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Review Article

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Semiconductor-attapulgite composites in environmental and energy applications: a review

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Abstract: Attapulgite, with abundant reserves, low price, a special structure, excellent adsorption, thermal stability, and catalytic performance, is often used as a catalyst or catalyst support, offering broad development prospects. In order to understand and fully utilize attapulgite resources, this paper introduces the common preparation methods of attapulgite and explores the effects of different modification methods (*e.g.* thermal modification, acid modification, etc.) on attapulgite performance. The article focuses on the current status of semiconductor-attapulgite composites in the fields of wastewater treatment, air pollution, and energy, and briefly describes examples of their applications in other fields. Finally, the development prospects of the composites in the field of environment and energy are summarized, and the challenges are discussed.

Keywords: attapulgite; semiconductor; composites; environmental; energy

1 Introduction

With the increase of industrialization, the world is facing increasingly serious problems of energy depletion and environmental pollution. Extreme climatic phenomena triggered by fossil energy, such as photochemical haze and acidic precipitation[1], as well as pollution of the atmosphere[2,3], water[4,5] and soil[6,7] caused by exhaust gases and wastewater from industrial activities, are continuously eroding our ecosystem. In the face of increasing energy resource problems, researchers are committed to promoting the widespread use of clean energy sources such as solar, wind, and water[8–11] to slow down the overexploitation of the Earth's resources. Countless researchers have devoted themselves to the study of environmentally functional materials in order to restore the environmental health of the Earth, develop clean energy, ensure the sustainable development of the country, guard our living environment, and promote the core driving force of the country's shift to a green and efficient development model.

Attapulgite (ATP), also known as Palygorskite (PAL), is a layered chain of hydrated magnesium silicate minerals. The composition of natural concave earth is complex, often containing montmorillonite, kaolinite, carbonate, and other minerals. It is widely distributed in the United States, Spain, China, and other countries, with especially abundant reserves in eastern China, particularly in Jiangsu, Anhui, and Guizhou.[12,13]

Attapulgite, which mineralogically belongs to the sea-foam group, is a magnesium silicate mineral with the ideal chemical formula $Si_8Mg_5O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$. Its structure is shown in Figure 1.[14] The mineral is interconnected by the shared vertices of silica-oxygen tetrahedra and magnesium-aluminum octahedra, forming a unique three-dimensional network. The crystal structure features numerous zeolite channels and pores, resulting in a large specific surface area.[15,16]

Due to its abundant reserves, low price, stable physical and chemical properties, as well as its excellent adsorption, loading and catalytic properties[17,18], attapulgite has a wide range of applications in the fields of industry, agriculture, energy and so on.[6,19,20] For example, in petrochemical industry, it can be used as a catalyst or catalyst carrier for catalytic cracking and hydrolysis.[21] In environmental treatment, due to its strong adsorption of organic dyes and heavy metal ions, it is often used in wastewater treatment and soil remediation.[22,23] In agriculture, attapulgite can also be used as a soil conditioner to improve soil aeration and water retention. Because of its ion-exchange property, it can slow release the nutrients in fertilizers, thus reducing fertilizer loss.[24,25]

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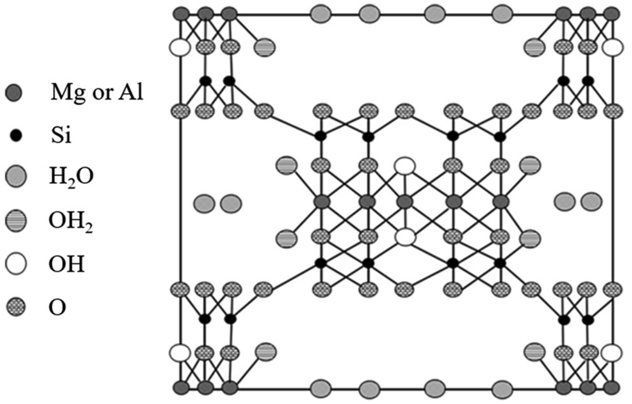

Figure 1: Ideal crystal structure model for attapulgite clay.

With the deepening of research, researchers have found that natural attapulgite has shortcomings such as easy agglomeration, high impurities, and poor selectivity, which cannot meet the experimental needs. Additionally, it fails to fully utilize the advantages of attapulgite itself. Therefore, researchers are exploring various methods to modify attapulgite, optimize experimental schemes, and develop new types of attapulgite composite materials to broaden the application field and enhance the functionality of attapulgite materials.

Semiconductor materials are usually referred to as materials whose conductivity at room temperature is between that of a conductor (e.g. most metals, graphite, etc.) and an insulator (e.g. ceramics, wood, etc.). These materials have controllability, a wide range of applications, stable performance, and other advantages. In the era of rapid development of intelligent electronic equipment, semiconductor materials play a significant role in providing power for various new materials such as high-frequency electronic devices, solar batteries, light-emitting diodes, transistors, etc. The specific types of semiconductor materials and their common applications are shown in Table 1. It is evident that the advancement of semiconductor technology drives progress in science and technology, making it an essential component of modern science and technology development[26] Fundamentals of semiconductors, 2005.

Currently, semiconductor-attapulgite composites have become a hot topic among researchers. Attapulgite possesses L-acid and B-acid centers, which have certain catalytic effects. Combined with the special pore structure of attapulgite clay, synergistic catalytic effects can be produced with catalysts to enhance catalytic efficiency.[27] The combination of attapulgite and semiconductor materials can significantly address the shortcomings of semiconductors, such as short lifetime of photogenerated carriers, agglomeration issues, and weak adsorption of pollutants, thereby greatly improving the low photocatalytic performance of catalysts.

For a long time, the author's group has been engaged in photocatalysis and multiphase catalysis, using semiconductors, precious metals and their composites for photocatalytic degradation of formaldehyde, catalytic reduction of nitroaromatics to amine-based compounds, catalytic formic acid to hydrogen, photocatalytic degradation of ciprofloxacin and other studies.[11,28–30]

This paper summarizes the relevant literature in the last decade, reviews the applications of semiconductor-attapulgite composites in the field of environmental treatment and energy, and finally looks forward to the prospects of semiconductor-attapulgite composites in other applications and the challenges them face.

2 Preparation of attapulgite composites

Since the discovery of attapulgite, people have been committed to the development and application of attapulgite composites. Due to the diversified structure of composite attapulgite materials, they play the role of fixing and providing microreaction sites. In recent years, a lot of new composite attapulgite materials have been developed and have shown a very important position in the fields of ecological management[19], energy[31], medicine[32], agriculture[24] and so on. There are many ways in which attapulgite composites can be prepared, and the common preparation methods are shown below.

Table 1: Common types, representative materials, and applications of semiconductors.

Types of semiconductors	Common materials	Applications
Element semiconductors	Si, Ge, P, Se	Transistors, far infrared detectors
Compound semiconductors	GaAs, ZnS, CuCl	Solar cell materials, semiconductor lasers
Oxide semiconductors	Cu_2O, ZnO, SnO_2	Transparent electrodes, electronic paper
Layered semiconductors	PbI_2, MoS_2, GaSe	Solid lubricants, photosensitive materials
Organic semiconductors	Polyacetylene, C_{60}	Organic light-emitting diodes, solar battery
Magnetic semiconductors	Eu, Mn	Spin transistors, magnetic sensor

2.1 Solvothermal synthesis

The target product is obtained by mixing a certain proportion of reactants and organic solvents and transferring the mixture into a steel kettle with a PTFE liner, where it reacts under high temperature and pressure. For example, Wang et al.[33] successfully prepared sulfur-doped SATP composites using the solvothermal method. The high concentration of sodium sulfide solution in the reaction process caused the internal layer chain structure of the attapulgite to change into a block structure. Part of the Al_2O_3 in the attapulgite structure would be converted into $Al_2(SO_4)_3$ and silicate. The high adsorption performance of SATP is not only suitable for the general environment but also enables high efficiency adsorption of dye molecules and metal ions under acidic or alkaline conditions.

2.2 Impregnation synthesis

Impregnation is a commonly used chemical synthesis method, typically utilized to uniformly deposit a substance in a solution onto the surface or interior of another substance. In the photocatalytic degradation of Novakrone blue and Novakrone yellow, Assis et al.[34] prepared TiO_2-ATP nanomaterials using a simple impregnation method. This method greatly improved the degradation efficiency of the materials and created economical photocatalysts with simple experimental methods, providing a new idea for the photocatalytic degradation of azodye-type reactive dyes.

2.3 Sol-gel synthesis

As a novel method of material preparation, the precursor substances prepared by mixing sol and gel are dried and heat-treated after the formation of the gel structure to finally obtain the desired target product. In the study of the adsorption of methylene blue, Chen et al.[35] found that cellulose-attapulgite nanocomposites prepared by the sol-gel method had the advantages of high adsorption and high alkali resistance. Additionally, Fu and Zhang[36] prepared attapulgite liquid crystal material (Fe_3O_4-ATP) with superparamagnetic properties by attaching Fe_3O_4 particles to the attapulgite using the co-precipitation method. This material allows control of the light intensity of the liquid crystals by the strength and direction of the external magnetic field. Additionally, the color of the liquid crystal phase can be adjusted by the concentration of the colloidal rod nanocomposites, offering a cost-effective method to fabricate new optical devices.

Table 2: Comparison of advantages and disadvantages of preparation methods for concave convex soil composite materials.

Preparation Method	Advantage	Disadvantage
Solvothermal synthesis	Controllable conditions, low production costs	High energy consumption, long time consumption
Impregnation synthesis	Easy to operate, low experimental requirements	Low stability, long cycle, low efficiency
Sol-gel synthesis	Low synthesis temperature, small product size	Long reaction time, involves harmful substances
Co-precipitation synthesis	Low experimental requirements, controllable experimental time	Large product size, generate by-products
Microwave synthesis	Fast heating speed, high thermal energy utilization	Difficult to control reactions, occurrence of side effects
Calcination synthesis	High stability, easy operation	High energy consumption, incomplete crystallization

In addition, the preparation of composite attapulgite materials are calcined[37], microwave method[38] etc. The advantages and disadvantages of these preparation methods are shown in Table 2, which shows that we can screen out the best method of synthesizing composite materials by understanding the advantages and disadvantages of various preparation methods and combining them with the reality.

3 Modification methods of attapulgite composites

3.1 High temperature modification

At high temperatures, the structural and interlayer water in the attapulgite will be gradually removed[39], leading to a reduction in interlayer spacing. This process may even result in the collapse of the crystal structure and the formation of an amorphous structure at higher temperatures. Heat treatment can enhance the thermal stability, increase the specific surface area, and improve the pore volume of attapulgite, thereby enhancing its performance as a catalyst and adsorbent. It is essential to carefully control the temperature during heat treatment to prevent the destruction of the material's structure and preserve its original properties.[40–42]

Shi et al.[43] investigated the effect of calcination temperature on attapulgite in cementitious materials. It was shown that the calcination temperature changes the mineral composition of the attapulgite, affecting the content of chemically bonded water in the material. After calcination at 500 °C, the content of reactive SiO_2 in the attapulgite increased from 3.56 % to 20.96 %, demonstrating optimal hydration activity. This temperature also facilitates the dissolution of silica, significantly reducing energy consumption in the cement industry and promoting the sustainable development of attapulgite in the industrial sector.

3.2 Acidification modification

Since there are a large number of impurities in the raw materials of attapulgite, most of which do not meet the requirements of fusion materials, researchers usually place attapulgite in an acidic solution to remove impurities in the raw materials, such as metal oxides, carbonates, and other large particles on the surface. This process increases the porosity and specific surface area, changes the electrically charged properties on the surface of the material[44–46], and enhances the active sites to improve adsorption performance. Utilizing acid-treated attapulgite to enhance adsorption performance, it is commonly engineered as a functional adsorbent for removing heavy metals and other hazardous substances from water bodies.

Tan et al.[45] used humic acid to modify attapulgite to alter its adsorption capacity and the mobility of U^{6+} in the liquid phase by modulating the surface charge of the material. The diameter of the HA-attapulgite aggregates increased significantly (1,120 nm → 1,485 nm) in the pH range of 2.0–9.0. This increase may be attributed to humic acid acting as a bridging agent during the adsorption process, leading to multilayered adsorption and the eventual formation of attapulgite-HA-attapulgite aggregates, which further enhances adsorption. Electrostatic attraction between the negatively charged humic acid on the surface and the positively charged attapulgite resulted in a strong complexation with U^{6+}, thus enhancing the adsorption of U^{6+} on the composite and provided an important theoretical basis for further research on U^{6+} removal.

3.3 Organic modification

Usually, organic compounds and attapulgite are inserted into the interlayer of attapulgite minerals through the ion exchange mechanism, which increases the interlayer distance, regulates the hydrophilicity or hydrophobicity of the material, and improves the selectivity and adsorption capacity of organic matter.[47–49] The organically modified attapulgite can be used as an adsorbent in the treatment of environmental pollution, with high adsorption capacity for organic pollutants such as oils and dyes. Additionally, this material is widely used in composite materials to enhance the mechanical properties and thermal stability of plastics, rubber, etc.

Li et al.[50] successfully prepared a polyaniline/attapulgite composite (PANI/ATP) and used it as an electrode material for liquid-phase electrochemical Pb removal. Under a voltage of −0.3 V, it was found that the electrosorption equilibrium of 0.1 mM Pb(II) was reached faster with the PANI/ATP paper electrode (approximately 3 min) than with the PANI paper electrode (approximately 5 min). This suggests that the incorporation of attapulgite increases the specific surface area of the composite material and shortens the electrosorption time. The negatively polarized PANI/ATP paper electrode was capable of electrostatic adsorption with Pb(II), combined with the chelating effect between aromatic imine groups and Pb(II), and synergized with the physical adsorption provided by attapulgite, resulting in an equilibrium adsorption capacity of 15.42 mg g^{-1}. This finding offers a new approach for using polymer clay composite electrodes in the removal of heavy metal ions.

3.4 Elemental doping modification

Ion exchange modification is the process of changing the cationic species in the interlayer of attapulgite through ion exchange reactions to enhance its original properties. By exposing the attapulgite to a solution containing different cations, the existing interlayer cations can be replaced. This modification not only increases the interlayer spacing of attapulgite but also enhances its adsorption and ion exchange capacities.[51,52]

Ren's group[53] conducted a study on the effects of heavy metals in soil on maize, in which ATP-nZVI composites were prepared. These composites utilized the large number of free cations (e.g., K^+, Na^+, and Mg^{2+}) in ATP-nZVI to exchange with the heavy metals, thereby removing the heavy metals from the soil. The effective Cd content in ATP-nZVI was determined using a $CaCl_2$ solution, resulting in a reduction of Cd mobility in the soil by 57.63 % and a decrease in TCLP content by 76.64 % compared to ATP and nZVI. This indicates that ATP-nZVI effectively improves Cd stability, reduces Cd mobility, and demonstrates better stability. The surface of ATP contains a large number of silanol groups. ATP-nZVI can interact with Cd in the soil to form an inner complex, change the morphology of Cd in the soil, reduce the content of Cd released into the soil, reduce the bioaccumulation of Cd in maize seedlings, remediate the soil, and promote the growth of plants. Therefore, ATP-nZVI is an effective material for the remediation of Cd-contaminated soil.

4 Research progress in environmental and energy

4.1 Wastewater treatment

With the rapid development of China's social economy and technology, various types of wastewater emissions are continuously increasing. Due to the incomplete urban wastewater treatment system, it is unable to effectively handle different types of wastewater. This not only poses a serious threat to the environment and water resources but also impacts the quality of life and environment of local residents.[54–56] Therefore, wastewater treatment has become one of the key research areas in current social development.

Heavy metals are commonly found in industrial wastewater and can damage organ function, leading to issues such as muscle paralysis, anemia, memory loss, and impacts on children's intellectual development when they enter the human body.[57,58] Among heavy metal ions, Cr(VI) is a common source of pollution that can significantly affect the growth of aquatic plants and animals.[59] In a study on the photocatalytic reduction of Cr(VI) and p-nitrophenol in water, Ma et al.[60] investigated the effect of the addition of ATP on the photocatalytic activity of CdS-ATP composites. The presence of ATP provided many active sites for the reaction, which facilitated the immobilization of the CdS nanoparticles and prevented the agglomeration of the material, thereby facilitating electron transfer. The attachment of CdS nanoparticles to the surface of the rod-shaped ATP can be clearly seen in Figure 2. When comparing all the composites synthesized in this experiment, a kinetic rate constant of 0.4467 min^{-1} was achieved for CdS-20 % ATP, enabling rapid photocatalytic reduction of Cr(VI) to Cr(III) in the system, with the degradation rate reaching 90 %, demonstrating excellent photocatalytic activity. It was concluded by the authors that the high photoreduction efficiency of the CdS-ATP composites in a short time may be attributed to the low impedance of the CdS-20 % ATP composites, which prolonged the lifetime of the photogenerated carriers. This practical value in the application of removing chromium-containing wastewater.

Antibiotics, as a common pollutant in water bodies, can affect the metabolism of plants and animals *in vivo*, leading to aberrations or mutations in plants and animals.[61,62] For example, Tan et al.[63] successfully synthesized Bi_2MoO_6/attapulgite composites and applied them for the removal of tetracycline and formaldehyde from water bodies. Compared with pure Bi_2MoO_6, the adsorption capacity of Bi_2MoO_6/attapulgite was greatly enhanced, and the reaction rate constant (k) for tetracycline was elevated to 1.70 times the original one. This enhancement was mainly attributed to the abundant active sites on the surface of the attapulgite preventing the agglomeration of the Bi_2MoO_6 particles and broadening the light-absorbing area of the composite. In the process of formaldehyde degradation, formaldehyde molecules can quickly combine with the hydroxyl groups on the surface of the attapulgite, while the photocatalytic reaction promotes the rapid conversion of formaldehyde molecules to CO_2, accelerating the degradation process. The possible mechanism of the reaction is shown in Figure 3.

Dye wastewater is commonly found in industrial wastewater such as printing and dyeing, textile, cosmetics, etc. Most of these dyes are difficult to be biodegraded and highly toxic, which will seriously affect the growth of plants and animals after entering the water environment.[64–66] Khatun's group[67] loaded different ratios of ZnO on the attapulgite to investigate the rate of its photocatalytic degradation of methylene blue. As shown in Figure 4, in the simulated daylight illumination experiments, the degradation rate of methylene blue increased with the increase of the proportion of attapulgite in the composite material, and ZnO/40 % attapulgite showed the best degradation effect with a degradation rate of 96 %. In the subsequent experiments, g-C_3N_4 was chosen to be doped with ZnO/30 % attapulgite. Under the same experimental conditions, the degradation rate of methylene blue by g-C_3N_4/ZnO/30 % attapulgite could be enhanced to 97 %, and the reaction rate constant of the ternary composite was increased to twice that of ZnO/30 % attapulgite, greatly improving the degradation efficiency of the dye. Wang et al.[68] successfully synthesized composites of attapulgite (ATP) and spherical zinc sulfide (ZnS) using a simple hydrothermal method, as shown in Figure 5a. In the experiment of photocatalytic degradation of rhodamine B, it was found that the mass ratio of ATP in the composites affected the dispersion of ZnS. A higher ratio of ATP reduced the agglomeration of ZnS, but an excessively high ratio led to a reduction in the active species, ZnS, affecting the photocatalytic performance of the catalysts. Experimental data showed that the 40 % ATP-ZnS composite effectively dispersed ZnS and exhibited the highest reaction rate constant ($K = 0.03004\ \text{min}^{-1}$), proving that the ATP composite could enhance photocatalytic activity. The main reason is that the 40 % ATP-ZnS composite has a smaller

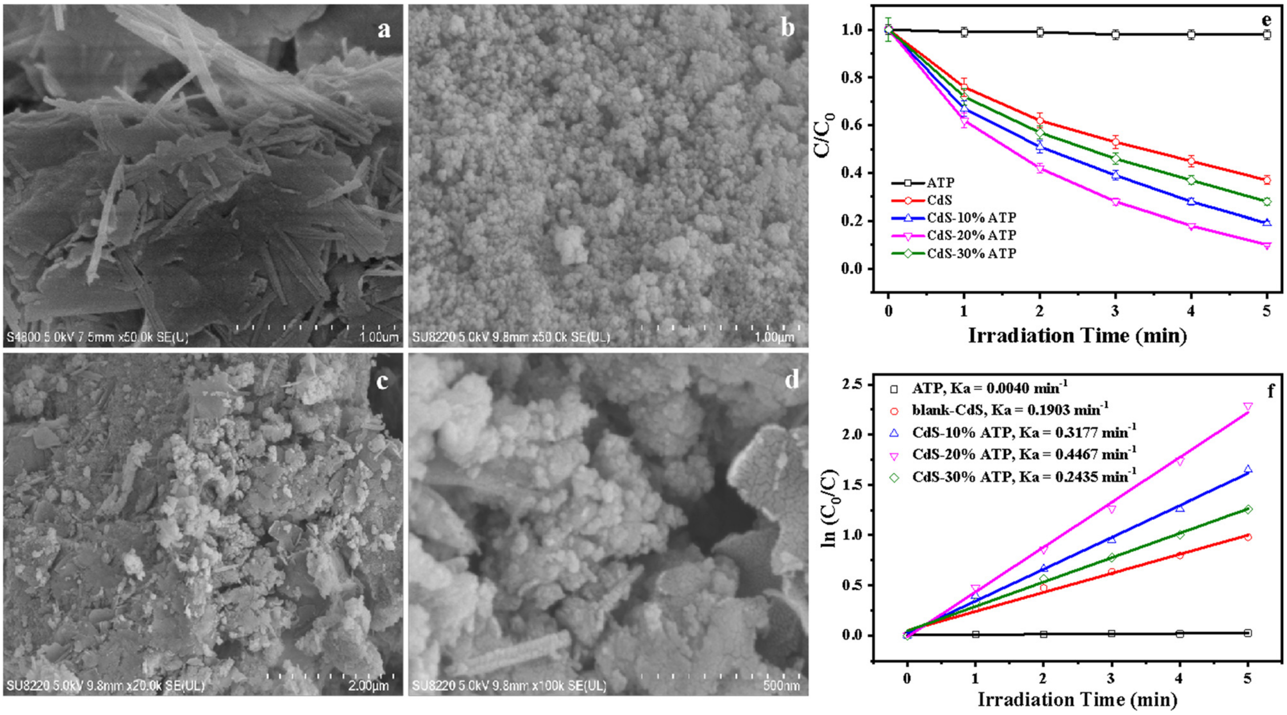

Figure 2: SEM images of ATP (a), blank-CdS (b), and CdS-20%ATP (c and d); results of photocatalytic reduction of Cr(VI) under simulated solar light irradiation for 5 min at room temperature: (e) With 5 % error bars and (f) apparent rate constant (k_a).

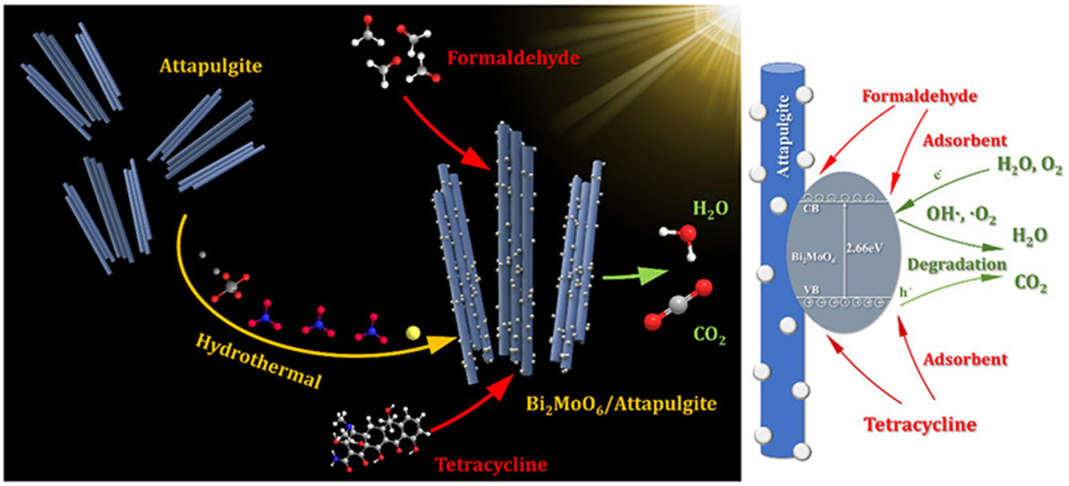

Figure 3: Possible photocatalytic mechanisms of Bi_2MoO_6/attapulgite.

bandgap than ZnS, enhancing the light absorption range and reducing the electron-hole pair recombination rate (Figure 5b–e).

In environmental waters, a large number of toxic organic compounds, such as phenol, chloroform, and formaldehyde, in addition to common heavy metals and dyes, are difficult to effectively remove due to their stable structure and low environmental concentration.[21,69,70] In the photothermal catalytic oxidation experiment of toluene, CeO_2: Yb^{3+}, Er^{3+}/ATP nanocomposites were synthesized by Huang et al.[71] using a simple precipitation method. The doping of rare-earth ions not only promoted the transfer of near-infrared light to visible light, increasing the photo-utilization of the composites, but also created a large number of oxygen vacancies, effectively facilitating the adsorption of oxygen. Meanwhile, the reactive intermediates (h^+, $\cdot O_2^-$, $\cdot OH$) generated by the oxygen vacancies accelerated the process of redox reactions in the

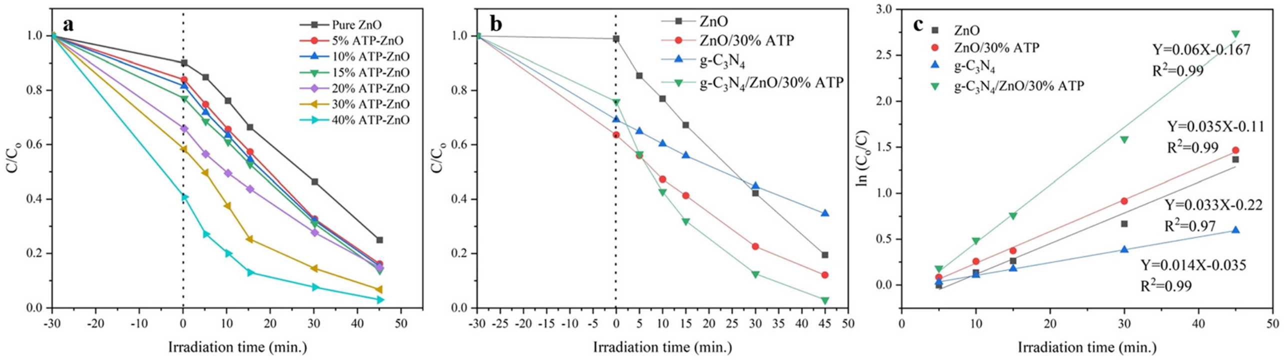

Figure 4: Under simulated sunlight irradiation conditions, (a) the effect of ATP with different ZnO loading levels and (b) the effect of various modified ZnO nanoparticles on photocatalytic degradation of methylene blue dye; (c) photocatalytic rate diagram of different modified ZnO nanoparticles.

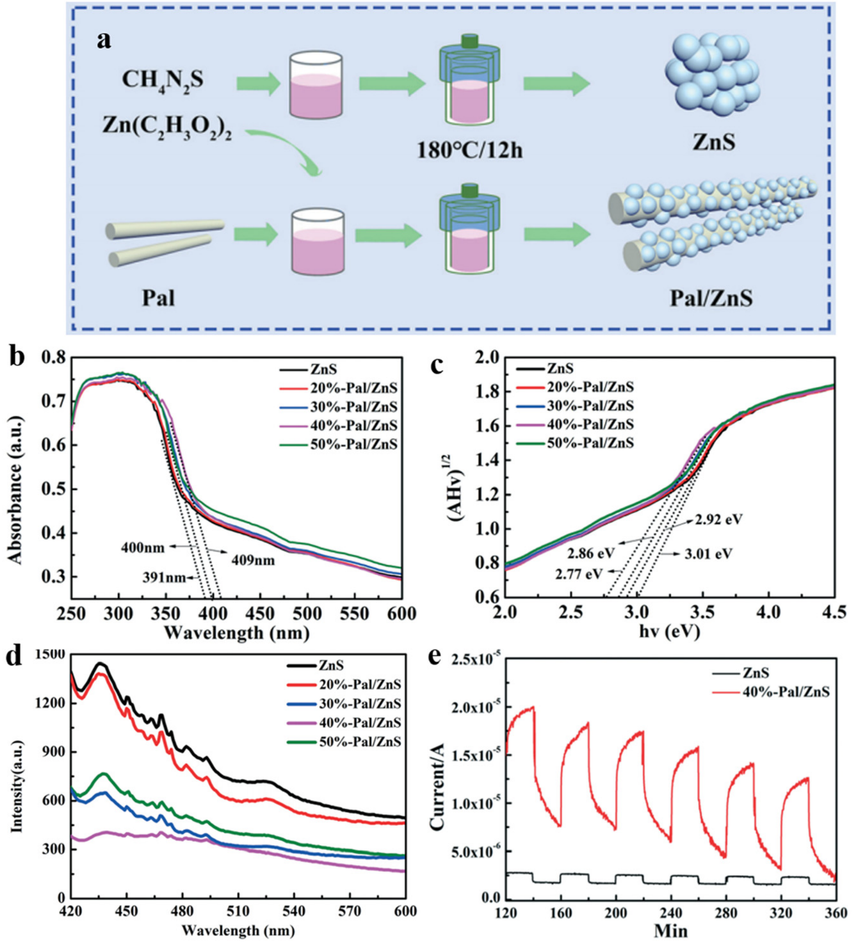

Figure 5: Schematic diagram of the preparation process of ZnS and ATP-ZnS composite materials (a), solid-state UV spectrum (b), bandgap energy spectrum (c), fluorescence spectrum (d), and photocurrent response spectrum of ZnS and 40 % ATP-ZnS (e).

photothermal catalytic process, providing a new approach for the photothermal catalytic degradation of organic compounds. The authors proposed a possible photocatalytic mechanism for photothermal catalytic oxidation of toluene, as illustrated in Figure 6.

4.2 Atmospheric pollution

With the development of industrial society and the consumption of traditional energy sources through combustion, the atmospheric environment is also experiencing serious

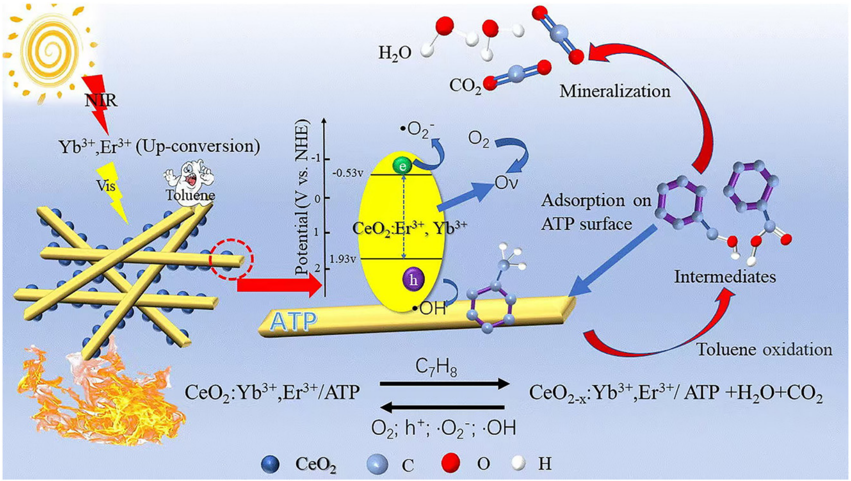

Figure 6: Schematic mechanism of photothermal catalytic oxidation of toluene over CeO_2:Yb^{3+}, Er^{3+}/ATP.

damage. Nitrogen oxides, carbon oxides, sulfur oxides, volatile organic compounds, and other pollutants are causing greenhouse effects, photochemical smog, and other adverse environmental conditions, as well as respiratory infections and diseases in humans.[72–74]

Li et al.[75] used a precipitation method to prepare CeO_2/Pr^{3+}/ATP ternary composite nanocomposites for the selective photocatalytic reduction of nitrogen oxides. In CeO_2/Pr^{3+}/ATP composites, a Z-type heterojunction exists, which results in enhanced visible light absorption of the ternary composites, facilitating the separation of electron-hole pairs. Specifically, CeO_2/Pr^{3+}/ATP (with a Pr doping molar fraction of 1 % and a mass ratio of ATP-loaded CeO_2/Pr^{3+} of 40 %) exhibited excellent performance in the photocatalytic removal of NO, achieving 90 % conversion and up to 95 % selectivity. The authors proposed a possible photocatalytic mechanism for this reaction, as illustrated in Figure 7.

Cao et al.[76] doped Sn onto In_2O_3 through a co-precipitation method, combined with microwave hydrothermal treatment and acid modification of attapulgite (H-ATP), ultimately successfully constructing Sn:In_2O_3/H-ATP composite material with an S-type heterojunction. During the experimental exploration of photocatalytic reduction of CO_2, it was found that due to the doping of Sn^{2+}, the localized surface plasmon resonance (LSPR) effect occurred on the surface of In_2O_3, broadening the light absorption range from the visible light region to the mid-infrared region and releasing high-energy hot electrons, demonstrating excellent photocatalytic reduction of CO_2 ability. As shown in Figure 8, under visible and infrared light irradiation, the CO production rates can reach 17.9 $\mu mol\,g^{-1}\,h^{-1}$ and 4.7 $\mu mol\,g^{-1}\,h^{-1}$, respectively, and the reduction performance remains stable in 5 cycles of experiments, providing an effective method for capturing and converting CO_2.

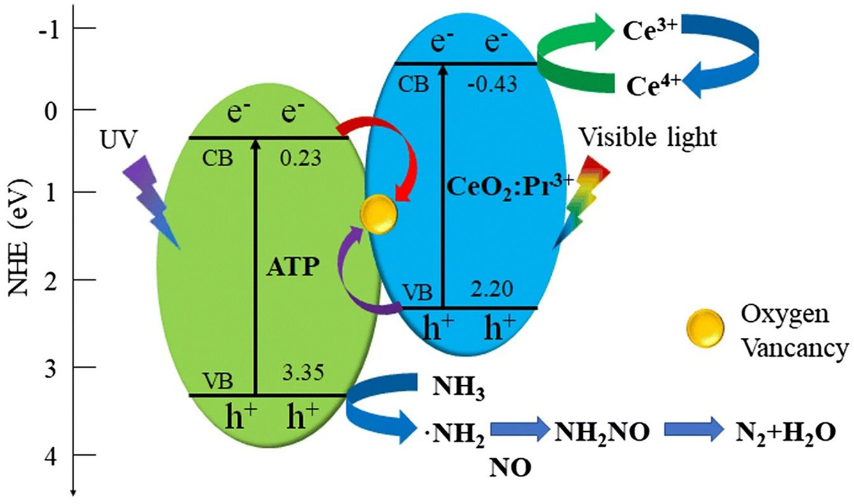

Figure 7: Mechanism diagram of CeO_2/Pr^{3+}/ATP photocatalytic oxidation of NO.

In the photocatalytic degradation experiment of acetone in air, a Cu-doped TiO_2/organic attapulgite (CTOA) nanocomposite material was successfully synthesized by Zhang's research group[77] using a simple method. Among them, CTOA-400 (with a Cu/TiO_2 molar ratio of 0.003) photocatalyst can achieve successful degradation of 90.35 % acetone within 6 h under ultraviolet light irradiation. At the same time, factors that enhance the photocatalytic activity of this reaction were explored by the authors: (1) Copper can capture and transfer electrons on the conduction band of TiO_2, thereby reducing the recombination rate of electron-hole pairs and accelerating the generation rate of hydroxyl radicals (·OH), (2) The highly hydrophobic organic attapulgite (OTA) increases the contact area between the catalyst and acetone, thereby enhancing the adsorption capacity of the catalyst, (3) By appropriately heat-treating the composite material, a CTOA catalyst with a micro-mesoporous nanocomposite structure is obtained, promoting the formation of TiO_2 crystals.

4.3 Energy

The large consumption of non-renewable resources such as coal, oil, natural gas and so on leads to energy shortages, the development and utilization of new energy sources can not be delayed[78], and accordingly the requirements for the relevant catalysts are getting higher and higher, and ATP

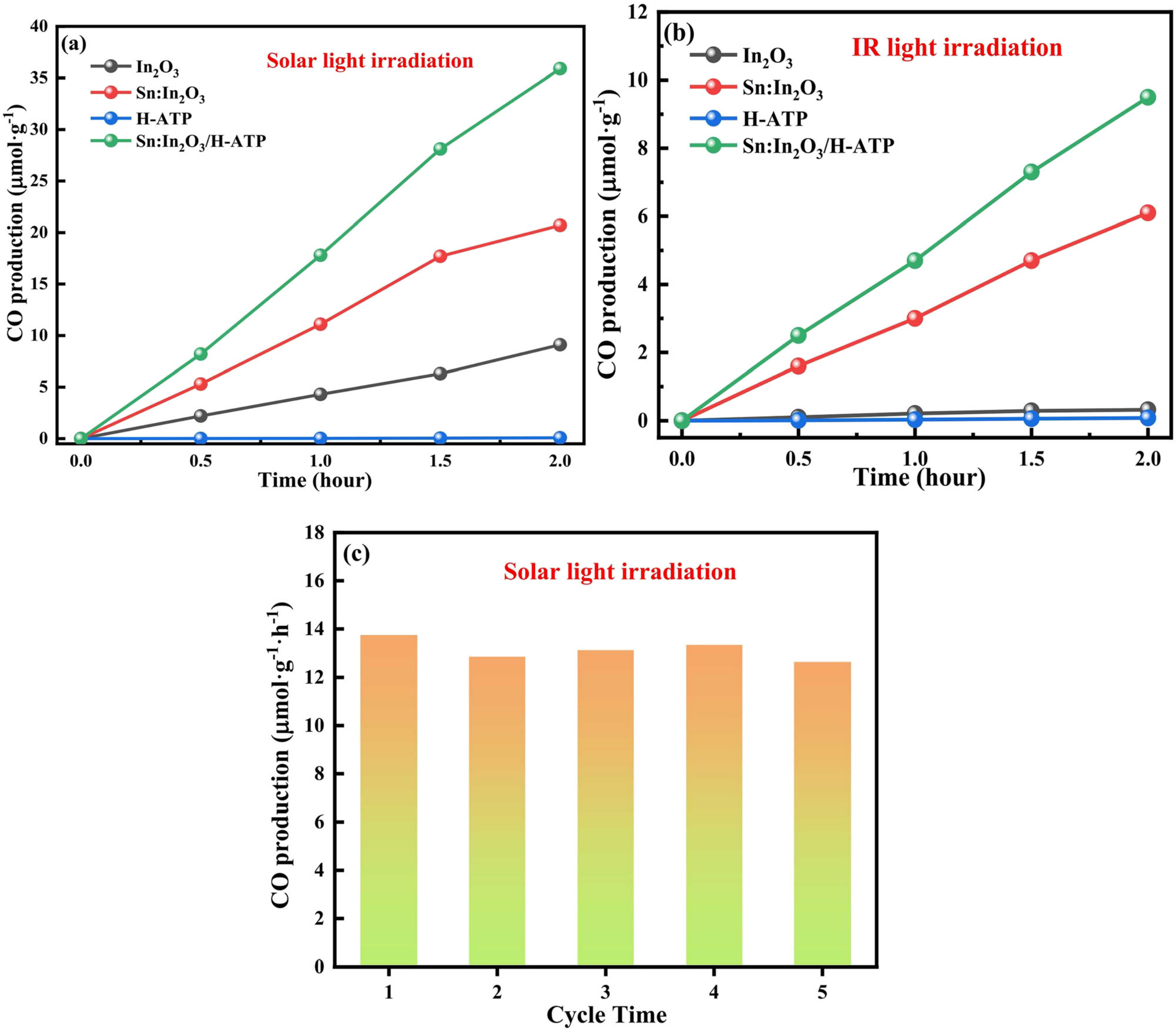

Figure 8: Time curves of CO production (a) under solar light and (b) under IR irradiation light photocatalytic CO_2 reduction over different samples. (c) Stability of Sn: In_2O_3/H-ATP after 5 cycles of CO_2 photoreduction to CO under solar light.

composites are being paid attention to and researched by virtue of their own special pore structure and economy.

4.3.1 Synthetic ammonia

In the experiment of photocatalytic nitrogen fixation, Yang's group[79] used $CuFe_2O_4$ to modify attapulgite and prepared a $CuFe_2O_4$/Fe-ATP composite clay material with a high nitrogen fixation rate. When comparing materials with different composite ratios, it was found that a $CuFe_2O_4$ composite mass ratio of 8 % resulted in the longest photoelectron lifetime (1.300 ns) and the highest photocurrent density. Under simulated solar irradiation conditions, the nitrogen fixation rate of the material reached 80 %, and the ammonia production rate was able to reach 390 $\mu mol \cdot g_{cat}^{-1} h^{-1}$. This may be due to the fact that iron ions entered the ATP skeleton, leading to the lattice reorganization of the composite material, forming a heterojunction structure, broadening the near-infrared light absorption range, and facilitating cellulose conversion.

Liu et al.[80] used a microwave hydrothermal method to load a new plasma $W_{18}O_{49}$ onto acid-modified attapulgite (H-ATP) and applied it in the study of photocatalytic nitrogen fixation. The study found that the surface of ATP treated with phosphoric acid was rough, which facilitated the loading of $W_{18}O_{49}$ on the surface. At the same time, the Z-shaped heterostructure formed by $W_{18}O_{49}$/H-ATP composite material had lower charge transfer resistance and faster interface electron transfer. The unique localized surface plasmon resonance (LSPR) effect increased the electron density, effectively enhancing the fixation of N_2. Under simulated sunlight and near-infrared light irradiation, the nitrogen fixation efficiency of 40 % $W_{18}O_{49}$/H-ATP can reach up to 138.76 $\mu mol\ g^{-1} h^{-1}$, which is three times that of $W_{18}O_{49}$ and four times that of H-ATP. The corresponding mechanism is shown in Figure 9.

4.3.2 Hydrogen energy

Conventional hydrogen production methods are limited by high energy consumption and pollution problems, so the development of efficient and environmentally friendly hydrogen production methods is deemed essential for achieving sustainable energy development.[81] CuS/P-ATP nanocomposites were successfully prepared by Zeng et al.[82] in hydrogen production experiments to investigate the mechanism of their photocatalytic decomposition for hydrogen generation. It was demonstrated that the S-type heterojunction structure formed between CuS and P-ATP can accelerate the separation of electron-hole pairs, and Figure 10 shows that 30 % CuS/P-ATP exhibits an excellent hydrogen evolution rate (286 $\mu mol\ g^{-1} h^{-1}$) and DFF generation rate (31 $\mu mol\ g^{-1} h^{-1}$), while maintaining 95 % selectivity for DFF. The mechanism of hydrogen production is as follows: under solar irradiation, plasma resonance occurs on the surface of CuS/P-ATP composites, generating high-energy hot electrons that migrate to the conduction band and participate in chemical reactions; the holes generated

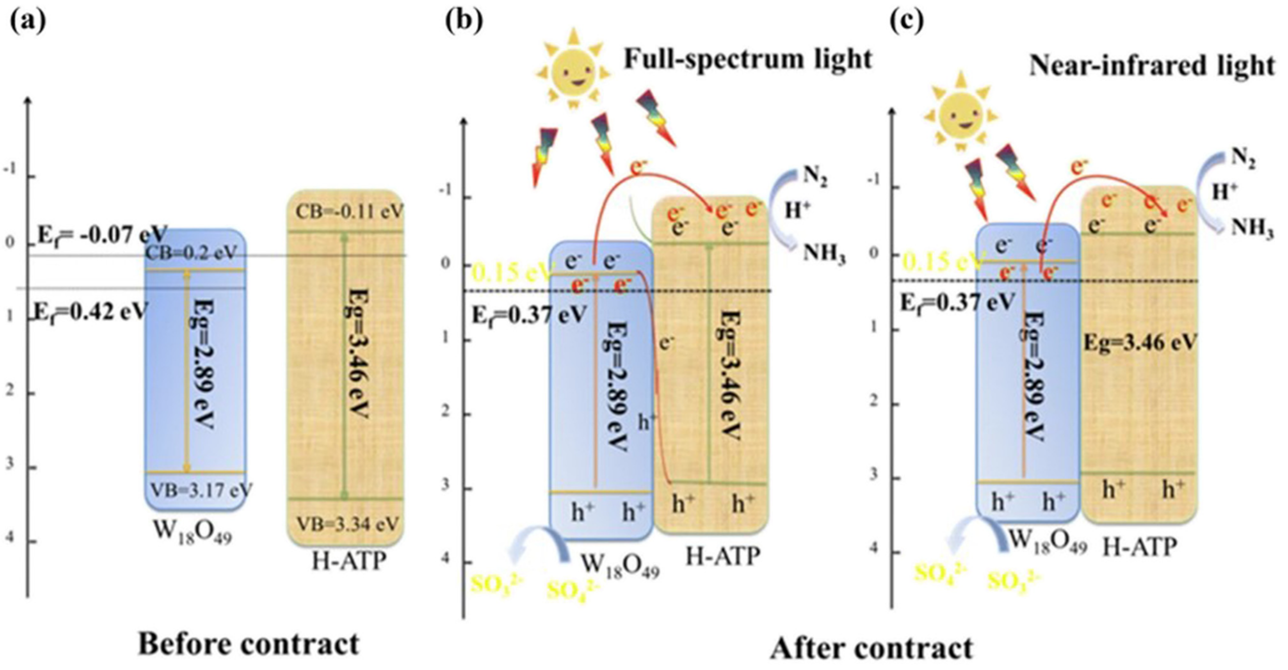

Figure 9: $W_{18}O_{49}$/H-ATP photocatalytic nitrogen fixation mechanism diagram.

by P-ATP oxidize HMF to DFF and release H^+, which undergoes a reduction reaction with the high-energy hot electrons on the surface of CuS, resulting in the generation of H_2. Under NIR light irradiation, the thermal effect increases the surface temperature of the material, facilitating the reaction between the hot electrons generated on the surface of CuS and HMF to produce DFF and release H^+ to generate H_2.

Liu et al.[83] determined the hydrogen precipitation activity of ATP/MoS_x composites by growing amorphous MoS_x on ATP *in situ*. In the aqueous solution of erythrosine B-TEOA, neither ATP nor sulfated ATP showed significant activity in photocatalytic hydrogen precipitation, while the hydrogen precipitation efficiencies of ATP/MoS_x and ATP/$Co(OH)_2$ were 18.7 μmol h^{-1} and 17.8 μmol h^{-1}, respectively, suggesting that MoS_x and $Co(OH)_2$ can be used as the active substances for hydrogen precipitation. To address the limitations of low activity and easy agglomeration of MoS_x, ATP/Co-MoS_x nanomaterials were prepared, and the hydrogen precipitation activity of the ATP/Co-MoS_x catalysts was about 67 times higher than that of MoS_x under visible light irradiation, with the apparent quantum yield at 500 nm as high as 47.7 %. In addition, the hydrogenation stability of ATP/Co-MoS_x catalysts was also improved. The main reason

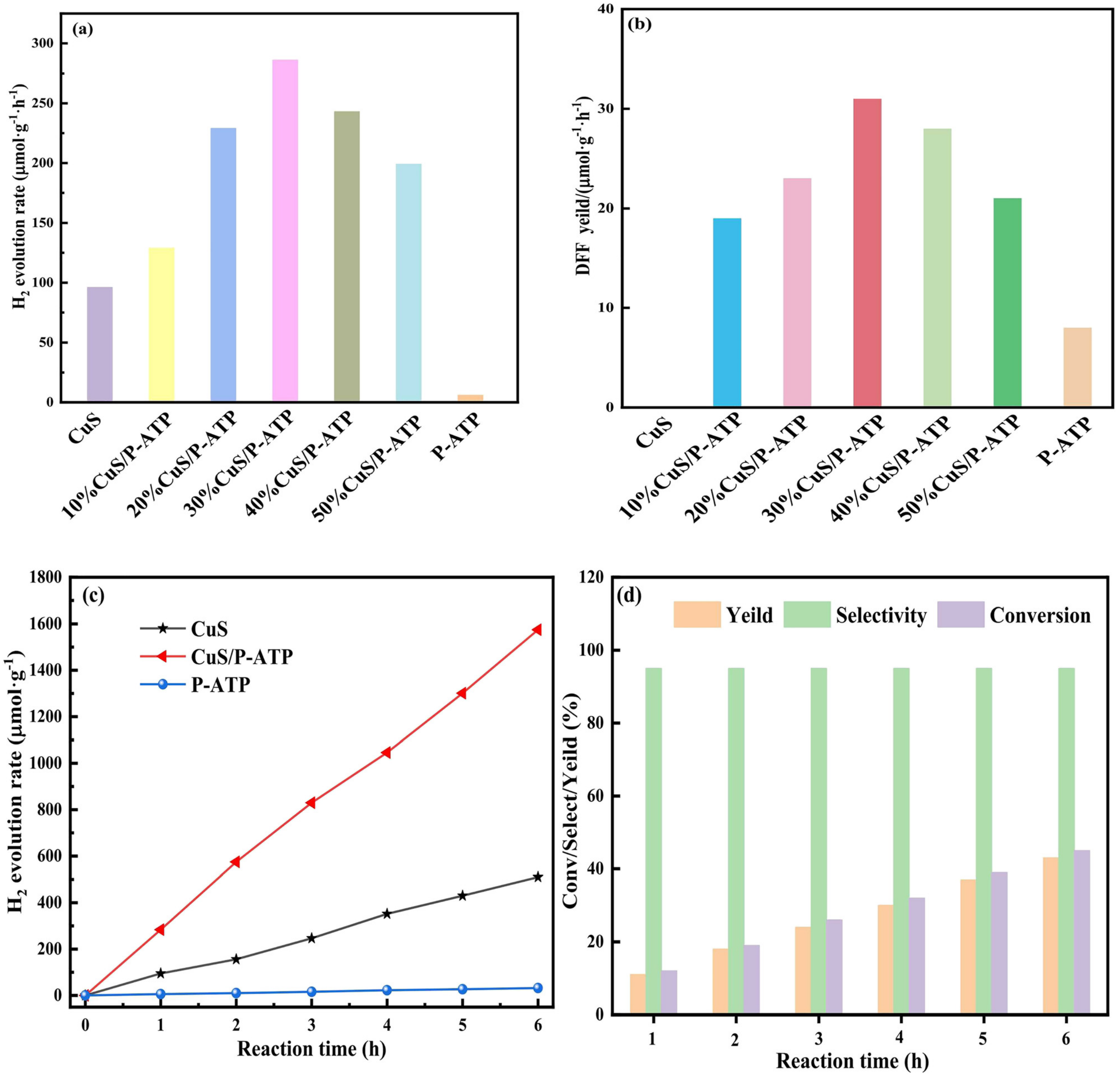

Figure 10: Under full spectrum irradiation, (a) photocatalytic hydrogen evolution activity of different materials and (b) oxidation activity of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DFF); (c) comparison of hydrogen evolution performance of CuS, P-ATP, and CuS/P-ATP under 6 hours of light irradiation, and (d) photocatalytic oxidation of 5-hydroxymethylfurfural (HMF) at different time intervals.

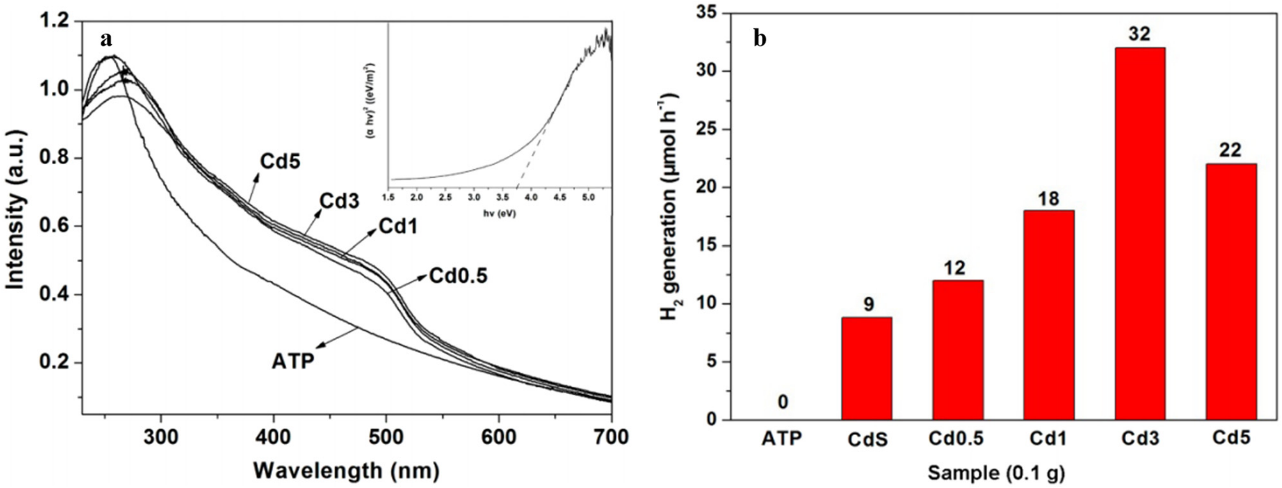

Figure 11: The comparison of (a) UV-vis absorption spectra and (b) visible light photocatalytic activities of CdS-ATP nanocomposites with different CdS nanocrystal loading amounts. Inset: Tauc equation plot of ATP.

is that the high specific surface area activity of ATP/Co$(OH)_2$ makes the in situ-grown amorphous Co-MoS_x smaller in size and uniformly dispersed, and the Co doping forms highly active “CoMoS” species, which can synergistically improve and regulate the active sites of ATP/Co-MoS_x to realize the high hydrogen precipitation activity.

In their experiments for the preparation of hydrogen energy, Zhang et al.[84] chose CdS-ATP nanocomposites as photocatalysts and investigated the decomposition of water to produce hydrogen under visible light using CdS-ATP. As shown in Figure 11, under the same experimental conditions, ATP did not produce hydrogen. However, after loading CdS nanoparticles, CdS-ATP exhibited significant photocatalytic activity. Specifically, Cd3 (3 wt% CdS) produced hydrogen at a rate of 32 μmol h^{-1}, and the rate of hydrogen production decreased as the loading amount increased. The authors concluded that the CdS nanoparticles altered the energy levels of the conduction and valence bands in the coupled system, thereby facilitating the separation and transfer of carriers and enhancing the photocatalytic activity. This finding opens up new possibilities for the development and utilization of attapulgite-based photocatalysts.

4.3.3 Second-generation fuels

Lignocellulosic biomass, as a carbon-based renewable energy source with the potential to partially replace fossil fuels, still faces significant challenges in the deoxygenation step during its conversion into biofuels. Hernando et al.[85] compared the deoxygenation performance of ZrO_2/ZSM-5-ATP and K/USY-ATP catalysts, and found that the coupling of the two catalysts increased the deoxygenation efficiency by nearly two times compared with the raw material, and the oxygen content of the bio-oil mass ratio was as low as 11.8 %, which was mainly attributed to the fact that the catalysts coupling configuration facilitated the conversion of oligomers and heavy compounds into light compounds, and promoted the ketonization reaction and hydroxylal condensation of the composites. This is mainly due to the coupling configuration of the catalyst, which facilitates the conversion of oligomers and heavy compounds into light compounds, and promotes the ketonization and hydroxyl aldehyde condensation of the composite materials, the synergistic effect of which further enhances the deoxygenation efficiency and inhibits coking phenomenon in the conversion of bio-oil. The coupling of ZrO_2/ZSM-5-ATP and K/USY-ATP catalysts is a faster and more efficient strategy for the preparation of high-quality biofuels than ZSM-5-based catalysts.

4.4 Other fields

The composite of clay minerals with antimicrobial materials has a significant synergistic effect, improving the stability, adsorption properties, and release control of antimicrobial materials. α-$AgVO_3$/ATP nanocomposites were prepared by Luo et al.[86] using the precipitation method, and the antimicrobial effect of the material was investigated. It was found that α-$AgVO_3$/ATP exhibited excellent catalytic activity in the photocatalytic inactivation of *E. coli*. ATP, serving as a stabilizer, dispersant, and growth-directing agent, effectively reduced the particle size of α-$AgVO_3$, increased the active sites, enhanced the adsorption capacity, accelerated the separation and transfer of photogenerated carriers, and provided a simple method to prepare efficient and low-cost photocatalysts for microorganism treatment.

Photochromic materials are currently widely used in fields such as optical storage, smart windows, and anti-counterfeit labels, but their application is limited due to low stability and slow color change rates. ATP/WO_3 composites were prepared by Dong's group[87] using amorphous tungsten oxide (WO_3), modified attapulgite (ATP), and polysiloxane. These composites formed superhydrophobic coatings (ATP/WO_3@fluoroPOS) with 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTES) and tetraethoxysilane (TEOS). Characterization showed that WO_3 particles, ranging in size from 5 to 10 nm, were uniformly dispersed on rod-shaped ATP. Photoluminescence experiments revealed that ATP/WO_3@fluoroPOS underwent rapid and highly reversible color conversion during UV irradiation and thermal erasure.

Fire causes serious loss of life and property, making flame-retardant materials essential for preventing the spread of fire and protecting personal safety. Gao's group[88] prepared poly(acrylic acid)/modified ATP/ZnO composites (PAA/BF-ATP/ZnO) via *in situ* polymerization using acrylic acid (AA), modified attapulgite (BF-ATP), and triethoxymethylene vinylsilane-modified ZnO as raw materials to enhance the flame-retardant and UV-resistant properties of cotton fabrics. It was found that the combination of BF-ATP and ZnO improved the flame retardancy and UV resistance of the material. The limiting oxygen index (LOI) of PAA/BF-ATP/ZnO in the appropriate ratio was 1.3 % higher than that of PAA/BF-ATP, and the burning rate was 0.24 mm s^{-1} lower, demonstrating its potential as a halogen-free and phosphorus-free flame retardant for cotton fabrics.

5 Conclusions

By introducing the research process on the preparation method and application area of attapulgite composites, the prospect of the application of attapulgite composites in the field of environment and energy is demonstrated. Researchers have combined the advantages of low cost, adsorptive, and catalytic properties of clay in the development and utilization of attapulgite, compositing it with other materials to further broaden the application value of attapulgite, such as using the adsorptive property of attapulgite to study the adsorption capacity of heavy metals and organic pollutants. Although the relevant research is still in the laboratory research stage, a large number of research results have been widely published. Due to its carrier nature, special pore structure, and excellent stability, attapulgite provides researchers with a good catalyst carrier in the preparation of semiconductor photocatalytic materials. Semiconductor materials, with their strong controllability, wide applicability, and stable performance, can expand the application fields of attapulgite and improve its functionality by combining with attapulgite. However, at this stage, semiconductor-attapulgite has made some progress in the fields of environmental treatment and energy, but semiconductor-attapulgite and its composites have been less studied in the fields of soil pollution remediation, medicine, and pharmaceuticals. For the research of semiconductor-attapulgite, it is necessary to continue to invest funds and manpower to study and explore new environmental functional materials in more depth, to make better use of the attapulgite resources and expand its application areas. At the same time, it is necessary to solve the challenges faced by the existing technology, promote the development of attapulgite composite materials in the field of environment and energy, and contribute to environmental protection and sustainable development.

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