.1. Photocatalytic Degradation of Organic Substances

Enormous quantities of organic pollutants such as synthetic dyes, fertilizers, solvents, and pesticides are being released into the environment and the aquatic ecosystem, which can cause serious environmental problems [1]. These organic compounds are mostly stable and do not undergo biodegradation or photodegradation naturally and hence cause harm to humans and animals in both the short and long term [40]. In addition, organic pollutants can harm human health by causing cancers and mutations, nausea, mental confusion, and Alzheimer’s. Thereby, searching for new technologies for the removal of organic pollutants is demanded. This is because the traditional techniques showed some restrictions and limitations such as unaffordable operation costs, poor removal efficiency, complicated processes, and low adaption to many organic structures [41][42]. AOPs can be used to eliminate organic pollutants from wastewater via direct and indirect processes where hydroxyl radicals are employed to hydroxylate or dehydrogenate the pollutants, and then, they will finally mineralize [43][44]. Therefore, the main advantage of using AOP for the degradation of organic pollutants is the complete destruction it guarantees instead of changing them into another phase, and without the need for toxic oxidants such as chlorination [45]. Photocatalysis can be utilized for degrading organic pollutants, as it provides good reproducibility, simplicity, high efficiency, and low cost. Photocatalysis can degrade organic pollutants into harmless products. The photocatalysis process is mainly a reaction between the organic pollutants and oxidizing and reducing agents, which are holes and electrons generated under UV or visible light irradiation on the photocatalyst's surface [37].

3.2. Microorganisms' Disinfection

Microbial pollution is among the most popular problems, as it is directly related to health and the environment [46]. Wastewater treatment plants cannot usually remove the pathogenic microorganisms because of the shortage in financial resources, which causes hazardous effects on public health [47]. Currently, pathogenic microorganisms contaminating water such as viruses, fungi, and bacteria and their corresponding infections are of particular concern. It is known that pathogens infections have been creating disasters such as cholera, which is caused by *Vibrio cholerae*, and plague, which is caused by *Yersinia pestis*. The enterotoxin-genic *Escherichia coli*, which causes diarrheal illness and passes through contaminated water, kills about 1.3 million children annually [48][49]. Referring to the WHO Guidelines for drinking water quality, drinking water is considered safe if it is free from fecal organisms including *Escherichia coli*, *Clostridium perfringens*, *Enterococcus* spp., Total coliforms, Thermotolerant coliforms [50]. The antibacterial photocatalytic mechanism begins by damaging the bacterial cell membrane, which causes damage to the internal components of the bacterial cell consequently. After that, the photocatalytic reactions will oxidize the remaining parts of the leaked bacterial cell [51][52].

3.3. Heavy Metals Reduction

Heavy metals are metals with high atomic weights, atomic numbers, and densities that are greater than 5 g/cm^3. The presence of heavy metals in water can cause poisoning of the living creatures, which leads to biodiversity damage, in addition to endangering human health when accumulating in the human body, causing cancers and organ failure. Examples of common heavy metals present in the environment are lead, cadmium, chromium, and arsenic [53][54]. Adopting strategies for the removal of heavy metal ions contaminating water is a great challenge for the scientific community currently. Some convenient methods such as chemical precipitation and reverse osmosis are used. However, these techniques showed some restrictions and limitations, as they cannot achieve complete removal of the metal ions, as well as the formation of sludge in large amounts, which are difficult to be disposed of and managed properly [55][56][57]. Furthermore, photocatalysis can provide a continuous operation, as it does not need energy input except light energy. In addition, the photocatalytic redox reactions do not produce polluting intermediates, which makes it a green process for heavy metals reduction. Moreover, photocatalysis works on depositing heavy metals to be easily reduced on the surface of the photocatalyst as solids to be directly separated from the solution [58][59][60][61].

3.4. Pharmaceuticals Photodegradation

Pharmaceutical waste is one of the most serious existing pollutants in water worldwide. There are several ways by which these pollutants were introduced to the environment such as hospital and domestic sewage, industrial discharge, and wastewater treatment plants. Pharmaceuticals are among the most significant contaminants of water, as they play a role in the alteration of the metabolic activity of the existing biota and hence can produce noticeable biochemical modifications. Currently, the world witnesses an extensive consumption of antibiotics, which caused an enormous increase in antibiotic wastes, and hence led to generating resistant bacteria, which threatens human health severely [62][63][64].

4. Conclusion

The investigation of the fundamentals of synthesis and applications of WS_2-nanostructured materials is still in continuous progress worldwide. The broad spectrum of applications in which WS_2 is employed has emerged from its superior properties as a TMD such as large specific surface area, tunable band gap, and high mobility. This entry focused on the recent research work conducted on WS_2-based nanomaterials and their significant role in the photocatalytic water treatment process including the degradation of organic substances such as dyes and pesticides, disinfection of water, and killing pathogens, reduction of heavy metals, and degradation of drugs and pharmaceuticals. The mechanism by which photocatalysis degrades pollutants in water was also explained. In addition, the entry highlighted the main techniques by which WS_2 nanostructures are synthesized such as hydrothermal, CVD, and LPE. It can be concluded that heterostructure construction is an essential solution to approach maximum degradation efficiency by reducing electron-hole pair separation and lowering the bandgap energy. Future research should consider the need of sufficient understanding of the growth conditions and behaviors of WS_2. In addition, optimizing the operation parameters and developing new effective designs to enhance the performance of WS_2 for water treatment applications is urgently needed. In addition, new studies must focus on incorporating WS_2 nanostructures in a hybrid/composite photocatalyst to extend its advantages as a green and cost-effective system for water purification and environmental remediation.

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