

Progress on photocatalytic degradation of organic pollutants by

Graphene/tio₂ composite materials

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Abstract: Graphene ? a New kind of carbon nano-materials with a large specific surface area Then Excellent electrical conductivity. When I is incorporated into TiO₂ Semiconductor to form a composite materials , TiO₂ Photocatalytic performance could do greatly enhanced and , composite has extensive application prospect in the field of photocatalysis . Graphene in titanium dioxide/graphene Nanocomposites can Promote effectively Separation of electron and hole, , and enhance The absorption efficiency inTiO₂ surface for Organic pollutions In certain Extent . In This Review , Preparation methods of graphene /tio₂ composite Nanomaterials and their application in Photocatalyticdegradation of organic pollutants are reviewed. and , mechanism to Photocatalytic enhancement by Graphene/tio₂ Composites is also analyzed. Finally , The future prospecton the trends of Graphene/tio₂ composite photocatalyst is also given .

Keywords: Graphene ; TiO₂ ; photocatalysis ; Nanomaterials ; degradation ; Organic pollutantsCatalyst

Hundred

photocatalytic oxidation technology (photocatalytic oxidation) Yes

A new green advanced oxidation technology , to directly use the sun light catalytic degradation of organic pollutants in waste water and air at ambient temperature and atmospheric conditions Dye the advantages of , with process simple , easy to operate , and degraded

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Total no two pollution , has broad application prospects in the area of environmental protection . the core of photocatalytic oxidation technology is the development of high efficiency photocatalyst . meshbefore , The research of Photocatalyst is more than TiO₂ , ZnO , SnO₂ , CdS , BiVO₄ , WO₃ , and so on , where TiO₂ has a high catalytic efficiency ,

Property Stability , Cheap and non-toxic , benefits such as reuse ^[1] , is considered an ideal Organic Light degradation catalysts . but

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Ti O₂ has a wider band width (anatase Ti O₂ 's throttling degree five g=3.2 [] EV), can only absorb short wavelengths of ultraviolet , and this divided light only for solar energy 3%~ 5, use of solar energy Low rate . also , in photocatalytic degradation , through light excitation generated electronic - hole pair with high activity , easy to replyclose , making photocatalytic reaction quantum inefficient . How to reduce Ti O₂ bandwidth and excitation of optical catalysts

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- Hole pair compound probability, Enhanced visible light response performance and photocatalytic performance become the focus of the current research on new photocatalytic materials. The researcher did a lot of modification research for this such as metal ions doping [2], Precious Metal sinks product [3], Semiconductor composite [4], Surface photosensitive [5] etc to improve TiO₂ photocatalytic activity of. Recent research finds, TiO₂ Light Catalyst with activated carbon [6], carbon nanotubes [7], Graphene [8] complex can be significantly Improve photocatalysis performance, where the compound with graphene is most noticeable.

Graphene (graphene) is a carbon atom from a single atom layer through sp² honeycomb two-dimensional carbon with hexagonal arrangement after hybridization new material [9], Its single-layer thickness is only 0.335 nm, is built with its His carbon material such as fullerene, carbon nanotubes (cnts), graphite basic structure Unit. vs. Fullerenes and cnts compared to graphene with better conductive properties [10] (room temperature electronic 迁移率 shift rate up to 2 × 10⁵ cm² • V⁻¹ • s⁻¹), mechanical Properties [11] (1060 GPa), Thermal conductivity [12] (3000 W • m⁻¹ • K⁻¹), and graphene also has a larger surface area [13] (Theoretical value is approximately 2630 m² • g⁻¹), can thus become a better performing catalyst carrier material. convert graphene to TiO₂ Combined preparation of graphene /tio₂ composite photocatalyst, with excellent electronic transmission performance and Super Large surface area Properties, significantly improve photocatalysis efficiency, can Enough to solve the bottleneck problem in photocatalytic reaction. article details about graphene /tio₂ Preparation of composite photocatalysis materials, analyzes the mechanism of graphene-enhanced photocatalysis and summarizes the near Recent studies on photocatalytic degradation of organic pollutants and the development prospects.

1. Graphene /tio₂ Preparation of composite materials

1.1 Preparation of graphene

Graphene was first in the Year by UK Manchester Large

Professor of physics Geim, and so on [14] through the micro-mechanical stripping of the. This method of preparing graphene is of high quality but extremely low productivity, cannot meet industrialization requirements. with the rapid preparation technology of graphene development, Researchers have developed numerous methods for preparing graphene, its apply a wider range of epitaxial growth methods [15], Chemical vapor deposition CVD law [16] and graphite oxide reduction [17] etc. where graphite oxide Restore can be efficiently produced in a relatively simple process High quality graphene, Is the current large-scale preparation of graphene unique valid way [18], preparation process as shown in diagram 1. The main If graphite powder is evenly dispersed in the concentrated sulfuric acid, strong oxygen, such as concentrated nitric acid Mixed acid, add oxidants such as potassium permanganate get oxidized stone ink, The oxidation process is to insert some hydroxyl groups between the graphite layer, carboxyl Group, and Epoxy-like oxygen-containing functional groups, To increase graphite layer spacing, and then Ultrasound-treated graphite oxide (go), then through water Reduction of a strong reductant such as hydrazine or by hot split restore, electrochemistry Reductive Graphite oxide (RGO).

Graphite Reduction is the simplest way to prepare graphene. Valid method, But this method and mechanical stripping method, Chemical vapor sinks Lake CVD not high purity compared to prepared graphene, But Most of the oxygen-oxidizing functions of the graphene oxide surface during the restore procedure The regiment can be restored, But the prepared graphene still retains a small number of Oxy-functional Group, thus graphite prepared by graphite reduction method graphene known as reduced oxide graphene (RGO) or functional graphite allyl. Now in the literature, the graphite for reduction by graphite by oxidation allyl and TiO₂ The combines the composite materials that are prepared with different names, Some of the text offer is called rgo/tio₂, and others are called directly gr/tio₂, This article unifies the method of reduction by graphite oxide graphene with TiO₂ combination of composite materials called RGO/ TiO₂, and other methods for the preparation of high-purity graphene with "" TiO₂ combined with a composite of composites called gr/tio₂.

1.2 Graphene /ti O₂ method for preparing composite materials

Graphene /tio 2 The composite photocatalyst was first in the 2008 Year by Williams etc [No] method of reducing graphene by ultraviolet irradiation from . current , graphene/tio 2 Composite Preparation method main Have sol - Gel method , Hydrothermal method , , in- situ growth, and so on . regardless of which method , its rationale is to grow titanium dioxide nanoparticles in oxidized stone by the hydrolysis of titanium dioxide, or through a ti's , precursor. ink surface , then chemically restored , hot Restore, and so on , Oxidation of graphene to graphene and get graphene . /tio2 compound material .

1.2.1 Sol - gel Sol - The Gel method is usually the first of the titanium body such as titanium alcohol salt (butyl titanate or titanium inorganic salts (four chloride titanium ()mix and stir with graphite oxide solution , Graphite oxide binds to titanium by hydrogen bonding forces and occurs condensation , Poly the Final form has a Ti- o-ti Three-dimensional network structure gel , then after baking and grinding to get graphene /Ti 0 2 Composite . sol - Gel method compared with other methods , process mature ,Graphene Easy doped and low preparation cost , The composites are of high purity. , but there are also longer preparation periods , Graphite in roasting process Reunion is not enough . in the Sol - Gel Preparation process , Graphite oxide The preparation method of a olefin , Doping of graphene , calcination temperature factors The has a significant effect on the photocatalytic properties of composites . by changing in hummers The oxidized graphene prepared by the method , degree of oxidation more thanhigh , Promote photocatalysis reaction . The addition of the graphene enhances the composite photocatalysis performance , But adding too much will make the primarycatalytic Ti 0 2 The catalytic efficiency of is affected , causes the composite material photocatalysis efficiency for materials [1] . reduction of oxidized graphene with oxidationgraphene compared to , stronger conductivity , thus roasting with the temperature + , reduction of graphene oxide increased , Composite's Strong conductive performance ,Enhanced photocatalytic activity , But the temperature is too high causes ablation of samples [1], The roasting temperature is generally controlled by the 550° C below .

Chen Chunming [a] using Sol - Gel Preparation Go / Ti 0 2 Complex composite material and further heat treatment so that go restore with performance excellent RGO/Ti 02 Composite . with photocatalytic degradation of a orange for research object , examines the calcination temperature , Graphene composite Effect of the amount on photocatalytic properties of composites . results show , Bake Burn temperature control in C, Graphene Doping to 3% (quality) prepared RGO/T 102 composite photocatalysis material main crystal phase is anatase mining TiO2, with Best Conductive performance , performance of photocatalysis performance most ok , degradation efficiency of methyl orange is significantly higher than single One-anatase TiO2. Shing etc [1] using Sol - Gel Rule Prepare rgo/tio2 composite materials for photocatalytic degradation of methylene blue and Rhodamine B, and study The comparison of a simple mixed-method preparation of rgo/tio2 Composite and go/tio 2 after the reduction of sodium borohydride RGO// TiO 2 photocatalytic degradation performance of composites . knot results show , on go / TiO2 Sodium borohydride restore procedure , Preserves down carboxylic groups with TiO2 Surface hydroxyl occurrences with form Ti - O - C Chemical Key , Strong rgo-tio2 between electronic transmissions , thus go/tio2 sodium borohydride reduction rgo/tio2 Composite material with simply RGO and TiO 2 Mixed composite composites have a certain range of properties compared to photocatalytic degradation.increase . 1.2.2 Hydrothermal hydrothermal method is preparation of graphene /tio 2 Composite Material Material common methods , It is the oxide of graphene and the four-butyl titanate , and so on a certain proportion of titanium source to move into high-pressure water hot kettle, etc. closed reaction container , under high temperature and pressure , Graphite oxide The olefin is reduced to graphene at the same time as the , step to get graphene /tio 2 composite photocatalyst . Hydrothermal preparation process , No need for duplicate composite materials for high-temperature roasting , It's good to avoid graphene. Reunion issues , and the prepared composite has a good crystallinity , Production High Purity . Pei Foyun etc [next] to eosin ,go and TiO 2 to original Preparation of Eosin by hydrothermal method rgo/tio2 Composite material material, The band gap of Composite was found by ultraviolet diffuse reflectance spectrometry by 3.25 EV down to 2.75 eV, extends the absorption range of the light , and The photocatalytic activity of the composites prepared by has also been significantly improved . High . Khalid etc [1] Use simple hydrothermal synthesis Rgo/tio2 composite , The addition of the graphene converts the spectral response of the

composite to a fan surround extend to visible light area , Increase utilization of visible light , and The photocatalytic activity of the composite is significantly stronger. , on visible light Next , degradation rate for methyl orange is significantly higher than pure TiO₂ . Zhao et al^[1]Graphite oxide and butyl titanate as raw materials through hydrothermal synthesis rgo/tio₂ composite photocatalyst , and methyl methylene blue as Target , rating RGO/TiO₂photocatalysis of Composites can be . results show ,RGO / TiO₂ The photocatalytic degradation of is significantly higher to pure TiO₂ Granular , and improved stability of composites . 1.2.3 in-situ growth method is also the preparation of graphene / TiO₂ One of the widely adopted methods of composite photocatalyst , This method is will TiO₂The precursor and the oxidized graphene compound , by controlling the precursor's hydrolysis , with oxygen-containing groups on graphene oxide as crystalline sites ,makes the TiO₂ nano-particles grow crystals on graphene oxide , and getting longer Big , and then restore oxidized graphene , Finally get the graphene /tio₂ Composite Light Catalyst . Liang wait^[1] to go and butyl titanate as original material by in-situ growth method rgo/tio₂ Composite . First , butyl titanate in Go surface hydrolysis generates an amorphous TiO₂ nanoparticles , and then undergo a hydrothermal reaction to crystallize into anatase type TiO₂, at the same time go get restored , Final rgo/tio₂ composite .

In addition to the common 3 outside , Some methods also to achieve graphene /tio₂ Preparation of composite materials , as self-assembly Law^[29-30]atomic layer deposition^[10], and so on , However, the cost of the preparation and the restrictions on technical conditions , These methods have less application in actual synthesis .

2. photocatalysis Promotion mechanism

Graphene /tio₂ Composite and pure TiO₂ compared with graphite The addition of the makes the photocatalytic activity of the composite significantly higher. , on The photocatalytic degradation of organic pollutants has broad application prospects .

It is now widely believed that graphene / TiO₂ composite photocatalytic degradation has The mechanism of the pollutant is : when TiO₂ energy equals or greater than band gap light (plus > five g) irradiation ,TiO₂ Price band (VB) Electronic on absorbing the energy of the photon, then jump 跃 to high-energy guide band (CB) , price with upper form into corresponding holes , to produce a luminous electron (e⁻)- void (H⁺) to . These electrons and holes can be adsorbed on TiO₂ on the surface of the particleOH or O₂ reaction Generation • OH and O⁻ free radicals such as , these free radicals have high activity , can be adsorbed organic contaminants catalytic degradation to CO₂,H₂O non-toxic harmless small molecules^[a]. But these luminous electrons , holes are very unstable , easily on TiO₂ particle interior or surface composite , reduce catalytic activity . when the is introduced into the photocatalysis system , available with graphene High carrier rate (2 X 10⁵ cm² • V⁻¹ • s⁻¹) features quickly fires Electron moved to graphene sheet structure , instead of accumulating in TiO₂ surface , Effective suppression of light-born electronics - void pair composite , can generate more highly active free radicals , significantly improve TiO₂ photocatalytic activity sex . kamat wait^[33-34] Pass to TiO₂ photocatalysis restore Go prepare rgo/tio₂ The process of the composite is studied by transient absorption spectroscopy Investigate the effect of graphene transfer on light electrons . research shows , with Increase in graphene addition , TiO₂ on the surface Ti⁴⁺ defect bit The amount of light electrons captured is decreasing , This part of the reduced light generator is apparently shifted to the graphene surface , confirms the graphene's light live electronic delivery , and they also study the use of the Step 跃 Move process further confirms that graphene acts as an electron receptor for Into the light raw electronic - The role of the separation . graphene with TiO₂ Duplicate timely , not aligned in graphene n electronic TiO₂ , Ti atoms occur to a certain degree of chemical formation Ti first C or Ti first O - C doped chemical key^[1] , To form a doped energy level , makes the TiO₂ Forbidden for width narrowed , a certain redshift ,extending response to visible light , increases the utilization of visible light . addition , Graphene Unique single origin child-layer two-dimensional planar structure and surface has a large number of n electronic and containing aromatic rings pollutant molecule occurrence n-n key conjugate action^[+] , can adsorb

more pollutant molecules, To improve photocatalytic degradation efficiency. diagram 2 for graphene /tio 2 schematic diagram of photocatalytic promotion of composite materials.

3. Graphene /tio2 Photocatalysis reduction of composites solution Performance

Graphene /tio 2 composite photocatalyst for waste water and air The contaminants in have better catalytic degradation, especially to methylene base Blue [All], rhodamine B [pdf], methyl Orange [all], 2,4- two chlorobenzene sour [/] etc organic pollutants, can be completely converted to H2O and CO2 etc Small Molecular substance. Zhang etc [a] using a simple one-step hydrothermal method To rgo/tio2 Composite for photocatalytic degradation of methylene blue (MB). graphene with TiO2 Composite allows light absorption of composite materials range extended to visible light area, still has under visible light high photocatalytic activity. and the benzene ring structure of graphene and the methylene methyl The base blue molecule exists stronger n-n key Action, can adsorb more sub methyl blue molecule and fully diffuse to graphene andTiO2 surface. addition, graphene acts as electron receptor, accelerating electron from TiO2 interface transition, significantly increases optical quantum efficiency. thus,rgo/tio2 The photocatalytic activity of a composite material is significantly higher than that of pure TiO 2, and Graphene holds There are more than carbon nanotubes (cnts)More excellent conductive properties [42-43], electronic move stronger, Can promote the light-born electron more effectively - void separation of pairs, A that is prepared as a carrier rgo/tio 2 Composite Material The photocatalytic activity of the material is also significantly higher than the same carbon content Cnts/tio2 composites, on waste water MB with high degradation efficiency, rgo/tio2 Composite to MB degradation mechanism as a diagram 3: . Chen etc [all] to TiCl3 and go as starting material using self-assembly method with p/n The of the heterogeneous knot go/tio 2 Composite materials for catalytic degradation of methyl orange. p/n heterogeneous knot formation not only can effectively promote the transfer of light-born electrons, significantly improves composite photocatalytic activity of materials, And can make the composite wavelength greater than the 510

nm The visible light of the fires, extend response to visible light, can be See light, showing high degradation efficiency for methyl orange. Li wait [a] Prepare Rgo/tio2composite materials for photocatalytic degradation of bisphenol A. the addition of graphene enables the photocatalytic activity of the composite to be enhanced increase, The also increases the adsorption of contaminants by composite materials Ability. under Ultraviolet illumination, RG0/ Ti 0 2 composite material to Bisphenol a photocatalytic degradation rate is pure Ti 0 2 (2.93 times).

in Graphene / Ti 0 2 During the preparation of the composite material, different ruler -inch oxidized graphene can be with Ti 0 2 particle composite preparation structure not same composite material. Dozens of nm go and size range in Hundreds of nm even a few microns go compared to, surface and Edge contains with more hydroxyl, carboxylic and epoxy-containing functional groups, thus with stronger hydrophilicity, has better dispersibility in solution. these go through oxygen-containing functional groups and TiO2 nanoparticles between interact to form a new type of core - shell structure of graphene /tio 2 Composite (r-ngot), The structure and TiO 2 load on sheet stonestructure on the graphene (r-lgot) vs., to increase graphene and TiO2 Direct contact Area, Accelerate Electronic transfer, significantly reduces light health e - compound probability of hole pair, displays higher photocatalytic activity sex [N], Two different structure of composite material preparation process as shown 4 shows. for kernel - shell structure's composites, graphene load on TiO2 granular surface, to accelerate electron transfer, Thus a composite material has a higher photocatalytic activity, But graphene is not a load The more the IS, the better the photocatalytic Properties of the composites are. Wang wait [I] Synthesis of graphene by hydrothermal method TiO2Nuclear nanoparticles - Shell composite materials for photocatalytic degradation of acetone in the air, and look at the the photocatalytic degradation of graphene in composite materials affect. results show that, Excessive load can cause graphene to light the Absorption enhanced so that the main catalytic TiO 2 To light Absorption Reduced, The efficiency of photocatalytic degradation of composites is reduced low. as shown 5, When the amount of graphene is

overloaded, TiO₂ To light The Utilization of the is reduced by a decrease in the amount of light generated by, making The photocatalytic activity of the composites weakens the. by comparing different graphite

Influence of the amount of butadiene load on the photocatalytic activity of composite materials, To determine the best load to 0.05% (quality), Graphene under this condition /tio₂ the highest photocatalytic activity of composite materials, photocatalytic degradation of acetone by rate is pure TiO₂ 1.7 Times.

to enhance the kernel - graphene and in Shell composites TiO₂ Interaction between the particles, make graphene wrap tighter, to To make surface modification to TiO₂[]. Lee wait [1] Use 3- Amino propyl Tri-ethyl siloxane to TiO₂ particle surface modification, makes the TiO₂ The surface introduces positively charged amino groups, and Go surface containing oxygen functional groups are negatively charged, go and modified TiO₂ The particles are between the in Electrostatic force, close together. on this side of the law Graphene /tio₂ core - Shell composite with higher photocatalysis active, band gap width also decreased, in visible light, to degradation efficiency of methylene blue is significantly higher than r-igot and TiO₂.

different shapes of TiO₂ and graphene compound, its photocatalytic activity has a significant difference. vs TiO₂ nanoparticles compared to, TiO₂ nanotubes (TNT) the photocatalytic activity increases with graphene, shows stronger degradation performance for contaminants. Zhou wait [2] using water Hot method rgo/tnt composites for photocatalytic degradation MB.

Research shows that, TiO₂ nanotubes and TiO₂ nanoparticles compared to RGO Better contact performance for, can be more effective in promoting the conversion of optical electrons move to graphene surface, better suppress light-born electronics - hole pair complex close, thus exhibit stronger photocatalytic activity. rgo/tnt complex composite material pair The photocatalytic degradation rate of MB is better than RGO / TiO₂ na rice particle, catalytic degradation mechanism as shown in the diagram 6 shows. other than, will TiO₂ Film and graphene composite preparation RGO-TiO₂ membrane Composite material, photocatalytic performance can also be significantly enhanced. Du wait [3] Stone Graphene Wrap to three-dimensional mesoporous TiO₂ Film, To synthesize a highly ordered Big Hole - mesoporous Rgo-tio₂ membrane composites. TiO₂ film with more Large specific surface area, to effectively increase the transport of contaminated material in the membrane ability and transfer efficiency of the excitation electron, thus rgo-tio² film composites show stronger photocatalytic activity, under ultraviolet light, The rate of degradation of methylene blue is macroporous - mesoporous TiO₂ film 1.6 times.

in Graphene /tio₂ Mixed System, introduces the 3 kinds of substances into graphene /tio₂/ ternary composites for other dopant, can benefit Properties of the dopant, Enhancing synergistic effect of three components, increase with, composite photocatalytic properties, increase degradation of contaminants [4]. Khalid wait [5] A hydrothermal method is used to prepare a Fe doped Graphite allyl /tio₂ Composite material, Fe The doping of the not only allows the catalyst to be banned The width narrows, Further expands the response to visible light and can Valid for excitation electronic - Detach the hole pair. for photocatalytic degradation methylene blue rgo/tio₂/fe Ternary composite material than rgo/tio₂, TiO₂ shows higher photocatalytic degradation efficiency. such as table 1 show, Add other doping such as Cu₂O, Ag, SiO₂, and so on Preparing ternary composite materials also increases the graphene separation charge Ability and extended composite response to visible light, to make ternary Composites exhibit a ratio of pure TiO₂ and the corresponding two-yuan composite system Higher photocatalytic activity.

Li, and so on [6] Study Magnetic materials Fe₃O₄ and Graphene /tio₂ Composite Preparation rgo/tio₂ /fe₃O₄ ternary composites for light reminders degrade methylene blue. This material not only has the advantages of the above ternary composite material The material Advantage, degradation rate of methylene blue is higher than rgo/tio₂, and added Fe₃O₄ Magnetic material enables composite photocatalyst to be external With magnetic conditions to achieve

separation, separating catalyst accept more easily, In the field of photocatalytic degradation of waste water Apply value, RgO/tio₂/fe₃O₄ Ternary composite photocatalyst system prepare and magnetic separation process as shown 7 Show.

Graphene /tio₂ The Composite can not only make organic compounds in waste water pollutant catalytic degradation to H₂O and CO₂, Air formaldehyde [1],- toluene, [P]and other volatile organic pollutants also have a better drop Solution effect. Jo[+] by Chemical mixing method Rgo/tio₂ compound Materials for photocatalytic degradation of toxic emissions -- toluene. with graphene have larger surface area and surface has more N can be with and toluene molecule occurrence n-n key conjugate effect, can adsorb more

diagram 7 RgO/ti₂O₃/fe₃O₄ Preparation of the ternary composite photocatalyst and schematic diagram of magnetic separation

fig.7 Preparation of RgO/tio₂/fe₃O₄ composite photocatalyst and magnetic separation process

The toluene molecule for, and the doping of graphene can significantly improve the composite material material photocatalytic activity. in visible light conditions, RG0/ Tioncompound The degradation rate of the material to toluene is much higher than that of pure Ti O₂.

4. Epilogue

using graphene for excellent conductivity, High specific surface area and special single-atom layer two-dimensional planar structure features and Ti Composite Preparation new composite photocatalyst, not only increase the pollutant molecule's adsorption capability, and Graphene /Ticomposites can effectively promote light electron - detach from hole pair, increase photocatalysis quantum efficiency and widening Tilight Absorption range, Increase utilization of visible light, It has a wide application in photocatalytic degradation of organic pollutants. Before view. However graphene /TiO₂ Composite photocatalyst still in development early period, to reach the actual application level, The also requires the following 3 Square surface for further research: ① in graphene /Ticomposite photocatalysis degradation mechanism, The current theory is essentially a comparison of the experimental results from the light reminders reaction, which is inferred from the, lacks strong solid verify, So for graphene/Ti? Composite photocatalytic activity effect Further research is required; ② in Graphene / Ti Preparation of composites, The current graphene and Ti Composite will inevitably cause damage to the graphene conjugate structure, cause lower conductivity of graphene, and the interaction between the two less powerful, cannot play synergies effectively, so, to Graphene, The composite method for Ti is also a more in-depth study, Discover both A new method that can make a better combination without damaging the structure of graphene; ③ Current research using graphene /Ti (composite photocatalysis Most degradable pollutants are organic dyes, photocatalytic degradation of it His kind of contaminants need further study., to extend its application Scope.

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