Article

Preparation and Photocatalytic Performance of Fe₃O₄@H-TiO₂—Experimental Research and Dynamic Model

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Abstract: In this experiment, the preparation method and photocatalytic properties of H-TiO₂ composite catalyst were studied. In this reaction, Fe₃O₄ was selected as the carrier of the catalyst. In this experiment, titanium tetraisopropoxide was used as the titanium source to synthesize H-TiO₂, and then NaBH₄ was used to reduce titanium dioxide to prepare hydrogenated titanium dioxide. In this experiment, the co-precipitation method was used to prepare the composite Fe₃O₄@H-TiO₂ photocatalyst, and the magnetic inspection of the composite catalyst was performed. In this experiment, the photocatalytic degradation curve of the composite photocatalyst Fe3O4@H-TiO2 under ultraviolet lamp and simulated sunlight was studied. According to the amount of photocatalyst, the kinetic equation of Fe₃O₄@H-TiO₂ photocatalyst with different qualities was studied, and the kinetic model of Fe₃O₄ @H-TiO₂ photocatalyst was studied.

Keywords: Fe₃O₄@H-TiO₂; kinetics; photocatalysis; model; degradation

1. Introduction

Over the past decade, the technical and economic importance of photocatalysis has increased significantly. The development of photocatalysis is inseparable from the development of nanotechnology. For example, the introduction of nanoparticle photocatalysts has greatly improved the catalytic efficiency of specific materials. From anti-fog, anti-microbial and self-cleaning surfaces to water and air purification and solar hydrogen production, a wide range of applications have been developed, many of which have entered commercial products. More and more research has made photocatalysis technology more mature and its application areas are constantly expanding. Research and application focuses include anti-stick or anti-fingerprint coatings, soil repellency and decomposition of organic matter (such as microorganisms or fats).

When exposed to light, photocatalysts trigger or accelerate chemical reactions, such as causing the decomposition of organic molecules. Due to the large specific surface area of nanocatalysts, the reactivity is significantly improved compared to larger particles or bulk materials. The market capacity increased from US$85.1 million in 2009 to US$158.4 million in 2014. It is widely used in the fields of water pollution treatment and air disinfection and purification. At the same time, the derived photocatalytic glass and photocatalytic cement have also been promoted and used in real life. Pollution refers to any physical, chemical or biological imbalance that may occur in the environment such as water, air, and soil. Due to the scarcity of water resources, there are currently serious environmental problems. If we include the uneven distribution of drugs worldwide in the list of organic pollutants in water, the problem will be even more serious. Most water chemical pollutants and their metabolites are highly persistent in wastewater because they continuously pollute water resources. It has been mentioned that phenol degrades by direct photolysis under ambient conditions, but according to the US Food and Drug Administration (FDA), phenol is still one of the most commonly detected compounds in organic

wastewater. In Mexico, there are no laws regulating the concentration of this pollutant in wastewater, so the content of phenol in printing and dyeing wastewater in the environment is increasing, and there is no effective method to treat this type of compound. However, in recent years, the application of high-intensity ultrasound has been greatly developed. This method shortens the synthesis time, generates structures with atypical morphology and texture, leads to changes in crystallinity and specific surface area, and has achieved good results in degrading organic compounds. At present, there are not many topics on the degradation of emerging pollutants such as phenol by ultrasonic materials, so the synthesis of such compounds is a green and effective nanophotocatalyst synthesis strategy. In addition, photocatalytic oxidation technology is a green technology that can be used to purify water pollution. The principle of this technology is to use light to make semiconductor materials excited. This is not a conventional redox reaction. However, the rapid fusion of electrons and holes, the large gap and the restriction of mass transfer are all difficulties that need to be overcome in the practical application of the technology. Nano-titanium dioxide can block ultraviolet rays and a kind of transparent things that can produce color effects. Because of its transparency and UV-shielding properties, it caused a huge sensation as soon as it appeared on the market. It is widely used in skin care products, material protection, plastic product manufacturing, and advanced ceramics. Many data on the practical application of titanium dioxide in the photocatalytic industry show that compared with some semiconductors, titanium dioxide's unique photon absorption and reactant adsorption characteristics make it widely praised in practical applications [1]. TiO_2 has a very low photon efficiency, which is less than 10% for most degradation reactions. Electrochemical experiments show that the H-TiO_2 carrier can improve the adsorption and desorption effect and thus enhance its catalytic activity. The $Fe_3O_4@H$-TiO_2 catalyst adsorbs pollutants in an economical and effective manner. This scheme is expected to improve the efficiency of the photocatalytic process and prevent the catalyst from being separated from the reaction system by filtration or magnetization. In addition, the proposed catalyst composite $Fe_3O_4@H$-TiO_2 catalyst is synthesized by ultrasonic radiation. It is expected to improve the photoactivity of structural properties such as specific surface area, type and pore size, and present the properties of mixed oxides.

1.1. Photocatalytic Principle of $Fe_3O_4@H$-TiO_2

The photocatalytic principle of $Fe_3O_4@H$-TiO_2 is essentially the role of H-TiO_2, and the main difference between H-TiO_2 and TiO_2 is the sensitive range of light waves. Titanium dioxide (TiO_2) is mainly introduced into the environment in the form of nanoparticles through wastewater treatment plants. When cosmetics are used and the products are washed down the sink, cosmetic pigments including titanium dioxide enter the wastewater. Once in the sewage treatment plant, the pigments are decomposed into sewage sludge and then injected into the soil or distributed in the soil surface layer, and then released into the soil. Because these nanoparticles remain in sewage sludge, 99% of them are entangled on land rather than in aquatic environments. In the environment, the solubility of titanium dioxide nanoparticles is negligibly low, and once particle aggregates are formed in soil and water environments, they show stable stability. During the dissolution process, water-soluble ions usually dissociate from nanoparticles into solution when thermodynamically unstable. The solubility of TiO_2 increases when the content of dissolved organic matter and clay in the soil is high. The photocatalytic properties of nano-titanium dioxide were discovered by Akira Fujishima in 1967 and published in 1972. The process on the surface of titanium dioxide is called the Honda-Fujishima effect. Titanium dioxide in thin film and nanoparticle form has the potential to be used for energy production: as a photocatalyst, it can split water into hydrogen and oxygen.

The resulting hydrogen can be used as a fuel. The process can be made more efficient by adding oxides to the carbon. The efficiency and durability are improved by increasing the disorder in the surface grid structure of the titanium dioxide nanocrystals, allowing

infrared light to be absorbed. Visible light active nano-anatase and rutile are now widely used in photocatalysis. Under exposure conditions, many electron-carrying hole pairs appear on the surface of the H-TiO_2 example. Its chemical formula is: H-TiO_2+ $h\lambda \rightarrow TiO_2(e^- + h^+)$

The electrons and holes that appear are still very active and chemically very active. They each have very strong reducing and oxidizing properties and will fuse if not carefully considered. These unstable electrons and holes move in the valence band and conduction band to the surface of H-TiO_2 and the adsorbate. When crossing the interface and adsorption on the external surface, chemical reactions may occur [2].

1.2. Factors Affecting the Photocatalytic Activity of nano-Fe_3O_4@H-TiO_2

1.2.1. Effect of Grain Size

The activity of photocatalysts is related to the size of catalyst crystal particles. Through a large number of experimental studies, it is found that the smaller the catalyst crystal particles are, the more conducive to the photocatalytic reaction. The reasons can be summarized as follows: First, the smaller the radius of the photocatalyst crystal particles, the larger its specific surface area, because different values of the specific surface area will affect the number of active particles and the activity of adsorbed organic matter. The larger the specific surface area, the more organic matter is adsorbed, and the higher the efficiency of the reaction, thereby enhancing the efficiency of photocatalysis. The smaller the grain size, the faster the migration rate of electrons and holes generated by photocatalysis, thereby shortening the time required for electrons and holes to reach the surface of the catalyst crystal, allowing them to reach the particle surface more quickly, and ultimately reducing the possibility of recombination in the carrier body, thereby ultimately improving the photocatalytic efficiency. In actual practice, it is necessary to determine the range of particle radius.

1.2.2. Influence of Light Wave Range

Photocatalysts are substances that do not react in themselves under light exposure conditions, but can promote chemical reactions. Photocatalysts achieve catalytic effects by converting natural light energy into energy for chemical reactions, converting nearby oxygen and water molecules into free negative ions with strong oxidizing power. They can decompose almost all inorganic and organic substances that are harmful to the ecology and human body. They can not only promote reactions, but also make perfect use of nature, save resources and reduce additional pollution [3]. Waves of different lengths have different energies, and the sensitivity of catalysts to light also varies with wavelength, so another factor that affects photocatalytic activity is light waves. Ultraviolet rays and visible light have different effects on active catalysis.

1.3. Factors Affecting the Performance of Fe_3O_4

1.3.1. Size of Fe_3O_4

Conventional laboratory synthesized Fe_3O_4 has micron and nanometer scales. Nanomaterials have superior physical and chemical properties compared with atomic or bulk materials due to their mesoscopic effect, small target effect, quantum size effect and surface effect. In recent years, Fe3O4 has been widely studied due to its superparamagnetism, high coercivity and low Curie temperature. In addition, Fe_3O_4 has good biocompatibility and is non-toxic.

Ferroferric oxide is an iron oxide, and its chemical formula is Fe_3O_4or$FeO.Fe_2O_3$. It is widely found in magnetite in nature. There are several commonly used methods to obtain ferroferric oxide: the first is to burn iron powder in oxygen, the second is the high-temperature reaction of iron and water, the third is the heating reaction of iron and nitrogen dioxide, and the fourth is the reaction of iron oxide and hydrogen.

It is well known that it is very important to ensure the narrow size distribution, good dispersibility and high magnetic response of Fe_3O_4 MNPs in tissue fluids. However, the magnetic attraction coupled with the inherent large surface energy (>100 dyn/cm) makes it easy to aggregate Fe_3O_4 MNPs in fluids. Therefore, a large number of synthetic polymers such as poly(vinyl alcohol) phosphate, polyethylene glycol, polyamide, poly(glycidyl methacrylate), poly(acrylic acid), chitosan (CS) and o-carboxymethyl chitosan have been used as coating agents to modify the surface of iron oxide particles. Although polymer coating can reduce the aggregation of MNPs, it also increases the overall size of the particles, thereby limiting the expression of magnetic properties, tissue distribution, metabolic clearance and penetration into the interstitial space. Therefore, it is of great significance to develop an effective surface modification method to prepare Fe_3O_4 with narrow particle size distribution and good dispersibility using small molecule compounds in aqueous or non-aqueous solutions.

This paper studies the method of modifying Fe_3O_4 with sodium nitrate and oleic acid to prepare Fe_3O_4 with narrow particle size distribution and good dispersibility.$MNPsFe_3O_4$ MNPs were synthesized by coprecipitation at different temperatures and modified by disodium citrate and oleic acid, respectively. The effects of temperature and modifier on the crystal structure, morphology, dispersibility, size distribution and magnetic properties of Fe_3O_4 MNPs were studied.

1.3.2. Other Factors Affecting the Performance of Fe_3O_4

- Total iron concentration (mol L-1)
- Temperature/T (°C)
- Sodium nitrate concentration/(mol L-1)
- Oleic acid concentration (ml L-1)

1.4. Hydrogenated TiO2

To hydrogenate titanium dioxide, the commonly used reducing agents include active metal elements, active metal hydrides, certain non-metal elements, stannous chloride ($SnCl_2$), alkali metal elements, non-metal hydrides, salts at low valence, potassium borohydride KBH_4, sodium borohydride $NaBH_4$, and ethanol C_2H_5OH. Among them, H_2 and $NaBH_4$ are Commonly used hydrogen donors for titanium dioxide hydrogenation. The method of using hydrogen and sodium borate to carry out chemical reactions through the path of ion loss is the classic chemical reduction method. The reference methods of using $NaBH_4$ for reduction include $NaBH_4$ mixed calcination reduction of TiO_2 supported nitrogen-doped graphene and $NaBH_4$ (0.1M) reduction of titanium dioxide nanotubes [4].

The H_2 method is commonly used to place TiO_2 in a quartz tube furnace and pass high-purity hydrogen to raise the temperature to 550oC, heat treat for 2 hours, and cool to obtain H-TiO_2, but this method is dangerous and the conditions are complicated. For anatase nanopowder, $NaBH_4$ should be mixed and calcined to reduce TiO_2 to carry nitrogen-doped graphene, while amorphous titanium dioxide is more likely to choose $NaBH_4$ (0.1M) to reduce TiO_2 nanotubes.

One-dimensional nanomaterials have been widely used due to their unique surface morphology, large current carrying capacity and good mechanical strength. In particular, nanomaterials are hailed as attractive candidates for field emission materials due to their high aspect ratio and sharp tips. Carbon nanotubes, as a popular material, are the best materials for future field emission (FE). Unfortunately, they are easily oxidized and ablated under low vacuum conditions and rapidly degrade, which hinders their practical application in field emission devices. Various one-dimensional metal oxide nanomaterials, including TiO_2, SnO_2, Fe_2O_3, and ZnO_6 with nanotube, nanorod and nanowire morphologies, have been widely studied to expand field emission candidate materials due to their excellent antioxidant ability. Among various one-dimensional metal oxide nanomaterials,

TiO$_2$ nanotube arrays (TNAs) prepared by anodization have the advantages of low working performance (4.5 eV), good electrical contact performance, and easy access method. However, TiO$_2$ nanotube arrays (TNAs) can work stably under lower vacuum and higher oxygen partial pressure. So far, TNAs have not fully met the requirements for practical application in FE. There are still some fundamental obstacles to overcome, including a slightly high turn-on field and relatively low emission current density due to their low conductivity and high electron affinity. Various approaches have been reported, including hydrogenation, thermal reduction, and high-energy laser ablation. For example, in our previous work, high-purity hydrogen or solid NaBH$_4$ as a reducing agent to reduce TNAs. Although the reduction strategy can introduce a certain amount of oxygen vacancies in TNAs, the experimental process usually requires multiple steps, high temperature, long time, special instruments and strict conditions, which limits its practical application. In addition, high-quality tubular structures are difficult to obtain because these strategies in turn lead to damage to the nanotubes or inhomogeneity of the composition. Therefore, studying a low-cost and simple way to prepare R:TNAs remains a difficult problem that researchers need to think about. Recently, Xing et al. 23 found that reduced TiO$_2$ nanoparticles were successfully synthesized at a lower temperature using a strong reducing agent NaBH$_4$ in a liquid environment. During the hydrothermal process, NaBH$_4$ easily hydrolyzes and releases reduced H$_2$ and atomic hydrogen: $8Ti^{4+}+NaBH_4+2H_2 \rightarrow 8Ti^++NaBO_2+8H^+$

Under this reduction condition, atomic hydrogen promotes the reduction of Ti^{4+} to generate Ti^{3+}, which improves the conductivity. Therefore, NaBH$_4$ liquid phase treatment is expected to be an effective way to reduce the preparation cost of TNAs and improve the iron properties of TNAs. The composite magnetic Fe$_3$O$_4$ improves the iron properties in two aspects.

1.5. Fe$_3$O$_4$@H-TiO$_2$ Composite Method

1.5.1. Powder Sintering Method and Thermal/Bonding Method

Thermal method or bonding method, physical composite method and powder sintering method. The powder sintering method is to ultrasonically treat the powdered H-TiO$_2$ nanotubes in deionized water or other solutions to form a uniformly dispersed suspension, then add the carrier to be loaded and place it on a magnetic stirrer to stir them fully. After stirring, the nano H-TiO$_2$ powder will be evenly coated on the surface of the carrier, and then the carrier coated with nano H-TiO$_2$ will be sintered at a temperature below 450°C. The thermal/bonding method is used for carriers that are not resistant to high temperatures. This experiment uses this method. First, the required PDMS glue is prepared, and then the powdered H-TiO$_2$ nanotubes are coated on the surface of the carrier, and then the glue is dipped, and the above steps are repeated until the nano H-TiO$_2$ powder is evenly coated on the surface of the carrier; this method is simple and convenient.

The physical composite method requires hydrogenation of TiO$_2$.

1.5.2. Preparation of Fe$_3$O$_4$@H-TiO$_2$ by Impregnation Method

The key to the impregnation method is impregnation, so it is called the impregnation method. The steps for preparing the catalyst are quite special, and it is the most widely used production process in the catalyst industry today. The impregnation method contains a co-catalyst, and is based on the active component. It uses a salt solution to impregnate a porous carrier, and then penetrates into the interior of the substance to make the catalyst efficient. Generally, the solution with the active substance is added to impregnate various carriers. When the impregnation reaches stability, the excess solution is poured out, and then the same activation, drying and roasting steps as the precipitation method are carried out. After the water vapor evaporates, the salts of the active components can

be retained in the interior of the carrier. The salts of such metals and their oxides are regularly dispersed in the small pores of the carrier. After heat treatment and activation, the obtained carrier catalyst will be highly dispersed.

The active liquid must be impregnated onto a carrier. Common porous carriers include silica, activated carbon, aluminum silicate, diatomaceous earth, pumice, asbestos, clay, magnesium oxide, activated clay, and alumina. They can be used in powdered form or in the form of granules after molding. Oxide carriers such as silica and alumina, like many activated carbons with adsorption capacity, can be easily wetted by aqueous solutions. In addition, capillary forces ensure that the solution is quickly absorbed into the entire structure, possibly filling the capillaries on one side. The dissolution of gases can also facilitate this process. However, there are some carriers that are difficult to wet, such as extremely graphitized carbon or carbon that has difficulty adsorbing oxygen. Such carriers need to be impregnated in an organic solution or under vacuum conditions [5].

1.5.3. Deposition-Precipitation (DP)

The deposition-precipitation method is to add the metal oxide carrier to the aqueous solution to make a suspension, and then continuously stir it, keep the temperature and pH constant, let it deposit on the surface of the carrier, and then carry out filtering, washing, drying, roasting and other steps to obtain the supported gold catalyst. This method is the most effective for the preparation of high-quality nano-gold catalysts.

1.5.4. Fe_3O_4@H-TiO_2 Chemical Composite Method

The samples of Fe_3O_4@H-TiO_2 composites were prepared under ultrasonic irradiation and directly impregnated with titanium salts.

A mixture of titanium isopropoxide, ethanol and hydrochloric acid; put the prepared ferroferric oxide in an ice bath. The ultrasonically irradiated mixture of ferroferric oxide and titanium isopropoxide is treated to obtain a sample of Fe_3O_4@H-TiO_2 [6].

1.6. Application of Fe_3O_4@H-TiO_2 Photocatalysis

1.6.1. Disinfection Application

Due to its good inactivation ability against a wide range of harmful microorganisms, photocatalysis is considered a viable alternative to traditional disinfection methods such as chlorination, which can produce harmful byproducts. Photocatalysis is a versatile and effective process that can be used for disinfection of air and water substrates. In addition, photocatalytic surfaces are being developed and tested for use in "self-disinfecting" materials. Research on photocatalytic disinfection technology has shown that the process has applications in indoor air and environmental hygiene, biological and medical applications, laboratory and hospital applications, pharmaceutical and food industries, plant protection applications, wastewater and wastewater treatment, and drinking water disinfection. This paper briefly introduces the research process of different photocatalytic disinfection technologies and biological experiments, focusing on the practical application of today's technology and methods.

The application of photocatalytic processes is a viable way to solve environmental problems in the future. The disinfection of bacteria is particularly important because traditional methods, such as chlorination, are chemically intensive and have many associated disadvantages. For example, in water treatment applications, chlorine used for disinfection can react with organic materials to produce highly carcinogenic chloroorganic compounds. In addition, some pathogens, such as viruses, certain bacteria such as Legionella, and protozoa, such as Cryptosporidium and Giardia lamblia cysts, are known to be resistant to chlorine disinfection. Other treatment methods, such as ozone oxidation and irradiation using germicidal lamps (254nm), also have their own problems and limitations, such as the lack of microcolony variants for the latter. Fe_3O_4@H-TiO_2, which is commonly used in photocatalytic processes, is non-toxic, chemically stable, cost-effective, reusable,

and does not cause substantial loss of catalytic capacity. Heterogeneous photocatalysis using Fe_3O_4@H-TiO_2 is a safe, harmless, and environmentally friendly process that does not produce any harmful byproducts. In-depth research has been done on the photocatalytic removal of organic, inorganic, and microbial pollutants. Sunada et al. reported the operating mechanism of titanium dioxide photocatalytic bactericidal activity. It is due to the combination of cell membrane damage and gradual oxidative attack on internal cell components until the cell dies [7].

1.6.2. Wastewater Treatment

In recent years, environmental safety has attracted much attention, and water environment safety has gradually entered people's field of vision. Nano-titanium dioxide photocatalysis can prevent environmental pollution from the source and ensure the basic nature of industrial production. Nano-photocatalytic technology has great potential in environmental safety. This article focuses on the role of nano-titanium dioxide photocatalytic technology in the field of sewage treatment, and briefly introduces the relevant scientific research results of nano-titanium dioxide photocatalytic technology in sewage treatment. At the same time, it is pointed out that in the actual environmental safety treatment process, the technology using nano-titanium as a photocatalyst has some obvious defects. Finally, the development prospects of photocatalytic technology are discussed.

The world is concerned about the pollution of dyes, pesticides, heavy metals and other pollutants in the water environment. Fe_3O_4@H-TiO_2 is an improved variety of traditional photocatalysts. It has increased magnetic properties for easy recycling, while hydrogenation increases the width of the absorbed light wave. Although there are many methods for sewage treatment, such as microbial method, adsorption method, ion exchange method, etc., the application of these methods is limited by high cost, low degradation efficiency, secondary pollution, and complex process. Fe_3O_4@H-TiO_2 photocatalysis is a chemical method. This method has significant effects, low cost, simple and easy operation, and has broad application prospects in the future. Semiconductor photocatalysis, developed in 1972, is a new way to treat sewage [8]. It has attracted widespread attention as a potential way to solve wastewater treatment and prevent environmental deterioration.

1.6.3. Air Purification

Fe_3O_4@H-TiO_2 photocatalyst is a functional material for environmental purification. The hydroxyl radicals generated by Fe_3O_4@H-TiO_2 can kill the energy bonds of organic gas molecules, decomposing them into single gaseous molecules, making the degradation of gas and organic matter faster. It degrades toxic and harmful substances in the atmosphere into water and carbon dioxide, achieving the effect of purifying the air.

Japan began research and development of photocatalyst air purification products in 1990 and quickly put them on the market [9].

1.6.4. Road Construction Materials

In the 1980s, Japan regularly sprayed photocatalysts in traffic-intensive areas to degrade automobile exhaust. Today, road construction materials with purification capabilities include sunshades, cement, and paint. The Bird's Nest Stadium and the Shanghai World Expo Pavilion in China are both sprayed.

2. Experimental Section

2.1. Experimental Reagents

Analytical grade ethanol, titanium tetraisopropoxide, hydrochloric acid, deionized water, $NaBH_4$ (99.99%), graphene oxide, dimethylformamide (analytical grade), nitrogen, sodium nitrate (chemical grade), oleic acid (chemical grade), $FeCl_3 \cdot 6H_2O$ (analytical grade), $FeCl_2 \cdot 4H_2O$ (analytical grade), NaOH (analytical grade), phenol (analytical grade), etc.

2.2. Experimental Instruments

Glass slide, covered crucible, ultrasonic device, microporous membrane, spectropho-tometer, 250mL volumetric flask, beaker, etc.

2.3. Synthesis of TiO2

Titanium tetraisopropoxide (97%) was used to obtain amorphous TiO_2 colloid. The TiO_2 gel in ethanol was then refluxed at 373 K for 22 h and different amounts of hydro-chloric acid were added. The resulting colloidal nanocrystals were centrifuged, washed with ethanol and water, and dried at room temperature. Powdered titanium dioxide crys-tals were obtained. Sintering at 773 K for 2 h removed the organic solvent and improved the crystallinity. The colloidal TiO_2 nanocrystals were dip-coated on a glass slide, dried, and sintered at 773 K for 2 h [10].

2.4. Preparation of Hydrogenated Titanium Dioxide

Typically, 4.0 g of titanium dioxide nanoparticle powder is put together with 2 g of $NaBH_4$ (99.99%) and ground thoroughly for more than half an hour. Then it is placed in a covered crucible and heated to 400°C for 12 hours at a heating rate of 10°C min-1. After being placed in the air and cooled to room temperature, the obtained black particles are thoroughly washed with ethanol and deionized water, and dried in a vacuum oven at 70 degrees Celsius. Production of black TiO_2, namely BTNG: Graphene oxide is generally dissolved in dimethylformamide at a concentration of 10 mg/ml [11]. The suspension is ultrasonically treated for 1 hour (200W, 100kHz) to obtain a uniform dispersion, and then transferred to a 50ml high-pressure flask. After heating at 200°C for 5 hours, the product is filtered through a microporous membrane (0.02μm) to obtain the product. Also availa-ble preparation of hydrogenated TiO_2 NGQDs: 1.0 g of titanium dioxide was added to 50 mL of 0.1 mL-1 NGQDs aqueous solution. The mixture was ultrasonically dispersed for 2 h, dried at 60 °C in a vacuum oven for 2 h, and then calcined at 200 °C under nitrogen flow (99.9%, 50 mL min-1) for 2 h. The dark gray powder obtained was represented by BTNG.

2.5. Preparation of Composite Fe3O4@H-TiO2 Photocatalyst

Analytical grade reagents ($FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, $NaOH$, C_2H_6O) were used as pro-duction materials. Chemical grade sodium nitrate and oleic acid ($C_{17}H_{33}COOH$) were used as modifiers. First, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ with a molar ratio of 1:2 were dis-solved in ethanol or deionized water at different temperatures, and then sodium hydrox-ide solution (3 mol·L^{-1}) was added to the above solution, and constant magnetic stirring was performed for half an hour until the pH value was equal to 10. Then, sodium nitrate, oleic acid and were added to the suspension respectively, and the obtained Fe_3O_4 MNPs were modified for 12 hours, and hydrogenated titanium dioxide was added. The obtained material was aged, incubated for 30 minutes, and cooled at room temperature. The ob-tained particles were separated by magnetic separation and washed with deionized water and alcohol several times until the pH value reached 7. The product was vacuum dried at 60 degrees Celsius for six hours to obtain $Fe_3O_4@H-TiO_2$ photocatalyst [12, 13].

2.6. Study on the Dynamics of Simulated UV Light Irradiation

Take 200ml of phenol with a concentration of 20mg/L, pour it into a 500ml beaker, add a certain amount of $Fe_3O_4@H-TiO_2$ photocatalyst (0.5g, 1.0g, 2.0g respectively), stir with a magnetic stirring device, irradiate under ultraviolet light for 150 minutes, and take samples every 25 minutes. Take 10ml and filter it with a microporous membrane to check the concentration of phenol, use a spectrophotometer to measure the absorbance, use the Lambert-Beer law to calculate the mass concentration of phenol, and construct an appar-ent reaction kinetic model.

2.7. Study on the Dynamics of Simulated Sunlight Irradiation

Take 200ml of phenol with a concentration of 20mg/L, pour it into a 500ml beaker, add a certain amount of $Fe_3O_4@H\text{-}TiO_2$ photocatalyst (0.5g, 1.0g, 2.0g respectively), stir it with a magnetic stirring device, irradiate it under simulated sunlight for 150 minutes, and take samples every 25 minutes. Take 10ml, filter it with a microporous membrane, measure the phenol concentration, measure the absorbance with a spectrophotometer, and use the Lambert-Beer law to calculate the phenol mass concentration, and establish a table view reaction kinetic model [13].

3. Analysis and Results

3.1. Magnetic Properties of $Fe_3O_4@H\text{-}TiO_2$
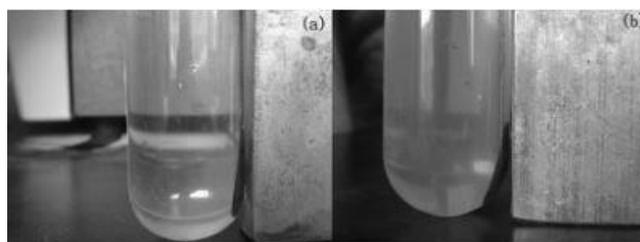
Figure 1. Magnetic separation experiment of $Fe_3O_4@H\text{-}TiO_2$ catalyst.

Magnetic separation pictures of ferroferric oxide in aqueous solution before and after loading. From the above picture, when ferroferric oxide is loaded on the surface of titanium dioxide, the $Fe_3O_4@H\text{-}TiO_2$ catalyst can still be magnetically separated well under the influence of the magnetic field, proving that the magnetism of Fe_3O_4 has not changed, which has a positive effect on the recycling of the catalyst[14].

3.2. Photocatalytic Degradation Curve of Phenol

The initial concentration was 2 mg/L, recorded as C0, and the reaction lasted for 150 minutes. The phenol concentration was measured every 25 minutes, recorded as C1, C2, C3, C4, C5, and C6. The concentrations of the UV lamp at 25-minute intervals are shown in Table 1.

Table 1. Phenol concentration measured at various time points under ultraviolet light.

light source	Catalyst quality	C1/(mg/L)	C2/(mg/L)	C3/(mg/L)	C4/(mg/L)	C5/(mg/L)	C6/(mg/L)
UV lamp	2.0g	1.826	1.635	1465	1.313	1.176	1.054
	1.0g	1.850	1.712	1.576	1.466	1.357	1.256
	0.5g	1.955	1.890	1.831	1.773	1.717	1.663

According to Table 1, the degradation curves of catalysts of different qualities under ultraviolet light are shown in Figure 2 below.
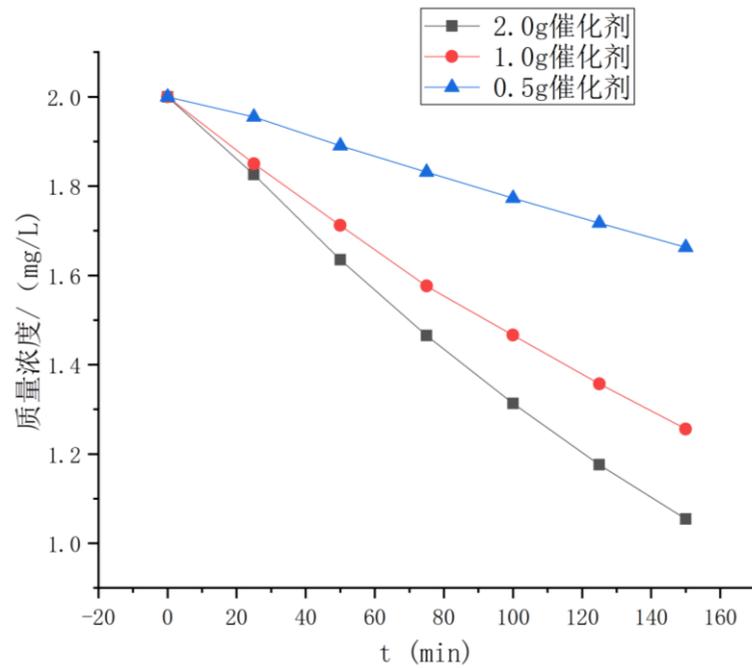
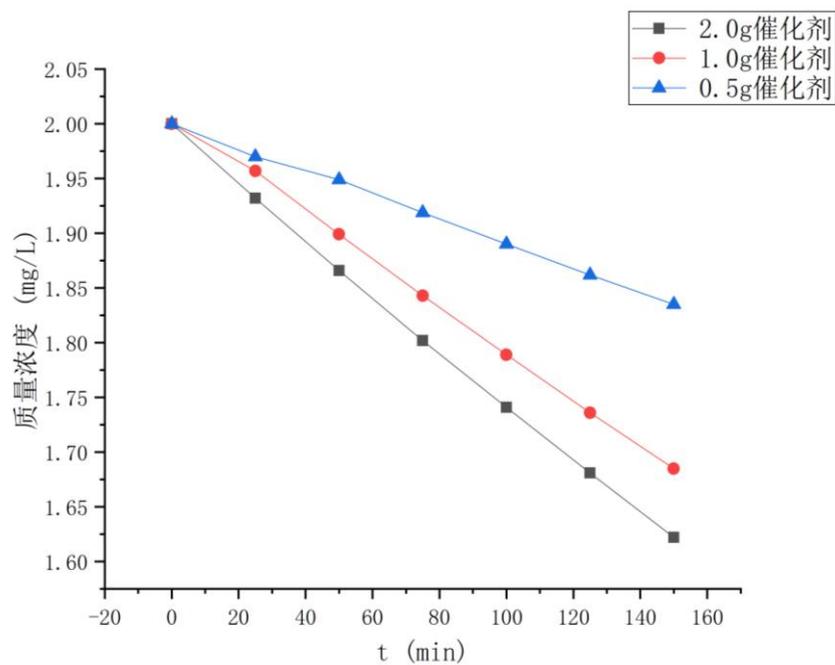**Figure 2.** Degradation curves of catalysts of different qualities under UV light.

Table 2. The concentrations every 25 minutes under simulated sunlight are shown in.

light source	Catalyst quality	C1/(mg/L)	C2/(mg/L)	C3/(mg/L)	C4/(mg/L)	C5/(mg/L)	C6/(mg/L)
Simulating sunlight	2.0g	1.932	1.866	1.802	1.741	1.681	1.622
	1.0g	1.957	1.899	1.843	1.789	1.736	1.685
	0.5g	1.970	1.949	1.919	1.890	1.862	1.835

According to Table 2, the degradation curves of catalysts of different qualities under simulated sunlight are shown in Figure 3 below.

Figure 3. Degradation curves of catalysts of different qualities under simulated sunlight.

The widely accepted kinetic model for photocatalytic degradation is the Langmuir-Hinshelwood (LH) model.

$$R=-=\frac{dC_s}{dt}\frac{k_1 KC_s}{1+KC_s}$$

Where: r-total rate of reactants [mg/(L.min)]

C_s-reactant concentration (mg/L)

t-reaction time (min)

k_1- reactant rate constant (min^{-1})

K - adsorption constant of reactants on catalyst

When C_s is very small, KC_s is much less than 1, and KC_s can be omitted, and the reaction rate will satisfy the first-order apparent reaction kinetics. At the beginning of the reaction, t is equal to 0, C_t=C. Substituting these conditions into the equation, the equation can be transformed to obtain:

$$-\ln(\frac{C_t}{C_0})=k_2 t$$

Where: k_2 first order apparent reaction kinetic constant (min^{-1})

C_t-concentration of reactant at a given time (mg/L)

C_0-initial concentration of reactant (mg/L)

t-reaction time, (min)

Since the photocatalytic degradation of phenol conforms to the first-order apparent kinetic equation, the general formula is:

$$r=k[C_6H_5]^1$$

r-rate [mg/(L.min)]

k-reaction rate constant (min^{-1})

$[C_6H_5]$-phenol concentration (mg/L)

Table 3. Reaction kinetic equations under ultraviolet light.

Fe_3O_4@H-TiO_2 catalyst quality	Reaction kinetics equation
2.0g	ln(C0/C)=0.0044t-0.019
1.0g	ln(C0/C)=0.0031t+0.0003
0.5g	ln(C0/C)=0.0013t-0.0098

The photocatalytic degradation under ultraviolet light conforms to the kinetic model LH model and is a first-order reaction.

Table 4. Dynamic equations for simulating sunlight irradiation.

Fe_3O_4@H-TiO_2 catalyst quality	Reaction kinetics equation
2.0g	ln(C0/C)=0.0014t-0.0009
1.0g	ln(C0/C)=0.0012t-0.0085
0.5g	ln(C0/C)=0.0006t-0.004

The photocatalytic degradation under simulated sunlight irradiation conforms to the kinetic model LH model and is also a first-order reaction.

Table 5. Phenol degradation rate under different conditions.

light source	Catalyst quality	Reaction rate constant/min^{-1}	Reaction rate /[mg/(L.min)]
Ultraviolet light	2.0g	0.0044	0.086
	1.0g	0.0031	0.06
	0.5g	0.0013	0.026
Simulating sunlight	2.0	0.0014	0.028
	1.0	0.0012	0.024
	0.5	0.0006	0.012

4. Experimental Conclusion

(1) Using chemical grade sodium nitrate and oleic acid ($C_{17}H_{33}COOH$) as modifiers can reduce the aggregation effect of Fe_3O_4 and obtain nanoparticles with more uniform size distribution.

(2) Analysis of the phenol degradation curves of photocatalysts of different weights (2.0g, 1.0g, 0.5g) under UV light and simulated sunlight every 25 minutes shows that the phenol degradation curve is roughly linear. The degradation effect of 2.0g photocatalyst is the best among the three groups. The degradation effect is best under UV light. And under ultraviolet light, the maximum degradation rate is the corresponding group of 2g photocatalyst, which is about 42.28%.

(3) In this experiment, the kinetic model of photocatalytic degradation of phenol is the LH model, and it is a first-order reaction. In the comparative experiment of this experiment, the maximum reaction rate constant is 0.086 mg/(L.min). In addition, the reaction rate of the same mass of catalyst irradiated by UV light is greater.

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