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2D Nanomaterials for Photocatalytic Hydrogen Production

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Abstract

Photocatalytic hydrogen production technology is a simple and effective hydrogen production method. The article introduces the latest progress of 2D nanomaterials and composite heterostructures in the photocatalytic hydrogen evolution reaction, and discusses in detail advanced methods for the synthesis of 2D nanomaterials. The interaction of strong in-plane chemical bonds and weak van der Waals forces makes these materials promising in surface applications. In addition, the article also elaborated on the use of 2D nanomaterials for photocatalytic hydrogen production, and emphasized the importance of structural defects and doping in the electronic structure. Finally, the article also provides a new perspective on the prospects and challenges of using 2D nanomaterials for photocatalytic hydrogen production.

Keywords

Photocatalytic Hydrogen Production; 2D Nanomaterials; Electronic Structure.

1. Introduction

Hydrogen is considered to be a clean and sustainable form of energy in the future. The importance of hydrogen as a fuel stems from the high energy produced by combustion (122 kJ/mol), far exceeding gasoline or other forms of fossil fuels. The process is not harmful to the environment and will not produce any harmful by-products. Currently, the hydrogen production process involves the production of carbon dioxide. Therefore, looking for viable alternatives other than producing any greenhouse gas is a key research direction. The use of solar energy to produce photocatalytic hydrogen on the surface of the catalyst is a promising alternative to solve the current energy and environmental crisis.

Since 1972, the ability to use photocatalytic materials to produce hydrogen has been proven. In order to generate four electrons, the surface of the nanocrystal needs to be hit by four photons with appropriate energy in a short time. The solar photon flux density is estimated to be 2000 μmol·s-1m-2. Therefore, it takes at least 4 ms for photons to be absorbed by nanoparticles, and the lifetime of charge carriers is estimated to be 1 μs. Therefore, it is extremely difficult to obtain solar flux to complete the water splitting reaction. In order to reduce recombination and shorten the moving distance of charge carriers, two-dimensional (2D) structured nanomaterials can meet these requirements. Even at low flux densities, the layered structure helps the light absorption process, and the generated charge carriers only need to travel a small distance [1].

2D materials exhibit the unique ability to confine electrons in ultra-thin layers, resulting in superior optical and electronic properties. Strong in-plane covalent bonds provide a place for the formation of many heterojunctions and heterostructures. In addition, 2D materials possess a high specific surface area, which makes the surface reactive. Such as water splitting. Graphene is the first 2D material to exhibit unique electronic, mechanical and optical properties. The entire graphene revolution has led to new research areas with similar structures. 2D transition metal disulfides (TMDs) have gained widespread attention in recent years. TMDs are made by extruding a hexagonal metal atom layer (M) with a stoichiometric amount of MX2.22 between two layers of chalcogen atoms (X).

These pieces are joined together through covalent interaction, and adjacent pieces are joined together through van der Waals interaction, thus forming the 3D crystal structure. Depending on the combination of transition metal and chalcogen atoms, there are 40 different types of molybdenum disulfide. The arrangement of these atoms in the crystal structure determines the physical and chemical properties. In the case of molybdenum disulfide, the optical and electronic properties change as the number of layers decreases. Moreover, the molybdenum disulfide in the bulk has an indirect band gap, which is transformed into a direct band gap in several layered flakes. Similarly, 2D Graphite Carbon Nitride (C_3N_4) is another layered structure that has been widely studied, with significant electrical and optical properties. Low-dimensional catalysts have become interesting candidates for various applications. Visible light absorption and compatible band gaps of these materials make them convincing candidates for H_2 production. The electronic properties of this structure play a vital role in the catalytic reaction mechanism of these materials. The adsorption or binding of any reactant depends on the electronic structure density of the Fermi level. The stronger combination is related to the height of the center of the electronic structure relative to the Fermi level. Therefore, understanding the energy band structure is essential for developing strategies for designing effective catalysts, which can radically increase catalytic yields. However, these structures have limitations, such as unstable structure, high exciton recombination, poor band gap, etc. [2].

There have been many studies introducing 2D nanomaterials. In the past five years, great progress has been made in manufacturing and increasing hydrogen production. This article introduces the latest developments in the use of 2D nanomaterials and their nanoheterostructure composite materials for photocatalytic water splitting reactions.

2. Using 2D nanomaterials to produce hydrogen by photocatalysis

2.1 The basis of photocatalytic hydrogen evolution reaction

The first is the ability to provide better charge transfer mobility. Secondly, it combines a simple synthesis method with an effective reaction mechanism. Finally, photons play an important role in preventing nanostructures from reaching photoactive sites.

As early as 1958, people began to search for the best H_2 catalyst. Parsons et al. observed that catalytic evolution is directly related to the formation of heat on the catalyst surface (H_2). In addition, by using computational chemistry, Norskov and his colleagues established the ability to predict binding energy, which in turn helped to understand the efficiency of H_2 production [3].

The water splitting reaction includes two basic reactions, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = 0.00\ V \tag{1}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^0 = +1.23\ V \tag{2}$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

$$\Delta E^0 = 1.23\ V,\ \Delta G^\circ = +237.2\ kJ/mole \tag{3}$$

Therefore, the entire research program is to find a photocatalytic surface that has the potential to absorb light and generate electron-hole pairs. These electrons and holes can then proceed in the HER reaction and OER reaction on the catalyst surface. However, in order to achieve this goal, it is important that the conduction band (CB) edge of the catalyst should be more negative than the reduction potential of H^+ to H_2 (0.00 V), and the valence band (VB) edge of the surface should be greater than the oxidation potential of H_2O to O_2 (1.23 V) Correction. In short, the band gap of semiconductors is estimated to be 1.23 volts, but due to heat loss, a wider approximation or suitable semiconductor band gap is between 1.5 and 2.5 eV [4].

At present, hydrogen production is achieved through steam reforming. In this process, methane reacts with steam in the presence of a catalyst at high temperature and pressure, and is converted into carbon monoxide and hydrogen. The carbon monoxide produced in this step is reused for exposure to excess steam to obtain carbon dioxide and more H_2.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (5)$$

2.2 Hydrogen production by 2D nanomaterial photocatalysis

2.2.1 Photoelectrochemical (PEC) water splitting

Japanese scientists have published research on the use of titanium dioxide electrodes to generate hydrogen under ultraviolet light. Since then, this idea has been extended to particle systems. In the past 50 years, significant progress has been made in this field. Under light irradiation, the plasma chemiluminescence activity that generates hydrogen occurs inside the plasma chemiluminescence cell (Figure 1 (a)). It consists of a working photoanode and a reflective photocathode for hydrogen evolution. The photoanode is composed of a semiconductor material for oxygen evolution. These electrodes are placed in an electrolyte solution, and wires are used to connect the current loop between the electrodes to complete the circuit. Semiconductors with band gaps greater than 1.23 V can be used as photoelectrodes for hydrogen generation. This can provide an external bias to initiate the reaction. However, the use of additional bias voltage often results in partial depletion of electrons in the photosensitive surface of the semiconductor. This loss leads to the formation of the surface space layer and the associated energy band bending. This process will inevitably reduce the recombination rate and extend the life of charge carriers.

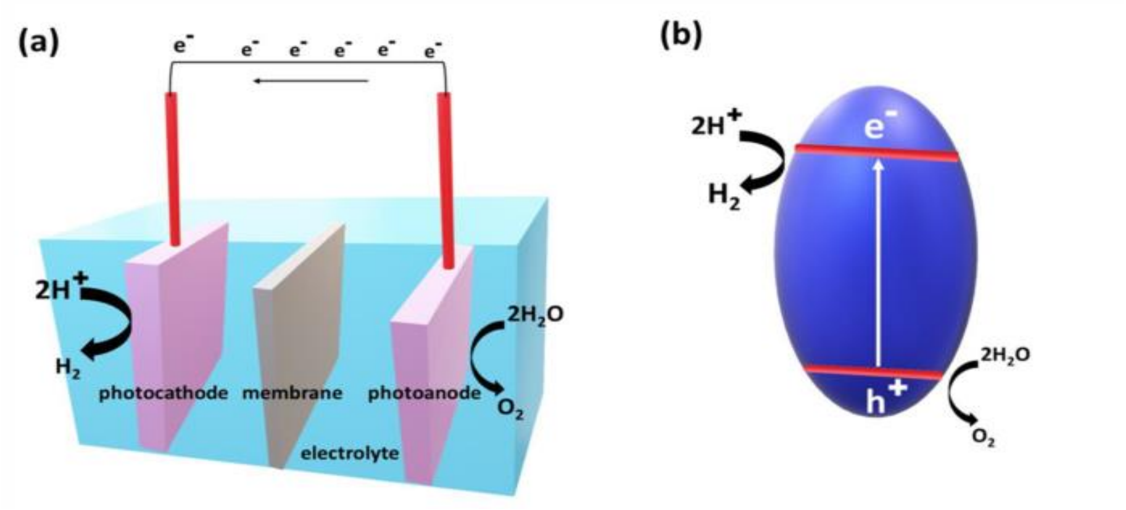

Figure 1. (a) PEC, (b) schematic diagram of photocatalytic water splitting to produce hydrogen

In the past ten years, some scholars have conducted a lot of research, emphasizing the application of 2D nanostructures in electrochemical hydrogen production. The photocatalytic electrochemical activity and the photocatalytic water splitting reaction are measured by evaluating the amount of hydrogen or oxygen produced by the reaction. The H_2 productivity is usually measured in $\mu mol \cdot h^{-1} g^{-1}$, and the photocurrent density is measured in $mA \cdot cm^{-2}$. The wavelength and intensity of incident radiation are several other parameters worthy of attention. However, each reaction setting is different and produces different results. Therefore, in order to compare the results, two parameters are used, namely quantum yield (QY) or apparent quantum yield (AQY).

2.2.2 Photocatalytic water splitting

In this process, by irradiating the surface of the catalyst with sunlight or visible light, a high yield of H_2 is produced. A catalyst, or more clearly defined as a photocatalyst, is a semiconductor material that contributes to the water splitting reaction and is not converted or consumed in the process (as shown in Figure 1(b)). This is a more reliable process compared to previous options. Because of the high efficiency of converting solar energy into hydrogen, the operation method is also very simple. Irradiating the semiconductor surface with sufficient energy will generate electron-hole pairs. These electron-hole pairs are very unstable and tend to recombine easily. However, structural or electronic manipulation helps transport charge carriers to initiate chemical reactions on the catalyst surface. In order to illustrate the efficiency of the water splitting reaction under sunlight, PEC and photocatalytic water splitting reactions are related to another parameter of the conversion efficiency of sunlight to H_2 under illumination.

2.2.3 Mechanical peeling

The mechanical peeling of the bulk layered material is usually referred to as the "scotch tape method". This is one of the most pioneering technologies for isolating single-layer 2D nanomaterials introduced by Novoselov et al. The use of chemical stripping results in a tampered structure with huge defects. Isolating the monolayer seems to be a challenging task, and the process is more like a transitional stage. On the other hand, mechanical exfoliation is used as a viable technique to separate hundreds of layers of 2D nanomaterials. In this technique, a piece of "transparent" tape is used to scrape the layered material from the bulk material. As a result, the micron-sized fragments of the 2D nanoparticles are peeled off, and then transferred to the Si/SiO_2 substrate by wet or dry transfer methods. Unlike the traditional scotch tape method, the researchers introduced an intermediate viscoelastic surface to peel off the flakes, which resulted in a significant increase in yield and reduced contamination of the flakes. Huang et al. improved the mechanical cleavage technique by introducing a process of pretreating the substrate with oxygen plasma, which resulted in the removal of environmental adsorbates (As shown in Figure 2). Finally, a heat treatment is performed to introduce peeling and obtain better interface contact with the substrate and bulk crystals. This technology improves the surface area and increases the yield of nanosheets produced. Although this technology has become a basic means of peeling layered materials, it also has its own limitations. With this technology, high yield and production of sheets with controlled sizes and shapes cannot be achieved. In most cases, the demand for the base layer of the release sheet is undoubtedly another factor that limits any practical application that requires a large yield and moderately stable sheet. This technology certainly lacks these aspects, so alternative methods have been explored [5].

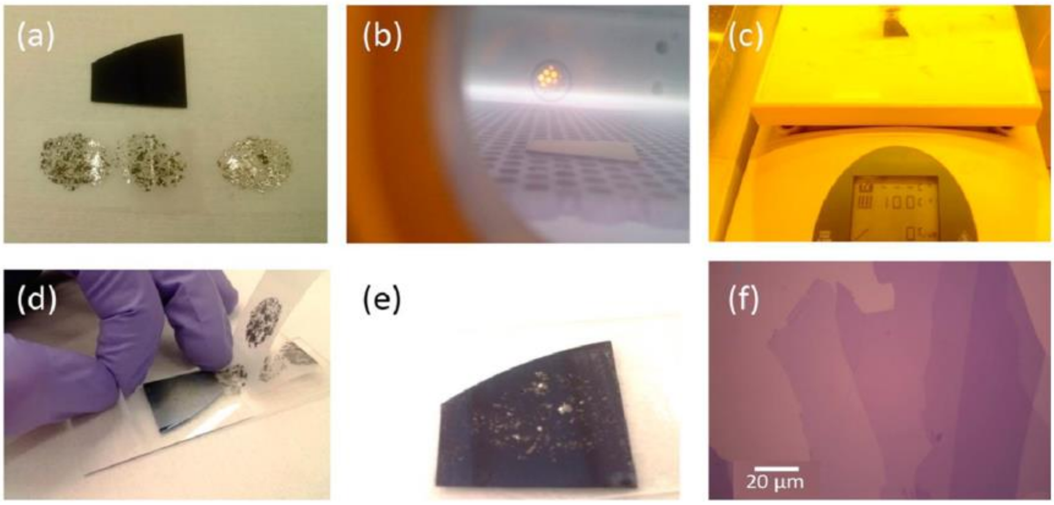

Figure 2. A typical peeling process of graphene, using a transparent tape method improved by micromechanical cleavage technology

2.2.4 Liquid-based peeling

Similar to mechanical exfoliation, the synthesis method of exfoliating the layered body material in a liquid can lead to the synthesis of 2D nanomaterials. Ultrasonic treatment force or mechanical thrust is applied to a liquid solvent in which a large amount of powder material is suspended. Nanosheets of graphene, TMDs, metal organic frameworks (MOFs) and several other materials have been obtained through liquid exfoliation. Exfoliation produces high aspect ratio nanosheets with high surface area, which is bound to be beneficial for applications related to high surface area. The most common method of synthesizing exfoliated layered crystals is oxidation. The use of compatible oxidants results in the introduction of hydroxyl or epoxy functional groups between the sheets, resulting in water embedding and significant large-scale ultrasonic peeling. The use of suitable stabilizers can prevent re-aggregation, and further reduction can remove oxides and introduce defects. The synthesis of graphene in the form of reduced graphene oxide (rGO) is the best example of this synthesis. Intercalation is another way to use the space between the layered structures to introduce guest molecules, which helps to separate the flakes from their interlayer adhesion. Further ultrasonic treatment or heat treatment resulted in complete peeling. The addition of surfactants helps to stabilize the process. In order to synthesize several layers of graphene, Shih et al. introduced different types of halogen inserts to introduce strain, and finally obtained double-layer or triple-layer graphene sheets. Siong et al. studied the effect of lithium intercalation between molybdenum disulfide layers. The wide gap (0.615 nm) between the TMDs provides space to accommodate a wide range of molecules, which allows further evaluation of the electronic and optical properties of the molybdenum disulfide layer when intercalating lithium ions. However, this method does have the disadvantage of being sensitive to environmental conditions. Another method in liquid stripping technology is ion exchange. This refers to maintaining neutrality by replacing existing ions, thereby introducing an ionic charge that is opposite to the charge of the layered sheet.

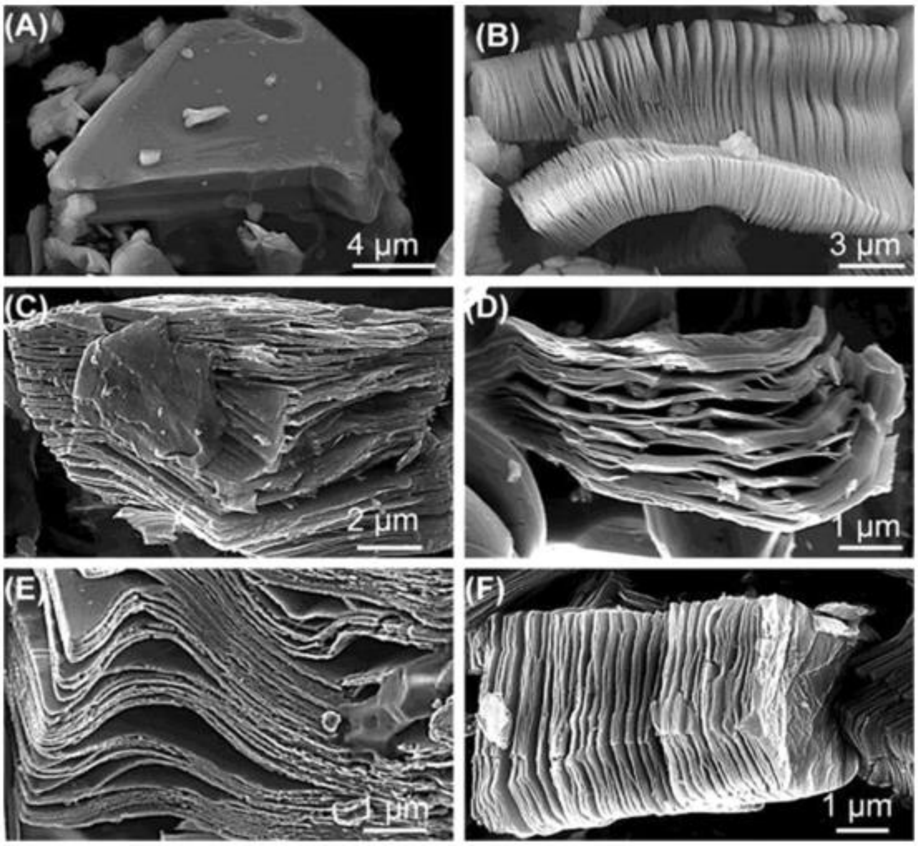

Figure 3. Particles of (A) Ti3AlC2 before (B) Ti3AlC2, (C) Ti2AlC, (D) Ta4AlC3, (E) TiBalC and (F) Ti3AlCN before and after high frequency treatment

The introduction of ions such as large organic molecules (such as quaternary ammonium cations, propylammonium cations, etc.). Another relatively simple technique is to apply ultrasonic waves in a solvent to induce the exfoliation of the layered material. Studies have shown that the correct choice of solvent leads to the stable synthesis of a large number of 2D materials. The matching of the surface energy of the solvent and the layered material contributes to stability and reduces the possibility of re-aggregation. Ternary metal carbide is a good example of liquid exfoliation. This kind of layered solid structure has a strong bond. Najib et al. reported the synthesis of a series of 2D transition metal carbides and carbonitrides from their largest phase in hydrogen fluoride. Here, the largest phase represents the chemical composition $Mn^{+1}AXn$, where n=1, 2, or 3. "M" represents an early transition metal, and elements from groups 13 and 14 are represented as "A". It is observed that the A layer of the largest phase is more chemically active because they bind weaker than the M-X bond. Different maximum stages are immersed in different concentrations of hydrogen fluoride for different time intervals. The resulting powder was sonicated at different time intervals to produce a layered structure of MXenes (Figure 3).

2.2.5 New materials

2D materials have always been the focus of interest. Their improveable properties and wide range of applications make them interesting candidates for various energy and environmental applications. 2D nanosheets provide less opportunity for the incident photon flux to propagate and improve efficiency even at low intensities. There have also been reports of the formation of p-n nano heterojunctions, which illustrates the importance of surface chemistry in the construction of heterojunctions on semiconductor surfaces. Kamoto et al. studied the H_2 production efficiency of rhodium-doped calcium niobate nanosheets, which are manufactured by stripping off their original parent material. Compared with the parent material, the production efficiency of the 2D sheet is increased by 165 times. This 0D/2D heterojunction provides sufficient active sites and charge separation for photogenerated charge carriers. The composite material showed the maximum productivity ($949.9 \mu mol \cdot h^{-1} g^{-1}$) compared with its original matrix. Some scientists have proved that within a certain period of time, by introducing pretreatment in liquid N_2O, 2D quantum dots can be formed from the exfoliated sheet of 2D nanomaterials. This process is a huge leap in the existing lipopolysaccharide strategy. Because the low-temperature treatment inevitably brings about the process of obtaining the original 2D structure in a single layer form, the solvent specific to each peeling is no longer required. Most importantly, any other impurities such as surfactants can be easily avoided.

3. Prospects and challenges

In the past ten years, the scientific community has made significant research progress in the conversion of solar energy into energy. In short, 2D nanomaterials and their composite arrangement show higher hydrogen production efficiency. In addition, by introducing a second component such as a co-catalyst, the transport of charge carriers is enhanced. The new synthesis method of 2D composite structure enhances visible light absorption and also improves the stability of the material against light corrosion. Therefore, these new heterojunctions are a kind of promising photocatalytic hydrogen production materials. Although significant progress has been made in the past decade, there are still huge obstacles to photocatalytic water splitting reactions. In addition to material synthesis and its core challenges, there is another field related to hydrogen storage. Hydrogen with low volumetric energy can be compressed into liquid or gaseous state, which requires a lot of energy, which will eventually lead to an increase in production costs. The problems of commercialization and the lack of technical support ultimately prevented consumers from buying hydrogen-fueled vehicles until the adequate supply of fuel was ensured. These are challenges that need to be addressed in the future.

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