Preparation and Photocatalytic Reaction of Nano-Tio2

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Abstract: Tio2 heterogeneous photocatalytic energy can realize many reactions which are difficult or impossible to achieve under normal conditions under mild conditions. Various methods for preparing nano TIO2 are introduced by gas phase method and liquid phase method. The hydroprecipitation method and the sol-gel method are introduced, and the supercritical fluid drying method and its advantages are described. The mechanism of photocatalytic reaction and the influencing factors of catalytic activity are introduced. The photocatalytic activity of Tio2 as photocatalyst is used. The application of inorganic and organic degradation in protection, anti-virus sterilization in health care, and organic synthesis have also been elaborated; future research work is expected.

1. Introduction

Since the Japanese scholars Fujishima and Honda discovered hydrogen photoelectrocatalytic decomposition of water on n-type semiconductor TIO2 single crystal electrodes in 1997, multiphase photocatalysis technology has attracted great attention from scientists and technicians. Currently, in multiphase Among the semiconductor catalysts used in photocatalytic reactions, Tio2 is favored for its non-toxicity, high catalytic activity, good stability and strong anti-oxidation ability. However, TIO2 has a wide band gap and can only utilize solar energy. 3% of solar energy. In order to improve the utilization of solar energy, in recent years, scholars from various countries have made a lot of fruitful exploration and research work on the preparation of high-activity nano-TIO2, multi-phase photocatalytic mechanism and improving the photocatalytic efficiency of Tio2. Tio2 photocatalytic sputum has broad application prospects in completely degrading organic pollutants in air and wastewater, which in turn has deepened the understanding of the depth and breadth of the mechanism of heterogeneous photocatalysis.

2. Preparation of 2 nm Tio2

The gas phase method is to oxidize TIO2 at high temperature to prepare TIO2. eD gusas P-25 Tio2 is prepared by gas phase method, which contains about 100% of anatase type (urti le) 3 0 %, non-porous structure, average particle size of about 20n m, specific surface area (50 ± 15) mZ·g- ,. Shi Liyi et al. 13 In the high temperature tubular aerosol reactor, the gas phase oxidation of IT1C4 is used to prepare nanometers. TIO2, the influence of residence time and reaction temperature on particle morphology was investigated. It was found that the particle size of Tio2 increased with the extension of residence time and the reaction temperature. The content of rutile Tio2 increased with the extension of residence time. When the reaction temperature reached 1 30 At 0 °C, the rutile Tio2 content is the largest. IT CI; the initial oxidation reaction is formed by the formation of the sharp-type TIO2 cluster, and then the Ruiqin-type Tio2 cluster is transformed into the rutile-type Tio2 cluster or further grown into a sharp Qinling type TIO2 particles. At high temperature, although the Ruiqin type Tio2 molecular cluster is converted into rutile TIO2 molecular clusters at a high rate, once grown into a sharp-minded Tio2 particle, the crystal form has been transformed. The process is terminated. As the reaction temperature increases, the crystal transition rate also increases. When the reaction temperature reaches 130 °C, on the one hand, the homogeneous nucleation rate greatly increases with increasing temperature. On the other hand, TIO2 The concentration of lattice defects in the particles is greatly reduced at high temperatures, which slows the rate of crystal

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transformation. These two opposite effects cause the rutile TIO2 content to reach a maximum at 130 °C. The nano-TIO2 prepared by gas phase method has higher activity. The reason can be attributed to the large surface area, the small number of composite centers prepared at high temperatures, and the mixed crystal effect.

3. Tio2 photocatalytic reaction and application

Nano TIO2 is an n-type semiconductor. Theoretically, as long as the light energy (hv) absorbed by the semiconductor is not less than its forbidden band width, the electrons on the valence band (e-) can be excited to transition to the conduction band at the valence band. Corresponding holes (+h) are generated, and then +h and e- interact with HZO, O:, etc. adsorbed on the surface of TIO2 to form highly reactive groups such as ·OH, ·02 -, of course, generated holes And electrons and composites may also be excited by Tio2 to produce +h and e - , which also occurs in ordinary TIO2, but due to the small particle size of nano TIO2, the time from +h and e - migration from the inside to the surface of the crystal Greatly shortened, thus reducing the probability of +h and e-complexing, thus having the unparalleled photocatalytic activity of ordinary Tio2. Sometimes in order to further improve the photocatalytic activity, reduce the recombination probability of photogenerated holes and electrons, additionally to the system Add some strong oxidants or reducing agents. These strong oxidants (or reducing agents) can effectively capture electrons, thus achieving efficient separation of holes and electrons.

There are two main crystal forms of TIO2, namely Ruiqin ore and rutile. The two crystal forms are composed of interconnected iT 06 octahedrons. The difference lies in the degree of distortion of the octahedron and the way of interconnection. Figure 2 shows the unit structure l9 of two crystal forms, each iT +4 is surrounded by six octahedrons composed of 0 - 2 . The octahedron of rutile TIO2 is irregular and slightly orthorhombic; The octahedron of type TIO2 exhibits obvious orthorhombic distortion, and the symmetry is lower than that of the former. The iT-iT bond length of the iron oxide type TIO2. (03 79, 0.3 04n m) is longer than the bond length of the rutile type Tio2 (0.3 5 7,0.2 9 6n m) is large, and the bond length of iT -O (0.19 3 4, 0.19 8n m) The bond length of this rutile Tio2 (0.19 4 9, 0.19 8 0n m) is small. The rutile type Tio2 Each octahedron is connected to the surrounding 10 octahedrons (two co-edges, 8 common apex angles), and each octahedron in the Ruiqin mine type TIO2 is connected to the surrounding 8 octahedrons (4 co-edges, 4 A total of these vertices. These structural differences lead to different density and electronic band structure of the two crystal forms.

In general, the photocatalytic activity of the Ruiqin type TIO2 is 20 higher than that of the rutile type Tio2, because: (1) the rutile type TIO2 has a smaller forbidden band width (the sharp-mine type TIO2 is 3.3e from The rutile TIO2 is 3.1 ev), and its positive conduction band hinders the reduction reaction of oxygen. The sharp-type Tio2 lattice contains more defects and dislocations, resulting in more oxygen vacancies to capture electrons. The rutile type Tio2 is the most stable crystalline structure of Tio2, has a better crystallized state, has fewer defects, photogenerated holes and electrons are easily recombined, and catalytic activity is affected to some extent; (3) rutile TIO2 has low photocatalytic activity It may also be related to the sharp drop in surface area caused by massive sintering of particles during high temperature processing. At present, there is some debate on the photocatalytic activity of different crystalline forms of TIO2. iB ckley et al. believe that photocatalysis of single sharp iron phase and rutile phase The activity is poor, and the mixed crystal has higher catalytic activity. Tao Yuewu et al. also obtained the same conclusion in the study of photocatalytic degradation of gas phase acetone and acetaldehyde on Tio2. It may be (equivalent to the presence of two semiconductor, constituting the compound semiconductor) by the coexistence of a certain ratio to the anatase type TIO2 and rutile Tio2, may cause photogenerated holes and electrons efficient separation occurs, reduce the risk of their recombination.

The particle size also affects the photocatalytic activity of Tio2. The smaller the particle size of the particles, the larger the number of particles per unit mass, and the larger the specific surface area, which is beneficial to the photocatalytic reaction on the surface, so the photocatalytic reaction rate and efficiency are also higher. High. When the size of the particle is in the or nmr, a quantum effect

occurs, which becomes a quantized particle, which leads to a significant band gap broadening, so that the hole-electron pair has a stronger oxidation-reduction ability, and the catalytic activity will follow. The degree of quantization of the size increases. The quantization of the size also enables the semiconductor to obtain a higher charge transfer rate, and the probability of recombination of holes and electrons is greatly reduced, which is also beneficial to improve the efficiency of the photocatalytic reaction. The large surface area means that there is more chance of a recombination center on the surface. When the recombination plays a major role, the activity decreases as the degree of quantization increases. In addition, the degree of quantization of the size increases. When the forbidden band is widened and the absorption line is blue-shifted, the degree of photosensitization of Tio2 will be weakened, and the utilization of light energy will also be reduced. Therefore, in the actual process, one should be selected. Suitable particle size range.

4. Applied research

The application of Tio2 in this area is a new field that has only emerged in recent years, but it has become one of the research hotspots. It is generally added to the liquid environment in which the virus survives, and then irradiated with ultraviolet light. In a relatively short period of time, the virus can be basically killed. The anti-sterilization mechanism of Tio2 is that TIO2 is irradiated by ultraviolet light, and a large amount of ·OH is formed on the surface. ·OH attacks the virus cells to inactivate it. The concentration of ·OH produced is not large, and the anti-virus effect is not ideal. It takes a long time. Cia et al. also reported the experiment of killing cancer cells with Tio2. They found that the killing power of cancer cells after adding TIO2. They are much better than UV light alone. They proposed the killing mechanism of Tio2 on cancer cells. They demonstrated that Tio2 passes photocatalytic pair by using UV light, TIO2 alone and Tio2 under light. Cancer cells play a killing role. The killing of cancer cells by Tio2 is carried out simultaneously from the inside and outside of the cells. Because the particle size of nano TIO2 is relatively small, it is easy Inside the human cell, on the surface and inside of cancer cells, the oxidation of holes +h and ·OH is generated by light. Therefore, all the promoters that are beneficial to the formation of OH will make the killing effect more thorough. C ia et al. In the presence of oxygen, humans added the promoter superoxide dismutase SOD to the system to promote the formation of ·OH. It was found to have a good killing effect on cancer cells. Although the application of Tio2 in this area has just started. There is still a lot of work to be done, but its potential for application in this area is great.

The photocatalytic reaction of organic compounds can also be carried out by using Tio2. Jenk: The experimental group carefully studied the photolysis process of 4-p-phenol in the TIO2 suspension, and found that 4-grasphenol was converted into two intermediates under photocatalysis. , ie hydroquinone and 4-octal catechol, then hydroquinone is converted to 1,2,4-benzenediol, 4-chlorocatechol is converted to 4-chloro-1,2,5 Pyrogallol and a small amount of 1,2,4-benzenetriol, and finally 1,2,4-benzenetriol and 4-1,2,5-benzenetriol further open-ring mineralization to COZ, HZO, lC First-class inorganic small molecules. Ldodo et al. investigated the degradation process of 4-nitrophenol under the action of TIO2 (anarite) / TIO2 (rutile) photocatalyst, and with Tio2 (Ruiqin) / 1A203 Comparing the two catalysts, it was found that both photocatalysts were active. The FITR measurement showed that there were only L acid and no B acid on both catalysts, and their activity increased with the increase of TIO2 content.

5. Conclusion

Heterogeneous photocatalysis is a frontier field of photochemical reactions that enables many reactions that are difficult or impossible to achieve (such as the decomposition of water, $\Delta rG >> 0$). Under mild conditions (generally The development and development of photocatalytic materials is one of the key to realize various chemical reactions through photocatalysis technology. Nano TIO2 has attracted much attention due to its unique advantages. In comparison, the sol-gel method combined with supercritical drying method is one of the most promising methods for preparing nano-Tio2.

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